BEFORE THE HON'BLE NATIONAL GREEN TRIBUNAL

PRINCIPAL BENCH AT DELHI

OA NO. 240/ 2024

IN THE MATTER OF:

SINGRAULI PRADOOSHAN MUKTI VAHINI APPLICANT

VERSUS

UNION OF INDIA AND ORS RESPONDENTS

REJOINDER BY THE APPLICANT IN RESPONSE TO THE CPCB FINAL REPORT DATED 10.09.2024

PAPER BOOK

(FOR INDEX: PLEASE SEE INSIDE)

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DATE: 02.03.2025

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REJOINDER/ OBJECTIONS ON BEHALF OF THE APPLICANT TO THE CBCB REPORT DATED 10.9.2024

MOST RESPECTFULLY SHOWETH:

1. That the above-titled Original Application has been filed to highlight the drastic long-term health impacts on the residents of Singrauli as a result of the industrialization of the region far beyond its carrying capacity, and to seek compensation as well as remedies to protect public health. The contents of the Original Application are relied on and not reiterated herein for the sake of brevity.

2. That vide order dated 15.03.2024, this Hon'ble Tribunal issued notice in the Original Application and directed Respondent No. 2, the Central Pollution Control Board (hereinafter referred to as '**CPCB**') to file a comprehensive report disclosing *"the extent of pollution in the area concerned* ***and its effect on the health of the local residents****."* (Emphasis supplied). Vide order dt. 22.05.2024, the CPCB filed an interim report that largely focused on the levels of pollution in the area and did not substantively deal with the health impact on the residents.

3. The Applicant filed IA No. 437/2024 dt. 09.09.2024 highlighting the lack of information on health impacts in the interim report filed by CPCB. Further, vide IA No. No. 437/2024 dt. 09.09.2024, the Applicant prayed before the Hon'ble Tribunal that a representative sub-committee be set up to examine the 'Long-term health impacts on the residents of the Singrauli region.'

The Final Report dated 10.9.2024 filed by CPCB.

4. That CPCB filed its final report dated 10.09.2024 (hereinafter referred to as '**final report'**) wherein the levels of pollution have been recorded but no significant comment has been made on the health impacts on the residents of Singrauli. The final report is merely a reiteration of the findings already submitted through the interim report. At the outset, it is submitted that the final report filed by the CPCB is not in compliance with the direction given by this Hon'ble Tribunal vide order da

15.03.2024. The objections of the Applicant to the final report of the CPCB and the inadequacies therein are as follows:

A. Air Pollution

5. That the final report filed by the CPCB does not provide any additional information as compared to the interim report. Both reports give monthly average data of PM2.5, PM10, SO2 and NO2, from April 2023 to March 2024, from two National Air Quality Monitoring Programme (NAMP) stations that are operated by the Regional Office, Uttar Pradesh Pollution Control Board (hereinafter referred to as '**UPPCB**'), located in Anpara and Renusagar, and the Continuous Ambient Air Quality Monitoring Stations (CAAQMS) operated by the industries, namely, NTPC Rihand, NTPC Shaktinagar, UPRVUNL at Obra.

6. The CPCB final report records levels of PM 2.5, PM 10, SO2 and NO2. However, coal burning also releases fluoride, CO2, methane and heavy metals into the atmosphere that cause air pollution and are detrimental to human health. The critical nature of such air pollutants is brought out in the scientific paper titled "Atmospheric emissions and pollution from the coal-fired thermal power plants in India". The continuing increase of air pollution in Singrauli region over a period of time is brought out in the paper "Long Term Air Quality Analysis in reference to Thermal Power Plants using Satellite Data in Singrauli Region, India. It is submitted that the CPCB study and report has excluded such critical pollutants.

A true and correct copy of the paper titled 'Atmospheric emissions and pollution from the coal-fired thermal power plants in India' by 'Guttikunda, S.K. & Jawahar, P.' published in Atmospheric Environment (2014) has been annexed herewith and marked as **R-1 (Pages 25 to 36).** A true and correct copy of the paper "Long Term Air Quality Analysis in reference to Thermal Power Plants using Satellite Data in Singrauli Region, India" by Romana, H. & Singh, R. & Shukla, Dericks in International Archives of the Photogrammetry, Remote Sensing and Spatial Information Sciences (2020) is **Annexure R-2 (Pages 37 to 42).**

7. Further, the study titled "Dark and Toxic under the Lamp: Industrial Pollution and Health Damage in Singrauli" (Annexure A-10 to the Original Application) also clearly states that:

> *"Based on the Central Institute of Mining and Fuel Research's calculation of the average concentrations of these elements in Indian coal (Banerjee et al 2000), we can estimate that about 1.9 metric tonnes of chromium (Cr), 4.2 tonnes of lead (Pb), 1.4 tonnes of arsenic (As), 1 tonne of nickel (Ni), and 0.1 tonne of mercury (Hg) are released into the environment from the coal burnt every day in Singrauli."*

8. Further, there is a lack of monitoring infrastructure, highlighted by the fact that the only continuous monitoring of heavy metal content in the atmosphere in the Singrauli region was carried out by the Banwasi Seva Ashram through June 2016-May 2017. The study monitored the presence of heavy metals such as arsenic, mercury and nickel in the atmosphere for a period of 1 year and clearly shows that the annual levels of arsenic and nickel are higher than the standards. It also

showed that the levels of heavy metals are higher closer to the industries. Studies undertaken in thermal power plants in India show that 80%–90% of mercury present in coals is released to air through stack gas (Agarwalla, H. & Senapati, R.N. & Das, T.B., Mercury emissions and partitioning from Indian coal-fired power plants, 100 Journal of Environmental Science. 28-33 (2021), https://doi.org/10.1016/j.jes.2020.06.035).

A true translated copy of the study titled 'Heavy Metals in Ambient Air of Sonabhadra' by Banwasi Sewa Ashram (2017) is annexed herewith and marked as **Annexure R-3 (Pages 43 to 64) .** A true and correct copy of the article titled 'Mercury Emissions and Partitioning from Indian coal-fired power plants' by Agarwalla, H. & Senapati, R.N. & Das, T.B. in the Journal of Environment Science (2021) is annexed herewith and marked as **Annexure R-4 (Pages 65 to 70).**

9. The CPCB report also does not take cognisance of the presence of fluoride in the atmosphere. Monitoring of fluoride by the Banwasi Seva Ashram that was carried out in association with the CPCB during 2002-2010 showed that the levels of fluoride in the atmosphere increased between 2003 and 2010. A true and correct copy of the study titled 'Environment Quality Monitoring in Singrauli Problem Area' by Banwasi Sewa Ashram in association with the Central Pollution Control Board (2010) is annexed herewith and marked as **Annexure R-5 (Pages 71 to 142).**

10. That the burning of coal leads to fluoride contamination not just of water but also of the atmosphere, and that fluoride release during coal combustion has resulted in environmental pollution, damage to plants and human and animal health. This has been shown through various studies including one titled "Fluorine in the environment, a review of its sources and geochemistry." Despite such established scientific findings, the CPCB final report has not incorporated any mechanism to measure fluoride levels in the atmosphere. A true and correct copy of the article titled 'Fluorine in the environment- a review of its sources and geochemistry' by Ron Fuge in Applied Geochemistry is annexed herewith and marked as **Annexure R-6 (Pages 143 to 185).**

11. That electrostatic precipitators and other environmental pollution mitigation technologies only partially capture heavy metal pollution, and such heavy metal pollutants in the atmosphere can travel up to 200-400 kms away, thereby causing air pollution in regions far away from the thermal power plants (Guttikunda, S. et al., Regulating Air Pollution from Coal-Fired Power Plants in India, Economic & Political Weekly Vol I January, 2015) . A true and correct copy of the article titled 'Regulating Air Pollution from Coal-Fired Power Plants in India' by Guttikunda, S. et al. in Economic & Political Weekly (January 2015) is annexed herewith and marked as **Annexure R-7 (Pages 186 to 191).**

12. The fact that the only long-term monitoring study of presence of heavy metals in the atmosphere is conducted by locals shows their commitment to correctly understand the state of air pollution in the region. Further, the fact that such infrastructure has not been set up by the CPCB and other state PCBs shows their lack of initiative.

13. It is submitted that the exact location of the continuous air quality stations should have been given so that the Applicant could examine whether the data is representative of the conditions in which the Applicants live.

14. That as per judgement dated 06.12.2017, three continuous monitoring systems for monitoring of mercury in the air were to be installed by the industries in the two districts of Sonbhadra and Singrauli. CPCB in association with SPCBs was to guide the industries in the location of the monitoring stations. However, it is submitted that data from these monitoring stations has not been shared till date. Further, it is unknown whether such monitoring systems were even set up and whether CPCB provided any support in determining the location of these monitoring systems.

B. Carrying Capacity

15. That the final report submitted by CPCB does not make any comment on the carrying capacity of the region. The CPCB has submitted, along with the final report, copies of letters written to UPPCB asking for

details of carrying capacity studies, *if* they have been carried out. Further, as per the final report, the UPPCB responded to the aforesaid letter by providing data related to air quality and water quality but have not submitted any document related to carrying capacity, thereby making it unclear whether such a study was conducted.

16. It is submitted that in case such carrying capacity studies have not been carried out, it is in gross violation of the Hon'ble Tribunal's order dated 28.08.2018 in **O.A. No.164/2018- Ashwani Kumar Dubey v. Union of India (hereinafter referred to as 'order dt. 28.08.2018')** wherein the Pollution Control Boards and the Ministry of Environment, Forest and Climate Change had been asked to assess the carrying capacity of the entire Singrauli region. The judgement dt. 28.08.2018 stated *"the regional carrying capacity of the entire Singrauli region is to be assessed before allowing any expansion scheme with respect to the existing industries. This assessment is the prerequisite for such consideration in future."*

17. That it has been 6 years since the aforesaid judgement and there has been continuous expansion in the region as is evident from the environmental clearances for expansion of Singrauli (Shaktinagar) Thermal Power Plant by 2*800MW and Mahan Thermal Power Plant by 2*800MW which were granted in 2020 and 2022, respectively. It is reiterated that as per the Hon'ble Tribunal's judgement dated 28.08.2018, such expansion should have been sanctioned only after

carrying capacity studies were conducted. However, CPCB has not shared any details of such carrying capacity studies, if they were conducted.

D. Health Impacts

18. It is submitted that this Hon'ble Tribunal vide order dated 15.03.2024, had directed the CPCB to file a comprehensive report disclosing the effects of pollution on the health of the local residents. Instead of collecting specific data and conducting a study to prepare the report, the CPCB has simply asked the Chief Medical Officer (hereinafter referred to as 'CMO'), Sonbhadra to share health status of patients who have visited the public health centres in the district. It is submitted that it was not the responsibility of the CMO, Sonbhadra to conduct a health study, and therefore he has simply shared the data requested of him.

19. That the data shows the number of patients that approached Community Health Centres (hereinafter referred to as '**CHC**') with lung related diseases and were referred to medical institutes for further diagnosis. However, the diagnostic reports have not been shared, highlighting one of the gaps in the data relied on by the CPCB. Regarding the rate of miscarriage in the region, the CMO has simply given the number of patients in 2023-24 as 0 for all the CHCs, with the remark: "Not dealing with gynae cases."

20. That the data submitted by the CMO, Sonbhadra cannot be representative of the health status of the area as it only reveals information on the fraction of the population that approached governmental health care services. Data relating to those individuals who show initial signs of illness such as fluorosis and deterioration of lung function but have not yet approached government medical institutions will not be included in this list. Further, those individuals who choose to go to private health centres will also not form part of this data. As per the National Family Health Survey 2019-21 Uttar Pradesh, only 24% of households in rural Uttar Pradesh go to public health sector services including Community Health Centres, Public Health Centres and government hospitals. This signifies that others who access private health care services or other services are not accounted for in the data submitted by CPCB.

21. That the CPCB report has not sufficiently dealt with health impacts. This is shown by the finding that the report has not gathered any data on the health impacts of mercury toxicity despite various studies that have found that the levels of mercury in the blood, nails and hair of residents of Singrauli has increased over time. (*Mercury in India,* Part 2 - Usage and releases, Toxics Link (2003); Sahu, Ramakant & Saxena, Poornima & Johnson, Sapna & Mathur, H.B. & Agarwal, H.C., *Mercury pollution in the Sonbhadra district of Uttar Pradesh, India, and its health impacts*, Toxicological and Environmental Chemistry 96.10.1080/02772248.2014.939980). A true and correct

copy of the report titled 'Mercury in India' by Toxics Link (2003) is annexed herewith and marked as **Annexure R-8 (Pages 192 to 216).** A true and correct copy of the article titled *'Mercury pollution in the Sonbhadra district of Uttar Pradesh, India, and its health impacts'* by Sahu, Ramakant & Saxena, Poornima & Johnson, Sapna & Mathur, H.B. & Agarwal, H.C. in Toxicological and Environmental Chemistry is annexed herewith and marked as **Annexure R-9 (Pages 217 to 230).**

22. That the Core Committee recommendations, which were accepted by the Hon'ble Tribunal vide judgement dated 28.08.2018, required the district administration to conduct a long-term study to estimate the magnitude of the health-related problem in the area.

23. That as per order dated 28.08.2018, the district administration was also required to provide training of the health care workers in the region, including doctors, for identifying the sources of diseases due to fluoride/mercury emission/discharge and treatment of affected patients. Further, the order also accepted the submission that as the patients with clinical manifestations suggestive of fluorosis were also noted to have severe malnutrition, mineral and nutrient supplements for these areas should be ensured by the district administration. Further, a Standard Toxicological Testing and Analysis Laboratory was to be set up in the region. None of these have been carried out, despite 6 years having passed since the order.

24. The CPCB and other governmental agencies have not complied with the orders of the Hon'ble Tribunal as per judgement dated 28.08.2018 or addressed the health concerns of the residents of the region. In fact, the only comprehensive study of the health impact of the region has been conducted by the Hazards Centre and the Banwasi Sewa Ashram, albeit with limited resources and facilities. Details of the said study have been reported by the Applicant in page 646- 647 of Annexure A1 in IA No. 437/2024 dt. 09.09.2024 filed by the Applicant.

25. In the aforesaid study presented by the Applicants, a systematic sampling was carried out, and the health of every fourth family in 52 villages spread across the district Sonbhadra was surveyed, to the east of the reservoir. Between the year 2018 to 2023, follow up health studies were conducted by the affected persons at their own behest, owing to the lack of initiative from the concerned authorities. The findings of all such studies have been shared with this Hon'ble Tribunal as per aforesaid Annexure A1, and they show the consistent deterioration of the health of the local residents. Despite disclosing and sharing the results of the study with the CPCB, no comment on the same has been made in the final report.

26. The study presented by the Applicant, conducted in 2023, reports deteriorating lung function among residents, increase in percentage of respondents showing signs of heavy metal toxicity with symptoms such as blue line on gums and tremor in hands and increase in

percentage of residents showing signs of fluorosis. These findings highlight the need for a comprehensive and credible study on the long-term health related impacts of pollution on residents in the region of Singrauli.

27. That the study presented by the Applicant has been conducted with limited resources by the affected persons themselves and cannot be a substitute for a comprehensive health survey in terms of the judgement dt. 28.08.2018. It is submitted that such a health survey/study, which collects the medical history and conducts a medical examination of every resident of the villages within a distance of 30 kilometres of the polluting industries, needs to be carried out by an expert body with participation from the residents. The health survey presented by the Applicant was conducted in villages located 3 to 40 kilometres from the industries. Therefore, air and water monitoring stations set up at these specific locations will aid in correlating data and establishing the credibility and accuracy of results. Therefore, participation of and consultation with Applicants is important for a bipartite study so that locations, samples, and test methods can be mutually agreed upon.

28. That despite the order dated 15.03.2024 passed by this Hon'ble Tribunal in the present matter directing the concerned authorities to conduct a comprehensive study of the health impacts of pollution on the residents of the Singrauli region, such a comprehensive study has not been conducted. It is also submitted that the need for a

comprehensive study of health impacts has been highlighted by this Hon'ble Tribunal in various judgments including judgement dt. 28.08.2018. Such a study is essential for assessing the compensation due to the residents and in the absence of a robust and comprehensive report on the health impacts of pollution in the region, determining the compensation due to victims and payment of the same is inadvertently delayed. Till date, relief in the form of compensation has not been provided to the various Applicants and other residents of the region.

29. That such a health survey/ study must be accompanied by setting up of Standard Toxicological Testing and Analysis Laboratory as per order dt. 28.08.2018, to facilitate appropriate diagnosis and testing. The need for better monitoring, detection and testing laboratories has been established through various orders of this Hon'ble Tribunal but little has been done to establish such trustworthy infrastructure.

30. That multiple reports filed and accepted before this Hon'ble Tribunal, including the final report filed by the CPCB in the current matter clearly acknowledge that Singrauli is a Critically Polluted Region ('CPR').

31. That the Applicants have collated a list of Studies undertaken in Singrauli-Sonbhadra related to pollution and health over the years has been annexed herewith and marked as **Annexure R-10**

(Pages 231 to 233). The Applicants crave leave to produce such of these studies as are not on record, should the same be directed.

C. *Water Pollution*

32. As per the final report, CPCB analysed only 11 ground water samples and 6 surface water samples. Sonbhadra has 1429 villages, as per 2011 census, with each village having at least 60-70 hand pumps and 5-10 wells, in addition to surface water sources such as ponds and check dams. The health study conducted by the Applicants was undertaken in 52 villages which would have more than 3,770 drinking water sources. A representative sample of 3,770 water sources with 95% confidence level and 5% confidence interval would require 350 samples to be tested. It is submitted that the number of samples taken for the CPCB study fall grossly short of the abovementioned ideal number and this itself shows that the CPCB study and results cannot be representative of the water quality of such a large area.

33. That the shortcomings of the CPCB report are further highlighted since the CPCB findings are contradictory to other studies done in the region at the same time. Out of the 11 samples of groundwater, only one sample taken at Anpara was found to contain fluoride that was higher than the permissible limit of 1.5mg/l (max). However, as per an article published in 2023, titled "*Fluoride in groundwater of industrial town of Sonbhadra district, Uttar Pradesh, India: probable release mechanism and potential health risk assessment,*" a study was conducted of Sonbhadra district wherein 128 samples of groundwater

were taken pre and post monsoon and levels of fluoride in groundwater recovered from Anpara and Renukoot, both falling within the Singrauli region, were found to be above the permissible limit. They further state that the source of fluoride in Renukoot region is due to mixing of fluoride laden surface water as well as fluoride from granitic rocks containing fluorinated minerals, and the source is fly ash in Anpara region, and conclude that based on studies in India and across the world, coal burning activities are the major cause of fluoride in this region. A true and correct copy of the article titled '*Fluoride in groundwater of industrial town of Sonbhadra district, Uttar Pradesh, India: probable release mechanism and potential health risk assessment'* by Ahamad, A., Janardhana Raju, N., Madhav, S. *et al.* in Environ Geochem Health (2023) has been annexed herewith and marked as **Annexure R-11 (Pages 234 to 255).**

34. Similar contradictory findings were found for other toxic elements. The CPCB final report states that arsenic metal was within permissible limits in all drinking water samples whereas mercury is found slightly exceeding the specified limit in two samples, out of eleven that were taken. Further, as per the final report, three other metals (total chromium, cadmium and lead) were not detected in any samples. However, as per an article published in 2024, titled "*Assessing water quality and human health risk near coal mines and industrial area of Singrauli, India: special emphasis on toxic elements*", a study was conducted of heavy elements contributing towards water pollution in the Singrauli area and it was found that levels of fluoride, manganese,

arsenic, molybdenum and nickel were above the permissible limit for drinking usage. Further, the study found that arsenic, manganese, cadmium, molybdenum, cobalt, and nickel were the key heavy elements contributing towards water pollution in the Singrauli area and fluoride was one of the major contaminants. This study analysed 54 ground and surface water samples, and 6 drain samples. A true and correct copy of the article titled "*Assessing water quality and human health risk near coal mines and industrial area of Singrauli, India: special emphasis on toxic elements*" by Jha, S., Sinha, S., Mahadevappa, P. et al. published in Environ Geochem Health (2024) is **Annexure R-12 (Pages 256 to 279).**

35. Further, there is a relationship between the atmospheric pollution in the region and water pollution (Banwasi Seva Ashram, Environment Quality Monitoring in Singrauli Problem Area, Central Pollution Control Board, 2010 (*supra)*; Monitoring of drinking water sources commissioned by 21 *Gram sabhas* (2016); Semerádová, S., Sucharová, J., Mičaník, M., Sýkora, F., & Jašíková L, (2022) *Atmospheric deposition as a possible source of water pollution,* VTEI, 2022,4. DOI: 10.46555/VTEI.2022.05.006). The article "Dark and Toxic under the Lamp: Industrial Pollution and Health Damage in Singrauli", attached as Annexure A-10 to the above original application describes water analysis commissioned by residents of 21 *gram sabhas* of the region where well water was found to contain more mercury than hand pump water, indicating that a possible source of

mercury at locations of some distance from mines and industries is fallout from the atmosphere. A true and correct copy of the Monitoring of drinking water sources commissioned by 21 Gram Sabhas (2016) is **Annexure R-13 (Pages 280 to 359).** A true and correct copy of the article titled '*Atmospheric deposition as a possible source of water pollution'* by Semerádová, S., Sucharová, J., Mičaník, M., Sýkora, F., & Jašíková L (2022) in **Annexure R-14 (Pages 360 to 371).**

36. That the aforementioned studies highlight that a scientific study of the water pollution of the region should not have relied merely on 11 groundwater samples. Further, the contradictory results of the CPCB report and the aforementioned studies highlight the inaccuracy of the CPCB report.

37. Further, such contradictory results highlight the need for tripartite or bipartite testing and sampling with a third sample reserved for testing by an independent laboratory in the event of the results of the two parties being different. Such a protocol for water sampling is as per the recommendations of the Core Committee, which were accepted vide judgment dt. 06.12.2017 passed by this Hon'ble Tribunal in O.A. No. 276 of 2013- Ashwani Kumar Dubey v. Union of India and O.A. No. 20/2014- Jagat Narayan Viswakarma & Ors. v. Union of India & Ors (hereinafter "judgment dt. 06.12.2017").

38. That as per judgement dt. 06.12.2017, three continuous monitoring systems for monitoring of mercury in the surface and groundwater were to be installed by the industries in the two districts of Sonbhadra and Singrauli. CPCB in association with the State Pollution Control Boards (herein after referred to as '**SPCB**') was to guide the industries in the location of the monitoring stations. However, it is submitted that data from these monitoring stations has not been shared till date. Further, it is unknown whether such monitoring systems were set up and whether CPCB provided any support in determining the location of these monitoring systems.

The Ld. NGT has the jurisdiction to address pollution related health impacts.

39. That as per Section 15(4) of the National Green Tribunal Act, 2010, this Hon'ble Bench is competent to take cognisance of damage caused to public health due to pollution. Relevant part of the section is extracted below:

> *"(4) The Tribunal may, having regard to the **damage to public health**, property and environment, divide the compensation or relief payable under separate heads specified in Schedule II so as to provide compensation or relief to the claimants and for restitution of the damaged property or environment, as it may think fit."*
>
> *(emphasis supplied)*

40. That in order to assess the damage to public health, this Hon'ble Tribunal is competent to direct a detailed and comprehensive study of the health related impacts of pollution in the Singrauli region and subsequently determine relief in the form of compensation.

41. In light of the above facts and circumstances, the applicants reiterate their request for setting up a representative sub-committee to examine the *'Long-Terms Health Impacts of the Residents of the Singrauli Region'* including assessment of the prevalence of diseases as a result of emission of fluoride, mercury and heavy metals, assessment of the health facilities provided by the District Administration as well as setting up of appropriate Standard Toxicological Testing and Analysis Laboratory.

PLACE: New Delhi

DATE: 02.03.2025

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BEFORE THE HON'BLE NATIONAL GREEN TRIBUNAL

PRINCIPAL BENCH AT DELHI

ORIGINAL APPLICATION NO. 240 OF 2024

IN THE MATTER OF:

SINGRAULI PRADOOSHAN MUKTI VAHINI & ORS. ...APPLICANTS

VERSUS

UNION OF INDIA & ORS. ...RESPONDENTS

AFFIDAVIT

I, Rameshwar, representative of Singrauli Pradooshan Mukti Vahini, s/o late Manraj, aged 72 years, r/o Pad Rach, Chopan Sonebhadra do hereby solemnly affirm and declare on oath as under:

Ticket Rs. 10/-
Renu Kumari
Dudhi Sonebhadra

1. That I am the authorized representative of the Applicant No.1 in the above-titled Original Application and am conversant with the facts and circumstances of the case and competent to swear this affidavit.
2. That I say that the contents of the accompanying Rejoinder have been drafted by my counsel under my instructions. I say that the contents thereof are true and correct to the best of my knowledge.
3. All annexures are true copies of their respective originals
4. The contents of this affidavit have been read and explained to me in Hindi and I state that the contents thereof are true and correct to my knowledge.

DEPONENT

VERIFICATION

Verified at Delhi on this 03rd day of ~~February~~ FEB, 2025 that the contents of the above affidavit are true and correct to my knowledge and belief and no part of it is false or incorrect and nothing material has been concealed therefrom.

DEPONENT

NOTARY
GOVT. OF U.P.

APPLICANT NO. 1

THROUGH

SRISHTI AGNIHOTRI SANJANA SRIKUMAR SANJANA GRACE THOMAS

ADVOCATES

No. 46, Upper Ground Floor,

Hemkunt Colony,

New Delhi-110048

Place: New Delhi

Date:

VERIFICATION

I, Rameshwar, authorized representative of Singrauli Pradooshan Mukti Vahini, s/o Mankey, aged about 70 years, r/o Padkala do hereby verify that the contents of the paragraphs stated above have been read and explained to me in Hindi and I state that the contents are true to the best of my knowledge and I have not suppressed any material fact.

APPLICANT NO. 1

Atmospheric Environment 92 (2014) 449–460

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Atmospheric emissions and pollution from the coal-fired thermal power plants in India

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HIGHLIGHTS

- Review of emission factors and emissions analysis for coal-fired power plants.
- Review of environmental regulations for air pollution from coal-fired power plants.
- Particulate pollution analysis via CAMx dispersion model.
- Health impacts of particulate pollution from coal-fired power plants.

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ABSTRACT

In India, of the 210 GW electricity generation capacity, 66% is derived from coal, with planned additions of 76 GW and 93 GW during the 12th and the 13th five year plans, respectively. Atmospheric emissions from the coal-fired power plants are responsible for a large burden on human health. In 2010–11, 111 plants with an installed capacity of 121 GW, consumed 503 million tons of coal, and generated an estimated 580 ktons of particulates with diameter less than 2.5 μm ($PM_{2.5}$), 2100 ktons of sulfur dioxides, 2000 ktons of nitrogen oxides, 1100 ktons of carbon monoxide, 100 ktons of volatile organic compounds, and 665 million tons of carbon dioxide. These emissions resulted in an estimated 80,000 to 115,000 premature deaths and 20.0 million asthma cases from exposure to $PM_{2.5}$ pollution, which cost the public and the government an estimated INR 16,000 to 23,000 crores (USD 3.2 to 4.6 billion). The emissions were estimated for the individual plants and the atmospheric modeling was conducted using CAMx chemical transport model, coupled with plume rise functions and hourly meteorology. The analysis shows that aggressive pollution control regulations such as mandating flue gas desulfurization, introduction and tightening of emission standards for all criteria pollutants, and updating procedures for environment impact assessments, are imperative for regional clean air and to reduce health impacts. For example, a mandate for installation of flue gas desulfurization systems for the operational 111 plants could reduce the $PM_{2.5}$ concentrations by 30–40% by eliminating the formation of the secondary sulfates and nitrates.

1. Introduction

India, at 210 GW, has the 5th largest electricity generation sector in the world (with captive power plants generating 31 GW more), with targets of additional 76 GW in the 12th five year plan (2012–2017) and another 93 GW in the 13th five year plan (Prayas, 2011, 2013). Thermal power plants account for 66% of generation, hydro for 19% and others (including nuclear energy) for 15%. In India, coal is the primary fuel of choice and accounts for 50–55% of the power generation and will only get larger in the coming years (Chikkatur et al., 2011; WISE, 2012; Prayas, 2013).

In India, the supply of electricity lags behind the demand. According to the Central Electricity Authority (CEA), in 2010–11, of the 122 GW peak demand, only 110 GW was supplied – which amounted to a shortfall of 10% (CEA, 2012). A third of the population that lives in rural India does not have access to electricity. Even those with access in urban India have to endure frequent power

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cuts and load shedding, which results in use of in-situ diesel generator sets (Guttikunda and Jawahar, 2012; Guttikunda and Calori, 2013).

Coal-fired power generation comes with significant costs to environment and human health. The water runoff from coal washeries carries pollution loads of heavy metals that contaminate ground water, rivers, and lakes – thus affecting aquatic flora and fauna (Finkelman, 2007). Fly-ash residue and pollutants contaminate soil and are especially harmful to agricultural activities. Most importantly for human health, combustion of coal releases emissions of sulfur dioxide (SO_2), nitrogen oxides (NO_x), particulate matter (PM), carbon monoxide (CO), volatile organic compounds (VOCs), and various trace metals like mercury, into the air through stacks that can disperse this pollution over large areas. The 2010 global burden of disease (GBD) study listed the outdoor air pollution (PM and ozone pollution) among the top 10 health risks in India, with as estimated 695,000 annual premature deaths from respiratory illnesses, compromised immune systems, and cardiovascular conditions (IHME, 2013). The known sources of outdoor air pollution in India include emissions from power plants, manufacturing industries, vehicle exhaust, cooking and heating in the households, generator sets, nature dust, on-road dust resuspension, garbage burning, and seasonal agricultural burning.

Previously, the studies on power plants in India focused on coal usage trends, resource management, greenhouse gas emissions, and innovation in use of renewable energy (Chikkatur and Sagar, 2009; Chikkatur et al., 2011; Prayas, 2011; Chaudhary et al., 2012; Ghose, 2012; WISE, 2012; Prayas, 2013) and total emissions inventories for base year 2005 or older (Streets et al., 2003; Reddy et al., 2005; Ohara et al., 2007; GAINS, 2012). Of the estimated annual anthropogenic emissions in India, the thermal power plants account for ~15% for $PM_{2.5}$, ~30% for NO_x, and ~50% of SO_2 (GAINS, 2012). Studies based on satellite measurements (Lu and Streets, 2012; Prasad et al., 2012) looked at the influence of power plant emissions on the column NO_x concentrations, including the influences of other sources, but there is limited bottom-up analysis on dispersion of emissions from the coal-fired power plants.

Given the plans to greatly expand the contribution of coal to the Indian power sector (Chikkatur et al., 2011; WISE, 2012; Prayas, 2013), it is vital that decision makers understand the hidden costs of air pollution from power plants. In this paper, we present an updated list of operational coal-fired power plants in India, their generation capacities, coal consumption rates, and evaluation of the health impacts of their pollution via dispersion modeling. We also discuss the current environmental regulations for power plants in India or their lack of.

2. Data and methods

2.1. Coal-fired power plants in India

The installed power generation capacity in India grew at an average annual rate of 8% in the 1970s and at 10% since the 1980s (WISE, 2012; Prayas, 2013). The characteristics of operational coal-fired power plants in India are presented in Table 1 and the location of these plants is presented in Fig. 1. The database of plants documented by CEA was further updated with information from websites and annual reports of the state electricity boards and private electricity generation companies (CEA, 2011; CEA, 2012). The database includes geographical location in latitude and longitude, number of boiler units and size of all known power plants operated by both public and private entities.

Power plants are clustered at pit heads of coal mines in Central India, in northern Andhra Pradesh, western Maharashtra, northern Chhattisgarh, West Bengal, Bihar, Jharkhand, and Orissa. Some large power plants are located on the coast, for the availability of cooling water from the sea and ease of importing coal. While the coastal winds are beneficial in some cases, the impacts are still at large for cities in the vicinity. For example, Chennai (Tamilnadu) and Ahmedabad (Gujarat), each host two coal-fired power plants of more than 1000 MW electricity generation and located closer to the city premises. Chennai, being a coastal city, records a smaller fraction of the power plant emissions in their ambient measurements, compared to Ahmedabad, which is in-land (Guttikunda and Jawahar, 2012). In Delhi, up to 8% of the ambient PM pollution can be attributed to the coal-fired power plants of 2000 MW, operated within 60 km from the city center (Guttikunda and Goel, 2013). Similar shares are expected for the cities of Mumbai, Ahmedabad, Kolkata, and some medium to smaller size cities like Nagpur, Raipur, Ranchi, Kota, Bhatinda, Raichur, with power plants in the vicinity of 100 km.

Table 1
Summary of annual coal consumption at the power plants in India in 2010–11.

State	Number of plants	MW	Coal million tons	kg coal/kWh 2006–07	% Installed units <210 MW
Andhra Pradesh	8	10,523	47.4	0.72	65%
Bihar	3	2870	10.2	0.94	77%
Chhattisgarh	8	9480	44.5	0.72	39%
Delhi	2	840	4.8	0.77	100%
Gujarat	11	14,710	55.9	0.65	69%
Haryana	5	5860	23.9	0.70	35%
Jharkhand	6	4548	12.0	0.75	86%
Karnataka	5	3680	14.6	0.69	64%
Madhya Pradesh	4	6703	33.1	0.79	79%
Maharashtra	13	17,560	71.5	0.73	51%
Orissa	8	8943	40.7	0.73	76%
Punjab	3	2620	13.2	0.66	82%
Rajasthan	4	3490	13.2	0.67	44%
Tamilnadu	8	6210	25.8	0.72	95%
Uttar Pradesh	11	11,997	56.0	0.80	86%
West Bengal	12	10,695	36.1	0.69	75%
Total	**111**	**120,727**	**503**	**0.73 ± 0.10**	**70%**

2.2. Coal characteristics

Indian coal (Gondwana coal) has high ash content (35–45%) and low calorific value (averaging 3820 kcal/kg in 2003–04 and 3603 kcal/kg in 2010–11). The sulfur content in Indian coals is less than those observed in the United States (1.0–1.8%) and Chinese coals (0.5–1.0%). The sulfur content in the Indian coal has a consumption-weighted average of 0.6% (Reddy and Venkataraman, 2002).

The high ash content and low calorific value affects the thermal power plant's operational efficiency and increases emissions per kWh generated. As a comparison, power plants in India use about 0.72 ± 0.10 kg of coal to generate 1 kWh, while a power plant in the USA of the same technology would consume 0.45 kg of coal per kWh (Chikkatur, 2008). The estimated annual coal consumption rates by state are listed in Table 1. The average thermal efficiency of the coal-fired power plants in India between 2004 and 2011 remained 32–33% (CEA, 2012) while this is peaking above 35% for the power plants in China (Seligsohn et al., 2009).

The high silica and alumina content in Indian coal ash is another problem, as it increases ash resistivity and reduces the collection efficiency at the electrostatic precipitators (ESPs). To address this issue, the government has mandated the use of coal whose ash content has been reduced to at least 34% in power plants in urban, ecologically sensitive, and other critically polluted areas. The

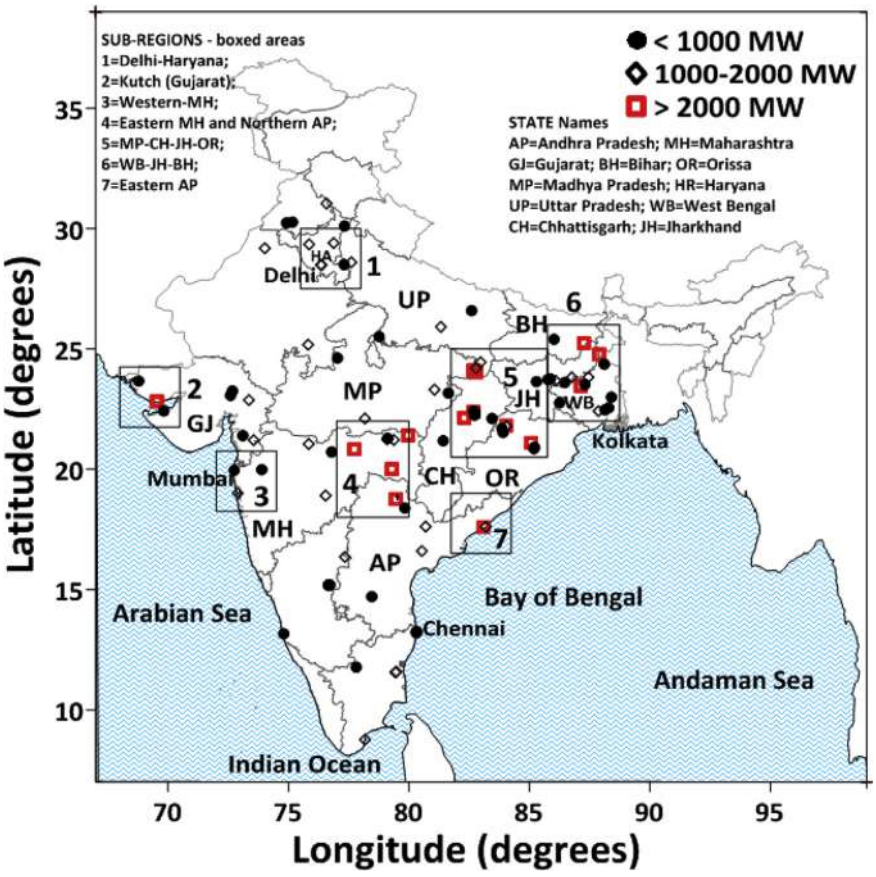

Fig. 1. Geographical location of the operational coal-based public and private power plants in India in 2012.

compliance with this mandate has been uncertain due to lack of access to the continuous monitoring data from the stacks.

Coal obtained from opencast mines has greater ash content – much of India's coal is mined using open caste methods and is likely to continue as such. In 2005, about 110 MT of coal ash was generated in India from more than 70 thermal power plants. Estimates for 2012 put this at 170 MT per annum (Bhangare et al., 2011).

2.3. Chemical transport dispersion model

Atmospheric dispersion modeling was conducted to study the impact of the emissions from the coal-fired power plants on the ambient PM concentrations and their health impacts. The modeling schematics are presented in the Supplementary Material. We utilized the ENVIRON – Comprehensive Air Quality Model with Extensions (CAMx), an Eulerian photochemical dispersion model, suitable for integrated assessments of gaseous and particulate air pollution over many scales ranging from sub-urban to continental. The model formulation, advection and scavenging schematics, chemical solvers, and gas-to-aerosol conversion mechanisms, are detailed in the model manual (http://www.camx.com). The model utilizes full gas phase SAPRC chemical mechanism (Carter et al., 2000) (217 reactions and 114 species) with two mode coarse/fine PM fractions including gas to aerosol conversions, for SO_2 to sulfates, NO_x to nitrates, and VOCs to secondary organic aerosols (SOA). The removal processes include dry deposition schemes using an updated approach with 26 landuse patterns and wet deposition due to predominant meteorological conditions. The most important advantage of CAMx is the use of 3D meteorology and independently controled plume rise and emission release point for each power plant, according to the stability profile at the plants location (Turner et al., 1986).

There are other atmospheric dispersion models, equally capable of carrying out this modeling exercise. The CAMx model was selected for its modular nature in characterizing and treating the plumes from point sources. Recent CAMx applications for similar modeling exercises include Huang et al. (2010) – an urban scale study to quantify the contributions of various sources to PM_{10} pollution in Beijing, China; Sun et al. (2012) – a regional study to simulate the changes in ozone concentrations due to new NO_x emission regulations in the power plants in Eastern USA; Emery et al. (2012) – a study on sources of background ozone concentrations over the USA and its policy implications; Wu et al. (2013) – a regional study evaluating the control policies for the sources of $PM_{2.5}$ in the Pearl River Delta region.

For the modeling domain, the meteorological data (3D wind, temperature, pressure, relative humidity, and precipitation fields) is derived from the National Center for Environmental Prediction (NCEP) (NCEP, 2012) global reanalysis database for the base year 2010–11 and processed through WRF 3.5 meteorological model at 1 h temporal resolution. An example animation for the wind speeds and wind directions at the surface level, mixing layer height, and precipitation fields, for one month are presented in the Supplementary Material. The initial conditions for the dispersion model were extracted from the MOZART global chemical transport model, for which an interface is available with the CAMx model. To further localize the initial conditions, the model was looped over each month for 10 days before starting the model calculations for the study analysis. The boundary conditions are also extracted from the MOZART global chemical transport model. After initializing the

model, the emissions from only the power plants were utilized in order to isolate the impacts of these emissions on the ambient concentrations.

The study domain extends from 7°N to 39°N in latitudes and 37°E to 99°E in longitudes at 0.25° grid resolution (Fig. 1). The vertical resolution of the model extends to 12 km stretched over 23 layers, with the lowest layer designated at 50 m and six layers within 1 km to advance vertical advection closer to the ground level.

2.4. Health impacts

In India, the morbidity and mortality burden of outdoor air pollution, is particularly costly in terms of work days lost, lost productivity, and loss in terms of gross domestic product, approximately USD 23.4 billion and 1.7% of national GDP in 2009 (World-Bank, 2012). Since, most of the pollution related deaths occur within a year or two of exposure, reducing PM pollution from sources like transport and power plants has immediate benefits for health and national economy. The direct link between outdoor air pollution and human health has been extensively documented under the 2010 GBD study (IHME, 2013). Epidemiological studies conducted in India have consistently demonstrated higher rates of respiratory and cardiovascular diseases in populations exposed to PM, NO_x, and ozone pollution (Chhabra et al., 2001; Pande et al., 2002; Gupta et al., 2007; Wong et al., 2008; CBHI, 2010; Siddique et al., 2010; Balakrishnan et al., 2013).

The total health risk for mortality is quantified using the relative risk functions for various endpoints defined as

$$\delta E = \sum_{i=1}^{\#grids} \frac{(RR_i - 1)}{(RR_i)} * \delta POP_i * IR \quad (1)$$

$$RR_i = \exp(\beta * \delta C_i) \quad (2)$$

The total health risk for morbidity is quantified using the following equation for various endpoints

$$\delta E = \sum_{i=1}^{\#grids} \beta * \delta C_i * \delta POP_i \quad (3)$$

where

δE = number of estimated health effects (various end points for mortality and morbidity).
IR = incidence rate of the mortality and morbidity endpoints. A total death incidence rate for India is set at 7.1 per 1000 inhabitants.
δPOP = the population exposed to the incremental concentration δC in grid i; defined as the vulnerable population in each grid. The gridded population is estimated using GRUMP (2010) for the model resolution of 0.25°. The total population of 1.2 billion is adjusted to Census-India (2012) by state totals, with the urban centers accounting for 30% of the total.
RR = relative risk for mortality and morbidity end points.
β = the concentration–response function; which is defined as the change in number cases per unit change in concentrations per capita. For all-cause mortality in this study, the function is defined as 3.9% change in the mortality rate per 4 μg/m^3 of change in the $PM_{2.5}$ concentrations (Hart et al., 2011). The uncertainties involved in the risk assessments are detailed in IHME (2013) for long term integrated exposures. The morbidity effects are calculated as cases of asthma attacks, chronic bronchitis, hospital admissions, and work days lost, for which the concentration–response functions are extracted from Abbey et al. (1995) and World-Bank (2012).
δC = the change in concentrations from the ambient standards in grid i; an output from the CAMx dispersion model as the annual average $PM_{2.5}$ concentration due to the coal-fired power plant emissions.

This methodology of relative risk and concentration–response function was applied for similar studies – IHME (2013) and Ostro (2004) for GBD assessments for 2010 and 2000 respectively; Bell et al. (2006) for health impacts of urban air pollution in the cities of Santiago, Mexico city, and Sao Paulo; GAINS (2012) for Asia and Europe regional studies evaluating the impacts in terms of life years lost due to baseline air pollution or benefits in life years saved due to future controls; Yim and Barrett (2012) for premature deaths in the United Kingdom caused by long-range transport of combustion emissions from the European Union; Cropper et al. (2012) for benefits of better environmental regulations in controlling pollution from coal fired power plants in India; Guttikunda and Jawahar (2012) for health impacts of urban air pollution in 2 large, 2 medium, and 2 small cities in India; Guttikunda and Goel (2013) for a megacity Delhi and its surrounding satellite cities.

3. Results and discussion

3.1. Atmospheric emissions

For 2010–11, the total estimated annual emissions are 580 ktons for $PM_{2.5}$, 1200 ktons for PM_{10}, 2100 ktons of SO_2, 2000 ktons of NO_x, 1100 ktons of CO, 100 ktons of VOCs and 665 million tons of carbon dioxide (CO_2). The total estimated emissions by state are presented in Table 2. The total emission rates are calculated based on the boiler size, coal consumption rates, and control equipment efficiencies, which is collected from thermal power plant performance reports (CEA, 2011; CEA, 2012). For the emissions input to the dispersion model, the annual emissions were further segregated by month, based on the coal-consumption data by month from the power plants. The diurnal cycle of the emissions was kept constant by month.

3.1.1. Emission factors

We summarized the regional emission factors for the coal based power plants in Table 3 in both tons/PJ and tons/h. The latter is for comparisons with any data available from the online monitoring. Previously published studies are regional estimates either for all of India and for all the power plants in Asia, and most are estimated for the base year 2000–05 and prior. A serious lack of monitoring data availability from the stacks, results in uncertainty estimates of emission factors. The overall uncertainty in the total emission estimates is ±20%, stemming from the variations in the information at the plant level on in-use coal characteristics, coal consumption rates, efficiencies in control operations, and emission factors.

3.1.2. Emission regulations

Comparative emission rates as gm/kWh for NO_2, SO_2, and $PM_{2.5}$ is presented in IEA (2012) for France, Germany, Italy, United Kingdom, China, India, Russia, the United States, Canada, Japan, South Africa, and Australia (Supplementary Material). Under the current emission regulations, the emissions rates are the highest in Russia and India. China, the United States, the European Union (EU) and Australia have stronger regulations (Table 4). Even with 55% of the installed coal-based generation capacity, there is a conspicuous lack of regulations for SO_2, NO_x, and Mercury emissions. There is also no continuous and open emission monitoring data available at

Table 2
Total annual emissions (rounded) from coal based power plants in India in 2010–11.

State	$PM_{2.5}$ tons	PM_{10} tons	SO_2 tons	NO_x tons	CO tons	VOC tons	CO_2 million tons
Andhra Pradesh	51,500	107,500	199,500	187,500	104,000	9500	62.8
Bihar	15,500	31,000	43,000	39,500	22,500	2500	13.5
Chhattisgarh	39,000	84,000	187,000	172,500	97,500	9000	58.9
Delhi	7500	14,500	20,500	20,000	11,000	1000	6.4
Gujarat	53,000	111,000	214,000	220,000	122,500	11,500	74.0
Haryana	23,500	50,000	100,500	93,500	52,500	5000	31.7
Jharkhand	15,500	31,500	50,500	48,500	26,500	2500	15.9
Karnataka	17,500	36,000	61,500	58,500	32,000	3000	19.4
Madhya Pradesh	49,500	100,000	139,500	130,500	73,000	7000	43.9
Maharashtra	80,500	167,000	300,500	278,500	156,500	14,500	94.6
Orissa	40,000	85,000	171,000	159,500	89,500	8500	53.9
Punjab	16,500	34,000	56,000	53,000	29,000	3000	17.5
Rajasthan	14,500	30,000	55,500	52,000	29,000	3000	17.5
Tamilnadu	36,500	74,000	108,500	104,500	56,500	5500	34.2
Uttar Pradesh	83,500	168,500	235,500	225,000	122,500	11,500	74.1
West Bengal	40,000	83,500	152,000	143,000	79,000	7500	47.8
Total	**580,000**	**1,200,000**	**2,100,000**	**2,000,000**	**1,100,000**	**100,000**	**665.4**

the plant level, which makes enforcement of what standards do exist, nearly non-existent.

3.1.3. Particulate emissions

The total PM emissions from the power plant stacks are regulated as concentrations and vary with boiler size. For example, for the plants with generation capacity more than 210 MW, the PM concentration limit is 150 mg/Nm^3 and for the plants with generation capacity less than 210 MW, the limit is 350 mg/Nm^3. These limits are much weaker compared to those practiced limits in Australia, China, USA, and EU. The limit for the smaller plants is 150 mg/Nm^3, if they are located in an urban, ecologically sensitive, and other critically polluted areas – which is at the discretion of MoEF. A breakup in the emissions regulation at 210 MW also led to installation of smaller boilers at most of the power plants (Table 1). Approximately 70% of the operational units in the country are of the size less than or equal to 210 MW and these units tend to have the worst net efficiency and plant load factor. The newer plants are mostly 500 MW or higher with the best net efficiency of more than 33% (CEA, 2012).

Differential emission regulations also tend to result in use of control equipment with low efficiency and higher emissions. For example, the Kolghat power plant in West Bengal state has 6 units of 210 MW and the Raichur power plant in Karnataka state has 7 units of 210 MW, each with a total generation capacity of more than 1000 MW, are allowed to adhere to the lower emission standard, only because the individual boiler size is less than or equal to 210 MW.

PM is the only pollutant for which any pollution controls are widely applied. A schematic of a coal-fired power plant is presented in Fig. 2 that shows flue gas from the boilers at high temperature and velocity passing through heat exchangers to recycle the residual energy. This then enters the particulate control equipment (ESPs and cyclone bag filters) for removal of entrained ash. ESPs are installed in all coal-fired power plants in India. As removal efficiencies at ESPs are higher for coarse particles, most of the PM dispersing from the top of the stack is in the size range of respirable PM (10 μm or less). Lu et al. (2010) measured fractions of 50–60% $PM_{2.5}$ and 90–95% PM_{10} in the total filterable PM in the flue gas at a 660 MW power plant. The PM in the flue gas also contains high concentrations of heavy metals such as arsenic, lead, cadmium, mercury, copper, and zinc, which not only contributes to potential health hazard than the bottom ash (Finkelman, 2007), but also increases the resistivity and reduces the ESPs collection efficiency to as low as 98%. Reddy et al. (2005) measured the chemical composition of the bottom ash, fly ash, and flue gas from a coal fired power plant in the western India and estimated 1–7% of zinc, 2–7% of copper, 5–8% of manganese, 7–10% of cobalt, 12–18% of

Table 3
Regional emission factors database.

Resource	Base year	$PM_{2.5}$	PM_{10}	SO_2	NO_x	CO	VOC
This study[c,a]	2010–11	49–68	90–138	174–192	177–189	100	9
Streets et al. (2003)[a]	2000			400–762	219–562		
GAINS (2012) (base)[d,a]	2000–05	53–261	18–374	69–1380	100–270		1–15
GAINS (2012) (controlled)[e,a]	2000–05	13–27	19–43	27–69	20–54		1–15
Ohara et al. (2007)[f,a]	2000			504	267	154	
Garg et al. (2006)[g,a]	2000		251	367	205	56	
Lu and Streets (2012)[h,a]	1996–2006				177–410		
This study[i,b]	2010–11	0.3–1.4	0.6–2.8	1.0–4.0	0.9–3.7	0.5–2.0	0.05–0.2
Kansal et al. (2009)[j,b]	2004–05		0.7–1.1	4.0–5.0	1.2–1.8		

[a] Units: tons/PJ.
[b] Units: tons/h.
[c] The range corresponds to the averages over the states.
[d] Base line factors for various technologies without or limited controls, global program.
[e] Base line factors with best available control technology for each pollutant, global program.
[f] The emission factor segregation was for China, Japan, and Others in Asia.
[g] Calculated as ratios of total emissions and coal consumption corresponding to the power sector, PM factor is for total suspended particulates.
[h] The range corresponds to coal fired boilers with and without low NO_x burner technology, by boiler size.
[i] Range corresponds to the estimated average emission rate per plant in each state.
[j] PM factor is for total suspended particulates; based on measurements at one station in Delhi per stack.

Table 4
Summary of emission standards for coal-fired power plants.

Country	PM	SO_2	NO_2	Mercury
India[a]	350 mg/Nm^3 for <210 MW 150 mg/Nm^3 for >210 MW	None	None	None
China[b]	30 mg/Nm^3 (proposed all) 20 mg/Nm^3 for key regions	100 mg/Nm^3 for new 200 mg/Nm^3 for old 50 mg/Nm^3 for key regions	100 mg/Nm^3	None
Australia[c]	100 mg/Nm^3 for 1997–2005 50 mg/Nm^3 after 2005	None	800 mg/Nm^3 for 1997–2005 500 mg/Nm^3 after 2005	In discussion based on USA standards
European Union[c]	Pre-2003 100 mg/Nm^3 for <500 MW 50 mg/Nm^3 for >500 MW Post 2003 50 mg/Nm^3 for <100 MW 30 mg/Nm^3 for >100 MW	Pre-2003 Scaled for <500 MW 400 mg/Nm^3 for >500 MW Post 2003 850 mg/Nm^3 for <100 MW 200 mg/Nm^3 for >100 MW	Pre-2003 600 mg/Nm^3 for <500 MW 500 mg/Nm^3 for >500 MW Post 2003 400 mg/Nm^3 for <100 MW 200 mg/Nm^3 for >100 MW	In discussion
USA[c,d]	37 mg/Nm^3 for old 6 mg/Nm^3 for new	245 mg/Nm^3 for old 50 mg/Nm^3 for new	61 mg/Nm^3 for old 42 mg/Nm^3 for new	
USA[c,e]	6.4 gm/GJ	640 gm/MWh	720 gm/MWh for old 450 gm/MWh for new	0.08 gm/MWh for lignite 0.01 gm/MWh for IGCC

[a] From Central Pollution Control Board (India) (http://cpcb.nic.in/Industry_Specific_Standards.php). Last accessed Feb 17th, 2013. Besides PM, only national ambient standards exist.
[b] From standards information in Chinese (http://www.zhb.gov.cn/gkml/hbb/qt/201109/t20110921_217526.htm). Last accessed Feb 17th, 2013. Prior to 2011, the standards were based on commissioning year (before 1996, 1997 to 2004, and after 2004).
[c] Power stations emissions handbook (http://www.ccsd.biz/PSE_Handbook). Last accessed Feb 17th, 2013.
[d] Emission rates are translated to mg/Nm^3 based on assumed plant efficiency.
[e] In official units; for mercury this is based on 12 month rolling average.

cadmium, 60–70% of selenium, 70–80% of mercury, and traces of arsenic, iron, lead, and chromium contained in the coal was emitted in the flue gas. Similar levels of entrainment were reported in an estimate of total trace metal emissions from coal fired power plants in China (Chen et al., 2013).

Besides flue gas PM emissions, fugitive dust from coal-handling plants and ash ponds (after the disposal from the plants) is a problem. According to CEA, after the combustion and application of control equipment, ash collection at the power plants ranged 70–80% of the total ash in the coal (CEA, 2011; CEA, 2012). It is assumed that the remaining ash is dispersed from the stacks. In 2003, an amendment notification from MoEF mandated 25% of bottom ash in all brick kilns within 100 km radius of any coal based thermal power plant and all building construction within 100 km for any coal-fired thermal power plant to use 100% ash based bricks, blocks, and tiles. To date, percentage of ash utilized in the construction industry is low – approximately 13% used for brick manufacturing and other construction activities.

3.1.4. Gaseous emissions

There are no legally mandated emission standards for SO_2. Only a handful of coal-fired power plants operate flue gas desulfurization (FGD) units and among those to be commissioned through 2020, only 7 power plants are listed to have FGD (Prayas, 2011). The FGD systems could range from in furnace control via limestone injection, wet scrubbing of flue gas, to capturing SO_2 in the flue gas through industrial processes (Fig. 2). Presence of a FGD system further improves removal of PM.

In India, for SO_2, only the stack heights are mandated assuming that the emissions will be dispersed to farther distances and thus diluting the ambient concentrations. For example, MoEF requires all power plants with generation capacity more than 500 MW to

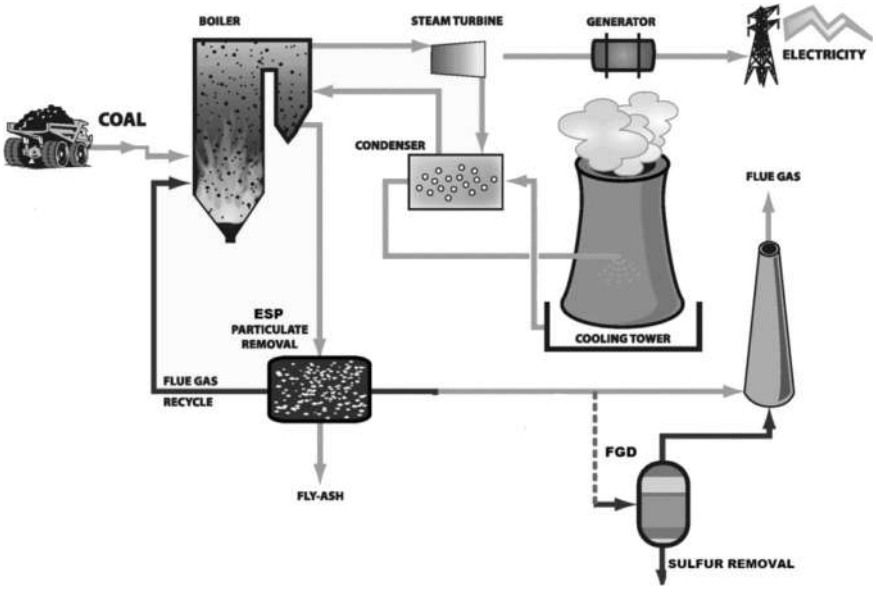

Fig. 2. Simplified schematics of coal-fired power plant operations.

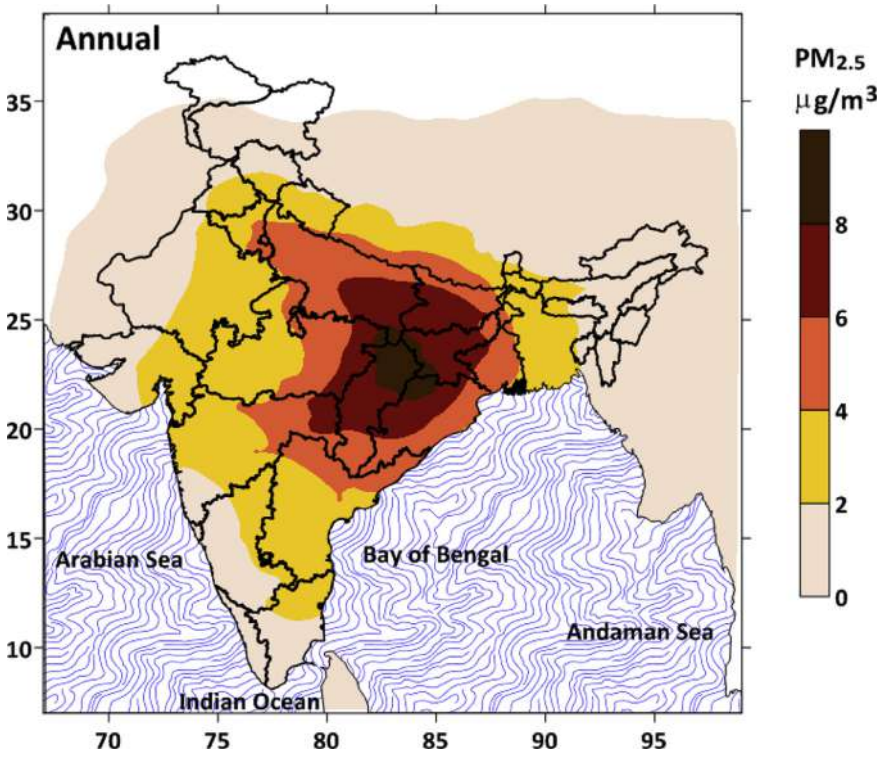

Fig. 3. Modeled annual average ambient $PM_{2.5}$ concentrations due to the emissions from coal-fired thermal power plants in India.

build a stack of 275 m; those between 210 MW and 500 MW to build a stack of 220 m; and those with less than 210 MW to build a stack based on the estimated SO_2 emissions using a thumb rule of height $= 14^*(Q)^{0.3}$ where Q is the estimated SO_2 emissions rate in kg/h. The stack heights for old power plants ranged between 150 m and 220 m.

Despite an estimated 30% of the total NO_x emissions in India originating from power generation (Garg et al., 2006; GAINS, 2012), there are no regulations to control these emissions. Some of the new installations and extensions are equipped with low-NO_x burners, with little details on their operational performance (Chikkatur et al., 2011).

3.1.5. Previous estimates

Few studies have reported emission rates and total emissions from the power plants in India. One national emissions inventory for the coal and gas based power plants is maintained by the GAINS program at the International Institute for Applied Systems Analysis (IIASA, Austria), which for the base year 2005, estimated total emissions of 490 ktons for $PM_{2.5}$, 1900 ktons for SO_2, 1300 ktons for NO_x, 43 ktons of VOCs. A major difference between GAINS and this study is in the database of plants, which is updated for the new installations and extensions for the existing plants, and assumed control efficiencies. A database of coal characteristics, control efficiencies, and emission rates is available online (GAINS, 2012). Another global emissions inventory by specific sectors is EDGAR with estimates for base year 2008 (http://edgar.jrc.ec.europa.eu). Average emission factors for PM, SO_2, NO_x, CO, and BC for all combustion sectors for base year 2000 are presented in Streets et al. (2003).

The CEA also reports, as part of the power plants performance evaluation, the emissions for total suspended PM in mg/Nm^3 (CEA, 2012). Since, these are not continuous measurements and mostly observed at select times during the year, it was difficult to either confirm or reject the estimates based on them. Kansal et al. (2009) studied the emissions from six coal and gas fired power plants in and around Delhi, based on the reported measurements, which tend to underestimate the contribution of power plant emissions to the region (Guttikunda and Goel, 2013). Similarly, based on intermittent measurements Cropper et al. (2012) estimated average emissions of 110 ktons/year for $PM_{2.5}$ from 92 coal fired power plants.

For NO_x, Prasad et al. (2012) studied the influence of thermal power plants on tropospheric NO_2 column measurements from the ozone monitoring instrument (OMI) onboard aura satellite (http://aura.gsfc.nasa.gov) and also studied the algorithm to deduce ground level concentrations, which could reflect the power plant emissions. This study particularly highlights the cluster regions over the states of Delhi, Haryana, Indo-Gangetic plains, and most of central India with the highest concentrations possibly originating from the power plants. Lu and Streets (2012) also studied the satellite data and further estimated the emissions based on boiler size and coal consumed for the period between 1996 and 2010, which overlays the changes in satellite observations to the newer installations and extensions commissioned during this period. They estimated a 70% increase in the column NO_x concentrations during this period, with the power plants contributing a total estimated 2300 ktons NO_x emissions for 2010.

3.2. Atmospheric dispersion

3.2.1. Ambient pollution

The atmospheric dispersion simulation was carried out for 11 days per month from 10th to 21st of each month and averaged to obtain monthly, seasonal, and annual concentrations. The modeled annual average $PM_{2.5}$ concentrations due to emissions from coal based power plants only are presented in Fig. 3. The modeled monthly average concentration maps and animations of modeled

daily average concentrations are presented in the Supplementary Material. The largest impact is felt over most of the central-east India including states of Maharashtra, Madhya Pradesh, Chhattisgarh, and Orissa, with the largest coal-fired power plants. Similar observations are reported based on satellite measurements of column NO_2 concentrations (Lu and Streets, 2012; Prasad et al., 2012).

For $PM_{2.5}$ concentrations in Fig. 3 includes fine PM, sulfate, and nitrate concentrations (from chemical conversion of SO_2 and NO_x emissions, using the predefined chemical mechanisms in CAMx). The concentrations are an incremental pollution from the coal-fired power plants only, which is considered in addition to the pollution from transport, domestic, and other industrial activities, on an annual basis. The population weighted concentration due to the coal-fired power plant emissions only is 3.6 $\mu g/m^3$. The national ambient annual average standard for $PM_{2.5}$ is 40 $\mu g/m^3$ and the WHO guideline is 10 $\mu g/m^3$.

The PM pollution in Central India, covering the states of Madhya Pradesh, Jharkhand, Orissa, and Chhattisgarh, is the highest due to the density of the power plants in the region and high installed generation capacity, due their proximity to the coal mines. The Delhi-Haryana region with the highest population density with more than 21.5 million inhabitants in Delhi and its satellite cities is exposed to higher PM pollution from coal-fired power plants. The range of modeled PM pollution in 7 sub-regions is presented in Table 5. The coastal regions experience the least of the PM pollution due to strong land-sea breezes, with much of the pollution dispersed over the seas. To date the inland power plants are still the majority in the country and a serious threat to human health and other environmental concerns.

- The Korba cluster (State: Chhattisgarh (CH)) has a combined generation capacity of 4380 MW between four power plants located within a 10 km radius. Major cities in the Korba region are Ranchi, Jamshedpur, Rourkela, Jabalpur, Nagpur, and Raipur (capital of Chhattisgarh).
- The Jhajjar cluster (State: Haryana) has a combined generation capacity of 2700 MW between two power plants within the radius of 10 km, with an additional power plant with 1000 MW under construction. The city of Delhi is 70 km from the Jhajjar cluster.
- The Mundra cluster (State: Gujarat (GJ)) has a combined generation capacity of 9620 MW between two private sector power plants located within 5 km radius. Major cities in the Mundra region are Jamnagar (major industrial port), Rajkot, and Ahmedabad (300 km away, with two local power plants of 1000 MW).
- The Mumbai cluster (State: Maharashtra (MH)) has one coal based power plant in Trombay and multiple gas powered plants.

While the impact of the emissions is felt within 200 km of the power plants, under windy conditions the influence can be tracked to distances as far as 400 km from the source region. The animated forward trajectories over one day for the coal-fired power plants in Korba, Jhajjar, Mumbai, and Mundra clusters, for three months (April, July, and October), is presented in the Supplementary Material. The forward trajectories illustrate that the emissions from these high stacks affects the regions and people far away from the source region and this should be accounted for in the environmental impact assessments of the coal-fired power plants, which under the current regulations is limited to only 50 km radius, from the power plant stacks (MoEF, 2010).

3.2.2. Seasonal variations

Generally, the wind speeds at 200 m or above are much faster than those observed at the ground level. The release of the emissions at the stack height plus any uplift due to the flue gas velocity and temperature, dictates the movement of the emissions and its vertical diffusion towards the ground. The forward trajectories presented in the Supplementary Material for the select clusters, further demonstrates the fast movement of the power plant plumes

Table 5
Installed capacity, modeled daily average $PM_{2.5}$ concentrations, health impacts of emissions from coal fired power plants for 7 regions at finer resolution in India in 2010–11.

No.	Cluster (size in degrees)	Regional features	No. of plants (those more than 1000 MW)	Installed capacity (MW)	Modeled $PM_{2.5}$[a] – median (95th percentile) $\mu g/m^3$	Estimated premature mortality within the region[b]
1	Delhi – Haryana (2.5° × 2.5°) (in-land)	Delhi is the national capital, listed among the top 10 cities with worst air quality in the world (WHO, 2011) and Haryana is an agricultural state	8 (5)	8080	3.9 (7.7)	6400–8800
2	Kutch (Gujarat) (2.5° × 2.5°) (coastal)	A coastal cluster, with two super-critical power plants in Mundra (Gujarat), both private, operated by Tata and Adani power groups	5 (2)	9900	1.0 (2.8)	100–120
3	Western-MH (2.5° × 2.5°) (coastal)	Including Mumbai, the most commercial and congested city in the country	3 (1)	2780	0.9 (2.3)	1700–2400
4	Eastern MH and Northern AP (3.0° × 4.0°) (in-land)	All plants are located closer to the coal belts of Chandarpur and Ghugus (Maharashtra – MH) and Singareni (Andhra Pradesh – AP)	10 (6)	14,800	3.2 (5.1)	1100–1500
5	MP–CH–JH-OR (4.0° × 4.5°) (in-land)	This cluster covers four states – Madhya Pradesh (MP), Jharkhand (JH), Chhattisgarh (CH) and Orissa (OR) and home to the largest coal fields of Jharia, Dhanbad, Korba, Singrauli, Karanpura, and Mahanadi	21 (10)	29,900	9.1 (23.1)	7900–11000
6	WB–JH–BH (3.0° × 4.0°) (in-land)	This cluster covers West Bengal (WB), JH, and Bihar (BH) sourcing mostly from Raniganj and Jharia coal belts	19 (7)	17,100	3.7 (5.6)	10700–14900
7	Eastern AP (2.5° × 2.5°) (coastal)	A coastal cluster including the port city of Vishakhapatnam	2 (2)	3000	0.8 (1.8)	1100–1500

[a] The $PM_{2.5}$ concentrations are modeled grid averages and is the concentration due to the emissions from the coal-fired power plants only, which is incremental to pollution from other sources in the region. For these sub-regional domains, the CAMx dispersion modeling was repeated @ grid resolution of 0.1°, equivalent of 10 km. Median and 95th percentile value is based on averages for all the grids in the select sub-regional domain.

[b] This is the estimate for the exposed population in the select geographical sub-region, but the influence of the power plant emissions reaches farther (illustrated in the forward trajectories – Supplementary Material).

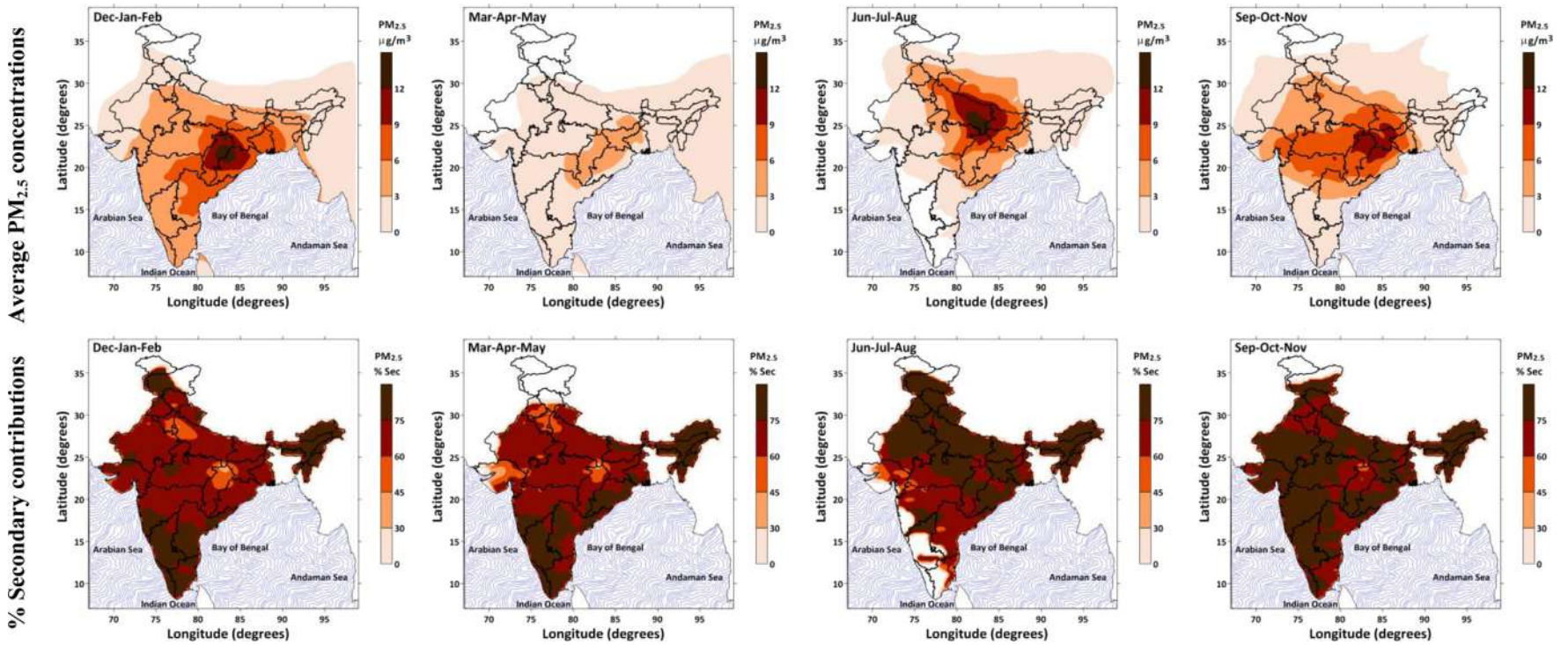

Fig. 4. Dispersion modeling results by season (Dec–Jan–Feb for winter; Mar–Apr–May for spring; Jun–Jul–Aug for summer; and Sep–Oct–Nov for fall) due to the emissions from coal fired thermal power plants in India (a) average $PM_{2.5}$ concentrations (b) percentage contribution of secondary (sulfates and nitrates) aerosols to average $PM_{2.5}$ concentrations by season.

in India. The meteorological conditions have a large variation in the subcontinent between the monsoonal and non-monsoonal months. This variation also affects the dry and wet deposition and the ambient concentrations of various pollutants. In Fig. 4, we present the seasonal average concentrations – Dec–Jan–Feb for winter, Mar–Apr–May for spring, Jun–Jul–Aug for summer, and Sep–Oct–Nov for fall season. The south-west monsoons from the Arabian Sea during the months of April to August tend to push and disperse the emissions upwards and north, while the north-east monsoons from the Bay of Bengal Sea during the months of October to November tend to push and disperse the emissions inland and south resulting in a wider spread of pollution. For the spring season, beginning of the south-west monsoon, strong winds and higher mixing heights were observed (Supplementary Material), which tend to lift the pollution higher into the troposphere, resulting in lower ground concentrations. In the later months, the cloud cover is higher, reducing the mixing heights, and increasing the ground level concentrations. There is much uncertainty in the monsoons and weather patterns that could not only influence the pollution patterns, but also there is growing evidence that the pollution from transport and industrial processes can affect the monsoonal patterns (Corrigan et al., 2006; Lau et al., 2009).

3.2.3. Secondary chemical contributions

The CAMx modeling system includes full gas phase SAPRC chemical mechanism, with gas and aerosol chemical conversions to support secondary particulate pollution assessment. With no FGD systems to control SO_2 emissions at most of the power plants, the secondary contributions are significant. SO_2, once airborne, further interacts with the hydroxyl radicals to form aerosol sulfates. The formation of aerosol nitrates is more complicated due to the involvement of the multiple nitrogen species and numerous chemical reactions with hydroxyl radicals and volatile organic compounds.

The percentage contribution of the secondary aerosols (sulfates and nitrates) to total $PM_{2.5}$ from the coal fired power plants in presented in Fig. 4. The maps are presented by season, Dec–Jan–Feb for winter, Mar–Apr–May for spring, Jun–Jul–Aug for summer, and Sep–Oct–Nov for fall season. The highest secondary contributions were estimated for the summer months. This is partly due to the higher photochemical activities and presence of oxidizing agents, which increase the oxidation of SO_2 and NO_x gases and their conversion rate to sulfates and nitrates.

From the coal-fired power plants, we estimate 30–40% of the PM pollution is secondary in nature, with the most coming from chemical conversion of gaseous SO_2 to aerosol sulfate. Since a majority of the power plants do not operate a dedicated FGD system, most of the SO_2 from coal combustion is emitted and ends up in respirable PM fraction, resulting in more health impacts. In the environmental impact assessment studies, which is required before commissioning any power plant, a provision for a FGD is discussed, but the power plants are not required to operate a FGD. The combined benefits of a FGD in conjunction with the already operational ESPs will have a significant effect on overall health impacts. We believe that FGD technology should become mandatory for all new power plants and a provision should be introduced to implement the same for the larger and older power plants to control SO_2 emissions and to reduce the overall $PM_{2.5}$ concentrations by at least 30–40%.

3.3. Mortality and morbidity estimates

The health impacts are calculated by overlaying the gridding population with the modeled $PM_{2.5}$ pollution from the coal fired power plants. Total premature mortality using for the range of mortality risks ranged between 80,000 and 115,000 per year. The estimated mortality and morbidity cases due to these emissions are summarized in Table 6. Using a conservative value of INR 2,000,000 (approximately USD 40,000) per life lost, based on the average life insurance policy's issued in India, the estimated premature deaths would result in a health cost of INR 16,000 to 23,000 crores (approximately USD 3.2 to 4.6 billion) annually.

In Table 5, we also present the estimated range of premature deaths for the population exposed in the sub-regions. The regions 1 (Delhi–Haryana–Uttar Pradesh) and 6 (West Bengal–Jharkhand–Bihar) are the densest, with average population density above 1000 per km^2, with peaks of more than 10,000 per km^2 in the cities of Delhi (capital of India) and Kolkata (capital of West Bengal). These regions also experience highest risk of exposure. These seven sub-regions account for 40% of the total premature deaths estimated for India.

4. Implications

Coal remains the main fossil fuel for power generation in India. In this study, we isolated the emissions from the coal-fired power plants and estimated a premature mortality rate of 80,000 to 115,000 due to their contribution to the ambient $PM_{2.5}$ concentrations. This number does not include the impacts of the water run-off and soil contamination due to the release of heavy metals. Combined with a strong demand for reliable electricity and consistent shortage in supply, it is doubtful that pollution will be controlled absent strong regulation for the operational 111 coal-fired power plants. There is a vast potential for controlling emissions from these plants and the resultant health impacts. The main conclusions from this analysis are the following

- To date, the pollution standards exist only for ambient air quality and not for individual power plants, which compromises the efforts to control any pollution. Only after standards are regulated at the plant level, can we proceed to the next steps of monitoring and enforcing, and reduce the impact of emissions from coal-fired power plants
- Going forward, coal-fired power plants should be subjected to tighter emission standards, similar to those found in emerging economies (like China) and developed economies (like EU, Australia, and USA). For example, a mandate for installation of FGD systems for the existing 111 coal-fired power plants could reduce the $PM_{2.5}$ concentrations by 30–40%, by eliminating the formation of secondary sulfates and nitrates, and some additional benefits to the primary particulates
- The efficiency improvement of existing older power plants, irrespective of the boiler size, should become a starting point for reducing overall coal consumption and associated atmospheric emissions
- Unlike pollution from the transport or domestic sector, pollution from stacks is a point source – meaning a finite and known

Table 6
Estimated 2010-11 health impacts due to emissions from the coal-fired power plants in India.

Effect	Health impacts
Total premature mortality	80,000 to 115,000
Child mortality (under 5)	10,000
Respiratory symptoms	625 million
Chronic bronchitis	170,000
Chest discomforts	8.4 million
Asthma attacks	20.9 million
Emergency room visits	900,000
Restricted activity days	160 million

number of units releasing emissions. Moreover, with a majority of the power plants operated by the public sector, mandating technologies that reduce pollution would seem to represent a simple solution.

- The stack emissions can be monitored relatively easily as compared to non-point sources (such as vehicles, garbage burning, domestic burning, and fugitive dust). While, the larger power plants are now equipped with continuous stack monitors, this information is not open to public, either for analysis or for scrutiny of the emission loads. This adds to the uncertainty of similar studies. Besides strengthening standards, newer policies are required for dissemination of information from the coal-fired power plants
- The environmental impact assessment procedures need to be revised, in order to include the health and environment damages due to long-range transport of pollution from the stacks, as high as 275 m, and travelling the distances of more than 300 km in less than 24 h. Currently, the procedure require assessment for an area of 50 km radius from the plants

In India, the amount of power generated from coal will remain high at least through 2030 (Prayas, 2011, 2013), and unless a better way is proposed to manage pollution from the coal-fired thermal power plants, the environmental effects and human health costs will be high.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2014.04.057.

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LONG TERM AIR QUALITY ANALYSIS IN REFERENCE TO THERMAL POWER PLANTS USING SATELLITE DATA IN SINGRAULI REGION, INDIA

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KEYWORDS: Air quality; NASA GES data; Anthropogenic activities; Thermal Power Plants; Singrauli region.

ABSTRACT

The exponentially growing population and related anthropogenic activities have led to modifications in local environment. The change in local environment, evolving pattern of land use, concentrations of greenhouse gases and aerosols alter the energy balance of our climate system. This alteration in climate is leading to pre-mature deaths worldwide. This study analyses the air quality of Singrauli region, Madhya Pradesh, India for the past 15 years. Otherwise known as Urjanchal "the energy capital" of India has been declared as critically polluted by CPCB. The study provides an updated list of thermal power plants in the study area and their emission effects on the local environment. The pollutants analyzed in the study are carbon dioxide, methane, nitrogen dioxide, Sulphur dioxide and particulate matter. Long term remotely sensed data was obtained from NASA Giovanni for past 15 years. Statistical analysis is used to characterize seasonal and annual variations of trace gases in the study area. The study concluded that Methane, Carbon dioxide, Nitrogen dioxide and Sulphur dioxide are on an increasing trend with an average rate of 1.03, 0.99, 2.15 and 1.09 annually. Secondly, Methane & SO_2, $PM_{2.5}$ & NO_2, PM_{10} & NO_2, CO_2 & Methane and $PM_{2.5}$ & PM_{10} have strong correlations with a 95% significance. Furthermore, Methane, SO_2 and CO_2 exhibit cyclic variation with change in season. The study also indicated that maximum aerosols present in the study area are a result of anthropogenic activities.

1. INTRODUCTION

Air pollution is heeded as a damnation for global environment. In addition to natural sources contributing to pollution, increased industrialization with inter-twined economic, technologic and political change aggravates the burden. Air pollution encases numerous trace gases including; Carbon dioxide (CO_2), Nitrogen dioxide (NO_2), Sulphur dioxide (SO_2), particulate matter ($PM_{2.5}$ & PM_{10}) carbon monoxide (CO) (Chen et al.,2007). Each pollutant may originate from different sources, however, are interlinked with fuel combustion and/or industrial activities. In addition to the crippling effect on the environment, pollutants have an adverse effect on human health, crops and ecosystem. In the year 2012, 3 million deaths were attributed to air pollution globally (WHO, 2016). Henceforth, it is pivotal to monitor the air quality and take informed decisions regarding its impact on the environment.

Air pollution has become a transnational issue, compelling organizations to work on a united front. The exponential rise in industrialization during past few decades have resulted in elevated concentration of greenhouse gases worldwide. While small concentration of greenhouse gases favor in warming the earth, the escalated concentration from anthropogenic activities, intensifies their effect. At a global level, industrialization established a shift in the air quality worldwide during mid-18th century. A rapid increase in SO_2 is observed from 1850 (1.36 M tonnes) to 1980 (71.25 M tonnes) in Europe. Similar patterns are seen for North and South America peaking at 30.46 M tonnes and 8.76 M tonnes respectively in 1980. Further, the SO_2 emission follows a decreasing trend. On the other hand, in Asia and Africa, the SO_2 emissions are increasing. Similarly, carbon dioxide emission annual trends grew much earlier in Europe and America than other regions around the world (OECD, 2014; Klimont et al., 2013). At present, China, is the lead emitter of carbon dioxide followed by United States, European Union, India and United Kingdom (Ritchie and Roser, 2020). Moreover, 49.04% of the global CO_2 emissions results from electricity and heat production sector. Emission of distinct pollutants and particulate matter (PMs), owing to industrial development, heavy motor vehicle uses and greater population density, has grown rapidly in demographic areas (Moorthy et al., 2016)

Globally, about 2/3rd of total electricity generated is produced from thermal power plants. It has been cogent that countries with strict emission regulations have low greenhouse gases emission. For instance, NO_x emissions have reduced by 50% in 2000 as compared to past decade in 6 states along Ohio River region comprising of West Virginia, Ohio, Illinois, Pennsylvania, Kentucky, Indiana (Frost et al., 2006). Furthermore, average NOx intensity in US is calculated to be 1.09g/kWh during 2010 (Tian et al., 2013). On the other hand, models predict 1.7-1.8 times increase of CO_2 emissions by 2030 and 2.6-2.7 times by 2050 in Russia. Similarly, an increase of 5.4% CO_2 has been estimated between 1990-2000 and an increase of 48.4% has been anticipated by 2010 (Hammons, 2006). An inventory study in China suggested that a coal fired thermal power plant emits 400-450mg/m^3 NO_x and 600-700mg/m^3 SO_2 (Liu and Wen, 2012). In another study, the authors also concluded that maximum greenhouse emissions result from coal fed thermal power plants. It was estimated that a total of 753890kt of NO_x was emitted from 31 Chinese provinces during the year 2010 (Tian et al., 2013). About 110 Ktons/years of $PM_{2.5}$ and 2300 Ktons of NO_x annually was emitted from coal based thermal power plants during 2010 (Wang et al., 2012).

In India, Sulphur dioxide emissions continue to grow and has become the world's second largest emitter after China (Smith et al., 2011). For instance, SO_2 emissions have increased from 1.95

million tonne (1878) to 2.47 billion tonne (2017) in India (Quéré et al., 2017). Similarly, methane emissions have hiked from 398.21 million tonne (1970) to 636.40 million tonne (2012) (Ritchie and Roser, 2020). It has been observed that CO_2 emissions have increased from 438.95 million tonnes (1990) to 1.30 billion tonnes (2010) (Oliver et al., 2016)
Furthermore, there are more than 100 thermal power plants across the country generating 66% of electricity, with coal as a primary fuel choice accounting for 50-55% of total power generation (Chikkatur et al., 2011; WISE, 2012; Prayas, 2013). However, such power generation implies a huge cost to environment (Guttikunda and Jawahar, 2014).

In this paper, the temporal variation of trace gases and particulate matter is analyzed using satellite data in Singrauli district, Madhya Pradesh, India. Although, ground based measurement techniques are more accurate in monitoring air quality, it has two major disadvantages. Firstly, the ground monitoring stations are sparsely and unevenly distributed in the area. Secondly, the uneven distribution of monitoring stations restricts a study area that can be analyzed. On the other hand, satellite data gives a broad spatial and temporal coverage and is now a future tool to understand national impacts of air quality (Lee et al., 2012). Furthermore, high quality ground-based measurements are lacking in developing countries like India and remote sensing techniques can provide coverage for larger areas. (Brauer et al. 2012) In other words, satellite data is a comprehensive information, visualization and validation to field measurements of air quality (Engel-Cox et al., 2004). Henceforth, an attempt has been made to monitor air quality using remotely sensed data.

This study aims to monitor greenhouse emissions in the study area for the past 15 years. The trace gases focused are carbon dioxide, nitrogen dioxide, methane, particulate matter and Sulphur dioxide. The remotely sensed data is used to visualize trend of trace gases in reference to installation of thermal power plants. Furthermore, a seasonal variation has been analyzed in the study to understand the variation of pollutant concentration. This will provide insight to cycle of pollutants and can be utilized to modify guidelines for operations of a coal fed thermal plant. Also, a correlation among the focused trace gases has been estimated in order to evaluate the dependency among trace gases. The visualization provided in the study will help understand the long-term and short-term variations of a pollutant. Additionally, this analysis will provide assistance to policy makers to enforce mitigation measures in the power sector to improve air quality.

2. MATERIAL AND METHODS

2.1. Study Area

The study site is located in Singrauli region of Madhya Pradesh, India. The study area is rich in natural and mineral resources, however, was covered with dense forests and inhospitable terrain in ancient times. Spread over a total area of 5675 sqkm, Singrauli has a population of 1,178,273. A 2°X2° grid [23 E, 81 N, 25 E, 83 N] was chosen, to cover whole Singrauli area. It has warm and temperate climate; The average annual rainfall is 1014mm. Singrauli area is the major power hub of the country. The availability of rich natural resources and raw material feeds the need of thermal power plant, aluminium industry, chemical industry, mining industry, and stone crushers established in this region. Due to the industrialization of the area environmental problems have been reported since few decades. CPCB and Ministry of Environment and forest after detailed environmental study have identified Singrauli as a critically polluted area since the year 1991 There are many Thermal Power plants in this region generating nearly 19284 MW of electricity (Table 2). Emissions from thermal power plants and coal mines are the major sources of pollution in the study area.

2.2. Data Used and Analysis

Data sets used in this work were downloaded from the Giovanni online data system, developed and maintained by the NASA GES DISC as described in table 1.
Aerosol optical depth is the quantitative estimate of the amount of aerosol present in the atmosphere and angstrom exponent is the measure of optical thickness of an aerosol. A scatter plot of AOD vs AE is used in this study to establish type of aerosols in atmosphere. Greenhouse gases such as nitrogen dioxide, sulphur dioxide, carbon dioxide and methane, absorbs heat radiations to keep the planet warm. However, anthropogenic activities have rapidly increased their concentration and monitoring and mitigation measures are need of the hour. Particulate matter are small particles such as dirt, soot or smoke. PM_{10} and $PM_{2.5}$ are the particles smaller than 10 micrometers and 2.5 micrometers respectively.
Trend analysis was performed in order to visualize and characterize the long-term and short-term variations of pollutant concentration. Cyclic variation of pollutants in pre-monsoon, monsoon, post-monsoon and winter seasons has been visualized. The trend of change has been compared with each new installation of a thermal power plant to anticipate the effect of new thermal power plant on pollutant concentration. Furthermore, correlations among different pollutants were estimated.

Table 1: Data source

S.No.	Trace Gas	Satellite	Spatial Resolution
1	AOD	MODIS	1ºX1º
2	AE		1ºX1º
3	SO2	OMI	0.25ºX0.25º
4	NO2		0.25ºX0.25º
5	CO2	AIRS	2ºX2.5º
6	CH4		1ºX1º
7	PM 2.5 and PM10	CPCB	Ground Observation

3. RESULTS AND DISCUSSION

Sulphur content in Indian coal (0.2 – 0.7%) is lower than the coal used in western countries. On combustion, most of the Sulphur is converted to SO_2. On the other hand, emission of NO_2 depends upon the design and condition of thermal power plant. Additionally, the high silica and alumina content in Indian coal increases ash resistivity and reduce the collection efficiency at the electrostatic precipitators. Henceforth, coal powered thermal plants act a large point source for SO_2 and NO_2 emissions. Details of thermal power plants installed in the study area are given in table 2.

Table 2: Thermal power plant details.

S. No	**Name**	**Location**	**Capacity (MW)**
1	NTPC	Vindhyachal	2000
2	NTPC	Shaktinagar	2000
	NTPC	Rihand	3000
3	Essar	Sasan	1200
4	Reliance	Sasan	3940
5	Jaypee	Nigre	1320
6	Hindalco	Baragawon	900
7	UPRVUNL	Anpara	2630
8	UPRVUNL	Obra	1094
9	Lanco	Anpara	1200

According to Environment protection amendment rules India, 2015, the emission standard limits of SO_2, NO_x and PM (mg/m^3) for new and old thermal power are described in table 3

Table 3: Standard emission limits for existing and new thermal power plants(mg/m^3)

SO_2		NO_x		PM	
Existing	New	Existing	New	Existing	New
200-600	100	300-600	100	50-100	30

As described in the literature, thermal power plants account for 15% of $PM_{2.5}$, 30% of NO_x and 50% of SO_2 emitted in the atmosphere (GAINS, 2012). Similar results were reported for thermal power plants in and around Delhi. A study conducted near thermal power plants of Singrauli concluded high BC concentration >200 $\mu g/m^3$ with peaks during early morning and evening hours, compared to the outside domain of the study region (Singh et al., 2018).

In this study, the change in trace gases levels are attributed with respect to thermal power plants. The straight lines shown in the figure 1 mark the start of a new thermal power plant in study area. As a new thermal power plant is installed, it takes a period of 6-8 months to attain its full capacity. As attributed from figure 1, the concentrations of Methane, SO_2 and CO_2 increases after a new TPP is introduced. Although, there were no new TPPs introduced after 2017, however, the collective effect of all the TPPs and limited emission control techniques affect the trace gases. It is evident that before the year 2007, CO_2 increased at a linearly. However, after 2012, CO_2 increased more steeply. Similarly, CH_4, NO_2 and SO_2 have elevated rate after 2012. The long-term and short-term changes of individual pollutants is explined below.

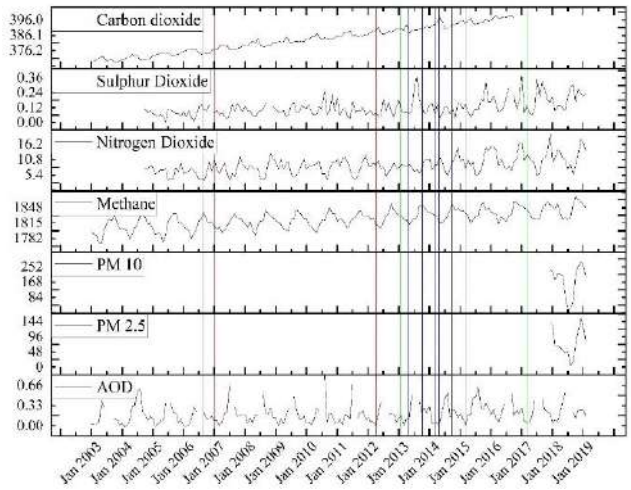

Fig 1: Trend of trace gases under observation. The straight lines in the figure mark the installation of new thermal power plant. The Red lines label for NTPC, Green for Essar, Blue for Reliance and Orange for Hindalco.

3.1. Carbon dioxide

Before industrialization, 0.03% of earth's atmospheric volume was comprised of carbon dioxide. However, as a result of fossil fuel burning it has increased by 25%. The resident time of stable CO_2 molecule is 3 years in the troposphere and more than 100 years in atmosphere (Raghuvanshi et al., 2006). This increased CO_2 concentration in the atmosphere has caused unprecedented climate abnormalities. This study has analyzed trend of CO_2 since the year 2003. It is evident from figure 2 that CO_2 content has increased linearly from a minimum value of 374.10 ppm in January 2003 till a maximum value of 403.68 ppm in June 2016. Every year since 2003 the annual rate of increase is approximately 0.99 times. Similarly, the overall CO_2 emission in the country has increased from 120.6 M tonnes in 1960 to 2238.4 M tonnes in 2014, approximately an increase of 19 times.

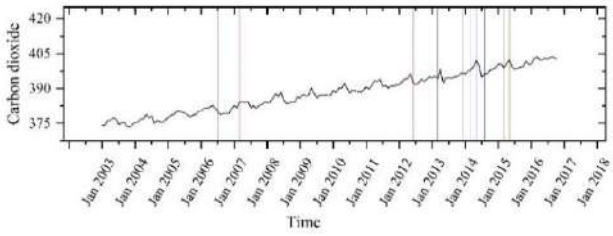

Fig. 2: Trend of Carbon dioxide.

Considering short term variation, CO_2 shows a cyclic variation annually as shown in figure 2. It is observed that in 2003, CO_2 increases from a minimum value of 374.10 ppm in January till a maximum value of 377.51 ppm in May. It then decreases to a value of 373.35 ppm in November. CO_2 obtains a maximum value of 378.89 ppm in May 2004. It is evident from the figure 2 that higher concentrations are observed during the months of May, June and July. On the other hand, the lower concentrations are observed during August and September. This can be attributed to rise of temperature during the months of April-June. Similar results were observed in a study of Gujarat (74 million tons), Maharashtra (94.6 million tons), Uttar Pradesh (74 million tons), Andhra Pradesh (62.8 million tons) and Chattisgarh (58.9). (Guttikunda and Jawahar, 2014). Furthermore, CO_2 emission has increased 5.6% from Indian thermal power plants during 2001-2010 (Mittal, 2012).

3.2. Methane

Methane is emitted from active, inactive, underground or surface coal mines. It is also emitted from the post-mining activities such as coal processing, storage and transportation. Methane is a prominent volatile organic compound, contributing to formation of ozone. In India, methane emissions have increased from 31.8 M tonnes (1990) to 73.4 M tonnes (2010) due to energy production alone(Ritchie and Roser, 2020. Literature has also suggested that methane emissions have increased at an rate of 1 percent annually(Raghuwanshi et al.,2006). In this section the methane emissions of Singrauli region since 2003 have been studied. It is clear from figure 3 that the emissions have increased from 1786.99 ppbv (2003) to 1887.79 ppbv (2018).

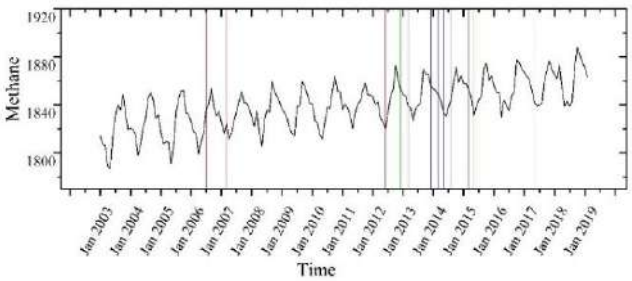

Fig. 3: Trend of Methane.

Conjointly, methane concentration shows a cyclic variation, where the minimum concentrations were observed during the month of April, May and June. On the contrary, the maximum concentrations were observed during September and October.

3.3. Nitrogen dioxide

Literature suggest that anthropogenic activities have progressed highly in emitting NO_2. This study shows variation of NO_2 over time since 2003 as described in figure 4. It is distinct that the concentration of NO_2 has increased over the span of time. It is established that due to strong vertical mixing and higher solar radiation, concentrations are higher during summer. On the other hand, due to stable thermal stability in winter, the NO_2 concentration increases significantly. The same can be seen from figure 4 where the minimum concentration values are observed during the months of July, August and September. On the other hand, the maximum values were observed in the months of November and December. Similarly, elevated emissions were observed in Andhra Pradesh (187500 tons), Chattisgarh (172500 tons), Gujarat (220000 tons), Maharashtra (278500 tons) and Uttar Pradesh (235500 tons) (Guttikunda and Jawahar, 2014). In an another study, it was estimated that during the period 2005-2014 NO_2 emissions have increased by 24.9% in Chennai, 6.13% in Delhi and 16.8% in Hyderabad (Duncal et al., 2015).

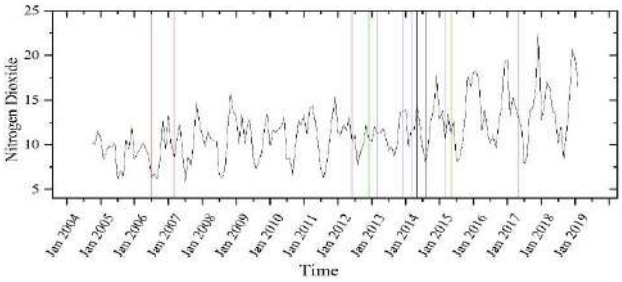

Fig. 4: Trend of Nitrogen dioxide.

3.4. Sulphur dioxide

Sulphur dioxide has a major influence on climate change, as, it is responsible for acid rain formation. (Menz and Seip, 2004). Other than energy sector, its emission depends on economic development. According to IPCC, global SO_2 trend will decline with decrease in development in future decades. In India, SO_2 levels have increased at an average rate of 1.05 since 2000.

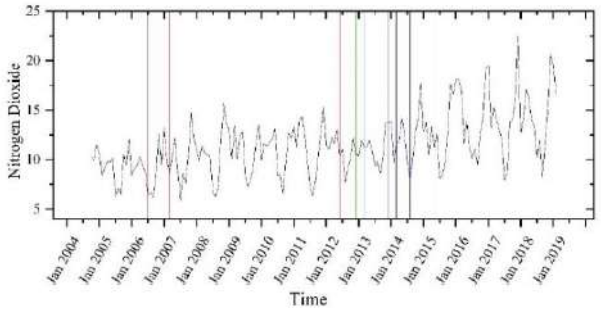

Fig 5: Trend of Sulfur dioxide.

The concentration of SO_2 over the period of last 15 years is shown in figure 5. The concentration has increased by 2.17 times. Furthermore, from the year 2007 till 2011, SO_2 levels had an increasing trend. The trend follows a cyclic pattern with decrease and increase in alternate years. On the other hand, there is no cyclic variation in the concentration of SO_2 within a year, i.e. no seasonal patterns are observed. It has been documented in other studies that SO_2 emissions have risen from 2.5 million tons (2001) to 3.8 million tons (2009), with an average annual rate of 169.39 thousand tons in India. Similarly, higher amount of emissions was observed in Andhra Pradesh (199500 tons), Chattisgarh (187000 tons), Gujrat (214000 tons), Maharashtra (300500 tons) and Uttar Pradesh (235500 tons) (Guttikunda and Jawahar, 2014).

3.5. Aerosol Optical Depth and Angstrom Exponent

Aerosol optical depth (AOD) is a measure of the extinction of the solar beam by dust and haze. In other words, particles in the atmosphere (dust, smoke, pollution) can block sunlight by absorbing or scattering the light. Type of aerosol can be determined with the help of Angstrom exponent and AOD scatter plot. According to the author, if AOD is less than 0.9 and AE is greater than 0.9, the aerosols are categorized as Anthropogenic aerosols. Similarly, AOD (>0.9) and AE (>1), biomass burning aerosols, (AOD, AE) (<0.7, <0.9), polluted continental and (AOD, AE) (>0.7, <0.6) dust aerosols (Tiwari et al., 2017). Angstrom exponent is a parameter that describes the relationship between optical thickness of an aerosol and wavelength of the light. It is inversely related to average size of the particles, therefore, the smaller the particle the larger the exponent.

Originated from both natural and anthropogenic activities, particulate matter in India, earlier, were mainly dust and carbonaceous compounds (Monks et al., 2009). However, emissions from fossil fuels and gigantic industries elevate atmospheric aerosols over Northern and Western India (Reddy and Venkataraman, 2002). The scatter plot of MODIS derived AOD and AE over the study area are reported in figure 6. It can be attributed, that the maximum number of aerosols reported can be classified under anthropogenic aerosols (figure 6).

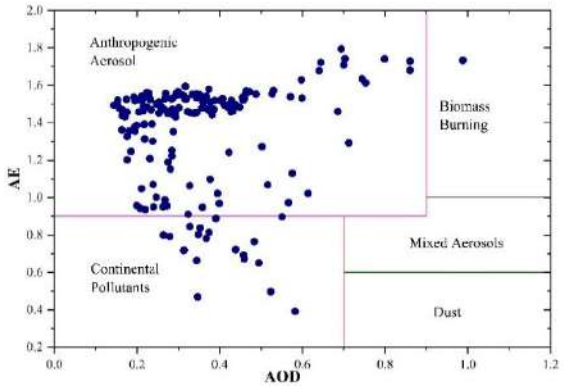

Fig. 6: Types of aerosols based on optical thickness.

3.6. Correlation Analysis.

The emitted greenhouse gases have individual residential period in the atmosphere, before there are removed. However, at the end of their residential period, few get oxidized and act as successor or pre-cursor of the other. Hence, increase in concentration of one trace gas can cause increase or decrease of the other. For instance, every molecule of methane has an 8-year residue period before its oxidation into CO_2 and water molecule. Similarly, 30-40% of particulate matter are secondary, produced from conversion of gaseous SO_2 and NO_x into aerosol sulphates and nitrates. In this study, table 4 represents correlation among the observed pollutant gases.

Table 4: correlation matrix of trace gases

	AOD	SO_2	NO_2	Methane	$PM_{2.5}$	PM_{10}	CO_2
AOD	1						
SO_2	0.093	1					
NO_2	0.55	0.093	1				
CH_4	-0.231	0.593	0.093	1			
$PM_{2.5}$	-0.236	0.385	0.599	0.423	1		
PM_{10}	0.016	0.363	0.665	0.478	0.824	1	
CO_2	0.199	0.281	0.468	0.482	NA	NA	1

The co-relation values thus obtained are at 95% and high significance level. Hence, it is articulate that; Methane & SO_2, $PM_{2.5}$ & NO_2, PM_{10} & NO_2, CO_2 & Methane and $PM_{2.5}$ & PM_{10} have strong correlations at significance level higher than 95%. Since majority of particulate matter comprises of sulphates and nitrates, the concentration of NO_2 and SO_2 affect its concentration. Similarly, as methane oxidizes into carbon dioxide therefore, have a strong correlation.

CONCLUSION

In India, over 100 coal powered thermal power plants remain the main source for electricity generation. They act as a large point source for pollution in the country detrimenting the environemnt and human health. The new standards aim to reduce emissions considerably, however, this study shows that the concentration of gases are still on an increasing trend. The analysis has following conclusion

- Methane, CO_2, NO_2 and SO_2 are on an increasing trend with an average rate of 1.03, 0.99, 2.15 and 1.09 annually.
- CO_2 & SO_2, PM_{10} & $PM_{2.5}$, PM_{10} & NO_2 and CO_2 & NO_2 have a co-relation at 99% significance.
- Methane, SO_2 and CO_2 exhibit cyclic variation with change in season. The maximum concentrations of methane, Sulphur dioxide and carbon dioxide are observed during post monsoon season. On the other hand, the minimum values of methane are observed during monsoon season, whereas, minimum concentrations of SO_2 and CO_2 are attributed during pre-monsoon season.
- Scatter plot of aerosol optical depth and angstrom exponent indicates that maximum aerosols present in the study area are result of anthropogenic activities.
- Thermal power plants act as a stationary source of emission. With every new coal fired thermal power plant the air quality has decreased in the study area.

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Measurement of toxic metals in the air of Sonbhadra-Singrauli area

1. Background:-

1.1. Toxic metals and their prescribed limits:-

1.11. Out of the 118 elements currently accepted in chemistry, 11 elements (Beryllium-Be, Chromium - Cr, Manganese-Mn, Cobalt Co, Nickel Ni, Arsenic As, Selenium Se, Cadmium Cd, Antimony Sb, Mercury Hg, and Lead Pb) have been considered extremely harmful and toxic for health by the US EPA (Environmental Protection Agency). Of these, except Beryllium, all others can be placed in the category of toxic heavy metals. These can harm health even in very small quantities when they enter the body through air, water or food.

In the drinking water standards set by the Bureau of Indian Standards, their maximum acceptable quantity is as follows:

Manganese (Mn) - 0.3 mg/l
Arsenic (As) - 0.05 mg/l

Chromium (Cr) - 0.05mg/l
Lead (Pb) 0.05mg/l
Mercury (Hg) - 0.001mg/l
Cadmium (Cd) - 0.01mg/l

It is clear that all these metals are harmful for health even in very small quantities, hence the presence of any of these elements even in small quantities in drinking water is harmful for health. The core committee appointed by NGT (National Green Tribunal) in its investigation found the quantity of many of these metals to be much higher than the standard in the water sources of many parts of Sonbhadra district.

1.12. Till 2009, no acceptable limit was fixed for any of these metals in air and their titration was also done here and there only in some research cases. In the new air quality standards issued in 2009, limits were fixed for three metals lead, arsenic and nickel but their regular titration is still not being done anywhere. The biggest difficulty in this is that these are present in air in very small quantities, and analyzing them in such small quantities is also difficult and expensive, also their quantity has to be collected

from a lot of air to make it analyzable. The standards that have been set are also based only on the annual average quantity and if the titration is done on any one day or only a few days of the year, then comparing it with the set standard of annual average will be meaningless.

1.2- Toxic metal pollution in Singrauli area:-

1.21. The problem of water and air pollution in Singrauli area began in 1965-66 after the establishment of Hindalco Aluminium and its successor Kanoria Chemical industries. Kanoria Chemical was originally an industry for making caustic soda (NaOH), which is an essential chemical for cleaning aluminium. Caustic soda is produced by electrolysis of sodium chloride (NaCl). In this process, mercury-Hg is used as the cathode. (In this, mercury in the form of metallic liquid continuously drips drop by drop which acts as the cathode). In this process, some portion of mercury dissolves in the chemical solution and finally goes into the effluent of the factory. In Kanoria Chemical, the effluent from the factory is poured into the Dongiyanala. Dongiyanala flows for about 3 km and joins the

Pantsagar lake. Thus, people with scientific understanding started to understand easily that some amount of mercury from Kanoria Chemical can continuously reach Pant Sagar Lake and can flow into Renu River below it, but we do not have any data to show that any special concern or measurement has been done in this regard.

1.22- Concern over the presence of harmful metals was first raised in the French market between 1988-90. This happened after the results of a study under EIA (Environmental Impact Assessment) conducted by the consulting company (EdF/CdF) on the loan sought from the World Bank for the expansion of NTPC's power projects came to light. According to this report, the amount of mercury and cadmium in the Pantsagar lake, the flow of Renu river, the wells and hand pump water around the Renu river and from Chopan to below it Son river were more than the prescribed standard amount in drinking water. That study (EdF/CdF) mainly blamed the pollution coming from Kanoria Chemical through Dongianaale as the source of these metals, especially mercury. Regarding the health problem, in 1993-94, ITRC (Indian

Institute of Toxicology Research, Lucknow) had also raised the issue of the presence of much more mercury than normal in the human blood of this area.

1.23-Registered in 1956 and in effect since 1965 under the able leadership of Late Prembhai, the active Banavasi Seva Ashram Govindpur not only worried about the problems of the society in the entire area (in which public health is also an important issue) but also investigated them in depth and made efforts to solve them. On the initiative of Banavasi Seva Ashram and with the help of Dunu Rai, a renowned scientist on the subject of pollution and health among social organizations and the Peoples Science Institute, Dehradun, when the flow of Dongiyanala was measured, the amount of mercury was found to be up to 1800 ug/l, which was more than the standard of 10 ug/l set for mercury.

When after 1990 Seva Ashram started producing water in this area when the issue of excessive pollution by industries started being raised, the entire focus was on fluoride (which was discharged in large quantities by the Hindalco

factory through the Murdhwa drain, and mercury and other chemicals discharged by Kanoria Chemicals through the Dongiana drain) and between 1995 and 2000, these drains were repeatedly measured to attract the serious attention of not only the industries, but also society and the government towards this problem.

It is clear that this type of effort and the pressure created by it would sooner or later have an impact on these industries as well and as a result the pollution caused by the wastewater from both these industries would reduce.

1.3 Studies conducted by Banavasi Seva Ashram from the year 2000 to 2015 –

1.31. By the year 2000, the amount of mercury in the Dongianaala flow had come down to 500 ug/l and the amount of fluoride in the Murdhwa Naala flow had come down to 10-12 mg/l. Soon it was realized that it would not only be difficult but also impossible that the pollution of these two industries located in Renukoot could be responsible for the fluoride and mercury

pollution in the entire area and it became more probable that coal contains not only mercury and fluoride but also many other metals in more or less quantity and the large thermal power plants of the region, which burn coal in such a large quantity (currently about 3 lakh tons per day), these harmful elements are being continuously thrown into the environment in abundance through ash, water discharge and pollution emitted in the air, which can also be the cause of severe pollution in the area. This idea gained strength in a big seminar organized at the Ashram in 1998, as a result of which, in the studies conducted from 1998-2010 in the laboratory established at Banvasi Seva Ashram with the help of PSI (Peoples Science Institute), (in which five years of studies were done with the help of Central Pollution Control Board CPCB New Delhi), it was found that both fluoride and mercury are contaminating the air, water, soil, vegetation etc. of this region through ash, water discharge and chimney emissions from coal and thermal power plants.

1.32-Public health and crop production study of the ashram between 2000-2015

In the health studies conducted by Banavasi Seva Ashram, not only the number of bone and health diseases but also the number of mental diseases (madness, paralysis) and reproductive system related diseases in the entire region made it clear that fluoride and mercury are having adverse effects on health in the entire region and due to the presence of these elements in air would be much more important than just being present in distilled water or ash, so their measurement in air is extremely important.

1.33-Case in NGT and Core Committee Report:-

(A) NGT case number OAN-276 of 2013 and OAN-20 of 2014
Chairman Dr. Tapan Chakraborty, some members Dr. Indramani Mishra, Dr. Vinod Tare

(B) Polluting industries- thermal power plants- 10 (21000 MW)

Cement Plant- 1 (Clicker 20 lakh ton per

annum, Cement 5 lakh ton per annum)
Coal mines - 16 (about 3 lakh tonnes per day)
Sponge iron - 1
Stone crusher-309
Explosives - 8 Chemicals - 12
Aluminium-2 (Alumina 0.9 million tonne per annum, Aluminium 0.7 million tonne per annum)

(c) Major solid waste- Fly ash- 1.1 lakh tonne per day, uncertain but very large quantity of overburden

Major air pollutants- 200 tonnes per day SPM, 100 tonnes per day PM10, 40 kg per day mercury

Water consumption - 40 lakh cubic meters per day

(d) Water quality study-

Kusmaha pond - Failed in iron, fluoride, mercury, cadmium, chromium
Murdhava Nala - Fails in Fluoride
Dogianala- failed in pH, fluoride
Surya Nala- Fails in iron, fluoride, nitrate
Pant Sagar water - all samples failed in mercury, chromium and cadmium limits, worrying
Renu river below the dam-all samples failed in mercury, worrying
Ground water - Kirwani, Parasi, Harhawa, Nakatu, Sirsoti, Chilkadod, Paraswar Raja, Govindpur, Kusmaha, Khairahi, Dibulganj, Jaitpur all places failed in mercury. Many places failed in fluoride, nitrate, trace metal

RO purified water-

Bajrangnagar, Dibulganj – Failed in Iron, Mercury, Cadmium, Nickel,
Paraswar Raja-failed in iron, aluminium, mercury

(E) Air quality-

Air quality monitoring system is very inadequate, measured PM10 often fails, later on, data from CAAQMS installed at Renukeshwar by Hindalco always fails in air hydrogen fluoride, mercury, fails most of the time in PM10, PM 2.5

(F) Effects on health-

Fluorosis is severe in Chopan and Myorpur blocks, almost everywhere

Symptoms of lead (Pb) poisoning are abundant in many places

Symptoms of mercury, arsenic, cadmium poisoning need in-depth study

Symptoms of silicosis- in daala and near highways

Recommendation of the Health Subcommittee-A standard toxicity study laboratory in the region

Intensive training of doctors and health workers in identification and diagnosis of pollution-related diseases

A comprehensive intensive health survey and management system in the area

2. Scheme of titration of toxic metals in normal air of Sonbhadra-Singrauli area:-

2.1- It is obvious that toxic metals in the atmosphere, such as the 11 toxic metals identified by EPA listed in 1.1, even in very small quantities, can be harmful to the health of humans and other animals and can accumulate in vegetation, water and soil and cause even more long-term and difficult problems. Also, the presence of such metals in the chimney gases emitted by various industries, especially mineral-based industries, can affect the quality of normal air and the health of animals. Yet, their regular and scientific measurement in air is not done in most countries, especially in India. Of these, those three metals in air (lead - Pb, arsenic - As, nickel - Ni) for which maximum tolerable limits have been determined by the Central Environmental Control Board (CPCB) and the Government of India, are also not being regularly measured. The following difficulties are faced in measuring these metals in normal air-

(a) Since they are present in very small quantities in the air, they would have to be

collected from a lot of air to collect sufficient quantity for analysis.

(b) Due to the change in the metals from time to time and even from moment to moment, the quantity present at any particular moment will not be of much importance. The harmful effects of these metals also occur only when they are gradually accumulated in water, soil, human body and other animals or vegetation etc. for a long time, hence it becomes necessary to measure them continuously and for a long time. This is the reason why their standard prescribed limits are also given only in the form of annual average quantity, not for any specific hour, day or short time.

(c) Air sample can be taken on filter paper for solid particles. Metals are not normally found in gaseous form in normal air but mercury, lead or arsenic can be found in gaseous form. At least this cannot be said about mercury. If any metal is present in the air in the form of gas, then its sample can be taken by absorbing it in a suitable

chemical solution but it is not easy to find a suitable solvent chemical.

(d) Toxic heavy metals cannot be titrated using common chemical analysis methods because they are present in very low quantities in any sample, and require special and very expensive equipment such as AAS. This type of expensive equipment, necessary chemicals and skilled scientific analysts require testing per sample, which makes it very expensive to test. Due to very low quantities, many times the result comes only BDL - Below Detection Limit (less than what can be measured) and the whole effort becomes futile and it seems appropriate or necessary to change the equipment and analysis method used. Due to these difficulties, the cost per sample of analysis or titration of these metals is much higher than the cost per sample titration of other air quality factors like PM-10, PM-2.5, SO2.

(e) Although standards for common quality factors like PM-10, PM-2.5, SO2 etc. are

determined on the basis of annual average, standard limits are also determined for daily (24 hours) quantity for many factors, and hence their annual average is also calculated by calculating the average on the basis of daily titration of 50-150 days in a year, either daily or every third day, twice a week or in such a sequence. If the same method is adopted for heavy metals, then we will have to analyze 50-150 samples in a year for these metals also. If the cost of this analysis is Rs. 1000 per sample per metal, then the annual cost of measuring heavy metals in air at one place will be Rs. 50000 to Rs. 150000 per metal per year. This expense will be after the cost incurred in collecting the sample. It is clear that this will be difficult as well as expensive. This is the reason why the titration of these metals is not being done even though it is necessary.

(f) Equipment available for collecting PM2.5 samples (based on EPA design) normally air sample is taken at 16.6 l/m3 and this sample is taken continuously during 24

hours 16.6 litre/m of air is drawn out. Thus, 1440 ml of air in 23904 (23.9 m3) litres of air samples can be obtained in 24 hours. On the other hand, for most gaseous factors, Air sample is taken at the rate of 1-1.5 litre/m. If we take the sample on the basis of 1 litre/m only air is sampled for heavy metals then 1.44 m3 of air will be drawn in one day, and if this is done continuously for 15 days then a total of 21.6 m3 of air will be drawn. In this way its amount will be approximately equal to the amount of air drawn in for PM-2.5 in 24 hours, and so the 47 mm filter paper that we use for PM-2.5 for 24 hours, the same filter paper and filter holder etc. will be able to take air sample for 15 days at 1 litre/ml. By drawing air at low speed in this way we can take samples over a long period of time on the same filter paper and the number of samples to be analyzed can be reduced considerably. Considering the above idea Huye Envirotech Instruments Pvt. Ltd. New Delhi (A reputed company manufacturer of air measuring instruments) with the help of IIT Delhi has developed a device which can

draw air continuously at 100 litres/min for a long time on the same 47 mm filter paper which is PM 2.5 is used for long term sampling of heavy metals.

(g) We decided to procure two units of the new instrument APM 586, which can take samples for a long time at 1 l/m, and use them for titrating heavy metals at two locations in the Sonbhadra-Singrauli area.

3. Detailed form of the scheme-

3.1. To purchase two instruments having the capacity to take air samples at 1 litre/m and to carry out these measurements, project assistance of Rs. 2 lakh was obtained from Guru Ganga Envirotech Trust New Delhi and two such units were purchased. The said units were operated on rechargeable batteries which were of 6 volts and could be charged up to 6.60 volts. It was found in an experiment that after running continuously for 15 days the battery also reaches 6 volts. It was also found in an experiment that even after this voltage gradually falls during these 15 days the air flow is not

affected at all. After charging this battery once there is no need to charge it again for 15 days.

3.2. In an experiment it was found that even after 15 days if a new charged battery is put in and the unit is started again immediately then for a full month (30 days) there is no problem of filter choking, motor pump overheating or any other type of problem. This instrument is completely battery operated, hence in this way air sample can be collected on the basis of 1 litre/m continuously for at least one month on the same filter paper, it is possible that samples for more than one month can also be collected on the same filter paper, but we did not try this.

3.3- Our initial thought was that we should collect these general air samples on a monthly basis so that a total of 12 samples are obtained for one place in a year, firstly we will be able to understand the difference in heavy metal content from month to month or the effect of weather and secondly if there is any sudden problem or analysis goes wrong then the entire result will not become meaningless. Keeping this

thought in mind we made a plan to take a separate sample every calendar month.

3.4. In this first attempt, we could have done the titration at only one place, but it would have been difficult to say whether the quantities found were due to the effect of industries or due to the general geographical conditions here. Therefore, we initially decided to do the titration at two places, one of which was convenient for us as Govindpur was the headquarters, which is located in the most polluted sub-region in this region. One thing an officer of the UP Pollution Control Board had said on the basis of some studies done between 2002-2005 that he does not know why all the mercury runs to Govindpur, as if mercury has a great affection for Banavasi Seva Ashram Govindpur. The second place we chose was Faripaan, which is about 40 km south-east of Govindpur, near the UP-Chhattisgarh border, and where industrial pollution has been found less in the reports so far.

4. Result

The results of the year-round titration of toxic metals are given in the table below

No.	Month	Led, pb (ng/m)3		Nickle (ng/m)3		Arsenic As(ng/ m3)		Mercury (ng/m3)	
		Govind pur	Faripan	Govind pur	Faripan	Govind pur	Faripan	Govind pur	Faripan
1.	June-16	34.6	38.3	12.8	13.7	45.5	46.5	26.5	2.6
2.	July -16	24.8	44.4	15.5	9.2	34.9	38.4	27.8	6.5
3.	August-16	29.2	25.5	27.6	7.7	19.5	18.2	31.8	3.8
4.	Rainy	29.5	36.1	18.6	10.2	31.6	34.4	28.7	4.3
5.	September -16	67.8	41.2	32.4	8.8	29.3	14.2	39.2	0.1
6.	October -16	42.5	ND	74.0	ND	24.6	ND	24.1	ND
7.	November -16	36.8	33.5	35.1	28.2	28.1	38.5	47.7	7.6
8.	After Rain	49.0	37.4	47.2	18.5	27.3	26.4	37.0	3.9
9.	December-17	62.1	71.3	41.9	27.3	39.5	44.1	17.4	2.8
10.	January-17	50.8	73.8	34.9	24.8	28.8	42.7	32.5	2.6
11.	Winter	56.5	72.6	38.4	26.1	34.2	43.4	25.0	2.7
12.	February-17	209.9	151.3	ND	ND	62.0	37.5	9.5	4.0
13.	March-17	47.9	0.9	34.2	5.7	34.9	5.9	21.7	9.3
14.	Sprint	128.9	76.1	34.2	5.7	48.5	21.7	15.6	6.7
15.	April-17	50.6	18.5	28.4	18.7	44.3	16.4	13.6	ND
16.	May-17	32.1	20.3	31.4	16.6	29.9	16.5	24.6	2.8
17.	Summer	41.4	19.4	30.0	17.7	37.1	16.5	19.1	2.8
18.	Annual Average	57.4	47.2	33.5	14.6	35.2	29.0	26.4	4.2
19.	PRESCRIBED LIMIT IN INDIA	2000		20		6		NP	

Note: Monthly sample was taken using NYROTECH APM 586 with a flow rate of 1.0 liter per minute.

- Statistics of titration throughout the year -

    - Govindpur had an average mercury level of 26.4 ng/m3, and Faripaan, located farther from industries, had an average mercury level of 33.5 ng/m3. There are no standards for ambient air in India.

    - The average arsenic content in the air of Govindpur was 35.2 ng/m3, and in Faripan it was 26 ng/m3. The average arsenic content in ambient air of industrial area, residential area and rural area should be less than 6 ng/m3.

    - The average nickel content in the air of Govindpur was 33.5 ng/m3, and in Faripan it was 14.6 ng/m3. The average nickel content in ambient air of industrial area, residential area and rural area should be less than 20 ng/m3.

The amount of toxic metals in the air of Sonbhadra is many times more than the standards. The amount of metals like arsenic is 6 times more than the standard in the air of Govindpur, and the amount of nickel is

also 1.5 times more than the standard. Faripaan, which is more than 50 kilometers away from the thermal power plants, and more than 30 kilometers away from Renukoot, has less amount of toxic metals in the ambient air than Govindpur. But here also the amount of arsenic is 5 times more than that of Manak. There is no standard for mercury.

Banvasi Seva Ashram
Govindpur Sonbhadra

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Mercury emissions and partitioning from Indian coal-fired power plants

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ABSTRACT

In India coal combustion is the single largest source of emission of mercury which is a wide-spread persistent global toxicant, travelling across international borders through air and water. As a party to the Minamata convention, India aims to monitor and reduce Hg emissions and stricter norms are introduced for mercury emissions from power plants (30 μg/Nm^3 for flue gas in stack).

This paper presents the results obtained during the experimental studies performed on mercury emissions at four coal-fired and one lignite-fired power plants in India. The mercury concentration in the feed coal varied between 0.12–0.27 mg/Kg. In the mercury mass balance, significant proportion of feed coal mercury has been found to be associated with fly ash, whereas bottom ash contained very low mercury. 80%–90% of mercury was released to air through stack gas. However, for circulating fluidised bed boiler burning lignite, about 64.8% of feed mercury was found to get captured in the fly ash and only 32.4% was released to air. The mercury emission factor was found to lie in the range of 4.7–15.7 mg/GJ.

1. Introduction

Mercury has become one of the major global air pollutants arising due to toxicity, bioaccumulation, persistence and long range transport. In atmosphere, Mercury is present in different forms and can travel long distances leading to global contamination (Selin, 2009). In aquatic ecosystems, mercury is converted to potent neurotoxin methylmercury which poses highest risks to human health (Karagas et al., 2012; Mckelvey and Oken, 2012). Due to its immense impact on human health and concern about its global transport, Minamata Convention on Mercury was adopted in October 2013. The Convention aims to regulate mercury and its compounds, with obligations for mining, use, emissions, releases, and disposal (Giang et al., 2015).

As per UNEP Global Mercury Assessment 2018, stationary combustion of coal is the second largest source of global anthropogenic emission of mercury behind Artisanal small scale gold mining (ASGM) (UNEP, 2018). It is estimated that depending on the execution of Best Available Technology (BAT), global mercury emission in 2050 may vary anywhere from −4% to +96% (Streets et al., 2009).

India is heavily dependant on coal to meet the energy demand of the country. Coal combustion is the single largest source of mercury emission in India, and coal fired power plants are major contributor in this sector. Mercury contents in Indian coal, is typically in the range of 0.003–0.34 g/tonne with average concentration of 0.14 g/tonne (UNEP, 2014). However due to a large volume of coal burnt, a significant amount of mercury is released in atmosphere. In India, about 637 MT of raw coal and 37 MT were combusted for generation of electricity in 2018–19 (Energy Statistics 2020). As rural electrification is priority of government of India, it plans to increase total power generation of the country and coal based thermal power plants will be an integral part of this plan (CEA report, 2012).

Coal when combusted in boilers at high temperature, majority of mercury in coal releases as elemental mercury (Hg^0) in the exhaust gas (Moretti and Jones, 2012). Depending on the chemical composition of flue gas i.e. presence of HCl, SO_2, fly ash etc. a fraction of Hg^0 is oxidised (Hg^{2+}) by some thermochemical process. $Hg^{2+}$is more soluble and also has a tendency to get adsorbed on the fly ash particles which leads to formation of particle bound mercury (Hg^p) (Park et al., 2008). Concentration of mercury emitted through stack largely depend on the mercury contents of coals being burnt as well as installed air pollution control devices like electrostatic precipitator (ESP), wet flue gas desulphurisation (WFGD), fabric filter (FF) etc. (Cao et al., 2008), Whereas, elemental mercury is difficult to remove by air pollution control devices. In Indian scenario, most of the power plants have particulate control devices like ESP and FF. However, in recent times installation of Flue gas desulphurisation (FGD) in power plants has gained pace

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with MoEF&CC notification for compulsory installation of FGD system in the existing and upcoming thermal power plants to curb SOx and presently many FGD projects are in various stages of implementation (Energy Statistics 2020).

Mercury speciation in flue gas is an important factor while assessing the environmental impact of Hg present in the atmosphere, as Hg^0, Hg^{2+} and Hg^p have different physiochemical properties and atmospheric lifetime. However, due to variability in the nature of coal and its composition, combustion conditions and use of oxidising additives during combustion, the proportion and quantities of different mercury species present in flue gases vary significantly.

In recent years, lot of studies have been carried out by experts to understand the partitioning of mercury and its removal efficiency by the commercial air pollution control devices in power plants. Shah et al. showed the extent of reduction in mercury emission from five coal power stations in Australia with ESP or FF as particle control technology (Shah et al., 2010). Bilirgen found that 34.5% reduction in mercury emission at stack can be achieved with optimal boiler control and low-NOx system +WFGD (Bilirgen and Romero, 2012). Lei studied the effect of chlorine and ash composition in mercury transformation across six coal based power plants in China (Lei et al., 2007). Zhang et al. investigated the partitioning, removal efficiency in Chinese power plants with different combinations of APCD like cold ESP, FF, flue gas desulfurization (FGD) (Zhang et al., 2008). Zhao studied mercury transformation in an ultralow emission power plant in China (S. Zhao et al., 2017a). Yokoyama et al. reported detail study of mercury emission from Japanese 700 MW power plant having SCR, ESP and WFGD as air pollution control device (Yokohama et al. 2000).

As the nature of coal used in Indian coal fired power generation differs from other countries, it is important to have full scale studies to be carried out to understand the mercury emission pattern. Till now, actual field studies carried out in Indian power plant in context of mercury emission are scanty because of the lack of reliable sampling and analysis data in Indian context (Reddy et al., 2005). Mercury mass balance studies at coal-fired power plants can help to improve our understanding on the impacts of coal quality and APCD configurations on mercury emissions. Estimated average mercury emission factors for Indian power plants with respect to coal sources, combustion technologies and configuration of APCD may be utilised for determining total mercury emissions from the sector and to reduce mercury emission through process optimization.

In this article, comprehensive mercury mass flow has been studied at five selected thermal power plant boiler units of India. amongst them, four are pulverised coal fired and one is circular fluidised bed system burning lignite. In addition to the total mass balance of mercury in the system, mercury speciation was also estimated. The partitioning of mercury in different combustion products was determined and mercury emission factors have been estimated.

2. Experimental method

2.1. Sampling site

Onsite sampling and tests were carried out in different boiler units of five coal-fired power plants in India, amongst them, four boiler units are pulverised coal fired of 500–660 MW capacity, whereas the other one is circulating fluidised bed (CFB) boiler of 135 MW capacity. All the boiler units have Electrostatic Precipitator (ESP) as only air pollution control device for removing particles from flue gases. The study was carried out in the year 2019. In India majority of the boilers are pulverised coal fired. A couple of lignite fired power plants are based on circulating fluidised bed boiler system. Details of boiler units studied are provided in the Table 1. During the test period, the boiler units were operating under steady full load boiler operation conditions.

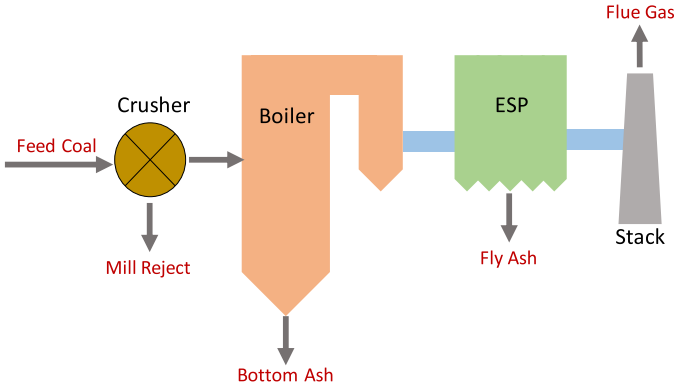

Fig. 1 – Sample collection point from boiler unit.

2.2. Sample collection method

Samples are collected by adopting standard sampling protocol. All the input and output materials were collected. Inputs included feed coal, whereas outputs are mill reject (MR), bottom ash (BA), fly Ash (FA) and flue gas. Flue gas samples were collected from stacks of boiler units at a good elevation where streamline gas flow could be obtained. Sample collection points are shown in Fig. 1. The onsite mercury determination in stack gases were performed by adopting EPA method 30B for total mercury and speciation of flue gas mercury (USEPA Method 30B). At the start of each run, average gas velocities and flue gas temperatures were measured using pre-calibrated pitot tube and temperature probes respectively. Requisite volume stack gas samples have been collected from the flue gas stream by inserting gas lined stainless steel probe through the sampling port of the stack. Gas volume was measured in the dry gas meter and vapour phase mercury in the gas was adsorbed in two different sorbent traps through the sampling port of the stack. Gas volume was measured in the dry gas meter and vapour phase mercury in the gas was adsorbed in two different sorbent traps. For total Hg concentration, activated carbon trap was used whereas for Hg speciation activated carbon along with KCl traps were utilised. The temperature of the probe was maintained at 125 °C to avoid condensation of mercury vapour before they are captured in the sorbent traps. The average value of mercury concentration of triplicate runs was considered for calculation. The following solid samples were collected simultaneously during each run of stack gas sampling -crushed coal from mill feeder, mill reject from bawl mills, bottom ash from boiler ash discharge point, fly ash from ESP hoppers.

2.3. Analysis method

The solid samples were properly crushed, pulverised, thoroughly homogenised and preserved in polythene bottles. Mercury concentrations of all the samples had been determined with the instruments Tri-cell DMA-80 (EPA Method 7473, Milestone, Italy) or RA915M with PYRO 915+analyser (Lumex, Russia). Determination of mercury combines the techniques of thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry (ASTM D6722–01).

Table 1 – Description of boiler.

Boiler unit	Capacity (MW)	Boiler type	Air pollution control device	Coal type	Location
Boiler A	500 MW	Sub-Critical PC-Boiler	Electrostatic Precipitator	Sub-Bituminous	West Bengal
Boiler B	500 MW	Sub-Critical PC-Boiler	Electrostatic Precipitator	Sub-Bituminous	West Bengal
Boiler C	660 MW	Super-Critical PC-Boiler	Electrostatic Precipitator	Sub-Bituminous	Madhya Pradesh
Boiler D	660 MW	Super-Critical PC-Boiler	Electrostatic Precipitator	Sub-Bituminous	Madhya Pradesh
Boiler E	135 MW	CFB boiler	Electrostatic Precipitator	Lignite	Rajasthan

PC-Boiler: Pulverised coal; CFB: Circulating Fluidised Bed.

Table 2 – Feed coal properties.

Unit	Ash%	Moisture %	Volatile Matter%	Gross calorific Value Kcal/Kg	C%	H%	N%	S%	Chlorine (mg/Kg)	Mercury mg/Kg
A	37.8	6.1	15.9	4201	45.48	3.92	1.57	0.36	1300	0.172 ± 0.004
B	42.2	3.3	22.3	4175	45.19	1.25	3.37	0.35	500	0.128 ± 0.005
C	39.7	9.6	21.9	4057	39.33	3.77	2.03	0.40	500	0.270 ± 0.010
D	35.2	9.8	21.7	3629	43.90	4.02	1.21	0.41	1300	0.243 ± 0.005
E	18.9	36.1	38.3	2937	32.88	0.57	6.96	0.18	500	0.163 ± 0.006

Table 3 – Partitioning of mercury in solid samples.

Mercury contents of solid samples (mg/Kg)				
Unit	Feed coal	Fly ash	Bottom ash	Mill reject
A	0.172 ± 0.004	0.106 ± 0.008	0.014 ± 0.003	0.261 ± 0.017
B	0.128 ± 0.005	0.064 ± 0.001	0.008 ± 0.004	0.640 ± 0.006
C	0.270 ± 0.010	0.065 ± 0.001	0.034 ± 0.002	0.031 ± 0.001
D	0.243 ± 0.005	0.085 ± 0.003	0.032 ± 0.001	3.535 ± 0.056
E	0.163 0.006	0.492 ± 0.011	0.012 ± 0.002	–

3. Results and discussion

3.1. Feed coal properties

The proximate analysis, Chlorine, Sulphur and mercury contents of collected coal samples were analysed and shown in the Table 2.

Coal samples: The analysis shows that the ash contents of coal samples vary between 35.2%–42.2%; moisture contents lie in the range of 6.0%–9.8%. The heat values of the coal samples are moderate to low and the gross calorific values of feed coal samples is in the range of 3600–4200 Kcal/Kg.

Lignite samples: The characteristics of the lignite samples are presented under Unit E in Table 2. Due to low rank, the air dried moisture is found to be high. The sample is having moderate ash content and heat values.

The total sulphur contents of the studied coal and lignite samples are in the range of 0.18–0.41%. Total chlorine content varied between 500 and 1300 mg/Kg. The mercury content of feed coal and lignite samples varies from 0.163–0.270 mg/kg. The values are comparable with average mercury concentration of Indian coals (UNEP 2014).

3.2. Partitioning of mercury in combustion products

During combustion, traces of mercury present in coal or lignite completely volatilises at high temperature as elemental mercury, due to its low boiling point. Under boiler ambient conditions, mercury vapours undergo thermo-chemical transformations. A part of the mercury may get oxidized under the influence of excess oxygen, halides and sulphur oxides present in flue gases. Catalytic role of particulates in oxidizing mercury in the vapour phase have also been reported. In the colder region of boiler, mercury may recondense and get adsorbed on fine ash particles and consequently captured by ESP. Due to milling and combustion at high temperature, feed coal mercury is partitioned in different products like fly ash, bottom ash, mill rejects, and flue gas.

Mercury content in feed coal varies largely was found in the range of 0.163 mg/Kg to 0.270 mg/Kg. Mercury concentrations of solid residues of power plants are presented in Table 3. Mercury contents of fly ash for pulverised coal fired boilers (A-D) found to be in the range of 0.064–0.106 mg/Kg. In the lignite fired circulating fluidised bed boiler (E), significant enrichment of mercury content in fly ash has been noticed. In all the boilers, mercury contents of bottom ash samples have been found to be much lower as compared to fly ash mercury values.

3.3. Relative enrichment factor (REF)

The relative enrichment factors (REF) were calculated to understand the partitioning of mercury after coal combustion process. The REF relates the mercury concentrations in the fly ash and the bottom ash to the concentration of mercury in the feed coal (Meij et al., 2002). Relative enrichment factor for mercury in fly ash and bottom ash were calculated as Eq. (1).

$$REF = \frac{C_i * C_{ash}}{C_{coal}} \quad (1)$$

where, REF is relative enrichment factor; C_i is the Hg concentration in fly ash or bottom ash, C_{ash} is the ash yield of coal, C_{coal} is the Hg concentration in coal.

The REF for Hg in fly ash and bottom ash are low (<0.23) for pulverised coal fired boilers which indicates volatile nature of mercury (Bhanagare et al., 2011). However, for circulating fluidised bed boiler, REF for fly ash is quite high (REF = 0.57) which indicates higher enrichment of Hg in fly ash in CFB boiler. The high mercury enrichment in fly ash for circulating fluidised bed boiler may be attributed to higher retention time of ash particles inside the boiler, lower boiler temperature and high unburnt carbon in the fly ash (Lei et al., 2007; Zhang et al., 2016; Zheng et al., 2017). The Loss on ignition of fly ash of circulating fluidised bed boiler was found to be 7.93%, whereas for pulverised coal fired boilers, the values range from 0.37–0.75%.

Table 4 – Mercury concentrations and speciation in flue gas.

Unit	Flue gas Hg (μg/Nm^3)	Oxidised Hg%	Elemental Hg%
A	18.5 ± 1.4	49	51
B	9.8 ± 0.35	45	55
C	29.4 ± 0.5	38	62
D	20.8 ± 1.8	42	58
E	9.2 ± 0.37	51	49

Table 5 – Mercury emission factors.

Unit	*G* (ton/hr)	*Q* (LHV) (kJ/kg)	*V* (Nm^3/hr)	*C* (μg/Nm^3)	MEF1 (mg/GJ)	MEF2 (mg Hg/ton of coal)
A	218	16,544.86	1,617,962	18.5	8.2	137.7
B	191	17,094.49	2,114,951	9.8	6.3	108.9
C	209	15,890.18	1,775,503	29.4	15.7	249.7
D	197	14,041.03	2,051,975	20.8	15.4	217.2
E	68.5	11,265.02	405,859	9.2	4.8	54.4

Mass Balance of boiler units

Unit	Hg Output/Hg Input (%)	Flue gas %	Fly ash %	Bottom Ash %	Mill Reject %
A	100.2	79.8	19.6	0.80	0.03
B	103.2	84.6	17.9	0.4	0.08
C	102.1	92.5	8.5	1.12	0.002
D	101.7	89.4	11.0	1.0	0.29
E	97.8	32.4	64.8	0.5	--

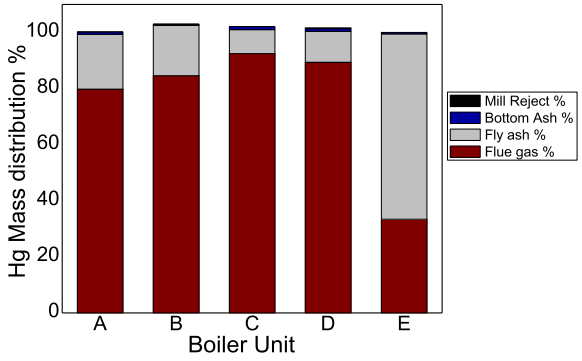

Fig. 2 – Distribution of mercury in combustion products.

3.4. Mercury in flue gas and speciation

Mercury being very volatile, it vaporises during combustion. Some mercury condenses on the fly ash and gets separated by ESP, and the rest emitted to the air. Table 4 shows the flue gas mercury concentrations and per cent elemental and oxidized mercury species present in flue gases. The total mercury concentration per unit volume in the flue gas samples studied have been found to lie in the range of 9–29 μg/Nm^3 (Table 4). The values are within the threshold limit of mercury emission norm of 30 μg/Nm^3 for Indian thermal power plants. It is observed that with increasing mercury contents of fuels, flue gas mercury concentration has also increased. However, other factors like boiler design, operational parameters, temperature profile inside the boiler and flue gas line, dust load in the flue gas stream, ESP efficiency etc. influence the flue gas mercury concentration. Low mercury emission level has been observed in circulating fluidised bed boiler flue gas (Table 4).

The speciation of elemental and oxidised mercury was measured with help of special sorbent traps having KCl and activated carbon as adsorbents. It is observed that oxidised mercury varies from 38% to 51% of total mercury emitted. Oxidised mercury concentration highly depends on interaction of elemental mercury in flue gas with different species like Cl_2, HCl, O_2, NOx, etc. present in flue gas (Wang et al., 2009). Oxidised mercury being more water soluble and reactive compared to elemental mercury can be easily removed by wet gas desulphurisation, whereas elemental mercury is inert in nature and is difficult to remove by air pollution control devices.

3.5. Mercury mass balance

The mercury mass balance has been worked out using the results of above analysis for the selected five boiler units. It indicates the distribution of the mercury within the system which allows us to understand the major mercury release pathways for better mercury management. For material balance exercise, material flow and other necessary data like coal feed rates, production of fly ash, bottom ash, mill rejects, plant load factor, ambient temperature and pressure, flue gas composition, stack dimension etc. have been collected from plant operators. To perform mercury mass balance calculation, it is assumed feed coal mercury is the only mercury input source and the feed mercury is partitioned in different outputs like fly ash, bottom ash, mill rejects and flue gas. It is also assumed that for pulverised coal fired boilers 80% of total ash is fly ash, 20% is bottom ash, whereas for circulating fluidised bed boiler 75% of total ash generated is fly ash and 25% is bed ash. In case of CFBC boiler, lime is added for SO_2 control. Lime contributes small mercury input into the system. Mercury content of lime is found to be 0.096 ± 0.003 mg/Kg and the value has been taken into account for overall mercury mass balance.

The partitioning of mercury in the products is presented in Fig. 2. The Table shows that major portion of feed mercury is emitted through stack. For the pulverised coal fired boilers (A-D) about 80–90% of total mercury, released to the atmosphere and rest portion remained associated with fly ash. Mercury concentration in fly ash was higher than that in bottom ash. Bottom ash and mill reject contained only a very small fraction of feed coal mercury.

The proportion of feed coal mercury distributed in the combustion products and mill rejects is depicted graphically in Fig. 2.

In case of Circulating Fluidised Bed boiler, mercury distribution pattern in the products have been found to be quite different. It is observed that major portion of mercury is associated with fly ash (64.8%). As previously discussed, in CFBC boiler due to high retention time of the ash particle in the boiler, high unburnt carbon and low boiler temperature, majority of the mercury gets associated with the fly ash and captured by the ESP. Only a small portion are emitted through flue gas (32.4%). Bed ash contained an insignificant percentage of input mercury (0.5%).

3.6. Mercury emission factor (MEF)

Mercury emission factor (MEF1), a relationship between mercury emission into the atmosphere and heat value of the consumed coal in thermal power stations, has been derived for all the studied plants using following equations.

$$\text{MEF1} = \frac{m}{G \times Q}$$

$$m = V \text{ x } C$$

where, MEF1 is mercury emission from flue gas per unit of Lower heating value (LHV) of coal, mg/GJ; m (mg/hr) is emission of mercury from flue gas; G (ton/hr) is coal consumption; Q (kJ/kg) is Lower heating value (LHV) of feed coal; V (Nm^3/hr) is flow rate of flue gas; C (ug/Nm^3) is concentration of mercury in flue gas.

The estimated MEF for five power plants are shown in Table 5. The MEF1 varied in the range of 4.8–15.7 mg/GJ. MEF1 values indicate that for boiler units' B and E, MEF1 values are much lower than the other units. This is corroborated by the findings that flue gas mercury concentrations are also lower (Table 4) as compared to other three boiler units. The MEF values for nine power plants in US varied in the 0.82–9.46 mg/GJ whereas for Chinese power plants it varied between 0.68–4.70 mg/GJ. The derived MEF1 for the plants under the present study are in the higher side compared to the US and Chinese coal power plants (US Department of energy, 1996; Gao et al., 2014; Wang et al., 2017; S. Zhao et al., 2017b; Wu et al., 2010). Similarly, Mercury emission factor (MEF2) in terms of the amount of mercury released in the atmosphere per tonne of coal combusted were also estimated. The estimated MEF2 values as shown in Table 5, ranges between 54 and 249 mg Hg/ tonne of coal. The estimated MEF2 are slightly higher than reported for Chinese power plant (Wang et al. 2010). The MEFs depend on various factors like mercury content in the feed coal, coal rank, efficiencies of air pollution control devices installed. Higher MEFs obtained for these plants may be attributed to the fact that the plants have only ESP as pollution control device; whereas coal fired power plants in China and US have additional air pollution control devices like FF, FGD, and SCR etc.

4. Conclusions

Comprehensive mercury mass balance studies have been performed for five selected Indian coal and lignite fired power plants. Mercury contents of feed coals, mercury emissions concentrations, partitioning of mercury in various combustion products, mercury speciation in flue gas and mercury emission factors have been derived. Relative enrichment factor for fly ash and bottom ash were also estimated. The mercury contents of feed coal and lignite samples varied within 0.163–0.270 mg/Kg. The REF values show that there is significant enrichment of mercury in fly ash, particularly for circular fluidized bed boiler. The mercury concentration of flue gases varied in the range of 9–29 $\mu g/Nm^3$. It may be noted that mercury concentrations of flue gas are always below the threshold limit of 30 $\mu g/Nm^3$ prescribed for Indian coal based power plants. The speciation results indicate that 50–60% emitted mercury are in elemental form. The mercury emission factor for the tested plants varied in the range of 4.8–15.7 mg/GJ. The mercury emission from Indian thermal power plants could be significantly reduced by modification and optimization of process parameters of ESP; installation of other air pollution control devices like FF, FGD, SCR and use of oxidizing additives during combustion.

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Environmental Quality Monitoring

in

Singrauli Problem Area

February 2009 to January 2010

Sponsored by

Central Pollution Control Board

Banwasi Sewa Ashram

Govindpur, Sonebhadra, U.P.

August 2010

Executive Summary

The Banwasi Sewa Ashram (BSA) was set up in 1954 in Sonebhadra District of Uttar Pradesh to work for the development of the forest dwellers, and in 1960 took up the cause of the people who were displaced by the emergence of the Pantsagar reservoir on the Rihand river. In later years, the development of an aluminium smelter, several coal mines, and thermal power plants added to the industrialisation of the area as well as further degradation and displacement.

The first comprehensive environmental impact study of the area was conducted in 1988 by Electricity de France/Charbonages de France (EdF/CdF) to predict what would be the impacts when power generation grew from a little over 6,500 MW to an eventual target of about 18,500 MW. Various studies were also carried out by other agencies over the next decade. And BSA began its own environmental studies in 1997.

BSA established its environmental laboratory in 1998 and was able to obtain a grant from the Central Pollution Control Board (CPCB) in 2002 to conduct detailed monitoring of air and water quality on the eastern side of the reservoir. CPCB awarded a second study in 2003-2004, and then a third study in 2005-2006. Eventually, a fourth study was awarded for 2009-2010. Each time the scope of the study was enlarged to cover more area and more parameters.

In these studies BSA has been able to obtain valuable technical inputs and assistance from institutions such as Envirotech, People's Science Institute Dehradun, Mahatma Gandhi Grameen Vishwavidyalaya Chitrakoot, Indian Institute of Technology Kanpur, and the expert guidance of Dr G D Agrawal, first Member-Secretary of the CPCB. This has considerably enhanced the technical capacity of BSA, in addition to deepening its commitment

This report presents the results of the monitored data for the year from February 2009 to January 2010 for 9 ambient air monitoring stations, 21 locations for monitoring surface water quality in the river, reservoir, and drains, and 14 locations for ground water monitoring in the Singrauli region – now recognised as a "problem area" by the CPCB. In addition, an effort has also been made to compare the results of 2009-2010 with data from the earlier years.

The findings from this study clearly show that the extent of air pollution has been worsening over the years and is more widespread than previously projected. Particulate matter is above the limits all over the region, as are gaseous Fluoride and Mercury. Sulphur Dioxide and Nitrogen Oxides values are still within limits although they display a steadily rising trend. The Pantsagar reservoir is showing signs of stress with high Dissolved Solids, low Dissolved Oxygen, and increasing Chemical Oxygen Demand.

Most of the pollutants are being discharged into the river and reservoir through drains that receive industrial effluents, including high concentrations of Fluoride and Mercury. The ponds on the eastern side of the reservoir also contain unacceptably high Mercury concentrations through the dry months. And these pollutants have leached through to the ground water which is also contaminated with Chlorides, Nitrates, Fluoride, and Mercury.

It has been noticed that some pollutant concentrations declined between 2003 and 2006, when the BSA was doing regular monitoring, and then increased again before BSA got the fourth award in 2009 – partly because of the steps taken by industries to mitigate pollution prior to 2006, and partly because of the subsequent increase in thermal power production in the region without much oversight by regulatory agencies.

Hence, apart from recommending continuous and regular monitoring by an independent citizen's body, this study also suggests that stringent measures have to be taken by the regulatory authorities to enforce mitigation measures, change process parameters where

necessary, and prosecute polluters. Some source identification of pollutants, analysis of causes of certain anomalous conditions, as well as impacts on living beings and environmental health – which have been highlighted by this and earlier studies – is also required and should be the target of future intensive research.

There have been questions raised whether institutions like Banwasi Sewa Ashram – originally set up to serve the cause of the forest-dwelling population – should be involved in scientific research of this kind. As this report illustrates, BSA now not only has developed the technical capacity and the support of competent individuals and institutions who have in-depth experience in the field of environmental studies but, more importantly, has a presence in and commitment to the Singrauli area which no other agency possesses.

When authorised regulatory agencies such as the State Pollution Control Boards fail to monitor and control the pollution is areas such as Singrauli, it is eventually up to the civil society organisations to act on the behalf of citizens and the marginalised people who presently have little voice in the governance of their own nation.

Contents

Introduction

The Banwasi Sewa Ashram (BSA) is located in Sonebhadra (earlier Mirzapur) District of Uttar Pradesh and was set up in **1954** to work for the development of the forest dwellers who were deprived of basic livelihood facilities and were being exploited and often working as bonded labour. In **1960** many scheduled and backward caste families, as well as tribals, who were displaced from the Rihand valley were also relocated in the area. The displacement from the valley was related to the submergence of 430sq.km of agricultural land by the Rihand dam and the emergence of the Pantsagar reservoir.

This also marked the beginning of the generation of 300MW of hydro-electric power from the dam, as well as the setting up in **1962** of the Hindalco aluminium smelter (capacity of 150,000tpa) and its ancillary units (Kanoria Chemicals producing 33,000tpa of Caustic Soda and Carbon Black manufacturing electrodes) near the dam. The discovery of extensive coal deposits in the Moher and Singrauli basins to the west of Pantsagar also led to the opening of the first open-cast coal mine at Jingurdah, and this catalysed the development of thermal power generation as well as further displacement of the people.

Beginning with the Renusagar Thermal Power Plant (TPP) in **1967**, five more Super Thermal Power Plants (STPP) have come up at Obra, Singrauli, Anpara, Vindhyachal, and Rihand. Coal production to feed these plants has increased correspondingly with 15 open-cast mines of National Coal Limited (NCL) exploiting the coal reserves (about 52 million tpa). Also in **1967** the UP State Cement Corporation set up a cement plant (800,000tpa) near Obra at Dala. As expected, all these industrial developments have led to significant environmental and social impacts in the region.

In **1988**, when total power generation was ***6,760***MW and the National Thermal Power Corporation (NTPC) was contemplating further expansion of capacity in its units at Singrauli, Vindhyachal, and Rihand, it commissioned m/s Electricity de France /Charbonages de France (EdF/CdF) to conduct an environmental impact study of the entire region. Through their study EdF/CdF concluded that not only was the then industrial development within tolerable limits of the environment but further expansion of power generation could take place (up to ***10,510***MW in the first phase and ***18,510***MW in the second) without “significant impact”.

A few other studies have also been carried out by other agencies such as the Geological Survey of India (GSI) at Jabalpur in **1992**, and by the Coal Mine Planning and Design Institute (CMPDI), Ranchi. The GHK/MRM study of **1993** also monitored air and water quality. Both NTPC and NCL have been regularly monitoring environmental parameters as well as commissioning studies by the University of Roorkee, the Indian Institute of Technology at Kanpur, the Industrial Toxicology Research Centre in Lucknow, and the Central Mine Research Institute, Dhanbad.

In **1997** the projected trend of power generation in MW was as follows:

TPP	1988	1992-97	1997-02	2002-08	2008-12
Rihand	1000	500	500	1000	
Anpara	630	1000		1500	
Renusagar	337	148			
Kanoria		25			
Vindhyachal	1050		1000	500	
Singrauli	2000			500	
Obra	1550				
New plants					6000
Total MW	**6567**	**8240**	**9740**	**13240**	**19240**

Environmental Impact Studies

Concerned at all these developments and their impacts on the people, as was being partially observed through the incidence of skeletal and dental deformities as reported by the medical clinics that BSA had set up on the eastern side of the reservoir, the Ashram organised a workshop in **1996** that was attended by representatives of the various industrial units, subject matter experts, and people from the affected villages. This workshop marked the first attempt to understand the impacts in their entirety and to move towards a comprehensive and participatory assessment methodology for social and environmental impact.

Subsequently, BSA initiated its first study of the environment in **1997** under the design and supervision of Dr G D Agrawal (Senior Professor and Head of Department of Environmental Engineering at the Indian Institute of Technology, Kanpur, and the first Member-Secretary of the Central Pollution Control Board, Delhi). During this study Suspended Particulate Matter (SPM) concentrations were measured at 10 stations on the eastern side of Pantsagar, and Lead and Arsenic were monitored at two stations near the Hindalco plant. In addition, BSA workers also carried out an assessment of the damage to fruiting trees and crops in 22 villages on the eastern and southern sides of the Pantsagar reservoir.

In the process BSA established its environment laboratory in **1998** through which it was able to monitor air, water, soil, seeds, and crops in the region under the wise guidance of Dr Agrawal. BSA has also been able to obtain valuable technical inputs and assistance from environment scientists Drs Ravi Chopra, Anil Gautam, and Ramesh Tripathi from the Environmental Quality Monitoring Group at the People's Science Institute, Dehradun, Dr Sadhna Chaurasia, Professor of Environment Science at Mahatma Gandhi Grameen Vishwavidyalaya, Chitrakoot, Dr Rajendra Prasad of Envirotech, Delhi, and Dr Mukesh Sharma, Professor and Head of Department of Environmental Engineering at Indian Institute of Technology, Kanpur.

The Central Pollution Control Board (CPCB), Delhi awarded its first study to BSA in **2002**. 4 locations for air sampling were selected for this study to monitor Suspended Particulate Matter (SPM), Respirable Suspended Particulate Matter (RSPM), Sulphur Dioxide (SO_2), Nitrogen Oxides (NO_x), Fluoride (F), and Mercury (both Gaseous and Particulate Hg). 8 sites were specified for sampling surface water in the Pantsagar reservoir and Rihand river, along with 5 village ponds and *bawadis*, and 5 drains carrying effluents. The parameters that were measured were pH, Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Chemical Oxygen Demand (COD), Dissolved Oxygen (DO), Electrical Conductivity (EC), Fluoride (F) and Mercury (Hg).

After evaluating the results of this study, CPCB awarded a second study to BSA for **2003-2004** that increased the number of air sampling stations to 6, with the addition of one filter paper per month for Benzene Soluble Fractions. The number of water sampling sites remained the same (although locations of 2 sites on the river were altered and another site was added for drains). 12 locations along the periphery of the reservoir were added for bio-monitoring during the non-monsoon period; and 10 sites were selected for ground water quality monitoring (depth, pH, Hardness, EC, COD, Nitrate, Chloride, F, and Hg). A preliminary survey for health impact was also carried out on the basis of existing medical records.

The above study was supposed to be for a period of two years but CPCB gave the next contract for **2005-2006**, beginning from September 2005. The Terms of Reference for this study were the same as earlier, except that 3 more stations were added for ambient air quality monitoring, 2 new sites selected for overflows from Effluent Treatment Plants (ETP), and ground water quality was measured in 3 more wells, while bio-monitoring was dropped. Meteorological data was also locally generated and/or procured from other

institutions. The parameters included Hardness, pH, EC, Iron, COD, F, Nitrate, Chloride, and Hg.

From September 2006 to January 2009, for over two years, CPCB reviewed the entire programme and eventually awarded another year-long study for **2009-2010** to BSA beginning February 2009. 6 older stations for ambient air quality were retained, 2 were dropped, and 3 new stations were selected for wider coverage of the spread of pollutants. The 21 locations for monitoring surface water quality in the river, reservoir, drains, and ponds remained the same as in the earlier period, except for the addition of another site for sampling ash pond overflows. The parameters remained the same as for the earlier period. Ground water monitoring was continued for the earlier 13 locations, with the addition of another one, for two times in the year.

This report presents the results of the monitored data for the year from February 2009 to January 2010 at all these locations and analyses the emerging trends. In addition, an effort has also been made to compare the results of 2009-2010 with earlier years, even though some of the monitoring locations and parameters may have changed slightly over the years, in order to understand the longer-term patterns and whether the monitoring exercise has had any perceived impact on the overall quality of the environment.

The February 2009 to January 2010 Study

Terms of Reference

In view of the area of the study being extensive, the exercise was undertaken in the following manner, as per the Terms of Reference stipulated by the CPCB Zonal office at Lucknow:

Ambient air quality (Total 9 locations):

- Air quality was monitored at each station in such a way that all the stations were operated uninterrupted for 2 days (48 hours) in every month.
- The monitoring was carried out round the year except on rainy days during the monsoon period.
- The parameters monitored were SPM, RSPM, SO_2, NO_x, F, and Hg (both gaseous as well as particulate). One filter paper per month was analysed for Benzene Soluble Fractions.
- The monitored parameters were compared to Indian and International Standards.

Surface Water Quality:

- Surface water quality was monitored at 22 locations, out of which 9 were on major drain outfalls, 8 were on the Rihand reservoir, and 5 were on village ponds. Additionally, 3 drains were monitored for collection of 24 hour composite samples. The parameters were pH, TSS, TDS, COD, DO, EC, F, and Hg.
- The monitoring at all locations was undertaken on a monthly basis, avoiding the monsoon season when the site was unapproachable.
- The monitored parameters were compared to Indian and International Standards.

Groundwater Quality:

- Groundwater quality monitoring was carried out at 14 locations.
- The monitoring was carried out once in the pre-monsoon (May-June) and once in the post-monsoon (October-November) periods.
- The monitored parameters were; pH, TSS, EC, TDS, COD, Chloride, F, Nitrate and Hg

Details of Monitoring Locations

Station Code	Location	Salient Details
A-1	Dhuma-Kewal	A remote village, visibly free from any type of polluting activity other thab usual rural activities, over 80 km east-north-east of coal mining and TPP complex, and 40 km east of Renukoot complex. Selected as a control site; located on roof of the school building.
AA-2	Jahra-Rajo	In the southern side of the Pantsagar reservoir, about 5 km east of the Rihand STPP township and likely to show the cumulative impact of emissions from RSTPP and its ash ponds as also transported pollutant from the tall stacks of

		Vindhyachal STPP and Singrauli STPP in the west.
A-3	Murdhawa-Renukoot	4 km east of Hindalco main gate on Varanasi-Shaktinagar highway. Likely to show immediate impact of Hindalco, Kanoria, and Carbon Black industries and also of the highway. Located on the roof of Hotel Padmini close to Radha-Krishna temple.
A-4	Dala-Bari	Located on the roof of a private house in Bari about 1 km east of the highway as it enters Dala from Chopan side. The station is likely to show impact of the nearby stone crushers and cement plant, as also the Obra STPP and associated transportation.
A-5	Kubari-Anpara	Located almost 5 km north from Anpara TPP to the north of the Pantsagar reservoir near the hilly range. Likely to show cumulative impact of air pollution from the coal mines on the area next to the Anpara and Renusagar TPPs.
AA-6	Navatoliya	Located north of the reservoir, about 3 km southeast of Bari-Dala station (A-4). Situated so as to capture the plume descent and gaseous and fugitive dust emissions from the Obra STPP, the cement plant, the stone crushers, and associated transportation.
AA-7	Lojhara	Located further east of Kubari-Anpara station (A-5), almost 9 km from the Anpara TPP and mid-way to Hindalco and Kanoria Chemicals (Renukoot) in the east. Likely to catch the long distance spread of pollutants from the Anpara and Renusagar TPPs as well as the Renukoot industries.
A-8	Govindpur	Located about 5 km southeast of Renukoot near the eastern highway, and is the centre of BSA. Selected to capture the south-eastern impact of pollution from the industries located in and near Renukoot.
A-9	Katauli	Located about 6 km east of Hindalco and expected to capture the plume descent from the Renukoot group of industries along with suspended particulates and gaseous emissions.
BS-2	Orangi	Located near the bridge where Murdhawa-Bijpur-Baidhan road crosses river Rihand. This is the point where the river enters Pantsagar reservoir and represents the upstream quality of river Rihand, acts as a reference station.
BS-5	Balia drain confluence	Located adjacent to the southern boundary of Singrauli STPP. The station receives sewage, coal mine effluents, and ash pond overflows from Vindhyachal STPP through the Balia drain at its confluence with the reservoir.
BS-8	Renusagar ash pond confluence	Located at the periphery of the Pantsagar reservoir south of the Anpara TPP where it receives the overflow from the ash ponds of the Renusagar TPP.
BS-9	Pipri-Sonwani	Located on the northern periphery of the reservoir, midway between the ash ponds of Anpara and Renusagar TPPs and the Rihand dam, to give the quality of the reservoir after cumulative discharges on the western side.

BS-11	Khamhariya	Located on the south-eastern periphery of the reservoir where it measures the cumulative impact of the discharges from the Rihand STPP and downstream of the Ajir river.
BS-13	Dongia drain confluence	Located about 200 m north of the ferry point (to avoid impact of the ferry) at the confluence of the Dongia drain with the reservoir. The Dongia drain carries the discharges from Kanoria Chemicals into the Pantsagar reservoir.
BS-15	Murdhawa drain confluence	Upstream of the Obra Dam, this point represents the river quality as it enters Obra reservoir including the downstream impact of the Murdhawa drain that carries the discharges of Hindalco and Carbon Black.
BS-16	Obra ash pond confluence	Only 0.5 km before the confluence with river Sone, this station gives the ultimate quality of river Rihand as it discharges into the Sone and carries the cumulative pollutants from the Pantsagar reservoir and the Obra TPP.
S-4	Balia drain	Located on the left bank of the drain, just upstream of the bridge leading to Khadia Project, the station indicates the quality of coal mine drainages. It is about 1 km before the confluence of the drain with the Pantsagar reservoir
S-12	Dongia drain	Located about 1 km downstream of the railway bridge on the drain and about 0.5 km before it joins Pantsagar reservoir. The station essentially monitors the overall discharge of effluents from Kanoria Chemicals.
S-14	Murdhawa drain	Located near the Varanasi Renukoot road bridge on Murdhawa drain. The drain appears to receive some Hindalco discharge besides a lot of township waste waters.
S-20	Bina ETP	These three stations were chosen at the outlets of the respective Effluent Treatment Plants from three clusters of coal mines at Bina, Kakri, and Dudhichua in order to assess the water quality of effluents after treatment and the performance of the ETPs.
S-21	Kakri ETP	
S-22	Dudhichua ETP	
S-23	Anpara Ash Pond	These two new stations were selected at the point where the overflows from the ash ponds of the Anpara TPP and the Singrauli STPP were draining out of the ash ponds and flowing towards the Pantsagar reservoir.
S-24	Singrauli Ash Pond	
S-25	Rihand drain	This is also a new station that measures the discharge from the Rihand STPP and ash pond into the reservoir.
S-17	Kirwani pond	These are three village reservoirs that were created by constructing small earthen dams along natural drainage channels. All the three ponds are intensively used by people for agriculture and also for bathing, washing and cattle watering etc. The purpose was to monitor the quality of the flows from the respective catchments into these village ponds.
S-18	Chetwa pond	
S-19	Bakulia pond	
BSA-1	Govindpur *bawadi*	The Govindpur *bawadi* is a large pit that is used mainly for cattle-watering.

BSA-2	Govindpur pond	The pond has been created by constructing a small earthen dam and is used for bathing, washing, irrigation etc.
SG-1	Hand pump near water intake point, Obra	
SG-2	Hand pump near Rotary Health Centre, Renukoot	
SG-3	Hand pump near slum next to Dongia drain, Renukoot	
SG-4	Hand pump near Renusagar Inter College	
SG-5	Hand pump near Kubari Primary School, Anpara	
SG-6	Hand pump near Behind Bina Stadium, Bina	
SG-7	Hand pump near Orangai	
SG-8	Hand pump near *bawadi* at Chetwa	
SG-9	Hand pump near *bawadi* at Bakulia	
SG-10	Hand pump at Jhirgadandi	
SG-11	Hand pump at Khamariya	
SG-12	Hand pump behind Ashram School, Govindpur	
SG-13	Hand pump at Primary School, Katauli	
SG-14	Hand pump near Supachuan	

The locations of these stations in **Maps 1 to 4**, along with the protocol for sampling and analysis, are given in ***Annexure I***.

Methodology

In order to ensure proper execution and progress of envisaged activities and timely review of expenditure a four member Project Management Committee was constituted with the following members:

1. Dr G D Agrawal – former Head, Department of Environmental Engineering, IIT Kanpur
2. Dr Ravi Chopra – Director, People's Science Institute, Dehradun
3. Dr Sadhna Chaurasia – Professor, MGCG Vishwavidyalaya, Chitrakoot
4. Dr Ragini Prem – Secretary, Banwasi Sewa Ashram

In addition, from time to time, assistance was sought from Dr R Prasad, Envirotech, New Delhi and Dr Anil Gautam, People's Science Institute, Dehradun, who participated in the orientation of the research team and selection of new stations.

A seven member team was formed by BSA to undertake the actual monitoring exercise comprising of:

1. Shri Hemant Prabhakar – B.Sc
2. Shri Chandra Shekhar – Inter Science
3. Shri Raju – M.Sc (Env)
4. Kum. Shalini – M.Sc (Env)
5. Shri Bhanu Pratap – M.Sc (Env)

6. Shri Sajal – M.Sc
7. Shri Dhanraj - driver

BSA possessed the following equipments which were serviced and calibrated at Envirotech, New Delhi for the purposes of this study:

a. Respirable Dust Sampler APM 460 – 1 no.
b. Respirable Dust Sampler APM 460BL – 1 no.
c. Thermoelectrically cooled gaseous attachment APM 411TE – 2 nos.
d. Generator set Birla Yamaha – 1 no.
e. Spectrophotometer – 1 no.
f. Balance – 1 no.
g. COD apparatus – 1 no.
h. pH meter – 1 no.
i. EC meter – 1 no.
j. DO meter – 1 no.

The methodology followed for monitoring was as specified in the CPCB manual (Central Laboratory Test Methods DOC: CB/CL/TH/9/C). Detailed descriptions of sampling were provided to the CPCB Zonal office with each quarterly report. Two members of the BSA team participated in replicate analysis of samples at the CPCB Zonal office laboratory for three days at the end of December 2009, as part of an Analytical Quality Control exercise. The results of the analysis conducted by the BSA staff were provided to the CPCB Zonal office for cross-verification. In June 2010 the preserved samples of RDS filter paper were transported to Lucknow by a member of the BSA team for analysis of Benzene Soluble Fractions as given in ***Annexure III***. *However, the results of the above analyses by the CPCB Zonal office have not been made available to BSA and, hence, are not included as part of this report*.

The monitoring protocol and results of the sampling and analysis for nine ambient air quality stations, eight river and reservoir quality stations, five village ponds, nine stations for effluent flows, and samples from fourteen hand pumps to assess ground water quality, in the period from February 2009 to January 2010, are presented in **Tables 1 to 6** given in ***Annexure III***. A graphical representation of the results for 2002, 2003-2004, 2005-2006, and 2009-2010 in the **Figures 1 to 45** is given in ***Annexure II***. These results for 2009-2010, as well as the trends from the discontinuous data available between 2002 and 2010, are discussed in the sections below.

1. Ambient Air quality

Ambient air quality was measured at nine stations for 2009-2010 (Map 1). There were three new stations from 2005-2006, namely Lojhara (north of the Reservoir), Navtoliya (north-east) and Jarha-Rajo (south of the reservoir) identified for air monitoring. The parameters to be monitored included Suspended Particulate Matter, Respirable Suspended Particulate Matter, Sulphur Dioxide, Nitrogen Oxides, Fluoride (gaseous), and Mercury (gaseous and particulate). The detailed results are given in Table 1 in ***Annexure III***.

RSPM and SPM

As may be seen from Table 1a and Fig.1, the RSPM value was observed ranging from 39 at Dhuma-Kewal (the control station) to 377 µg/m^3 at Navtoliya (east of Dala) for eight stations excluding Bari-Dala. As expected, the highest value at Bari-Dala was 1290 µg/m^3 because of the presence of a large number of stone crushers. However, what is notable is that even for the control station of Dhuma-Kewal the values exceeded the permissible limit of 60 µg/m^3 in the early summer months, while all other stations exceeded the limit for all twelve months, except for Katauli in the three rainy months. At all locations the values dipped in the wet months between June and October, but increased significantly in the dry summer. A corresponding trend is observed for SPM (Table 1b, Fig.2), with Bari-Dala as the station with extremely high values going up to 2127 and 2089 µg/m^3 in December and April respectively. Even Dhuma-Kewal exceeds the limit of 140 µg/m^3 in March and April. All other stations, without exception, exceed the limits for all the twelve months.

If one were to compare the results for 2009-2010 with data available for other preceding years (Figs.1 and 2) it is clear that minimum values during the monsoon months have been steadily rising over the years and have crossed the permissible limits in the latest round of monitoring. At the same time, maximum values seem to be coming down and the variation over the year is significantly lower for 2009-2010 – and this may be because of more effective performance of ESPs during the dry months. The only exception is Bari-Dala where the pollution levels are outstandingly high and there is no amelioration perceived because of lack of control measures for the stone crushers.

SO_2 and NO_x

SO_2 values given in Table 1c and Fig.3 are seen to be generally lower than the permissible limit of 60 µg/m^3, except occasionally between March and June, for Kubri-Anpara, Lojhara, Murdhawa-Renukoot, and Govindpur. This clearly indicates the cumulative impact of pollution from the nearby stacks of industrial units in the western and northern part of the region – especially since Bari-Dala in the north does not display a similar pattern and the control Dhuma-Kewal remains stable at a value lower than 6 µg/m^3. Interestingly, Katauli, to the east of the Renukoot, also shows a peak in values during the summer months, but this does not cross the limit. NO_x values (Table 1d and Fig.4) also show a peaking pattern in the summer months, with some stations such as Murdhawa-Renukoot, Kubri-Anpara, Bari Dala, Lojhara, and Jarha Rajo giving concentrations higher than the permissible limit. Again Dhuma-Kewal remains stable with a maximum concentration of 10 µg/m^3, with values 3-4 times lower than for all other stations, even during the wet season. This pollution may thus be traced to the degree of transportation in the region.

The trends over time (Figs.3 and 4) seem to indicate that, while the peaks remain high during the summer, the average levels of gaseous pollution reduced between 2003-2004 and 2005-2006, but have begun steadily rising in 2009-2010 for both SO_2 and NO_x.

Dhuma-Kewal is the only station that remains relatively stable. Hence, the adverse impacts of growth in power generation and transportation in the area are quite clear.

F and Hg

Gaseous Fluoride (Table 1e) is higher for Murdhawa-Renukoot, touching a peak of 10.5 $\mu g/m^3$ in May, which is to be expected because of the presence of the Hindalco smelter at Renukoot. However, for some inexplicable reason, it also reaches a maximum of 15 $\mu g/m^3$ at Kubri-Anpara during February. But there is a similar peak going over 7 $\mu g/m^3$ for Lojhara, Katauli, and Murdhwa-Renukoot in the same month. This may indicate a large emission from Hindalco in that month since all the stations lie roughly in the same east-west line. Otherwise F remains below 5 $\mu g/m^3$ for all stations for the rest of the year. Gaseous Mercury (Table 1f) was not monitored for the rainy season but it too shows a peak similar to F in the months of February and May. It is found below the detectable limit for the reference site at Dhuma-Kewal, but is unacceptably higher than the permissible level of 12 ng/m^3 for all other stations. It consistently reaches levels higher than 500 ng/m^3 for Lojhara, Murdhwa-Renukoot, and Kubri-Anpara, again lying within the same belt for high F emissions. Particulate Hg (Table 1g) was also not monitored during the rainy season but it shows a similar pattern of being low in the control site at Dhuma-Kewal, but higher than the permissible limit (3 $\mu g/m^3$) for the rest of the stations for most of the year. Particularly high values of over 8 ng/m^3 may be seen during the winter months for Murdhawa-Renukoot, Lojhara, Govindpur, Bari-Dala and Navtoliya stations, all lying adjacent to each other in the northern part of the region.

The comparison with previous data (Figs. 5, 6, and 7) indicates that gaseous F has been steadily rising since 2003-2004 but gaseous Hg decreased from 2003-2004 to 2005-2006 and is again showing a rising trend, particularly between the months of February and May. Particulate Hg, on the other hand, rose sharply in 2005-2006 and has since declined, although not to 2003-2004 levels.

2. Water quality of Rihand River and Pantsagar Reservoir

The eight stations at the confluence of various drains with the reservoir and one station at the control point upstream of the reservoir, that were monitored in 2005-2006, were also selected for the present study (Map 2).

pH

As given in Table 2a and Fig.8 the pH levels vary within permissible limits for all stations except for one exception for the confluence of the Renusagar ash pond drain with the reservoir, where the value reaches 9.4 during December. Values generally are higher in winter and lower in the rainy season.

Compared to earlier years (Fig.8), the reservoir as a whole is tending towards an average pH of 8 without any of the peak acidic or alkaline discharges from the Dongia, Balia and Khamaria nalas seen in 2003-2004.

TSS

Just before its entry into the reservoir at Orangi, the Rihand river shows very good water quality with negligible TSS that goes up significantly to between 200-300 mg/l during August and September (Table 2b). But the remaining stations also show a similar trend with values below 60 mg/l during the non-monsoon months. Values tend to go well over the permissible 100 mg/l during the August to October period for all stations, although they are lower than what the river brings to the reservoir, except for the confluence with the Balia nala (bringing a load of 376 mg/l from the coal mining region) during August.

Compared to the monitoring of earlier years (Fig.9) it is apparent that the huge loads in the Obra region have significantly reduced as well as at other stations such as Khamaria, Renusagar, Pipri, Dongia, Obra, and Balia nalas. Thus, it would seem that measures have been taken upstream on these drains to mitigate the impact somewhat.

TDS and EC

As has been reported earlier, the values for TDS and EC follow identical patterns (Tables 2c and 2d). All the values are below the permissible levels for TDS, but at the confluence with the Dongia nala there is a surge above 700 mg/l during August, September, and January. This indicates that there are excessive releases upstream from the Kanoria Chemicals that have not been adequately treated and mitigated.

When seen against the data for earlier years (Figs. 10 and 11) it is apparent that there was significant improvement in 2005-2006 when there were smaller spikes up to 600 mg/l at the confluences with the Renusagar and Pipri drains, but this improvement has been negated in 2009-2010 when values are going well over the 2003-2004 levels for almost all stations.

DO and COD

DO levels remain between 6 and 8 mg/l for almost all stations, indicating a fairly healthy water quality even though COD levels range between 150 to 250 mg/l during the August-September season (Tables 2e and 2f). Only the Balia nala confluence crosses the limit and goes up to 298 mg/l in January. Hence, the ability of the reservoir to cope with influents appears to still be adequate.

However, a comparison with previous trends (Figs. 12 and 13) shows that while the COD levels are rising for most stations, the DO levels do not demonstrate the wide variation between 6 and 12 mg/l that they had earlier. In other words, the capacity of the reservoir to process polluting loads is declining.

F and Hg

Fluoride levels at all stations remained well below the permissible level and ranged from a minimum of 0.2 mg/l at Orangi upstream of the reservoir to maxima of 1.5 mg/l at the confluence upstream of Obra (which receives the effluents from the Murdhawa nala) in May and 1.4 mg/l for the confluence with the Dongia nala in January (Table 2g) – indicating that the main pollutants in this regard come from the industries at Renukoot. Mercury, on the other hand, was well above the permissible limit at all stations – even at the reference point of Orangi in April, May, and January (Table 2h). But the huge spikes in values were in April when values reached massive levels of over 2 µg/l at the confluences with Balia, Khamaria, and Dongia drains with levels going up to 8.3 µg/l for the Balia nala and a surprising 6.3 µg/l at the confluence at Khamaria.

Looking at the trends over time (Figs.14 and 15) Fluoride levels in the reservoir have clearly gone down, but Mercury levels remain disturbingly high with some dilution after the rainy months.

3. Water quality of Village Ponds

Five village ponds, including two within the campus of Banwasi Sewa Ashram, were monitored to assess the water quality of surface storages that were not fed by any effluent drains and were dependent only on rain-fed runoff (Map 2) All these ponds are on the western side of the reservoir.

pH

The pH values for all the five ponds remained well within the limits prescribed (Table 3a) with only the Kirwani pond occasionally touching 9 in the summer months.

Compared to earlier monitored data for the same ponds (Fig.16), the average values have increased slightly although the previous peaks reached by the Govindpur pond in 2003-2004 have not been repeated.

TSS

Values for 3 of the ponds at Bakulia, Kirwani, and Chetwa indicate that values of TSS are high for August and Kirwani waters continue to remain over the limit during September and October too (Table 3b). However, the pond and *bawadi* at Govindpur do not cross the limit at any time although the pond shows the same behaviour of high concentrations during the wet season while the *bawadi* peaks in January.

A comparison with the earlier period (Fig.17) shows that the trend is almost the same except in the case of the Govindpur *bawadi* whose peak in July has significantly flattened out.

TDS and EC

As expected, TDS and EC data are very similar in its pattern (Tables 3c and 3d). TDS values are all lower than 615 mg/l, except for the Govindpur pond which reaches a maximum value of 730 mg/l in May. But these values are all less than one-third of the permissible limit of 2100 mg/l in surface waters.

The graphs over the past (Figs.18 and 19) show that there has not been much change except that the peaks for the Bakulia pond and Govindpur *bawadi* have declined.

COD and Hg

Tables 3e and 3f present the data for these two parameters, except that Hg has not been analysed during the monsoon months. COD remains below the limit of 250 mg/l except when the pond at Bakulia goes up to a maximum of 352 mg/l in August, indicating that there is a significant flow of pollutants into the pond. The Govindpur *bawadi* similarly shows a peak in November but it remains below the limit at 208 mg/l. The highest values of Mercury are 4.3 and 4.2 µg/l for the ponds at Kirwani and Chetwa in the months of March and January respectively. But even otherwise, the values for all the ponds remain unacceptably high through the dry months and far above the prescribed limit of 0.01 µg/l. The source of such high levels of Mercury in surface waters therefore, is an issue of grave concern.

As Fig.20 indicates COD in the current year follows a pattern similar to that of previous years, except for the high peak in Bakulia in August 2009. Fig.21, however, reveals that Mercury levels were much higher in 2005-2006 but slightly lower in 2003-2004 (except for the Bakulia pond).

4. Effluent quality in Drains

Nine stations on various drains entering the Pantnagar reservoir were monitored, with three located on the eastern edge and 6 on the western side, as in 2005-2006 (Map 3).

pH

Table 4a provides the range of pH that remained between 7 and 9 for most of the locations except for the Dongia and Murdhawa drains which increased to 13.2 and 9.7 respectively in the winter. Thus, the effluents discharged from the Renukoot industrial area remained as significant as before.

The earlier data (Fig.22) reveals much greater fluctuations in pH for both these drains, hence some mitigation efforts have yielded results.

TSS, TDS and EC

TSS values remained below 500mg/l for all the drains through the year (Table 4b). The higher values, as expected, are monitored for Balia drain (265mg/l) and Dongia drains. TDS and EC show identical patterns with the Dongia drain going well over the TDS limit of 2100 gm/l from February through August, with a maximum load of 5210 mg/l before it is diluted by monsoon run-off (Tables 4c and 4d). Thus, the pollution load in Dongia drain remains a significant issue.

In earlier years TSS was much higher going up to as much as 3700 mg/l for the Balia drain and 2600 mg/l for the Kakri ETP drain (Fig.23), so there has been some mitigation. But the patterns for TDS and EC (Figs.24 and 25) remain the same as before, although the months for the peaks and troughs have changed, with the Dongia drain carrying the heaviest loads from the Renukoot area.

DO and COD

DO values could not be measured for most of the drains between March and October (Table 4e), except for Balia and Murdhawa drains which varied between a low 2 mg/l and a reasonable 5.5 mg/l over the year. The Dongia drain was marked by a complete absence of DO. The values for COD (Table 4f) revealed that these three drains ranged between 200 to 500 mg/l, while the others generally remained below the limit of 250 mg/l.

As far as past trends are concerned, DO was significantly higher in the drains both in 2003-2004 and 2005-2006, except for the total absence of DO in the Dongia and Murdhawa drains in the 2003-2004 period (Fig.26). COD was about the same or lower in 2003-2004 but increased significantly in 2005-2006.

F and Hg

The level of Fluoride was assessed in the drains and the results are given in Table 4g. All the values are well below the given limit of 15 mg/l, except for one peak of the Singrauli Ash Pond overflow that surprisingly soars up to 24 mg/l in April. The values of the Murdhawa drain are generally higher than those of the others and this is expected. Similarly, one Mercury value for the Rihand Ash Pond overflow suddenly shoots up to an inexplicable 34 µg/l in February while the Dongia drain levels remain between 7.5 to 17.4 µg/l through the year (Table 4f). Values from the other drains are also generally much higher than the limit of 0.01 µg/l. Thus, more Fluoride and Mercury-bearing effluents are

being regularly discharged into the Murdhawa and Dongia drains respectively from all the industrial units.

The pattern over previous years (Figs. 28 and 29) shows that Fluoride content in the effluents was decreasing from 2003-2004 but has increased subsequently, and Mercury pollution has a parallel trend, particularly for the Dongia drain.

5. Quality of composite Drain samples

The composite samples from the three stations on the Balia, Dongia, and Murdhawa drains were analysed and the results are presented in Table 5. These follow the same trends as the grab samples in general (Table 4). However, there are certain significant differences that may be remarked upon.

pH

The patterns are very similar to those of the grab samples (Tables 4a and 5a), but the peaks above the limit in early summer are less for all three stations, while there are higher pH values up to and beyond the limit (particularly for the Murdhawa nala) in the post-monsoon period.

Looking at the long-term trends (Fig.30) average pH values are consistently increasing for the Dongia drain and remaining about the same for the other two.

TSS

TSS values of composite samples are quite different from grab samples (Tables 4b and 5b) in that they decline for grab samples in the August to January period, while the composite samples show a distinct rise in August to October period. This suggests that the industries use the monsoon period to discharge significant quantities of wastes into the drains, although the discharges do not violate the norms and remain below 400 mg/l.

Previous data is available only for the 2003-2004 monitoring (Fig.31) and that shows that the discharges in that year were much higher and throughout the year, ranging from 900 to 1400 mg/l. Hence, it is evident that the industries have taken some measures to control their releases of solid/suspended wastes, even during the rainy period.

TDS and EC

The TDS/EC values for composite samples followed the same pattern as the grab samples with a pronounced peak of over 4500 mg/l for the Dongia nala in June that decreases below the limit after August with dilution from the rains. The other two drains remained below 1000 mg/l, averaging about 500 mg/l (Tables 4c and 5c).

Earlier data (Figs.32 and 33) shows that TDS values were much higher for Dongia nala and did not come down below the limit even during the rains for both 2003-2004 and 2005-2006. Average values for Balia and Murdhawa nalas have remained about the same around 500 mg/l.

COD

COD values show that both Balia and Dongia nalas carry loads above the permissible limit of 250 mg/l for the whole year, with high peaks in March and September-October, while the Murdhawa drain values conform to the limit only in April, May, and December (Table 5e). The corresponding values were generally higher for the grab samples especially in the March to May period (Table 4e). Hence, this confirms that there is a heavy discharge of pollutants into the reservoir from the various industrial units adjoining these drains.

Data from previous studies (Fig.34) indicates that there has been a steady rise in COD levels over the past years in all three drains, with recent discharges well above the standards set by the CPCB.

F and Hg

Fluoride was monitored throughout the year for Murdhawa and Balia nalas only (Table 5f). The values of the composite samples were slightly higher than those for grab samples although the pattern was roughly the same with peaks in the post-monsoon season (Table 4e). But values remained below the limit of 15 mg/l with the Murdhawa nala giving a maximum of 8.1 mg/l in October. Mercury, on the other hand, was very high in all three drains, with the Dongia nala giving a maximum value of 25.1 μg/l in May declining to 13.1 μg/l by July with the rains (Table 5g). The other two drains averaged around 2.5 to 3 μg/l. But all these values greatly exceeded the limit of 0.01 μg/l.

In comparison to this, the values for Fluoride in previous years were less for the Balia nala and more for the Murdhawa and Dongia nalas in 2003-2004 (Fig.35). Mercury levels in earlier years were less for Dongia nala but more for the Balia and Murdhawa nalas (Fig.36). In other words, the decline noticed earlier for Fluoride and Mercury bearing discharges into the Dongia drain has not been sustained.

6. Monitoring of Ground water sources

Monitoring of ground water sources was carried out in May and November 2009 and the results are presented in Table 6. Samples were collected from 14 locations comprising of available hand pumps (Map 4).

pH and TSS

pH values remained within the prescribed limits of 6.5 to 8.5 (Table 6a). Values increased slightly in the post-monsoon period for 5 hand pumps at Renukoot, Bina, Orangi, Bakulia, and Jhigradandi (Fig.37). TSS increases were more noticeable, particularly for the hand pumps near Obra and Dongia. But the values remained below 30 mg/l and well within the limit of 100 mg/l.

Ground water had not been monitored in 2003-2004, but measurements of pH in 2005-2006 had indicated no value higher than 7.5 in October 2005, indicating a heavy dilution effect from the rains.

TDS and EC

EC patterns were the same as TDS variations for almost all the hand pumps (Tables 6b and 6c). Samples from Renukoot, Orangi, and Katauli just exceeded the limit (500 mg/l) in the pre-monsoon period but these declined subsequently (Figs. 39 and 40). However, hand pumps at Chetwa, Bakulia, Jhigradandi, Khamariya, and Govindpur showed a marked increase between 15 mg/l (Khamariya) to 184 mg/l (Bakulia) in TDS values for the post-monsoon period (Figs.39 and 40) – the hand pumps at Obra, Orangi, and Supachuan additionally showed an increase in EC values. All these hand pumps should therefore be examined for how the ground water has been contaminated after the rains.

Earlier values for EC had reached over 1000µMhos/cm for two samples in October 2005 that declined to 800µMhos/cm in May 2006, and another two samples where the values were 750/990µMhos/cm in October 2005 as compared to 360/390µMhos/cm in May 2006.

Chloride and Nitrate

Both Chloride and Nitrate values in all ground water samples were well within the prescribed limits (Tables 6e and 6f). The highest value for Chloride was 102 mg/l at Renukoot and for Nitrate it was 4.1 mg/l at Chetwa. Chloride values declined uniformly after the rains except for the hand pump at Bakulia (Fig.41). Nitrate values, on the other hand, increased for several hand pumps located at Obra, Renukoot, Dongia, Kubari, Bina, and Orangi (Fig.42).

Relatively higher chloride content was found in three wells in May 2006. While three wells indicated nitrate content higher than 20 mg/l in May 2006, indicating significant pollutants entering the ground water at those locations.

COD

There are no prescribed limits for COD in ground water. Most of the values were below 80 mg/l (Table 6g). The only exceptions being the hand pump at Bina (a huge jump post-monsoon to 160 mg/l) and Renukoot (pre-monsoon 96 mg/l). In 8 of the samples, there was decline in the post-monsoon period (Fig.43). Correlating with the values for TDS, Chlorides, and Nitrates above, it is evident that the hand pumps at Obra, Kubari, Bina, Chetwa, Bakulia, Katauli are the worst affected.

In 2005-2005 also only two samples displayed high COD values above 150mg/l in October 2005, as compared to lower values in May 2006.

F and Hg

Fluoride was recorded at more than 1.2 mg/l in ground water sources at Jhigradandi, Govindpur, and Katauli before the monsoon, with Govindpur giving the highest value of 2.4 mg/l. Post-monsoon the limits were exceeded by samples from hand pumps at Renusagar, Orangi (the reference station), Chetwa, Jhigradandi, Khamariya (highest at 1.9 mg/l), Govindpur, and Supachuan (Table 6h). Fluoride concentrations increased in 5 of the hand pumps after the rains (Fig.44). Mercury concentrations were far above the stipulated limit of 0.01 µg/l in all the sources, other than post-rains at Obra, Renukoot, and Jhigradandi, going up to a maximum of 3.9 µg/l at Bina (Table 6i). Concentrations generally declined after the rains except for the hand pumps at Renusagar, Orangi, Chetwa, and Katauli (Fig.45).

In 2005-2006 Fluoride values were generally lower than 3mg/l, except in 3 wells where it was significantly higher at 5.64, 7.7, and 9.92mg/l. But significantly high levels of Mercury (above 5µg/l) were found to be present in May 2006 in six sources, of which three were those with high Fluoride content.

Discussion and Conclusions

AMBIENT AIR

The data clearly shows that Dala in the north continues to be the highest emitter of particulate matter. All other stations are also recording both SPM and RSPM above the limits the year round with the exception of the reference station at Kewal in the rainy season. But what is of greater concern is the rise in levels in Kewal in the summer months as this indicates a general rise in dust emissions for the whole area. A comparison with earlier years shows that minimum values for particulates during the monsoon months have been steadily rising over the years and have crossed the permissible limits in the latest round of monitoring. At the same time, maximum values are coming down and the variation over the year is significantly lower for 2009-2010.

SO_2 values are higher in the western and northern part of the region although they are generally below the limits except in the summer. NO_x values also show a peaking pattern in the summer months when a few stations cross the limits. The trends over time indicate that, while the peaks remain high during the summer, the average levels of gaseous pollution reduced between 2003-2004 and 2005-2006, but have begun steadily rising in 2009-2010 for both SO_2 and NO_x.

Gaseous F is expectedly higher in the Renukoot region but it also reaches a peak in the same month as Kubri, Katauli, Murdhawa, and Lojhara, all of which lie roughly in the same east-west line. Gaseous Hg too shows a peak similar to Fluoride and is unacceptably higher than the permissible level for all stations other than Kewal. Particulate Hg is higher than the permissible limit for all stations for most of the year, particularly in the northern part of the region. Gaseous F has steadily increased from 2003 onwards, gaseous Hg decreased from 2003-2004 to 2005-2006 but is now again showing a rising trend, while particulate Hg rose sharply in 2005-2006 but has now declined, although not to 2003-2004 levels.

The above features may be interpreted to indicate:

- more effective performance of ESPs during the dry months
- no mitigation of pollution from stone crushers in the Dala region
- increased cumulative impact of pollution from clusters of industrial units
- NOx pollution is linked to higher transportation density in the region
- Fluoride and Mercury contamination is linked to higher industrial production

RESERVOIR and EFFLUENTS

The pH levels vary within permissible limits for all stations, except for the Renusagar ash pond overflow, in the reservoir. Values are generally higher in winter and lower in the rainy season. The reservoir as a whole is tending more and more towards an average pH of 8 without any of the spikes seen in 2003-2004, and this pattern is seen in pH of the drains discharging into the reservoir too. When the river enters the reservoir it has low TSS that rises during the monsoon months and a similar pattern is seen for the rest of reservoir. However, TSS discharges from other drains into the reservoir have markedly declined over the years.

TDS and EC follow identical patterns and all TDS values are below permissible levels, even for an inexplicable surge in the rainy season at the confluence with the drain coming from Kanoria Chemicals when the drain itself carried its lowest loads. Earlier, there was significant improvement at this confluence in 2005-2006 even though this

drain discharged a heavier TDS load well above the limit that year. But all other drains have been carrying more pollutants over the years, as is reflected in a pattern of high TDS and EC, lower DO levels, and higher COD demands, in both the drains as well as at the confluences with the reservoir.

Fluoride levels at all stations in the river and reservoir remained below the permissible levels although the main pollution in this regard comes from the industries at Renukoot and Obra. The drains discharging into the reservoir are also within the limit for this parameter, except for one surge from the Singrauli ash pond. Fluoride levels in the reservoir have clearly gone down over the years. Mercury, on the other hand, was well above the permissible limit at all reservoir stations – even at the upstream reference point. The huge spikes took place in the summer at the confluences, where all the drains are also discharging high concentrations of Mercury into the reservoir, particularly through the Dongia nala.

From the above observations, it may be concluded that:

- the capacity of the reservoir to degrade polluting loads is declining
- industries have taken some measures to control their releases
- they probably use the monsoon period to discharge significant quantities
- the earlier marked decline of these discharges has not been sustained
- Mercury levels remain high with some dilution after the rains
- more Fluoride and Mercury-bearing effluents are being regularly discharged

PONDS

The pH values for all the ponds remained well within the limits although they too have increased slightly over the years. TSS values are high for August and partly during September and October too, and the peak value demonstrated earlier by the Govindpur *bawadi* has ameliorated significantly. TDS values are all within the permissible limit and there has not been much change over time. COD also remains below the limit except for one pond at Bakulia in August. The Mercury concentrations for all the ponds remain unacceptably high through the dry months and far above the prescribed limit, with the highest values at Kirwani and Chetwa in the months of March and January respectively. Mercury levels were much higher in 2005-2006 but slightly lower in 2003-2004.

The critical issue that emerges is:

- the source of such high levels of Mercury in the ponds must be traced

GROUND WATER

pH and TSS values were within the prescribed limits although increases were noticeable for the latter in the post-monsoon period. Some samples just exceeded the limit for TDS in the pre-monsoon period but these declined subsequently, while others (mainly in the eastern plains) showed a marked increase for the post-monsoon period, as in the earlier monitoring in 2005-2006. Both Chloride and Nitrate values in all ground water samples were well within the limits, with the former declining uniformly after the rains, and the latter increasing for several hand pumps located mainly in the industrial areas. One pump in the coal mining area showed a huge increase in COD post-monsoon. Several hand pumps also recorded high Fluoride concentrations, particularly after the rains. And Mercury concentrations were far above the stipulated limit in almost all the sources (including the reference station), with concentrations generally declining after the rains.

Thus, the following inferences emerge:

- contaminants from the air and surface are leaching into the ground with the rains
- but post-monsoon Chloride and Mercury declines indicate dilution

Recommendations

- ✓ Unless strong measures are immediately taken by regulatory authorities, the increase in particulate matter in the air of the region cannot be arrested. Particular attention has to be given to the operation of stone crushers in the north and the performance of electro-static precipitators and ash pond management in the coal-based power plants.
- ✓ While Sulphur Dioxide and Nitrogen Oxides remain largely within limits, their increase is clearly linked to the rapid growth in coal combustion and transportation related to power generation (an addition of almost 4000MW between 2002 and 2008) and both these have to be mitigated if air quality is to improve.
- ✓ The high concentrations of Fluoride and Mercury in the air indicate the substantial impact of fugitive and stack emissions of aluminium smelting, caustic manufacture, and coal combustion in the industrial belt. Significant process changes are required if these are to be mitigated.
- ✓ It is clear that the Balia, Dongia, and Murdhawa nalas are discharging inadequately treated wastewater into the Pantsagar reservoir and the river downstream of the Rihand dam. Both regular operation and independent monitoring of wastewater treatment plants and ash ponds is necessary.
- ✓ The Pantsagar reservoir is steadily deteriorating with significantly high levels of TSS, Fluoride, and Mercury being discharged into it through various drains that receive industrial effluents from treatment plants and otherwise. Previously recorded declines have been reversed because of lack of independent supervision.
- ✓ Mercury concentrations in the surface water bodies reveals that it may be entering the water through the air route with the sources being both the thermal power plants as well as the manufacture of caustic soda. These need to be regularly monitored and regulated.
- ✓ Considerable Fluoride and Mercury contamination in ground water sources is seen in different pockets of the region and is an area of significant concern because they are both leaching into the ground suggesting different sources including the reservoir and rain water flows – which need to be traced.
- ✓ The perceived decline in environment quality between 2006 and 2009 may be because of the absence of citizen pressure on both polluters as well as regulators. Hence, a system of regular and continuous monitoring (including bio-monitoring) and reporting to regulators by independent institutions should be vigorously pursued.
- ✓ Such a monitoring protocol can further investigate the anomalies that previous studies have illustrated as well as trace the sources of pollution – particularly of Fluoride and Mercury – and establish the range, spread, and impact of pollution in the region. It will also be crucial to determine whether further development of theram power and industrial expansion is viable for the region.

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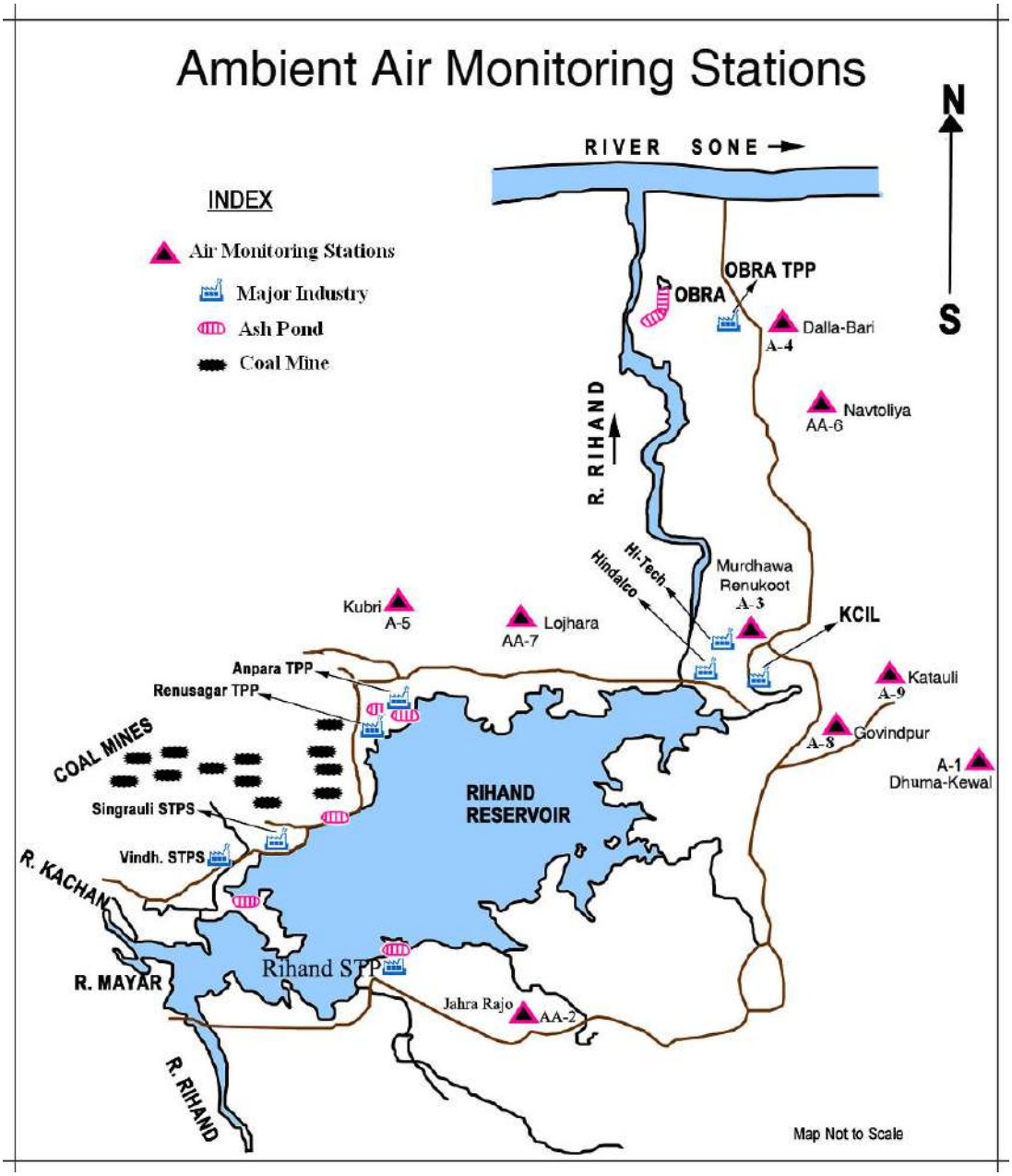
Annexure I

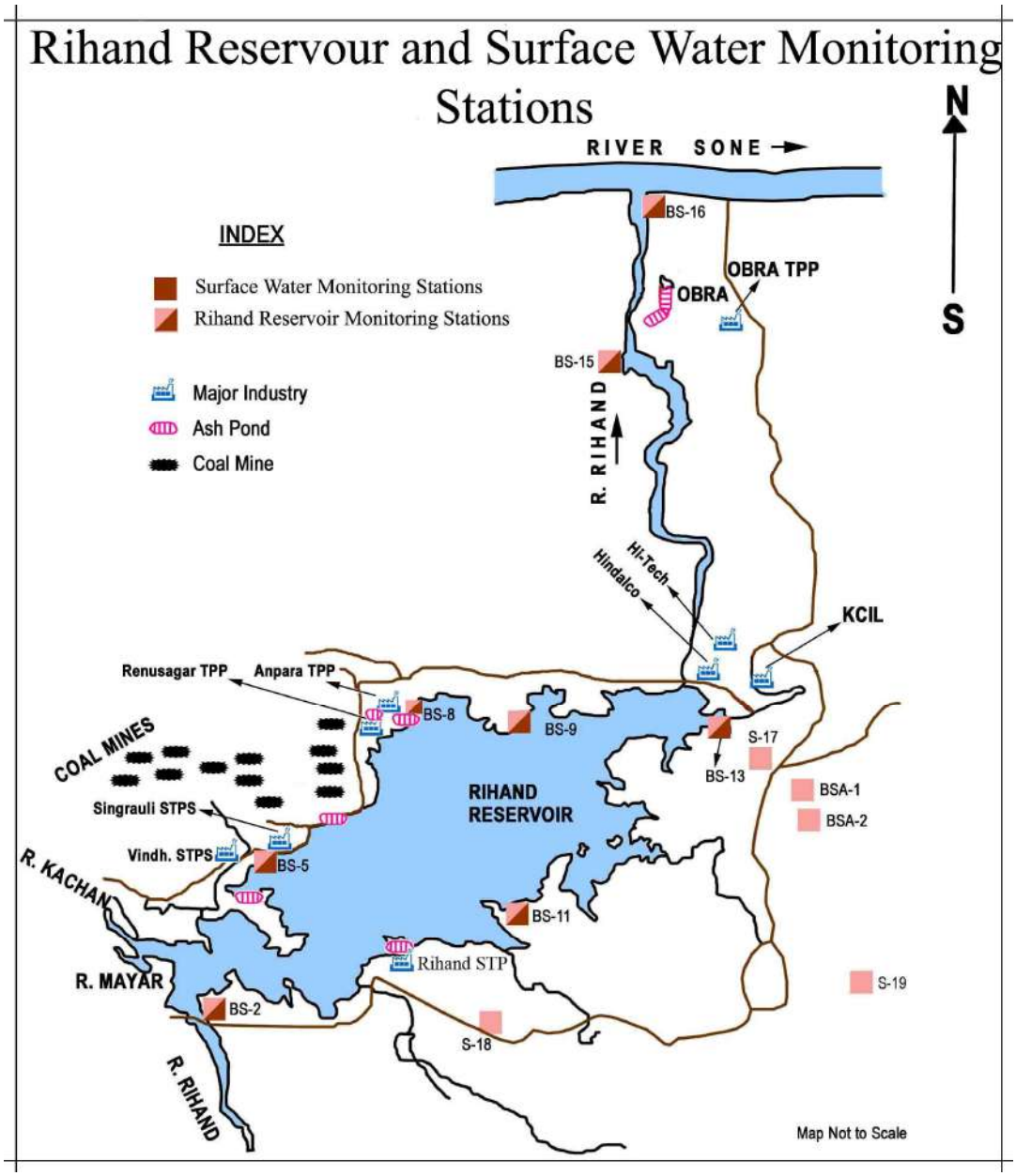
Locations of Monitoring Stations

Environment Quality Monitoring, Singrauli

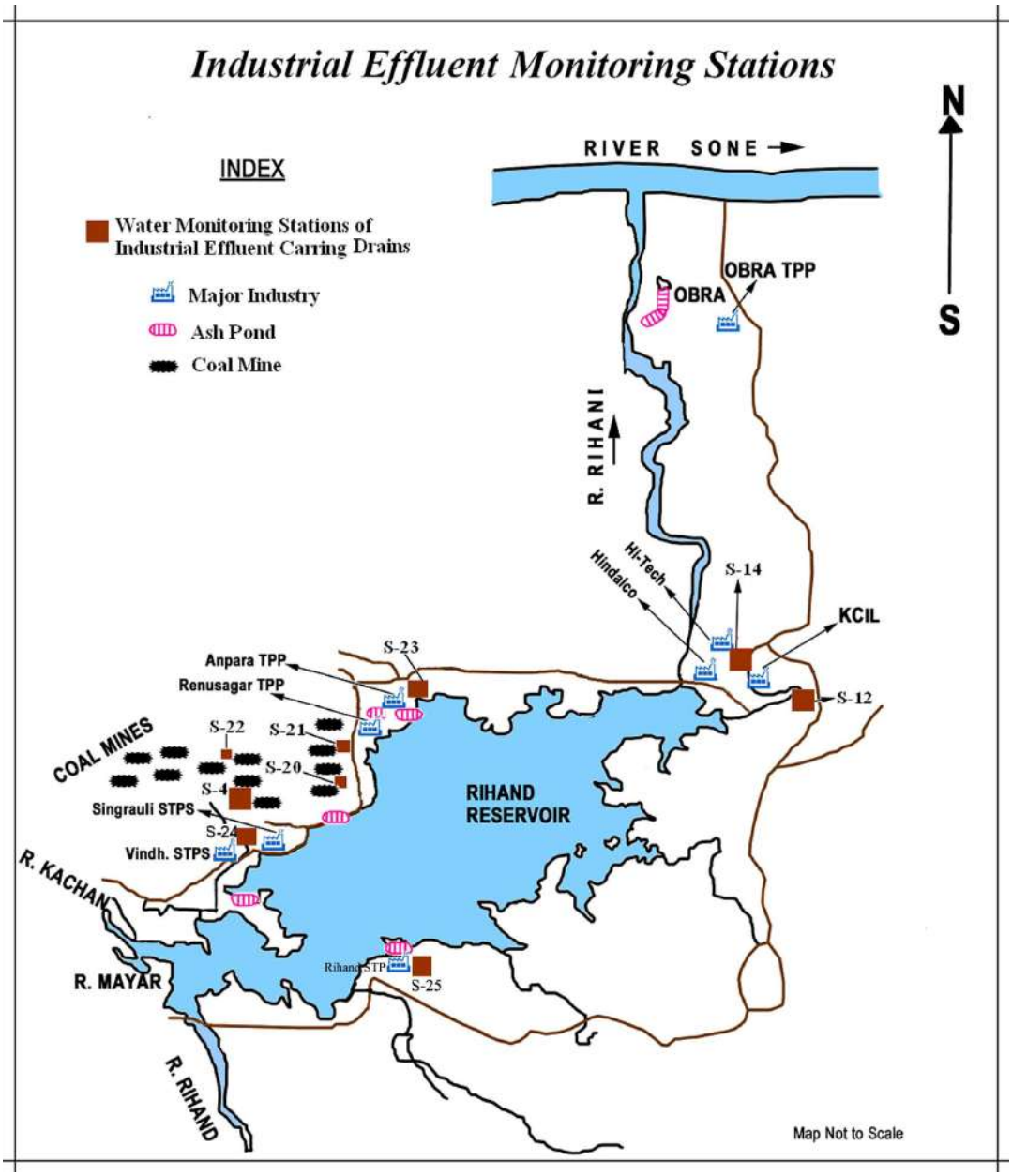
2009-2010



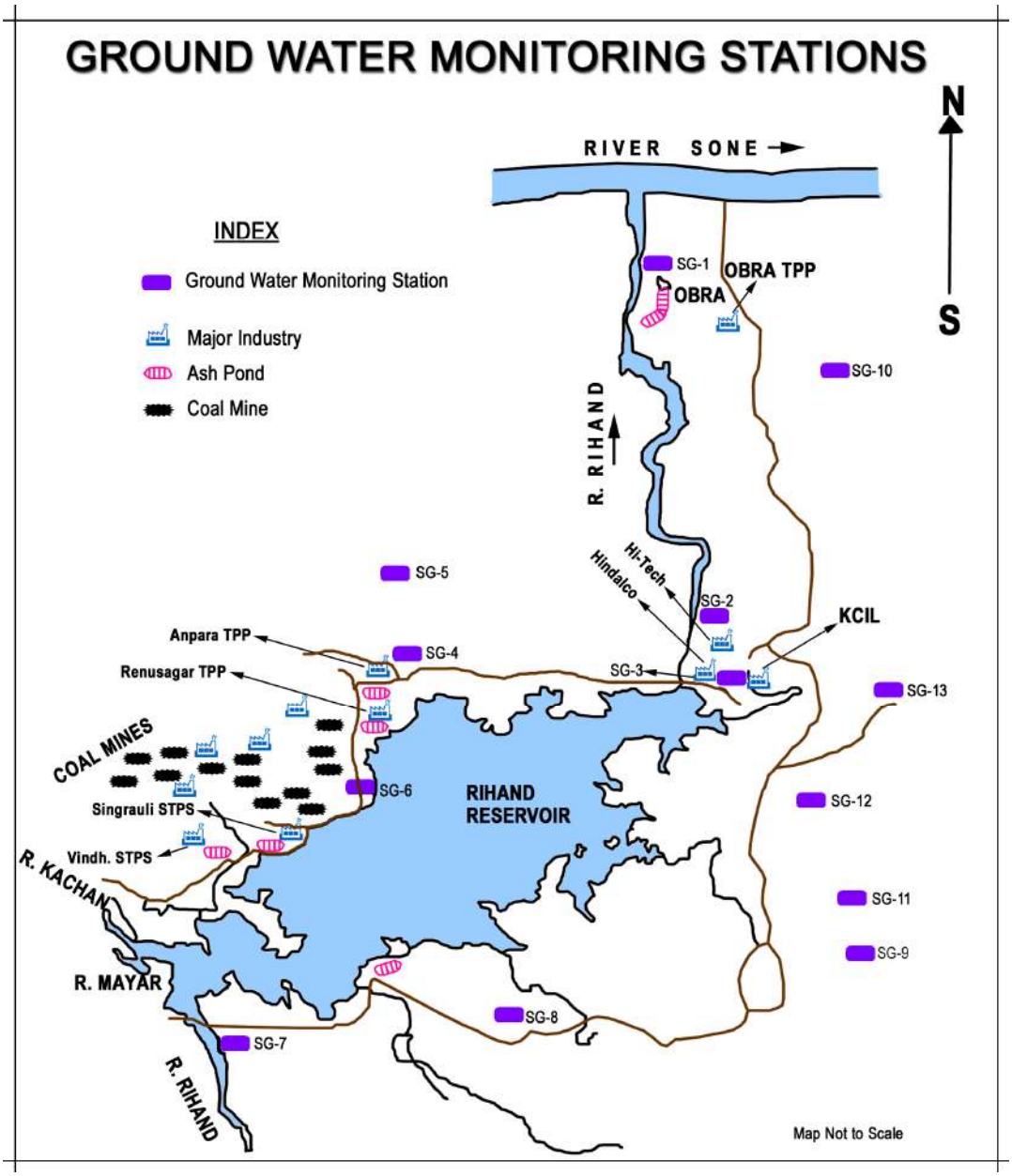
Map 1: Location of Ambient Air Monitoring Stations



Map 2: Location of Surface Water Monitoring Stations



Map 3: Location of Effluent Monitoring Stations



Map 4: Location of Ground Water Monitoring Stations

Protocol followed for air and water quality monitoring and analysis

S.No.	Parameter	Method followed
	A. Air quality	
1	SPM, RSPM	High Volume Sampler with Cyclonic Flow technique; Envirotech make RDS Model APM-451 and 460. Measurements were done gravimetrically.
2	SO_2	Modified West and Gacke method.
3	NO_x	Sodium Arsenite method
4	Fluoride	Ambient air is collected by bubbling air through a solution of Sodium Hydroxide and the sample analysed using Ion Selective Electrode.
5	Mercury	Ambient air is collected by bubbling air through an acidic solution of Potassium Dichromate (20% HNO_3 and 4% Potassium Dichromate – w/v). The gaseous samples are treated as liquid samples and analysed using a Mercury Analyser.
	B. Water quality	
1	TSS	The basic principle involved is gravimetric. A well mixed sample is filtered through a wet fiberglass filter and the residue is dried to a constant weight at 103-105ºC. The increase in weight of the filter paper represents the Total Suspended Solids.
2	TDS	The basic principle involved is gravimetric. A well mixed sample is filtered through a standard fiberglass filter and the filtrate is evaporated to dryness in an oven at 103-105ºC. The increase in weight represents the Total Dissolved Solids.
3	EC	Portable EC meter – Systronics make.
4	pH	Battery Operated Pocket pH meter, calibrated each day before use.
5	DO	Modified Alkyl Azide method.
6	COD	Close Reflection method.
7	Fluoride	Ion Selective Electrode method.
8	Chloride	Argentometric titration method.
9	Hardness	EDTA titration method.
10	Nitrate	PDA method
11	Mercury	Cold Vapour method using Mercury Analyser.

Annexure II

Trends from 2003 to 2010
Environment Quality Monitoring, Singrauli
2009-2010

Fig.1 Ambient Air RSPM µg/m^3

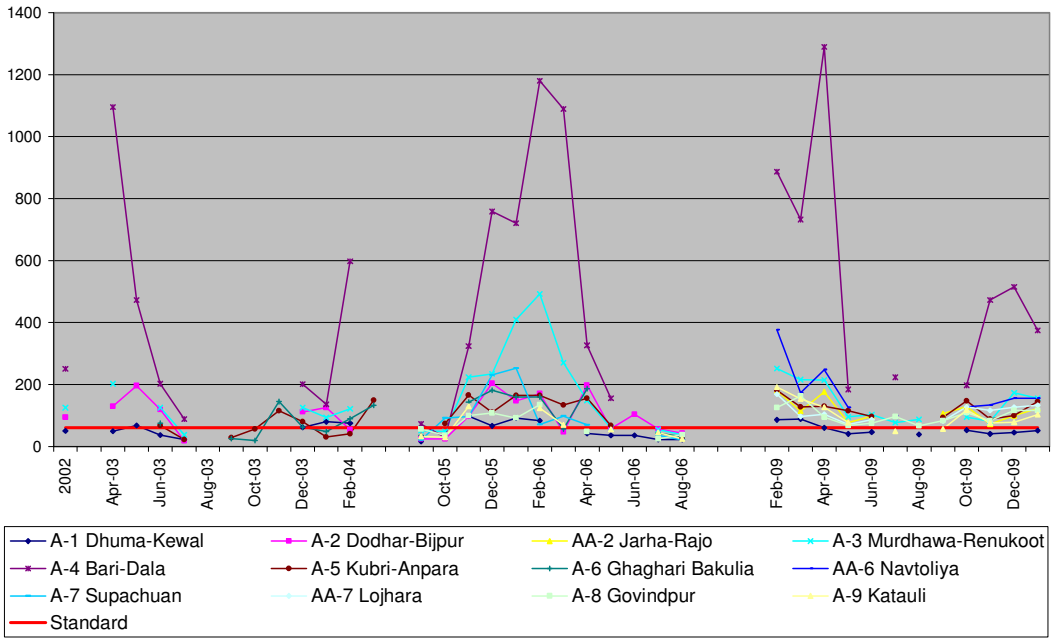


Fig.2 Ambient Air SPM µg/m^3

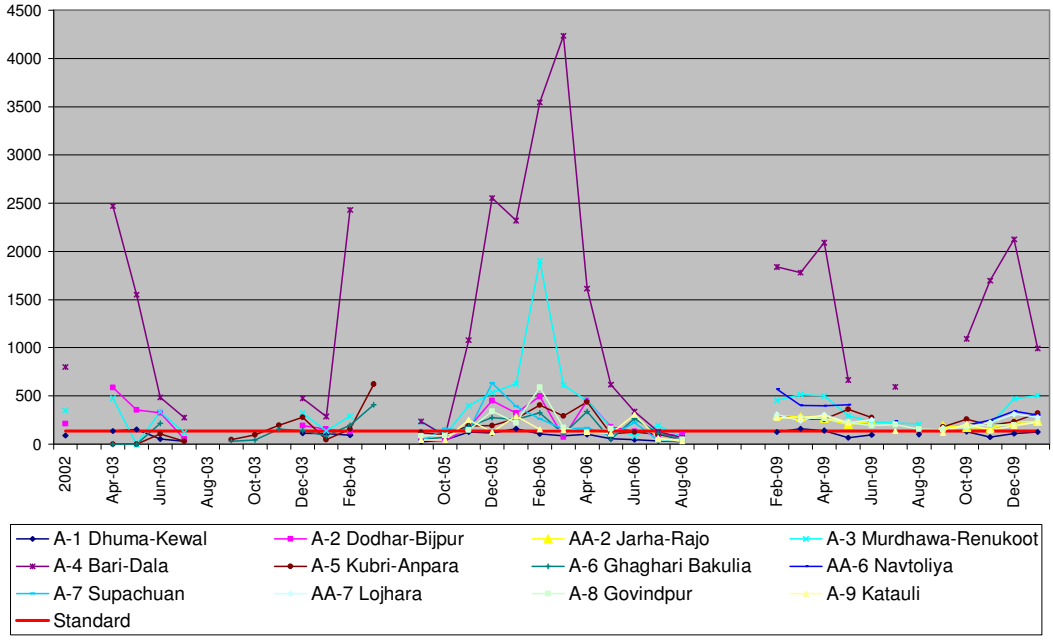


Fig.3 Ambient Air SO_2 µg/m^3

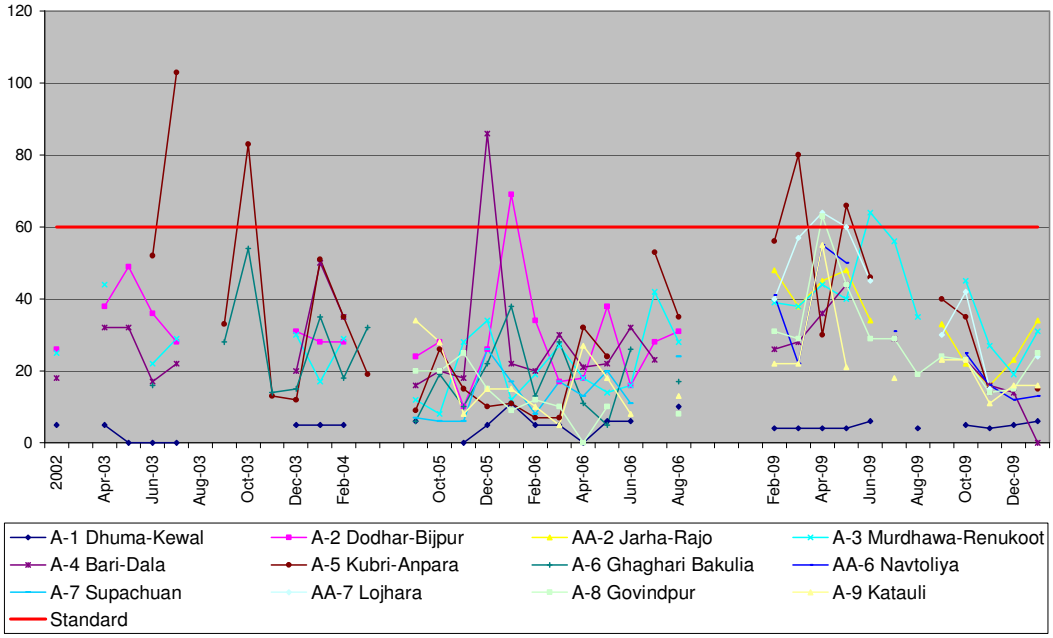


Fig.4 Ambient Air NO_x µg/m^3

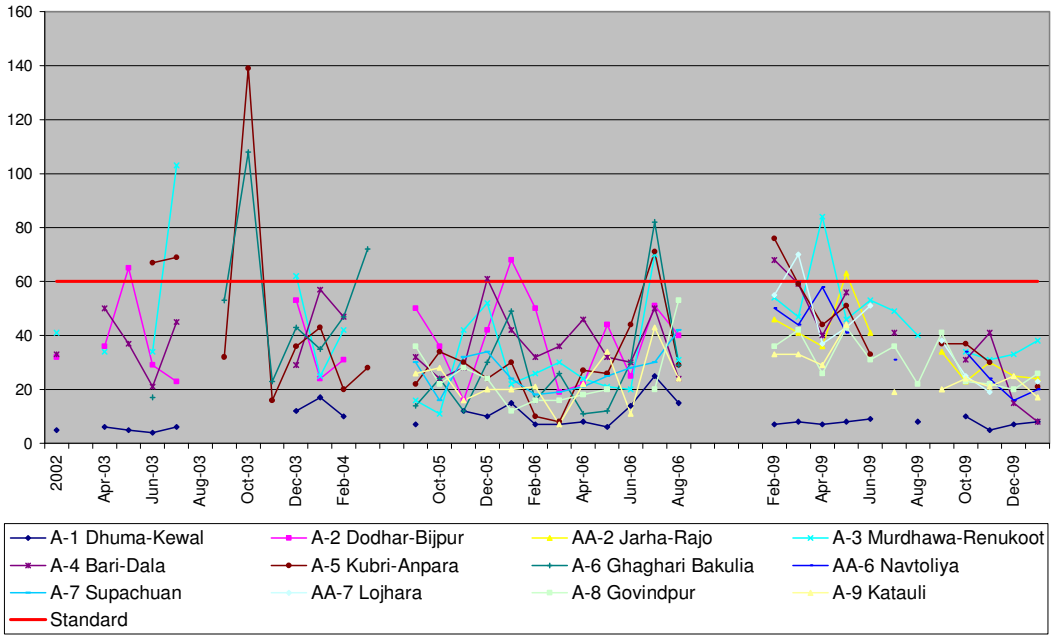


Fig.5 Ambient Air F µg/m^3

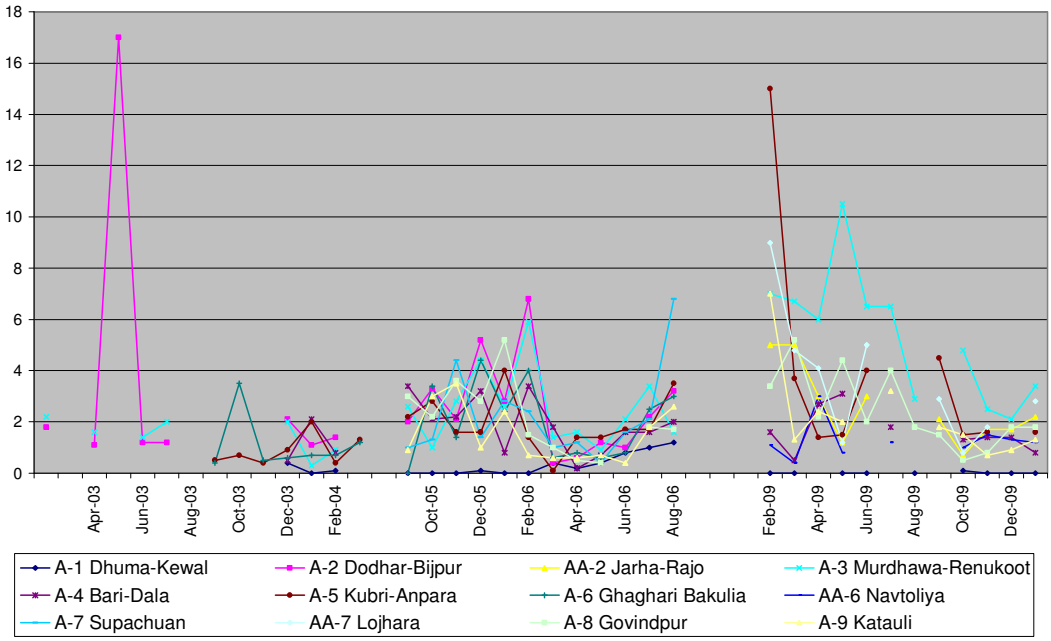


Fig.6 Ambient Air Hg gaseous ng/m^3

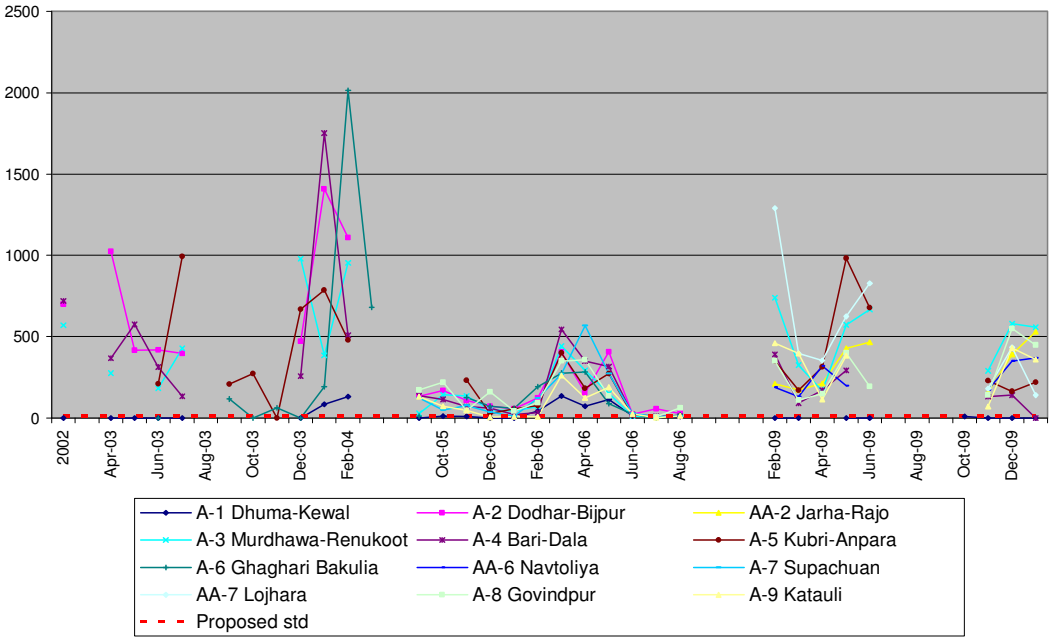


Fig.7 Ambient Air Hg particulate ng/m^3

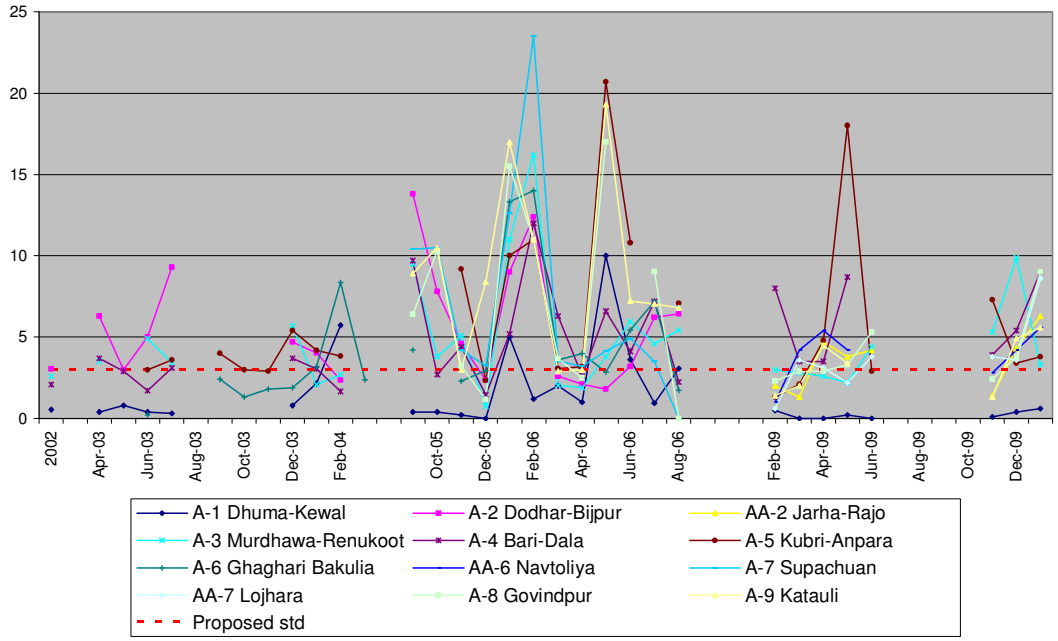


Fig.8 Reservoir pH

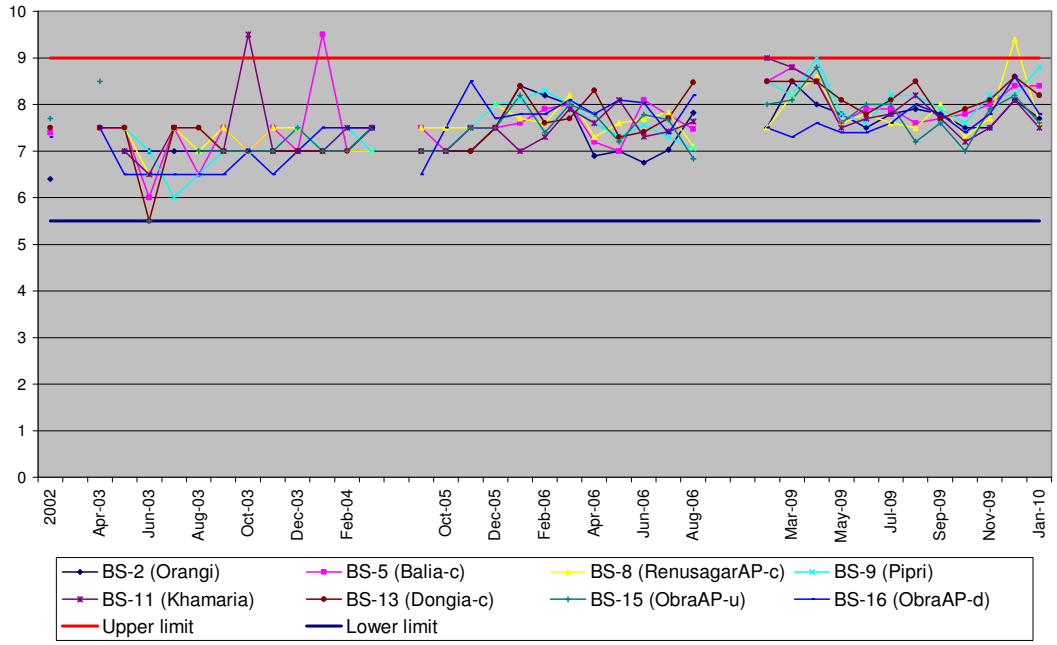


Fig.9 Reservoir TSS mg/l

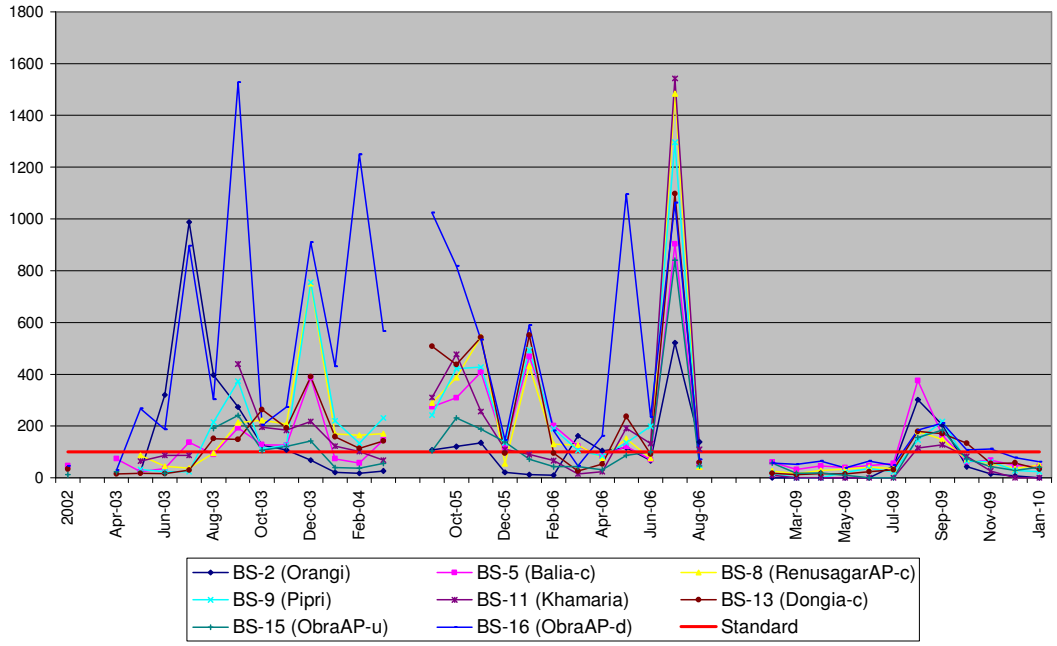


Fig.10 Reservoir TDS mg/l

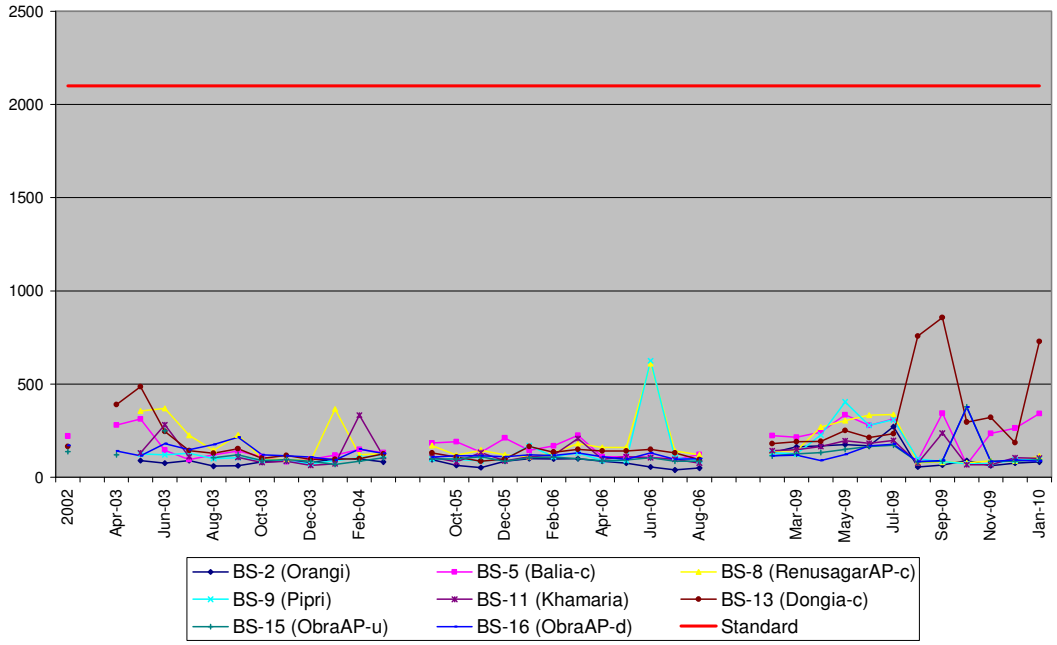


Fig.11 Reservoir EC µMhos/cm

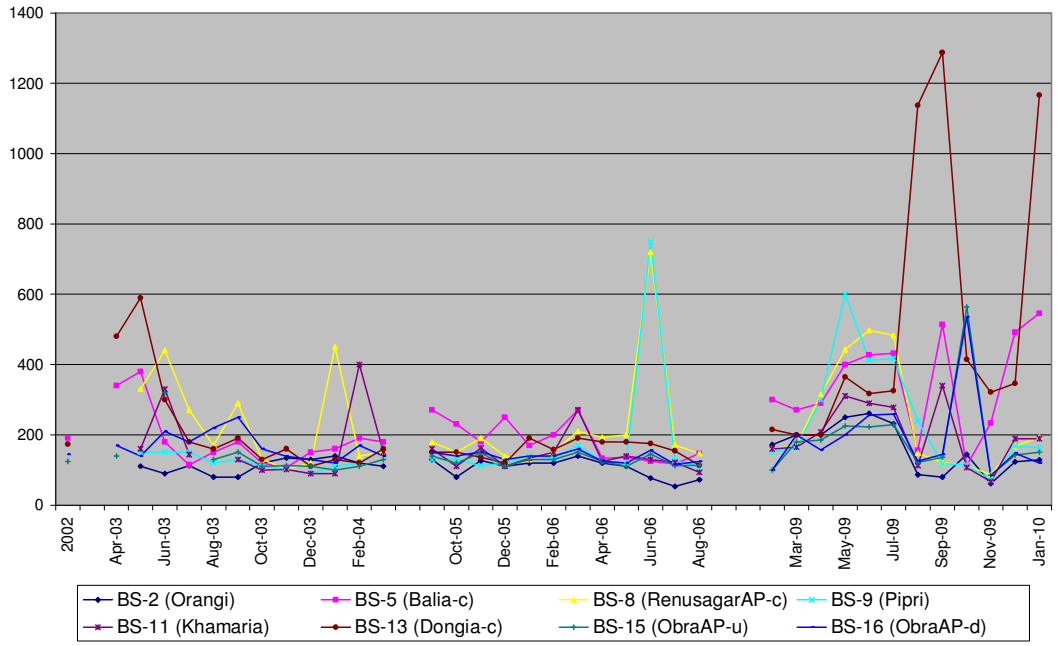


Fig.12 Reservoir DO mg/l

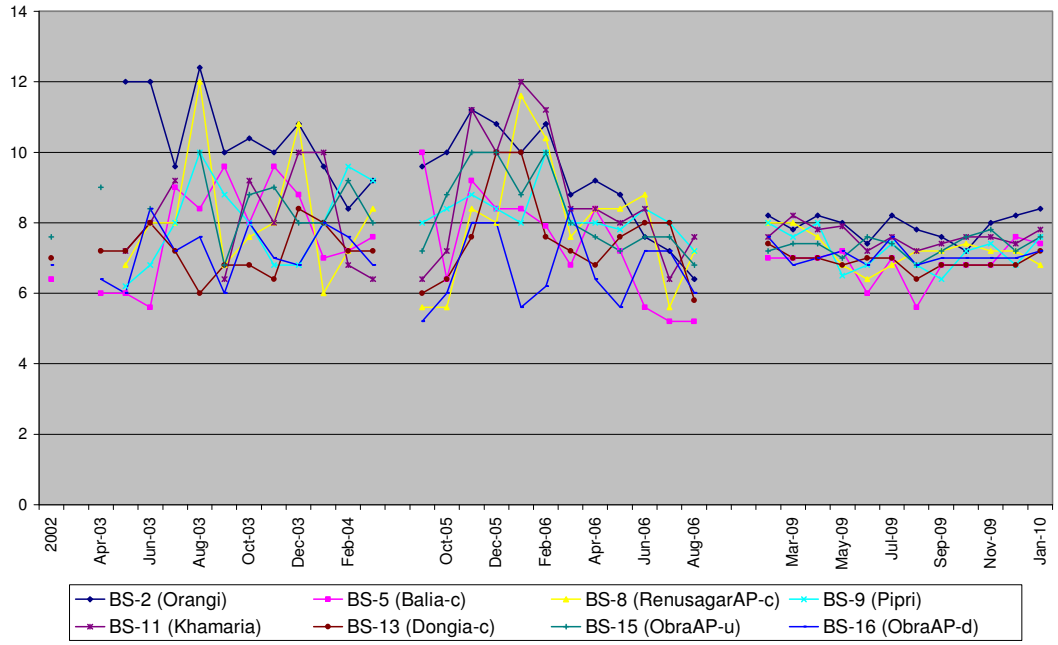


Fig.13 Reservoir COD mg/l

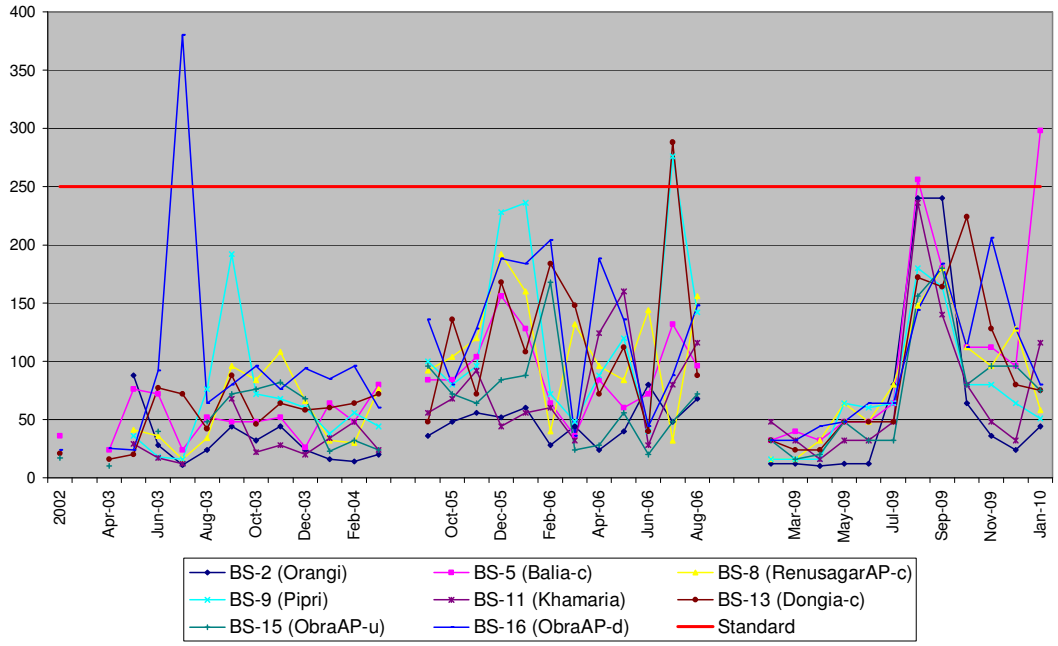


Fig.14 Reservoir F mg/l

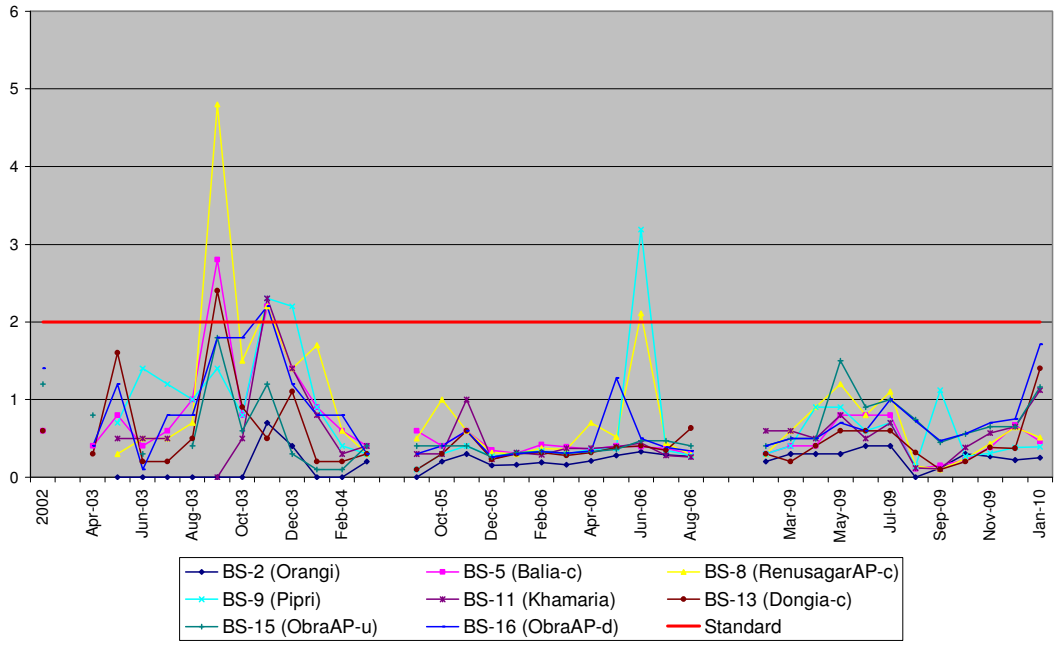


Fig.15 Reservoir Hg µg/l

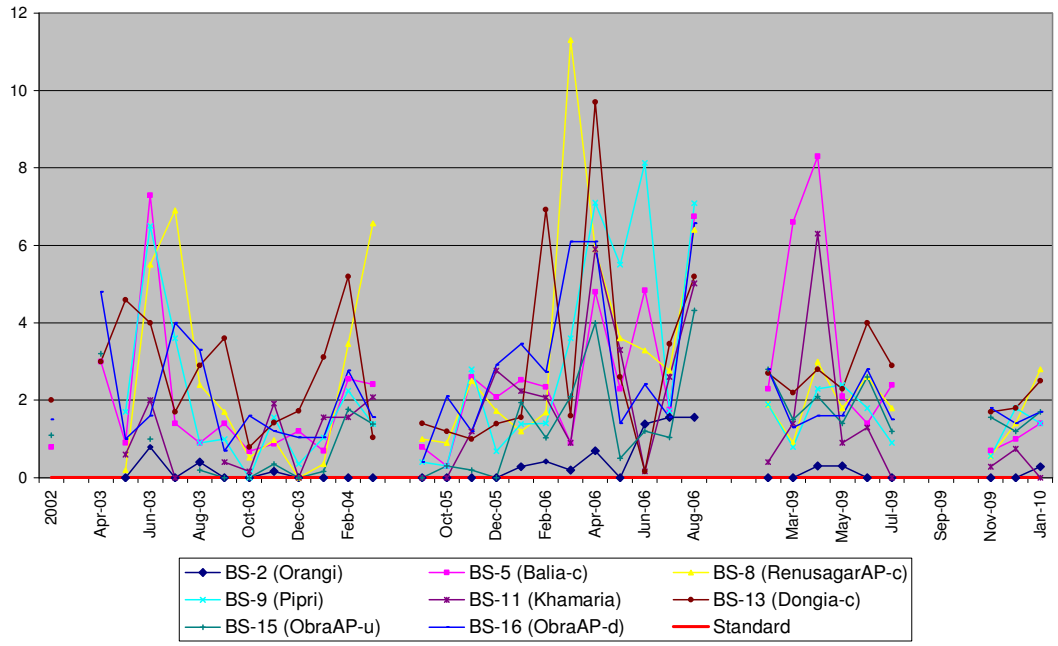


Fig.16 Ponds pH

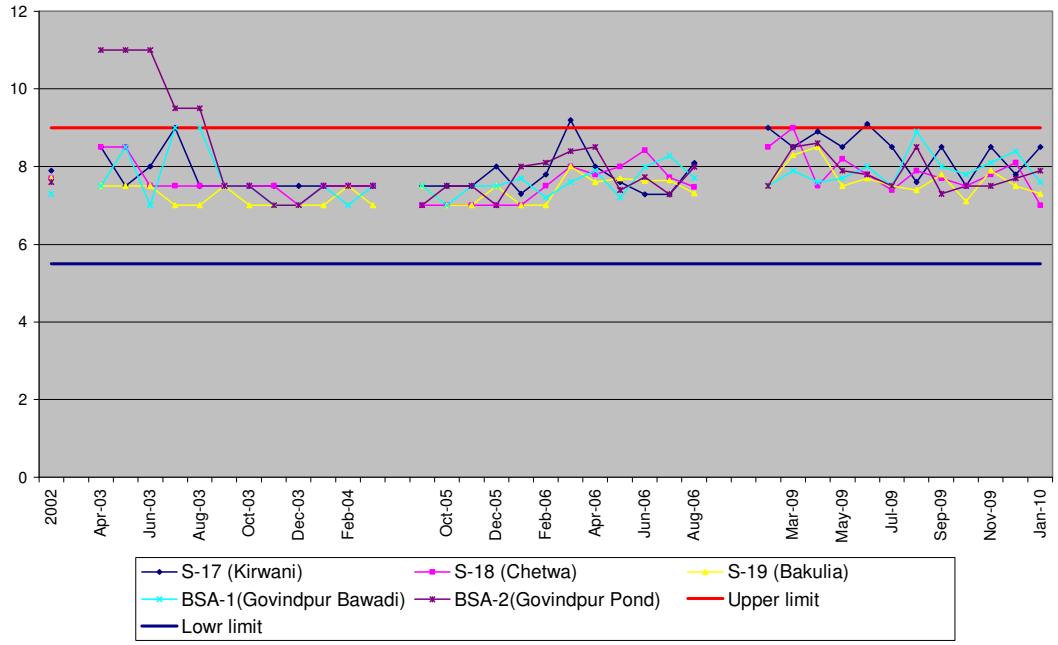


Fig.17 Ponds TSS mg/l

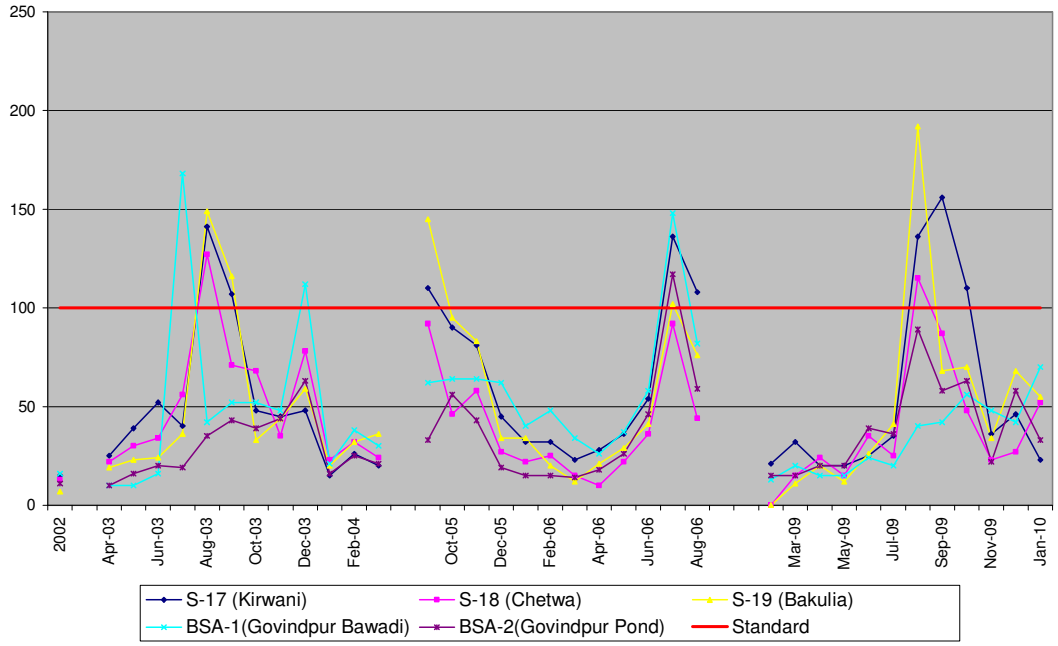


Fig.18 Ponds TDS mg/l

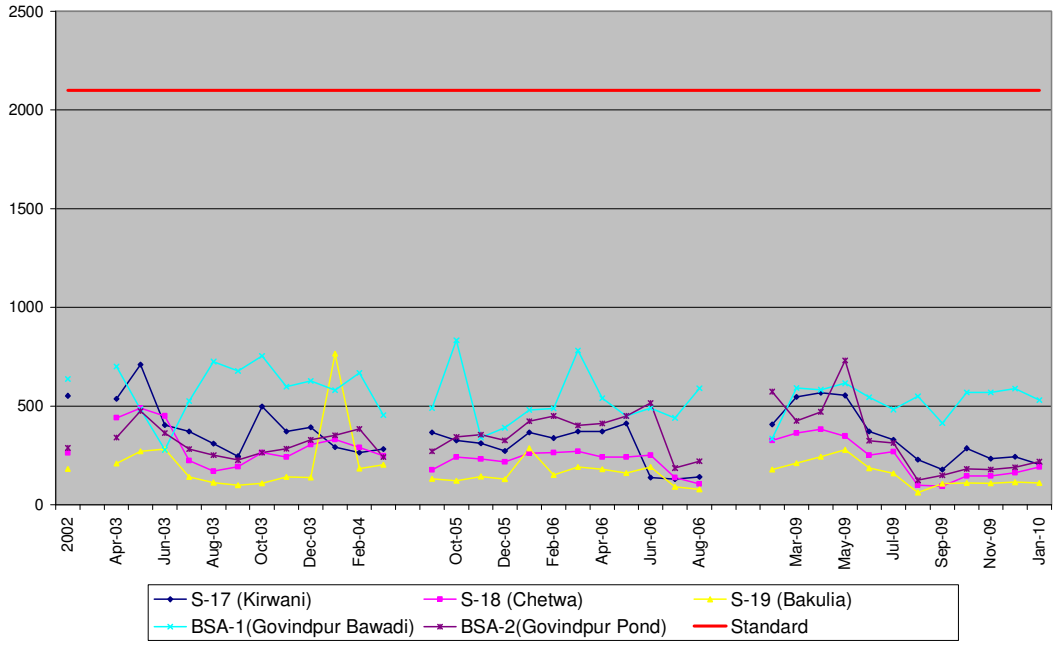


Fig. 19 Ponds EC µMhos/cm

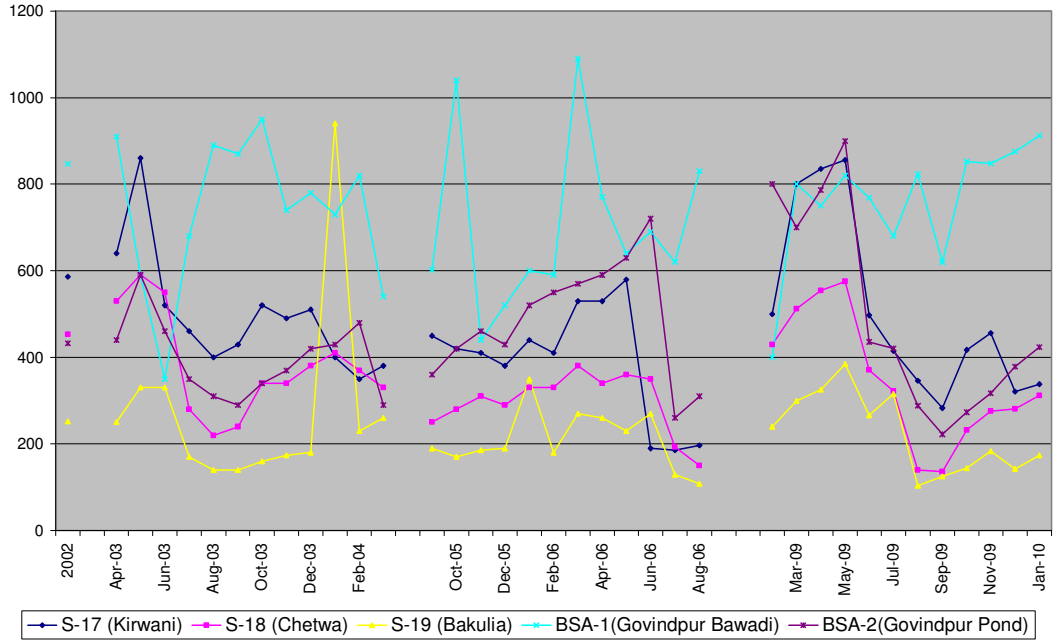


Fig.20 Ponds COD mg/l

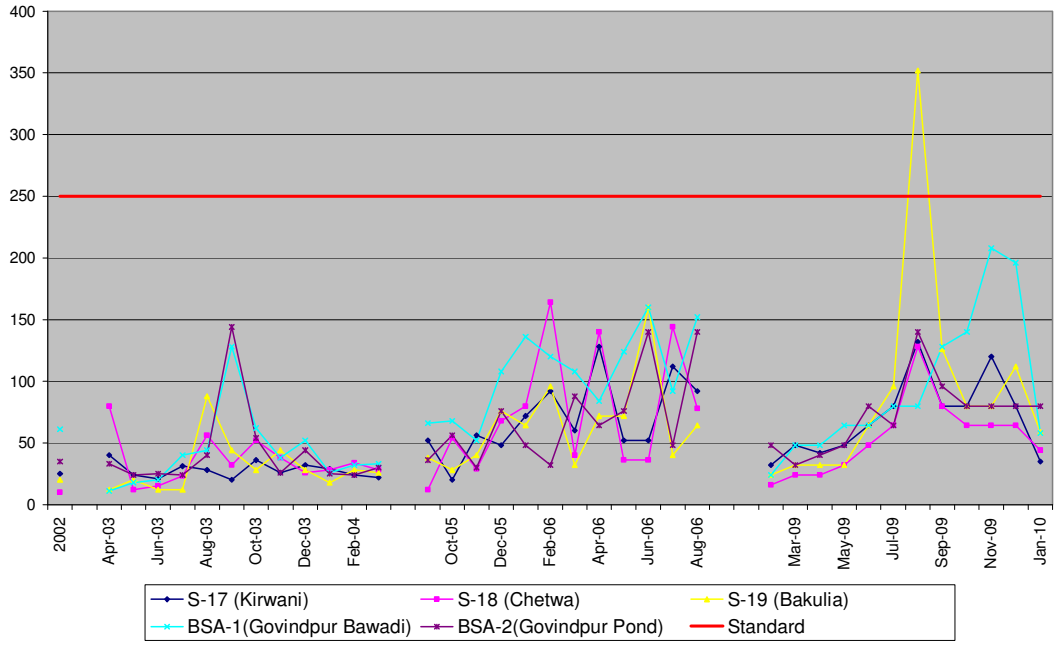


Fig.21 Ponds Hg µg/l

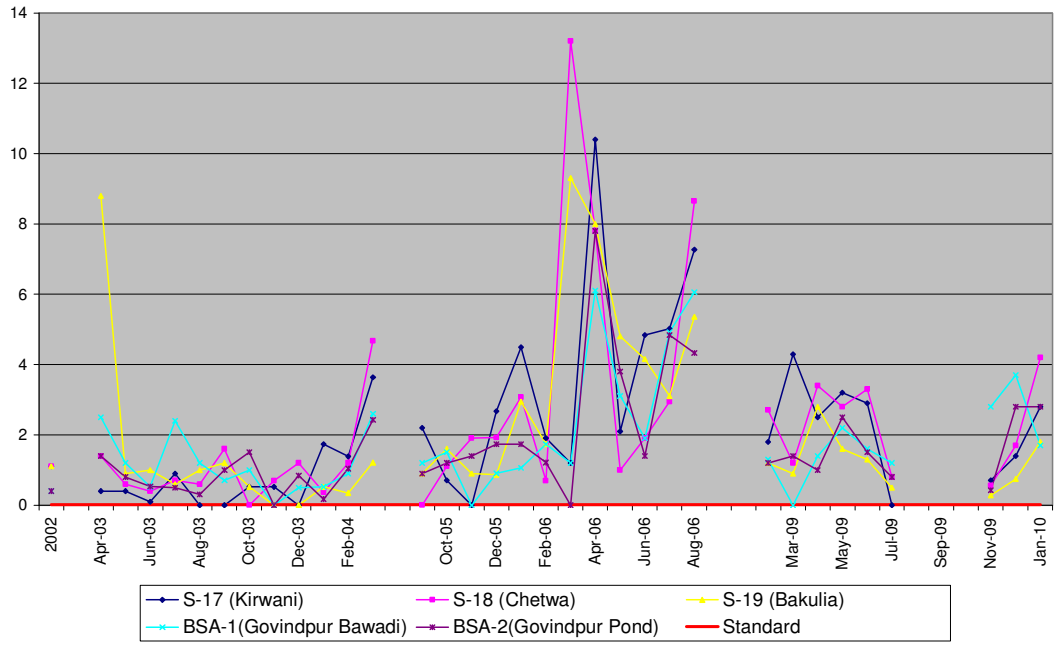


Fig.22 Drains pH

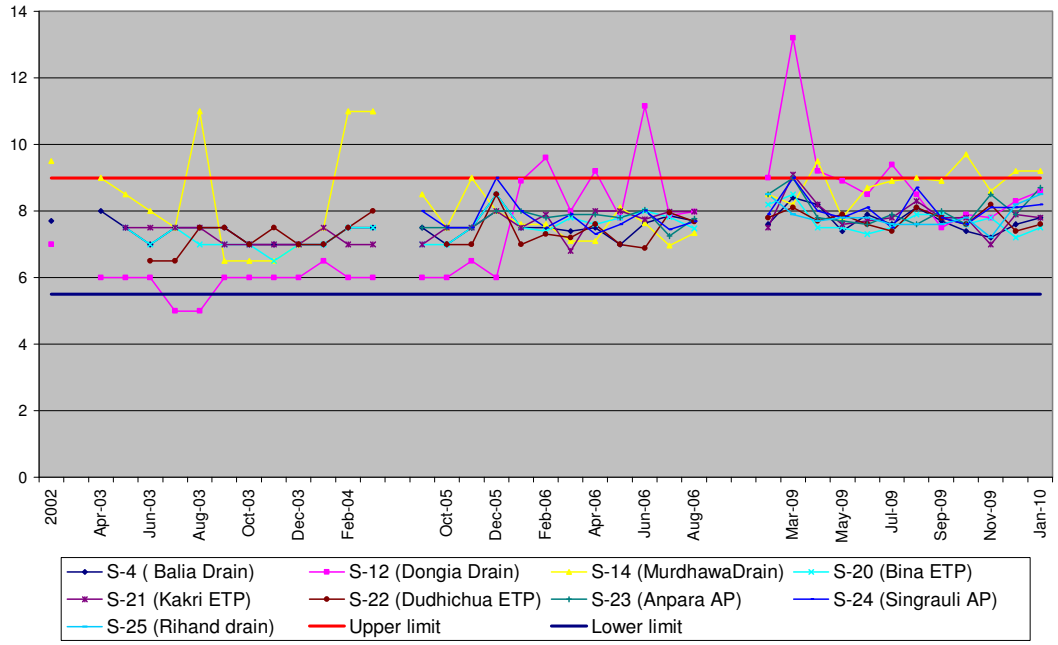


Fig.23 Drains TSS mg/l

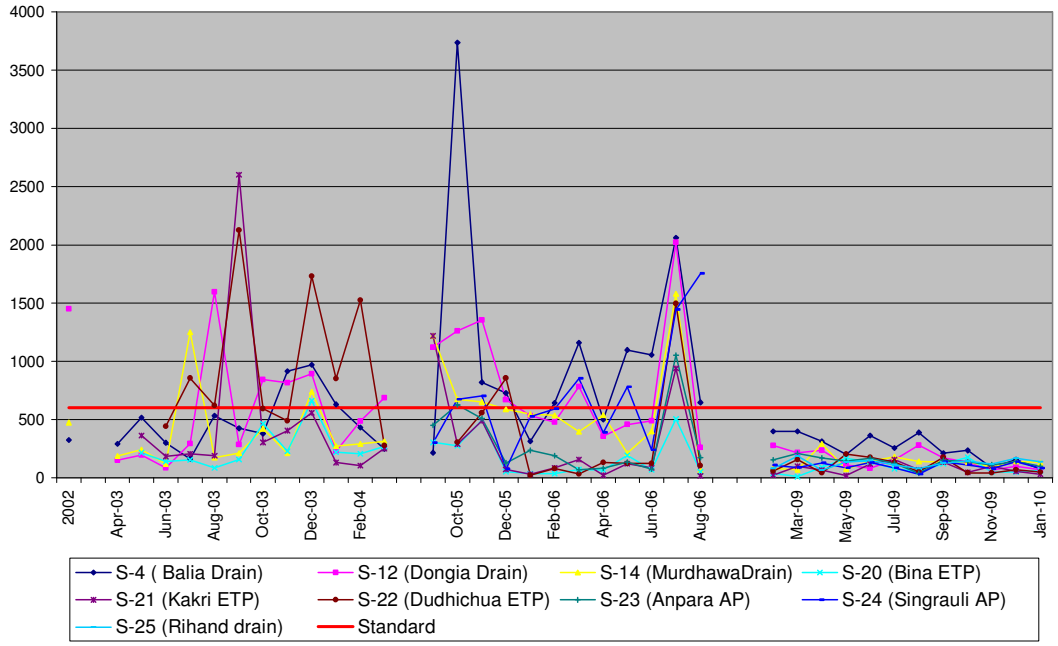


Fig.24 Drains TDS mg/l

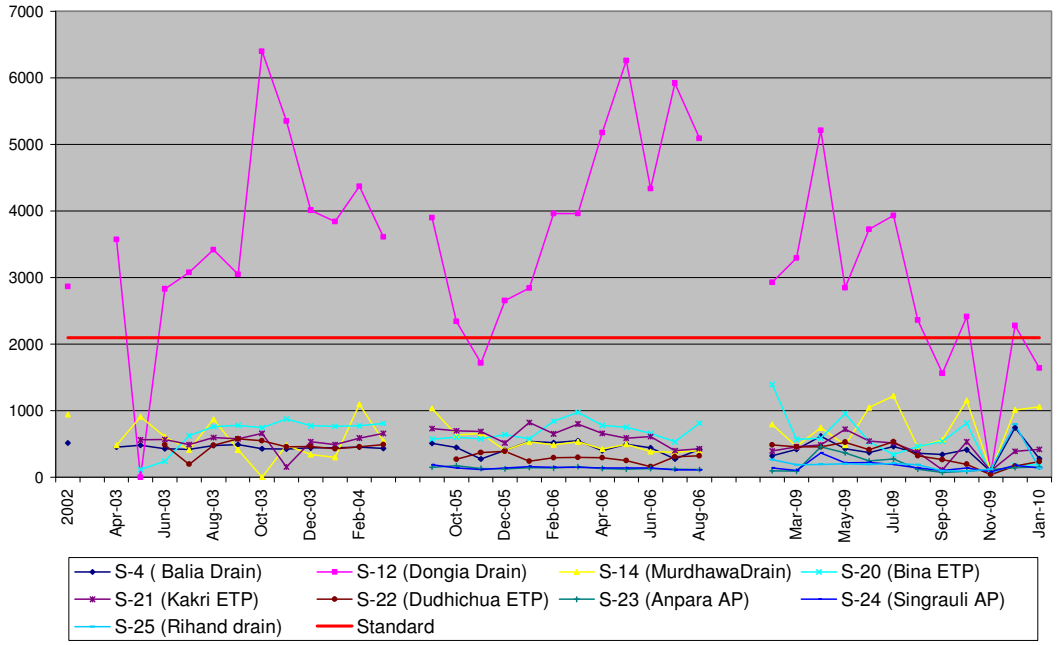


Fig.25 Drains EC µMhos/cm

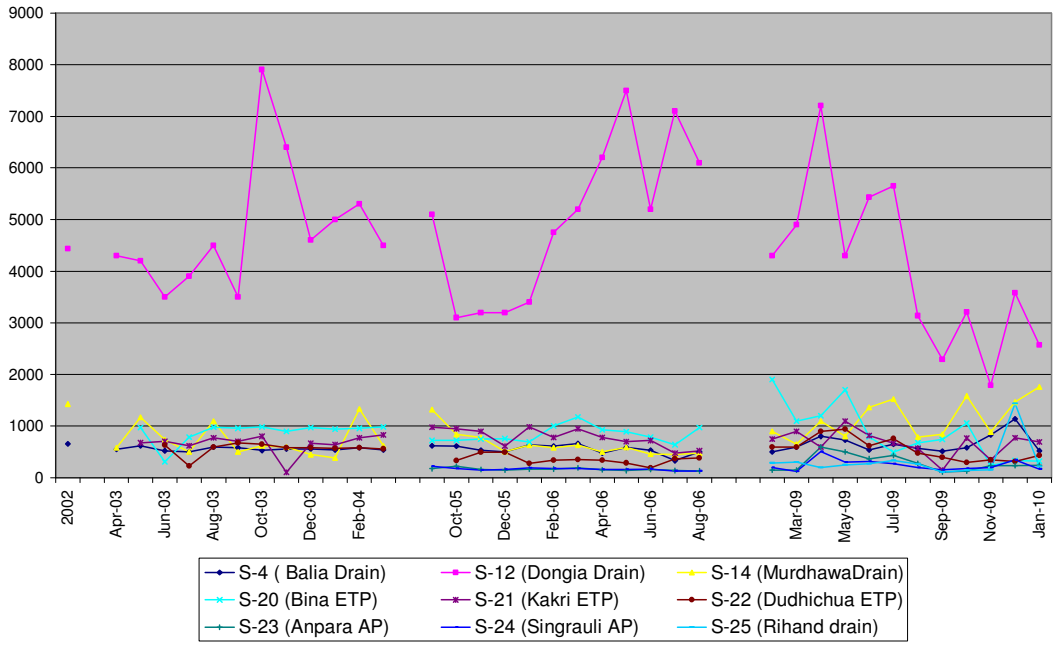


Fig.26 Drains DO mg/l

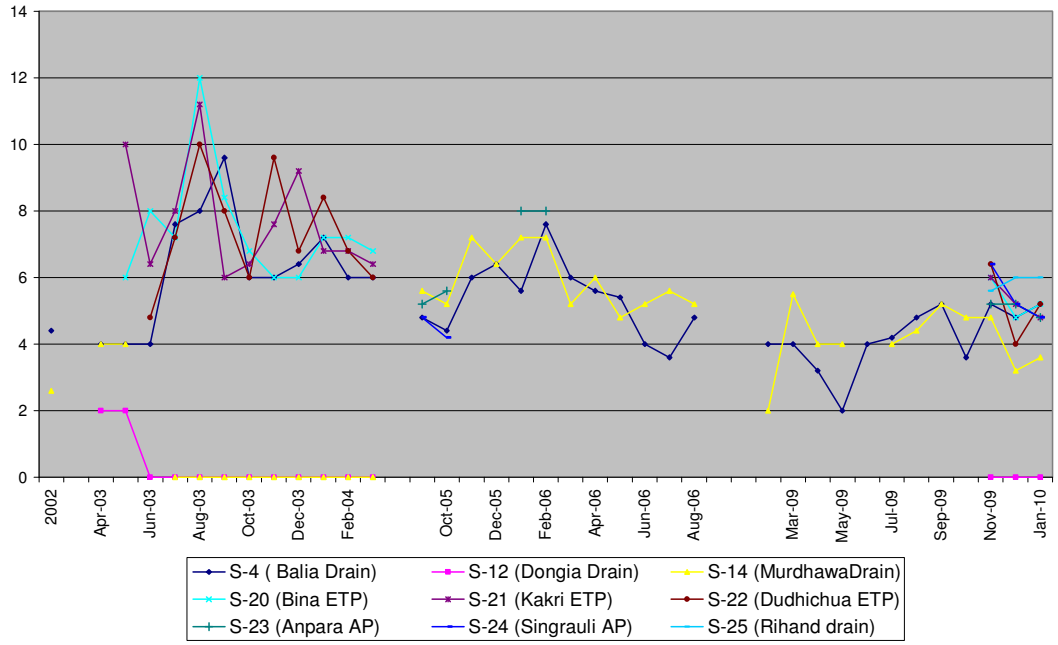


Fig.27 Drains COD mg/l

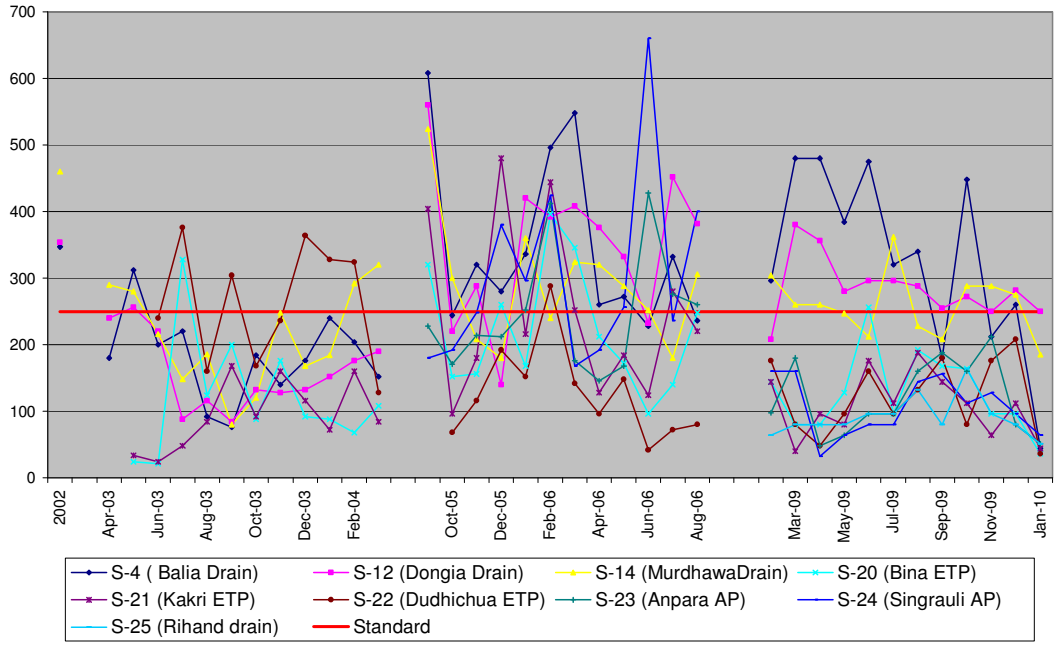


Fig.28 Drains F mg/l

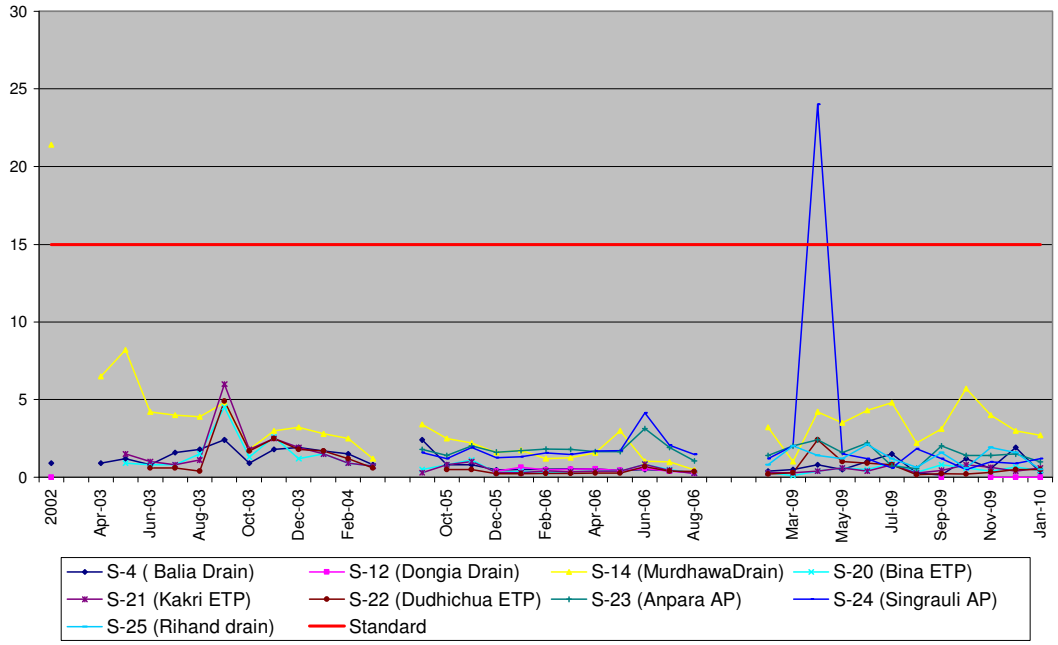


Fig.29 Drains Hg µg/l

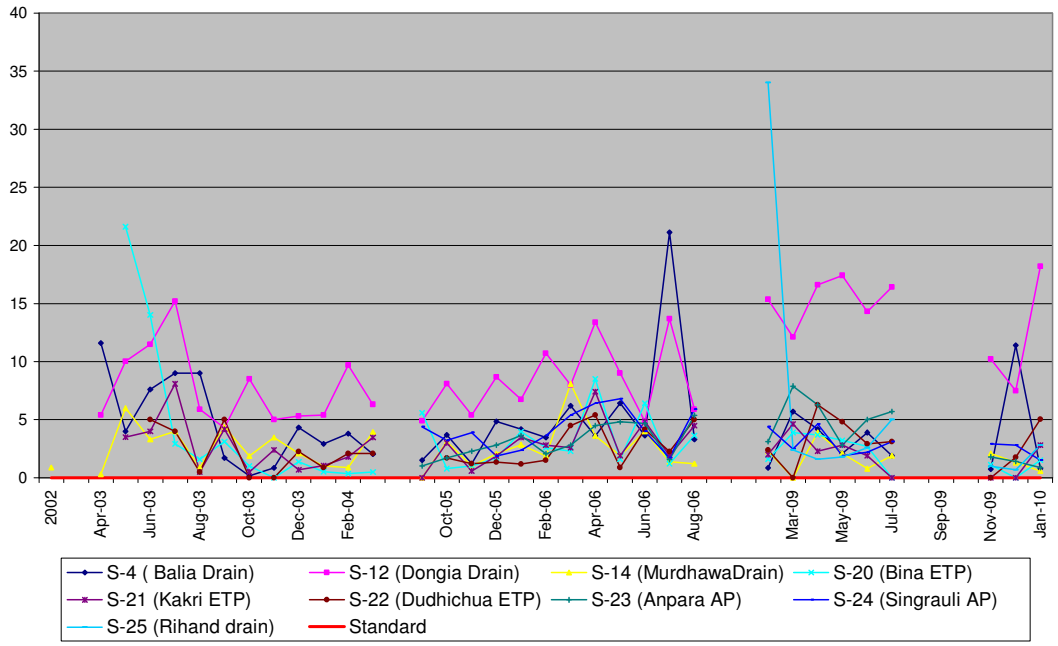


Fig.30 Composite effluents pH

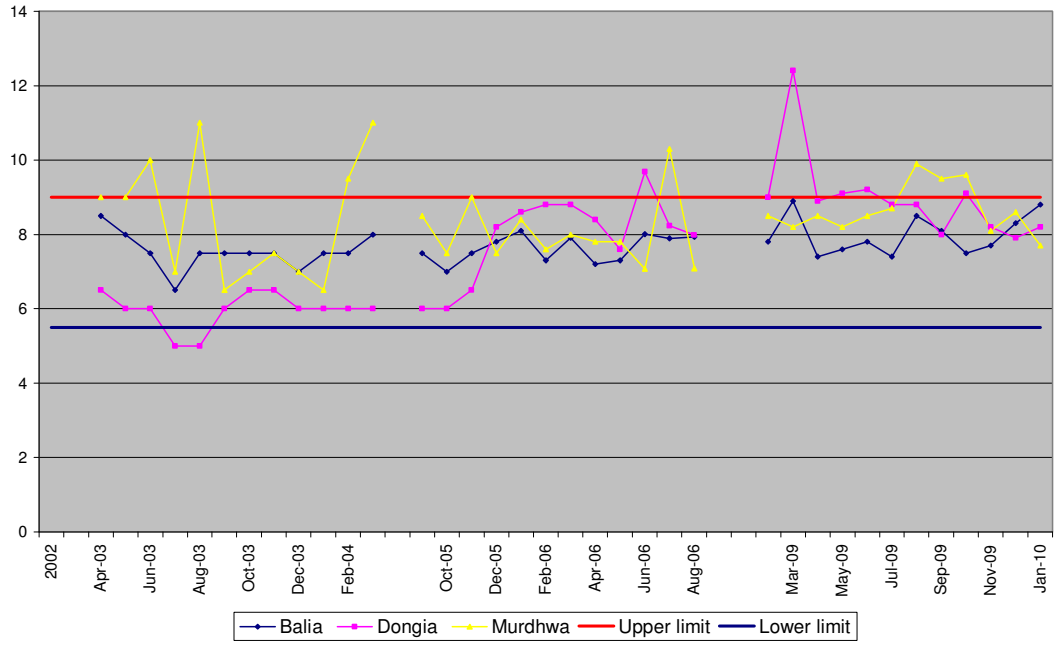


Fig.31 Composite effluents TSS mg/l

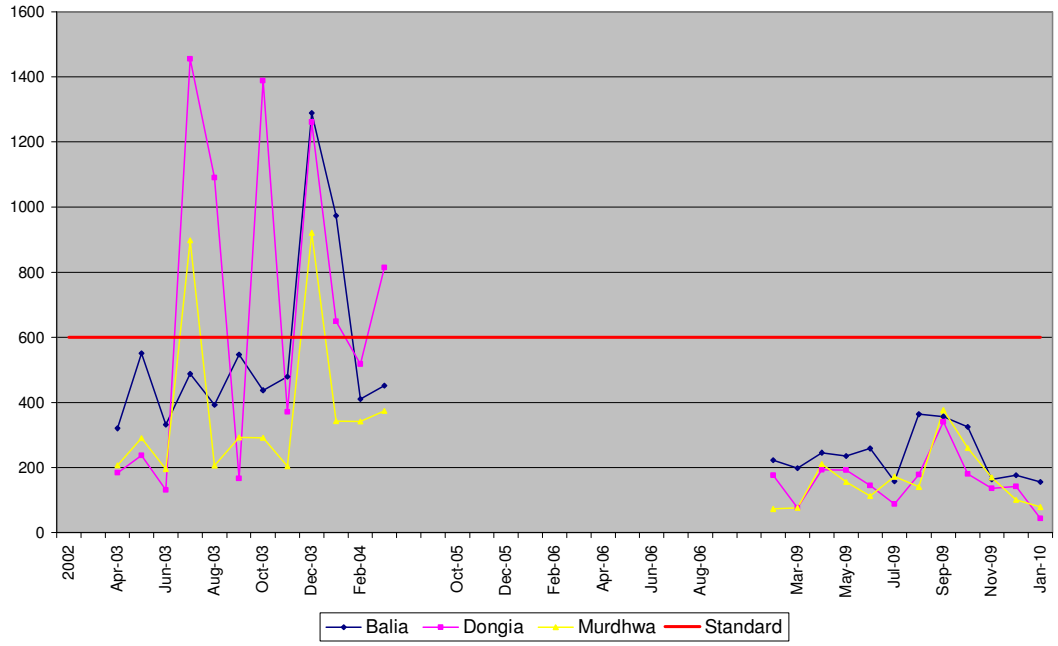


Fig.32 Composite effluents TDS mg/l

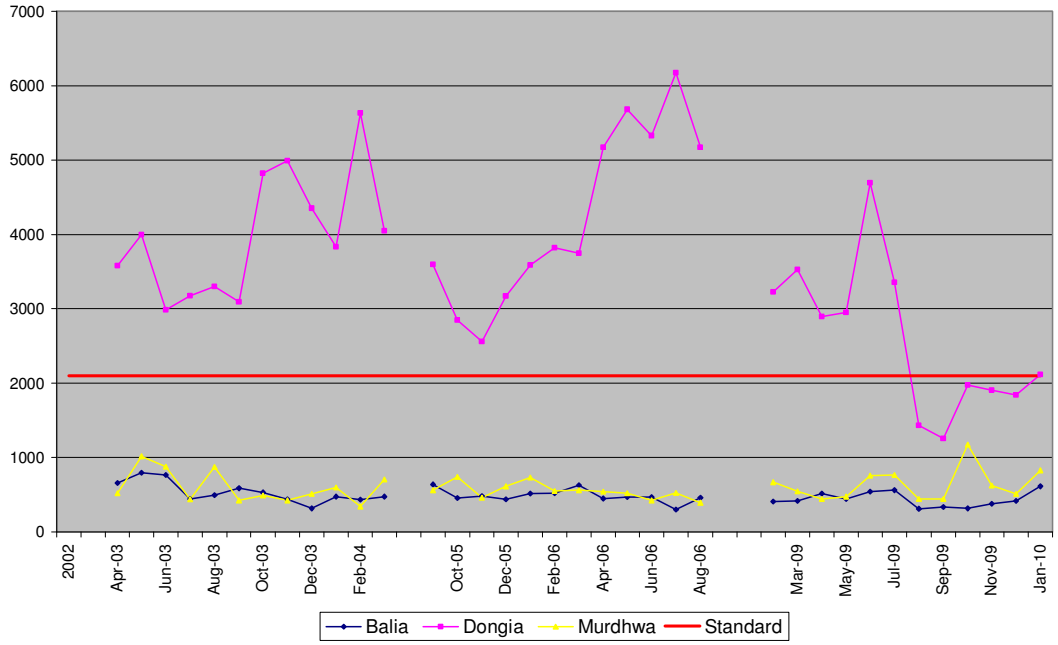


Fig.33 Composite effluents EC µMhos/cm

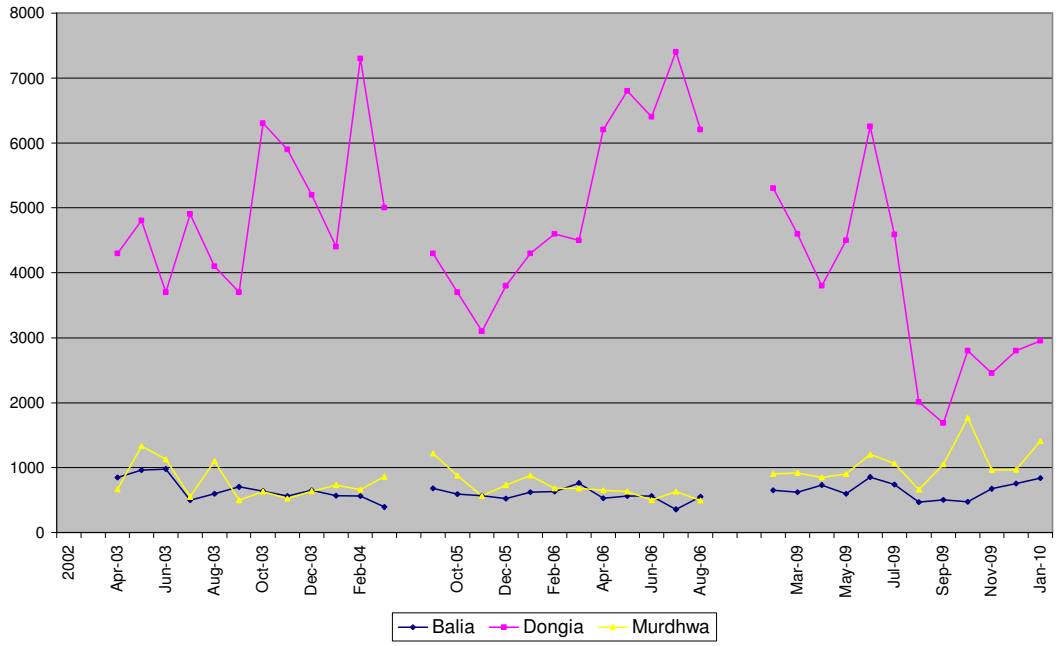


Fig.34 Composite effluents COD mg/l

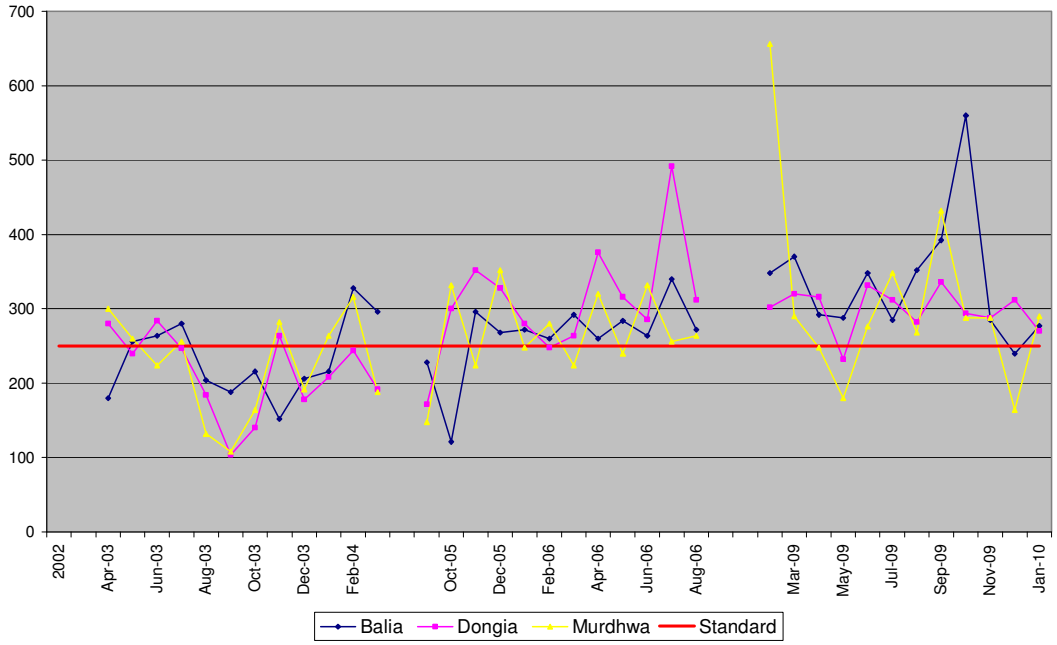


Fig.35 Composite effluents F mg/l

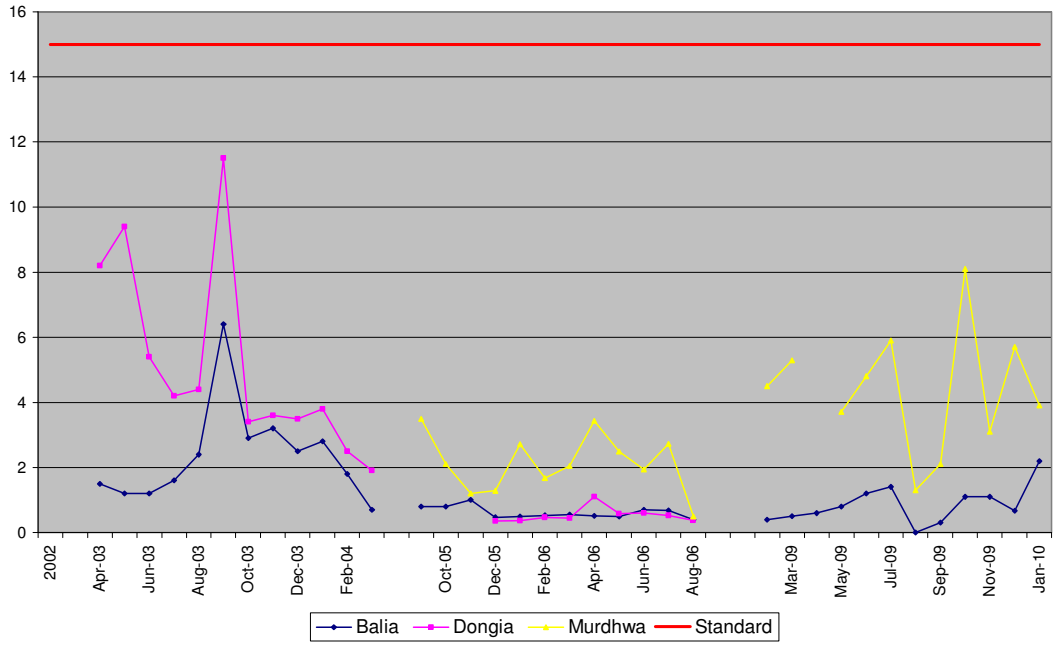


Fig.36 Composite effluents Hg µg/l

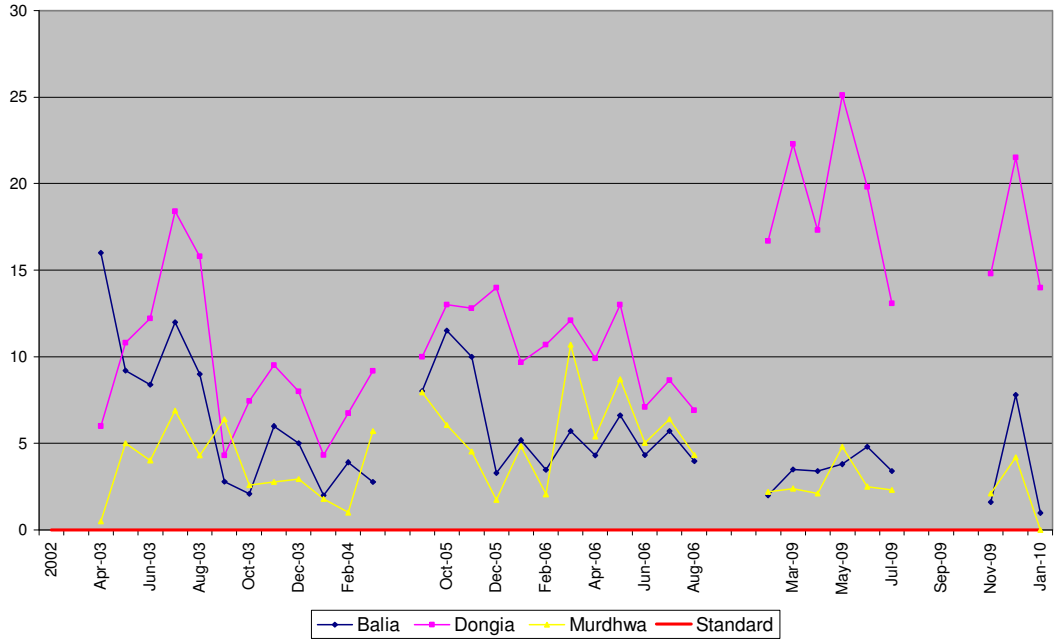


Fig.37 Ground water pH

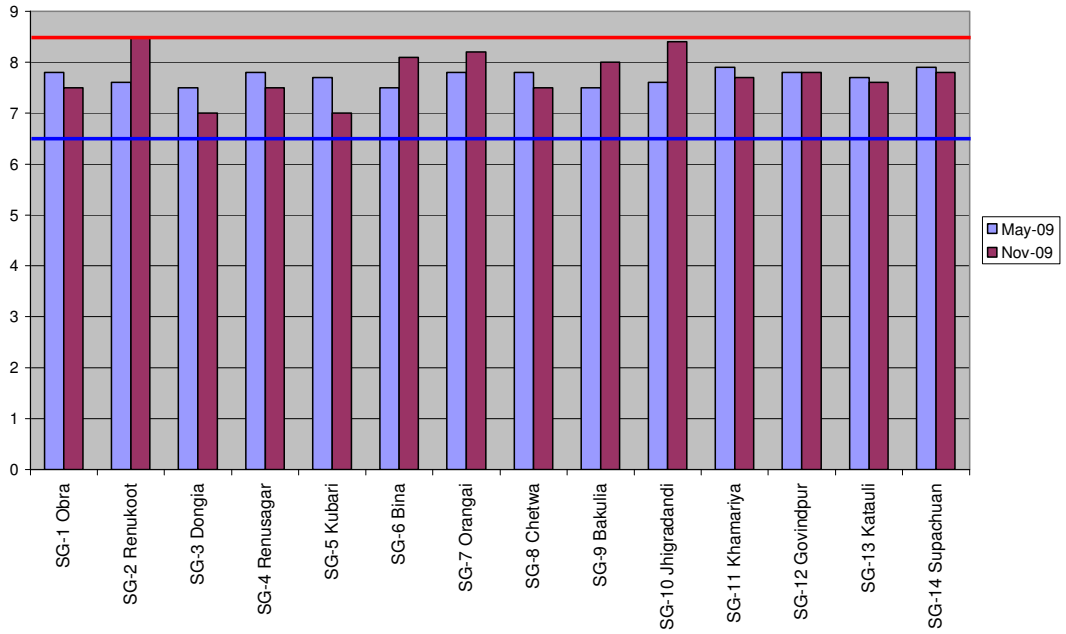


Fig.38 Ground water TSS mg/l
(limit 100 mg/l)

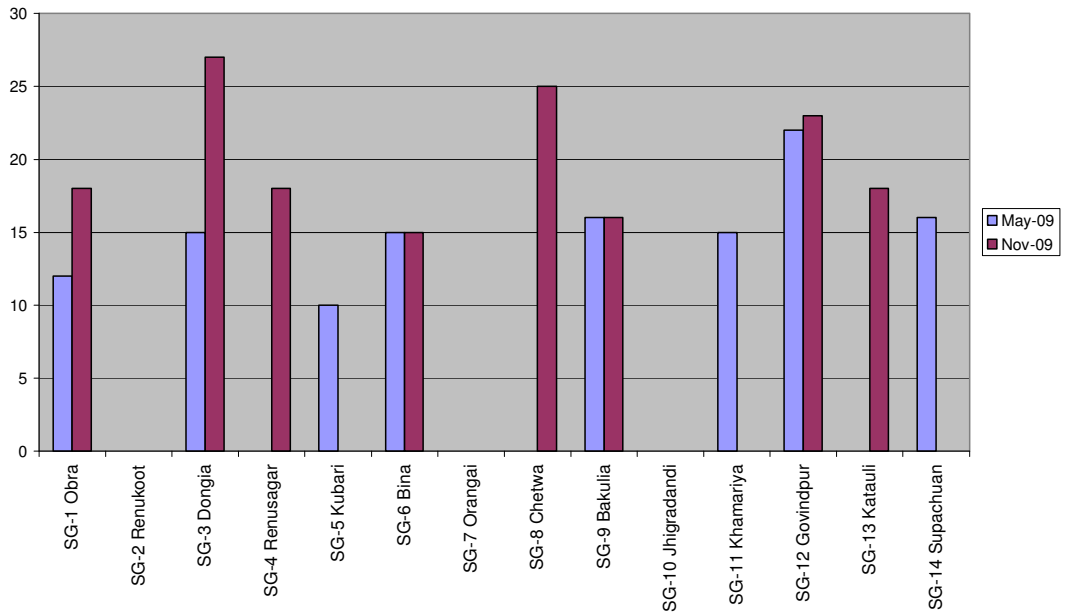


Fig.39 Ground water TDS mg/l

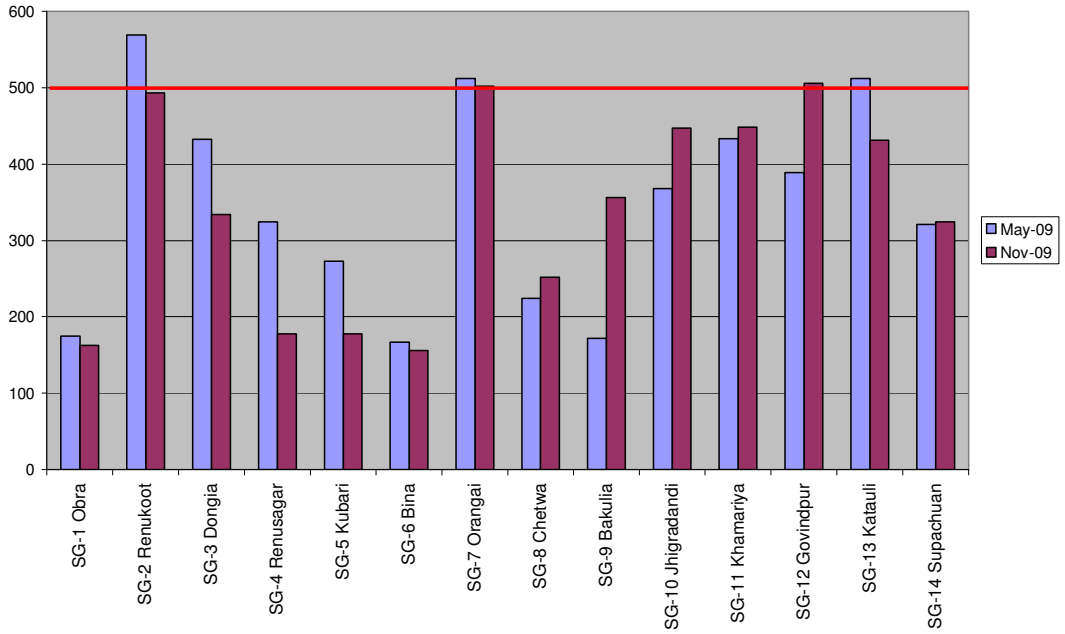


Fig.40 Ground water EC µmhos/cm

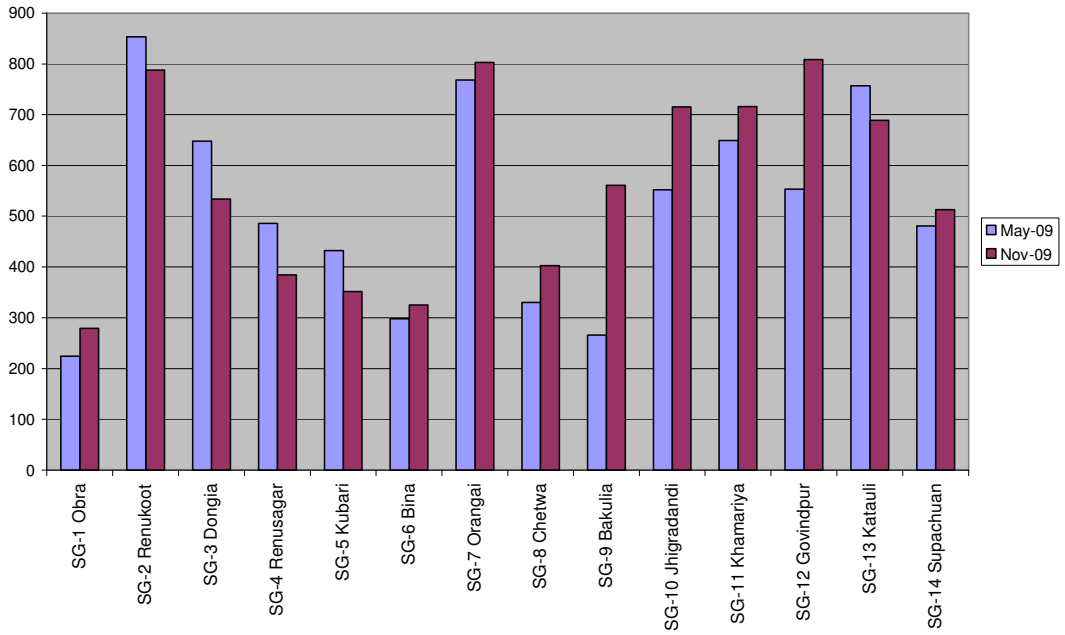


Fig.41 Ground water Chloride mg/l
(limit 250 mg/l)

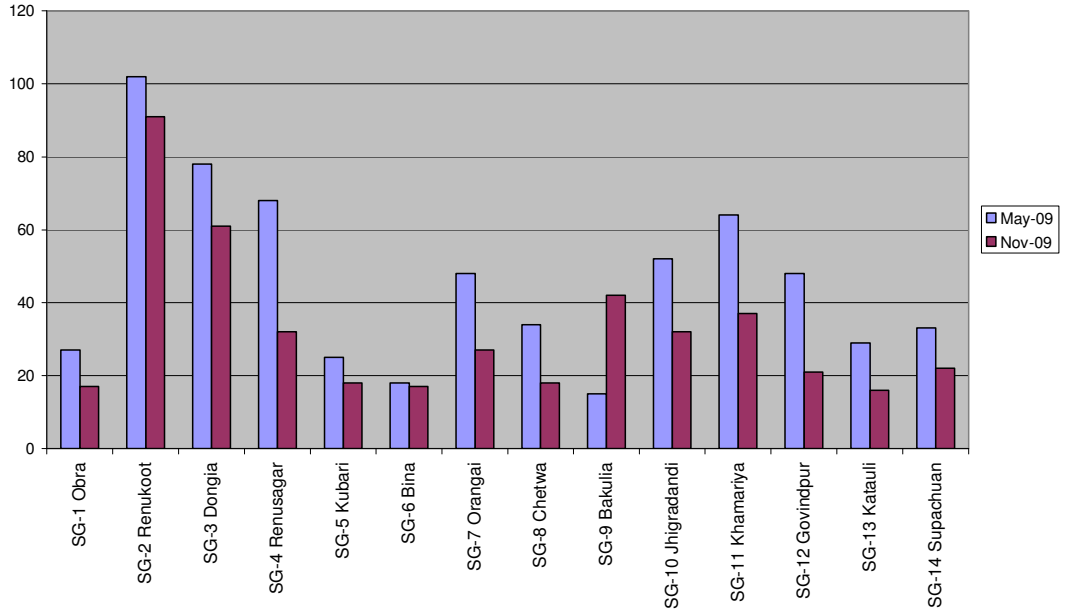


Fig.42 Ground water Nitrate mg/l
(limit 45 mg/l)

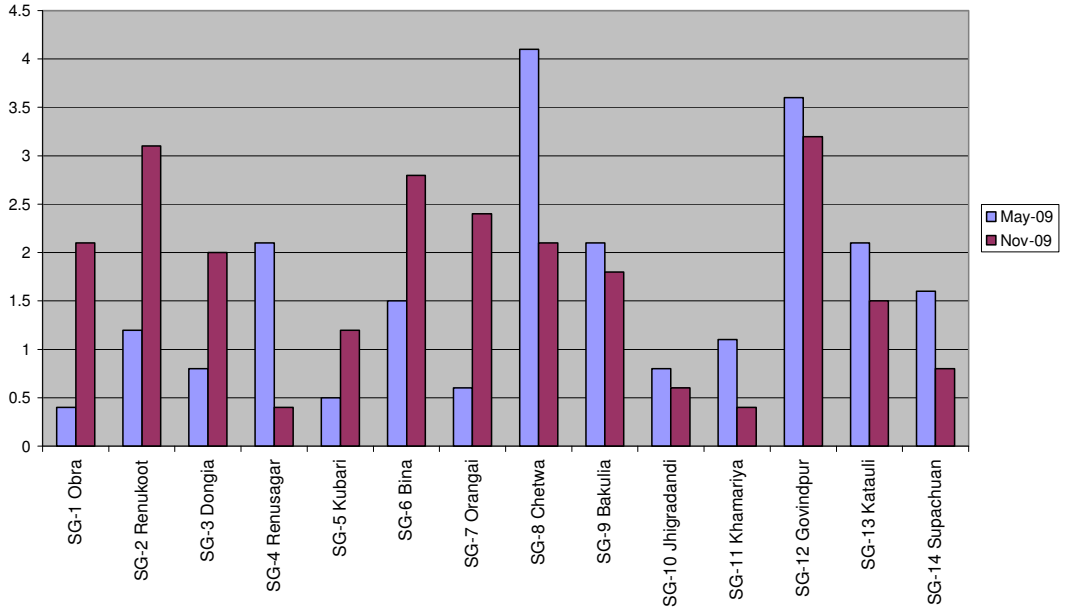


Fig.43 Ground water COD mg/l

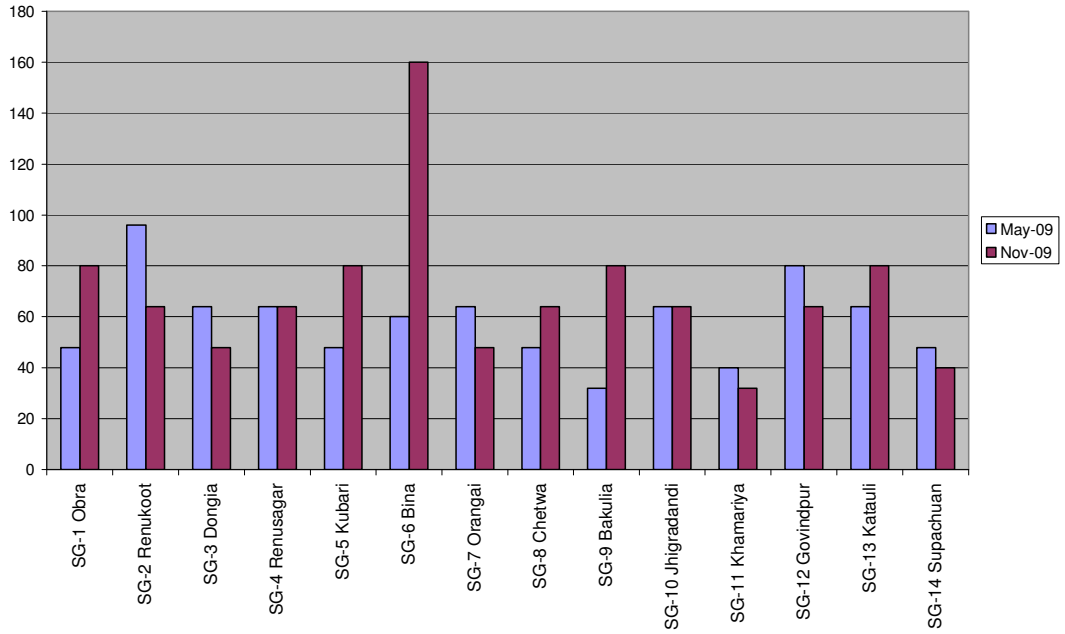


Fig.44 Ground water Fluoride mg/l

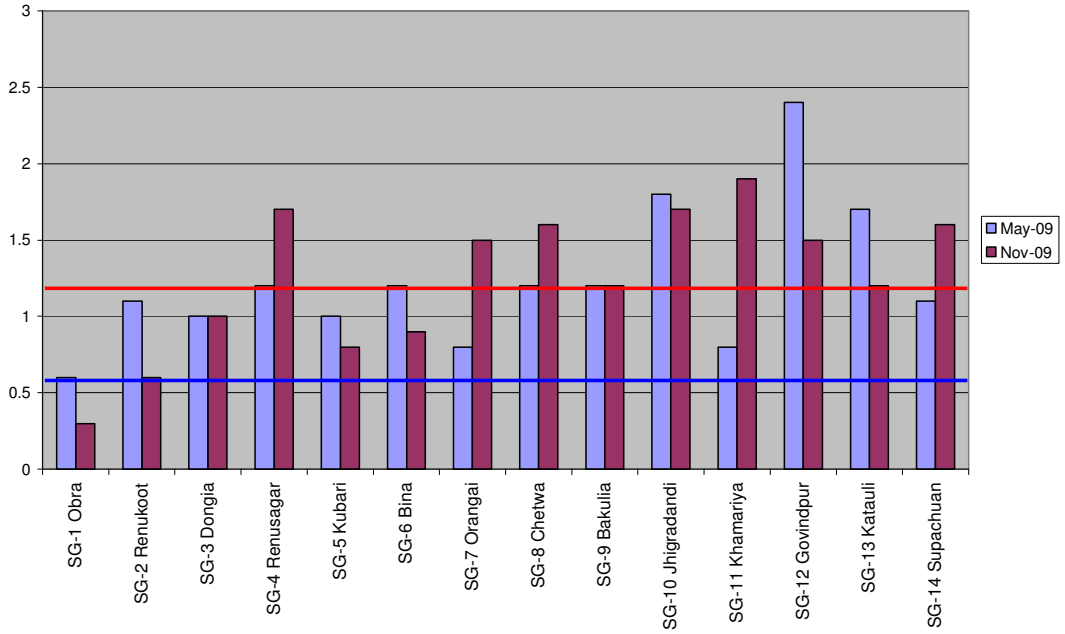
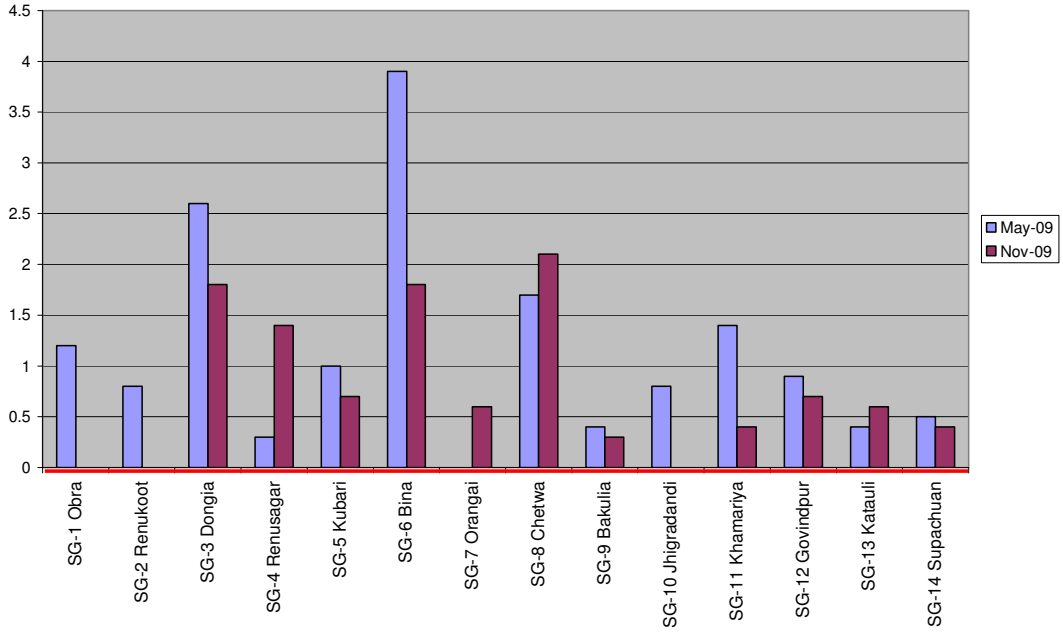


Fig.45 Ground water Hg µg/l



Annexure III

Detailed monitoring results

Environment Quality Monitoring, Singrauli
2009-2010

Table 1: Ambient Air quality													
The High Volume Sampler was operated uninterrupted at each station for 2 days in every month, except on rainy days. 8-hourly samples were collected for SPM and RSPM, 4-hourly samples for SO2 and Nox, and 12-hourly samples for F and Hg													
	Table 1a	**RSPM µg/m^3**			**Limit = 60**								
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
A-1	Dhuma-Kewal	86	88	60	41	47		39		53	40	45	51
AA-2	Jarha-Rajo	180	114	177	77	98			106	129	72	99	123
A-3	Murdhawa-Renukoot	252	216	215	96	103	77	87		94	81	173	156
A-4	Bari-Dala	887	732	1290	184		223			197	473	515	374
A-5	Kubri-Anpara	181	128	130	115	97			93	147	88	100	145
AA-6	Navtoliya	377	173	248	125		99			128	134	156	156
AA-7	Lojhara	169	97	104	71	86			82	128	117	126	133
A-8	Govindpur	125	163	95	68	75	97	66	84	109	84	116	116
A-9	Katauli	192	153	126	77		49		56	118	76	78	103
	Table 1b	**SPM µg/m^3**			**Limit = 140**								
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
A-1	Dhuma-Kewal	127	162	142	69	100		102		132	76	112	128
AA-2	Jarha-Rajo	297	282	268	204	241			194	174	166	229	237
A-3	Murdhawa-Renukoot	457	518	499	297	234	222	208		184	204	468	503
A-4	Bari-Dala	1836	1780	2089	667		597			1094	1697	2127	995
A-5	Kubri-Anpara	292	263	259	364	275			183	261	196	234	322
AA-6	Navtoliya	571	401	399	411		240			196	248	344	304
AA-7	Lojhara	309	243	307	226	253			171	174	223	311	281
A-8	Govindpur	276	271	268	226	193	207	156	148	185	200	201	228

A-9	Katauli	274	276	296	221		137		120	213	146	191	228
	Table 1c	**SO_2 µg/m^3**			**Limit = 60**								
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
A-1	Dhuma-Kewal	4	4	4	4	6		4		5	4	5	6
AA-2	Jarha-Rajo	48	38	45	48	34			33	22	16	23	34
A-3	Murdhawa-Renukoot	39	38	44	40	64	56	35		45	27	19	31
A-4	Bari-Dala	26	28	36	44		29			23	16	14	0
A-5	Kubri-Anpara	56	80	30	66	46			40	35	14		15
AA-6	Navtoliya	41	22	55	50		31			25	16	12	13
AA-7	Lojhara	40	57	64	60	45			30	42	15		24
A-8	Govindpur	31	29	63	44	29	29	19	24	23	14	15	25
A-9	Katauli	22	22	55	21		18		23	23	11	16	16
	Table 1d	**NO_x µg/m^3**			**Limit = 60**								
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
A-1	Dhuma-Kewal	7	8	7	8	9		8		10	5	7	8
AA-2	Jarha-Rajo	46	41	36	63	41			34	23	30	25	24
A-3	Murdhawa-Renukoot	54	47	84	46	53	49	40		34	31	33	38
A-4	Bari-Dala	68	59	40	56		41			31	41	15	8
A-5	Kubri-Anpara	76	59	44	51	33			37	37	30		21
AA-6	Navtoliya	50	44	58	41		31			34	24	16	20
AA-7	Lojhara	55	70	37	43	51			38	25	19		23
A-8	Govindpur	36	42	26	43	31	36	22	41	23	22	20	26
A-9	Katauli	33	33	29	44		19		20	24	21	25	17
	Table 1e	**gaseous F µg/m^3**											
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
A-1	Dhuma-Kewal	0	0		0	0		0		0.1	0	0	0
AA-2	Jarha-Rajo	5	5	3	1.2	3			2.1	0.7	1.7	1.7	2.2
A-3	Murdhawa-Renukoot	7	6.7	6	10.5	6.5	6.5	2.9		4.8	2.5	2.1	3.4
A-4	Bari-Dala	1.6	0.5	2.7	3.1		1.8			1.3	1.4	1.4	0.8
A-5	Kubri-Anpara	15	3.7	1.4	1.5	4			4.5	1.5	1.6		1.6
AA-6	Navtoliya	1.1	0.4	3	0.8		1.2			1	1.5	1.3	1.2
AA-7	Lojhara	9	4.8	4.1	1.2	5			2.9	0.8	1.8		2.8

A-8	Govindpur	3.4	5.2	2.2	4.4	2	4	1.8	1.5	0.5	0.8	1.8	1.8
A-9	Katauli	7	1.3	2.4	2		3.2		1.8	1.5	0.7	0.9	1.3
	Table 1f	**gaseous Hg ng/m^3**			**Proposed limit = 12**								
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
A-1	Dhuma-Kewal	0	0		0	0				10	0	0	0
AA-2	Jarha-Rajo	210	172	213	428	465					156	390	530
A-3	Murdhawa-Renukoot	740	325	165	572	667					290	580	560
A-4	Bari-Dala	390	91	171	292						130	140	0
A-5	Kubri-Anpara	350	171	313	982	678					230	164	220
AA-6	Navtoliya	190	130	321	199						174	350	370
AA-7	Lojhara	1290	397	354	625	829					180	436	140
A-8	Govindpur	350	109	149	400	194					140	550	450
A-9	Katauli	460	397	115	384						70	430	360
	Table 1g	**particulate Hg ng/m^3**			**Proposed limit = 3**								
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
A-1	Dhuma-Kewal	0.5	0	NM	0.2	0					0.1	0.4	0.6
AA-2	Jarha-Rajo	2	1.3	4.7	3.8	4.2					1.4	4.3	6.3
A-3	Murdhawa-Renukoot	3	2.8	2.6	2.2	4.4					5.3	9.9	3.3
A-4	Bari-Dala	8	3.5	3.5	8.7						3.9	5.4	9
A-5	Kubri-Anpara	1.3	2.1	4.8	18	2.9					7.3	3.4	3.8
AA-6	Navtoliya	1	4.2	5.4	4.2						2.8	4.2	5.6
AA-7	Lojhara	0.6	3.6	3.1	2.2	3.8					3.8	3.6	8.6
A-8	Govindpur	2.3	2.9	2.9	3.3	5.3					2.4	3.8	9
A-9	Katauli	1.4	2	4.5	3.4						1.3	4.9	5.6

Table 2: Surface water quality in River and Reservoir													
Grab samples were collected once on a monthly basis, while avoiding the monsoon season													
	Table 2a	**pH**		**Upper limit = 9; lower limit = 5.5**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
BS-2	Orangi	7.5	8.5	8	7.8	7.5	7.8	7.9	7.8	7.5	7.5	8.1	7.7
BS-5	Balia-c	8.5	8.8	8.5	7.6	7.9	7.9	7.6	7.7	7.8	8	8.4	8.4
BS-8	Renusagar AP-c	7.5	8.2	8.6	7.6	7.8	7.6	7.5	8	7.3	7.7	9.4	7.6
BS-9	Pipri	8.5	8.2	9	7.8	7.6	8.2	8.2	7.9	7.6	8.2	8.2	8.8
BS-11	Khamaria	9	8.8	8.5	7.5	7.7	7.8	8.2	7.7	7.2	7.5	8.1	7.5
BS-13	Dongia-c	8.5	8.5	8.5	8.1	7.8	8.1	8.5	7.7	7.9	8.1	8.6	8.2
BS-15	Obra AP-u/s	8	8.1	8.8	7.6	8	8	7.2	7.6	7	7.9	8.2	7.6
BS-16	Obra AP-d/s	7.5	7.3	7.6	7.4	7.4	7.6	8	7.8	7.4	7.8	8.6	7.8
	Table 2b	**TSS mg/l**		**Limit = 100**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
BS-2	Orangi	0	0	0	0	0	46	301	204	43	15	7	0
BS-5	Balia-c	60	32	45	39	47	56	376	165	61	67	48	43
BS-8	Renusagar AP-c	26	16	28	34	41	36	180	148	70	56	36	50
BS-9	Pipri	17	0	0	21	35	24	146	217	65	62	28	24
BS-11	Khamaria	10	0	0	0	0	0	114	128	83	27	0	0
BS-13	Dongia-c	18	12	16	15	24	31	180	170	134	56	57	34
BS-15	Obra AP-u/s	58	18	19	10	0	0	156	183	73	42	28	41
BS-16	Obra AP-d/s	58	52	64	38	64	48	183	212	107	112	78	62
	Table 2c	**TDS mg/l**		**Limit = 2100**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
BS-2	Orangi	132	163	168	175	168	272	56	65	90	62	76	81
BS-5	Balia-c	222	215	242	335	278	312	89	343	70	234	263	341
BS-8	Renusagar AP-c	139	142	270	305	332	337	80	81	78	87	87	112
BS-9	Pipri	130	125	226	405	278	309	98	84	72	72	92	98
BS-11	Khamaria	142	147	165	195	182	198	75	236	67	67	105	102
BS-13	Dongia-c	180	189	192	252	212	232	758	858	296	321	185	729
BS-15	Obra AP-u/s	115	125	132	150	165	172	81	85	378	85	85	94

BS-16	Obra AP-d/s	115	119	89	122	168	178	84	90	376	84	92	86
	Table 2d	**EC µmhos/cm**											
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
BS-2	Orangi	172	200	200	250	261	232	87	80	144	62	123	129
BS-5	Balia-c	300	270	290	400	427	432	156	514	112	234	492	545
BS-8	Renusagar AP-c	160	170	315	443	498	482	148	121	113	87	167	194
BS-9	Pipri	152	162	300	600	412	418	240	118	115	72	168	163
BS-11	Khamaria	160	165	208	310	290	278	112	340	107	67	189	189
BS-13	Dongia-c	215	200	200	365	317	326	1137	1287	414	321	346	1166
BS-15	Obra AP-u/s	100	180	185	225	223	229	121	136	564	85	143	150
BS-16	Obra AP-d/s	100	200	157	200	256	259	126	144	536	84	148	120
	Table 2e	**DO mg/l**											
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
BS-2	Orangi	8.2	7.8	8.2	8	7.4	8.2	7.8	7.6	7.2	8	8.2	8.4
BS-5	Balia-c	7	7	7	7.2	6	7	5.6	6.8	6.8	6.8	7.6	7.4
BS-8	Renusagar AP-c	8	8	7.6	6.8	6.4	6.8	7.2	7.2	7.4	7.2	7.2	6.8
BS-9	Pipri	8	7.6	8	6.5	6.8	7.4	6.8	6.4	7.2	7.4	6.8	7.6
BS-11	Khamaria	7.6	8.2	7.8	7.9	7.2	7.6	7.2	7.4	7.6	7.6	7.4	7.8
BS-13	Dongia-c	7.4	7	7	6.8	7	7	6.4	6.8	6.8	6.8	6.8	7.2
BS-15	Obra AP-u/s	7.2	7.4	7.4	7	7.6	7.4	6.8	7.2	7.6	7.8	7.2	7.6
BS-16	Obra AP-d/s	7.6	6.8	7	7.2	6.8	7.6	6.8	7	7	7	7	7.2
	Table 2f	**COD mg/l**		**Limit = 250**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
BS-2	Orangi	12	12	10	12	12	80	240	240	64	36	24	44
BS-5	Balia-c	32	40	32	48	48	64	256	180	112	112	96	298
BS-8	Renusagar AP-c	16	16	32	64	48	80	148	180	112	96	128	58
BS-9	Pipri	16	16	16	64	60	64	180	164	80	80	64	51
BS-11	Khamaria	48	32	16	32	32	48	236	140	80	48	32	116
BS-13	Dongia-c	32	24	24	48	48	48	172	164	224	128	80	75
BS-15	Obra AP-u/s	32	16	20	48	32	32	156	180	80	96	96	75
BS-16	Obra AP-d/s	32	32	44	48	64	64	144	184	112	206	128	80
	Table 2g	**F mg/l**		**Limit = 2**									

Code	Station	Feb-09	Mar-09	Apr-09	May-09	Jun-09	Jul-09	Aug-09	Sep-09	Oct-09	Nov-09	Dec-09	Jan-10
BS-2	Orangi	0.2	0.3	0.3	0.3	0.4	0.4	0	0.12	0.3	0.27	0.22	0.25
BS-5	Balia-c	0.3	0.4	0.4	0.8	0.8	0.8	0.11	0.15	0.22	0.38	0.67	0.46
BS-8	Renusagar AP-c	0.3	0.6	0.9	1.2	0.8	1.1	0.14	0.1	0.24	0.43	0.64	0.51
BS-9	Pipri	0.3	0.4	0.9	0.9	0.6	0.7	0.14	1.12	0.27	0.31	0.38	0.39
BS-11	Khamaria	0.6	0.6	0.5	0.8	0.5	0.7	0.12	0.11	0.38	0.57	0.65	1.12
BS-13	Dongia-c	0.3	0.2	0.4	0.6	0.6	0.6	0.32	0.1	0.2	0.38	0.37	1.4
BS-15	Obra AP-u/s	0.4	0.5	0.5	1.5	0.9	1	0.74	0.45	0.56	0.65	0.65	1.16
BS-16	Obra AP-d/s	0.4	0.5	0.5	0.7	0.6	1	0.72	0.47	0.56	0.7	0.75	1.71
	Table 2h	**Hg µg/l**		**Limit = 0.01**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
BS-2	Orangi	0	0	0.3	0.3	0	0				0	0	0.28
BS-5	Balia-c	2.3	6.6	8.3	2.1	1.4	2.4				0.7	1	1.4
BS-8	Renusagar AP-c	1.9	0.9	3	1.8	2.6	1.8				0.56	1.4	2.8
BS-9	Pipri	1.9	0.8	2.3	2.4	1.8	0.9				0.56	1.8	1.4
BS-11	Khamaria	0.4	1.4	6.3	0.9	1.3	0				0.28	0.75	0
BS-13	Dongia-c	2.7	2.2	2.8	2.3	4	2.9				1.7	1.8	2.5
BS-15	Obra AP-u/s	2.8	1.5	2.1	1.4	2.6	1.2				1.56	1.2	1.7
BS-16	Obra AP-d/s	2.8	1.3	1.6	1.6	2.8	1.5				1.8	1.4	1.7

Table 3: Surface water quality in Ponds													
Grab samples were collected once on a monthly basis, while avoiding the monsoon season													
	Table 3a	**pH**		**Upper limit = 9; lower limit = 5.5**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-17	Kirwani	9	8.5	8.9	8.5	9.1	8.5	7.6	8.5	7.5	8.5	7.8	8.5
S-18	Chetwa	8.5	9	7.5	8.2	7.8	7.4	7.9	7.7	7.5	7.8	8.1	7
S-19	Bakulia	7.5	8.3	8.5	7.5	7.7	7.5	7.4	7.8	7.1	7.9	7.5	7.3
BSA-1	Govindpur *Bawadi*	7.5	7.9	7.6	7.7	8	7.5	8.9	8	7.8	8.1	8.4	7.6
BSA-2	Govindpur Pond	7.5	8.5	8.6	7.9	7.8	7.5	8.5	7.3	7.5	7.5	7.7	7.9
	Table 3b	**TSS mg/l**		**Limit = 100**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-17	Kirwani	21	32	20	20	25	35	136	156	110	36	46	23
S-18	Chetwa	0	15	24	15	35	25	115	87	48	23	27	52
S-19	Bakulia	0	11	20	12	26	41	192	68	70	34	68	55
BSA-1	Govindpur *Bawadi*	13	20	15	15	24	20	40	42	56	48	42	70
BSA-2	Govindpur Pond	15	15	20	20	39	36	89	58	63	22	58	33
	Table 3c	**TDS mg/l**		**Limit = 2100**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-17	Kirwani	406	546	567	554	371	327	228	177	286	234	242	205
S-18	Chetwa	326	362	381	346	251	268	98	92	145	145	162	190
S-19	Bakulia	178	210	242	278	186	159	62	106	110	108	114	109
BSA-1	Govindpur *Bawadi*	335	592	582	615	543	481	549	413	568	568	587	531
BSA-2	Govindpur Pond	572	425	470	730	324	312	124	148	182	178	188	217
	Table 3d	**EC µmhos /cm**											
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-17	Kirwani	500	800	835	856	497	415	346	283	417	456	321	338
S-18	Chetwa	430	512	554	575	371	322	140	136	232	276	281	312
S-19	Bakulia	240	300	325	385	266	315	104	125	144	184	142	174
BSA-1	Govindpur *Bawadi*	400	800	750	820	769	680	823	619	852	848	875	912
BSA-2	Govindpur Pond	800	700	786	900	436	421	288	222	273	317	379	423
	Table 3e	**COD mg/l**		**Limit = 250**									

Code	Station	Feb-09	Mar-09	Apr-09	May-09	Jun-09	Jul-09	Aug-09	Sep-09	Oct-09	Nov-09	Dec-09	Jan-10
S-17	Kirwani	32	48	42	48	64	80	132	80	80	120	80	35
S-18	Chetwa	16	24	24	32	48	64	128	80	64	64	64	44
S-19	Bakulia	24	32	32	32	64	96	352	126	80	80	112	59
BSA-1	Govindpur *Bawadi*	24	48	48	64	64	80	80	128	140	208	196	58
BSA-2	Govindpur Pond	48	32	40	48	80	64	140	96	80	80	80	80
	Table 3f	**Hg µg/l**		**Limit = 0.01**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-17	Kirwani	1.8	4.3	2.5	3.2	2.9	0				0.7	1.4	2.8
S-18	Chetwa	2.7	1.2	3.4	2.8	3.3	0.8				0.56	1.7	4.2
S-19	Bakulia	1.2	0.9	2.8	1.6	1.3	0.5				0.28	0.75	1.8
BSA-1	Govindpur *Bawadi*	1.3	0	1.4	2.2	1.6	1.2				2.8	3.7	1.7
BSA-2	Govindpur Pond	1.2	1.4	1	2.5	1.5	0.8				0.42	2.8	2.8

Table 4: Effluent quality in Drains flowing into the Reservoir													
Grab samples were collected once on a monthly basis, while avoiding the monsoon season													
	Table 4a	**pH**		**Upper limit = 9; lower limit = 5.5**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-4	Balia Drain	7.6	8.4	8.2	7.4	7.9	7.6	8.1	7.7	7.4	7.2	7.6	7.8
S-12	Dongia Drain	9	13.2	9.2	8.9	8.5	9.4	8.5	7.5	7.9	7.8	8.3	8.6
S-14	MurdhawaDrain	8.5	8.2	9.5	7.8	8.7	8.9	9	8.9	9.7	8.6	9.2	9.2
S-20	Bina ETP	8.2	8.5	7.5	7.5	7.3	7.5	7.9	7.9	7.6	7.8	7.2	7.5
S-21	Kakri ETP	7.5	9.1	8.2	7.6	7.7	7.8	8.3	7.8	7.8	7	7.9	7.8
S-22	Dudhichua ETP	7.8	8.1	7.7	7.9	7.6	7.4	8.1	7.8	7.6	8.2	7.4	7.6
S-23	Anpara AP	8.5	9	7.8	7.7	7.6	7.9	7.6	8	7.6	8.5	7.9	8.7
S-24	Singrauli AP	7.9	9	8	7.8	8.1	7.5	8.7	7.8	7.6	8.1	8.1	8.2
S-25	Rihand drain	8.5	7.9	7.7	7.8	7.8	7.6	7.6	7.6	7.8	7.2	8.2	8.5
	Table 4b	**TSS mg /l**		**Limit = 600**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-4	Balia Drain	399	397	312	199	363	256	390	213	236	85	157	75
S-12	Dongia Drain	276	215	234	110	81	152	280	170	134	65	97	67
S-14	MurdhawaDrain	80	70	291	76	145	178	140	134	136	92	139	129
S-20	Bina ETP	38	11	90	165	135	79	51	120	176	49	50	61
S-21	Kakri ETP	24	97	65	20	117	156	70	135	45	98	55	30
S-22	Dudhichua ETP	59	157	43	203	176	133	53	175	43	41	70	50
S-23	Anpara AP	153	208	170	144	165	125	38	150	136	112	140	98
S-24	Singrauli AP	107	89	127	84	132	85	30	138	112	78	138	82
S-25	Rihand drain	80	185	66	134	148	112	78	127	143	118	168	137
	Table 4c	**TDS mg/l**		**Limit = 2100**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-4	Balia Drain	322	419	615	426	374	462	362	343	412	85	743	278
S-12	Dongia Drain	2927	3290	5210	2846	3725	3932	2358	1558	2412	65	2278	1638
S-14	MurdhawaDrain	795	465	745	478	1045	1222	452	561	1155	92	1012	1055
S-20	Bina ETP	1396	565	589	955	530	342	461	536	812	49	176	192
S-21	Kakri ETP	396	457	485	720	543	512	380	108	529	98	389	419

S-22	Dudhichua ETP	487	458	455	527	412	532	319	265	197	41	167	236
S-23	Anpara AP	96	94	456	363	248	272	119	76	91	112	145	156
S-24	Singrauli AP	140	101	366	215	222	195	135	104	136	78	176	136
S-25	Rihand drain	264	190	192	198	197	208	189	98	93	118	796	132
	Table 4d	**EC µmhos /cm**											
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-4	Balia Drain	500	600	800	728	535	650	568	514	583	834	1145	520
S-12	Dongia Drain	4300	4900	7200	4300	5438	5650	3137	2287	3214	1792	3578	2568
S-14	MurdhawaDrain	900	650	1100	800	1365	1522	791	841	1582	884	1467	1758
S-20	Bina ETP	1900	1100	1200	1700	795	496	678	745	1060	234	329	325
S-21	Kakri ETP	750	900	600	1100	814	672	570	150	763	343	772	689
S-22	Dudhichua ETP	600	600	900	945	618	758	482	397	295	346	315	432
S-23	Anpara AP	150	150	600	500	366	435	278	114	136	236	239	246
S-24	Singrauli AP	200	125	510	300	315	275	197	156	176	198	346	167
S-25	Rihand drain	290	300	200	252	276	335	264	112	139	156	1435	213
	Table 4e	**DO mg/l**											
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-4	Balia Drain	4	4	3.2	2	4	4.2	4.8	5.2	3.6	5.2	4.8	5.2
S-12	Dongia Drain										0	0	0
S-14	MurdhawaDrain	2	5.5	4	4		4	4.4	5.2	4.8	4.8	3.2	3.6
S-20	Bina ETP										6	4.8	5.2
S-21	Kakri ETP										6	5.2	4.8
S-22	Dudhichua ETP										6.4	4	5.2
S-23	Anpara AP										5.2	5.2	4.8
S-24	Singrauli AP										6.4	5.2	4.8
S-25	Rihand drain										5.6	6	6
	Table 4f	**COD mg/l**		**Limit = 250**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-4	Balia Drain	296	480	480	384	475	320	340	180	448	212	260	44
S-12	Dongia Drain	208	380	356	280	296	296	288	255	272	250	282	250
S-14	MurdhawaDrain	304	260	260	247	212	362	228	208	288	288	275	185
S-20	Bina ETP	144	80	80	128	256	96	192	168	164	96	96	36

S-21	Kakri ETP	144	40	96	80	176	112	188	144	112	64	112	44
S-22	Dudhichua ETP	176	80	48	96	160	96	132	180	80	176	208	36
S-23	Anpara AP	98	180	48	64	96	96	160	188	160	212	80	51
S-24	Singrauli AP	160	160	32	64	80	80	144	156	112	128	96	64
S-25	Rihand drain	64	80	80	80	96	96	132	80	164	96	80	51
	Table 4g	**F mg/l**		**Limit = 15**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-4	Balia Drain	0.4	0.5	0.8	0.5	1	1.5	0.28	0.15	1.2	0.56	1.9	0.32
S-12	Dongia Drain								0		0	0	0
S-14	MurdhawaDrain	3.2	1	4.2	3.5	4.3	4.8	2.2	3.1	5.7	4	3	2.7
S-20	Bina ETP	0.3	0.1	0.4	0.6	0.5	0.9	0.32	0.8	0.6	0.38	0.67	0.43
S-21	Kakri ETP	0.3	0.3	0.4	0.6	0.4	0.8	0.28	0.45	0.8	0.64	0.4	0.59
S-22	Dudhichua ETP	0.2	0.3	2.4	1	0.9	0.8	0.18	0.22	0.2	0.32	0.48	0.48
S-23	Anpara AP	1.4	2	2.4	1.6	2.2	0.7	0.56	2	1.4	1.4	1.5	0.98
S-24	Singrauli AP	1.2	2		1.5	1.2	0.6	1.84	1.2	0.5	0.98	0.89	1.2
S-25	Rihand drain	0.8	2	1.4	1.2	2.1	1.2	0.64	1.6	0.6	1.9	1.6	0.48
	Table 4h	**Hg µg/l**		**Limit = 0.01**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-4	Balia Drain	0.86	5.7	4.2	2.1	3.9	1.9				0.76	11.4	0.8
S-12	Dongia Drain	15.35	12.1	16.6	17.4	14.3	16.4				10.2	7.5	18.2
S-14	MurdhawaDrain	2.3	0	3.9	2.1	0.8	1.9				2.1	1.3	0.6
S-20	Bina ETP	1.6	3.9	3.7	3.2	2.7	0				1.1	0	1.5
S-21	Kakri ETP	2	4.6	2.3	2.8	1.9	0				0	0	2.8
S-22	Dudhichua ETP	2.4	0	6.3	4.8	2.9	3.1				0	1.78	5.04
S-23	Anpara AP	3.1	7.9	6.3	2.8	5	5.7				1.8	1.4	0.9
S-24	Singrauli AP	4.4	2.5	4.6	1.9	2.2	3.1				2.9	2.8	1.5
S-25	Rihand drain	34	2.4	1.6	1.8	2.6	5				0.98	0.7	2.8

Table 5: Industrial Effluent Carrying Drains (Composite)													
These drains were monitored by collection of 24 hour composite samples once on a monthly basis, with a sampling frequency of one hour													
	Table 5a	**pH**		**Upper limit = 9; lower limit = 5.5**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-4	Balia	7.8	8.9	7.4	7.6	7.8	7.4	8.5	8.1	7.5	7.7	8.3	8.8
S-12	Dongia	9	12.4	8.9	9.1	9.2	8.8	8.8	8	9.1	8.2	7.9	8.2
S-14	Murdhawa	8.5	8.2	8.5	8.2	8.5	8.7	9.9	9.5	9.6	8.1	8.6	7.7
	Table 5b	**TSS mg/l**		**Limit = 600**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-4	Balia	222	198	246	235	258	158	364	356	325	164	176	156
S-12	Dongia	176	76	193	192	145	88	178	340	180	135	142	43
S-14	Murdhawa	73	76	210	155	112	172	140	376	260	169	100	78
	Table 5c	**TDS mg/l**		**Limit = 2100**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-4	Balia	408	421	516	445	542	562	314	336	318	378	417	612
S-12	Dongia	3227	3530	2893	2950	4696	3356	1434	1256	1972	1908	1842	2115
S-14	Murdhawa	672	549	443	477	758	768	443	443	1175	623	510	826
	Table 5d	**EC µmhos /cm**											
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-4	Balia	650	620	730	600	856	738	471	504	477	671	758	835
S-12	Dongia	5300	4600	3800	4500	6253	4585	2011	1689	2801	2456	2798	2954
S-14	Murdhawa	900	920	850	900	1200	1068	664	1050	1762	960	964	1412
	Table 5e	**COD mg/l**		**Limit = 250**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-4	Balia	348	370	292	288	348	285	352	392	560	285	240	277
S-12	Dongia	302	320	316	232	332	312	282	336	294	288	312	270
S-14	Murdhawa	656	290	248	180	276	348	268	432	288	288	164	290
	Table 5f	**F- mg/l**		**Limit = 15**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-4	Balia	0.4	0.5	0.6	0.8	1.2	1.4	0	0.3	1.1	1.1	0.67	2.2

S-12	Dongia												
S-14	Murdhawa	4.5	5.3		3.7	4.8	5.9	1.3	2.1	8.1	3.1	5.7	3.9
	Table 5g	**Hg µg/l**		**Limit = 0.01**									
Code	**Station**	**Feb-09**	**Mar-09**	**Apr-09**	**May-09**	**Jun-09**	**Jul-09**	**Aug-09**	**Sep-09**	**Oct-09**	**Nov-09**	**Dec-09**	**Jan-10**
S-4	Balia	2	3.5	3.4	3.8	4.8	3.4				1.6	7.8	0.98
S-12	Dongia	16.7	22.3	17.3	25.1	19.8	13.1				14.8	21.5	14
S-14	Murdhawa	2.2	2.4	2.1	4.8	2.5	2.3				2.1	4.2	0

Table 6: Ground water quality from hand pumps

Monitoring was carried out once in pre-monsoon period, and once in post-monsoon period

T 6a	pH	limit=6.5-8.5	
Code	Station	May-09	Nov-09
SG-1	Obra	7.8	7.5
SG-2	Renukoot	7.6	8.5
SG-3	Dongia	7.5	7.0
SG-4	Renusagar	7.8	7.5
SG-5	Kubari	7.7	7.0
SG-6	Bina	7.5	8.1
SG-7	Orangi	7.8	8.2
SG-8	Chetwa	7.8	7.5
SG-9	Bakulia	7.5	8.0
SG-10	Jhigradandi	7.6	8.4
SG-11	Khamariya	7.9	7.7
SG-12	Govindpur	7.8	7.8
SG-13	Katauli	7.7	7.6
SG-14	Supachuan	7.9	7.8

T 6b	TSS mg/l	limit=100	
Code	Station	May-09	Nov-09
SG-1	Obra	12	18
SG-2	Renukoot	0	0
SG-3	Dongia	15	27
SG-4	Renusagar	0	18
SG-5	Kubari	10	0
SG-6	Bina	15	15
SG-7	Orangi	0	0
SG-8	Chetwa	0	25
SG-9	Bakulia	16	16
SG-10	Jhigradandi	0	0
SG-11	Khamariya	15	0
SG-12	Govindpur	22	23
SG-13	Katauli	0	18
SG-14	Supachuan	16	0

T 6c	TDS mg/l	limit=500	
Code	Station	May-09	Nov-09
SG-1	Obra	175	163
SG-2	Renukoot	569	493
SG-3	Dongia	432	334
SG-4	Renusagar	324	178
SG-5	Kubari	273	178
SG-6	Bina	167	156
SG-7	Orangi	512	502
SG-8	Chetwa	224	252
SG-9	Bakulia	172	356
SG-10	Jhigradandi	368	447
SG-11	Khamariya	433	448
SG-12	Govindpur	389	506
SG-13	Katauli	512	431
SG-14	Supachuan	321	324

T 6d	EC µmhos /cm		
Code	Station	May-09	Nov-09
SG-1	Obra	225	279
SG-2	Renukoot	853	788
SG-3	Dongia	648	534
SG-4	Renusagar	486	384
SG-5	Kubari	432	352
SG-6	Bina	298	325
SG-7	Orangi	768	803
SG-8	Chetwa	330	403
SG-9	Bakulia	266	561
SG-10	Jhigradandi	552	715

T 6e	Chloride mg/l	limit=250	
Code	Station	May-09	Nov-09
SG-1	Obra	27	17
SG-2	Renukoot	102	91
SG-3	Dongia	78	61
SG-4	Renusagar	68	32
SG-5	Kubari	25	18
SG-6	Bina	18	17
SG-7	Orangi	48	27
SG-8	Chetwa	34	18
SG-9	Bakulia	15	42
SG-10	Jhigradandi	52	32

T 6f	Nitrate mg/l	limit=45	
Code	Station	May-09	Nov-09
SG-1	Obra	0.4	2.1
SG-2	Renukoot	1.2	3.1
SG-3	Dongia	0.8	2
SG-4	Renusagar	2.1	0.4
SG-5	Kubari	0.5	1.2
SG-6	Bina	1.5	2.8
SG-7	Orangi	0.6	2.4
SG-8	Chetwa	4.1	2.1
SG-9	Bakulia	2.1	1.8
SG-10	Jhigradandi	0.8	0.6

SG-11	Khamariya	649	716
SG-12	Govindpur	553	809
SG-13	Katauli	757	689
SG-14	Supachuan	481	513
T 6g	**COD mg/l**		
Code	**Station**	**May-09**	**Nov-09**
SG-1	Obra	48	80
SG-2	Renukoot	96	64
SG-3	Dongia	64	48
SG-4	Renusagar	64	64
SG-5	Kubari	48	80
SG-6	Bina	60	160
SG-7	Orangi	64	48
SG-8	Chetwa	48	64
SG-9	Bakulia	32	80
SG-10	Jhigradandi	64	64
SG-11	Khamariya	40	32
SG-12	Govindpur	80	64
SG-13	Katauli	64	80
SG-14	Supachuan	48	40

SG-11	Khamariya	64	37
SG-12	Govindpur	48	21
SG-13	Katauli	29	16
SG-14	Supachuan	33	22
T 6h	**Fluoride mg/l**	**limit=0.6-1.2**	
Code	**Station**	**May-09**	**Nov-09**
SG-1	Obra	0.6	0.3
SG-2	Renukoot	1.1	0.6
SG-3	Dongia	1	1
SG-4	Renusagar	1.2	1.7
SG-5	Kubari	1	0.8
SG-6	Bina	1.2	0.9
SG-7	Orangi	0.8	1.5
SG-8	Chetwa	1.2	1.6
SG-9	Bakulia	1.2	1.2
SG-10	Jhigradandi	1.8	1.7
SG-11	Khamariya	0.8	1.9
SG-12	Govindpur	2.4	1.5
SG-13	Katauli	1.7	1.2
SG-14	Supachuan	1.1	1.6

SG-11	Khamariya	1.1	0.4
SG-12	Govindpur	3.6	3.2
SG-13	Katauli	2.1	1.5
SG-14	Supachuan	1.6	0.8
T 6i	**Mercury µg/l**	**limit=0.01**	
Code	**Station**	**May-09**	**Nov-09**
SG-1	Obra	1.2	0
SG-2	Renukoot	0.8	0
SG-3	Dongia	2.6	1.8
SG-4	Renusagar	0.3	1.4
SG-5	Kubari	1	0.7
SG-6	Bina	3.9	1.8
SG-7	Orangi	0	0.6
SG-8	Chetwa	1.7	2.1
SG-9	Bakulia	0.4	0.3
SG-10	Jhigradandi	0.8	0
SG-11	Khamariya	1.4	0.4
SG-12	Govindpur	0.9	0.7
SG-13	Katauli	0.4	0.6
SG-14	Supachuan	0.5	0.4

RDS F Paper Samples delivered to CPCB Zonal office on 15 June, 2010 for analysis of Benzene Soluble Fractions

S.No.	Station	Code	Date	F Paper code
February				
1	Kewal	A-1	12/02/09	26
2	Jarha Rajo	AA-2	12/02/09	01
3	Murdhawa	A-3	01/02/09	61
4	Bari Dala	A-4	21/02/09	05
5	Kubari	A-5	10/02/09	30
6	Navtolia	AA-6	07/02/09	03
7	Lojhara	AA-7	12/02/09	23
8	Govindpur	A-8		
9	Katauli	A-9	26/02/09	60
March				
10	Kewal	A-1		
11	Jarha Rajo	AA-2	01/03/09	33
12	Murdhawa	A-3	18.03.09	10
13	Bari Dala	A-4	30.03.09	41
14	Kubari	A-5		
15	Navtolia	AA-6	31/03/09	28
16	Lojhara	AA-7		
17	Govindpur	A-8	07/03/09	02
18	Katauli	A-9	23/03/09	20
April				
19	Kewal	A-1	11/04/09	43
20	Jarha Rajo	AA-2	06/04/09	48
21	Murdhawa	A-3	21/04/09	11
22	Bari Dala	A-4	25/04/09	32
23	Kubari	A-5	09/04/09	58
24	Navtolia	AA-6	01/04/09	30
25	Lojhara	AA-7	11/04/09	54
26	Govindpur	A-8	23/04/09	06
27	Katauli	A-9	24/04/09	17

S.No.	Station	Code	Date	F Paper code
August				
55	Kewal	A-1	20/08/09	16
56	Jarha Rajo	AA-2		
57	Murdhawa	A-3		51
58	Bari Dala	A-4		
59	Kubari	A-5		
60	Navtolia	AA-6		
61	Lojhara	AA-7		
62	Govindpur	A-8	02/08/09	30
63	Katauli	A-9		
September				
64	Kewal	A-1		
65	Jarha Rajo	AA-2	22/09/09	38
66	Murdhawa	A-3		
67	Bari Dala	A-4		
68	Kubari	A-5	13/09/09	02
69	Navtolia	AA-6		
70	Lojhara	AA-7		
71	Govindpur	A-8	12/09/09	04
72	Katauli	A-9	01/09/09	11
October				
73	Kewal	A-1	26/10/09	40
74	Jarha Rajo	AA-2		
75	Murdhawa	A-3		
76	Bari Dala	A-4		
77	Kubari	A-5		
78	Navtolia	AA-6		
79	Lojhara	AA-7		
80	Govindpur	A-8		
81	Katauli	A-9		

May				
28	Kewal	A-1	21/05/09	24
29	Jarha Rajo	AA-2	13/05/09	21
30	Murdhawa	A-3	28/05/09	35
31	Bari Dala	A-4	25/05/09	33
32	Kubari	A-5	17/05/09	12
33	Navtolia	AA-6	21/05/09	43
34	Lojhara	AA-7	19/05/09	01
35	Govindpur	A-8	13/05/09	01
36	Katauli	A-9	20/05/09	04
June				
37	Kewal	A-1		
38	Jarha Rajo	AA-2	02/06/09	56
39	Murdhawa	A-3	31/06/09	14
40	Bari Dala	A-4		
41	Kubari	A-5	16/06/09	30
42	Navtolia	AA-6		
43	Lojhara	AA-7	28/06/09	31
44	Govindpur	A-8	21/06/09	05
45	Katauli	A-9		
July				
46	Kewal	A-1		
47	Jarha Rajo	AA-2		
48	Murdhawa	A-3		
49	Bari Dala	A-4		
50	Kubari	A-5		
51	Navtolia	AA-6		
52	Lojhara	AA-7		
53	Govindpur	A-8	11/06/09	07
54	Katauli	A-9		

November				
82	Kewal	A-1	25/11/09	69
83	Jarha Rajo	AA-2		
84	Murdhawa	A-3	08/11/09	02
85	Bari Dala	A-4		
86	Kubari	A-5		
87	Navtolia	AA-6		
88	Lojhara	AA-7	13/11/09	54
89	Govindpur	A-8	12/11/09	42
90	Katauli	A-9	30/11/09	12
December				
91	Kewal	A-1	24/12/09	57
92	Jarha Rajo	AA-2	22/12/09	58
93	Murdhawa	A-3	30/12/09	32
94	Bari Dala	A-4	18/12/09	03
95	Kubari	A-5	28/12/09	19
96	Navtolia	AA-6	20/12/09	11
97	Lojhara	AA-7	27/12/09	25
98	Govindpur	A-8	11/12/09	49
99	Katauli	A-9	04/12/09	24
January				
100	Kewal	A-1	30/01/10	48
101	Jarha Rajo	AA-2	26/01/10	26
102	Murdhawa	A-3	24/01/10	47
103	Bari Dala	A-4	16/01/10	14
104	Kubari	A-5	24/01/10	35
105	Navtolia	AA-6	15/01/10	20
106	Lojhara	AA-7	22/01/10	37
107	Govindpur	A-8	30/01/10	52
108	Katauli	A-9	11/01/10	01

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Fluorine in the environment, a review of its sources and geochemistry

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Fluorine in the environment, a review of its sources and geochemistry

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Abstract

While F is an essential constituent of some rock-forming minerals such as fluorite and apatite, its major occurrence in the lithosphere is within hydroxysilicate minerals where F^- occupies OH^- lattice sites. The majority of the F occurring in the secondary environment derives from natural weathering processes with some soils derived from F-rich parent rocks containing over 1weight (wt) % F. Other natural sources of F are vulcanicity, wind-blown dust and a minor marine-derived component, with biomass burning, being in part natural, also a source. Several anthropogenic sources of environmental F have also been identified. Of the anthropogenic sources, the application of phosphate fertiliser, which probably adds over 2.3 Mt a^{-1} F to soils globally, represents the largest. While much of this is strongly retained in soils, in acidic conditions some may be transferred to groundwater. In some abandoned mine sites in the UK where fluorite was associated with the mineralisation, soil F contents of up to 8 wt % have been recorded with plants growing on the sites containing up to 1wt % F.

The rapid growth of urban areas in India, Pakistan and Bangladesh has resulted in an upsurge of brickmaking in Asia, with these 3 countries plus China accounting for over 75% of global brick production. As a result there is a large number of unregulated brick kilns which emit HF into the surrounding environment. Based on an annual global brick production of 1,500 billion and the F contents of brick clays, it is estimated that about 1.8 Mt a^{-1} F are released to the environment from brick manufacture. This suggests that brickmaking is the largest source of atmospheric F emissions dwarfing that of coal combustion, 0.2 – 0.3 Mt a^{-1}, phosphate fertiliser production, 0.07 – 0.10 Mt a^{-1}, aluminium smelting, 0.041 Mt a^{-1}, and even vulcanicity, 0.3 – 0.7 Mt a^{-1}. However, it is apparent that atmospheric F emissions are not transported globally and as such their effects are manifested only in the local environment. Emissions from industry sited close to urban centres can impact these environments together with domestic coal combustion and the release of F from high octane fuels in motor vehicles.

A more recent source of F in the environment stems from the large number of fluorocarbon compounds in everyday use. Degradation of some of these fluorocarbon compounds together with pyrolysis of fluoropolymers and burning of household refuse has resulted in the deposition of organofluorine compounds such trifluoroacetic acid in the environment.

1. Introduction

Fluorine is ubiquitous in the environment with most deriving from natural sources, these being: normal weathering processes resulting in F release from rocks and minerals, volcanic activity and marine aerosol emission, together with biomass burning, being in part natural. However, there are several sources of anthropogenically-derived F which in some areas represent a threat to the biosphere. Anthropogenic sources can be broadly subdivided into

those deriving from industrial processes, which include coal fired power generation, brick making and ceramic manufacture, aluminium production and phosphate fertiliser production, and those deriving from agricultural practices such as phosphate fertiliser and sewage sludge application, and the use of F-containing herbicides and pesticides etc.

It has been suggested that F is an essential element for humans and other animals (Underwood, 1977; Adriano, 1986) but this has not been proven unequivocally (Fordyce, 2011). However, it is well known that in low concentrations fluorine, in the form of F^-, is beneficial to human health. The early work of Dean (1938) and his co-workers (Dean et al., 1941, 1942) showed that small quantities of ingested F^- promote the development of healthy teeth and help to protect them from caries. It has also been suggested that dietary F^- promotes strong bone formation (Jha et al., 2011) and possibly aids the prevention of osteoporosis (Ozsvath, 2009). However, while ingestion of relatively small quantities of F^- have a beneficial effect on teeth and bone, ingestion of elevated concentrations of F^- has a harmful effect, causing dental and skeletal fluorosis (Fewtrell et al., 2006). Dental fluorosis has been estimated to affect in excess of 70 million people globally with at least 2.7 million people in China and India alone suffering from skeletal fluorosis (Fawell et al., 2006), while some workers suggest that the numbers affected by fluorosis globally are as high as 200 million (Ayoob and Gupta, 2006). UNICEF (2016) lists 27 countries where fluorosis is endemic.

The major pathway of F into the body, as F^-, is via drinking water and Dissanayake (1991) suggests that concentrations of 0.5 – 1.5 mg L^{-1} will promote healthy teeth, with concentrations in excess of 1.5 mg L^{-1} causing dental fluorosis and concentrations in excess of 4 mg L^{-1} resulting in skeletal fluorosis. The World Health Organization (WHO, 2017) suggests a guideline value of 1.5 mg L^{-1} in drinking water. However, it is apparent that there are modifying influences such as the amount of water consumed on a daily basis, which generally reflects climate, *e.g.* in Ghana it has been shown that dental fluorosis occurs in areas where the concentration in the water is 1.5 mg L^{-1} (Craig et al., 2015). The major problems with regard to human fluorosis are manifested in areas where the domestic water supply derives from F-rich groundwaters. In the majority of cases, the source of F in these waters is natural. The global distribution of F-rich waters has been reviewed by Edmunds and Smedley (2013) and Ali et al. (2016).

In some cases F-rich foods can contribute to the overall body load (Ozsvath, 2009) with the tea plant, in particular, being a natural concentrator of F (Fordyce, 2011) with dental and even skeletal fluorosis having been shown to result from drinking tea (Fung et al., 1999; Kakumanu and Rao, 2013). Other modifying effects are the diets of affected populations, with low-protein diets exacerbating the problem (Fordyce, 2011), in addition, it has been demonstrated that low calcium and Vitamin D intakes are associated with increased fluorosis (Patel et al., 2017). It has also been shown that domestic animals can suffer from fluorosis due to consumption of high-F^- waters (Choubisa, 2012).

Dental and skeletal fluorosis are the major problems resulting from F intoxication, however, other adverse health outcomes have been postulated. These outcomes include cancer of various organs, low IQs in children, renal problems and interference with endocrine systems amongst others (Ozvath, 2009). However, there is limited proof of these outcomes and

research is ongoing. A detailed account of the health problems associated with F^- intake is beyond the scope of this review and the reader is referred to reviews by Ozvath (2009) and Fordyce (2011) for a broader discussion of the topic.

The aim of this review is to discuss and assess the relative importance of the various natural and anthropogenic sources of environmental F.

2. Fluorine geochemistry

2.1. Lithogeochemistry

Fluorine is the lightest of the halogen group and is the most electronegative element. As such it is highly reactive and it is widely stated in the literature that elemental fluorine does not exist naturally in the free state but, recently, Schmedt auf der Günne et al. (2012) have demonstrated the presence of F_2 in a radioactive variety of fluorite, antozonite, using NMR spectroscopy. However, F normally exists in nature as the F^- ion.

Fluorine is a lithophile element (Levinson, 1980) being concentrated in the crust of the Earth (Hanley and Koga, 2018). Rudnick and Gao (2014) indicate that relatively few attempts have been made to estimate the F content of the upper continental crust but suggest a figure of 557 mg kg^{-1}, derived from the average of previous estimates. These authors suggest that the bulk continental crust contains 553 mg kg^{-1}. Earlier estimates such as those of Wedepohl (1995) suggest that the F content of the bulk crust (525 mg kg^{-1}) is somewhat different to that of the upper continental crust (611 mg kg^{-1}), due to the element's lithophile behaviour.

Of the rock-forming minerals in which F is an essential constituent only fluorite (CaF_2) and, to a lesser extent, topaz ($Al_2SiO_4(F,OH)_2$) are relatively common (Koritnig, 1972), while cryolite (Na_3AlF_6) and bastnäsite ($(Ce, La, Nd)CO_3F$) can occur in some granitic pegmatites (Bailey, 1977), and villaumite (NaF) can occur in some peralkaline, nepheline-containing igneous rocks (Stormer and Carmichael, 1970) and has also been identified in evaporate minerals in Lake Magadi, Kenya (Nielsen, 1999). Several other minerals which contain F as an essential component have been identified in pegmatitic rocks and in metasomatically/ hydrothermally altered rocks (Koritnig, 1972).

In most rocks these F-containing minerals account for a relatively small percentage of the total F content. The major control on the lithogeochemistry of F is the similarity of the F^- and the OH^- ions with ionic radii of 131 pm and 135 pm, respectively (Li et al., 2017). Due to this similarity the F^- ion easily substitutes for the OH^- ion in rock-forming minerals. It is, therefore, not surprising that hydroxyl-containing silicates and apatite are the major hosts of F in the lithosphere.

A summary of concentrations in the major rock types is included in Table 1. According to Koga and Rose-Koga (2018) in the rocks which make up the continental crust F predominantly ranges up to 900 mg/kg, being fairly evenly distributed within the major rock types. However, within the different rock types there are wide variations in F content. In general, the F content of igneous rocks increases with silica content being highest in felsic and lowest in ultramafic rocks. Fluorine is considered to be an incompatible element in that

during crystallisation of a melt it does not enter early forming minerals so becoming strongly concentrated in the late stage melt and is enriched in the final differentiates (Stormer and Carmichael, 1971; Fuge, 1977). Thus granitic pegmatites can contain concentrations of over 1wt % F. Fluorine also becomes concentrated in the late stage hydrous fluids which can lead to hydrothermal and metasomatic alteration of the granites resulting in extreme F enrichment (Table 2). In addition, alkalic and silica undersaturated igneous rocks are also generally F-rich, with some carbonatites containing up to 2.5wt % F. (Table 2).

Of the common sedimentary rocks only shales are relatively enriched in F, ranging up to about 800 mg kg^{-1}, with sandstones and carbonates generally containing <300 mg kg^{-1} (Table 1). However, sedimentary phosphorites are strongly enriched in F with concentrations in the region of 4 wt % (Table 2).

2.2. Soil geochemistry and plant uptake

The fluorine content of most soils ranges between <10 and 1000 mg kg^{-1}, however, values in excess of 1wt % have been recorded in uncontaminated soil (Table 3). The F content of soils reflects that of the parent material, for example, high F soils occurring over F-rich granites (Table 3). However, retention of F in a soil generally reflects its clay content as clay minerals strongly adsorb F^- (Weinstein and Davison, 2004) with the greatest adsorption occurring in slightly acidic soils (Liu et al., 2014). As a result clay-rich soils tend to be rich in F (Weinstein and Davison, 2004). In addition to the adsorption of F by clays in soil, according to Liu et al. (2014), F^- replaces OH^- in the clay minerals.

Davison and Weinstein (2006) state that soils are a source of F for the biosphere but also act as a sink for atmospherically deposited F. They further suggest that F added to the soil from the atmosphere tends to be leached down the profile, resulting in surface soils being generally lower in F than deeper soil horizons. However, the strong ability of clay minerals to adsorb F^- causes it be retained in the sub-surface horizons. Aluminium and Fe oxyhydroxides are also strong adsorbents of F^- in soil and aid in the immobilisation of atmospherically deposited F (Cronin et al., 2000). The ability of soils to retain F is well illustrated by the case of Mt. Etna volcano, Italy, where large quantities of F-rich gases are evolved continuously. The groundwaters in the aquifers occurring on the flanks of the volcano, which are important sources of potable water, have been protected due to the retention of F by the soils (D'Alessandro et al., 2012).

The bioavailabilty of soil F is generally low, particularly in soils with a pH of 5.5 – 6.5, so that little soil F is incorporated in plants (Weinstein and Davison, 2004). In addition, soil-derived F is prevented from being incorporated into the aerial parts of plants through exclusion by the roots (Davison and Weinstein, 2006). However, it is generally accepted that where there is a source of atmospheric F it is incorporated in plants by uptake through the leaves, with direct aerial uptake being the dominant pathway (Davison and Weinstein, 2006). According to Weinstein (1977) F^- is the most phytotoxic air pollutant.

2.3. Fluorine in waters

Unpolluted surface waters are generally low in F^- with De Vos et al. (2006) quoting values ranging from <0.05 – 1.6 mg L^{-1} with a median of 0.1 mg L^{-1} for stream waters analysed for the FOREGS Geochemical Atlas of Europe. The highest values generally reflect geological influences such as F-rich granites, recent volcanics or fluorite mineralisation, with some reflecting input of F-rich groundwater. Surface waters impacted by F-rich hydrothermal waters can be strongly enriched, with values of up to 2800 mg L^{-1} quoted by Ali et al. (2016).

Groundwaters can become strongly concentrated in F^- with some values for global groundwaters quoted by Ali et al. (2016) ranging up to over 20 mg L^{-1}. The F content of waters is controlled by fluorite solubility and hence the Ca content of the water (Edmunds and Smedley, 2013). In general, F-rich groundwaters fall into the following categories (Edmunds and Smedley, 2013; Ali et al., 2016):-

i) Those occurring in arid/semiarid areas where there has been evapoconcentration resulting in Na-rich/Ca-poor waters
ii) Old groundwaters – where there has been water-rock interaction with Ca-Na exchange resulting in low Ca waters
iii) Those occurring in crystalline basement rocks
iv) Those occurring in areas of alkalic igneous rocks (*e.g.* Great Rift Valley, East Africa)

As stated earlier, F–rich groundwaters used as potable water sources have resulted in serious fluorosis in many countries. The global occurrence of these waters is reviewed by Edmunds and Smedley (2013) and Ali et al. (2016).

3. **Uses of fluorine**

Fluorite or fluorspar (CaF_2), derived from hydrothermal deposits, is the only mineral mined as a commercial source of F (Hayes et al., 2017), with 6 Mt extracted globally in 2017, the bulk of this extraction being in China (63%) and Mexico (26%) (U.S. Geological Survey, 2018). A relatively minor source is also afforded by fluorosilicic acid (H_2SiF_6), which is a by-product of the manufacture of phosphate fertiliser, via phosphoric acid, from F-containing apatite. Fluorine has a wide range of uses in industry and manufacturing. Fluorite itself is used in the steel industry as a flux, improving the fluidity of the melt. It is also used in the ceramics industry, glassmaking and manufacture of fibreglass, and in coatings on welding rods (U.S. Geological Survey, 2018).

The major use of fluorite is, however, in the production of HF which is then used in the production of fluorine gas and in the manufacture of the very many F-containing chemicals and materials in use globally (Harsanyi and Sandford, 2015). The major uses of HF, as listed by Villalba et al. (2007), are the production of fluorocarbons and the manufacture of synthetic cryolite and AlF_3, for use in the Hall-Héroult process for the isolation of Al metal from Al_2O_3, however, Kvande (2011) suggests that in modern systems, relatively small quantities of cryolite are used up in this process.

The C – F bond is extremely strong and difficult to rupture, hence, fluorocarbon compounds are very stable (Key et al., 1997). Organofluorine compounds have found use in a large

variety of everyday human activities. Many fluoropolymers are manufactured and have a wide range of uses, being very stable, non-corrosive and resistant to heat, they are used extensively in industry, for example, as lubricants which can withstand high temperatures, wire insulation materials and in vacuum pumps (Villalba et al., 2007). In addition, fluoropolymers are used for waterproof roofing materials and waterproof clothing and as non-stick surfaces on cookware in addition to many other uses (Harsanyi and Sandford, 2015).

Fluorine is incorporated into a large variety of compounds that are used in medicine and agriculture. The incorporation of F in pharmaceuticals has been found to improve their biological reactivity and to enhance their bioavailability (Böhm et al., 2004; Maienfisch and Hall, 2004). Prior to the 1970s F-containing medicines were rarely used (Böhm et al., 2004), however, according to Wang et al. (2014) there are about 200 pharmaceuticals now in use which contain F and, according to Harsanyi and Sandford (2015), 20% of all new pharmaceuticals entering use daily are F-containing. In addition, the major anaesthetics in use currently are fluorinated gases (Harsanyi and Sandford, 2015). Fluorine is also incorporated into many agrochemicals with Tomoya and O'Hagan (2014) suggesting that about 25% of herbicides currently in use contain F. According to Jescke (2010) the use of F-containing agrochemicals has shown a steady increase since the 1950s with major expansion in their use from the 1980s. These F-containing compounds are used as insecticides, fungicides, herbicides, acaricides and nematicides (Jescke, 2010) with many continuing to be developed (Jescke, 2017).

Hydrofluoric acid is also used for etching glass and in the manufacture of semiconductors for the microelectronics industry. It is also used in oil refineries as an alkylation catalyst to obtain high-octane fuels. Villalba et al. (2007) also note the use of HF for the enrichment of uranium by converting it to UF_4 and, subsequently, UF_6. Sulfur hexafluoride is another important compound manufactured from F and, due to its inertness, has many uses in the electrical industry, in particular, but also finds use in the medical field and as a general tracer gas. Fluorine is incorporated into toothpaste and mouthwashes to help prevent tooth decay and in some countries and regions is added to water supplies to aid dental health.

4. Natural sources of fluorine in the environment

4.1. Vulcanicity

Fluorine is released from volcanoes predominantly as HF gas (Symonds et al., 1988) with minor amounts emitted in other gases such as Si-containing compounds (D'Alessandro, 2006). Gaseous HF interacts with and is adsorbed onto the surface of volcanic ash (Óskarsson, 1980) and during eruptions the majority of F release is by way of ash (Bellomo et al., 2007). However, over 90% of F release occurs during quiescent degassing (Symonds et al., 1988) and during this phase it is released as HF (Bellomo et al., 2007). Francis et al. (1998) found that during quiescent degassing of Mount Etna, Sicily, Italy, 190 t of HF are released daily, which amounts to an annual release of almost 70,000 t, making it the largest point source of atmospheric F emissions on Earth.

While F-rich gases impact the whole environment in volcanic regions, the major concern regarding volcanogenic F is its impact on drinking waters and the deposition of F-containing ash on plants and soils in the vicinity of the eruption, the major pathway into the biosphere being via impacted waters and crops etc (D'Alessandro, 2006; Ranjan and Ranjan, 2015). Fluorine in volcanic ash is solubilised in the digestive systems of grazing animals (Cronin et al., 2003) and there are many examples of grazing animals developing chronic fluorosis as a result of ingestion of F-rich ash with both domestic and wild animals being affected (Cronin et al., 2003; Weinstein et al., 2013; Ranjan and Ranjan, 2015). Severe dental fluorosis has been recorded in juvenile red deer following an eruption of the Puyehue–Cordon Caulle volcano, Argentina, in 2011 (Flueck and Smith-Flueck, 2013). Major problems of fluorosis in livestock have been recorded in Iceland where magmas are F-rich (D'Alessandro, 2006). The first description of fluorosis in sheep was given after the 1693 eruption of Hekla (Fridriksson, 1983), while the Laki eruption in 1783-84 resulted in catastrophic loss of life for both humans and domestic animals due to the impact of the estimated 7 Mt of HF released (Williams-Jones and Rymer, 2015). In addition to causing fluorosis in grazing animals, the extreme phytotoxicity of HF caused crops to perish, so resulting in starvation of animals and humans, the major reason for the catastrophic loss of life after the Laki eruption (Weinstein et al., 2013). Flueck (2016) reports that ruminants are particularly prone to fluorosis from ingested volcanic ash with fluorosis in grazing animals in Patagonia being manifested some months after the deposition of the ash.

Volcanic activity has resulted in F^- enrichment of surface and groundwaters in many countries (Stewart et al., 2006; Flaathen and Gislason, 2007). Impacts on water can be from dissolution of HF gas but for the most part F enrichment in water is due to its interaction with ash, with ash leachate studies suggesting that concentrations of soluble F^- range up to several thousand mg L^{-1} (Witham et al., 2005). Gislason et al. (2011) found that ash from the 2010 eruption of the Eyjafjallajökull volcano, Iceland, had 6.9% F in its surface coating and that 16% of this was soluble in pure water. The major pathway into humans is through drinking waters (D'Aessandro, 2006) with Baxter et al. (1999) recording dental fluorosis in populations of villages on São Miguel Island, in the Azores, due to drinking spring water from the caldera of the Furness volcano. In Goma, Democratic Republic of the Congo, rainwater is a major source of potable water and, due to its interaction with a plume deriving from the Nyiragongo and Nyamulagira volcanoes, is enriched in F^- which has resulted in dental fluorosis in the population (Balagizi et al., 2017).

Volcanic emissions have been suggested to be the major source of F to the atmosphere (Friend, 1989; Tavener and Clark, 2006). Some attempts have been made to estimate the annual global total of HF release from volcanoes. The most commonly quoted values in the literature are those of Symonds et al. (1988) who suggested a value of 0.06 – 6 Mt and Halmer et al. (2002) who derived a value of 0.7 – 8.6 Mt. However, more recently, Pyle and Mather (2009) have been critical of previous estimates for this global flux on the basis of the methods used for the estimation. These authors further quote an estimate of 0.5 ± 0.2 Mt for the annual global flux of arc-related volcanoes, which they suggest dominate the global volcanic efflux. While F emissions from mid-ocean ridges and intraplate volcanics are also

likely to produce significant quantities of HF, it seems probable that global atmospheric emissions from volcanoes may not be as great as previously thought.

4.2. Marine-derived fluorine

It has been proposed that marine aerosols and spray make a very significant contribution to atmospheric F and to its geochemical cycle (Friend, 1989; Taverner and Clark, 2006). Friend (1989) suggested that the annual marine flux of F, supposed to be 0.4 to 1 Mt, to the atmosphere is second only to the volcanic flux, while Taverner and Clark (2006) quote values of between 1 and 2 Mt. However, other authors (*e.g.* Cadle, 1980; Lewandowska et al., 2013) suggest the lower value of 20,000 t for this flux.

The mean F content of seawater is 1.3 mgL^{-1} (Carpenter, 1969) and it has been suggested that marine-derived F is an important component in the hydrogeochemical cycle of F. Sugawara (1967) quoted data for samples of Japanese precipitation that imply that F^- is strongly enriched relative to Cl^- and that the major source is seawater, while Carpenter (1969) also states that most F in global precipitation derives from the sea. It has been suggested that F is emitted from seawater in gaseous and particulate forms, the gaseous component being HF (Friend, 1989; Taverner and Clark, 2006). According to Carpenter (1969), relative to Cl, F is preferentially enriched in marine emanations to the atmosphere with the F/Cl ratio of precipitation being 10-1000 times that of seawater. Neal et al. (1990) in a study of rainfall in mid Wales, UK, also suggested that there is some enrichment of F relative to Cl.

However, Wilkniss and Bressan (1971) demonstrated that, in general, there was no preferential enrichment of F^- in marine-derived aerosols; these authors also found that where F^- concentrations were elevated in aerosols it was due to a high dust content. This was confirmed by Barnard and Nordstrom (1982) who found no significant difference between the F^- content of pristine coastal and inland rainfall samples collected in the USA. There was no correlation with Na concentrations (as a proxy for sea salt), which was interpreted as indicating no enrichment from the sea. It was also concluded that the major source of F^- in rainwater was anthropogenic. Saether et al. (1995) in a study of F^- in precipitation in southern Norway also concluded that there was no preferential enrichment from the sea surface with their data suggesting that, in general, less than 1.5% of F^- in precipitation derives from the sea, with the majority deriving from anthropogenic sources. In addition, De Angelis and Legrand (1994) in a study of F^- in ice and firn from Greenland found that there was an insignificant sea-salt particle contribution.

However, some authors have suggested that coastal rainfall is enriched in F^-, with Linder and Frysinger (2007) reporting that rainfall from within 10 km of the coast of South Carolina had a mean F^- content of 0.17 mg L^{-1} compared with 0.06 mg L^{-1} between 40 and 50 km from the coast. Lewandowska et al. (2013) found F^- to be enriched in marine-derived PM_{10} aerosols over a coastal site in Gdynia, Poland when airspeeds increased to over 10 m sec^{-1}, the F^- content correlating significantly with the Na content. It has also been reported that in some coastal areas of mid Wales, UK, stream water and runoff are relatively enriched in F^- reflecting a marine input (Neal, 1989; Neal et al., 1990; BGS, 1999). In addition, Mikkonen

et al. (2018) have demonstrated that coastal soils in Victoria, Australia are enriched in F^- relative to those from inland areas with F^- content correlating with Na^+ content.

Despite the conflicting evidence it seems likely that the contribution of marine-derived F to the atmosphere has been over estimated and is fairly insignificant when compared to the volcanic and anthropogenic fluxes. While marine derived F may well influence the chemistry of coastal rainfall, runoff and soil, it seems likely that its influence only extends about 10-20 km inland.

4. 3. Wind-blown dust

Weinstein (1977) suggested that wind-blown soil could make a significant contribution to atmospheric F content. On the basis that in the USA alone about 30 Mt of soil are removed annually by wind action, this would add about 6,000 t of F to the atmosphere. Analytical data on ice cores from Greenland (De Angelis and Legrand, 1994) and the French and Swiss Alps (Preunkert and Legrand, 2001) suggest that wind-blown dust, deriving from soils, constitutes a significant source of F^- in precipitation. Indeed, Preunkert and Legrand (2001) state that prior to 1930 wind-blown dust was the dominant source of atmospherically deposited F^-. While the source of F^- through the 1930s to 1980 was predominantly anthropogenic, Preunkert and Legrand (2001) found that from 1980 to 2000 wind-blown dust accounted for 18 ± 2% of the F^- in ice cores from the Alps.

4.4. Biomass burning

Biomass burning can result from natural processes and from human actions, with the latter being both intentional, as in the agricultural practice of stubble burning, and from accidental fires (Yadav and Devi, 2018). While the great majority of biomass fires are anthropogenically sourced, natural fires tend to destroy larger areas of vegetation than human induced fires (Yadav and Devi, 2018). For this reason, the author has included biomass burning under the general heading of natural processes.

Several authors have commented on the potential contribution of biomass burning to atmospheric releases of fluorine (e.g. Weinstein and Davison, 2004). De Angelis and Legrand (1994) found elevated F concentrations deriving from biomass burning, in high latitudes, in the Greenland ice cap, while Lewandowska et al. (2013) report biomass burning as a source of F in PM_{10} aerosols in the Baltic Sea area of Poland. More recently Jayarathne et al. (2014) have attempted to determine the degree of F emission from biomass burning experimentally. Different biomass types were subjected to combustion in the laboratory and the degree of F emission was determined. On the basis of the results, Jayarathne et al. (2014) suggest that biomass burning releases significant amounts of fine particulates ($PM_{2.5}$) containing F. The degree of F release varied with plant type and with geographic distribution.

Jayarathne et al. (2014) estimate that 76,000 t of F are released annually from biomass burning, which they suggest is comparable to that released from coal combustion.

5. Industrial sources of fluorine in the environment

5.1. Coal combustion

Coal combustion has been suggested to be one of the major sources of anthropogenic F (Weinstein and Davison, 2004), while F has been listed as one of the most hazardous elements emitted during coal combustion (Yang et al., 2017). The world average for the F content of coal has been calculated to be 88 mg kg^{-1} (Ketris and Yudovich, 2009) and a high percentage of this is released during combustion. Chen et al (2013) suggested that almost 80% of the F in coal is released to the atmosphere at 800 ^{o}C, this being in gaseous and particulate forms (Doley et al., 2004), with Yu et al. (2004) demonstrating that 100% of the F in coal is released at 1100-1200 ^{o}C.

Several studies have shown that F release during coal combustion has resulted in environmental pollution, damage to plants and fluorosis in animals and humans. Doley et al. (2004) state that emissions from coal-fired power stations represent the largest individual source of atmospheric F in Australia with impacts on plants being recorded. Burns and Allcroft (1964) recorded fluorosis in grazing animals in the vicinity of coal-fired power stations in the UK. Fidanci and Sel (2001) reported that F emissions from the Yatağan coal-fired power station in Muğla Province, SW Turkey, have resulted in chronic fluorosis in sheep. Studies in Europe have shown that fluorosis occurs in wild animals as a result of emissions from coal-fired power stations such as in the NW of the Czech Republic (Zemek et al., 2006; Kierdorf et al., 2012).

However, it is in China that the worst problems associated with F release from coal combustion have been manifested as it is a major producer of coal and consumes about half of the global total production (BP, 2018; Finkelman and Tian, 2018), it being the country's major energy resource (Chen et al., 2013; Yang et al., 2017). Chinese coals contain an average of 130 mg kg^{-1} F (Dai et al., 2012) with coals from some regions of southern China such as Guizhou Province having been found to contain as much as 3575 mg kg^{-1} (Dai et al., 2015). Chen et al. (2013) claimed that F emissions from coal combustion increased steadily through 2005 to 2009, estimating that in 2009, over 162,000 t F were emitted.

Human fluorosis due to F release from the combustion of coal indoors has only ever been reported from China (Dai et al., 2012). Dental and skeletal fluorosis due to coal combustion have been reported in several Chinese provinces (Ando et al., 1998; Finkelman et al., 1999), with over 18 million people affected in 2000 (Li et al., 2003). It is likely that much of the exposure to F derives from the burning of coal in open stoves and utilisation of the stoves to dry and preserve foodstuffs, such as corn and chillies (Ando et al., 1998; Zheng et al., 1999; Finkelman et al., 2002) with some also deriving from direct inhalation (Ando et al., 1998; Dai et al., 2012). Dai et al. (2007) recorded F contents of corn and chillies dried over open fires as 1419 mg kg^{-1} and 110 mg kg^{-1}, respectively. While it has been suggested that the source of F is directly due to its release from coal (Li et al., 2003; Liu et al., 2007), some authors have implicated the use of F-rich clay, used to bind the coal into briquettes, as a major source of F release during combustion (e.g. Wu et al., 2004; Dai et al., 2007). Dai et al. (2007) in a study

of fluorosis in Zhijin County, Guizhou Province, quote mean values for F of 237 mg kg^{-1} in coal, 2262 mg kg^{-1} in the clay binder and 828 mg kg^{-1} in the coal/clay mixture.

Hong et al. (2017) have highlighted F emissions related to subsurface coal seam fires and determined F in soils and plants in the vicinity of such a fire in Inner Mongolia, which has been burning for over 50 years. Fluorine contents of up to 1670 mg kg^{-1}, with a mean of 1250 mg kg^{-1}, were recorded for soils in the vicinity of the fire, compared to a background of 240 mg kg^{-1}. Plant leaf samples in the vicinity of the fire showed a mean value of 523 mg kg^{-1} with a background of 76 mg kg^{-1}. In addition, an urban area in the vicinity was impacted with soils having F contents of 552 mg kg^{-1}. Coal seam fires are natural phenomena that occur in many countries (Finkelman, 2004) and as such could be serious sources of F contamination on a local basis.

In addition to the problems caused by coal combustion, it has been shown that coal waste can also be a source of environmental F contamination. Gao et al. (2016) determined F in coal waste in China to range up to 1885 mg kg^{-1} with the mean content being 525 mg kg^{-1}. Soils in the vicinity of the waste tips contain 320-860 mg kg^{-1} F compared to 180-550 mg kg^{-1} in background soils. The authors further suggest that spontaneous combustion of coal spoil heaps releases 90% of the contained F which makes a significant addition to atmospheric F pollution, which could account for 40% of atmospheric F emissions in China.

While the majority of the F occurring in coal is lost to the atmosphere during combustion, some is retained in fly ash collected in electrostatic precipitators. Figures for the F content of fly ash generally suggest relatively low concentrations, with Tsubouchi et al. (2011) quoting values for Japanese fly ash ranging from 20-130 mg kg^{-1} and Deng et al. (2016) values of 84-326 in ash deriving from various Chinese coals, while Córdoba et al. (2012) suggest a value of 123 mg kg^{-1} for fly ash from a Spanish power plant. However, Ramya et al. (2013) quote a value of 2,024 mg kg^{-1} for fly ash from two power stations, near Nagpur, central India. As fly ash is frequently disposed of in lagoons there is some concern that groundwaters may be impacted but Ramya et al. (2013) found that there is only moderate contamination of groundwater, ranging up to 3.1 mg L^{-1} with most below 1.5 mg L^{-1}.

Coal combustion has been suggested to be the major anthropogenic flux of F to the atmosphere (Taverner and Clark, 2006), the annual flux having been estimated to be between 12,000 and 102,000 t (Jayarathne et al., 2014). However, as noted above, Chen et al. (2013) calculated that F emissions from coal combustion in China in 2009, were over 162,000 t. With China being responsible for utilising about 51% of the global coal output (BP, 2018), it seems likely that total global F emissions from coal combustion are in the range of 200,000 – 300,000 t, which is 2-3x higher than previous estimates.

5.2. Brickmaking

The manufacture of bricks has long been recognised as a source of environmental F contamination (*e.g.* Ost, 1907; Oelschläger, 1965). Bricks, along with tiles and drainage pipes, are made from clays and clay-rich rocks and the process involves roasting at temperatures of 900 – 1200 ^{o}C with temperatures of 1000 ^{o}C or more being favoured.

Fluorine is housed in the OH-containing minerals, such as the clays and micas etc., and most of this is evolved, mainly as HF and SiF_4, during the high temperature roasting (Troll and Farzaneh, 1978; Weinstein and Davison, 2004). Bonvicini et al. (2006) suggest that 57-82% of the F in brick clays is lost during firing at 1000 ^{o}C, while Xie et al. (2003) found that during roasting of soils used for brickmaking in southern China, the amount of F emitted increased from 57.2% to 85.4% between 700 and 1100 ^{o}C. In a study of variously sourced brick clays from the UK, Fuge and Hennah (1989) demonstrated that, in general, over 80% of F occurring in the brickmaking rocks was lost during roasting at 1000 ^{o}C (Table 4).

In the developed world the brickmaking industry, along with other industries with potential to emit F, has been heavily regulated and F emissions have been greatly reduced (Cape et al., 2003). However, there is still a problem with F release during brick making in the developing world where large quantities of bricks are manufactured to facilitate the rapid growth of urban areas, to the extent that Khalid et al. (2017) describe brick making as the fastest growing industry in southern Asia. In 2010, 1,500 billion bricks were produced globally with China, India, Pakistan and Bangladesh producing over 75% of them (Baum, 2010). While brick production in China is being modernised and becoming less of a pollution source, much of the brickmaking in the rest of the developing world is artisanal and heavily polluting (Schmidt, 2013). Many of the brickmaking facilities, which are in close proximity to urban areas, are poorly regulated and are serious sources of F emission (Ahmed et al., 2012). For example, Ahmed et al. (2012) state that in the urban and peri-urban area of the large city of Peshawar, Pakistan, there are some 400-450 brick kilns, with each producing some 800,000 bricks per month. Fluorine emissions from these kilns have been shown to cause foliar damage to fruit trees in the region and to reduce crop yields of bean and maize significantly (Ahmed et al., 2012, 2014). Many of the kilns use low quality coal along with waste oil and rubber tyres to fire the kilns (Jha et al., 2008; Khalid and Mansab, 2015). Rajarathnam et al. (2014) estimate that 25 Mt of coal are used in brick kilns in India annually. It is, therefore, likely that in addition to F released from clays during firing of the bricks, some is also released from the fuels.

On the basis that the manufacture of 1000 bricks requires approximately 3 t of clay (BGS, 2007), the 1,500 billion bricks being produced annually would require 4.5 billion tonnes of clay. Clays and clay-rich rocks used for brickmaking would generally be expected to contain 450 - 800 mg kg^{-1} F (Koritnig, 1972; Xie et al., 2003) of which about 80% would be expected to be lost during firing (Fuge and Hennah, 1989; Xie et al., 2003). Assuming a mean F content of 500 mg kg^{-1}, suggests that in the region of 1.8 Mt F is released from roasting of brick clays annually. Notwithstanding that in many countries clean technology has been introduced into the brickmaking industry, it is apparent that the industry represents the major anthropogenic flux of F to the atmosphere, dwarfing that of coal.

The ceramic industry is also based on baking of clays to make tiles etc and, consequently, suffers from the same problems as the brick-making industry. Bonvicini et al. (2006) state that F emission during the production of ceramic tiles in the Sassuolo District, Modena and Reggio Emilia provinces, Italy is 727 t a^{-1} of which they estimate 73 t a^{-1} is emitted to the atmosphere. According to Bonvicini et al. (2006), the Sassuolo District produces about a $^{1}/_{4}$ of

the global output ceramic tiles. On this basis the global F release from ceramic tile production is estimated to be about 290 t a^{-1}. However, no figures are available to enable estimation of F release from the manufacture of other ceramic items such as sanitary ware.

5.3. Aluminium smelting

Aluminium metal is produced from aluminium oxide by the Hall-Héroult process, whereby the Al_2O_3 is dissolved in molten cryolite (Na_3AlF_6), with some added AlF_3, and is subjected to electrolysis at 960 ^oC. During the electrolytic process F is released into the atmosphere in both gaseous and particulate forms, the gaseous releases are almost entirely HF but minor quantities of other F-containing gases such as CF_4 and C_2F_6 are also produced (Tjahyono et al., 2011; Kvande, 2014). The particulate species are Na and Al fluorides and cryolite (World Aluminium, 2018).

In the late 1940s and 1950s there was a major expansion of global Al production utilising the Hall-Héroult process and as a result there were several examples of serious F pollution in the vicinity of Al smelters. In Norway large areas of pine forest were destroyed and grazing animals were affected (Robak, 1969; Arnesen et al., 1995), in Ontario, Canada, cattle suffered from severe fluorosis (Krook and Maylin, 1979), in Scotland, UK, farm animals suffered from severe fluorosis (Gilbert, 1985) and in N. Wales, UK, Walton (1985, 1987) recorded concentrations of up to 8500 mg kg^{-1} F in bones and damage to teeth of small rodents. As a result of the early problems associated with Al smelting the industry adopted clean technologies using scrubbing systems etc, resulting in a dramatic decrease in F emissions (Ouellet, 1987; Vike and Håbjørg, 1995; Preunkert and Legrand, 2001). Cape et al. 2003) suggested that emissions of F had fallen by a factor of 100 in the previous 50 years. Subsequently, F emissions have been reduced even further and it has been estimated that modern Al smelters produce 15 – 30 kg of F per tonne of Al produced but scrubbing reduces this to < 300 g per tonne (Tjahyono et al., 2011).

However, environmental problems related to F release from Al smelters still occur. Rodriguez et al. (2012) determined the concentrations of F deposited on deciduous tree leaves around an Al smelter in Puerto Madryn, Patagonia. The highest value recorded was over 3650 mg kg^{-1} with analysis of several species revealing that there was a distance decline in F concentrations from the smelter to 6 km away. Talovskaya et al. (2015) report F concentrations in snow melt water around the Al smelters at Bratsk, Krasnovarsk and Sayanogorsk in SW Siberia. Concentrations of F in the melt water were 37 mg kg^{-1} at 0.5 km from the Sayanogorsk smelter, 18 mg kg^{-1} at 3 km from the Bratsk smelter and 12 mg kg^{-1} at 1 km from the Krasnovarsk smelter. In all cases there was pronounced distance decline in F contents of snow melt and in the case of the Sayanogorsk and Krasnovarsk smelters, values of 0.5 to 1 mg kg^{-1} were recorded at 29-30 km distance. In Victoria, Australia, in the vicinity of the Portland Al smelter, dental and skeletal fluorosis have been identified in kangaroos (Hufschmidt, et al., 2011; Kierdorf et al., 2016). The Portland smelter is recorded as having emitted just under 110 t of F-containing compounds during the period July 2013 – June 2014 (Kierdorf et al., 2016).

The world production of primary Al in 2017 was 63 Mt (World Aluminium, 2018). According to Tjahyono et al. (2011), most large Al smelters limit F emissions to 0.5-0.6 kg F/t Al. This should have resulted in the release of between 32,000 and 38,000 t of F, however, on the basis of the F emission intensity (kg F/ t Al) of 0.64 for 2017 quoted by World Aluminium (2018) the amount of F released would have been 41,000 t. This is somewhat higher than previous estimates (Jayarathne et al., 2014).

5.4. Phosphoric acid and phosphate fertiliser manufacture

Phosphoric acid is manufactured from phosphate rock, which is essentially composed of apatite. Two methods are utilised for the production of phosphoric acid, a wet process and a thermal process (Weinstein and Davison, 2004; Villalba et al., 2008). In the wet manufacturing process the phosphate rocks are reacted with acid, which can be hydrochloric, nitric or sulfuric acid, however, for the manufacture of fertilisers sulfuric acid is used. The thermal process involves conversion of the phosphate rock to elemental phosphorus which is subsequently converted to phosphoric acid. The production of fertilisers utilises 88% of the phosphate rock extracted globally (UN Food and Agriculture Organisation, 2017) and the wet method of phosphoric acid production for fertiliser manufacture accounts for about 90% of global phosphoric acid production (Tayibi et al., 2009).

Phosphate rock, which is extracted from several countries, contains appreciable quantities of F with those being utilised for fertiliser production generally containing from 2-4% F (EFMA, 2000). During the wet process much of the F is converted to HF and SiF_4 (Weinstein and Davison, 2004) with 10-15% of these compounds being volatilised (EFMA, 2000). In addition, for every tonne of H_3PO_4 produced, about 5 to 5.4 t of waste phosphogypsum (mainly $CaSO_4$) are also produced, this being stored in ponds (EFMA, 2000; Villalba et al., 2008). This waste product also contains F with Tayibi et al. (2009) listing values of 0.15 – 1.20 wt % F in phosphogypsum from world sources. The phosphogypsum pond waters also typically contain 4-14 g L^{-1} F (Weinstein and Davison, 2004). In the thermal process much less F is released, with some SiF_4 produced during the initial conversion of the phosphate rock to phosphorus (Villalba et al., 2008).

The volatilisation of F-containing compounds during the wet process has in the past been deemed responsible for serious environmental damage such as the destruction of forest areas in Brazil (Klumpp et al., 1996). Most modern plants have efficient scrubbing systems which according to EFMA (2000) are capable of removing more than 99% of the F-containing compounds. However, it is apparent that even in modern plants there is significant evolution of F-containing compounds. Mirlean and Roisenberg (2007) in a study of F^- distribution around a phosphate fertiliser plant in Rio Grande Brazil reported F^- values in rainwater of up to 3.04 mg L^{-1} within 2 km of the plant, the rainwater also having a pH of 4.1. Groundwater near the plant had a correspondingly low pH of 4.1 and elevated F^- content of 4.79 mg L^{-1}. The fine fractions of soils (<63 µm) in the vicinity of the plant were found to contain up to 2.37 wt % F^-. While the source of the F^- and the acidity in the waters was thought to reflect HF release, the concentrations in soil were thought to be due to appreciable particulate deposition, their F^- contents being similar to those in the fertilisers produced. In the vicinity

of a phosphate fertiliser plant in Tunisia, Mezghani et al. (2005) identified chlorosis and necrosis in plants; the plants were found to contain significantly greater F than those of background samples (up to 4x), with F content showing a distance decline over 16 km. This corresponded with measurements of atmospheric F contents. Kierdorf et al. (2016) report that the phosphate fertiliser plant in Portland, Victoria, Australia emitted 17 to 35 t of F^- compounds a year between 2002/2003 and 2013/2014.

In addition to the release of F-containing compounds during the manufacture of phosphoric acid, it is apparent that significant quantities are also released from the waste phosphogypsum piles and from the associated water (Weinstein and Davison, 2004; Villalba et al., 2008). Arocena et al. (1995) demonstrated that in phosphogypsum F is strongly enriched in the finest fractions (from 2.5 to 5.7 x) so making it more susceptible to leaching and transport. Dartan et al. (2017) found elevated F^- in soils, up to 884 mg kg^{-1}, in the region of fertiliser production units in Turkey. The authors concluded that the source of the F^- was mainly from atmospheric transportation from the phosphogypsum piles.

It is apparent that F contamination can also occur as a result of extraction of phosphate rock. Tanouayi et al. (2016) report that dental fluorosis is endemic in the phosphorite mining region of Hahotoe–Kpogame, Togo. The authors concluded that F^- pollution of waters, soils and vegetables grown in the region, as a result of the mining, is responsible for the fluorosis problems.

According to the U.S. Geological Survey (2018), global extraction of phosphate rock was 263 Mt in 2017; 88% of all phosphate rock extracted globally is converted to phosphate fertiliser, mostly by the wet process (UN Food and Agriculture Organisation, 2017). Assuming that the mean F content of the phosphate rock is 3 wt % (most sedimentary phosphate rocks, the major occurrence, contain > 3%) and that 10-15% of this is volatilised during production (EFMA, 2000) then in the region of 0.694 – 1.04 Mt of F^- would be expected to be released. EFMA (2000) claim that modern phosphate fertiliser plants would scrub out 99% of these releases which would suggest that from 6,900 – 10,400 t of F^- would be released annually from phosphate fertiliser production, assuming all plants have efficient scrubbing systems. However, this would be the amount released as gas during the acidification process and would not include any particulates or any subsequent releases from the phosphogypsum. A previous estimate of gaseous and particulate F release during phosphate fertiliser production of 28,000 t is listed in Jayarthne et al. (2014).

5.5. Previous mineral extraction

It has been demonstrated that in the UK, soils in the vicinity of past mining activity where fluorite mineralisation occurs are seriously impacted by F contamination. Fuge and Andrews (1988) quote values for soils in areas adjacent to fluorite-containing mine waste piles in the N. Pennine region of up to almost 2 wt % F and in NE Wales up to 3,500 mg kg^{-1} F. Andrews et al. (1989) also recorded concentrations of 1wt % F in soils over tailings in the Pennine region with 300 – 1000 mg kg^{-1} F in vegetation; these authors also note the occurrence of dental fluorosis in field voles in the area. Cooke et al. (1976) report F values of up to 3.8 wt % in tailings in the Derbyshire Peak District with vegetation on the tips containing up to 1 wt

% F, these being some of the highest values recorded in plants (Weinstein and Davison, 2004). More recently Geeson et al. (1998) recorded soil F concentrations of up to 8 wt % in agricultural soils in the Peak District of Derbyshire with Othoo and Abrahams (2016) reporting elevated F in the bones of grazing animals in that region.

China-clay extraction in the St Austell area, Cornwall, has also resulted in F contamination of the local environment. The fine tip material contains up to 1.47 wt % F, soils in the vicinity of the tips contain up to 3,300 mg kg^{-1} F and unwashed grasses up to 3,240 mg kg^{-1} F, while the main river draining the area contains 0.44 – 1.25 mg L-1 (Fuge and Andrews, 1988).

5.6. Other industrial sources

Several other sources of environmental F from industrial sources have been mentioned in the literature. Fluorite is used as a flux in the manufacture of steel. Villalba et al. (2007) stated that 1.95 Mt of fluorite was used in the global steelmaking industry in 2003, with over 75% of this consumption being in the developing world. During the steelmaking process HF and SiF_4 are emitted (Semrau, 1957), while it seems that much of the F is retained in the residual slag with Yang et al. (2014) quoting values of 0.44 – 3.37 wt % F (mean 2.02%) in slag from a Swedish steel plant. While there have been instances of serious environmental problems linked to release of F from steelmaking plants, such as the occurrence of fluorosis in farm animals in northern England (Burns and Allcroft, 1964), Weinstein and Davidson (2004) suggest that minor amounts of HF are released to the atmosphere during steelmaking, quoting a value of 104 t a^{-1}.

The use of F-containing materials in the glass and fibreglass, and enamel industries has also resulted in environmental contamination, with HF being emitted (Semrau, 1957). It has been suggested that as much as 20% of the F involved is volatilised in the glassmaking process (Semrau, 1957) with high concentrations of F recorded in some plants in the neighbourhood of glassmaking and enamel factories (Koritnig, 1972). However, Weinstein and Davidson (2004) point out that in developed countries there are now very efficient scrubbing systems in place in glassmaking factories and these have ceased being important sources of environmental F. In addition, data in Villalba et al. (2007), point to the limited amount of fluorite used in the glass and enamel industries relative to that used in the steel industry (<3%). It would seem, therefore, that current emissions from the glassmaking industry are of only limited concern.

There are several industries in which HF is used such as in the manufacture of fluorocarbons and the many other F-containing products. It is essential in the manufacture of semiconductors with Weinstein and Davidson (2004) stating that about 32 t a^{-1} of HF were released by the semiconductor industry into the USA environment during the 1990s. Hydrofluoric acid is used in the petroleum industry as a catalyst in the upgrading of light alkenes, such as butene and propene, to produce alkylates, which are important additives in high octane fuels. About 2 kg of HF are used per m^3 of alkylate (Villalba et al., 2007). Lewandowska et al. (2013) suggest that F is emitted from motor vehicle exhaust as a result of its incorporation into fuels, citing it as a source of F in aerosols in urban areas on the Baltic coast of Poland.

6. Agricultural sources of fluorine in the environment

6.1. Application of phosphate fertiliser

As outlined in section 5.4., phosphate fertiliser is manufactured from phosphate rock, which generally contains 2-4 wt % F (EFMA, 2000). During the process some of the F is lost to volatilisation and some is transferred to the waste phosphogypsum. However, it is apparent that appreciable quantities of F are retained in the fertiliser (Table 5). In addition, Cronin et al. (2000) suggest that HF gas scrubbed out of the effluent gases is frequently added back into the fertiliser during subsequent processing, so increasing the F content of the final product. In a study of phosphate fertilisers used in India, Ramteke et al. (2018) found that between 3.14 and 74.8 % of the original F remains in the fertiliser.

Loganathan et al. (2007) calculated that single superphosphate fertiliser applications to soil in New Zealand amounting to 10-30 kg of P ha^{-1} a^{-1} added between 1 and 6 kg F ha^{-1} a^{-1}. Ramteke et al. (2018) suggested that during 2011-2012, 10.2 Mt of single superphosphate fertilizer was applied to soils in India along with 4.79 Mt of diammonium phosphate. Using these figures Ramteke et al. (2018) calculated that 128,000 ± 14,550 t a^{-1} of F^- were added to soil in India.

As F^- is strongly retained in most agricultural soils due to its adsorption by clay minerals and Al- and Fe- oxyhydroxides etc, where phosphate fertiliser has been applied over several years it has been shown that there is a build-up of soil F. Loganathan et al. (2003) and Hedley et al. (2007) carried out studies of soils in New Zealand with a history of prolonged periods of phosphate fertiliser application. Comparison of sites with similar soil types where there had been no phosphate fertiliser applications to those where phosphate fertiliser had been applied over several years showed marked increases of F content, such as 116 to 259 mg kg^{-1}, after application of 765 kg P ha^{-1} over 20 years as single superphosphate, and 133 to 226 mg kg^{-1}, after application of 60 kg P ha^{-1} a^{-1} for 10 years as single superphosphate. However, a more recent study of a trial site in Ireland, where 930 kg P ha^{-1} had been applied over 31 years as triple superphosphate, demonstrated that while the content of F in the soil had increased by 60 kg ha^{-1}, the increase was statistically insignificant (McGrath and Tunney, 2010).

As F^- added to soil during phosphate fertiliser application is generally strongly bound it is not taken up by vegetation and so there is limited intake of F from herbage into grazing animals. However, Loganathan et al. (2007) suggest that much of the added F tends to remain in surface soils, thus, ingestion of the fertilised soils represents a pathway for F into grazing animals (Cronin et al. 2000). Hedley et al. (2007) state that F intake to livestock is mainly from soil ingestion and that a build-up of F in soils following long term application of phosphate fertilisers poses a potential risk of fluorosis.

In 2017 global extraction of phosphate rock was 263 Mt (U.S. Geological Survey, 2018) and 88% of this was converted to phosphate fertiliser (UN Food and Agriculture Organisation, 2017). Literature data for the F^- content of phosphate fertilisers suggests that it ranges widely between 0.14 and 3.8 wt % (Table 5). Assuming phosphate fertilisers contain an average of 1wt % F^- then at least 2.3 Mt of F^- are added to agricultural soils annually, which make it the largest source of anthropogenically-derived F. However, the fertiliser-derived F is strongly

held in soil and is essentially bio-unavailable to plants but could pose a threat to grazing animals due to soil ingestion (Cronin et al., 2000; Hedley et al., 2007).

In addition to the problems of fertiliser F with regard to grazing animals there is also a problem of potential contamination of groundwater. Loganathan et al. (2007) suggest that in more acidic soils F^- can migrate down the soil profile and into shallow groundwater. However, it seems more likely that such a migration of F^- will occur under more alkaline conditions (Pickering, 1985). Groundwater contamination with F^- deriving from phosphate fertiliser has been suggested to occur in West Bengal, India and in the Punjab, Pakistan. In West Bengal, Kundu and Mandal (2009) found that elevated F^- in groundwater was positively correlated with the amount of single superphosphate fertilizer applied to soils in the area. In Punjab, Farooqi et al. (2009) recorded concentrations of up to 22.8 mg L^{-1} F^- in groundwater that the authors claimed derived from F^- which had accumulated in soils due to phosphate fertiliser application. It was suggested in the case of the Punjab that F^- had been mobilised due to the high alkalinity of the soils resulting from the use of fertilisers.

6.2. Other agricultural sources

Application of sewage sludge to agricultural land is widely practised and is a major source of disposal. Davis (1980) showed that application of sewage sludge containing 33,000 mg kg^{-1} F to pasture in an area of the UK resulted in fluorosis in cattle, possibly linked to excessive uptake of F in ryegrass and/or due to soil ingestion. The excessive F content of the sludge in question was due to an influx of F into the sewage system from an industrial source. In view of the present day regulation of industrial outfalls such extreme F concentrations in sewage sludge are less likely. According to Kabata-Pendias and Pendias (2001) sewage sludge would normally be expected to contain from 2-740 mg kg^{-1}, with the US EPA (1985) quoting a mean value of 86 mg kg^{-1} and a 95^{th} percentile of 739 mg kg^{-1} for sewage sludge in the USA.

Fluorine in sewage sludge is likely to derive from many sources. In addition to natural sources such as weathering of rocks and leaching from soil together with wind-blown dust, there are many anthropogenic sources. Fluoride is added to potable water in some areas to aid dental health, similarly it is added to toothpaste and mouthwashes. In addition, many pharmaceuticals contain F, along with herbicides and insecticides etc. The F content of sewage sludge added to agricultural land is subject to limitation, e.g. 200 mg kg^{-1} in the UK (Department for Environment, Food & Rural Affairs and Environment Agency, 2018), and is, therefore, likely to add considerably less F to soils than phosphate fertiliser. However, it seems from Davis (1980) that F added to soil in sewage sludge is considerably more bioavailable than that from phosphate fertiliser.

A large number of organofluorine agrochemicals are in common use as insecticides, fungicides, herbicides, acaricides and nematicides (Jescke, 2010) with most being aromatic compounds (Weinstein and Davison, 2004). Most of these agrochemicals are polyfluorinated and are not subject to de-fluorination and undergo only limited biodegradation (Key et al., 1997) so it seems likely that they remain in soil or are transferred to surface or groundwater.

Groundwater in many parts of the world is enriched in F^- (Edmunds and Smedley, 2013; Ali et al., 2016) and some of these waters are used for irrigation of agricultural land. Scholz et al. (2015) found that experimental irrigation of plants with water containing 3 or 5 mg L^{-1} resulted in little root uptake but there were significant increases of foliar F due to overhead irrigation. The use of F-rich waters to irrigate agricultural land was suggested by Botha et al. (1993) to be, in part, responsible for the occurrence of fluorosis in farm animals in a region of South Africa.

7. Anthropogenic sources of fluorine in the urban environment

Many of the sources of environmental F discussed in the earlier sections can seriously impact urban environments, for example when F-emitting industries are sited in the peri-urban environment. In several cities in SE Asia artisanal brick-making results in major F emissions which impact the urban environment (Schmidt, 2013). In SW Siberia the Krasnovarsk aluminium smelter impacts the city of the same name. Coal combustion within homes in China has resulted in fluorosis, while Lewandowska et al. (2013) suggested that one source of elevated F contents of aerosols in urban areas on the Baltic coast of Poland was burning of coals for domestic heating. Lewandowska et al. (2013) also highlighted the role of motor vehicles in F pollution of urban aerosols which they suggested were derived from inclusion of F in high octane fuels and from teflon seals used in the construction of the vehicles.

As a result of the many uses of F in modern society, significant quantities of F-containing materials occur in municipal solid waste (MSW). During incineration of MSW much of the F is released as HF with amounts of up to 20 mg Nm^3 (m^3 at STP) occurring in the gas emitted, this being reduced to 0.01 – 0.1 mg Nm^3 after treatment (Quina et al., 2011). Emissions of HF from incinerators are strictly controlled with a maximum admissible content of 1 mg Nm^3 (Quina et al., 2011). Weinstein and Davidson (2004) indicate that combustion of fluoropolymers would not only release HF but would also release organofluorine compounds including trifluoroacetic acid (TFA). It is worth noting that while modern incinerators are subject to stringent emission standards, uncontrolled burning of refuse and bonfires in gardens and backyards could represent a significant local source of HF and organofluorine compounds in urban environments.

8. Fluorinated organic compounds in the environment

A large number of fluorinated organic compounds occur in the environment and while about 30 of these occur naturally, the vast majority are of anthropogenic origin (Weinstein and Davidson, 2004). Most naturally occurring organofluorine compounds derive from biological sources (Key et al., 1997) but some have been identified in volcanic and geothermal gases and within minerals such as fluorite (Gribble, 2002). Key et al. (1997) point out that all known biologically-derived organofluorine compounds contain only one atom of F while in contrast many human-made fluorocarbons contain multiple F atoms, with over a million containing the trifluoromethyl group (CF_3) (Solomon et al., 2016). The C-F bond is the strongest in nature (Key et al., 1997) and while organofluorine compounds containing one or two F atoms are generally de-fluorinated in the environment, those that contain multiple F

atoms are not de-fluorinated and undergo limited degradation (Key et al., 1997; Solomon et al., 2016).

Manufactured organofluorine compounds have a wide range of uses, from agricultural and pharmaceutical products through to the fluoropolymers used in the manufacture of many items. The major concern is with compounds where all of the H atoms in the C-H bonds are replaced by F, the perfluorinated compounds (PFCs), particularly those with long chains, with 6 or more carbons (Solomon et al., 2016). PFCs are water and grease repellents and have been widely used as stain resistant sprays, for carpets and upholstery for instance, in water-proof clothing, cleaning products, latex paint and fire retarding foams (Calafat et al., 2007; Stahl et al., 2011). PFCs have been widely used in food packaging with a recent study of fast food packaging in the USA detecting them in 20 – 56% of the various packaging materials (Schaider et al., 2017). PFCs are persistent in the environment and have found their way into the biosphere, where they have been found to bioaccumulate and biomagnify (Houde et al., 2006), and humans where they can bioaccumulate in the brain, liver, lung, bone and kidney (Perez et al., 2013). It has been estimated that 98% of the USA population have detectable PFCs in blood (Kataria et al., 2015). The major pathways into humans are via diet, with fish, shellfish and potatoes being major contributors (Ji et al., 2012), together with drinking water and inhalation of indoor air (Stahl et al., 2011).

PFCs have been linked to several human health problems including cancers, thyroid disease and immunotoxicity (Schaider et al., 2017) and have been shown to affect the renal system (Kataria et al., 2015). In addition, PFCs can cross the placental barrier into the foetus (Yang et al., 2016) with this being linked to reduced foetal growth (Callan et al., 2016). Some of the long chain PFCs are now listed as persistent organic pollutants (POPs) and in some cases their manufacture has been banned.

The most well-known and notorious fluorocarbon compounds are the chlorofluorocarbons or CFCs. They were introduced in the mid-1900s in refrigeration and air conditioning systems, in fire extinguishers and as propellants in aerosol cans etc. In the 1970s it was realised that the CFCs were causing serious ozone depletion. Their production was limited in the 1990s and they are being totally phased out (McCulloch, 2003). The CFCs have essentially been replaced with hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) that do not result in ozone depletion (Weinstein and Davidson, 2004).

In addition to being involved in ozone depletion, the CFCs along with HFCs and HCFCs are serious greenhouse gases and together with other F-containing gases such as SF_6 and NF_3 represent 2% of global greenhouse gas emissions (IPCC, 2014). According to the US EPA (2018) in 2016, 92% of the F-containing greenhouse gases derived from the CFC substitutes with small amounts deriving from such sources as aluminium production and semiconductor manufacture. The F-containing greenhouse gases have long atmospheric lifetimes ranging up to several thousand years (US EPA, 2018).

Degradation of some of the CF_3-containing compounds released into the environment such as the HFCs and the HCFCs will result in the formation of trifluoroacetic acid (TFA – CF_3COOH) (Boutonnet et al., 1999). In addition some TFA is released to the environment

through its manufacture (Key et al., 1997), from pyrolysis of fluoropolymers (McCulloch, 2003) and the burning of household waste (Weinstein and Davidson, 2004). TFA is stable in the environment (Boutonnet et al., 1999) and rapidly forms acetate salts such as CF_3COONa (Solomon et al., 2016). TFA, mainly in the form of its salts, occurs in air, soils, precipitation and surface water but its concentration in these media shows large geographic variations; while its concentration is low in remote areas of the world (Boutonnet at al., 1999), it is elevated in the atmosphere and rainfall of urban and industrial areas (Weinstein and Davidson, 2004). It tends not to be retained in soils and is probably carried into groundwater (Solomon et al., 2016). According to Solomon et al. (2016) TFA accumulates in playas, salt-lakes and the sea due to evapoconcentration, however, its concentration in seawater is considerably greater than would be expected from accumulation through the recent past, suggesting an additional natural source. Seawater in close proximity to hydrothermal vents in the seabed has been found to be enriched in TFA and such hydrothermal outputs have been suggested to be a source of its natural enrichment in seawater (Solomon et al., 2016).

De Angelis and Legrande (1994) suggest that increased F^- contents of Greenland snow in the late 1900s are, in part, a result of CFC degradation, while Preunkert and Legrande (2001) state that degradation of HCFCs may have contributed to the F^- budget of Alpine snow during 1980 – 1995.

9. Conclusions

Fluorine in the environment mainly derives from weathering of the lithosphere, its major reservoir in the lithosphere being OH-containing minerals where F^- substitutes for OH^-. Of the other natural sources of environmental F, vulcanicity is the most important but wind-blown dust and biomass burning make significant contributions. While it has been suggested that marine-derived F is a major source to the environment it seems likely that its contribution has been over estimated and that it constitutes only a minor fraction of the total additions.

While concentrations of up to 8 wt % F have been recorded in soils of fluorite mineralised areas of the UK with up to 1wt % F recorded in plants, the most significant anthropogenic source of environmental F is the addition of phosphate fertiliser to agricultural soils, which is estimated to add at least 2.3 Mt annually. While much of this is strongly held in soil, it is possible that some of the F will be mobilised into groundwater. Of the other anthropogenic sources coal combustion has been widely held to be the major contributor. However, it seems likely that at present brickmaking is the major anthropogenic source of F. The rapid growth of urban areas in India, Pakistan and Bangladesh has seen a corresponding growth of brickmaking in these countries and together with China they are responsible for over 75% of global brick production. As many of the brick kilns in operation in these countries are artisanal and unregulated they represent a serious source of HF emissions. Using data from the literature it is possible to estimate that global brick production releases about 1.8 Mt a^{-1} F. From data in Table 6 it can be estimated that total gaseous emissions of F from anthropogenic sources are in the order of 2.2 Mt a^{-1}, suggesting that F emissions from brickmaking far

outweigh those of coal combustion, Al smelting and the manufacture of phosphate fertilisers, and even the major natural source of vulcanicity.

Studies on ice cores from Greenland and from the French and Swiss Alps reveal that their contained F is derived from relatively local sources (De Angelis and Legrand, 1994; Preunkert and Legrand, 2001). Therefore, it seems likely that while atmospheric F emissions represent a major threat to local environments, they are not transported globally. Within the urban environment, the occurrence of industrial sources of F emission in the periurban environment can have an impact, while domestic coal combustion and the release of F from high octane fuels in motor vehicles are also potential sources.

Fluorine has a wide range of uses in modern society it being incorporated into many compounds used in medicine and agriculture, and in the many fluoropolymers currently manufactured. Degradation of some of these fluorocarbon compounds, along with pyrolysis of fluoropolymers and the burning of household refuse containing them has resulted in the recent deposition of organofluorine compounds in the environment.

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Table 1. Fluorine abundances in crustal rocks from literature compilations (mg kg^{-1})

Rock type	1	2	3
Ultramafic rocks		50 – 100	20
Basalts & gabbros	400	300 – 500	300
Intermediate rocks	500	500 – 1200	
Granites	735	520 – 850	800
Rhyolites		300 – 700	
Shales	740	500 – 800	700
Sandstones	270	50 – 270	200
Carbonates	330	50 – 350	300

1. Levinson (1980); 2. Kabata-Pendias and Pendias (2001);
3. Reimann and Caritat (1998)

Table 2. Fluorine-rich rocks (mg kg^{-1})

Rock type	Range	Mean (no.)	Ref.
Greisenised granite, Germany		20,400 (24)	1
Greisenised granite, SW England, UK	8,040 – 27,700	15,500 (5)	2
Granite pegmatites, SW England, UK	365 – 22,700	7,550 (14)	2
Fluorite granite, St. Austell, SW England, UK	1,070 – 10,400	4,380 (11)	2
Granite, central Colorado, USA	70 – 260,000	1,100 (459)	3
Phonolites/trachytes/nephelinites, Eastern rift	1000 – 4,900	2,500 (27)	4
Carbonatites, Africa	216 – 25,200	6,500 (12)	5
Sedimentary phosphorites, global	37,000 – 40,000	38,500 (4)	6

1. Koritnig (1972); 2. Fuge and Andrews (1988); 3. Wallace (2010); 4. Hayes et al. (2017);
5. Dawson and Fuge (1980); 6. EFMA (2000)

Table 3. Fluorine in soils (mg kg^{-1})

Source	Range	Mean (no.)	Ref.
World		200	1
World		400 (median)	2
Former USSR	30 – 320	200	3
USA	<10 – 3700	430	4
UK	113 – 580	350 (144)	5
New Zealand	212 – 617	357	6
World - podzols	<10 – 1,100	130	7
World - cambisols	<10 – 800	385	7
World - rendzinas	<10 – 840	360	7
World – kastanozems & chernozems	10 – 1,194	550	7
World - histosols	10 – 335	220	7
Sn/W mineralised area, SW England	1,335 – 5,250	2410 (54)	5
Fluorite mineralised area, Colorado	40 – 7160	630 (209)	8
F-rich granites, SW England	370 – 12,600	1930 (178)	9

1. Levinson (1980); 2. Reimann and Caritat (1998); 3. Vinogradov (1967);
4. Shacklette and Boerngen (1984); 5. Fuge and Andrews (1988);
6. Loganathan et al. (2006). 7. Kabata-Pendias and Pendias (2001); 8. Wallace (2010);
9. Fuge (unpublished data)

Table 4. Comparison of fluorine content of brick-making clays before and after roasting (mg kg^{-1})

Material	Range	Mean
Chinese soils – clay-rich[1]	295 – 800	490
Chinese soils after roasting at 1100 ^{o}C[1]	53 – 112	74
Marine deposited clays, UK[2]	501 – 993	807
Marine clays, UK, after roasting at 1000 ^{o}C[2]	70 – 332	154
Non-marine deposited clays, UK[2]	263 – 572	390
Non-marine clays, UK, after roasting at 1000 ^{o}C[2]	<50 – 237	75

1. Data from Xie et al. (2003)
2. Data from Fuge and Hennah (1989)

Table 5. Fluorine in phosphate fertiliser (%)

Material	Range	Mean	Ref.
Phosphate fertiliser, global	0.85 – 3.80		1
Single superphosphate, New Zealand	1.08 – 1.84		2
Triple superphosphate, New Zealand	1.30 – 2.40		2
Monoammonium phosphate, New Zealand	1.60 – 2.20		2
Diammonium phosphate, New Zealand	1.20 – 3.00		2
Single superphosphate, India	0.42 – 1.16	0.86 (4)	3
Diammonium phosphate, India	0.14, 1.07	0.61 (2)	3
Ammonium nitrophosphate, India		1.33	3

1. Kabata-Pendias and Pendias (2001); 2. Cronin et al. (2000);
3. Ramteke et al. (2018)

Table 6. Sources of fluorine in the environment

Source	Estimate Mt a^{-1}	Ref.
Vulcanicity	0.3 – 0.7	1
Biomass burning	0.076	2
Coal combustion	0.2 – 0.3	3
Brickmaking	1.8	3
Al smelting	0.041	3
Manufacture of phosphate fertiliser	0.07 – 0.10*	3
Application of phosphate fertiliser	2.3	3

*Amount released in gas. Total including F released in particulates and from phosphogypsum is much higher – Jayarathne et al. (2014) quote a total value of 0.28 MMT a^{-1}.

1. Based on data in Pyle and Mather (2009) 2. Jayarathne et al. (2014);
3. Current paper

- The majority of the F occurring in the secondary environment derives from natural weathering processes.
- In abandoned mine sites where fluorite mineralisation occurred, soil F contents range up to 8 wt %, with plants growing on the sites containing up to 1wt % F.
- The application of phosphate fertiliser is the largest anthropogenic source of F in the environment, probably adding over 2.3 Mt a^{-1} F to soils globally.
- Global brick production is estimated to release about 1.8 Mt a^{-1} F, making it the largest source of F emissions to the atmosphere.
- Other anthropogenic sources of F emissions to the atmosphere are coal combustion, 0.2 – 0.3 Mt a^{-1}, phosphate fertiliser production, 0.07 – 0.10 Mt a^{-1} and aluminium smelting, 0.041 Mt a^{-1}.
- Vulcanicity has been estimated to release 0.3 – 0.7 Mt $a^{-1}$to the atmosphere.
- More recently, degradation of fluorocarbon compounds together with pyrolysis of fluoropolymers and burning of household refuse has resulted in the deposition of organofluorine compounds in the environment.

Regulating Air Pollution from Coal-Fired Power Plants in India

SARATH GUTTIKUNDA, PUJA JAWAHAR, DEBI GOENKA

Coal remains the main fossil fuel for power generation in India. The health impacts of air pollution from these coal-fired power plants include numerous premature deaths and frequent asthma attacks. In the future, the amount of power generated from coal will remain high, at least through 2030, and unless we find a better way to manage these power plants, the environmental effects of growing air pollution, greenhouse gas emissions and the cost to human health will all be high.

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The Indian economy is the third largest in the world at $4.7 trillion (purchasing power parity, PPP at 2012 estimates) spurred by growth across manufacturing, construction, and service sectors. Not coincidentally, it is also the fourth largest consumer of electricity in the world. The demand for electricity from a growing economy of this scale is huge – peak demand was approximately 122 gigawatts (GW) of power in 2011. Peak supply (at 110 GW) could barely keep up with peak demand in 2011. The gap between the supply and demand for electricity is crucial to understand the power sector in India.

In India a third of the population in rural areas does not have access to electricity and those areas on the grid are not assured of uninterrupted supply. The blackout in July 2012, that paralysed 600 million people in 22 states in the northern, eastern, and north-eastern India, is testament to how tenuous the power situation is in the country. According to the Northern Regional Load Dispatch Centre, Uttar Pradesh, Punjab, and Haryana were responsible for overdraw that led to tripping in the transmission lines, and resulted in a shortage of over 32 GW on 30-31 July 2013 and a blackout for three days. While this was the major episode that drew attention to the grid, there are frequent power cuts in most parts of the country. In the urban sector, these cuts are severe in the winter and summer months, when heaters or air conditioners are in full service. These needs are usually supplemented by in situ large, medium, and small diesel generator sets at hotels, hospitals, malls, markets, large institutions, apartment complexes, cinemas, and farmhouses and these form an additional source of air pollution to the already deteriorating quality of air in cities.

The power sector in India is consequently dealing with two competing priorities: (a) to provide necessary power to fuel a growing economy, and (b) to reduce the environmental and social costs of providing this power.

In this article, we draw attention (or lack thereof) towards addressing the environmental costs of electricity generation, assess the air-pollution-related health impacts of emissions from coal-fired power plants, and an analysis of the current environmental regulatory framework for coal-fired power plants in India.

Coal-Fired Power Plants

India has the fifth largest electricity generation sector in the world at 210 GW in 2012. In the Twelfth and Thirteenth Five-Year Plans, additional capacity of 76 GW and 93 GW are planned (Prayas 2013). Of the total electricity generated, thermal power plants (gas and coal) account for 66%, hydroelectricity for 19%, and the remaining 15% from other sources including natural gas and nuclear energy.

We used the list of thermal power plants documented by the Central Electricity Authority (CEA) as a starting point to build our database of operational coal-fired power plants in the country (CEA 2011, 2012). We updated this database for 2011-12 representing a total generation capacity of 121 GW. We also include in the database geographical location in latitude and longitude, the number of boiler units and size of all known power plants operated by both public and private entities. The power plant characteristics by state are presented in Table 1 (p 63). The geographical distribution of the coal-fired power plants in India is presented in Figure 1 (p 63).

- The Korba cluster (Chhattisgarh) has a combined generation capacity of 4,380 megawatt (MW) between four power plants located within a 10 km radius. Major cities in the Korba region are Ranchi, Jamshedpur, Rourkela, Jabalpur, Nagpur, and the capital Raipur.
- The Jhajjar cluster (Haryana) has a combined generation capacity of 2,700 MW between two power plants within

the radius of 10 km, with an additional power plant with 1,000 MW under construction. Delhi is 70 km from the Jhajjar cluster.

Table 1: Summary of Annual Coal Consumption at the Power Plants in India in 2011-12

State	Number of Plants	MW	Coal (Million Tonnes)	kg coal/kWh 2006-07	Installed Units <210 MW (%)
Andhra Pradesh	8	10,523	47.4	0.72	65
Bihar	3	2,870	10.2	0.94	77
Chhattisgarh	8	9,480	44.5	0.72	39
Delhi	2	840	4.8	0.77	100
Gujarat	11	14,710	55.9	0.65	69
Haryana	5	5,860	23.9	0.70	35
Jharkhand	6	4,548	12.0	0.75	86
Karnataka	5	3,680	14.6	0.69	64
Madhya Pradesh	4	6,703	33.1	0.79	79
Maharashtra	13	17,560	71.5	0.73	51
Odisha	8	8,943	40.7	0.73	76
Punjab	3	2,620	13.2	0.66	82
Rajasthan	4	3,490	13.2	0.67	44
Tamil Nadu	8	6,210	25.8	0.72	95
Uttar Pradesh	11	11,997	56.0	0.80	86
West Bengal	12	10,695	36.1	0.69	75
Total	111	1,20,727	503	0.73±0.10	70

• The Mundra cluster (Gujarat) has a combined generation capacity of 9,620 MW from two private sector power plants located within a 5 km radius. Major cities in the Mundra region are Jamnagar (major industrial port), Rajkot, and Ahmedabad (300 km away, with two local power plants of 1,000 MW).

• The Mumbai cluster (Maharashtra) has one coal-based power plant in Trombay and multiple gas-powered plants.

This data was gathered from websites and annual reports of the state electricity boards for public[1] and private sectors.[2]

Emissions and Health Impacts

Air pollution is a complex mixture of pollutants with sources ranging from fossil fuel burning in transportation, power generation, industries, and domestic sectors to natural sources such as dust storms and forest fires. In this study, our objective was to isolate the health impacts of the emissions from the coal-fired power plants. In 2011, we estimated that the 111 coal-fired power plants consumed 503 million tonnes of coal in total – emitting 580 kilotonnes particulates with diameter less than 2.5 micrometres ($PM_{2.5}$), 2,100 kilotonnes of sulphur dioxides (SO_2), 2,000 kilotonnes of nitrogen oxides (NO_x), 1,100 kilotonnes of carbon monoxide (CO), 100 kilotonnes of volatile organic compounds (VOCs) and 665 million tonnes of carbon dioxide (CO_2).

These emissions resulted in an estimated 80,000 to 1,15,000 premature deaths and more than 20 million asthma cases from exposure to total $PM_{2.5}$ pollution, which cost the public and the government an estimated Rs 16,000 crore to Rs 23,000 crore ($3.2 to $4.6 billion). The health impacts analysis of these emissions was carried out via state-of-the-art dispersion modelling system (CAMx) and the use of health risk coefficients established by epidemiological studies (Guttikunda and Jawahar 2013). We believe that the health impacts discussed here is an underestimation, and does not include the impacts of the water run-off and soil contamination due to the release of heavy metals like zinc, copper, manganese, cobalt, cadmium, selenium, mercury, arsenic, iron, lead, and chromium.

The particulate matter (PM) pollution from coal-fired power plants (presented in Figure 2, p 64) in central India covering Madhya Pradesh, Jharkhand, Odisha, and Chhattisgarh, is the highest due to the density of the power plants in the region and higher installed generation capacity because of its proximity to coal mines. The Delhi-Haryana region with the highest population density, with more than 21.5 million inhabitants in Delhi and its satellite cities, also experiences substantial PM pollution from coal-fired power plants.

The coastal regions experience the least of the PM pollution due to strong

Figure 1: Geographical Location of the Operational Coal-based Public and Private Power Plants in India in 2012

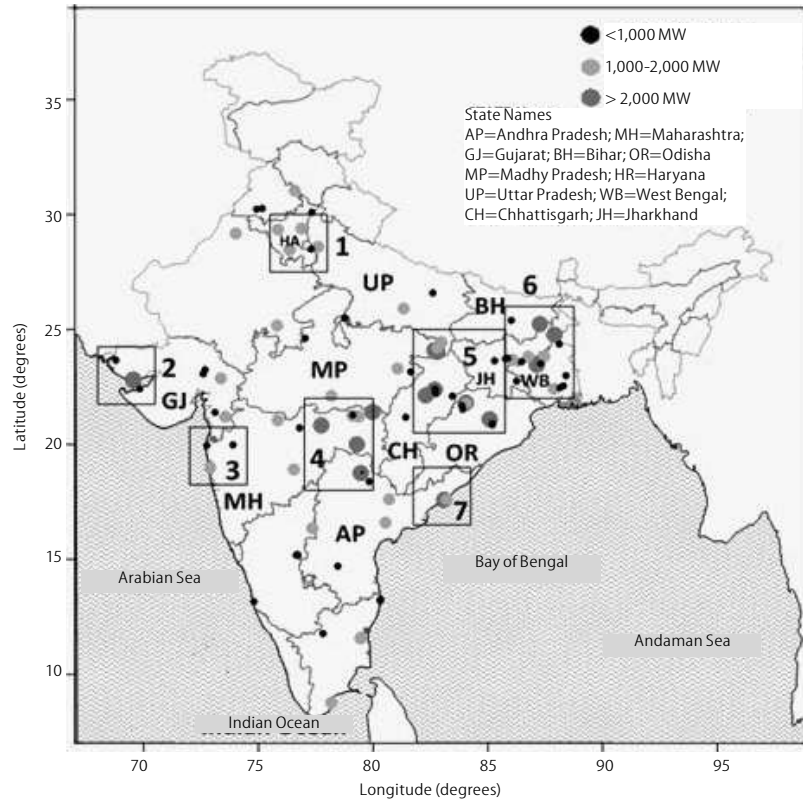


Figure 2a: Modelled Annual Average Ambient $PM_{2.5}$ Concentrations due to the Emissions from Coal-Fired Thermal Power Plants in India

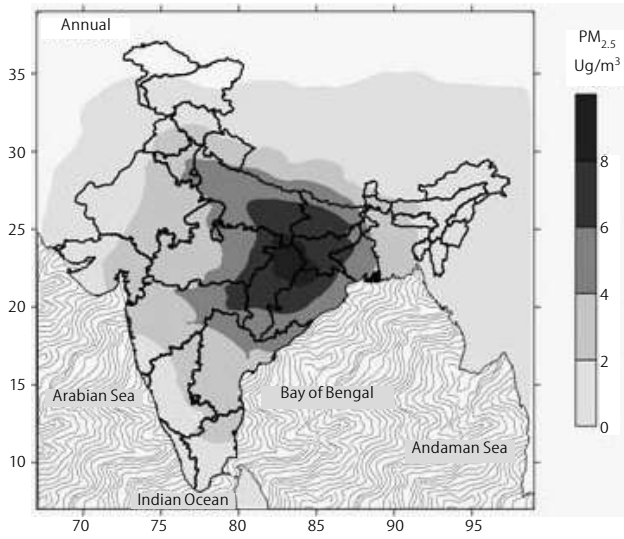
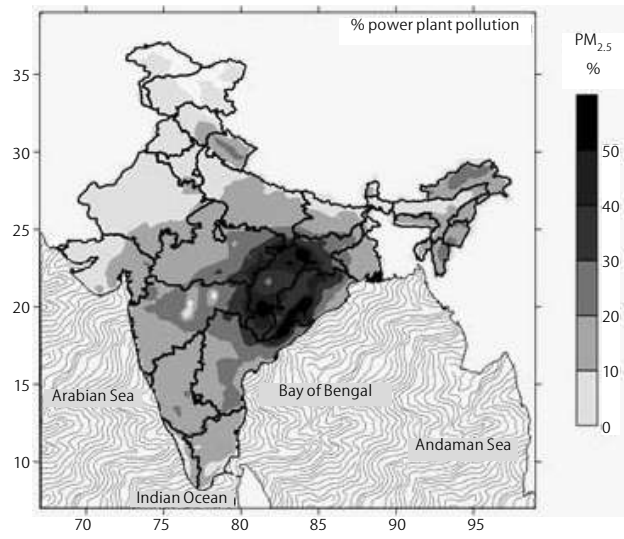


Figure 2b: Per Cent Contribution of Coal-Fired Power Plants to Annual Average Ambient $PM_{2.5}$ Concentrations in India



(Based on Satellite Measurements – van Donkelaar et al 2010).

land-sea breezes, with much of the pollution dispersed over the seas. While the air pollution from these coastal power plants is diluted over the seas for some months, they are equally threatening to water and soil quality, due to pollution from coal washeries and ash dumps. Till date the inland power plants are still the majority in the country and a serious threat to human health and other environmental concerns.

While the impact of the emissions is felt within 200 km of the power plants, under windy conditions the influence can be tracked to distances as far as 400 km from the source region. The animated forward trajectories[3] illustrate that the emissions from these high stacks affects regions and people far from the source region. The plumes travel long distances, while the pollution levels get diluted, these receptor points still experience an increase in the ambient concentration and also an increase in the morbidity and mortality risks. Impacts also include deposition of heavy metals, sulphur oxides, and ozone on agricultural land.

Environmental Regulations

Despite the volume of coal use in the power generation sector and the corresponding emissions and health impacts, there are very few regulations in place to address the environmental and health costs of coal. Till date, pollution standards only exist for ambient air quality and not for individual power plants. Only after standards are set and regulations mandated at the plant level, can we proceed to the next steps of monitoring and enforcing policy, so as to have lesser environment and health impact due to coal-fired power plants. For particulate matter emissions, the emission standard in India lags to those implemented in China, Australia, the United States (US), and the European Union (EU) (Table 2). For other key pollutants, there are no prescribed emission standards despite the fact that India is a relatively dense country and several power plants are close to residential areas.

All the stack emissions at the power plants are monitored and regulated as concentrations only and not in terms of

Table 2: Summary of Emission Standards for Coal-Fired Power Plants

Country	PM	SO_2	NO_2	Mercury
India[a]	350 mg/Nm^3 for <210 MW 150 mg/Nm^3 for >210 MW	None	None	None
China[b]	30 mg/Nm^3 (proposed all) 20 mg/Nm^3 for key regions	100 mg/Nm^3 for new 200 mg/Nm^3 for old 50 mg/Nm^3 for key regions	100 mg/Nm^3	None
Australia[c]	100 mg/Nm^3 for 1997-2005 50 mg/Nm^3 after 2005	None	800 mg/Nm^3 for 1997-2005 500 mg/Nm^3 after 2005	In discussion based on the US standards
European Union[c]	Pre-2003 100 mg/Nm^3 for <500 MW 50 mg/Nm^3 for >500 MW Post 2003 50 mg/Nm^3 for <100 MW 30 mg/Nm^3 for >100 MW	Pre-2003 Scaled for <500 MW 400 mg/Nm^3 for >500 MW Post 2003 850 mg/Nm^3 for <100 MW 200 mg/Nm^3 for >100 MW	Pre-2003 600 mg/Nm^3 for <500 MW 500 mg/Nm^3 for >500 MW Post 2003 400 mg/Nm^3 for <100 MW 200 mg/Nm^3 for >100 MW	In discussion
US[c, d]	6.4 gm/GJ	640 gm/MWh	720 gm/MWh for old 450 gm/MWh for new	0.08 gm/MWh for lignite 0.01 gm/MWh for IGCC

a – from Central Pollution Control Board (India) (http://cpcb.nic.in/Industry_Specific_Standards.php). Last accessed 17 February 2013. Besides PM, only national ambient standards exist.
b – from standards information in Chinese (http://www.zhb.gov.cn/gkml/hbb/qt/201109/t20110921_217526.htm). Last accessed 17 February 2013. Prior to 2011, the standards were based on commissioning year (before 1996, 1997 to 2004, and after 2004) .
c – Power stations emissions handbook (http://www.ccsd.biz/PSE_Handbook). Last accessed 17 February 2013.
d – in official units; for mercury this is based on 12 month rolling average.

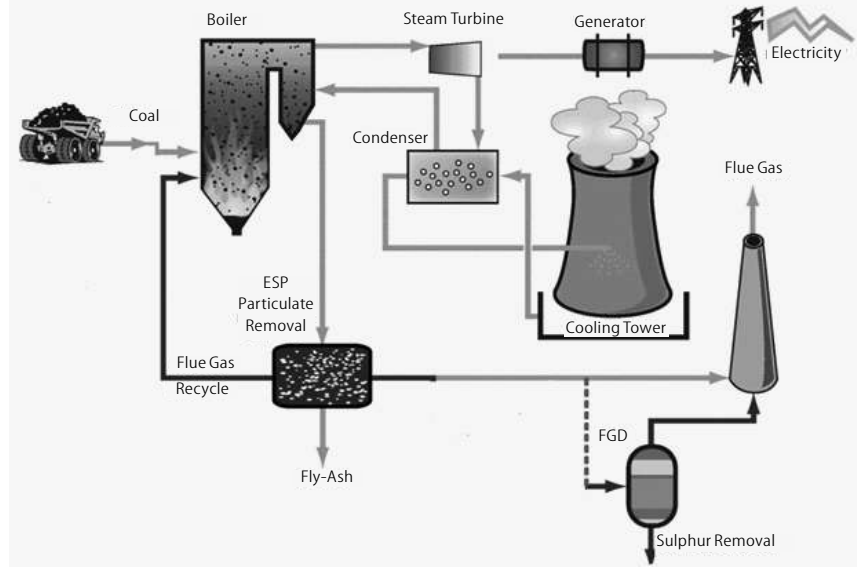
total emissions per plant. For example, for PM, the plants with generation capacity more than 210 MW, the concentration limit in the flue gas is 150 mg/Nm^3 and for the plants with generation capacity of less than 210 MW, the limit is 300 mg/Nm^3. These limits are much higher than those currently practiced in Australia, China, US, and EU. The limit for the smaller plants can be reverted to 150 mg/Nm^3, if they are located in an urban, ecologically sensitive, and other critically polluted areas – which is at the discretion of Ministry of Environment and Forests (MoEF). A break-up in the emissions regulation at 210 MW also led to installation of smaller boilers at most of the power plants (Table 1). Approximately 70% of the operational units in the country are of the size less than or equal to 210 MW and these units tend to have the worst net efficiency and plant load factor. The newer plants are mostly 500 MW or higher with the best net efficiency of more than 33% (CEA 2012). Hence, efficiency improvement of existing, older power plants and tightening of emission standards for all sizes should become a critical component for reducing coal consumption and atmospheric emissions. Differential emission regulations also tend to result in use of control equipment with low efficiency and higher emissions.

Particulate matter is the only pollutant for which any pollution controls are widely used in India. A schematic of a coal-fired power plant is presented in Figure 3 that shows flue gas from the boilers at high temperature and velocity passing through heat exchangers to recycle the residual energy. This then enters the particulate control equipment (electro-static precipitators (ESPs), and cyclone bag filters) for removal of entrained ash. ESPs are installed in all coal-fired power plants. As removal efficiencies at ESPs are higher for coarse particles, most of the PM dispersing from the top of the stack is in the size range of respirable PM (10 mm or less). Lu, Wu and Pan (2010) measured fractions of 50-60% $PM_{2.5}$ and 90-95% PM_{10} in the total filterable PM in the flue gas at a 660 MW power plant. The PM in the flue gas also contains high concentrations of heavy metals such as arsenic, lead, cadmium, mercury, copper, and zinc, which not only contributes to potential health hazard than the bottom ash (Finkelman 2007), but also increases the resistivity and reduces the ESPs collection efficiency to as low as 98%. Reddy et al (2005) measured the chemical composition of the bottom ash, fly ash, and flue gas from a coal-fired power plant in the western India and estimated 1%-7% of zinc, 2%-7% of copper, 5%-8% of manganese, 7%-10% of cobalt, 12%-18% of cadmium, 60%-70% of selenium, 70%-80% of mercury, and traces of arsenic, iron, lead, and chromium contained in the coal was emitted in the flue gas. Similar levels of entrainment were reported in an estimate of total trace metal emissions from coal-fired power plants in China (Chen et al 2013).

Besides flue gas PM emissions, fugitive dust from coal-handling plants and ash ponds (after disposal from the plants) is a problem. According to CEA, after the combustion and application of control equipment, ash collection at the power plants ranged 70%-80% of the total ash in the coal. It is assumed that the remaining ash is dispersed from the stacks. In 2003, an amendment notification from the MoEF mandated 25% bottom ash in all brick kilns within a 100 km radius of any coal-based thermal power plant and all building construction within 100 km for any coal-based thermal power plant to use 100%-ash-based bricks, blocks, and tiles. Till date the percentage of ash utilised in the construction industry is low.

The ambient $PM_{2.5}$ concentrations presented in Figure 2 includes two fractions – primary PM emissions, which is a result of the ash content in the coal and the secondary PM, which is a result of chemical reactions converting SO_2 and NO_x emissions to particulate forms of sulphates and nitrates. We estimate the secondary PM pollution accounts for 30%-60% of the total ambient $PM_{2.5}$ pollution from the power plants. While most of the power plants operate ESPs to control the dust emissions, only a handful a power plants operated flue gas desulfurisation (FGD) units, which are effective in controlling the SO_2 and NO_x emissions. Among those to be commissioned through 2020, only seven power plants are listed to have FGD (Prayas 2011). The FGD systems could range from in furnace control via limestone injection, wet scrubbing of flue gas (Figure 3) and is known to further aide in removal of PM. In India, there are no mandated emission standards for SO_2 and only the stack heights are mandated assuming that the emissions will disperse to farther distances, diluting the plume concentrations. For example, MoEF requires all power plants with generation capacity more than 500 MW to build a stack of 275 m; those between 210 MW and 500 MW to build a stack of 220 m; and those

Figure 3: Simplified Schematics of Coal-Fired Power Plant Operations



with less than 210 MW to build a stack based on the estimated SO_2 emissions using a thumb rule of height = $14*(Q)^{0.3}$, where Q is the estimated SO_2 emissions rate in kg/h. The stack heights for old and new power plants ranged between 150 m and 275 m.

Despite an estimated 30% of the total NO_x emissions in India originating from power generation (Garg et al 2006), currently, there are no regulations to control these emissions for coal-fired power plants. Some of the new installations and extensions are equipped with low-NO_x burners, with little details on their operational performance (Chikkatur et al 2011).

Regulating for Cleaner Power

Coal remains the main fossil fuel for power generation in India. Supplies of other fuel sources such as naphtha and natural gas are not stable and need to be imported, which led to their lesser growth in this sector. Unlike pollution from the transport or domestic sector, pollution from power plants is a point source. This means that there are a finite and known number of units from where pollution is released and thus can be controlled better. Moreover, with a majority of the power plants run by the public sector, mandating technologies that reduce pollution would seem to represent a simple solution. However, power plant regulation has thus far lagged far behind other emerging economies and power plants by themselves have no incentive to improve pollution control. Combined with a strong demand for reliable electricity and lack of supply it is doubtful that pollution will be controlled in the absence of strong regulation and enforcement.

Of all the operational coal-fired power plants in the country, 70% are of the size less than or equal to 210 MW and these units tend to have the worst net efficiency and plant load factor. We believe that a bifurcated environmental standard for PM emissions led to this different sizes of power generation units. For example, the Kolghat power plant in West Bengal has six units of 210 MW and the Raichur power plant in Karnataka state has seven units of 210 MW, each with a total generation capacity of more than 1,000 MW, are allowed to adhere to the lower emission standard, only because the individual boiler size is less than or equal to 210 MW. The efficiency improvement of existing older power plants and tightening of emission standards for all sizes should become a starting point to reduce coal consumption and atmospheric emissions. Going forward, coal-fired power plants should be subject to tighter emission standards based on those found in emerging economies (like China) and developed economies (like EU, Australia, and the US).

The stack emissions being point sources, are limited in number, and can be monitored relatively easily as compared to non-point sources (such as vehicles, garbage burning, domestic burning, and fugitive dust). Some of the larger power plants are now equipped with continuous monitors for the criteria pollutants. However, this information is not available in the public domain, either for analysis or for scrutiny of emission loads. This adds to the uncertainty of the estimates, for analysing the impacts of the emissions, understanding the contribution loads, and for planning. If the emission standards need strengthening or new policies to be introduced for clean power and clean environment, the information dissemination should be more open, otherwise, the enforcement of the limited standards that do exist is nearly non-existent.

From the power plants, we estimate 30-60% of the PM pollution is secondary in nature, with the most coming from chemical conversion of SO_2 emissions. Since a majority of the power plants in the country do not operate a dedicated

FGD system, most of the SO_2 from coal combustion is emitted and ends up in respirable PM fraction, resulting in more health impacts. In the environmental impact assessment studies, required before the commissioning of a power plant, a provision for an FGD for all power plants is discussed for future years, but not yet mandated. We believe that FGD technology should become mandatory for all new power plants and a provision should be introduced to implement the same for the larger and older power plants to control SO_2 emissions. The combined benefits of an FGD in conjunction with the already operational ESPs at most of the power plants will benefit not only ambient particulate pollution and related health impacts, but also a reduction in deposition of these gases over agricultural lands.

As part of environment impact assessment, the planning and commissioning of power plants should include influences of long distance transport, beyond 50-200 km. Since, the size of power plants is expected to increase in the coming decades, with the mandated stack heights of 275 m, the emissions can be expected to travel and influence areas even farther than that, and consequently result in additional health impacts.

What Can Be Done?

Ultimately, the government, and citizens' groups need to demand clean power, keeping in mind that health impacts of the emissions from power plants in India can be severe. An environmental outlook study concluded that a least-cost policy mix to reduce air pollution in developing economies of Brazil, China, India, and South Africa is made up of 50% end of pipe measures and 50% of shifting to cleaner energy sources (OECD 2012). In the future – while the share of power generation from coal is projected to decline (IEA 2012) – the amount of power generated from coal will remain high at least through 2030, and unless we find a better way to manage power plants, the environmental effects due to growing air and CO_2 emissions and the human health cost will be high. The way forward for coal-fired power plants in India is

- to make the emission standards for particulates more stringent and introduce new emission standards for other pollutants,
- enforce the standards by revising the current environment impact assessment procedures, which do not factor human health as a primary indicator,
- make the implementation of FGD for reduction in emissions of multiple pollutants,
- introduce continuous monitoring at the plant stacks, such that the data is in the public domain in real time.

NOTES

1 The public sector entities include – National Thermal Power Corporation; Indraprastha Power Generation Company; Haryana Power Generation Corporation; Punjab State Power Corporation; Rajasthan Rajya Vidyut Utpadan Nigam; Uttar Pradesh Rajya Vidyut Utpadan Nigam; Gujarat State Electricity Corporation; Madhya Pradesh Power Generation Company; Chhattisgarh State Power Generation Company; Maharashtra State Electricity Board; Andhra Pradesh Power Generation Corporation; Karnataka Power Corporation; Tamil Nadu Electricity Board; The West Bengal Power Development Corporation; Orissa Power Generation Corporation; and Calcutta Electric Supply Corporation.

2 The private sector entities include – Jindal Power; CPL India; Azure India; Adani Power; Reliance Power; and Tata Power.

3 Available at http://www.urbanemissions.info.

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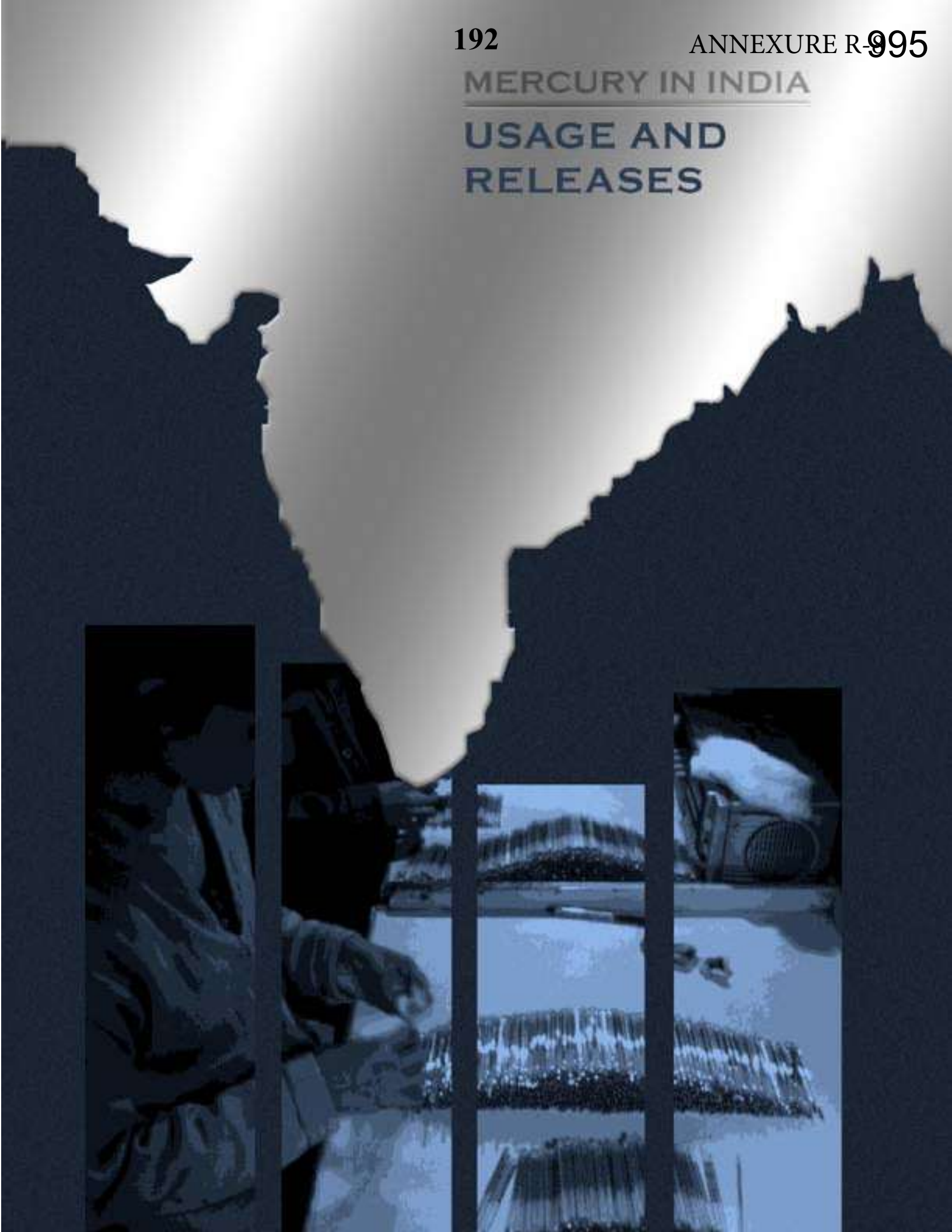
MERCURY IN INDIA

USAGE AND RELEASES



MERCURY IN INDIA

- Mercury's ability to alloy with most metals, liquidity at room temperature, ease of vaporising and freezing and electrical conductivity make mercury an important and very popular industrial metal.

- It has 3,000 industrial uses, primarily in the caustic soda-chlorine production, the manufacturing of thermometers and other instruments and of electrical apparatus, as well as the formulation of various compounds. Paints and industrial instruments are also among the major uses of mercury.

- While developed countries have stopped using the mercury cell process in the chlor-alkali industry because of environmental and health hazards, mercury use in chlor-alkali industry is still very prevalent in India.

- The loss of mercury is 100 per cent in the production of caustic soda, that is, 394 gm/tonne of caustic soda produced. Thus with an annual capacity of 475.6 thousand tonnes in 1999-2000, on an average nearly 150-200 tonnes of mercury is lost in production of caustic soda by the mercury cell process annually.

- The Government of India has banned the commissioning of new mercury cell based chlor-alkali plants since 1991. Thus it has become mandatory for new chlor-alkali plants to instal the modern membrane cell technology

- On an average India produces 10 to 12 million instruments a year including clinical and laboratory thermometers as well as blood pressure monitors (sphygmomanometers), consuming about 15 tonnes of mercury annually.

- Additionally, mercury exists in medical waste and emitted through medical waste incinerators. Even if very expensive cleaners are installed in the stacks, there are still mercury emissions into the nearby ecosystem because mercury, which exists as a contaminant in medical waste, is combusted at high temperatures, vaporises and exits the combusting gas exhaust stack.

CHAPTER 1
USAGE AND RELEASES

Mercury and its compounds have found various usages through the ages. Properties such as the ability to alloy with most metals, liquidity at room temperature, ease of vaporising and freezing and electrical conductivity make mercury an important and very popular industrial metal. Among its current 3,000 industrial uses, its primary uses are caustic soda-chlorine production, the manufacturing of thermometers and other instruments and of electrical apparatus, as well as the formulation of various compounds. Paints and industrial instruments are also among the major uses of mercury.

Mercury is used in electrical switches; it is highly suitable for use in thermometers. Mercury dissolves numerous metals to form amalgams. Mercury is used to make vapour lamps, which are widely used because they are powerful sources of ultraviolet and visible light.

Mercuric oxide is a constituent of mercury batteries.

Mercurous chloride, or **calomel**, is a white, relatively insoluble salt. It is used in calomel electrodes, which are commonly used in electrochemistry, and in medicine as a cathartic and diuretic. Sometimes, calomel is also used as a teething powder for young children.

Mercuric chloride, or corrosive sublimate, is highly poisonous because it is very soluble. It was used for deliberate poisonings as early as the 14th century. It is now used as a disinfectant, in preparation of other mercury compounds, and in anti-fungal skin ointments.

Mercuric sulphide occurs in a red form and an amorphous black form. The red form (vermilion) is used as a colouring material. It is sometimes used to colour tattoos red, but it causes significant skin irritations and obstructions of the lymphatic system.

Mercuric fulminate is an explosive that is sensitive to impact and is used in percussion caps for ammunition and detonators.

Mercurochrome is an organic mercury compound that is used on wounds as an anti-bacterial agent.

Environmental and toxicity concerns have reduced the use and consumption of mercury metal in the industry. Over the years, there has been a phase-out of mercury by various consumers. Several European countries, especially Scandinavian countries, have completely phased out the use of mercury in day-to-day life.

However, concerns about the detrimental effects of mercury are yet to be taken on board in India.

Mercury Usage and Releases in India

Mercury finds a wide variety of applications in India. It is, however, impossible to examine all its applications as part of this study. Therefore, only a few major users are mentioned and discussed here.

The largest consumer of mercury is the chlor-alkali industry, which manufactures caustic soda and chlorine as a by-product using electrolytic process with mercury electrodes. The second-largest consumption of mercury is for the production of electrical apparatus, mercury vapour lamps, electrical switches, fluorescent lamps, etc. Mercury is also used in the manufacturing of instruments, such as thermometres, barometers, etc. Mercury finds application in metallurgy and mirror coating and as a coolant and neutron absorber in nuclear power plants as well. In addition, mercury is used in the health care sector for blood pressure monitoring instruments, feeding tubes, dilators and batteries, dental amalgams and also used in laboratory chemicals like zenkers solution and histological fixatives. The third-largest consumption of mercury in India takes place during the production of mercury-based compounds used as fungicides.

Chlor-alkali Industry

Chlor-alkali production is the manufacturing of caustic soda and chlorine. India's chlor-alkali industry is small in comparison with the rest of the world's production, and it still uses the outdated mercury cell technology extensively. Chlorine and caustic soda, the outputs of this industry, are used as the raw material for industries like paper and pulp, textiles, metal processing, planting, soap, organic solvents, PVC plastics, etc.

It is important to note that chlorine from the caustic soda industry finds a major application in PVC plas-

MAJOR CONSUMERS OF MERCURY IN INDIA

Mercury	Consumers	Amount (estimated)
Elemental mercury	Chlor-alkali industry (Mercury cell process)	100-150 tonnes annually
Elemental mercury	Instrument manufacturing 1. Clinical thermometer 2. Laboratory thermometer 3. Blood pressure monitors 4. Barometers 5. Other instruments	20 tonnes annually
Elemental mercury Mercury oxide Mercury salts	Electrical apparatus manufacturing 1. Electric switches 2. Electric lamps a) Fluorescent lamps b) Mercury vapour lamps 3. Batteries	Data not available
Mercury compounds	Fungicides a) Phenyl mercury acetate b) Methoxy ethyl mercury chloride	Data not available
Mercury oxide Mercury compounds	Other products a) Paints b) Cosmetics	Data not available
Elemental mercury Mercury oxide	Health set-ups a) Drugs and pharmaceuticals b) Dental amalgams c) Others	Data not available

Caustic Soda Usage Pattern ('000 tonnes)			
End Use	**1990**	**1995**	**2000**
Paper/paper board	160	235	300
Miscellaneous	113	133	160
Soaps and detergents	110	115	130
Chemicals	90	105	120
Aluminium	86	110	110
Exports	15	35	93
Rayon grade wood pulp/viscose yarn/VSF	89	89	89
Cotton textiles	77	77	77
Fertilisers	40	50	72
Dyes and intermediates	35	42	50
Pharmaceuticals	31	34	38
Petrochemicals	13	22	35
Demineralisation	16	20	26
Power	16	20	26
Oil drilling	8	10	12
Vegetable oils	8	9	10
Rayon tyre cord	9	9	9
Mineral and metals	4	5	6
Total	**920**	**1,120**	**1,363**

(Source: The Hindu Survey of Indian Industry, 1995.)

tic. Almost 60 per cent of PVC is chlorine compound by weight.[1] Here the growth of PVC, a highly toxic plastic, has been synonymous with the growth of the chlor-alkali industry.

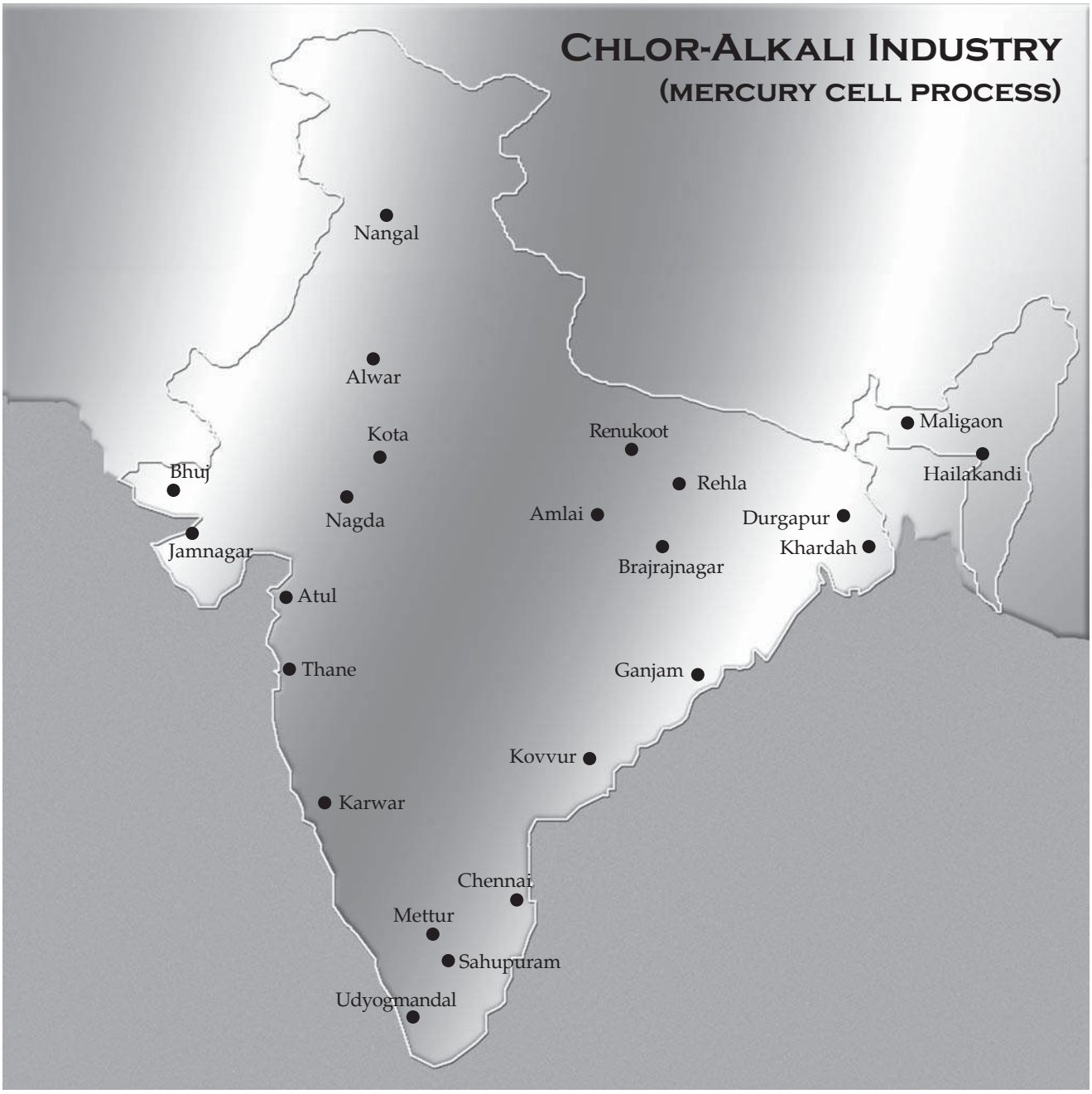
Chlor-alkali is one of the 10 most energy-intensive industry sectors in India. Historically, the caustic soda industry had always been plagued by the problem of high-energy consumption and mercury pollution. The high-energy consumption has a direct bearing not only on a country's most essential resource but also on the cost of production.

As mentioned earlier, caustic soda and chlorine are two basic chemicals being used in various products. The usage pattern of caustic soda is depicted in the table above.

An increase in the production of paper, aluminium, soaps and detergents, chemicals and other miscellaneous items, has naturally led to an increased requirement of caustic soda and chlorine. It should, however, be noted that the caustic soda and chlorine market has been a cyclical one. It is expected that the present trend will continue for a few more years.

On the other hand, chlorine has also shown a tremendous growth pattern over the years. There has been increased production of paper and pulp, PVC, paraffin wax and inorganic chemicals. The present trend of growth will continue, as in the case of, for instance, caustic soda.

Since the first 5-tonnes-a-day plant was opened in



Mettur in Tamil Nadu in 1936, the chlor-alkali industry has grown in India to produce almost 1.51 million metric tonnes in 2000. There are two processes currently used by the chlor-alkali industry, the older mercury cell and the more modern membrane cell. The production of caustic soda by mercury cell started in the 1950s and now accounts for 32 per cent of total caustic soda production.

In the mercury cell process, mercury is used in the basic electrolysis process of splitting sodium chloride (common salt) into chlorine gas and caustic soda, and hydrogen is released.

According to the Alkali Manufacturers Association of India, there are at present 42 caustic soda units functioning in the country with a total installed capacity of 2.23 million metric tonnes as on March 2000, which is about 5 per cent of the world's annual production. Membrane cell process accounts for 66 per cent of the total production while mercury cell accounts for nearly 34 per cent. Of the 42 manufacturing units, 11 units are completely based on the mercury cell processes, 12 units have both mercury and membrane cell processes, 18 units have the membrane cell process alone and there is only one unit using diaphragm cell process.

In other words, there are still 23 units, which wholly or partly use the mercury cell process for caustic-chlorine production. The list of these 23 units along with their respective production processes is given in

The Mercury Cell Process: A typical mercury cell has positively charged electrodes (anodes) made of either high quality graphite or specially coated titanium metal. The anodes are fixed to the vessel of the cell. Mercury, which is liquid at ordinary temperatures, is the negatively charged electrode (cathode). Its place is at the bottom of the cell. However, it is not stationary. The vessel is installed at a slight inclination so that mercury can flow down and be re-circulated with the help of a pump. In between the cathode and the anodes is the brine solution (electrolyte), which is also in constant circulation. The vessel is long and has a rectangular cross section. It is made of steel and has arrangements for chlorine outlet, electricity input and for brine and mercury re-circulation. Each cell has a secondary cell where mercury flows from the primary cell.

In a mercury cell, the following reaction takes place during the passing of electric current under 3 to 4.5 volts:

2 NaCl + electrical energy =	2 Na	+	Cl_2	
sodium chloride	sodium		chlorine gas	
(electrolyte)	(at cathode)		(at anode)	

Chlorine gas moves up and is taken out through pipes. The highly reactive sodium liberated at the cathode, which is mercury, immediately forms sodium mercury amalgam. It flows out to the secondary cell also known as denuder which is a small circular chamber packed with loose inert material, through which de-mineralised water flows. No electricity is used. The following reaction takes place:

2 Na-Hg	+	2 H_2O	=	NaOH	+ H_2	+ Hg
sodium - mercury		water		sodium hydroxide	hydrogen	mercury

Water reacts with sodium and forms sodium hydroxide (caustic soda liberating mercury for re-circulation to the primary cell to act as cathode again and again. Hydrogen is simultaneously liberated.

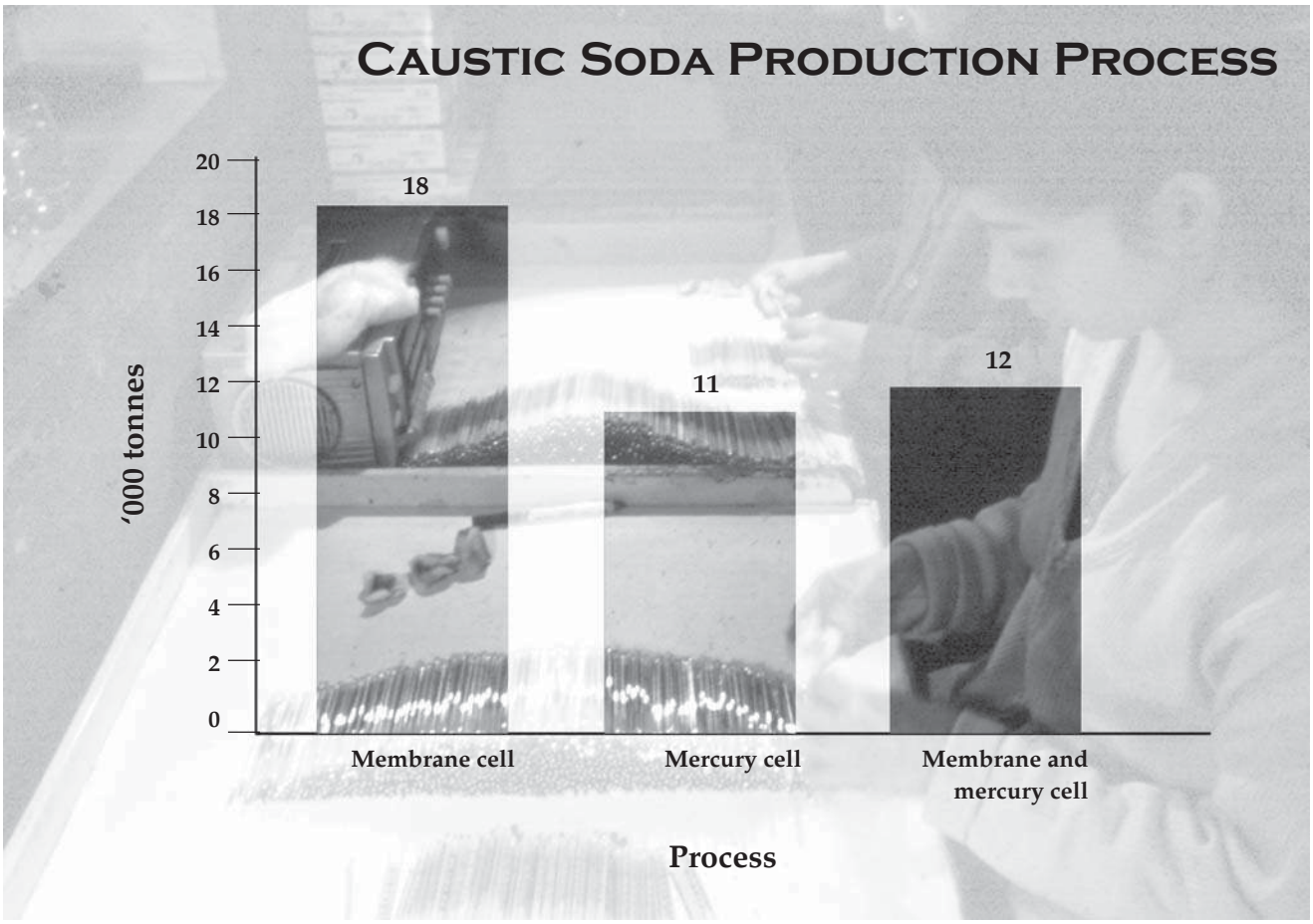
Thus the net reaction of chlor-alkali production can be rewritten as:

2 NaCl + 2 H_2O + electrical energy = 2 NaOH + Cl_2 + H_2

CHLORINE USAGE PATTERN ('000 TONNES)

End Use	1990	1995	2000
Pulp and paper	140	170	210
PVC	115	150	200
Chlorinated paraffin wax	72	80	100
Inorganic chemicals	65	70	75
Organic chemicals	40	45	55
Pesticides and insecticides	38	45	50
Miscellaneous	30	40	50
Water treatment	16	25	42
Pharmaceuticals	15	18	20
Rayon grade wood pulp	10	10	10
Total	**541**	**653**	**812**

(Source: The Hindu Survey of Indian Industry, 1995.)



the Annexure.

The chlor-alkali industry is the largest user of mercury in India; however, the amount of caustic soda-chlorine produced using mercury cells has declined over the years. Though India's chlor-alkali industry is small in comparison to the rest of the world, it still largely uses the outdated mercury cell technology extensively. While developed countries have stopped using the mercury cell process in the chlor-alkali industry, because of environmental and health hazards, mercury use in chlor-alkali industry is still very prevalent in developing countries like India. Mercury consumption by the chlor-alkali sector is at least 50 times (1.5-2 gm/tonne to 150 gm/tonne)[2] higher than the average European consumption.

Alternatives to Mercury Cell

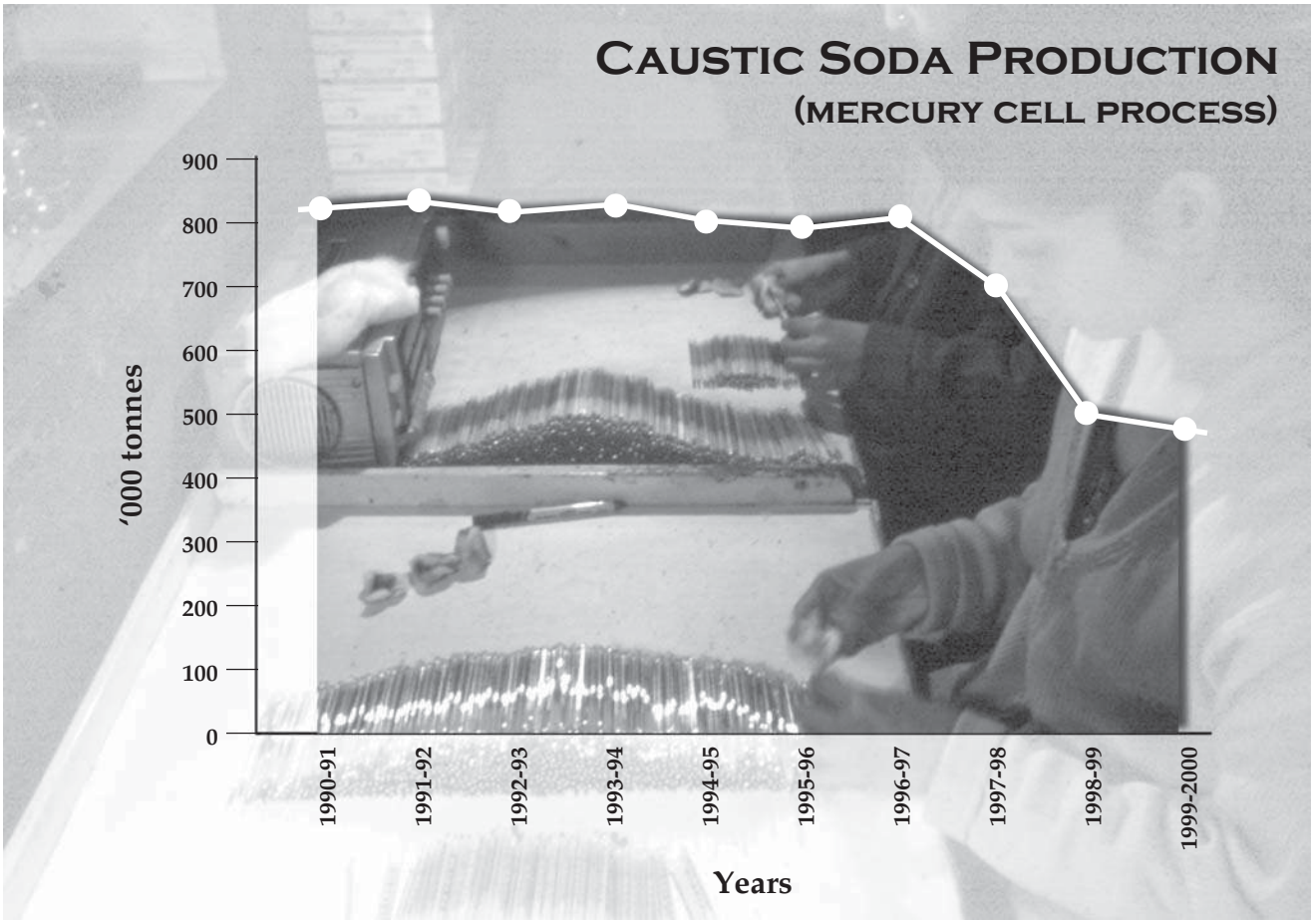
The membrane cell process is an efficient alternative, as there is no usage of mercury and it consumes less energy as well. The only problem highlighted by the industry in the conversion of mercury cell based caustic-chlorine plants to membrane cell process is the involvement of high costs of conversion. The cost of conversion of a 100 tonnes per day mercury cell to a membrane cell plant is Rs 650 million, that is, US$ 13 million. As the industry excuses itself by saying that servicing of this capital will nullify the savings made in energy consumption.

Legislation

The Government of India has banned the commissioning of new mercury cell based chlor-alkali plants since 1991. Thus it has become mandatory that new chlor-alkali plants should be installed with the modern membrane cell technology, which is more energy efficient and less polluting. However, there has been a lack of initiative on the part of the government and industry to do away with the existing mercury cell-based caustic soda-chlorine producing units. The industry, on its part, is demanding soft loans from government institutions to convert these plants. Cuts in the import duty on membrane cells have also been demanded as they have high duty charges.

The trend in the graph also suggests that mercury cell technology is being phased out. The production of caustic soda has reduced from 835 thousand tonnes in 1990-91 to 475.6 thousand tonnes in 1999-2000, thus showing the phasing out of the mercury cell technology by the industry.

The Central Pollution Control Board (CPCB) has published a number of documents between 1981 and 1985 as 'Comprehensive Industry Document Series and



Programme Objective Series' on various aspects of the chlor-alkali industry (*see page 17*). The documents try to review the status of this industry with special reference to the mercury cell process. There have also been case studies on some chlor-alkali units using the mercury cell technology.

The figures in the graph above suggest that consumption of mercury in the mercury cell technology depends on the age and maintenance of the cathodes of mercury in the plants: the old cell house will consume more mercury as compared with the new cell house. Thus, consumption of mercury varies from one unit to another. Mercury consumption in the mercury cell process varies from 75-80 gm to 394 gm per tonne of caustic soda produced.

There is also variation in the mercury consumption in the mercury cell process, depending on the mercury cells, their type and maintenance in the unit. If the cell is new or maintained properly, mercury consumption will be less, and vice versa.

On the basis of the figures given above, we can say that, on an average, around 150 gm of mercury is consumed per tonne of caustic soda produced in India. The total production of caustic soda by mercury cell processes in 1999-2000 was 475.6 thousand tonnes. Thus the consumption of mercury in the mercury cell process in the production of caustic soda was 71 tonnes in 1999-2000.

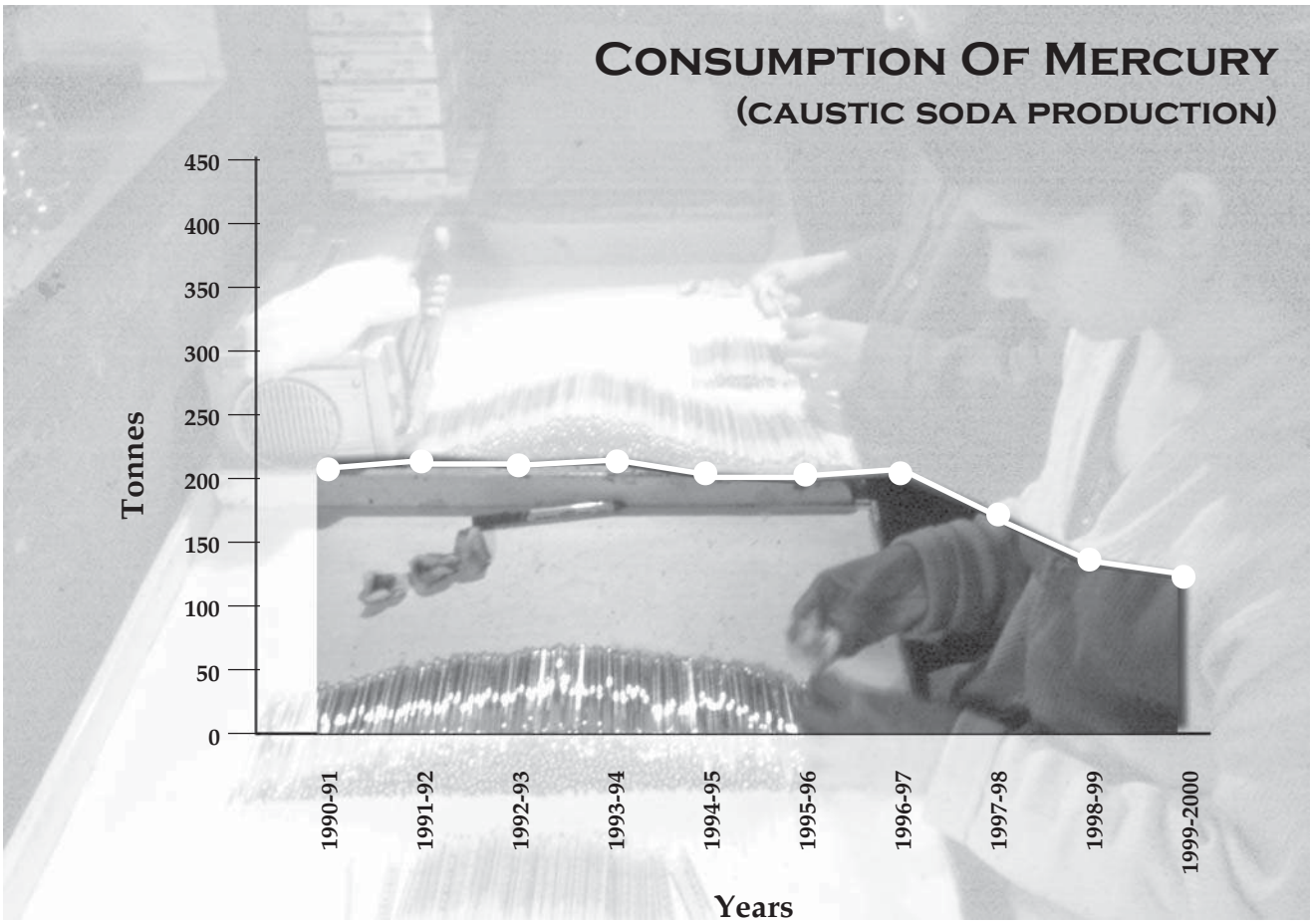
Though it is very difficult to estimate accurate figures, on an average we can say that around 70 to 80 tonnes of mercury is consumed by the mercury cell technology of chlor-alkali production.

The graph on the next page shows reducing mercury consumption in the mercury cell process of chlor-alkali production over time because of mercury's toxicity concerns for the environment and the Government of India's mandate (as mentioned earlier).

Releases from Chlor-alkali Industry

There is an immediate environmental impact from the use of mercury in the mercury cell process. Although mercury does not take part in the reaction, it is always lost to the environment during the process, often as a contaminant in brine sludge. Thus caustic-chlorine production by mercury cell process is declining and production by the membrane cell process is on the rise.

Mercury discharges to land, water and air mostly come from the mercury cell process of the chlor-alkali industry. The quantity of mercury that is consumed in the production of one tonne of caustic soda is nearly the same as the amount lost in the same production process!



Thus it can be said that 90 to100 per cent of the consumed mercury is lost during the production process.

A study released by the CPCB in 1977 suggests that the average mercury consumption of the chlor-alkali industry be targeted as 394 gm/tonne of caustic soda produced.[3]

The loss of mercury is 100 per cent in the production of caustic soda, that is, 394 gm/tonne of caustic soda produced.

MERCURY LOSS FROM CHLOR-ALKALI PLANTS

Source	Gm Hg/tonne NaOH	Percentage
Water	1	0.3
Hydrogen	5	1.3
Products	22	5.6
Handling loss	50	12.7
Unknown*	62	15.6
Brine mud	254	64.5
Total	**394**	**100**

Thus with an annual capacity of 475.6 thousand tonnes in 1999-2000, on an average nearly 150-200 tonnes of mercury is lost in production of caustic soda by the mercury cell process annually.

Another study suggests that about 0.23 kg of mercury is lost per tonne of caustic soda produced.[4]

Thus, on the basis of this study, we can say that on an average 110 tonnes of mercury are lost in the production of caustic soda by the mercury cell process annually.

It is also very important to note that mercury loss from the mercury cell process varies from one plant to another, as it also depends on the age and maintenance of the plant. If the mercury cells are old then the loss will be greater.

Hence, in light of the above discussion, it can be estimated that around 100-150 tonnes of mercury are emitted annually by the chlor-alkali industry.

Process-wise Caustic Soda Production ('000 tonnes)

Year	Membrane	Mercury	Diaphragm	Chemical	Total
1990-91	115.8	835.0	66.2	1.1	1,018.0
1991-92	155.4	845.9	52.1	0.9	1,054.4
1992-93	220.0	825.8	50.6	5.3	1,101.7
1993-94	232.2	831.9	44.5	6.7	1,115.3
1994-95	356.0	796.0	50.3	5.0	1,207.4
1995-96	491.2	772.6	41.7	3.2	1,308.7
1996-97	527.7	789.6	3.3	-	1,320.7
1997-98	740.0	676.5	3.0	-	1,419.5
1998-99	975.4	514.9	-	-	1,494.8
1999-2000	1,035.4	475.6	-	-	1,514.0

CPCB Documents

Name	Industry	Mercury Consumption
Comprehensive Industry Document Series: 1981-82: 'Minimal National Standards Caustic Soda (Mercury cell) Industry'	Basis of mercury supplied to industry	394 gm/tonne caustic soda produced
Programme Objective Series: 1985: 'An Assessment of Mercury Pollution Problem at Kothari Industries Ltd, Chennai'	Kothari Industries Ltd, Chennai	75-80 gm/tonne caustic soda produced
Programme Objective Series: 1982-83: 'Mercury Transfer to Environment from Chlor-alkali Industry: A Case Study'	Hindustan Heavy Chemicals, Khardah, West Bengal	150 gm/tonne caustic soda produced

Instrument Manufacturing Industry

Mercury is used in many medical and industrial instruments for measurement and control functions. These instruments include all types of thermometers such as clinical, laboratory and meteorological ones, as well as blood pressure monitors (sphygmomanometers) and barometers.

Mercury has been used in the instrument manufacturing industry because of its unique physical and chemical properties. Mercury's linear expansion is uniform, between -39 to 359 degrees and, if mixed with 8 per cent of thallium, its coefficient of expansion expands to -55 to 600°C. Beside these usages, mercury is used in barometers to measure atmospheric pressure. These instruments are found in major research laboratories, hospitals and clinics, school and college laboratories, meteorological observatories, clinical thermometers and in some common household items.

Thermometer Industry

The thermometer industry in India is essentially a small sector industry with a capacity of 40,000 to 50,000 pieces per month.

Clinical Thermometers

Mercury was found to be highly suitable for use in clinical as well as other types of thermometers because it does not moisten glass and has a uniform thermal expansion, though there are very serious concerns

about the impact of its disposal practices (water pollution and occupational health). Clinical thermometers are largely manufactured in the small-scale sector in India. The industry is localised in north India and is based in Delhi and in the nearby towns of Aligarh, Ambala, Sonepat, etc (*see box below*)

On an average, around 425 thousand clinical thermometers are produced in India in a month, which means 5 million annually. A clinical thermometer contains approximately 0.61 grams of mercury. Thus with an annual capacity of 5 million clinical thermometers, about 3.1 tonnes of mercury are required annually for their manufacture.

Laboratory Thermometers

Laboratory thermometers are bigger in size than clinical thermometers and are used in various laboratories of educational and research institutions for research purposes. The laboratory thermometer industry is based in Delhi, Ambala, and few other places in India, mostly in the unorganised sector.

On an average, about 300,000 laboratory thermometers are manufactured annually in India. A laboratory thermometer contains approximately 3 gm of mercury. Thus, about 900 kg of mercury is consumed to produce 300,000 laboratory thermometers in one year.

Clinical Thermometer Manufacturers

Company	Production (pieces per month approx)
Unitech Thermometers (Delhi)	40,000-50,000
Hanimax Thermometers (Delhi)	50,000-60,000
Hindustan Thermometers (Delhi)	50,000-60,000
Wilkho Thermometers (Delhi)	30,000-35,000
MCP (Medical Products) (Delhi)	40,000-45,000
Locally made (unorganised sector) (Delhi)	25,000-30,000
Hick Thermometers (Aligarh)	60,000-70,000
Maharana Thermometers (Sonepat)	50,000-55,000
Locally made (unorganised sector) (Ambala)	50,000-60,000
Total	**395,000-465,000**

(Source: Personal communication)

Laboratory Thermometer Industry

Place	Production (pieces per year approx)
Delhi	100,000
Ambala	100,000
Other parts of India (unorganised sector)	100,000
Total	**300,000**

(Source: Personal communication)

Blood Pressure Monitors (Sphygmomanometers)

Although many liquids could be used in pressure measuring devices, mercury is used in sphygmomanometers because its high density requires less space. Blood pressure monitors, one of the important instruments used in the health care sector, are found in all hospitals and clinics. They are used to measure and monitor the blood pressure of the patients, especially heart patients. These instruments are also being used in households and gaining importance day-by-day. Like the other thermometer companies, blood pressure monitor making companies are mostly localised in and around Delhi.

In all, about 200,000 blood pressure monitoring instruments are manufactured annually in India. A blood pressure monitor contains approximately 60 gm of mercury. Thus about 12,000 kg of mercury is consumed to produce 200,000 blood pressure monitoring instruments annually.

Barometers

Barometers are one of the important instruments used in meteorological departments, and can also be found in weather stations and educational and research institutions. Barometers are used to measure atmospheric pressure and are helpful in analysing and forecasting weather. The barometer manufacturing industry is based in Kolkata where the company National Instruments produces them.

Generally all the barometers manufactured are of one standard size and contain approximately 5 kg of

Sphygmomanometer Industry

Place	Production (pieces per year approx)
Delhi	100,000
Other parts of India	100,000
Total	**200,000**

(Source: Personal communication)

mercury. On an average, around 25 pieces a year are manufactured in India, generally on the basis of orders given by various institutions. Thus, about 125 kg of mercury is annually required in the manufacturing of barometers.

Thus, the instruments manufacturing industry is a major consumer of mercury in India. It will take time to replace mercury by a viable alternative in this industry. On an average, the instrument manufacturing industry consumes around 16 tonnes of mercury per year.

Alternatives

There is a trend to shift towards safer mercury-free alternatives to these measuring instruments as these instruments have a short life span and their disposal means the release of toxic mercury in the environment. Digital measuring instruments are the best available al-

Glass Thermometer Manufacturing Process

The production of glass thermometers begins by cutting glass tubes to the required length and size. Next, either a glass or metal bulb, used to hold the mercury, is attached to the base of the tube. The tubes are filled with mercury in an isolated room. A typical mercury filling process is conducted inside a bell jar. Each batch of tubes is set with open ends down into a pan, and the pan set under the bell jar, which is lowered and sealed. The tubes are heated to about 200°C, and a vacuum is drawn inside the bell jar. Mercury is allowed to flow into the pan from either an enclosed mercury addition system or a manually filled reservoir.

When the vacuum in the jar is released, the resultant air pressure forces the mercury into the bulbs and capillaries. After filling, the pan containing the tubes is manually removed from the bell jar. Excess mercury in the bottom of the pan is re-filtered and reused in the process.

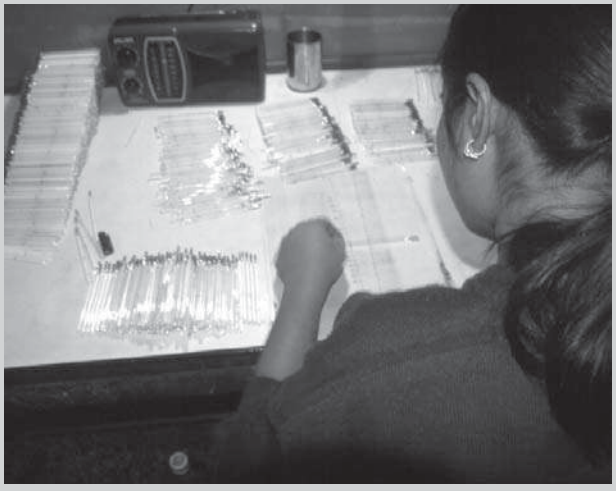
Excess mercury in the tube stems is forced out the open ends by heating the bulb ends of the tubes in a hot water or oil bath. The mercury column is shortened to a specific height by flame heating the open ends. The tubes are cut to a finished length just above the mercury column, and the ends of the tubes are sealed. All this is done manually. Lastly, the temperature scale is etched on to the tube, completing the assembly.

Visit to a typical thermometer factory, Delhi

The thermometer factories in Delhi are generally located in residential areas. At first sight, the factory that we went to visit looked like a residential house. The factory is on the ground floor and the proprietor lives upstairs.

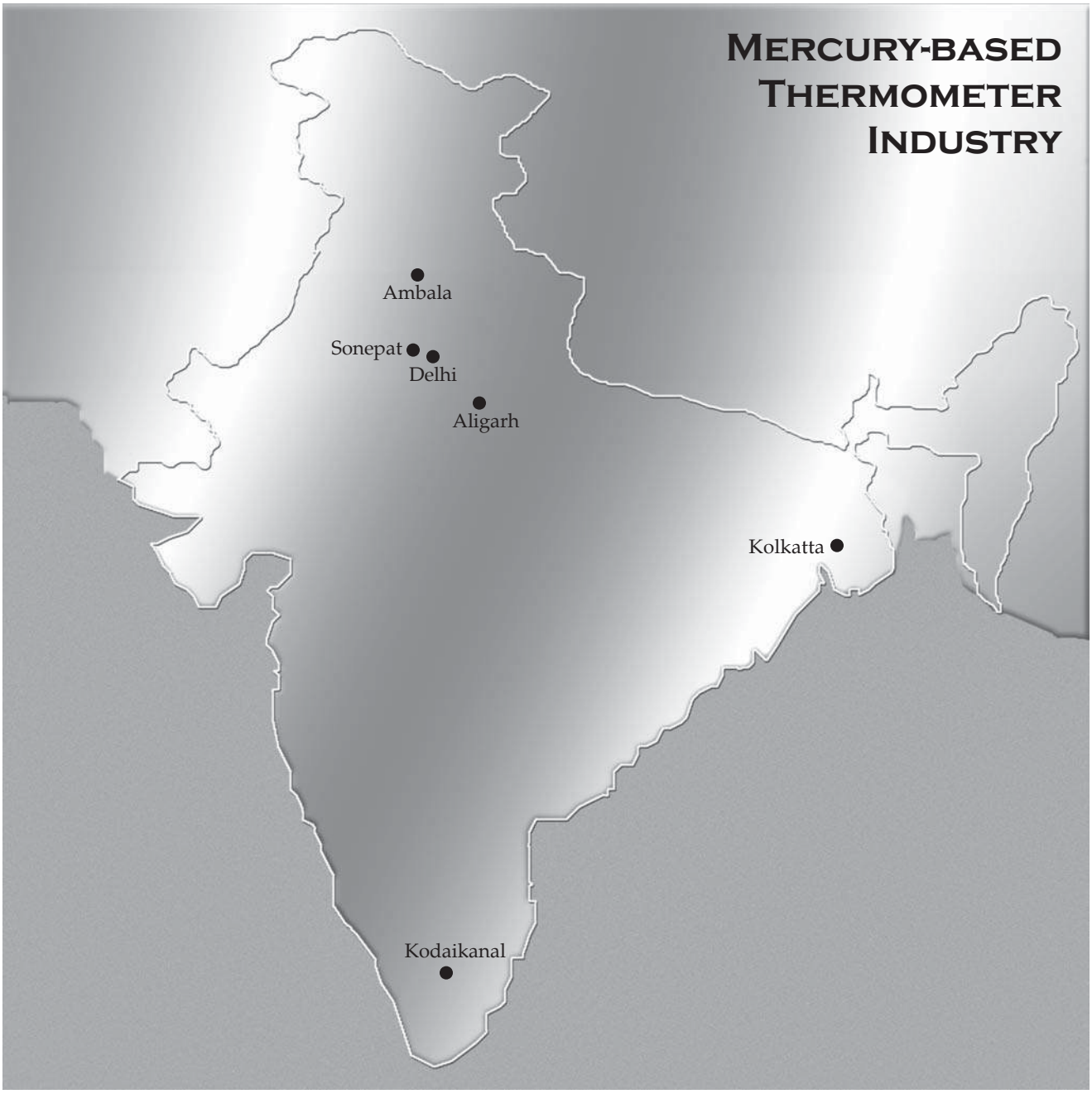
The location of this thermometer factory clearly highlights the problem of mushrooming of small-scale industries in residential areas. Both liquid and solid wastes find their way into the municipal waste facilities.

There has been a tremendous decline in the growth of these industries because, since the early 1990s, China has been dumping its mercury-based clinical thermometers in the Indian market. Chinese thermometers are said to look attractive, be accurate and, above all, be cheaper than Indian thermometers. The production cost of these Chinese thermometers is said to be Rs 6 as compared to the Indian price of Rs 10-15. This is because they do not have to import raw materials such as mercury and fine glass, like India has to do. Part of India's such imports come



from China!

There is now a trend among producers to import these cheap Chinese thermometers and to market them under their own brand names rather than manufacturing them on their own, because importing remains cheaper than producing.



ternative to mercury-based instruments and have been used widely in the developed countries. They are very costly as compared to the mercury-based instruments but prove their cost-effectiveness in the long run, as they are very accurate and have longevity. Thus, the cost factor would even out in the long run.

Releases from Instrument Manufacturing Industry

The weight of mercury in each of these instruments is dependent on the type and grading. Average mercury content is 1 gm per thermometer, a range of +/- 0.0012 per cent. There is a breakage rate of 30 to 40 per cent in the manufacturing of these instruments, especially thermometers.

On an average India produces 10 to 12 million instruments a year including clinical and laboratory thermometers as well as blood pressure monitors (sphygmomanometers), consuming about 15 tonnes of mercury annually. Due to breakage during the manufacturing process of these instruments, broken glasses with trace amounts of mercury are also accumulated in tonnes. Manufacturing units use all the traditional and modern methods to recover mercury from these broken glass pieces. If not properly recovered, however, there is a grave danger of mercury entering our environment and bodies, as the broken glass pieces can land up in municipal waste dumps and in drains, causing

Mercury Thermometer Factory, Kodaikanal

In 1977, a second-hand mercury thermometer factory owned by Cheseborough Ponds was exported from the USA and bought by Ponds India Ltd. It was located in the southern Indian town of Kodaikanal, Tamil Nadu. The town is a famous hill resort and host to a few dozen boarding schools.

The thermometer factory changed hands in 1997, when Hindustan Lever Ltd bought it from Ponds India Ltd. Hindustan Lever is 51 per cent owned by Anglo-Dutch multinational Unilever. According to Hindustan Lever Ltd, mercury for the thermometers was imported primarily from the United States; the finished thermometers were exported back to the United States and then further distributed to markets in Germany, the UK, Australia, Spain and Canada.

The factory, now closed, was situated at an altitude of 2,000 metres amidst the flourishing tropical montane forest of the Western Ghats, one of the world's biodiversity hotspots. To the east of the factory wall, the land slopes steeply to the Pambar Shola forest, which was recently designated as a sanctuary by the Tamil Nadu government. The company secured a special exemption from the Tamil Nadu government to establish its factory on the ridge of the Pambar Shola slope, on the grounds that the factory was non-polluting.

It was one of the largest thermometer manufacturing plants in the world, producing 100,000 to 150,000 pieces a month, thus consuming nearly 75 kg of mercury per month (or 900 kg of mercury annually). Till its closure it manufactured around 165 million thermometers. The plant's operations were stopped because it was carrying illegal dumping of its mercury-bearing waste in the surroundings. The slopes where the wastes are dumped are part of the Pambar Shola watershed, draining water through the Pambar River, which eventually ends up in the plains

leading up to the temple city of Madurai.

Over the years, the factory used these slopes as a dumping ground for all kinds of wastes, including broken mercury-containing thermometers and other potentially mercury-contaminated wastes.

A few years ago, production fell owing to declining demand in Western markets where environmental and public health concerns over mercury have led to the replacement of mercury thermometers by non-mercury thermometers.

At the factory, the highly hazardous mercury-bearing wastes were stored haphazardly in open and torn sacks, with the contents spilling onto the workspace, frequented by barefooted and unprotected workers. Reports gathered from several workers indicate serious health effects including a variety of neural disorders, tremors, infertility and loss of appetite.

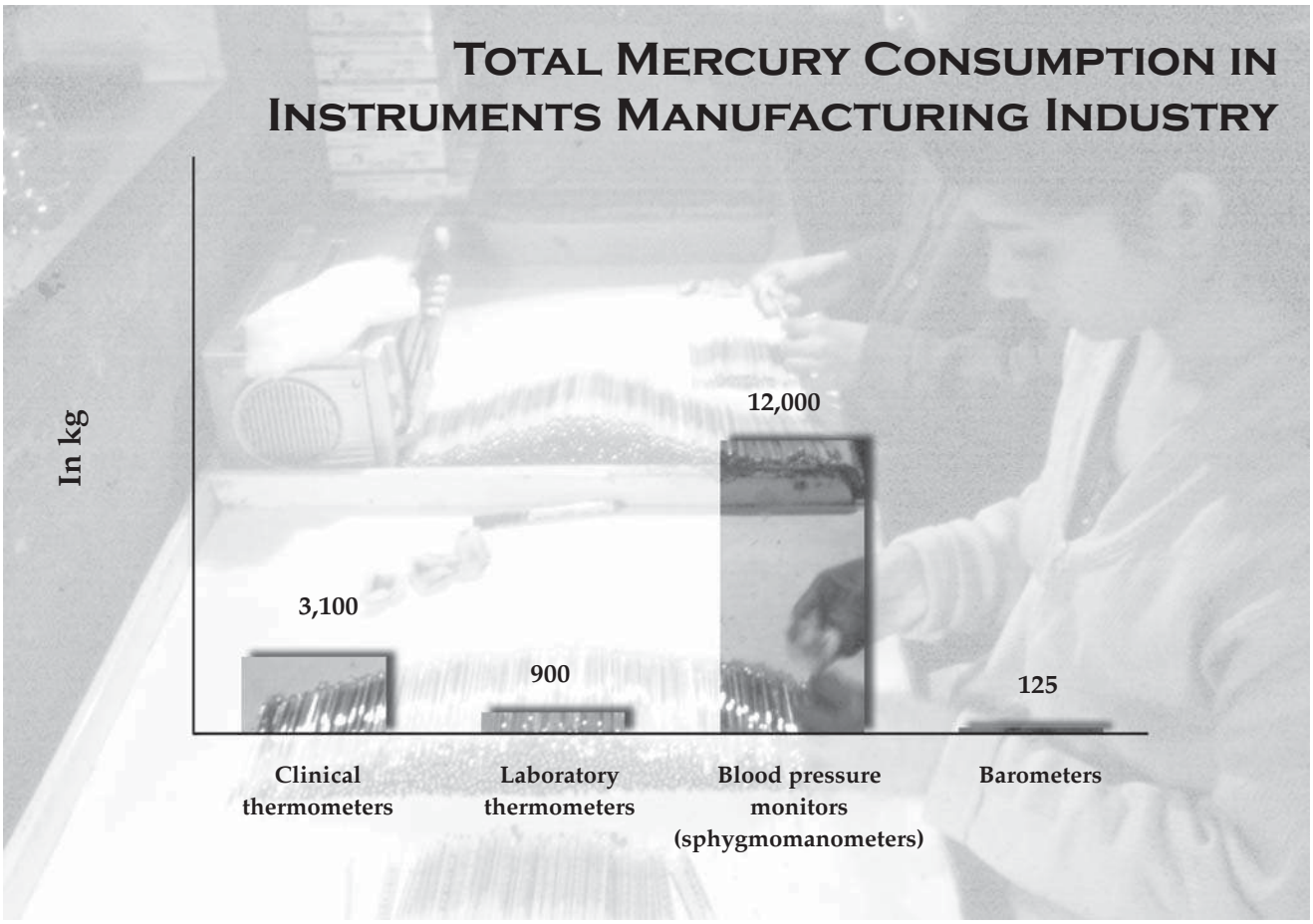
According to the waste merchant at the dumpsite, children with bare feet and hands used to recover half a litre of mercury, while a local merchant purchased broken thermometers containing hazardous waste for less than five cents per kilo. Many of the broken thermometers were stamped with Baxter or Medline, two US medical product suppliers.

serious threat to both surface and ground water sources.

The Kodaikanal thermometer factory has highlighted the harm a mercury-based thermometer plant can do to the environment. The Hindustan Lever Ltd thermometer plant has been guilty of dumping tonnes of broken glass waste (with traces of mercury in it) in the local forest and of selling some of it to the local waste dealers. Broken glass with traces of mercury was not stored properly; it was kept in the open, resulting in washing of mercury during the rains and draining into nearby streams and rivers. The company, in its report to the Tamil Nadu Pollution Control Board, assesses the amount of mercury released into the environment from its factory site in Kodaikanal at 539 kg (stating a statistical variance of 'between 43 kg minimum to 1,075 kg maximum').[5]

Electrical Apparatus Manufacturing Industry

Mercury is widely used and consumed in the electrical apparatus industry. Though the actual quantity used is not very large, usage-wise mercury plays a major role. Mercury is one of the best electrical conductors among metals and is used in many areas of electrical apparatus manufacturing. In India, the main manufactured apparatuses are electric switches and lamps.



Total Mercury Consumption in Instruments Manufacturing Industry

Name	Unit (in kg)	Used/unit
Clinical thermometers	3,100	0.61 gm
Laboratory thermometers	900	3 gm
Blood pressure monitors (Sphygmomanometers)	12,000	60 gm
Barometers	125	5 kg
Total	**16,125**	

Electric Switches

Mercury switches are used in thermostats and some alarm type clocks. Electric switches containing mercury have been manufactured since the 1960s with approximately 1 lakh produced annually. No information on locations of manufacturers, of electric switches that specifically contain mercury, is available. The electric switch is an important household item; its presence is necessary in every building and house where electricity is available. Mercury switches are also used in automobiles, thus playing an important part in the automobile industry.

Electric Lamps

Electric lamps containing mercury include fluorescent, mercury vapour, metal halide and high-pressure sodium vapour lamps. These lamps are used for both indoor and outdoor applications including heat lamps, lights of high-ceiling rooms, film projection, photography, dental examinations, photochemistry and street lighting. These lamps are both manufactured in India as well as imported. The main mercury-containing electric lamps manufactured in India are:

Fluorescent lamps: All fluorescent lamps (both tubes and bulbs) contain elemental mercury in the form of mercury vapour, put inside the glass tube. Mercury has a unique combination that makes it the most efficient material for use in fluorescent lamps. In fluorescent lamp production, pre-cut glass bulbs are washed, dried and coated with liquid phosphorus emulsion that deposits a film on the inside of the lamp bulb. The glass bulb is then exhausted on exhaust machines and approximately 15 to 250 mg of mercury is added. Some of

PRODUCTION OF FLUORESCENT LAMPS

Years	Number (in millions)
1980-81	2.36
1985-86	3.55
1990-91	5.07
1993-94	6.36
1994-95	7.71
1995-96	9.77
1996-97	11.36
1997-98	14.50
1998-99	13.23
1999-2000	12.49

(Source: Monthly Abstract of Statistics, Central Statistical Organisation, Govt of India.)

the mercury combines with the emulsion on the interior of the bulb and remains there over the life of the bulb. The glass bulb is filled with an inert gas and sealed. After the lamps are sealed, metal bases are attached to the ends and are cemented in place by heating.

All fluorescent lamps operate by discharging an electric arc through mercury plasma enclosed in a glass tube. The ultraviolet (UV) photons emitted by the de-excitation of mercury atoms are converted to visible light by a phosphor coating on the inside of the glass tube.

Fluorescent lamps save a lot of energy and last 10 to 20 times longer than incandescent light bulbs. They provide the same high-quality light with less than one-quarter the electricity consumption.

The major companies manufacturing fluorescent lamps in India are Philips, Laxman Sylvania, Osram, Surya, Crompton Greaves, GE Lightings and some local companies including ABBA Lightings, etc.

Mercury vapour lamps: Mercury and metal halide lamps consist of an inner quartz arc tube enclosed in an outer envelope of heat resistant glass. The quartz arc tube contains a small amount of mercury ranging from 20 mg in a 75-watt lamp to 250 mg in a 1000-watt lamp. According to the manufacturers, no other substance has been found to replace mercury. However, this needs to be re-examined. High-pressure sodium vapour lamps consist of an inner, high purity alumina ceramic tube enclosed in an outer envelope of heat-resistant glass. The ceramic tube contains a small amount of sodium-mercury amalgam, ranging from 8.3 mg of mercury in a 50-watt lamp to 25 mg in a 1000-watt lamp.

The major companies manufacturing mercury vapour lamps are Philips, Laxman Sylvania, Osram, Surya, GE Lightings, Crompton Greaves; local companies include ABBA Lightings, etc.

Battery Production

A battery is a device that converts chemical energy into electrical energy. The battery is made up of an anode (positive electrode), a cathode (negative electrode) and an electrolyte. Different materials may be used to make the anodes and cathodes, such as zinc, mercury oxide and silver oxide, lead acid, carbon and nickel and cadmium.

Mercury has been used in batteries for two purposes. The first use is as a component in the zinc-mercury amalgam used as the anode in mercury oxide and alkaline batteries and as a component in the cathode of mercury oxide batteries. Its second use is to inhibit side reactions and corrosion of the battery casing material in carbon-zinc and alkaline batteries. Most primary batteries and some storage batteries contain mercury in the form of mercury oxide (HgO), zinc amalgam (Zn-Hg), mercuric chloride ($HgCl_2$), or mercurous chloride (Hg_2Cl_2).

Mercury batteries have a zinc anode, mercuric oxide cathode, and an electrolyte of an aqueous solution of potassium hydroxide or sodium hydroxide. The cell has a solid cathode of mercuric oxide and contains 33 to 50 per cent mercury or mercuric oxide. This cannot be reduced without proportionally reducing the energy content of these batteries. The battery cell contains a caustic electrolyte and can have the same adverse health effects as alkaline batteries.

Mercuric oxide batteries fall into two categories: button cell and larger sizes. Most mercuric batteries sold for personal use are button cells. Button cells are small, circular, relatively flat batteries that are used in transistorised equipment, walkie-talkies, hearing aids, electronic watches and other items requiring small batteries.

Mercuric oxide batteries are widely used for applications including medical, industrial and military applications and other non-household devices.

The major companies manufacturing dry cell and other types of batteries are: Eveready, BPL, Novino, Nippo, Panasonic, Energiser, etc, though multinational companies have started producing mercury-free batteries. In India, there are companies that make batteries on a very small scale, and the use of mercury in their operations is unaccounted.

Releases from Electrical Apparatus Manufacturing Industry

There has been no documented case of mercury release from the production process of these industries, though there could be breakage rate in production of fluorescent and mercury vapour lamps. The process of mercury recovery from broken glasses, as also their way of disposal, can release mercury in the environment.

Fungicide Industry

A pesticide that kills fungi is called a fungicide. Fungicides are based on the broadly toxic elements; cop-

per, mercury and sulphur were among the earliest agrochemicals. Copper sulphate and mercury chlorides have been used since the 18th century. Though synthetic systemic compounds have largely superseded them, mercury-based compounds are still an integral part of the pesticide industry. Diseases such as rusts, mildew and blights spread rapidly once established. Fungicides are thus routinely applied to growing and stored crops as a preventive measure, generally as foliar sprays or seed dressings.

Organo-mercurial compounds are used as fungicides. In India, mercury is used to produce organo-mercurial compounds and their production constitutes the third-largest consumption of mercury in the country. Farmers use fungicides for seed dressing.

In India various organo-mercurial compounds are sold in the market under different brand names, for instance Ceresan, Aretan, Agallol, to be used as fungicides. Though these are very effective in seed treatment, various studies have proved that mercury in the fungicide enters seeds when treated, further persists in the plant tissues, translocates in the food crop in trace amounts and finally finds its way into the human food chain. The impact of seed dressing is enormous since it is applied to a large volume of seeds, which are subsequently sowed over millions of acres, thereby causing widespread dispersal of mercury.

Some typical compounds of this category are methyl mercury nitrite, methyl mercury dicyandiamide, methyl mercury acetate, phenyl mercury acetate (PMA), ethyl mercury chloride, methoxy ethyl mercury chloride (MEMC), etc.

India has banned the use of some organo-mercurials like phenyl mercury acetate (PMA), ethyl mercury chloride, and restricted the use of methoxy ethyl mercury chloride (MEMC) as fungicides, because they get accumulated into the plants through treated seeds. The mercury poisoning incident in Iraq, in 1956, is well known worldwide, where people consumed bread made of wheat, treated with methyl mercury acetate. The wheat was treated to sow and by mistake it came to Iraq through relief.

In India all the fungicides in use have to be registered under the Insecticides Act, 1968. The mercury-based compounds used as fungicides registered on a regular basis under section 9(3) of the Insecticides Act, 1968, are:

- Ethyl mercury phosphate
- Ethyl mercury chloride*
- Ethoxy ethyl mercury chloride
- Mercuric chloride
- Methoxy ethyl mercury chloride (MEMC)*
- Methyl mercury chloride
- Phenyl mercury acetate (PMA)*
- Phenyl mercury chloride
- Phenyl mercury urea
- Tolyl mercury acetate

(*Only these three are manufactured in India.)

The use of phenyl mercury acetate (PMA) has been banned in India since 1973, with effect from 1.1.73, but it was still produced for export. In 1999, its manufacturing was also banned in India with effect from 26.3.1999.

The use of methoxy ethyl mercury chloride (MEMC) has been banned since 2001 with effect from 17.7.2001, by the Ministry of Agriculture, except for seed treatment of potatoes and sugarcane in the country.

The data provided by the Directorate of Plant Protection, Ministry of Agriculture, (*in the table below*) shows that in the last five years no organo-mercurial compounds have been produced, imported or exported to India, though consumption is on a slight increase. It leads to the conclusion that there is a large stockpile of these compounds in India. The Directorate of Plant Protection states that "as per the FAO inventory of stockpiles of obsolete pesticides in India, 3,346 tonnes of stock are present". There is a possibility that a large quantity of these would be organo-mercurials.

The data given by the Ministry of Environment and Forests shows that India has a stockpile of 44 tonnes

Organo-mercurial Compounds

	1995-96	1996-97	1997-98	1998-99	1999-2000
Production (in MT)	0	0	0	0	0
Import (in MT)	0	0	0	0	0
Export (in MT)	0	0	0	0	0
Consumption (MEMC) (in MT)	81	73	82	87	85

(Source: Dr P.S. Chandurkar, Plant Protection Adviser, Directorate of Plant Protection, Ministry of Agriculture, Govt of India)

of organo-mercurial compounds and there is restricted use of these stocks in agriculture. How is this possible when the annual consumption figures given by the Directorate of Plant Protection are of 80 tonnes on average?[7] There seems to be a huge data gap in production and consumption figures between the various governmental agencies responsible for handling organo-mercurial compounds.

Mercury in Health Set-ups

Mercury is widely used in the health care sector. Mercury and mercury-containing products are used in patients' areas and pathology laboratories, in clinical procedures and in medicines. At least 20 different medical products contain mercury and many mercury-containing solvents and degreasers are found in laboratories, housekeeping departments, and kitchen and maintenance areas. Mercury is an ingredient in some proprietary formulas used to manufacture medical and industrial supplies.

This section tries to view the role of mercury in the health care sector in India.

Source of Mercury in Hospitals

1. Thermometers and thermostats
2. Blood pressure monitors (sphygmomanometers)
3. Dilators and batteries
4. Dental amalgams
5. Laboratory chemicals like zenkers solution and histological fixatives

Hospitals and clinics, big or small, are the largest consumers of these instruments.

The industrial and chemical uses of mercury are manifold in the medical community: besides the instruments, hospitals have mercury in fluorescent and high-intensity lamps, in thermostats and switches and in a variety of generators, manometers and batteries. Non-medical uses of mercury include cleaning solutions, preservatives, paints and anti-fouling agents for wood and other surfaces. Beside these instruments and non-medical uses, other health care sectors that use mercury or mercury-based products are:

Dental amalgams: Mercury is used in dentistry, primarily in amalgam fillings for teeth. The dentist drills out the cavity and then fills the cavity with amalgams. Dental amalgams are typically 40-50 per cent elemental mercury by weight. Mercury has the unique property of mixing well with various metals. In dental amalgams, mercury is mixed with copper, gold and silver to form an amalgam. Dental amalgams represent a significant source of overall mercury exposure and are probably the population's major source of elemental mercury vapour.

Medicines: Mercury and mercury-compounds have been used in the manufacturing of medicines but the details are not known. Ayurveda in India uses mercury for the treatment of several diseases as a part of '*Rasayan Shastra*' or metal therapy. Using mercury in medicines has cured cases of blood cancer and multiple sclerosis. The therapeutic powers of metals like mercury have been the object of a constant fascination for the alchemists of the ancient and medieval world.[8]

Ayurveda and Rasathanthra (treatment using mercury): The Dravidians adopted this method of treatment in the Samhitha period. This treatment involves the purification of metals like gold, iron, etc, that later take the form of medicines. *Rasahridayathanthram* by Vagwadacharya is the first Sanskrit work on Rasathanthra. There are references to the uses of *rasa* (mercury) metals and gems in the Charaka and Sushrutha samhithas. It is ascertained that mercury has the ability to make the body strong and sturdy.[9]

Mercury in Other Products

Mercury is found in a variety of household products, including batteries, fluorescent light tubes and bulbs, electrical switches and thermometers. The use of mercury in many of these applications is regulated by government agencies or controlled voluntarily by industry groups. A brief summary of product-specific use of mercury:

Paints

Producers have progressively discontinued the use of mercury in most paints sold in the market. Mercury was earlier used as a biocide in two categories of paints. Marine anti-fouling paints utilised mercury (mercury oxide) as an agent to hinder the growth of algae after the paint was applied to the bottom of the ships. Latex paints used a variety of mercury compounds such as phenyl mercury acetate (PMA), as a biocide after its application as well as a preservative to control microbial growth in the paint can during storage.

Cosmetics

Mercury compounds were previously used in skin bleaching creams and as preservatives in a variety of cosmetics. Mercury is used as a preservative, especially in cosmetics intended for use in the area of the eye. Besides this, mercury sulphide, a red-coloured powder, is also present in the traditionally used sindoor, used by Hindu women in India. Mercury sulphide is also used in red colour making, especially during the festival of Holi.

Air Emissions

Mercury is released in the air by burning fossil fuels such as coal, mineral oil, incineration as well as goods and items containing mercury in trace amounts. This process does not use mercury, but mercury gets released and is further accumulated, as mercury remains persistent in the environment.

The major contributors of adding mercury to the environment via air emissions are:

- Coal fired thermal power plants.
- Medical waste incinerators.
- Municipal waste incinerators.

Thermal Power Plants

India is the third-largest producer of coal in the world. Coal is the most abundant fossil fuel resource and is the primary fuel for energy in India. The coal reserves of India have been estimated, by the Geological Survey of India, to be 2,11,593.61 million tonnes as on January 1, 2000.[10]

Coal is the dominant energy source in India, accounting for more than half of the country's requirements. Seventy per cent of India's coal production is used for power generation, with the remainder being used by heavy industry and public use. Domestic supplies satisfy most of India's coal demand.

In India, the power and steel sectors, at present, are the major consumers, taking 89 per cent share of the total coal produced. The installed capacity of coal-based electricity generation has increased from 800 MW in 1973 to 50,000 MW in 1994-95 and is expected to go up by another 50,000 MW in the next 15 years. Thermal power plants are currently using about 220 million tonnes of coal per year, which account for about 75 per cent of the total coal production. The demand of coal for thermal power stations will increase year after year. There are around 75 thermal power plants in the country, which currently generate around 75 per cent of India's power.[11]

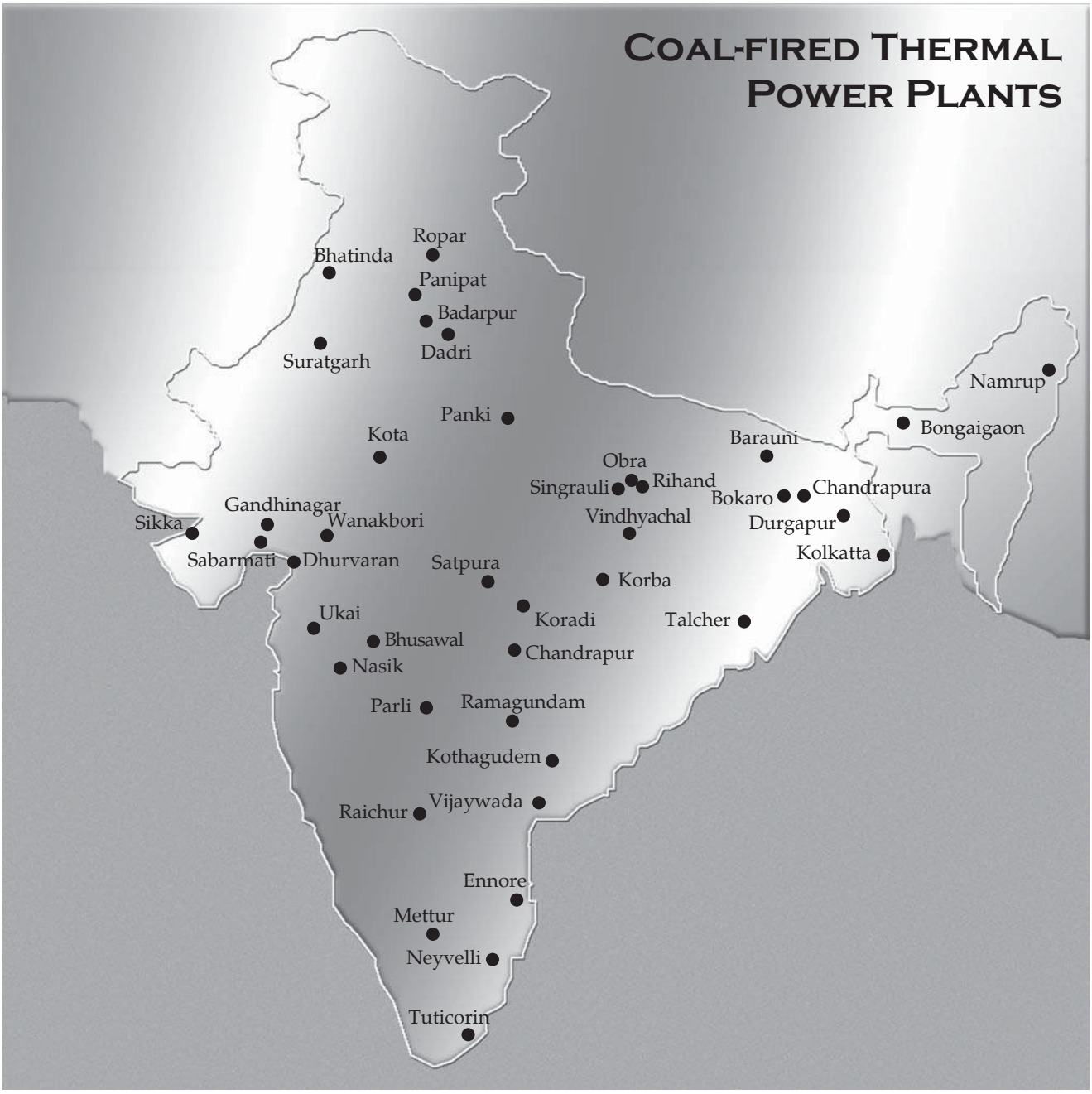
Most of India's coal is characterised by low trace element concentration. The quality of coal depends upon its rank and grade. Indian coal is of mostly sub-bituminous rank, followed by bituminous and lignite (brown coal). The ash content in Indian coal is approximately 35 to 55 per cent.[12]

Emissions from Coal Burning: The smokestacks of thermal power plants spew a broad range of toxic substances into the air. These vapours include known carcinogens such as mercury, heavy metals, dioxins, furans and PCBs. During combustion, many of these metals like Fe, Al, Mn, Co, Ni, Cd, Hg, Pb, Zn, Cd, As, etc, volatilise at furnace temperatures, and toxic and harmful quantities of these elements are released in the environment. Coal contains mercury as a natural component along with other elements in trace amounts (0.04-0.7 mg/kg).[13]

Given the large quantity of coal burned in thermal power plants as well as in industrial, commercial and residential burners, considerable amounts of mercury are released into the environment.

Thermal power plants are the second largest source of mercury emissions in India. As the coal is combusted in the utility boiler, mercury is vaporised and released as a gas. Pollution controls employed by utilities to curb other pollutants are not effective in removing mercury. At present, there are no commercially viable control technologies for mercury. As a consequence, this highly toxic form of air pollution continues to go largely unabated.

Thus coal becomes a repository of toxic metals. For example, a super thermal power plant consuming 8 million tonnes of coal containing x grams per tonne of any toxic metal, will pump into the surrounding eco-



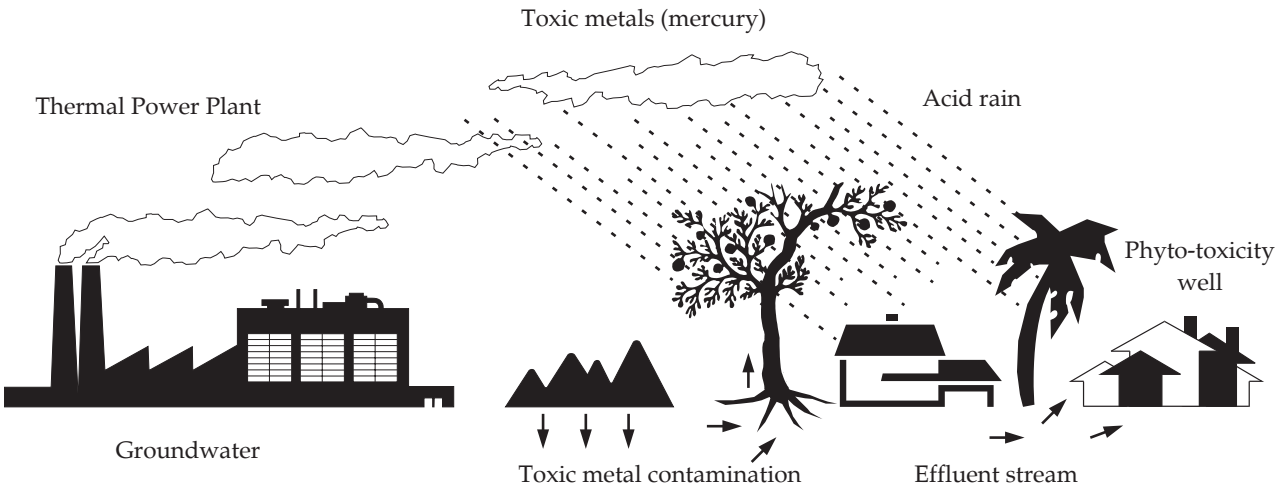
system 8x million grams of the metal.

Mercury in coal: In India there was uncertainty over the actual concentration of mercury in coal: there have been several studies, but not a single concrete one. The mercury content of coal produced by different mines varies widely according to the location, making it quite difficult to propose estimates.

The studies, which show concentration of mercury in coal samples in India, are mostly academic-oriented. A study by K.C. Sahu shows mercury content in a coal sample as 0.11 ppm. On the other hand, samples of Pathankhera coalfields in Gondwana basin, in Madhya Pradesh, analysed in a study by R.R. Nandgaonkar show mercury content in coal in the range of 0.8 to 0.20 ppm.[14]

A World Bank document in the year 2000 on the National Thermal Power Corporation (NTPC) showed results for mercury concentrations in coal analysis done by NTPC in the range of 0.11 to 0.14 ppm while another study of coal analysis, done by the Roorkee University, India, showed mercury to be in the range of 0.8 to 11.4 ppm. The Bank noted the discrepancy among the two results and requested NTPC to redo the study after consulting with other reputable laboratories and agencies in India to establish a standard test procedure that would be consistent with the coal testing procedures used in the USA. After a year, the new findings showed mercury concentrations in coal in the range of 0.17 to 0.32 ppm, significantly higher than coal in USA and

Fall-out of Coal Combustion from a Thermal Power Plant



Europe where mercury emission from thermal power plants has been of concern.

The Central Pollution Control Board (CPCB) conducted a study on 'Mercury balance in thermal power plants'.[15] The CPCB analysed 11 coal samples and found the average mercury concentration to be of 0.272 ppm (ranges between 0.09 to 0.487 ppm). Though these data are inadequate, it is still an attempt to assess the total mercury pollution potential from coal in India.

Mercury emissions from coal: On an average, India annually consumes 325 million tonnes of coal in sectors such as coal-fired thermal power plants, iron and steel plants, cement plants, foundries, fertiliser production, paper manufacturing, etc. The power sector, which accounts for over 70 per cent of the total coal consumption, annually consumes around 220 million tonnes.

The total mercury pollution potential from coal in India is estimated to be 77.91 tonnes per annum, considering average concentration of mercury in coal as 0.272 ppm. About 59.29 tonnes per annum mercury is mobilised from coal-fired thermal power plants alone.[16]

The mercury emanating from the thermal power plants' stacks is 58.05 per cent gaseous and 2.4 per cent in particulate form. About 32.5 per cent is retained in the ashes (fly ash and bottom ash). The remaining 7.05 per cent could not be accounted for.

Thus, mercury being persistent in the environment, its presence in the air in this amount could enter bodies through the oral route and prove a great threat to people, especially those living in the vicinity of these thermal power plants.

The 75 thermal power plants consume around 220 million tonnes of coal for power generation, producing 65-75 million tonnes of fly ash. Thermal power plants' coal consumption is likely to reach 400 million tonnes per year, which would represent 150 million tonnes of ash generation. With such high growth projections for these plants, the future of mercury emissions in India is really grim.

Beside this, the fly ash generated by thermal power plants is also a huge concern because of its environmental impacts. The impact of ash-ponds near thermal power plants on the local environments is usually stated to be the following:

- Leaching of trace elements, in particular heavy metals, into surface water and ground water.
- Accumulation of heavy metals in soils and plants around ash ponds.

On an average, around 65 million tonnes of fly ash are generated every year in India by 75 thermal power plants. For every megawatt of power generated, about 0.6 to 0.7 tonnes of ash is produced.[17] Heavy metals are largely concentrated on the surface of fly ash.

The disposal of fly ash is extremely water and land intensive. Large tracts of land are acquired for fly ash disposal, leading to air, water and soil contamination. In India, mercury is concentrated as 0.1 ppm as a trace element in the fly ash.[18] The present modes of disposal in water bodies pose grave danger for the populations.

The leachability of heavy metals from fly ash is well documented. However, the concentration of leached ions is not likely to have a significant impact on surface water bodies where periodic high flows will prevent accumulation of leached contaminants. The influence of leached trace elements on ground water quality is an area of major concern, because of the possibil-

ity of progressive accumulation of leached trace elements into ground water beneath an ash pond. Data pertaining to ground water contamination is scanty and more studies are required.[19]

Singrauli – hotbed of mercury pollution: The Singrauli region has a long and sorry history. Some 30 years ago, the Singrauli area in Central India was inhabited by a rural, self-sufficient population, and by rich wildlife. Today, it is considered the energy capital of India, with a huge artificial reservoir, giant coal mines, five super thermal power plants, and several industrial complexes.

The five giant super thermal power plants in Singrauli area, which supply 10 per cent of India's power, stand responsible for 16.85 per cent, that is, 10 tonnes per annum, of the total mercury pollution resulting from power generation.

Since 1988, there have been a number of studies on the presence of mercury in the water bodies of the Singrauli region. A study on mercury contamination in the Singrauli area was done by the Industrial Toxicology Research Centre for NTPC to assess the environmental risk to human population related to mercury contamination in the Singrauli area. Work monitoring and analysis of mercury contamination was completed in 1998 and a report was prepared, but it remained confined to the NTPC offices.

According to the World Bank's year 2000 document, the study indicates sufficiently high levels of mercury concentrations in humans, plants and animals to cause concern for the Singrauli area.

NTPC did not disseminate the results of this study to the general public, primarily because of its concern about the public reaction. The NTPC, indeed, claims that its power stations are not a major contributor to the mercury problem in the area!

The impact of mercury emissions from thermal power plants and fly ash on the environment and the health of people living in the area can be traced through a study done by the ITRC. A representative of the ITRC presented the study at a World Bank meeting; it is titled 'The status and magnitude of mercury contamination in the human population in and around industrial zones along Gobind Ballabh Pant Sagar (GBPS) Reservoir', in Singrauli, Madhya Pradesh. It is an epidemiological study, tracing mercury levels in the local people's bodies. The probable source of mercury contamination has mostly been food items.

The table below shows that the proportion of mercury in the blood samples was high in Dibulganj, Anpara, Renukoot and Parasi. The samples belonged to people between 10 and 60 years of age. The people from whom samples were taken had been living in the area for five to 10 years and had specific food consumption patterns. A regular monitoring and clinical surveying of subjects residing in the area is required. There is also

MERCURY LEVELS IN RELATION TO GEOGRAPHIC LOCATIONS IN SINGRAULI

Areas	Hg blood (μg/ml)		
	Numbers	Mean	SE
Anpara Bazar, Anpara Colony and Village	188	36.93	6.15
Balia Nala, Bansi and Bina	184	13.75	1.08
Chilka Dhand	118	12.61	0.86
Dibulganj	94	67.81	18.90
Dudhi, Kauwa Nala, Kakri and Kota Basti	58	6.76	0.75
Mamuar	60	13.17	1.17
Meurpur	117	10.00	0.86
Parasi	48	16.33	3.32
Rehata	75	16.21	1.04
Renukoot	21	31.15	1.94
Shakti Nagar	97	2.09	0.10

(Source: Paper presented by ITRC in World Bank meeting.)

a need for further and in-depth studies for accurate appraisal of the situation.

Another study by researchers concludes that serious mercury pollution is occurring in GBP reservoir and other surface waters of Singrauli, posing a grave threat to the health and livelihood of the population. The major cause of pollution, which appears in the study, is the deposition of mercury transported via the air route from the emissions of large thermal power plants.[20]

Medical Waste Disposal

According to the US Environment Protection Agency, medical waste incinerators are one of the largest sources of mercury pollution in the environment. Studies show that there is up to 50 times more mercury in hospital waste than in general municipal waste, and the amount of mercury emitted by medical waste incinerators represents more than 60 times the emissions' level from pathological waste incinerators.[21]

Mercury is found in blood pressure monitors, thermometers and thermostats, dental amalgams, oesophageal dilators, cantor tubes, miller abbot tubes, etc. Mercury-containing products are used in patient areas and pathology labs, in clinical procedures and in medicines. At least 20 different medical products contain mercury and many mercury-containing solvents and degreasers are found in labs, housekeeping departments, kitchens and maintenance areas.

The storage rooms may also be filled with used, damaged or outdated equipment or supplies that contain mercury. Mercury is an ingredient in some proprietary formulas used to manufacture medical and industrial supplies. Breakage, waste disposal or spills from these products release mercury into the atmosphere or drains, where it can persist.

Some products that formerly contained mercury are no longer manufactured. However, the old products are still a part of the environment. In fact, broken or obsolete equipment is often the primary source of mercury waste at many hospitals and clinics.

Industrial and chemical uses of mercury are manifold in the medical community: we use mercury intentionally in fluorescent and high-intensity lamps, in thermostats and switches and in a variety of generators, manometers and batteries. Non-medical uses of mercury are also present in a variety of products: in cleaning solutions, preservatives, paints and anti-fouling agents for wood and other surfaces.[22]

In India, hospitals and clinics generally dispose their waste by burning or incinerating it. Medical waste incinerators aim to disinfect wastes, but in the process, all the materials on which infections may exist are burnt.

Given that, much hospital material is also composed of mercury. Even if very expensive cleaners are installed in the stacks, there are still mercury emissions into the nearby ecosystem as mercury in medical waste is combusted at high temperatures, vaporises and exits the combusting gas exhaust stack.In India, medical waste incinerators are mostly small incineration units that burn around 50 to 175 kg/hour of infectious and non-infectious wastes generated from facilities involved in medical or veterinary care or research activities.

There is a serious lack of data on mercury emissions from medical waste incinerators. The city of Delhi alone has 61 medical waste incinerators. There is no account for the total number of incinerators in India.

Though the amount of mercury present in medical waste is very low in proportion to the total waste, it is enough to contaminate the ecosystem severely.

Municipal Solid Waste Disposal

Municipal solid waste is generally disposed off in three ways in India:

- Landfill dumping
- Open dumping
- Open burning

Municipal solid waste consists primarily of household garbage and other commercial, institutional and industrial solid wastes. Mercury is present in the form of various products in our day-to-day household items; clinical thermometers and blood pressure monitors are becoming an important part of our households. Besides this, mercury is present in electrical switches, mercury vapour lamps, fluorescent tube lights, alarm clocks, toys, singing greeting cards, talking refrigerator magnets, lighted athletic shoes, etc. Though present in trace amounts, it becomes very significant when assembled in garbage. Mercury batteries are a known source of mercury in municipal solid waste.

The disposal of any of the above-mentioned products in the municipal solid waste will lead to mercury emissions in the environment. Even if municipal solid waste is burnt openly or in a bhatti, the mercury present in the waste will be emitted in the environment and dispersed widely.

Municipal solid waste is dumped in landfills or even openly. The mercury present in waste can leach down to ground level and pollute ground water. In the rainy season, the mercury present in waste can be washed down to running water, later reaching rivers and oceans.

Sometimes improper municipal solid waste disposal practices in India lead to the dumping of waste into drains, the latter reaching and polluting other water sources.

Even though the amount of mercury present in municipal solid waste is small in proportion to the total amount of waste, the amount of mercury present in it is enough to cause environmental and health concerns to large population. In India, there are no estimates available for the annual uncontrolled mercury emissions from the disposal of municipal solid waste.

Summary

Historically, mercury has a variety of applications in India. Though its use in various industries has been decreasing over time, in others, such as thermometer production has not gone down. Industries such as the chlor-alkali industry have not yet phased out mercury usage and some plants are extremely 'leaky'.

Clearly, there are substitutes in all cases and the human and natural environment is at risk. Mercury needs to be eliminated totally, and government policy as well as the industry need to proactively make this happen.

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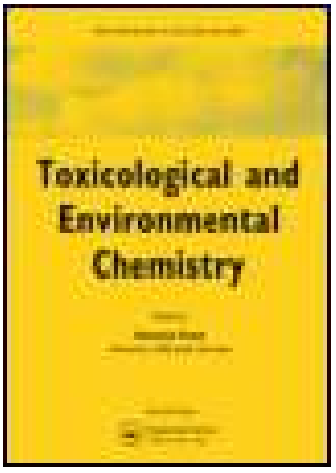

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Mercury pollution in the Sonbhadra district of Uttar Pradesh, India, and its health impacts

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The Sonbhadra district in the Singrauli area of Uttar Pradesh, India, has many coal mines and thermal power plants and is a critically polluted area. Many residents of this area reported adverse health conditions which may be linked to metal pollution, especially of mercury investigated here.

In May 2012, samples of water (23), soil (7), blood, hair, and nails from persons showing adverse health conditions selected at random were collected and analyzed for total mercury by atomic absorption spectrometry.

Twenty percent drinking water samples contained mercury from 3 to 26 μg L^{-1} (3–26 times the permissible limit). Soil samples had 0.5–10.1 mg kg^{-1} Hg.

The average concentrations of mercury in human blood, hair, and nails were found to be 34 μg L^{-1}, 7.4 mg kg^{-1}, and 0.8 mg kg^{-1}, respectively. Mercury concentrations in the blood of these persons were 45 and 28 μg L^{-1} on average in the case of men and women. This is much higher than the safe level of 5.8 μg L^{-1} set by the United States Environmental Protection Agency (USEPA).

It was concluded that all residents of Sonbhadra sampled could be suffering from mercury toxicity as the area is polluted by Hg released from the coal-fired thermal power plants.

Keywords: mercury pollution; thermal power plants; human blood; hair and nails; Sonbhadra

1. Introduction

The northeastern part of Madhya Pradesh, the Singrauli district, and the adjoining southern part of the Sonbhadra district of Uttar Pradesh are together known as the Singrauli region. The area remained unexploited until the construction of the Rihand Dam (Govind Ballabh Pant Sagar – GBPS) in 1961. The dam was constructed on the river Rihand, a tributary of the Son River at the village Pipri (Sonbhadra). As of now, many coal-fired thermal power plants have come up and extensive coal mining activities are going on. The area also has an aluminum smelting plant, chemical industry, cement industry, and other industrial and commercial operations. The thermal power capacity of the region stands at about 12,700 MW (10 thermal power plants) and the coal mining is about 83 million tonnes per annum (MTPA) (14 mines). Most of the coal mines are present at the border of Uttar Pradesh and Madhya Pradesh. Another 9200 MW of thermal power capacity is planned in the Singrauli region, as also another 50 MTPA of coal mining projects. The Central Pollution Control Board declared the Singrauli area as a critically polluted area (CPA), ranked the ninth most CPA of India and indexed 81.8 out of 100 (Central Pollution Control Board [CPCB] 2009).

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Mercury can be introduced into the environment by both natural and anthropogenic sources, including volcanic emissions, mining, industrial, and agricultural activities (Clarkson 1993). Coal contains Hg as a natural component along with other elements in trace amounts (Agrawal et al. 2008). Mercury contained in coal evaporates during combustion in boilers operating at temperatures above 1100 °C. Given the large quantity of coal burned in thermal power plants as well as in industrial plants, considerable amounts of mercury are likely to be released into the environment. Coal in the Sonbhadra district is estimated to contain 0.26 mg kg^{-1} Hg (Kumari 2010) and in the range of 0.42−10.1 mg kg^{-1} in seven samples of coal in different power plants in the Singrauli region (Personal Communication, June 15, 2012 − unpublished work). The Hg emanating from a thermal power plant's stack is 58% gaseous and 3% in particulate form. About 32% is retained in the ashes (fly ash and bottom ash). Up to about 70% to 80% of Hg vapor in the atmosphere is absorbed in the alveoli of human lungs (Cherian, Hursh, and Clarkson 1978; Sandborgh-Englund et al. 1998).

Mercury poisoning was first reported from the Minamata Bay area, Japan, caused due to consumption of fish and other seafood contaminated with mercury (Harada 1995). Subsequent studies have reported many cases of mercury pollution and adverse health effects (WHO 1991, 2000).

Human hair has been considered as a useful bio-indicator of mercury (Clarkson 1993). Health Canada has issued guidelines /recommendations for Hg exposure of humans and for correlation between Hg levels in blood and hair and possible consequences (Table 1).

Chronic exposure to Hg affects the nervous system, causing tremors, spasms and loss of memory, severe depression, increased excitability, delirium, hallucination, and personality changes. Renal damages have been observed in chronically exposed workers (Brigden, Santillo, and Stringer 2002).

Many residents of four areas, i.e., Anpara, Chilika Daad, Dibulganj, and Obra in Dudhi subdivision of the Sonbhadra district of Uttar Pradesh, showed adverse health conditions not related to normal diseases. In view of the presence of many coal-fired power plants, polluting industries, and coal mines in the area, a study was undertaken to assess the Hg pollution in the area.

2. Materials and methods

2.1. Water samples

Twenty-three samples of water (about 1 L) were collected from different places in polyethylene terephthalate bottles of 1 L capacity (Pearl Polymers Limited, India), stored at 4 °C away from direct sunlight, and brought to the laboratory for analysis. Details of the samples are given in Table 2; 15 drinking water samples (W01−04, W06−08, W14−16, W19−23), 3 surface water samples (W10, W13, W17), and 5 effluent samples (W05, W09, W11, W12, W18) were taken.

Table 1. Health Canada guidelines for mercury exposure of humans.

Biological materials	Blood Hg ($\mu g\ L^{-1}$)	Hair Hg (mg kg^{-1})
Normal acceptable range	<20	<6
Increasing risk	20−100	6−30
At risk	>100	>30

Table 2. Mercury in water samples from Sonbhadra.

Sample No.	Sample code	Sample location	Hg (μg L^{-1})
Drinking water		IS: 10500:2004 – desirable limit	**1.0**
		IS: 10500:2004 – permissible limit	**1.0**
1	W01	Hand pump at Dibulganj	26
2	W02	Well water from Kalika Singh's house, Anpara	8.0
3	W03	Water supplied by Renusagar Power Project (NTPC) to Garbandha village	ND*
4	W04	Well water, Garbandha village	ND
5	W06	Hand pump in Prahlad's house at Chilika Daad	3.0
6	W07	Hand pump at Chilika Daad near Kashmir Valley School	BDL**
7	W08	Water supplied by NTPC to Chilika Daad	ND
8	W14	Water from tap supplied by UPID, near gate of VIP colony, Renukut	ND
9	W15	Hand pump in front of Rambhajan's house at Kusmaha village – filtered water	ND
10	W16	Hand pump in front of Rambhajan's house at Kusmaha village – unfiltered water	ND
11	W19	Hand pump at Chilika Daad	ND
12	W20	Hand pump at Dibulganj in front of former Pradhan's house	ND
13	W21	Hand pump in front of the Govt. school at Kirwani village, in front of Kailash's house	ND
14	W22	Hand pump at Obra, Malviya Nagar	ND
15	W23	Hand pump at bus stand Renukut near Ramlila Maidan	ND
Surface water			
16	W10	Water from Renuka River at Obra	ND
17	W13	Rihand Dam where Dongiya Nallah drains into Rihand Dam (Renukut – Pipri)	10
18	W17	Obra Dam where Murdhawa Nallah† (Ganda Nala/Thad Pathar) meets	ND
Effluents		Prescribed limit in EPA Act, 1986	10
19	W05	Water from Ash Pond of Shakti Nagar NTPC	ND
20	W09	Water from Ballia Nallah	ND
21	W11	Jharia Nallah at Obra near Shushil's house	ND
22	W12	Dongiya Nallah at Renukut (Pipri) effluent of Aaditya Birla Chemicals (India) Ltd (ABCL)	127
23	W18	Murdhawa Nallah (Ganda Nala/Thad Pathar)	ND

*ND – not detected.
**BDL – below detection limit.
†Nallah – large drain.

Table 3. Mercury in soil samples from Sonbhadra.

Sample No.	Sample code	Sample location	Hg (mg kg^{-1})
1	S 01	Soil from Anpara Village, beside Anpara Power Plant	1.64
2	S 02	Chilika Daad near coal depot	1.75
3	S 03	Sector 10 at Obra	0.42
4	S 04	Soil near Rihand Dam and Dongiya Nallah (Renukut – Pipri)	10.1
5	S 05	Soil in front of Rambhajan's house at Kusmaha village	0.57
6	S 06	Soil in front of Kailash's house at Khairahi village	0.50
7	S 07	Soil from near Ramlila Maidan at Renukut	0.50

2.2. Soil samples

Seven soil grab samples of about 250 g were taken at a depth of 20–30 cm below the surface. They were kept in transparent polythene bags and brought to the laboratory for analysis (Table 3).

2.3. Blood, hair, and nail samples of local residents

Persons having some health problems other than normal diseases were selected at random and their health problems were recorded (Table 4). Blood samples of about 10 mL were collected in commercially available heparinized tubes (Vacuette, Greiner Bio-One, Kremsmünster, Austria). Hair and nail samples of about 500 and 200 mg each were also taken from the same persons and stored in polybags. All these samples were stored at −4 °C and brought to the laboratory for Hg analysis. The area studied and the sampling sites are shown in the maps (Figure 1 (A) and (B)).

All acids and reagents were of analytical grade (Merck, Darmstadt, Germany). A standard for mercury was also purchased from Merck. Ultrapure water was used (Elga USF Maxima Ultra Pure Analytical Grade DI Water System).

All glassware were soaked in 10% nitric acid overnight, cleaned with detergent solution, washed thoroughly, and finally rinsed with ultrapure water before use.

2.4. Digestion and analysis of total Hg in water and soil

The samples were digested according to the EPA methods 7470A and 7471B and analyzed by flameless atomic absorption spectrometry (AAS) (model M6, Thermo Scientific, Cambridge, UK) using sodium borohydride as the reducing agent. The detection limits were 2 μg L^{-1} for liquids and 10 μg kg^{-1} for solid samples.

2.5. Digestion and analysis of mercury in human blood, hair, and nails

For the determination of Hg in whole blood, 1 mL samples were digested (Application Note; Agilent Technologies 1997).

Before analysis, hair samples were washed successively with acetone, distilled water, again with acetone, and then dried at 40–45 °C for one hour. The dried samples, about 100 mg, were digested according to the procedure described by Leino and Lodenius

Table 4. Mercury in human blood, hair, and nail samples from Sonbhadra of persons showing adverse health conditions.

Sample No.	Sampling location	Age	Gender	Health conditions	Blood ($\mu g\ L^{-1}$)	Hair ($mg\ kg^{-1}$)	Nail ($mg\ kg^{-1}$)
1	Chilika Daad	45	Female	Abdominal pain, joint pain, white lesions (skin discoloration), burning extremities, electrifying feeling throughout body.	78.7	ND	ND*
2	Chilika Daad	47	Male	Joint pain, scaly skins. Uses tobacco and pan.	45.3	ND	ND
3	Chilika Daad	26	Male	Kidney problems, stomach ache.	29.5	ND	1.44
4	Chilika Daad	45	Female	Skin discoloration, joint pain.	ND	ND	0.90
5	Chilika Daad	41	Female	Joint pain, burning extremities.	ND	ND	0.18
6	Chilika Daad	26	Female	Starting case of skin discoloration.	ND	1.57	7.0
7	Chilika Daad	45	Female	Pink discoloration. Her husband an NTPC employee has tingling problem.	15.5	ND	0.16
8	Chilika Daad	08	Male	Diabetes from the age of 1.5 years.	38.7	30.7	ND
9	Dibulganj	50	Female	Abdominal burning, tingling, muscular spasm, joint pain.	17.8	31.3	No sample
10	Dibulganj	23	Male	Speaking difficulty, stammering.	26.2	15.3	ND
11	Dibulganj	33	Female	Swelling in legs, blurred vision, pain in legs.	61.5	10.7	2.09
12	Dibulganj	43	Female	Hip pain, skin discoloration, joint pain, because of stone in her abdomen she has been operated twice.	32.9	ND	ND
13	Dibulganj	16	Female	Burning sensation, on reading she sheds tears, abdominal pain.	23.6	26.5	ND
14	Kirwani	10	Female	Body pain, numbness in left side of body. Eats fish.	10.3	10.9	ND
15	Khairahi	38	Male	Burning extremities, electrifying feeling, joint pain, and muscular spasm. Eats fish two to three days in a week, takes alcohol/pan occasionally.	113.5	3.84	ND

(*continued*)

Table 4. (*Continued*)

Sample No.	Sampling location	Age	Gender	Health conditions	Blood ($\mu g\ L^{-1}$)	Hair ($mg\ kg^{-1}$)	Nail ($mg\ kg^{-1}$)
16	Khairahi	42	Female	Muscular spasm, blurred vision, joint pain from last four years, burning extremities. Eats fish two to three times in a month.	76.3	1.6	3.0
17	Obra	63	Male	Burning sensation in foot, swelling in legs, tingling, and blurred vision.	29.9	1.2	0.08
18	Obra	48	Male	Right leg has become short in length from last six to seven years, knee pain, trembling in hands, muscular spasm, burning extremities in foot.	29.6	ND	ND
19	Malviya Nagar, Obra	46	Female	Joint pain, blurred vision, swelled knees, not able to walk properly because of pain. Fisherman family eats fish two to three days in a week.	22.6	6.85	ND
Average concentration					**34.3**	**7.39**	**0.83**

*ND – not detected.

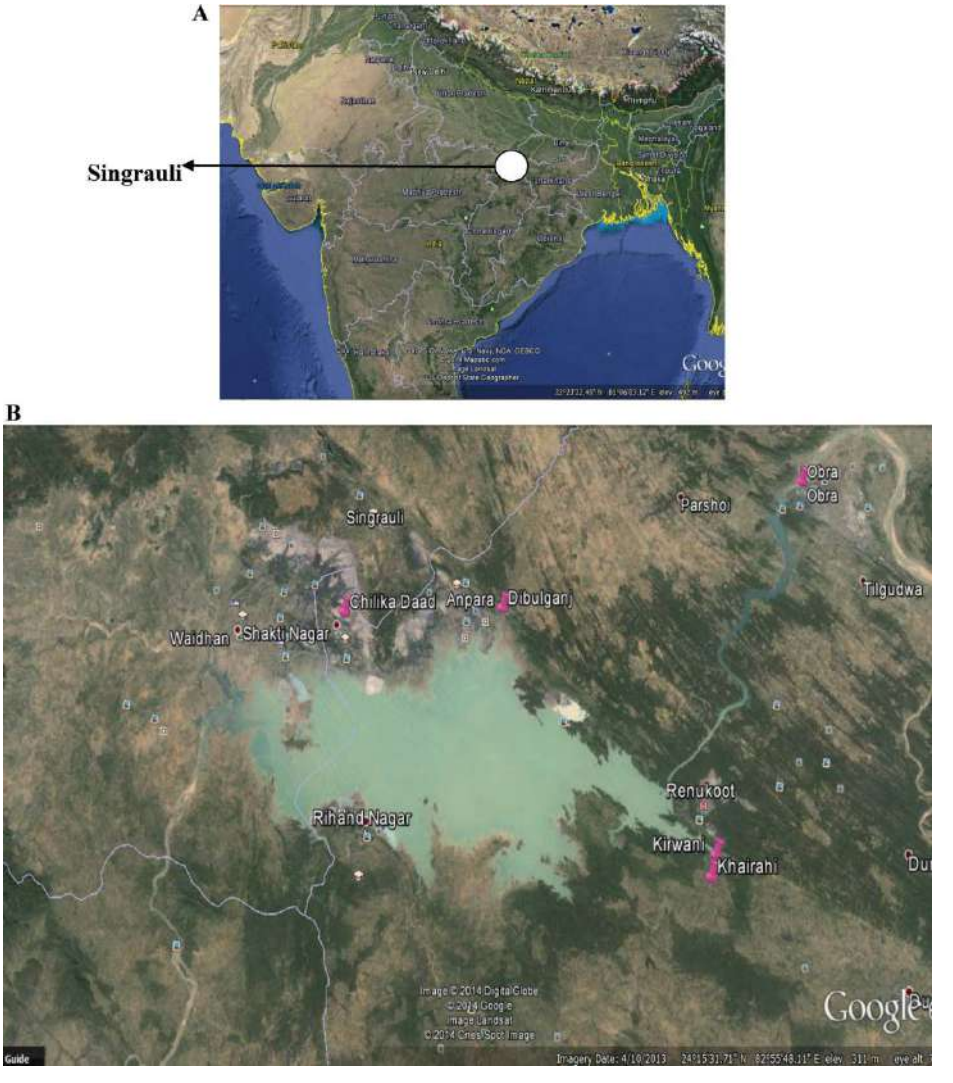

Figure 1. (A) Map of India showing Singrauli. (B) Detailed map of the Singrauli area showing sampled areas.

(1995). The digested samples were then analyzed by flameless AAS under borohydride reduction. The detection limit was 20 μg kg^{-1}.

Nail samples, about 100 mg each, were digested following the procedure described by Pallotti, Bencivenga, and Simonetti (1979). The detection limit was 20 μg kg^{-1}.

3. Results and discussion

3.1. Mercury in aqueous samples

Twenty percent of the drinking water samples contained mercury ranging from 3 to 26 μg L^{-1} which were 3–26 times higher than the permissible limit of 1 μg L^{-1}

(Table 2). Anpara, Dibulganj, Chilika Daad, and Obra are situated very close to thermal power plants. A study by the Industrial Toxicological Research Centre (ITRC), Lucknow, of the Singrauli area found that 15% drinking water samples had Hg at more than 1 μg L^{-1} (Srivastava, n.d.), the most probable cause being the combustion of large amounts of coal in the area. Naturally occurring levels of Hg in ground water and surface water are less than 0.5 μg L^{-1}, although local mineral deposits may give rise to higher levels (IPCS 2003). A few ground water samples and shallow wells surveyed in the USA exceeded 2 μg L^{-1} (Ware 1989).

One surface water sample (W13) and one industrial effluent (W12) contained 10 and 127 μg L^{-1} Hg.

The effluent from Aditya Birla Chemicals (India) Ltd. chlor-alkali plant had 12.7 times the permissible limit of Hg. Surface water near caustic chlorine industry and industrial effluents have been reported to contain 176 and 58–268 μg L^{-1} Hg, respectively (Srivastava, n.d.).

3.2. *Mercury in soil*

Mercury was found in all samples analyzed in the range of 0.42–10 mg kg^{-1} (Table 3), the highest in a soil sample (S 04) collected near the Rihand Dam where Dongiya Nallah (large drain) meets at Renukut – Pipri. This is 1.5 times the Canadian soil quality guidelines for agricultural and residential/parkland soil of 6.6 mg kg^{-1} (Canadian soil quality guideline 1999). The most probable reason of the very high mercury content of this soil is Dongiya Nallah as its water contains mercury at high concentrations (127 μg L^{-1}), carrying the effluent of a chlor-alkali plant. A soil sample collected earlier and analyzed in 2011 by Centre for Science and Environment-Pollution Monitoring Laboratory (CSE-PML) from outside Anpara thermal power plant near the fly ash pond contained 0.71 mg kg^{-1} of mercury. Anpara, Chilika Daad, and Obra are situated near the thermal power plants. Mercury emissions from massive coal consumption raise the Hg level to more than 1 mg kg^{-1} in soil. Elemental Hg fallout over the soil horizon in the vicinity of a steel plant which consumes a lot of coal was reported to be in the range of 60–836 g km^{-2} $month^{-1}$ and the particulate matter contained as high as 56 mg kg^{-1} Hg in dust fallout (Srivastava, n.d.).

3.3. *Mercury in human samples*

More than 500 residents of this region complained of health problems not generally related to common diseases. These varied from joint pain, body pain, skin discoloration, speaking difficulties, swelling in legs, blurred vision, burning sensations in extremities, muscular spasms, trembling of hands, kidney problems, etc., many of which are also seen in mercury poisoning. Blood, hair, and nail samples were collected from 19 persons of age 8–63 years from Chilika Daad, Dibulganj, Khairahi-Kirwani, and Obra selected at random from these residents.

The results of mercury in blood samples are given in Table 4, along with the details of the individuals and their health conditions. The average concentration of mercury in blood was found to be 34 μg L^{-1}. The United States Environmental Protection Agency (USEPA)'s limit of mercury in blood (5.8 μg L^{-1}) was exceeded in 84% of the samples. According to Health Canada guidelines (Table 1), 63% are in the category of increasing risk as they had blood mercury level between 20 and 100 μg L^{-1}, and one out of 19 persons is at risk as more than 100 μg L^{-1} of mercury was found. All these persons were showing different adverse health conditions. An ITRC study in Singrauli of 105 subjects

found that 66% of the subjects had more than 5 $\mu g\ L^{-1}$ Hg in blood as compared to 10% in control subjects (Srivastava, n.d.).

The highest concentration of mercury (113 $\mu g\ L^{-1}$) was found in a blood sample of a person (sample no. 15) of Khairahi village. He reported the problem of burning extremities, electrifying feeling, joint pain, and muscular spasm. He ate fish two to three days in a week. Two samples of *Rohu* fish (*Labeo rohita*) from the Rihand reservoir contained about 0.5 mg kg^{-1} methyl mercury (unpublished work). A mercury concentration of more than 100 $\mu g\ L^{-1}$ constitutes, according to Health Canada, a risk of mercury toxicity. The second highest concentration of mercury (79 $\mu g\ L^{-1}$) was found in a blood sample of a woman (sample no. 1) of Chilika Daad village. She had abdominal pain, joint pain, skin discoloration, burning extremities, and electrifying feeling throughout the body. This Hg level is in the increased risk category according to Health Canada.

Mercury vapor exposure in chlor-alkali workers for eight to nine years resulted in blood Hg level of 12 $\mu g\ L^{-1}$, and they tended to have increased number of electroencephalography abnormalities (Piikivi and Tolonen 1989). In another study, chlor-alkali workers with an exposure for 5.5 years had 10 $\mu g\ L^{-1}$ Hg in blood and the workers reported memory disturbances, sleep disorders, and also muscle fatigue and confusion (Piikivi and Hanninen 1989).

All men had mercury in their blood and were in the range of 26−113 $\mu g\ L^{-1}$, with an average concentration of 45 $\mu g\ L^{-1}$. All men exceeded the USEPA's safe level of mercury in blood of 5.8 $\mu g\ L^{-1}$ and they are in the increased risk category of Health Canada guidelines as they had more than 20 $\mu g\ L^{-1}$ of mercury in their blood (Figure 2).

Seventy five percent women had mercury in the range of 10.3−78.7 $\mu g\ L^{-1}$ in their blood with an average of 28 $\mu g\ L^{-1}$ which is higher than USEPA's safe level of mercury in blood (5.8 $\mu g\ L^{-1}$) (Figure 2). The concentration of mercury in the blood of women is

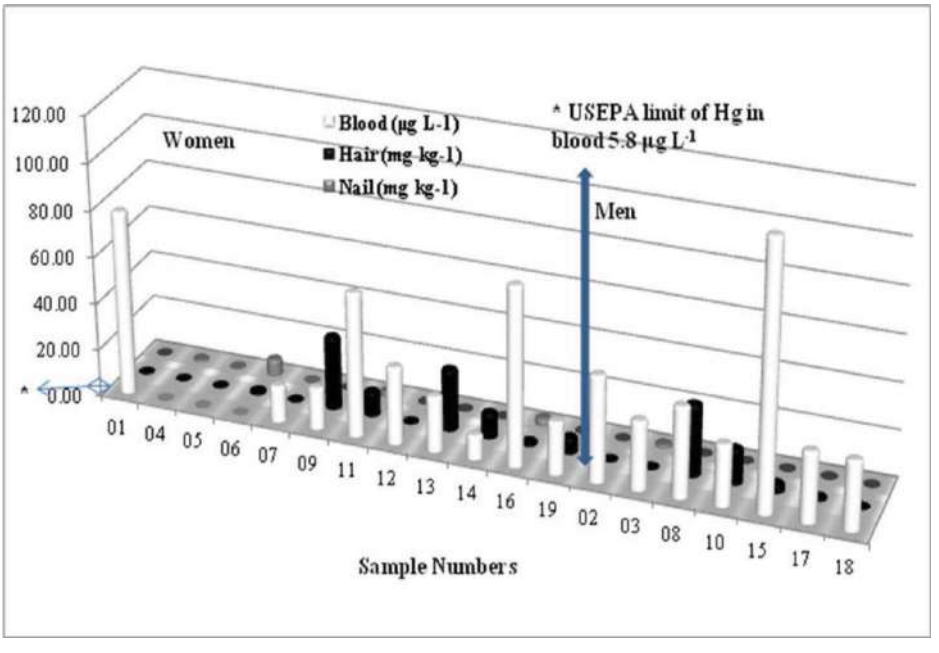

Figure 2. Mercury in human blood, hair, and nails of some residents of Sonbhadra.

lower than that in men probably due to the fact that all pulmonary volumes and capacities are about 20%–25% less in women than in men (Guyton and Hall 2006). It may indicate that uptake of mercury vapors from the inhaled air in the lungs of humans is an important method of mercury incorporation in the human body from the environment.

About 57% hair samples had mercury in the range of 1.2–31 mg kg^{-1}. Five persons had mercury between 6 and 30 mg kg^{-1} and were in the increased risk category of Health Canada guidelines, and 10% are in the risk category as they had more than 30 mg kg^{-1} of mercury in their hair.

The highest concentration of mercury (31.3 mg kg^{-1}) was found in a hair sample of a person (sample no. 9) from Dibulganj, who reported problems of abdominal burning, tingling, muscular spasm, and joint pain. The second highest concentration of mercury (30.7 mg kg^{-1}) was detected in the hair sample of a man (sample no. 8) from Chilika Daad. He had been suffering from diabetes since the age of 1.5 years. Hair samples of a person (sample no. 13) from Dibulganj had 26.5 mg kg^{-1} Hg who was having problems of burning sensation throughout the body (Table 4).

Concentrations of mercury in hair of more than 20 mg kg^{-1} may result in different symptoms such as vertigo and dizziness, headache, pain in limb extremities, reduction in vision, etc. as found in people in three fishing villages in the Tapajos river basin, Amazon (Harada et al. 2001). Some of these symptoms were also observed in some of the residents (Table 4).

Monitoring Hg levels in the hair of people throughout the world would indicate locations where people's body burden of Hg is high enough to show adverse health conditions. Concentrations of Hg in human hair from 35 countries ranged from 0.2 to 7.9 mg kg^{-1} (Airey 1983).

All hair samples from Khirahi-Kirwani and 80% samples from Dibulganj village had mercury while 67% of the samples from Obra village contained mercury, but only 25% samples from Chilika Daad village contained mercury. ITRC in an earlier study in Singrauli reported that hair of 48% of 1183 subjects contained more than 1 mg kg^{-1} Hg as compared to 25% in control subjects (Srivastava, n.d.).

Agusa et al. (2005) found that the Hg levels in the hair of residents from Phnom Penh, Kien Svay, and Tomnup Rolork of Cambodia were in the range of 0.54–190 mg kg^{-1}. The concentration of Hg in marine and fresh-water fish in the area ranged from <0.01 to 0.96 mg kg^{-1}, suggesting that fish was probably the main source of Hg for these Cambodian people.

Hair samples from Parakana Indian reservation in the vicinity of Tucurui water reservoir contained Hg in the range of 0.9–240 mg kg^{-1} with a mean value of 65 mg kg^{-1}. The Hg pollution in the area was high enough to cause health effects (Leino and Lodenius 1995).

Mercury was detected in 44% of the nail samples in the range of 0.16–7.0 mg kg^{-1}, and the average concentration was 0.83 mg kg^{-1}. The highest amount of mercury (7.0 mg kg^{-1}) was found in the sample of a person (sample no. 6) from Chilika Daad village (Table 4). The average concentration of Hg in men was 0.22 mg kg^{-1} and that in women was 1.22 mg kg^{-1}.

Mercury was detected in 63% nail samples from Chilika Daad while 33% of the samples from both Khairahi-Kirwani and Obra contained Hg. Only 25% samples from Dibulganj village had Hg.

Mercury in the range 3–84 mg kg^{-1} was detected in the fingernails of dental personnel (Helsby 1976).

4. Conclusions

Sonbhadra district of Uttar Pradesh in India is a part of the Singrauli area which has many coal-fired thermal power plants, coal mines, etc. Central pollution control board of India has put it in their list of "critically polluted areas." The investigation reported here tends to confirm it, as many residents of this area show adverse health conditions somewhat similar to mercury toxicity.

An enormous quantity of coal, which contains mercury, is used by the thermal power plants and other industries in the area releasing large quantities of mercury vapors in the atmosphere. Up to 80% of mercury vapor in the inhaled air is absorbed by the human body.

Drinking water samples analyzed showed up to 26 times higher mercury than permissible limits. Similarly, soil samples from that area also showed higher amounts of mercury. The concentrations of total mercury in the blood, hair, and nails of persons examined were found to be much higher than the USEPA's safe level of 5.8 μg L^{-1} in blood. The average concentrations of mercury in the blood of men and women were 45 and 28 μg L^{-1}, respectively. This difference in the mercury levels of affected men and women may be due to the fact that the respiratory volumes and capacities are about 25% less in women as compared to men. The mercury concentration found in the blood of women is about 38% less than that in men. It is very likely that absorption of mercury from the inhaled air is an important source of its uptake in human beings. The high concentrations of mercury in the blood and hair of residents indicate mercury poisoning of the affected residents.

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Studies undertaken in Singrauli-Sonbhadra related to pollution and health over the years

S. No.	Year	Conducted By	Title / Parameter	Publication
1.	1991	Electricité de France/Charbonages de France	Environmental Study of Singrauli Area.	National Thermal Power Corporation (NTPC)
2.	1991	Singh,, K P, Agrawal J S, Singh (BHU)	Environmental degradation of the Obra-Renukoot-Singrauli area, India and its impact on natural and derived ecosystems	The Environmentalist
3.	1993	TERI	Study of Environmental Issues in Coal Mining and Associated Costs	https://archive.org/stream/in.ernet.dli.2015.474584/2015.474584.Study-Of_djvu.txt
4.	1995/8	People's Science Institute	Water monitoring for fluoride mitigation plan	
5.	1997	Banwasi Seva Ashram	Air pollution and its impact on agricultural productivity in Sonbhadra	Unpublished
6.	2001	CPCB	Mass Balance of Hg in Singrauli	Unpublished
7.	2002-2010	Banwasi Seva Ashram in association with CPCB	Environmental quality monitoring - air, surface water, groundwater, effluent and reservoir water	Submitted to CPCB
8.	2008	AP Sharma, BD Tripathi	Magnetic mapping of fly-ash pollution and heavy metals from soil samples around a point source in a dry tropical environment	Environmental Monitoring and Assessment
9.	2008	Rai P K	Heavy metals in water, sediments and wetland plants in an aquatic ecosystem of tropical industrial region, India	Environmental Monitoring and Assessment
10.	2009	CPCB, IITD	Comprehensive Environmental Assessment of Industrial Clusters	
11.	2011	Singrauli: The Coal Curse	Fact finding report on Singrauli	Greenpeace
12.	2012	Shukla SK & Pandey DN	Environmental Restoration around the Rihand Dam	International Journal of Scientific and Research Publications
13.	2012	Centre for Science and Environment	Mercury Pollution in Sonbhadra District of Uttar Pradesh and its Health Impact	
14.	2013	G Areendran, P Rao, K Raj, S Mazumdar, K Puri	Land use/land cover change dynamics analysis in mining areas of Singrauli district in Madhya Pradesh, India	Tropical Ecology
15.	2014	Vasudha & Prem	Singrauli: Development, but at whose cost?	India Social Development Report 2014
16.	2014	Anand B, Sharma p, Sharma SN	Long Term Monitoring of Water Quality in the Gobind Ballabh Pant Sagar in the Region around a Thermal Power Plant	International Journal of Engineering Science Invention
17.	2014	Prabhakar K, Anand B, Sharma S N, Sharma P & Gupta SL (Central Soil n Materials Research station)	Influence of a Chemical Industry Effluent on Water Quality of Gobind Ballabh Pant Sagar – A Long Term Study	International Journal of Engineering Science Invention
18.	2015	NGT	Core Committee set up by the NGT for “Monitoring of potential hazards of industrial development in Singrauli area"	

19.	2015	Anand, B, Sharma, S N, Ratnam, M (Central Soil n Materials Research station)	Long term studies on the impact of sediments and effluents of a chemical factory on the health and water quality of Rihand dam project, UP	
20.	2016	People's Science Institute and 21 Gram Sabhas of Sonbhadra	Water quality monitoring of 21 villages in Sonbhadra	
21.	2016	Pandey, P, Verma M K, Mukhopadyaya R et al	Biological properties of selected overburdens of Singrauli area - Microbial population of overburdens	Nature Environment and Pollutant Technology
22.	2016-17	Banwasi Seva Ashram	Singrauli Sonbhadra kshetra ki ki vayu mein vishaile dhatuon ka anumapan	
23.	2018	People's Science Institute	PM monitoring of Sonbhadra region	https://hazardscentre.org/2023/05/16/gscc-final-report-air-quality-monitoring-in-singrauli-and-delhi-edit/
24.	2017	Ahmad, F, Goparaju L	Spatio-temporal dynamics of mines in Singrauli, India: An analysis using geospatial technology GIS images of mine expansion over years	Indian Society of Geomatics
25.	2018	AL Ulsham, CS Dubey, DP Shukla, BP Mishra	Sources of fluoride contamination in Singrauli with special reference to Rihand reservoir and its surrounding Sources of fluoride contamination in Singrauli	Journal of the Geological Society of India
26.	2018	Varshney R, Jamal A	Evaluation of reservoir water quality using water quality index in Govind Ballabh Pant Sagar reservoir, India	Rasayan Journal of Chemistry
27.	2020	NEERI	Study of Flora - Fauna and Ash Characterization for Backfilling of Ash from NTPC Vindhyachal STPS in Mine Voids of Gorbi Mines of Northern Coalfields Ltd.	
28.	2020	Romana, Singh, Shukla	Long term air quality analysis in reference to thermal power plants using satellite data in Singrauli region, India	
29.	2020	Ahamad A, Raju NJ, Madhav S & Khan AH	Trace elements contamination in groundwater and associated human health risk in the industrial region of southern Sonbhadra, Uttar Pradesh, India	Environmental Geochemistry and Health
30.	2021	Ahamad A, Raju NJ, Madhav S, Gossel W, Ram P, Wycisk P	Potentially toxic elements in soil and road dust around Sonbhadra industrial region, Uttar Pradesh, India: Source apportionment and health risk assessment	Environmental Research
31.	2022	Romana, Singh,Dubey, Shukla	Analysis of Air and Soil Quality around Thermal Power and Coal Mines of Singrauli Region, India	International Journal of Environmental Research and Public Health (IJERPH
32.	2023	Banwasi Seva Ashram, Hazards Centre	Singrauli: Dark and Toxic under the Lamp Health damage due to air pollution	Economic and Political Weekly
33.	2023	Ahamad A, Raju NJ, Madhav S & Ram P	Fluoride in groundwater of industrial town of Sonbhadra district, Uttar Pradesh, India: probable release mechanism and potential health risk assessment	Environmental Geochemistry and Health
34.	2024	Banwasi Seva Ashram, Hazards Centre	Sonbhadra - Comparative study of health issues of 13 villages where repeat surveys undertaken	
35.	2024	Jha S, Sinha s, Mahadevappa P, Hazra S, Sarkar S	Assessing water quality and human health risk near coal mines and industrial area of Singrauli, India: special emphasis on toxic elements	Environmental Geochemistry and Health
	Some studies that had been started but status of completion unknown			
36.		National Environmental Engineering	Study for assessment of cumulative impact of large number of power plants and coal mines etc. located in Singrauli Region (Singrauli district of MP and Sonbhadra	Sponsored by Mahan Coal Limited. Study was being undertaken in 2013-14.

		Research Institute (NEERI)	district of UP) and suggest appropriate measures to mitigate the identified impacts	
37.	2017-18	National Environmental Engineering Research Institute (NEERI)	Decontamination of Rihand reservoir would require ₹10,000 crore	https://www.downtoearth.org.in/pollution/how-effective-is-ngt-s-rs-79-cr-fine-on-singrauli-mines-power-cos--67299
38.		Central Water and Power Research Station (CWPRS) Khadakwasla Pune	A comprehensive study to assess the Rihand reservoir's water and sediment quality and to delineate water and sediment remediation and restoration measures	Work was to start in January 2021.
39.		National Environmental Engineering Research Institute (NEERI)	Source Apportionment study of Singrauli region and Capacity building of Environmental Monitoring & Management of Northern Coalfields Limited, Singrauli, Madhya Pradesh	Undertaken for NCL, mentioned in their annual report of 2022-23.

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ORIGINAL PAPER

Fluoride in groundwater of industrial town of Sonbhadra district, Uttar Pradesh, India: probable release mechanism and potential health risk assessment

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Abstract In the selected study region of Sonbhadra district, coal burning and mining activities are dominant. Previous studies reported F contamination in very few groundwater samples of this region. A detailed study is required to estimate the fluoride in groundwater of this area. Hence, a total of 128 groundwater samples were collected during post- and pre-monsoon seasons in the year 2017 to estimate the F^-, its geochemistry, and health risk assessment from Renukoot and Anpara industrial clusters of Sonbhadra district, Uttar Pradesh, India. The pH of groundwater samples varied from slightly acidic to alkaline during both seasons. Almost all the major cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) and major anions (HCO_3^-, Cl^-, SO_4^{2-}, and F^-) values in groundwater samples of both clusters were found within the permissible limit of World Health Organization (WHO) and Beauro of Indian standards except F^- in both seasons. The scatter plots of F^- with Ca^{2+}, Na^+, HCO_3^-, and pH are used to explain the release mechanism of fluoride in groundwater. Saturation indices (SI) calcite versus SI fluorite and SI dolomite versus SI fluorite plots of both clusters used to check the involvement of these minerals in fluoride enrichment of aquifers. F^- contamination in groundwater due to coal burning in coal mining and thermal power plant dominated region is discussed globally and locally both. The non-carcinogenic health risk due to consumption of fluoride-contaminated water is estimated by using target hazard quotient (THQ). THQ values of F^- showed that children are at high risk than adults in both clusters of the study area during both seasons. Pictorial representation is used to show the dental fluorosis cases in children of the study region.

Keywords Coal mining · Fluoride · Sonbhadra · Saturation indices · Target hazard quotient · Dental fluorosis

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Introduction

Groundwater is used for drinking purposes in superiority to surface water by approximately 1.5 billion people globally, and it is predicted that about 1.8 billion population may face an absolute shortage of water by 2025 (Ahamad et al., 2018; Madhav et al., 2021a; Hasan et al., 2019; Raju et al., 2009b). In

most developing and poor countries, groundwater is often consumed untreated (Bretzler & Johnson, 2015; Fentahun et al., 2023; Madhav et al., 2021b; Raju et al., 2011). Several types of contaminants are reported in groundwater globally, but due to the severe health impact of F^-, it is included among the top 10 most toxic chemicals for community health (Malek Mohammadi et al., 2017; WHO, 2016). In natural water, F^- mainly occurs as a monovalent ion. F^- contamination in groundwater is becoming a leading worldwide problem. Being a naturally occurring element, F^- is widely dispersed in the environment, and it comprises about 0.32% of the earth's crust (WHO 1984). F^- enters below the ground from different sources and enters humans through various pathways (Ghosh et al., 2013). Many rocks and sediments contain minerals like amphiboles, fluorite, cryolite, sellaite, apatite, mica, and topaz, which contain fluorides (Paikaray & Mahajan, 2023). Apart from the natural sources, various anthropogenic activities such as coal mining activities, emission from coal burning in various coal-dependent industries, brick production, landfills, application of phosphatic fertilizers, and production of cement, glass, ceramic, onsite sanitation systems also enrich F^- in the groundwater and contaminate it (Rawat et al., 2010; Sharma et al., 2017; Brindha & Michael, 2019; Soujanya et al., 2020). Fluoride contents in coals are commonly estimated in the range between 100 and 300 mg/kg. Muscovite and kaolinite are the main carriers of F^- in coal (Xiong et al., 2017). Oxidation of pyrite and weathering of aluminosilicate minerals during coal extraction operations may result in the release of fluoride into soil and groundwater. Atmospheric fluorine from burning coal is the greatest human-made source of fluoride contamination in the USA (Mukherjee & Singh, 2020; Wu et al., 2004). Approximately 85–90% of the fluorine in coal is also shown to be emitted as HF when the temperature exceeds 850 °C (Fuge, 2019; Liu et al., 2007). Fluorine is emitted in the form of HF, SiF4, and CF4 during combustion (Liu et al., 2007; Yan et al., 1999). Several studies are available on the presence of fluoride in coal, fly ash, and soil of China, but unluckily very little work has been carried out on the presence of fluoride in Indian coal and its impact on groundwater (Liu et al., 2007; Ren et al., 1999; Swaine, 1990). Rapid industrialization, increased coal mining activities, aluminum smelting plant, and installation of super thermal power plants to meet the increasing demand for electricity led to contamination of fluoride in the study area along with natural sources. Aluminum industries are one of the major emitters of fluoride in the atmosphere. The smelter and pot rooms are the primary work area from where fluoride is emitted either into the atmosphere or in soils as tailings (Pandey et al., 2015). Fluoride in water can be a hazard or a benefit depending on its strength. At low concentration (around 0.5 mg/L), it helps in the maintenance of teeth and bones. In the literature, it is already reported that the intake of contaminated water having a high concentration of fluoride results in serious human health diseases (Salve et al., 2008; Chouhan and Flora, 2010). Also, it is reported that long-term ingestion of fluoride (1.5 mg/L, WHO 1997) may lead to dental fluorosis (tooth mottling), and in extreme cases (> 3 mg/L), it may cause skeletal fluorosis (deformities in bone) (Raju et al., 2009a; Younas et al., 2019). Many developing countries such as Mexico (Liu et al., 2020), India (Mukherjee et al., 2019), China (Khair et al., 2014), Fiji (Prasad et al., 2018), and Iran (Aghapour et al., 2018) are facing high risk due to consumption of high concentration of F in drinking water. South Asia can be seen as the epicenter of fluoride contamination in groundwater. Most of the South Asian countries like India, Pakistan, and Sri Lanka are severely affected. Around 35 and 26 million populations of China and India, respectively, are suffering due to high exposure to F (Jadhav et al., 2015). To identify the different pathways, mechanisms, and sources of F in groundwater and health risk assessment in humans due to its consumption, numerous works were done at the global level as well as in India (Raju et al., 2009a; Ozsvath, 2009; Ghosh et al., 2010, 2013; Agalakova and Gusev, 2011; Raju et al., 2012; Raju, 2017; Tiwari et al., 2017; Admimall et al., 2018; Karunanidhi et al., 2020; Aravinthasamy et al., 2020; Haji et al., 2021; Masood et al., 2022; Qui et al., 2023; Iqbal et al., 2023; Hao & Wu, 2023). Although the industrial impact of coal-based F^- emissions and their health effects have been examined extensively, the relationship between coal mining and groundwater F^- contamination has received far less attention. In the Sonbhadra region, the literature is available on geogenic sources of F^- contamination in groundwater (Pandey et al., 2016; Raju et al., 2012, 2009a, 2009b), but in the current region a few published work have reported

F in coal, fly ash, soil, slurry water, and Rihand reservoir water and it was confirmed that coal mining and coal burning activities are responsible for the enrichment of F^- (Usham et al., 2018). But for the first time, this detailed study is carried out on F^- contamination in groundwater resources, health risk assessment, and identification of dental fluorosis cases in the selected study region. Hence, this study is mainly focused on (1) To assess the F^- contamination in groundwater, (2) To identify the source and mechanism of its release, (3) To study health risk assessment due to its consumption, and (4) Identification of dental fluorosis cases in the study region.

Study area & methodology

Study region

In the present study, two urban industrial clusters of Sonbhadra district comprising Renukoot (24°11′17.20″–24°14′21.72″N and 83°00′22.50″–83°03′39.10 ″E) and Anpara (24°07′23.76″–24°11′30.30″N and 82°41′48.12″–82°47′36.30 ″E) having 45 and 89.40 km^2 area, respectively, were selected to understand the industrial impact on groundwater resources. Both clusters consist of various industries such as Aluminum Smelting Plant, Chlor-alkali Plant, and Hi-tech Carbon Limited in Renukoot and Thermal Power Plant and Coal Mining activities in Anpara (Fig. 1). Study region has a typical dry-tropical climate with average rainfall ranging between 850 and 1300 mm. The area's overall geography is undulating, with plains, hills, and valleys interspersed. Until 1961, when the Rihand Dam (Govind Ballabh Pant Sagar) was built over the river Rihand, a tributary of the Son River, the study region was underdeveloped and unexploited. Coal mining has increased dramatically since then, with the majority of mines being along the Uttar Pradesh–Madhya Pradesh border. Currently, fourteen mines produce roughly 83 million tonnes of coal per year. Alongside this, several coal-fired thermal power facilities have been built that produce roughly 12,700 MW of electricity in the area (Ahamad et al., 2021).

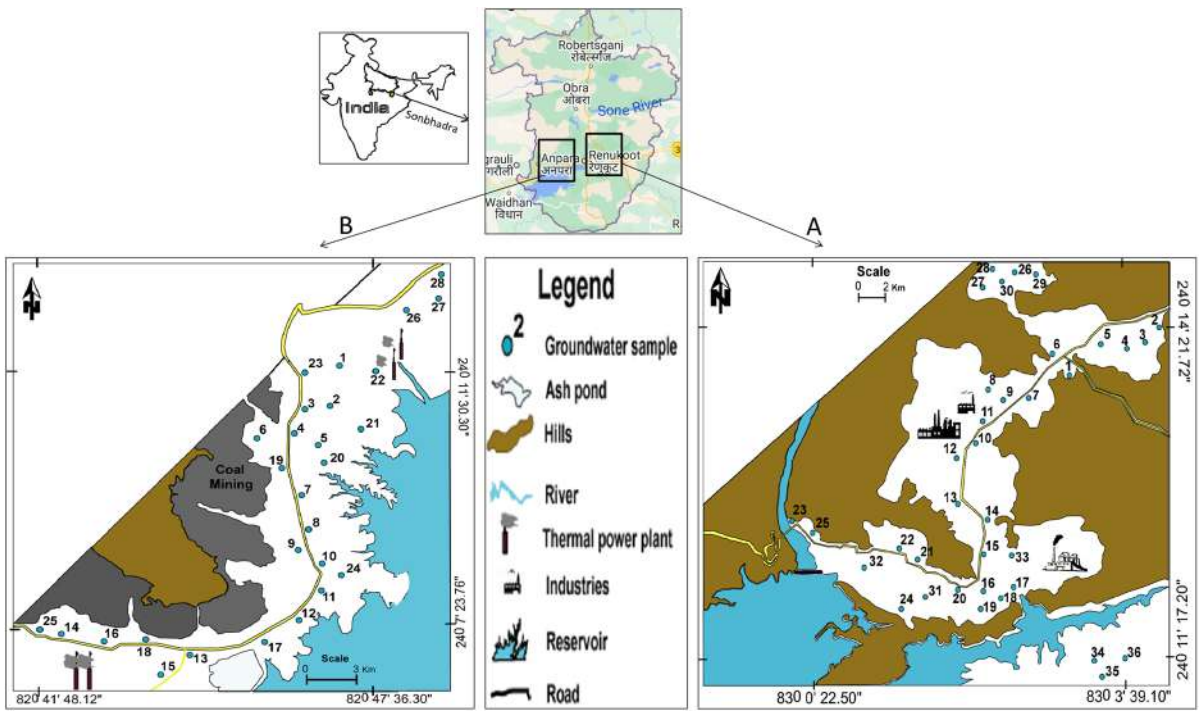

Fig. 1 Physiographic map of the two industrial clusters Renukoot (Cluster A) & Anpara (Cluster B) showing the sampling locations of the groundwater

Geology and hydrogeology

The geological map of the study region is shown in Fig. 2. The geology of the research area is heterogeneous, ranging from archaean (Bundelkhand granitic gneisses) to modern (Ganga) alluvium. The tract is located beneath the granitic complex of the Bundelkhand region and Sonbhadra's covering the Mahakoshal (Bijawar) and Vindhyan supergroup rocks. While the younger rocks in southern Sonbhadra are made up of coal-bearing Gondwana, the lower Vindhyan sediments of Sonbhadra are made up of deposits of cement-grade limestone, flux-grade dolomite, and building stone (Ahamad et al., 2020). According to the CGWB and the state tubewell department, fractures result in secondary porosity and porous formation in alluvial formations and hard rock areas. These fractures vary in depth from location to location. The presence of two distinct litho-units has a significant impact on the state of the local groundwater.

(1) The valley-filled area's unconsolidated sediments (alluvium).

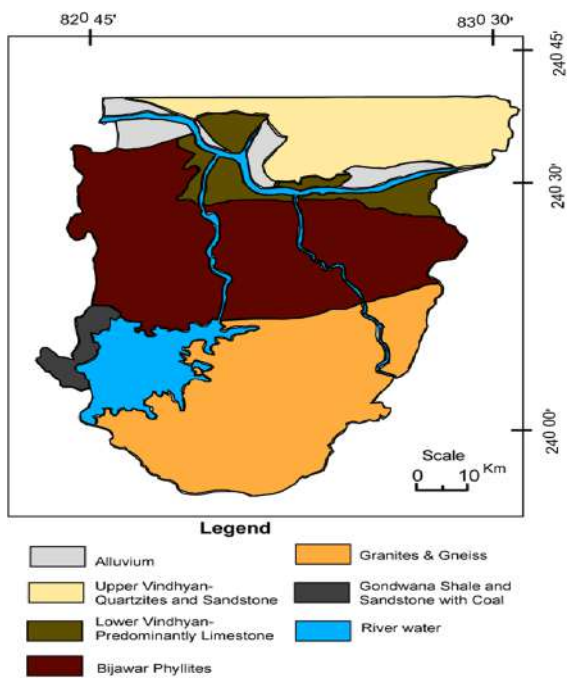

Fig. 2 Geological map of the study region

(2) The hard rock formation: consisting of Precambrian and Vindhyan formations.

Drainage, topography, and lithological behavior are the main factors that control groundwater. At shallow depths, groundwater is phreatic, while at deeper depths, it is formed by fractures and granular zones and in the study region average depth of water level varied from 13.66–14.68 mbgl during pre-monsoon while in post-monsoon, it varied from 10.29–12.89 mbgl. After the investigation of the long-term water level pattern, it is derived that the well depth shows the downfall pattern during the pre-monsoon period (Verma & Patel, 2021).

Groundwater sampling and analysis

The flowchart is shown below (Fig. 3), which gives the overall scheme of the study, from the sample collection, analysis, and interpretation to the F enrichment mechanism, health risk assessment, and identification of dental fluorosis patients. For pH, electrical conductivity (EC), and major cations (Ca^{++}, Mg^{++}, Na^{+}, and K^{+}) and anions (HCO_3^{-}, Cl^{-}, SO_4^{2-}, and F^{-}) analysis, a total of 128 groundwater samples in 500 ml Tarson polyethylene bottles were collected from borewells and hand pumps in the study region's two clusters, Renukoot (72 samples: 36 each for post- and pre-) and Anpara (56 samples: 28 each for post- and pre-). The groundwater samples were obtained at random from operable bore wells, excluding hand pumps, which are predominantly utilized for drinking and domestic purpose by inhabitants in the two clusters under investigation. The groundwater samples were collected, preserved, and then analyzed according to the APHA (1995) standard techniques. The global positioning system (GPS) was utilized to locate each sampling site. Before filling the bottles, labeling was done, and they were carefully rinsed with the sampled groundwater. The groundwater samples were collected only after 5–10 min of water flushing to stabilize the EC and remove the interference of standing water in the metal case. The pH and EC were measured using digital pH and EC meters (pH/Cond 340i SET 1) on the spot when the samples were collected. The groundwater samples were then kept at 4 degrees Celsius to avoid any substantial chemical changes.

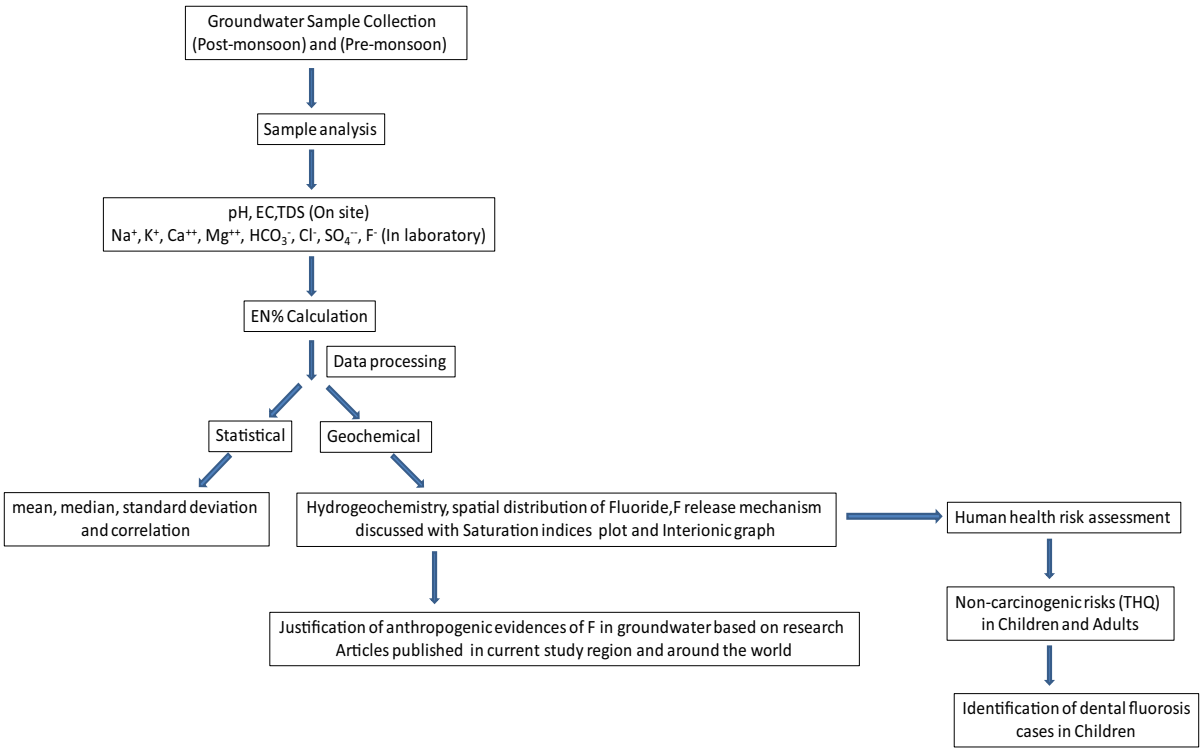

Fig. 3 Flowchart showing the methodology adopted to conduct this study

All of the analysis followed a regular procedure APHA (1995). Prior to the measurement of major cations and anions, samples were filtered using 0.45 µm filter papers in vacuum filtration equipment to remove suspended particles. Major cations, anions, alkalinity, and hardness were then measured in the samples. The EDTA titrimetric method was used to determine calcium, magnesium, and hardness while a flame photometer was used to determine sodium and potassium content (Elico model CL 378). $AgNO_3$ titration was used to calculate chloride. Electrometric titration was used to calculate carbonate, bicarbonate, and alkalinity. The content of fluoride was determined using a Thermo-Scientific Orion Ion Selective Electrode 4-Star. The sulfate concentration was determined by UV-3200 double beam spectrophotometer, Lab India.

Data treatment

The analytical data obtained were processed for detailed geochemical and statistical analysis. All the samples have electroneutrality (EN) % values within ± 5% in pre-monsoon and post-monsoon. Basic statistical parameters such as mean, median, standard deviation, and correlation were computed by using SPSS 16.0, Stat Soft STATISTICA 6, and Microsoft Excel version 2007. Coefficient of determination ($R^{2)}$ and Pearson correlation coefficient (r) methods are used to know the strength of association and direction of a relationship between the variables. Saturation indices of different minerals were computed using the PHREEQC Interactive 2.12 software. The inter-ionic relation graphs were made using Microsoft Excel version 2007. Different contour maps were used to depict the concentration of different parameters with the help of Arc GIS 9.3. The location map was made by using adobe illustrator 10.0.

Quality control and quality assurance for F^- analysis

Standard methodologies mentioned in APHA (1995) were used to ensure quality. Thermo Fisher Scientific, USA, provided 100 mg/L sodium fluoride stock solution for standard preparation. The stock solution was serially diluted with Millipore distilled water to produce a series of standard fluoride solutions

(0.1–10 mg/L). With the standards (0.05, 0.1, 1.0, 5.0, and 10 mg/L), the electrometer was calibrated to a slope of -59.2 ± 2 mV. TISAB III was added in a 10:1 ratio to all standards and samples. Twenty ml of each groundwater sample was taken, and 2 ml TISAB was added before measuring the fluoride value. The Instrument's accuracy was tested using blanks and duplicate samples, and the results were determined to be repeatable within ± 2% error. The samples were checked three times, and the average values were reported.

Health risk assessment in humans through exposure pathway

F^- is a very hazardous element that may cause severe cases of dental and skeletal fluorosis. There are several ways through which a person can ingest fluoride, but compared to oral routes (through food and water), inhalation and dermal absorption are negligible (O'Rourke et al., 1999; Masood et al., 2022; Karunanidhi et al., 2020; Aravinthasamy et al., 2020; Ahamad et al., 2019; Ahamad et al., 2020; Mukherjee & Singh, 2022). Non-carcinogenic risks can be examined through the target hazard quotient (THQ). The THQ is based on the ratio between an estimated dose of contaminant and the reference dose, below which there is no appreciable risk (Storelli, 2008). To calculate the THQ through water ingestion, the US Environmental Protection Agency (US EPA, 1989; Ahamad et al., 2019, 2020) equation is used. So, the non-carcinogenic health risk assessment due to the consumption of fluoride-contaminated water was estimated by using the following equation:

$$\mathrm{THQ} = \frac{\left(\mathrm{EF_r} \times \mathrm{ED_{tot}} \times \mathrm{SFI} \times \mathrm{MCS_{inorg}}\right)}{\left(\mathrm{RfD} \times \mathrm{BW_a} \times \mathrm{AT_n}\right)}$$

All the values for each parameter of this equation are adopted from the published previous research article (Ahamad et al., 2020). The RfD value for F is 0.06 mg/kg/day (Masood et al., 2022).

Result and discussion

Hydrogeochemistry

The statistical summary of pH, EC & different physicochemical parameters and their comparison with WHO 2011 and BIS 2012 standards are shown in Table 1. The pH value of groundwater samples for Renukoot and Anpara in post- and pre-monsoon varied from 6.30 to 8.00 (mean 7.1) and 6.6–8.10 (mean 7.15) and 7.04–7.80 (mean 7.36) and 6.93–8.00 (mean 7.31), respectively. The results displayed that the overall groundwater of both clusters is slightly acidic to alkaline in nature and within the permissible limit set by WHO and BIS. Very few samples of Renukoot (3% in post-monsoon) deviated from the standard range of BIS for pH. The pH values are almost homogenous in the entire study area pointing to similar geochemical processes (Fentahun et al., 2023) The variations in the EC values are an indicator of a wide range of activities and geochemical processes which control the ionic concentration of the groundwater (Kawo & Karuppannan, 2018; Raju et al., 2011). The EC value of groundwater samples for Renukoot and Anpara in post- and pre-monsoon varied from 373–1857 (mean 902 µS/cm) and 340.86–1775.13 (mean 849.79 µS/cm) and 561.67–1531.75 (mean 809.96 µS/cm) and 654.40–1645.02 (mean 892.26 µS/cm), respectively. The seasonal variation in EC may be due to the leaching of major cations and anions, especially salts from the soil, or the dissolution of minerals from the wall of the aquifer with the rise of the water table (Ahamad et al., 2019; Panneerselvam et al., 2023).

The Ca value of post- and pre-monsoon in Renukoot and Anpara region ranged between "22–138 (mean 77.64 mg/l) and 28–136 (mean 80.03 mg/l)" and "34–92 (mean 56.43 mg/l) and 40–102 (mean 56.86 mg/l)," respectively. The value of Mg in study area ranged between "8.55–65.69 (mean 24.42 mg/l) and 6.37–57.43 (mean 19 mg/l)" for Renukoot and "9.04–46.70 (mean 31.48 mg/l) and 7.35–48.17 (mean 32.97 mg/l)" for Anpara in post-monsoon and pre-monsoon, respectively. Ca and Mg values for the majority of the samples of both clusters were found within the WHO and BIS standards in both seasons. Lower concentrations of Ca and Mg are likely because of calcite and dolomite precipitation under alkaline pH conditions and cation exchange reactions occurring in the subsurface (Selvam, 2015; Younas et al., 2019). In the present study, Na ranged from "22.20–236.20 (mean 63.01 mg/l) and 17.80–247.70 (mean 61.88 mg/l)" for Renukoot and "14.60–168.40 (mean 62.73 mg/l) and 30.80–186 (mean 72.80 mg/l)" for Anpara during post-monsoon and pre-monsoon, respectively. In

Table 1 Statistical summary of physicochemical parameters in groundwater samples of Renukoot and Anpara clusters of Sonbhadra and its comparison with WHO and BIS standards during post-monsoon and pre-monsoon seasons

Renukoot														
Parameters	WHO (2011)	BIS (2012)	Post-monsoon						Pre-monsoon					
			Min	Max	Mean	SD	% samples exceeding WHO limit	% samples exceeding BIS limit	Min	Max	Mean	SD	% samples exceeding WHO limit	% samples exceeding BIS limit
pH	9.20	6.5–8.5	6.30	8.00	7.10	0.29		3.00	6.60	8.10	7.15	0.27		
EC	1500	–	373	1857	902	376	11	–	341	1775	850	335	6	–
Ca^{2+}	200.00	200.00	22.00	138.00	77.64	26.50			28.00	136.00	80.03	24.56		
Mg^{2+}	150.00	100.00	8.55	65.69	24.42	12.68			6.37	57.43	19.00	10.90		
Na^{+}	200.00	200.00	22.20	236.20	63.01	44.28	3.00		17.80	247.70	61.88	43.53	3.00	3.00
K^{+}	12.00		0.30	15.60	1.93	2.50	3.00		0.60	18.40	2.01	2.91	3.00	
HCO_3^{-}	600.00	600.00	62.00	484.00	233.22	91.34			48.00	516.00	239.17	89.70		
SO_4^{2-}	600.00	400.00	27.20	228.90	103.25	52.75			17.11	180.40	70.99	40.69		
Cl^{-}	600.00	1000.00	22.00	208.00	83.92	47.51			32.00	232.00	86.92	48.13		
F^{-}	1.50	1.50	0.02	5.10	0.48	0.87	14	14	0.19	5.50	0.71	0.92	14	14
Hardness	500.00	600.00	114.00	544.99	294.36	92.53	6.00		122.00	516.00	278.00	85.10	3.00	
Alkalinity			50.84	396.88	191.24	74.90			39.36	423.12	196.09	73.53		
Anpara														
Parameters	WHO (2011)	BIS (2012)	Post-monsoon						Pre-monsoon					
			Min	Max	Mean	SD	% samples exceeding WHO limit	% samples exceeding BIS limit	Min	Max	Mean	SD	% samples exceeding WHO limit	% samples exceeding BIS limit
pH	9.20	6.5–8.5	7.04	7.80	7.36	0.18			6.93	8.00	7.31	0.27		
EC	1500	–	561.67	1531.75	809.96	195.07	4	–	654.40	1645.02	892.26	202.20	4	–
Ca^{2+}	200.00	200.00	34.00	92.00	56.43	12.43			40.00	102.00	56.86	12.44		
Mg^{2+}	150.00	100.00	9.04	46.70	31.48	10.68			7.35	48.17	32.97	11.14		
Na^{+}	200.00	200.00	14.60	168.40	62.73	31.19			30.80	186.00	72.80	34.37		
K^{+}	12.00		0.30	9.30	1.20	1.69			0.20	10.10	1.47	1.79		
HCO_3^{-}	600.00	600.00	168.00	340.00	225.79	42.12			174.00	358.00	243.71	44.36		
SO_4^{2-}	600.00	400.00	9.36	87.02	39.34	22.50			15.90	102.30	48.17	22.55		
Cl^{-}	600.00	1000.00	36.00	176.00	97.57	39.06			32.00	182.00	106.00	41.73		
F^{-}	1.50	1.50	0.19	2.50	0.88	0.53	14	14	0.24	2.80	1.04	0.57	29	29
Hardness	500.00	600.00	160.00	344.00	270.43	49.95			188.00	346.00	277.63	45.26		

Table 1 (continued)

Parameters	WHO (2011)	BIS (2012)	Post-monsoon					Pre-monsoon				
			Min	Max	Mean	SD	% samples exceeding WHO limit	% samples exceeding BIS limit	Min	Max	Mean	SD	% samples exceeding WHO limit	% samples exceeding BIS limit
Anpara														
Alkalinity			134.48	278.80	183.97	35.46			142.68	293.56	198.91	37.30		

All parameters are in mg/l except electrical conductivity (EC) in (µS/cm) at 25°C

the whole study region, K ranged from "0.3–15.60 (mean 1.93 mg/l) and 0.6–18.40 (mean 2.01 mg/l)" for Renukoot and "0.3–9.3 (mean 1.2 mg/l) and 0.2–10.10 (mean 1.47 mg/l)" for Anpara during post-monsoon and pre-monsoon, respectively. Almost all samples of all the clusters are within the permissible limit of WHO and BIS for Na and K. The HCO_3 value of the study area of post- and pre-monsoon in Renukoot and Anpara regions ranged between "62–484 (mean 233.22 mg/l) and 48–516 (mean 239.17 mg/l)," "168–340 (mean 225.79 mg/l) and 174–358 (mean 243.71 mg/l)," respectively. If the most abundant anion in groundwater is HCO_3 then silicate weathering is the key source of abundant Na over Cl (Srinivasamoorthy et al., 2014). The SO_4 value of the study area of post- and pre-monsoon in Renukoot and Anpara regions ranged between "27.20–228.90 (mean 103.25 mg/l) and 17.11–180.40 (mean 70.99 mg/l)" and "9.36–87.02 (mean 39.34 mg/l) and 15.90–102.30 (mean 48.17 mg/l)," respectively. The value of Cl in the study area ranged between "22–208 (mean 83.92 mg/l) and 32–232 (mean 86.92 mg/l)" for Renukoot and "36–176 (mean 97.57 mg/l) and 32–182 (mean 106 mg/l)" for Anpara in post-monsoon and pre-monsoon, respectively. Among anions, HCO_3, SO_4, and Cl ions values were found below the prescribed limit of WHO and BIS for both clusters in both seasons. The F value of the study area of post- and pre-monsoon in Renukoot and Anpara regions ranged "0.02–5.10 (mean 0.48 mg/l) and 0.19–5.50 (mean 0.71 mg/l)" and "0.19–2.50 (mean 0.88 mg/l) and 0.24–2.80 (mean 1.04 mg/l)," respectively. The concentration of F in groundwater exceeded in 14% samples of the permissible limit prescribed by WHO (2011) and BIS (2012) in both seasons for the Renukoot cluster, while Anpara industrial cluster shown 14 and 29% samples exceeded the standard limit in post-monsoon and pre-monsoon seasons, respectively.

Spatial distribution of F^-

Renukoot cluster displayed a high value of F^- in the southern part (Fig. 4 A1 and A2) adjacent to the GBPS reservoir, which may be due to the mixing of F^- laden surface water with groundwater that contains F^- around 4.7 mg/l (Usham et al., 2018) as well as the release of F^- from granitic rocks

containing fluorinated minerals. In this region, we also have an aluminum smelting plant that releases HF into the atmosphere. Very high concentration of F^- is reported in different tree leaves of that zone already, which may act as a marker of F^- deposition in that region (Pandey et al., 2015). Anpara cluster displayed a high value of F^- (Fig. 4 B1 and B2) in the vicinity of coal mining and ash pond region, which may be due to the leaching of fly ash from the soil surface to the below ground or mixing of slurry water to the groundwater (Usham et al., 2018).

Anthropogenic evidences for high F^- in groundwater

Fluoride is considered a geogenic contaminant, and there are numerous studies at a global level that reported its origin from geological sources. In recent years, researchers have reported high levels of fluoride in groundwater due to various anthropogenic sources, i.e., coal mining, thermal power plant, aluminum smelting plant, fertilizers used in agricultural land, etc. The current study region is also dominated by a similar kind of industrial setup, i.e., coal mining and thermal power plant. The article published on fluoride contamination in this region has also reported that coal burning is the major source of the high concentration of fluoride in different environmental components. In this section, the authors tried to summarize similar studies which reported fluoride contamination at the global level, national level, and local levels. There are so many researchers around the world who reported high concentrations of fluoride in groundwater in coal mining regions (Table 2). Several researchers studied F contamination in various parts of the coal mining region of India and found its concentration beyond the permissible limit of

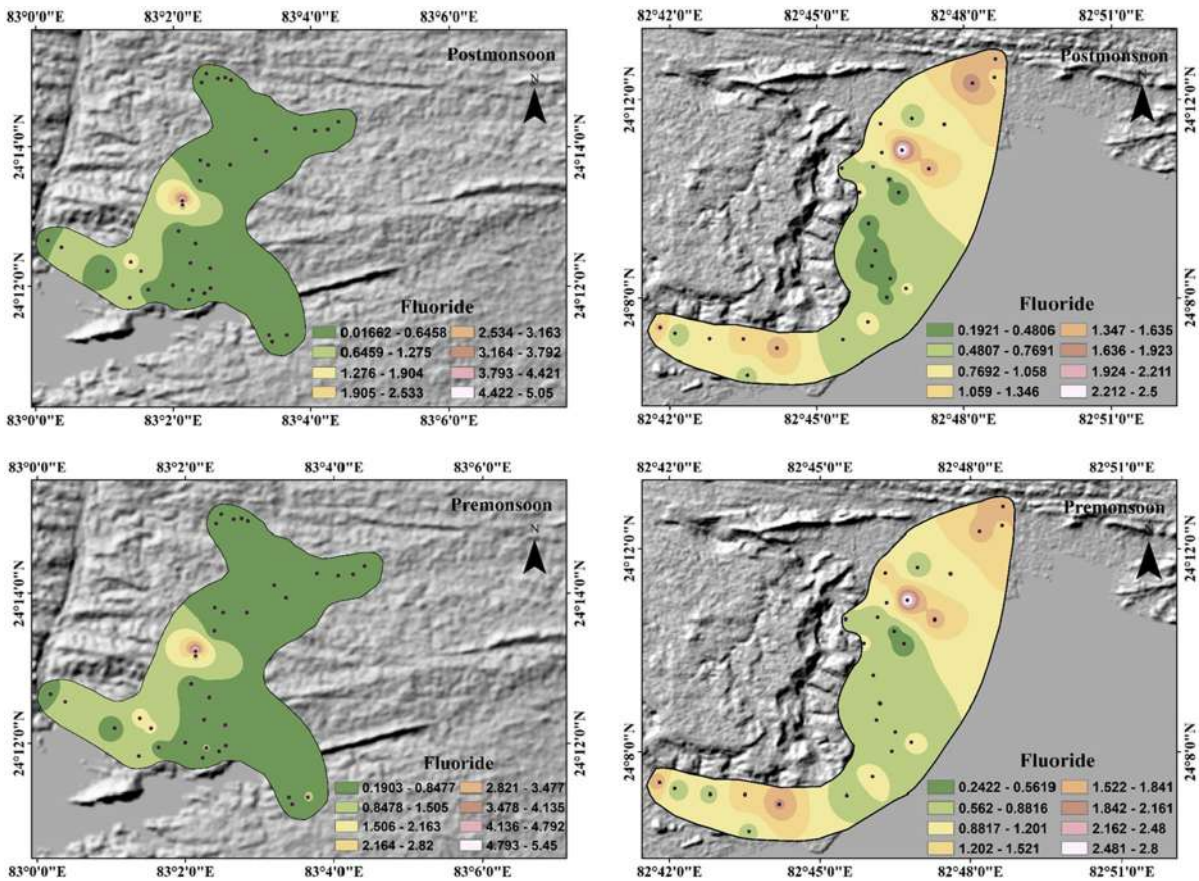

Fig. 4 Spatial distribution of F in groundwater samples of Renukoot (A1 & A2) and Anpara (B1 & B2) cluster during post-monsoon and pre-monsoon seasons

WHO. Yadav et al. (2021) found F concentration in the groundwater of Dhanbad in the range of 0.1 to 2.3 mg/l, which is below the maximum value reported in our study region. Selvam (2015) reported F in the groundwater of Tamil Nadu, which was found below the maximum value of Renukoot and above the value of the Anpara region during both seasons. Similarly, Mohanty et al. (2018) and Usham et al. (2018) also observed the F^- concentration beyond the permissible limit of WHO in the groundwater of Ramgarh district, Jharkhand, and Singrauli district, MP, respectively. Studies carried out in other parts of the world have reported the highest concentration of F^- (9.42 mg/l) in Shanxi Province, China, followed by Dargai Pakistan (8.65 mg/l), Taiyuan City Shanxi Province, China (5.70 mg/l) and Hongdunzi Coal Mine, Northwest China (5.60 mg/l), Shanxi Province of Northern China (3.49 mg/l), Zarand district, Kerman Province, Iran (3.45 mg/l) and coal mining areas of the Salt Range, Punjab Pakistan (1.8–2.7 mg/l) (Table 2). The

Table 2 F^- contamination in different environmental matrices

Location	F^- concentration	References
Groundwater		
Southern Sonbhadra (Renukoot)	0.02–5.10 mg/l post-monsoon & 0.19–5.50 mg/l pre-monsoon	This study
Southern Sonbhadra (Anpara)	0.19–2.50 mg/l post-monsoon & 0.24–2.80 mg/l pre-monsoon	This study
Rajrappa coal mining area of Ramgarh District, Jharkhand State of India	0.3–3.21 mg/l (pre-monsoon) 0.41–3.17 mg/l (post-monsoon)	Mohanty et al. (2018)
Katras block coal mine area Dhanbad district, Jharkhand, India	0.1–2.3 mg/l	Yadav et al. (2021)
southern coastal city, Tamil Nadu, India	0.16–4.8 mg/l pre-monsoon 0.2–3.2 mg/l post-monsoon	Selvam, (2015)
Singrauli, Uttar Pradesh	1.5 mg/l	Usham et al. (2018)
Sub-district Dargai, Pakistan	0.5–8.65 mg/l	Rashid et al. (2020)
Coal mining areas of Salt Range, Punjab Pakistan	ESR = 0.1–1.8 mg/L CSR = 0.1–2.7 mg/L TSR = 0.3–2.5 mg/L	Masood et al. (2022)
Zarand district, Kerman province, Iran	Up to 3.45 mg/L	Derakhshani et al. (2020)
Shanxi Province of Northern China	0.48–3.49 mg/l	Li et al. (2021)
Taiyuan city Shanxi Province, China	0.1–5.7 mg/l	Li et al. (2019)
Shanxi Province	0.03–9.42 mg/l	Yuan et al. (2020)
Hongdunzi Coal Mine, Northwest China	0.40 to 5.60 mg/L	Li et al. (2018)
Fluoride in coal		
China coal	25–1230 mg/kg	Wu et al. (2004)
Australian coal	15–458 mg/kg	Godbeer and Dalway (1987)
Canadian coal	31–580 mg/kg	Godbeer et al. (1994)
Austrian coal	137–564 mg/kg	Martinez-Tarazona et al. (1994)
Coal Dargai Pakistan	98 mg/kg	Rashid et al. (2018)
Xiangning mining area	2–911 mg/kg	Guohua et al. (2019)
Coal of Shanxi province	0.8–1443 mg/kg	Guohua et al. (2019)
Fluoride in different environmental samples of current study region		
Coal of Sonbhadra region	0.32–3.1 mg/kg	Usham et al. (2018)
Fly ash of Sonbhadra region	2.72–12.6 mg/kg	Usham et al. (2018)
Soil of Sonbhadra region	0.83–6.1 mg/kg	Usham et al. (2018)

reason mentioned for the high value of F^- in groundwater is due to the leaching of F^- from fly ash, acid mine drainage, atmospheric deposition, and particulate matter generated due to coal mining practices.

It is evident from the coal samples of different parts of the world that F^- concentration was reported very high in comparison to Sonbhadra region coal. The highest F concentration in coal was reported in the range of 0.8–1443 mg/kg of Shanxi province coal in China, followed by China coal (25–1230 mg/kg), Xiangning mining area (2–911 mg/kg), Canadian coal (31–580 mg/kg), Austrian coal (137–564 mg/kg), Australian coal (15–458 mg/kg), Coal Dargai Pakistan (98 mg/kg), and Coal of Sonbhadra region (0.32–3.1 mg/kg).

The study by Usham et al. (2018) has reported the presence of fluoride in fly ash (12.6 mg/kg), drain water (5.34 mg/l), soil (6.1 mg/kg), and coal (3.1 mg/kg) in Singrauli region. They confirmed the source of fluoride from the coal thermal power plant, which utilized coal from the Singrauli coal seam (1.6 mg/kg). They have reported the fluoride concentration in Rihand reservoir water up to 4.7 mg/l. The aquifers located in the surrounding of this reservoir possibly get recharged due to infiltration of the surface water.

In the Renukoot region, Pandey et al. (2015) reported the emission of F in the form of HF from the aluminum smelting factory and coal combustion in other industries located in this area. A high concentration of F^- was estimated in different plant leaves of trees grown in the study region. The highest fluoride value was found to be 33 mg/l. Various coal-dependent activities release the fluorinated compound into the air, and its deposition over the land surface causes enrichment of F^- in soil, and its leaching from the surface leads to enter F^- in groundwater resources. In the current study area, the high concentration of F^- is already reported in coal samples, fly ash samples, soil samples, slurry water, Rihand reservoir water, tree leaves, etc. Hence, there is enough evidence to support the statement that F^- in groundwater of the selected study area is contributed by all these anthropogenic sources along with some natural sources.

Geochemistry of high F^- value in groundwater

There are various procedures to control the groundwater geochemistry of the study region and enrich the aquifer with a high concentration of F^-. Groundwater fluoride is typically thought to come primarily from fluorite (CaF_2), particularly in granitic terrains (Sunitha et al., 2022). When groundwater responds with stone gneissic rocks for a drawn-out period, the fluoride fixations are ceaselessly improved, even after the groundwater arrives at a harmony state concerning fluorite (CaF_2) because of the evacuation of Ca^{2+} by precipitation of calcite ($CaCO_3$). The precipitation of calcite from Ca and CO_3 ions is made possible by weathered rock formations' sodium carbonate type water (Na-HCO_3), which also accelerates the dissolution of CaF_2, which results in the release of fluoride into the groundwater (Raju et al., 2012).

$$CaF_2 + 2NaHCO_3 = CaCO_3 + 2Na + +2F^- + H_2O + CO_2$$

During the course of synthetic enduring, the disintegration of fluoride species in normal water is controlled by calcium and represented by thermodynamic standards. The fluoride fixation in groundwater is constrained by mineral fluorite.

$$CaF_2 = Ca^{2+} + 2F^-$$

$$KCaF_2 = a(Ca^{2+})$$

$$a(F^-)^2 = 10^{-10.58} \text{at } 25\ ^\circ C$$

where K represents the solubility product constant and *a* denotes the activities of the corresponding ions. As a result, there is a negative correlation between calcium and fluoride activities (Reddy et al., 2010). The dissolution of fluoride from fluoride-rich minerals is also facilitated by calcite ($CaCO_3$)-rich minerals. Decreasing Ca concentrations are observed under alkaline conditions with a corresponding rise in Na noticed in highly fluoride-affected areas. Generally, the aquifers which have a high value of F contain a low concentration of Ca, a high concentration of Na, a high concentration of HCO_3, and alkaline pH. In the present study, it is observed that Renukoot and Anpara clusters show more than 1.5 mg/l WHO permissible limit of F, which is located in the surrounding Rihand reservoir. The scatter plots of fluoride with Ca, Na, HCO_3, and pH are used to explain the release mechanism of fluoride in groundwater. In this study, the graph between Ca and F (Fig. 5A1 and A2) displays a very low R^2 (coefficient of determination)

value (R^2 = 0.005 post and R^2 = 0.016 of Renukoot and R^2 = 0.004 post and R^2 = 0.11 pre of Anpara). The correlation coefficient between Ca and F was found negative or very weak (r = 0.08 post and r = −0.13 pre- of Renukoot and r = −0.06 post and r = −0.46 pre- of Anpara) (Tables 3 and 4), which justified the high value of F with low Ca value. The graph between Na and F (Fig. 5 B1 and B2) displays moderate R^2 (coefficient of determination) value (R^2 = 0.424 post and R^2 = 0.579 pre of Renukoot and R^2 = 0.179 post and R^2 = 0.236 pre of Anpara). The correlation coefficient between Na and F was found positive (r = 0.65 post and r = 0.76 pre of Renukoot and r = 0.42 post and r = 0.49 pre of Anpara), which justified the high value of F with high Na. The graph between HCO_3 and F (Fig. 5 C1 and C2) shows moderate R^2 (coefficient of determination) value (R^2 = 0.273 post and R^2 = 0.416 pre of Renukoot and R^2 = 0.151 post and R^2 = 0.16 pre of Anpara). The correlation coefficient between HCO_3 and F was found positive (r = 0.52 post and r = 0.65 pre of Renukoot and r = 0.39 post and r = 0.40 pre of Anpara), which justified that the high HCO_3 enhanced the dissolution of F in groundwater. The graph between pH and F (Fig. 5 D1 and D2) shows moderate R^2 (coefficient of determination) value (R^2 = 0.39 post and R^2 = 0.45 pre of Renukoot and R^2 = 0.33 post and R^2 = 0.31 pre of Anpara). The correlation coefficient between pH and F was found positive (r = 0.62 post and r = 0.67 pre of Renukoot and r = 0.58 post and r = 0.56 pre of Anpara), which leads to high F dissolution in groundwater under alkaline pH conditions.

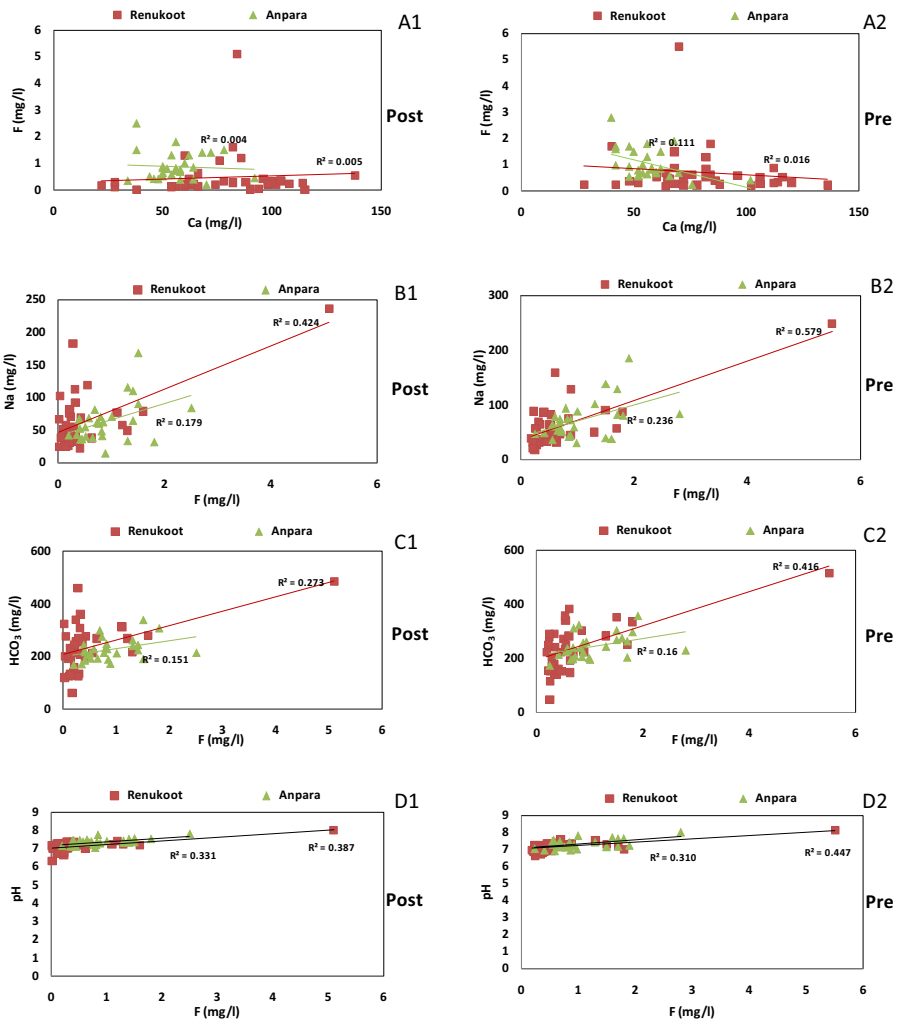

Fig. 5 Graph between F vs Ca, Na, HCO_3, and pH of Renukoot and Anpara clusters during post-monsoon and pre-monsoon

Table 3 Correlation between chemical constituents of groundwater in Renukoot during post-monsoon

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3-	$SO_4^{3}-$	C^{-}	F^{-}	pH	EC	TH	TA
Ca^{2+}	1.00											
Mg^{2+}	0.21	1.00										
Na^{+}	**0.50**	0.31	1.00									
K^{+}	0.28	0.16	0.15	1.00								
HCO_3^{-}	0.59	0.15	**0.74**	0.32	1.00							
$SO_4^{2}-$	**0.61**	**0.66**	**0.69**	0.11	0.39	1.00						
C^{-}	**0.62**	**0.62**	**0.77**	0.31	0.44	**0.78**	1.00					
F^{-}	0.08	−0.04	**0.65**	−0.03	**0.52**	0.12	0.31	1.00				
pH	0.26	0.00	0.43	0.15	0.38	0.16	0.27	**0.62**	1.00			
EC	**0.76**	**0.61**	**0.85**	0.26	**0.66**	**0.87**	**0.90**	0.35	0.34	1.00		
TH	**0.83**	**0.72**	**0.53**	0.29	**0.51**	**0.80**	**0.79**	0.03	0.19	**0.89**	1.00	
TA	**0.59**	0.15	**0.74**	0.32	**1.00**	0.39	0.44	**0.52**	0.38	**0.66**	**0.51**	1.00
Correlation between chemical constituents of groundwater in Renukoot pre-monsoon												
Ca^{2+}	1.00											
Mg^{2+}	0.27	1.00										
Na^{+}	0.26	0.40	1.00									
K^{+}	0.30	0.24	0.07	1.00								
HCO_3-	0.35	0.25	**0.72**	0.25	1.00							
$SO_4^{2}-$	**0.64**	**0.57**	**0.51**	0.20	0.18	1.00						
Cl^{-}	**0.55**	**0.66**	**0.75**	0.23	0.35	**0.79**	1.00					
F^{-}	−0.13	0.18	**0.76**	−0.04	**0.65**	0.12	0.40	1.00				
pH	−0.02	0.27	**0.55**	0.06	0.43	0.19	0.35	**0.67**	1.00			
EC	**0.67**	**0.67**	**0.82**	0.23	**0.60**	**0.81**	**0.91**	0.45	0.40	1.00		
TH	**0.86**	**0.72**	0.40	0.34	0.39	**0.76**	**0.74**	0.00	0.12	**0.83**	1.00	
TA	0.35	0.25	**0.72**	0.25	**1.00**	0.18	0.35	**0.65**	0.43	**0.60**	0.39	1.00

Saturation indices

To explore the possible mechanisms of F^{-} contamination further, saturation indices (SIs) of the groundwater samples were calculated. The fluoride concentrations found in groundwater are mainly dependent on the oversaturation of calcite, particularly in granite gneiss rock, due to the cation exchange process and water–rock interactions in the study region. Both CaF_2 and $CaCO_3$ provide Ca^{2+}, which influences the composition of the groundwater (Rashid et al., 2018). SI calcite vs. SI fluorite (Fig. 6 A1 and A2) and SI dolomite vs. SI fluorite (Fig. 6 B1 and B2) plots of both clusters indicate fluorite in under-saturated conditions, while calcite and dolomite both are in under-saturated to super-saturated condition. Most SI value of dolomite and calcite are either very close to zero or above zero, which means that these minerals will precipitate, reducing the Ca value in the system and increasing the dissolution of CaF_2 (Fluorite). This condition increases the F concentrations in the groundwater of the study region. Almost neutral to alkaline pH conditions favor the F^{-} enrichment, which increases the HCO_3^{-} value. The increased HCO_3^{-} value reacts with Ca^{2+} resulting in the enhancement of the precipitation of calcite, which finally helps in the reduction of Ca^{2+} and consequently stimulates the process of fluorite dissolution and intensifies the concentration of F^{-} in the groundwater environment (Wu et al., 2018).

Human health risk assessment

Non-carcinogenic Risk (NCR)

The presence of high content of fluoride in the aquifer due to natural and anthropogenic sources and the

Table 4 Correlation between chemical constituents of groundwater in Anpara duringpost-monsoon

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3-	$SO_4^{2}-$	C^{-}	F^{-}	pH	EC	TH	TA
Ca^{2+}	1.00											
Mg^{2+}	−0.15	1.00										
Na^{+}	0.27	0.02	1.00									
K^{+}	0.03	0.09	−0.07	1.00								
HCO_3-	0.31	0.31	0.47	0.10	1.00							
$SO_4^{2}-$	0.24	−0.12	0.46	0.38	0.27	1.00						
C^{-}	0.25	0.41	**0.70**	0.09	0.23	0.13	1.00					
F^{-}	−0.06	−0.29	0.42	−0.12	0.39	0.38	−0.11	1.00				
pH	−0.27	−0.31	0.17	0.18	0.04	0.28	−0.07	**0.58**	1.00			
EC	0.48	0.32	**0.89**	0.07	**0.63**	0.45	**0.76**	0.24	−0.03	1.00		
TH	0.49	**0.79**	0.19	0.10	0.46	0.04	**0.52**	−0.30	−0.44	**0.57**	1.00	
TA	0.35	0.38	0.42	0.11	**0.97**	0.21	0.27	0.24	−0.07	**0.62**	**0.55**	1.00
Correlation between chemical constituents of groundwater in Anpara during pre-monsoon												
Ca^{2+}	1.00											
Mg^{2+}	−0.36	1.00										
Na^{+}	−0.08	0.09	1.00									
K^{+}	0.07	0.11	−0.08	1.00								
HCO_3-	−0.02	0.37	**0.51**	−0.02	1.00							
$SO_4^{2}-$	0.04	0.00	0.40	0.45	0.23	1.00						
C^{-}	0.04	0.42	0.65	0.09	0.19	0.08	1.00					
F^{-}	−0.46	−0.09	0.49	−0.14	0.40	0.22	−0.06	1.00				
pH	−0.39	−0.14	0.04	0.18	−0.02	0.16	−0.17	**0.56**	1.00			
EC	0.12	0.39	**0.88**	0.04	**0.59**	0.34	**0.77**	0.23	−0.13	1.00		
TH	0.32	**0.77**	0.04	0.16	0.36	0.02	0.46	−0.41	−0.41	0.48	1.00	
TA	0.06	0.38	0.47	0.00	**0.97**	0.17	0.22	0.25	−0.14	**0.58**	0.42	1.00

dependency of the local population primarily on it for drinking purposes is putting human health at risk in the study region.

Target hazard quotient (THQ)

Table 5 summarizes the THQ values of the fluoride in the groundwater samples collected from the Sonbhadra. For adults, THQ values of F^{-} exceeded the safe limit by 6 and 7% for Renukoot and Anpara during post-monsoon, respectively. For adults, THQ values of F^{-} exceeded the safe limit by 8 and 21% for Renukoot and Anpara during pre-monsoon, respectively. THQ values of F^{-} For children exceeded the safe limit by 17 and 64% for Renukoot and Anpara during post-monsoon, respectively. THQ values of F^{-} for children exceeded the safe limit by 36 and 82% for Renukoot and Anpara during pre-monsoon, respectively. If the groundwater from the bore wells with a high THQ value (> 1) for the observed elements is used for a long and sustained period without adopting any remedial measures, these will have the potential to cause NCR human health risks to the consumers in the region. In the majority of the groundwater samples, the results highlighted a significant non-cancer health hazard across the study area as indicated by the presence of more than unity THQ values for F^{-}. Within this context, the current study assists in establishing a periodic monitoring network to evaluate the F^{-} contamination that reveals both the quality of groundwater and the level of associated health risk.

The THQ value of F^{-} for adults during post-monsoon in Renukoot and Anpara regions ranged between "0.01–3.30 (mean 0.31 mg/l) and 0.12–1.62 (mean 0.57 mg/l)," respectively. The THQ value of F^{-} for adults during pre-monsoon in Renukoot and Anpara regions ranged between "0.12–3.56 (mean 0.46 mg/l) and 0.16–1.81 (mean 0.68 mg/l)," respectively. For

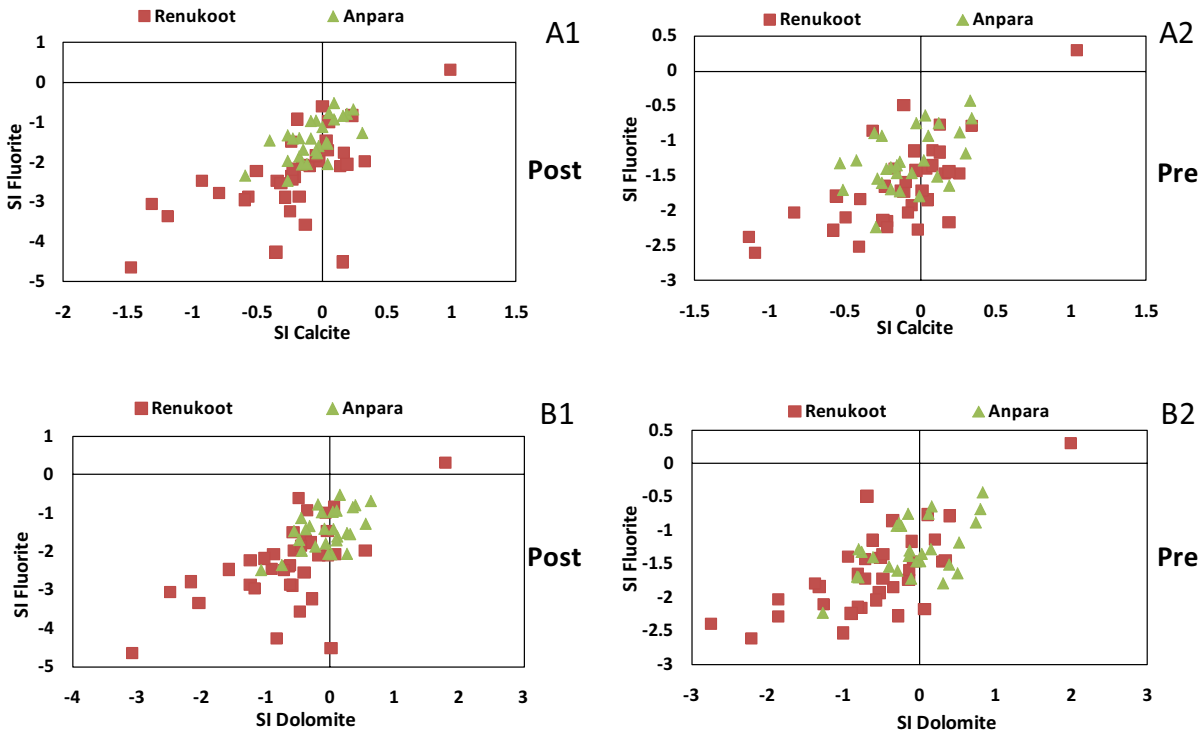

Fig. 6 Saturation index plot (A1 & A2) fluorite vs calcite, (B1 & B2) fluorite vs dolomite

Table 5 Statistical description of target hazard quotient (THQ) in adults and children of the study area

Parameter	THQ of F (Adult)				THQ of F (children)			
	Renukoot		Anpara		Renukoot		Anpara	
	Post-	Pre-	Post-	Pre-	Post-	Pre-	Post-	Pre-
Min	0.01	0.12	0.12	0.15	0.03	0.33	0.33	0.42
Max	3.29	3.56	1.62	1.81	8.93	9.63	4.38	4.90
Average	0.31	0.46	0.57	0.68	0.84	1.25	1.55	1.83
% sample exceeding	6%	8%	7%	21%	17%	36%	64%	82%

children, the THQ value of F^- during post-monsoon in Renukoot and Anpara regions ranged between "0.03–8.93 (mean 0.84 mg/l) and 0.33–4.38 (mean 1.55 mg/l)," respectively. For children, the THQ value of F^- during pre-monsoon in Renukoot and Anpara regions ranged between "0.33–9.63 (mean 1.25 mg/l) and 0.42–4.9 (mean 1.83 mg/l)," respectively. The radial plots of the THQ of all samples in both the clusters are shown in Fig. 7 (I and II) for adults and Fig. 7 (III and IV) for children during post-monsoon and pre-monsoon. The THQ value for children is observed to be very high compared to adults, which means that children within the study area are more prone to non-carcinogenic health risks of F^-. Similar research related to health risk assessment on the same model was done in India and other parts of the globe. Mukherjee and Singh (2019) observed higher fluoride toxicity in children than adults in the semiarid rural tract of Birbhum district, located in the eastern part of peninsular India, where F^- concentration in groundwater is estimated in the range of 0.3–9.36 mg/l. However, they included gender-based studies in their research work. Admilla et al. (2018) also reported a higher risk of F^- for children compared to adults in

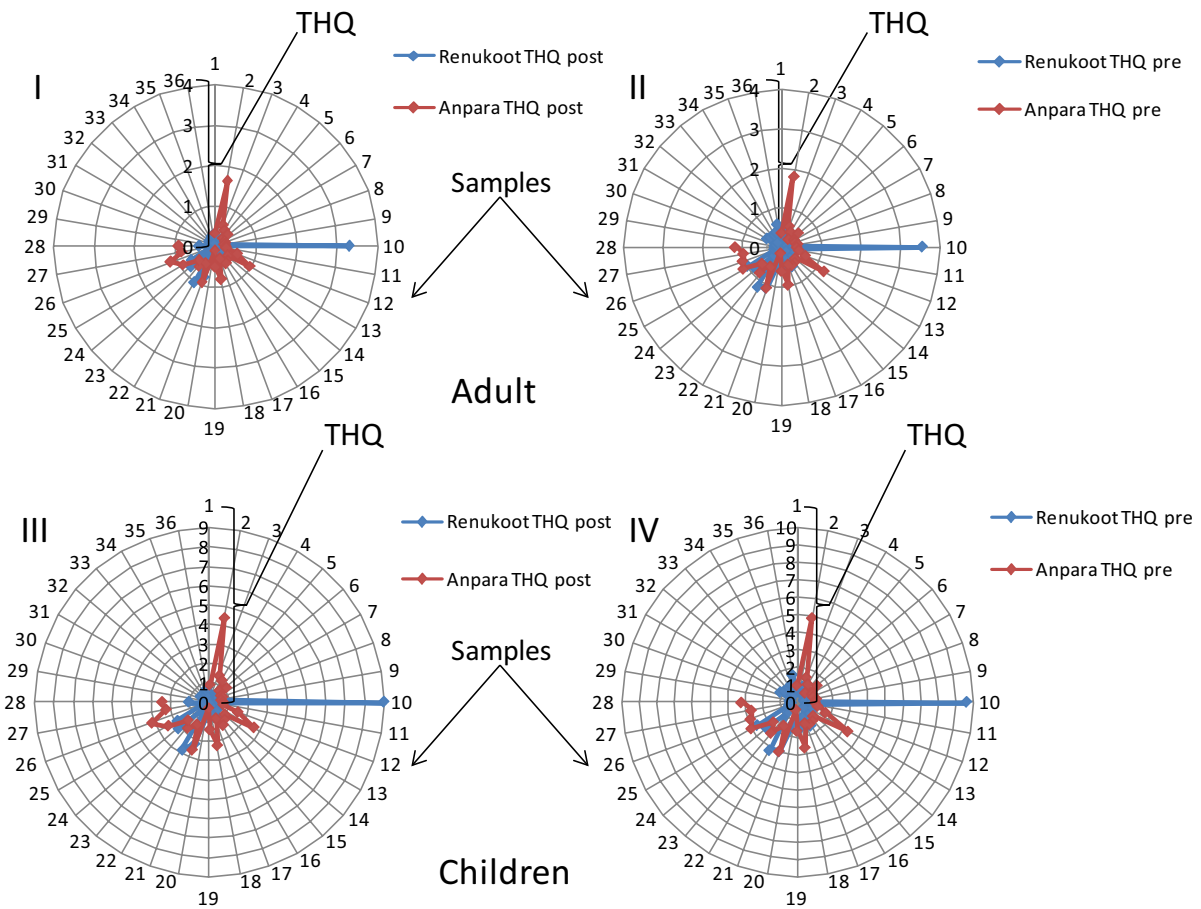

Fig. 7 Radar plot for target hazard quotient (THQ) of F of each sampling location during post- and pre-monsoon in the study area (I, II) for adults (III, IV) for children

the Nirmal district of Telangana (India). Narsimha and Rajitha (2018) found that the local population group in the Siddipet district of Telangana poses the fluoride toxicity order as children > men > women. Qiu et al. (2023) also reported a higher risk of F for children compared to adults in the mid-layer groundwater of the Huaibei mining area in North China. Iqbal et al. (2023) found that fluoride toxicity in South Punjab, Pakistan, followed the same order of health risk as children > and adults, which supports the current study's findings. A health survey related to fluorosis-affected children was also done. A few pictures of dental fluorosis-affected children of the study region are shown in Fig. 8.

Conclusion

Sonbhadra district is known as the energy capital of India. In the current study area of Sonbhadra district, coal burning and coal mining activities are dominant. All the groundwater samples of the study region were found to be slightly acidic to alkaline in nature during both the seasons. The cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) and anions (HCO_3^{-}, Cl^{-}, and SO_4^{2-}) values for the majority of the samples of both clusters were found within the permissible limit of WHO and BIS in both seasons. The concentration of F^{-} in groundwater samples exceeded 14% of the permissible limit prescribed by WHO and BIS in both seasons for the Renukoot cluster, while Anpara cluster showed 14 and 29% samples exceeded the standard limit in post-monsoon and pre-monsoon, respectively. The release

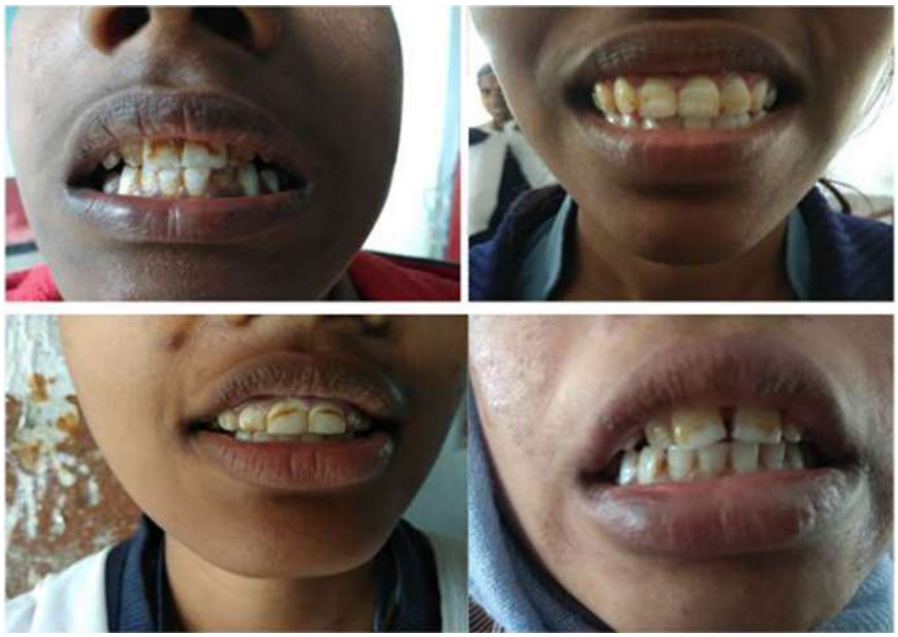

Fig. 8 Dental fluorosis cases in children of the study region

of fluoride from granitic rocks containing fluorinated minerals and the mixing of F^- laden surface water with groundwater contributed to Renukoot cluster's high F^- values in the southern portion adjacent to the GBPS reservoir. In the vicinity of coal mining and an ash pond, the Anpara cluster had a high F^- value, which suggests that fly ash may have leached below the soil surface. Based on different studies across the world and in India, it is confirmed that coal burning activities are the major sources of fluoride contamination in this region too. The published article of this region reported a high concentration of F^- in coal samples, fly ash samples, soil samples, slurry water, Rihand reservoir water, tree leaves, etc., which confirm the reason of F^- enrichment in this area. Scatter plot of F^- with different ions concluded that the aquifers which have a high value of F^- contain a low concentration of Ca, a high concentration of Na, a high concentration of HCO_3, and alkaline pH. Saturation indices (SI) of fluorite showed under-saturation, while calcite and dolomite were in under-saturated to super-saturated conditions. This has facilitated the release of fluoride into the groundwater. THQ values of F^- in adults exceeded the safe limit by 6 and 7% during post-monsoon and 8 and 21% during pre-monsoon for Renukoot and Anpara clusters, respectively. THQ values of F in children exceeded the safe limit by 17 and 64% during post-monsoon and 36 and 82% during pre-monsoon for Renukoot and Anpara clusters, respectively. Picture of the affected children showed mild to severe cases of dental fluorosis. The local population should immediately stop the consumption of groundwater of this region. The local government should start campaign about the health hazard of fluoride to make aware the people of the study area. Urgent actions are required by the government to curb the issue of F contamination in this region and provide the clean water to everyone that is the basic right of every individual of the world as per the United Nation sustainable development goal (SDG) 6. In future, researchers should focus on the work related to estimation of fluoride in biological samples, i.e., blood, urine, hair, etc.

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Declarations

Conflict of interest The authors declare no conflict of interests.

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ORIGINAL PAPER

Assessing water quality and human health risk near coal mines and industrial area of Singrauli, India: special emphasis on toxic elements

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Abstract Water contamination is a major environmental issue, especially in rapidly growing industrialized areas like Singrauli. This study addresses research gaps regarding the hydrochemical characterization, health risk assessment, and source identification of contaminants. Hydrochemistry shows the concentrations of Na^+, Ca^{2+}, F^-, Mn, As, Mo, Sr, and Ni were above the permissible limit for drinking usage. Water quality index (WQI), heavy metal pollution (HMPI), and evaluation indices (HMEI) revealed As, Mn, Cd, Mo, Co, and Ni were the key heavy elements contributing towards aqueous media pollution in the Singrauli area. Additionally, F was also considered one of the major contaminants. In health risk assessment, the higher values of hazard quotient (HQ) for non-carcinogens were associated with Mn, As, Mo, and F; and hazard index (HI) values > 1 were found in 70% and 55% of samples for children and adults, respectively. Carcinogenic risk (CR) for human health was associated with As. CR values in 56.7% (for adults) and 61.7% (for children) of the total samples exceeded 1×10^{-4}. Monte Carlo simulation was applied and highlighted the significant risk factors responsible for both carcinogenic and non-carcinogenic health impacts. 19.2%, 7.3%, and 6.9% of the simulated HQ values for adults and 30.1%, 16.9%, and 10.6% for children were above the safe limit for F, As, and Mn, respectively. Additionally, only 43.8% and 24.8% of the simulated HI for adults and children were within the safe limit. Irrespective of age groups, all the simulated values of As in CR were above 1×10^{-6}; and 60% (for adults) and 77.1% (for children) of the values were above 1×10^{-4}. This outcome emphasizes the urgency of pollution control measures, especially for As, F, and Mn, to safeguard public health. Moreover, a multivariate statistical approach revealed that both geogenic and anthropogenic sources were responsible for contamination. Therefore, regular monitoring, filtration, and purification are mandatory to ensure safe drinking water for human consumption.

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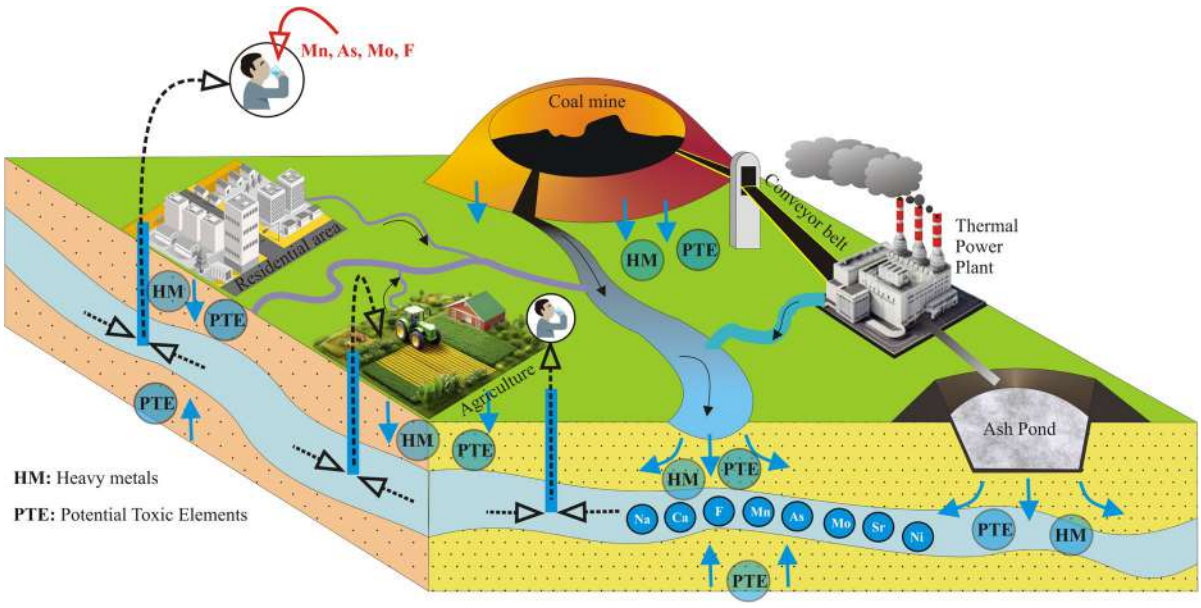
Graphical Abstract



Keywords Carcinogenic risk assessment · Health hazard index · Health quotients · Monte Carlo simulation · Principal component analysis · Public health

Introduction

Water contamination is one of the crucial environmental concerns that every country is currently prioritizing (Peng et al., 2022). Compromised water quality hinders progress towards the sustainable development goals of the world. Worldwide, 2.2 billion people are unable to access safe drinking water (SDGS, 2015). This compromised quality of the drinking water may be influenced by both geogenic and anthropogenic contaminants (Coyte et al., 2019; Dhakate et al., 2023; Ukah et al., 2018). The increase in human population in both urban and rural areas results in an equivalent rise in the amount of waste generated daily from residential, commercial, and industrial activities (Mohammadpour et al., 2023; Ozoko et al., 2022). These anthropogenic wasters disposes different types of potentially toxic pollutants, which further leach into aqueous media, thereby impacting the environment even at very low concentrations (Jiang et al., 2021; Ukah et al., 2020). Toxic elements are one of the most significant categories of contaminants that could enter the water supply regularly from both natural and anthropogenic sources (Kamani et al., 2023). Globally, about 80% of urban and industrial untreated wastewaters are released into the environment, endangering the future of ecosystems (Lin et al., 2022).

In India, primary causes of water pollution include improper handling of industrial wastes, disregard for the Central Pollution Control Board's guidelines, and low public awareness of suitable water consumption (Nivetha & Sangeetha, 2020). Adverse effects of anthropogenic water contamination are reported in several states, i.e., Tamil Nadu, Chhattisgarh, Odisha, Jharkhand, Madhya Pradesh, Assam, Meghalaya, and West Bengal (Gopinathan et al., 2022a; Khan et al., 2013; Mohanty et al., 2001; Singh et al., 2010, 2017; Usham et al., 2018).

Health risk and water quality assessment are an outstanding technique to identify the degree of impact of contaminated water in society (Mohammadpour et al., 2024). Quality indices, potential health risk assessment, along with probabilistic Monte Carlo

simulation by using toxic elements are important tools to study a comprehensive health risk assessment.

The present research area, Singrauli, the 'Energy Capital of India', is well-known for the active industries and coal mines. The presence of numerous active open-pit coal mines, thermal power plants, their effluents, and hybrid industrial frameworks in the study area impacted the land use, geomorphic features, water quality, and regular lifestyle of local inhabitants in the studied area. In the last few decades, inhabitants of the Singrauli area have suffered from serious illnesses, i.e., bronchopulmonary problems, cardiovascular disease, tuberculosis, fluorosis, cholera, and acute dysentery (Bose & Leitmann, 1996; DDMP, 2012; Usham et al., 2018). During monsoon season, waterborne diseases took the shape of epidemics (DDMP, 2012). Limited researchers have reported the presence of contaminants in the water from the north-eastern side of the studied area, i.e., the Sonbhadra District of Uttar Pradesh (Bhardwaj et al., 2020; Kumar et al., 2019; Ranjan et al., 2020; Sonkar & Jamal, 2019; Usham et al., 2018; Varshney et al., 2022). The sites in the vicinity of the coal mines are usually prone to contamination of the water by toxic heavy metals (HMs), which include carcinogenic and non-carcinogenic HMs (Gopinathan et al., 2022b, 2024; Liang et al., 2017; Yadav, 2021). However, in this rapidly industrializing area, where the inhabitants are relying on both surface and groundwater for their daily usage, there is a dearth of research regarding the type of contaminants, their sources, and the possible health risk assessment that needs to be addressed. The nature and likelihood of negative health effects in the population exposed to environmental pollutants can be ascertained through the comprehensive human health risk assessment. Both the potential and probabilistic health assessments help to estimate the significant health risk and potential threats on a definite condition (USEPA, 2018).

This study aims to: (1) assess physicochemical properties of surface and groundwater; (2) evaluate water suitability for drinking using various indices; (3) estimate human health risks from direct ingestion through probabilistic Monte Carlo simulations; and (4) identify contamination sources by multivariate statistical analysis. During this research, the authors were also focused on answering the hypothesis that the toxic elements in water, especially with regard to groundwater, could originate from several sources. Moreover, this study will help to provide an archive for future scientific correlation, development, and sustainable utilization of water resources, and to establish a point of reference for the regulatory authority monitoring groundwater for the purpose of tracking contaminants.

Study area

The study area in the Singrauli District is bounded by latitudes N 23°57'–N 24°15' and longitudes E 82°23'–E 82°40' (Fig. 1). Singrauli coalfield has two major basins, viz., the Moher sub-basin, which is situated in the northeast, and the cardinal basin in the southwest. This region has major open-cast coal mines and thermal power plants, generating nearly 20,000 MW of electricity. Major opencast mining projects are Amlohri, Nigahi, Jayant, Dudhichua, Khadia, Bina, and Jhingurda (Choubey & Shankaranarayana, 1990; Swarnakar et al., 2022). Additionally, the major thermal power plants are Sasan, Mahan, and Vindhyachal (NTPC) thermal power plants, and the aluminium industry of Hindalco is also situated in this area (Fig. 1). The presence of numerous mining structures and hybrid network grids of power plants already violates the natural framework. The concerned area experiences a tropical monsoon climate, with extreme temperatures of 47.2°C and 2°C during summer and winter, respectively (Khan et al., 2013). The area receives an annual average rainfall of 1118 mm. The two main seasonal rivers that flow through the Singrauli region are Kachan and Mayar.

Geological setting

Geologically, the area is mainly exposed to different rock types from Archaean to Palaeoproterozoic, predominantly granite, granite gneiss, phyllite, biotite schist, migmatite, and quartzite of the Chotanagpur Gneissic Complex and Mahakoshal Group of rocks, followed by sandstone, coal, and shale of the Lower Gondwana Group of rocks (Fig. 1). The entire area is structurally complex and tectonically active (Mohan et al., 2007). The Talchir sediments rest unconformably over the Precambrian basement in the east, and the younger Lower Gondwana sediments

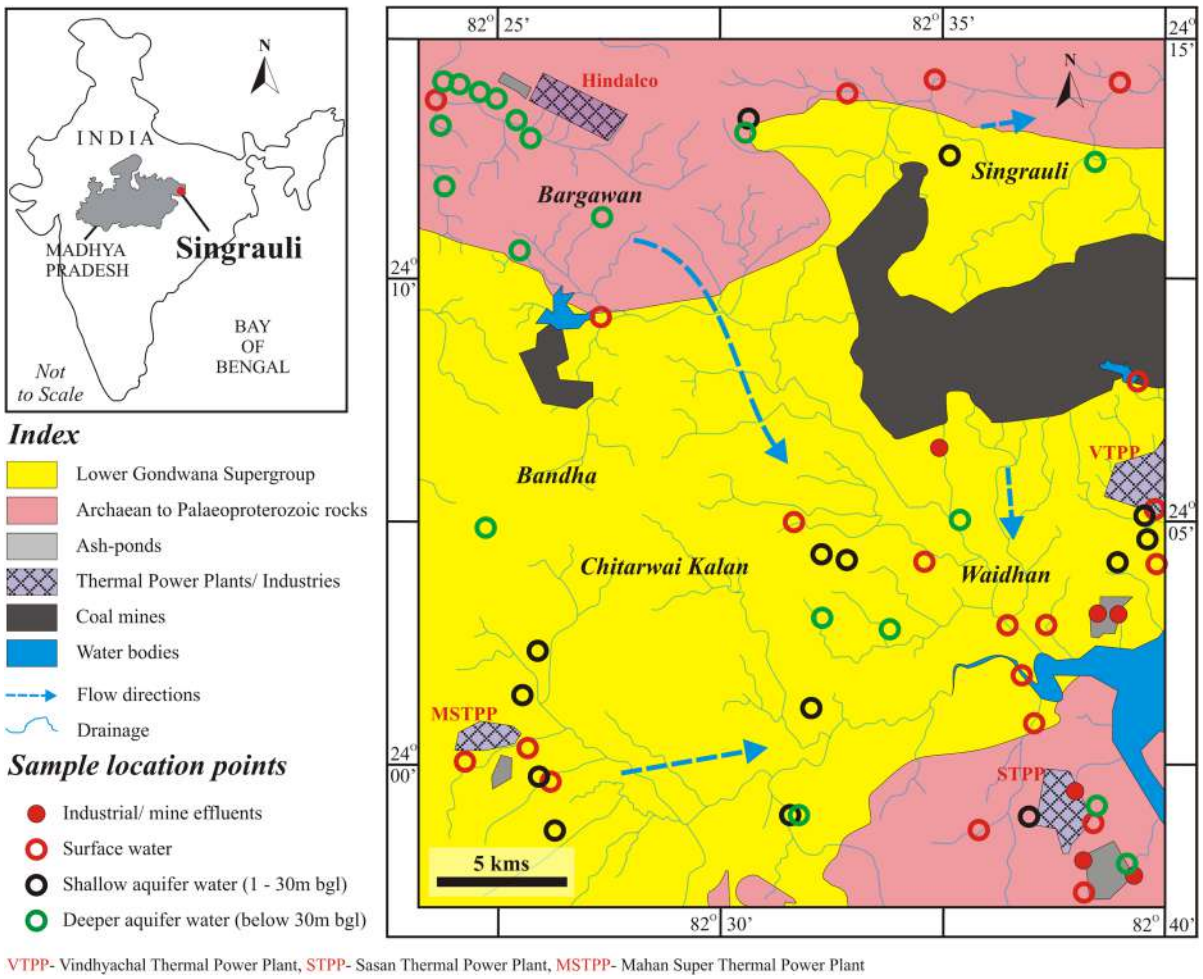


Fig. 1 Lithological map (modified after GSI, 2020) of the study area overlap with drainage distribution showing sample location points along with distribution of ash-ponds, coal-mines and thermal power plants/ industries

abut against the Precambrian rocks along an east–west trending fault at the north of the concerned area (Hota et al., 2012). Geomorphologically, the northern and southern parts of the area are primarily distinguished by structural hills and ridges. Hills, plateaus, and low-lying flats are the characteristic features of the Gondwana Supergroup of rocks, where the low-lying flats are mostly covered by agricultural activities.

Hydrogeology

CGWB (2021) has broadly identified two major aquifers, i.e., shallow aquifers (1–30 mbgl) and deeper aquifers (30–200 mbgl). The transmissivity and yield of these aquifers range from 0.19 to 27.68 m^2 day^{-1} and 0.40 to 8.20 lps, respectively, depending on the aquifer material. The groundwater level in this region varies between 0.83 and 25 mbgl in the pre-monsoon season and 1 to 25 mbgl during the post-monsoon season. The monitoring wells in this district have a high fluctuation range, which indicates poor aquifer storage capacity (CGWB, 2021). The annual extractable groundwater is 34,053.65 ham, whereas the annual 33,344.8 ham aquifer recharge takes place during the monsoon. The overall groundwater flow direction in the study area is towards the eastern side (Fig. 1). Singh and Kishore (2022) conducted an electrical resistivity survey within the Gondwana sequence at the central part of the study area, and three to four earth layers were identified. Among

which, the first layer contains lithomarge clay with a thickness of 0 to 5 m, and the third layer is fine-grained sandstone or fractured or weathered sandstone with a mean thickness of 10.5 m. These two layers are potential groundwater aquifer zones.

Materials and methodology

Sample collection, preparation and analysis

A total of 60 water samples were collected during the months of November to December to assess various water quality parameters in the Singrauli area and identify the major hydrogeochemical processes. Samples were collected from surface sources (i.e., check dams, flowing water, industrial/mine effluents) and from shallow and deeper sources (i.e., dug wells, tube wells, and bore wells). Sample location sites were selected randomly, but the points were systematically distributed. In random selection, sites were mainly selected in the populated area, whereas the water samples were collected systematically in the vicinity of industrial/mine areas and from aquifers of various depths throughout the area. Sample location points are displayed in Fig. 1. The data related to the depth of borewells and tube wells were collected from the Public Health and Engineering Department (PHED), Singrauli. Among the 60 samples, 6 were collected from industrial/ mine effluents (i.e., mine outlets, ash pond slurry, and decanted water); 20 samples were from the surface (flowing streams and check dams); 15 samples were from shallow aquifers; and 19 samples were from deeper aquifers. All samples were collected in 1-L high-density polyethylene (HDPE) bottles (for major ions). Apart from this, water samples were also collected in another set from each location in 250 ml polypropylene bottles, after filtration through Whatman filter paper (0.45 µm) and acidification to pH 2 with HNO_3 (Loring & Rantala, 1992) for metal analysis as per American Public Health Association (APHA, 2017) standard methods. The temperature, pH, total dissolved solids (TDS), electrical conductivity (EC), and turbidity were measured on-site from the unfiltered samples by using the 'Combo pH-EC kit' (HI-98130) and the 'Turbidity (EPA) portable meter' (HI-98703).

The parameters like Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, F^{-}, CO_3^{2-}, HCO_3^{-}, Cl^{-}, NO_3^{-}, SO_4^{2-}, alkalinity, and total hardness as $CaCO_3$ (TH) were analyzed for a complete analysis of the water samples. Ca^{2+} and Mg^{2+} were determined titrimetrically using standard EDTA. The HCO_3^{-} was estimated by the volumetric method, using H_2SO_4, phenolphthalein and methyl orange indicator (APHA, 2017). Chloride was estimated by $AgNO_3$ titration, and it was standardized by NaCl. Na^{+} and K^{+} were measured by the flame photometer (Model 1382 ESICO international Flame Photometer) with the standardized solution of 1000 mg L^{-1} NaCl and KCl solutions, respectively. SO_4^{2-} and NO_3^{-} were analyzed by colorimetric method with an UV–visible spectrophotometer (Model No. UV–Vis Spectrophotometer), and were standardized by Na_2SO_4; and $NaNO_3$, respectively. The fluoride concentration in water was determined electrochemically, using a fluoride ion selective electrode (APHA, 2017). The electrode used was an Orion fluoride electrode, coupled to an Orion electrometer. Standard fluoride solutions (within the ranges from 0.1 to 10 mg L^{-1}) were prepared from a stock solution (100 mg L^{-1}) of NaF. The concentrations of the selected heavy metals (As, Cd, Co, Cu, Fe, Mn, Ni, Mo, Pb, Sr, and Zn) in filtered water samples were analyzed directly by inductively coupled plasma mass spectrometry (Thermo Fisher ICP-MS iCAP Qc). Before analysis, the linearity and precision of this instrument were examined, calibrated, and checked with multi-elements standard (1094920100) by PerkinElmer and Merck. Charge balance errors of major cations and anions were within ± 10%.

Water quality analysis

Details of various physicochemical parameters are tabulated and compared with BIS (2012), WHO (2017), and USEPA (2018) guidelines in Table 1. In this study, water quality index (WQI), heavy metal pollution index (HMPI), and heavy metal evaluation index (HMEI) were calculated for water quality monitoring and assessment.

In WQI, the weight arithmetic method (Tyagi et al., 2013) was utilized on 24 parameters, i.e., pH, TDS, turbidity, TH, alkalinity, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, F^{-}, Cl^{-}, NO_3^{-}, SO_4^{2-}, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Mo, Cd, and Pb from the perspective of drinking

Table 1 Physicochemical parameters of water samples with their statistical summary and their respective guideline values

Parameters (Unit)	Statistical summary (n = 60)												Guideline values
	W1 (n = 6)			W2 (n = 20)			W3 (n = 15)			W4 (n = 19)			
	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	
pH	7.26	8.10	7.83	7.33	9.40	8.17	6.64	7.52	7.12	5.74	9.30	7.07	6.5–8.5[1]
Temp. (^{0}C)	20.6	25.8	22.9	17.5	32.2	22.2	25.5	28.2	26.8	22.8	28.0	26.7	–
EC (µS cm^{-1})	790	1150	927	170	1290	558	420	2380	1260	100	2410	918	–
TDS (mg L^{-1})	400	590	468	90	660	281	210	1190	630	50.0	1205	459	500[1]
T (NTU)	6.10	950	222	1.50	17.1	6.00	0.70	76.3	8.50	0.30	62.6	8.00	1.00[1]
TH (mg L^{-1})	330	530	410	100	380	208	160	710	411	30.0	900	315	200[1]
A (mg L^{-1})	38.0	215	116	60.0	325	194	155	455	310	25.0	400	225	200[1]
Ca^{2+} (mg L^{-1})	72.0	132	96.8	16.0	125	52.5	36.0	216	114	8.00	264	82.0	75.0[1]
Mg^{2+} (mg L^{-1})	26.0	36.0	32.1	8.00	45.0	19.5	9.70	41.3	26.8	2.40	58.4	25.3	30.0[1]
Na^{+} (mg L^{-1})	27.0	57.0	38.3	7.20	64.0	30.3	5.00	240	105	4.80	174	67.5	50.0[2]
K^{+} (mg L^{-1})	1.20	12.6	7.50	1.00	5.60	2.20	0.60	30.5	4.40	0.50	4.40	2.10	12.0[2]
HCO_3^{-} (mg L^{-1})	60.0	262	152	73.2	340	223	189	531	371	12.2	488	273	–
CO_3^{2-} (mg L^{-1})	0.00	0.00	0.00	0.00	36.0	8.50	0.00	0.00	0.00	0.00	12.0	0.60	–
Cl^{-} (mg L^{-1})	36.0	146	89.6	8.90	108	33.9	10.6	468	150	8.90	422	90.0	250[1]
F^{-} (mg L^{-1})	0.30	4.50	2.60	0.20	1.60	0.60	0.05	2.10	0.50	0.10	5.10	1.80	1.00[1]
NO_3^{-} (mg L^{-1})	bdl	11.0	2.30	bdl	28.0	2.40	bdl	104	34.5	bdl	132	23.3	45.0[1]
SO_4^{2-} (mg L^{-1})	50.0	235	175	10.2	245	35.4	5.00	185	87.6	3.50	300	74.9	200[1]

W1- water collected from industrial/ mine effluent; W2- water collected from surface water; W3- water collected from shallow aquifer; W4- water collected from deeper aquifer; T- turbidity; TH- total hardness as $CaCO_3$; A- alkalinity; bdl- below detection limit; [1]BIS (2012); [2]WHO (2017)

purpose. HCO_3^{-} and CO_3^{2-} were exempted from the calculation due to the absence of their standard values. WQI was calculated as:

$$WQI = \frac{\sum (Q_i \times W_i)}{\sum W_i} \quad (1)$$

where Q_i is the quality rating of the ith parameter and W_i is the unit weight. The ideal values for all the parameters were assumed to be zero except pH (i.e., pH = 7) (Sharmin et al., 2020), and the drinking standard values were taken from BIS (2012), WHO (2017), and USEPA (2018).

For HMPI, the concentration of heavy metals, i.e., Mn, Fe, Co, Ni, Cu, Zn, As, Cd, and Pb, were used to calculate Q_i and W_i, as expressed in Eq. 2,

$$HMPI = \frac{\sum (Q_i \times W_i)}{\sum W_i} \quad (2)$$

Another index regarding the heavy metal pollution is HMEI, which is calculated by following formula,

$$HMEI = \frac{\sum_{i=1}^{n} HM_{conc}}{HM_{MPC}} \quad (3)$$

where, HM_{conc} is the analyzed concentration of a particular heavy metal and HM_{MPC} is the maximum permissible concentration of the same heavy metal (BIS, 2012; USEPA, 2018; WHO, 2017). In this index, the threshold value is 1; samples with an index < 1.0 are considered fit, and samples with an index value > 1 are unfit for domestic usage (Singh et al., 2017).

Human health risk analysis

Consumption rate, exposure duration, and presence of contaminants, along with the intensity of the immunity factor, cumulatively controlled the effects of any contaminant on inhabitants. Consumption of contaminated water typically enriches metals and metalloids and poses serious effects on lives. Assessment of health risk was evaluated using Health Quotients (HQ) and Hazard Index (HI) for non-carcinogenic toxic elements, and total carcinogenic risk (CR) was estimated to determine the impact of carcinogenic toxic elements. Moreover, to assess the human health risk, firstly, the chronic daily intake (CDI) was calculated by Eq. 4 (Means, 1989; Wu et al., 2009). In this study, a health risk assessment was calculated based on the direct ingestion through the oral pathway for both adults and children.

$$CDI\left(mg\ kg^{-1}day^{-1}\right) = \frac{C_{HM} \times DI \times EF \times ED}{BW \times AT} \quad (4)$$

In Eq. 4, the values of each parameter were considered according to two distinct age groups, with average exposure duration (ED) of 24 and 6 years (USEPA, 1997), average body weight (BD) of 57 and 18.7 kg (ICMR, 2020), and average time of exposure (AT) of 8760 and 2190 days (USEPA, 2001) for adults and children, respectively. The average daily intake (DI) is considered to be 2 and 1 L day^{-1} for adults and children, respectively (Reddy & Sunitha, 2023; USEPA, 2000). The HQ is the ratio between CDI and oral reference doses of toxic elements (R_fD). The values of R_fD were considered as per USEPA, (2010).

$$HQ = \frac{CDI}{R_f D} \quad (5)$$

The total potential of the toxic elements on human health was calculated as expressed in Eq. 6. The hazard index (HI) was estimated to quantify the non-carcinogenic risk factor.

$$HI = \sum_{i=1}^{n} HQ = HQ_{Cu} + HQ_{Fe} + \ldots \quad (6)$$

In this research, carcinogenic risks (CR) caused by carcinogens through oral ingestion exposure pathways were also estimated by using CDI values and slope factor (SF) in Eq. 7. As and Cd were considered carcinogens to estimate the CR. The slope factors for As and Cd were considered as 1.5 and 0.38 (mg kg^{-1} $day^{-1})^{-1}$ respectively (Li et al., 2016; Xu et al., 2020).

$$CR = CDI \times SF \quad (7)$$

This conventional approach to potential risk assessment merely applies simple formulas and ignores the random variation of the concentrations of toxic elements (Mohammadpour et al., 2022; Shahsavani et al., 2023). In order to minimize the randomness and uncertainty in prediction and to better understand the impact of risk, Monte Carlo simulation was applied to quantify the human health risks of two different age groups (i.e., adults and children) via the

Table 2 Statistical summary of the heavy metals and toxic elements in water samples with their respective standard values and calculated unit weights (W_i)

AL- Acceptable limit (in mg L^{-1}); *PL*- Max. permissible limit (in mg L^{-1}); R_fD- Oral reference dose (in mg kg^{-1} day^{-1}); W_i- Unit weight; Statistical values are in mg L^{-1}; *bdl*- below detection limit; *NR*- No relaxation

[1]BIS (2012); [2]WHO (2017); [3]USEPA (2018); [4]USEPA (2010)

Heavy metals	Statistical summary ($n=60$)			Standard values			W_i
	Min	Max	Avg	AL	PL	R_fD[4]	
Mn	bdl	1.88170	0.11590	0.10[1]	0.30[1]	0.0140	0.0153
Fe	bdl	0.15950	0.10240	0.30[1]	NR[1]	0.7000	0.0051
Co	bdl	0.01842	0.00051	0.05[2]	0.05[2]	0.0030	0.0306
Ni	bdl	0.03587	0.00218	0.02[1]	NR[1]	0.0200	0.0765
Cu	bdl	0.01854	0.00124	0.05[1]	1.50[1]	0.0371	0.0306
Zn	0.05808	2.84966	0.20723	5.00[1]	15.0[1]	0.3000	0.0003
As	bdl	0.02334	0.00384	0.01[1]	0.05[1]	0.0003	0.1530
Sr	0.03303	6.61968	0.62299	4.20[3]	4.20[3]	0.6000	0.0004
Mo	bdl	0.21473	0.01012	0.07[1]	NR[1]	0.0050	0.0219
Cd	bdl	0.00033	0.00002	0.003[1]	NR[1]	0.0010	0.5099
Pb	bdl	0.00197	0.00053	0.01[1]	NR[1]	0.0035	0.1530
F	0.05	5.09000	1.15577	1.00[1]	1.50[1]	0.0600	0.0015

oral ingestion pathway in the Singrauli area. This probabilistic simulation method was used to simulate the impact of toxic elements (listed in Table 2) on the human health risks, and the output is represented by a probability distribution histogram. This simulation was implemented using Python programming, with random simulation iterations set to 10,000 to obtain probability distributions with different confidence levels (1–99%). The probability distribution of the toxic elements in water samples was ascertained by using the Anderson–Darling goodness-of-fit test. Subsequently, the contribution of individual toxic elements to the carcinogenic and non-carcinogenic risks on the human health was also estimated.

Statistical analysis

A multivariate statistical approach was undertaken in this study in order to identify and categorize the possible sources of measured parameters in the water samples. Among the 26 physicochemical parameters, the correlation among them was not well established because certain heavy metals in several water samples were below the detection limit. Moreover, consideration of these heavy metals also introduces uncertainties in multivariate analysis. Therefore, 7 trace elements (i.e., Fe, Co, Ni, Cu, Mo, Cd, and Pb) with more than 25% of the samples having concentrations below the detection limit were eliminated (Brindha et al., 2020), and the rest of the parameters were considered for statistical analysis. Furthermore, Kaiser–Meyer–Olkin (KMO) and Bartlett's test were utilized to check the adequacy and appropriateness of the hydrochemical dataset to apply dimension-reduction multivariate statistical techniques, like principal component analysis (PCA).

Result and discussion

Physicochemical parameters

Hydrochemical data for a total of 60 samples are given in Table 1 with respect to the maximum desirable and permissible limits recommended by BIS (2012), WHO (2017), and USEPA (2018). pH values range from 5.74 to 9.4, i.e., acidic to alkaline in nature. All flowing water and industrial/mine effluent water were alkaline in nature, whereas groundwater was acidic to alkaline. TDS values were mainly within the fresh water category, except for 5 groundwater samples from the Gondwana sandstone, which had TDS values > 1000 mg L^{-1}. Total hardness as $CaCO_3$ ranges from 30 to 900 mg L^{-1}; as per the standard values, 93.3% of water samples were in the hard to very hard category, which may cause severe kidney problems after long-term consumption (WHO, 2008). Along with total hardness, turbidity was also very high in the study area, ranging from 0.27 to 950 NTU. 85% of total samples and 73.5% of groundwater samples had turbidity greater than the permissible limit (WHO, 2017). 53.3% of samples had alkalinity above the permissible limit for drinking usage (BIS, 2012; WHO, 2017). Among 60 samples, 48.3%, 41.7%, and 33.3% samples had higher concentrations of Na^+, Ca^{2+}, and F^-, respectively, and were considered unsuitable for drinking as per permissible values (BIS, 2012; WHO, 2017). Among the HMs, the concentrations of Mn, As, Mo, Sr, and Ni in some water samples were above permissible limits (BIS, 2012; WHO, 2017). The detailed values of HMs are given in Table 2.

Hydrochemical facies and evolution process

Major anions (Cl^-, SO_4^{2-}, CO_3^{2-}, and HCO_3^-) and cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) of water samples were plotted on a piper diagram (Piper, 1944) for hydrochemical facies analysis. In the study area, water samples were categorized into four types: industrial/mine effluents, surface water, groundwater from shallow aquifers (1–30 mbgl), and groundwater from deeper aquifers (30–200 mbgl). The hydrochemical facies of surface water, i.e., flowing streams and check dams, were Ca–HCO_3, Ca–Mg–SO_4, and Ca–Mg–HCO_3 types. Industrial/mine effluents were Ca–Mg–SO_4 type water. Groundwater from shallow aquifers had mixed cations with HCO_3, SO_4, and Cl-type water. The deeper aquifer (30–200 mbgl) had Ca–Mg–HCO_3 type along with Ca–Mg–SO_4 and Na–Cl type water (Fig. 2). In Gibb's diagram (Gibbs, 1970) (Fig. 3), subsurface water chemistry was controlled by rock-weathering along with the influence of evaporation dominance. However, as the major ions in industrial/mine effluents were Ca^{2+}, Mg^{2+}, and SO_4^{2-} with TDS ranging from 400 to 590 mg L^{-1}; interpreting this water by Gibb's plot could not be justified on the basis of Cl^-, HCO_3^-,

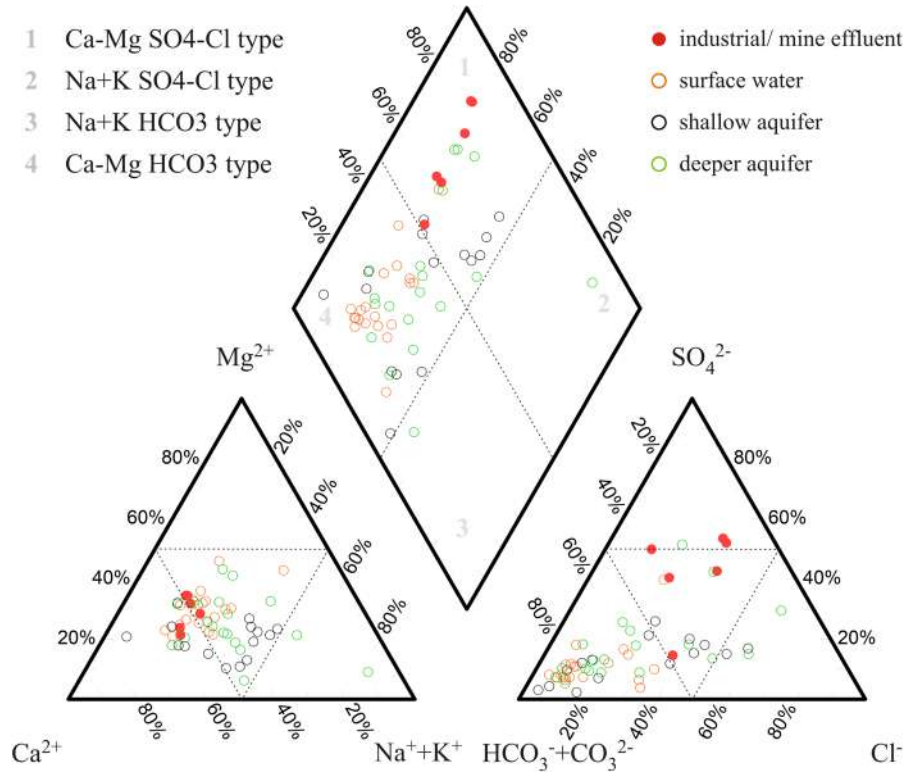


Fig. 2 Piper diagram showing hydrogeochemical facies variation of the surface and subsurface water

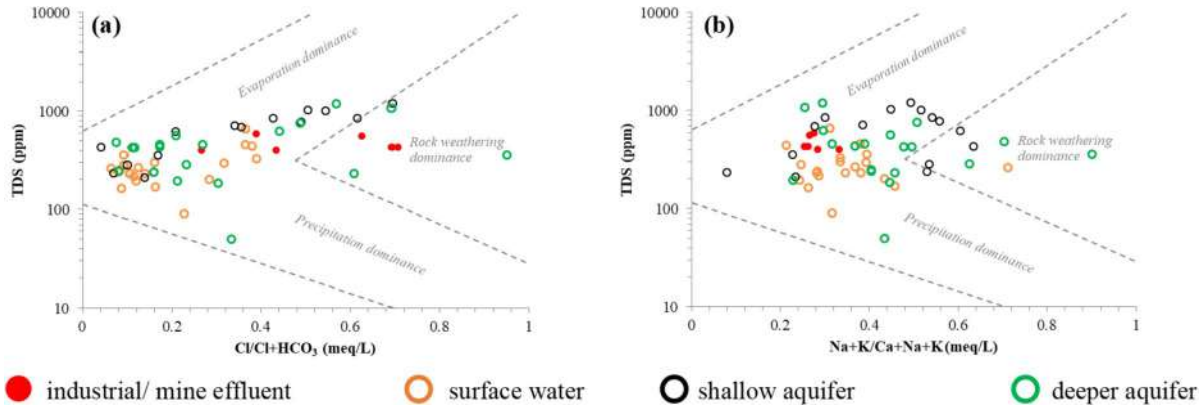


Fig. 3 Gibb's diagram of the water samples **a** $Cl^{-}/(Cl^{-}+HCO_3^{-})$ vs. TDS, and **b** $(Na^{+}+K^{+})/(Ca^{2+}+Na^{+}+K^{+})$ vs. TDS

and Na^{+} ions. Moreover, in the Singrauli area, overall water chemistry has a trend towards evaporation dominance, with increasing TDS indicating an influence of contaminants in surface water and groundwater (Fig. 3). The chloro-alkaline indices (CAI) were used to assess the ion exchange reactions between groundwater and its host rock (Schoeller, 1977). During cation exchange, the CAI values were negative. Ca^{2+} and Mg^{2+} ions present in water react with aquifer material to release Na^{+} ions. On the other hand, Na^{+} and K^{+} ions in the water were exchanged with Mg^{2+} and Ca^{2+} ions if the indices were positive, which indicates a base-exchange reaction. During this process, the host rocks were the primary sources of dissolved solids in the water. In Fig. 4a, the majority of surface water and groundwater from both aquifers

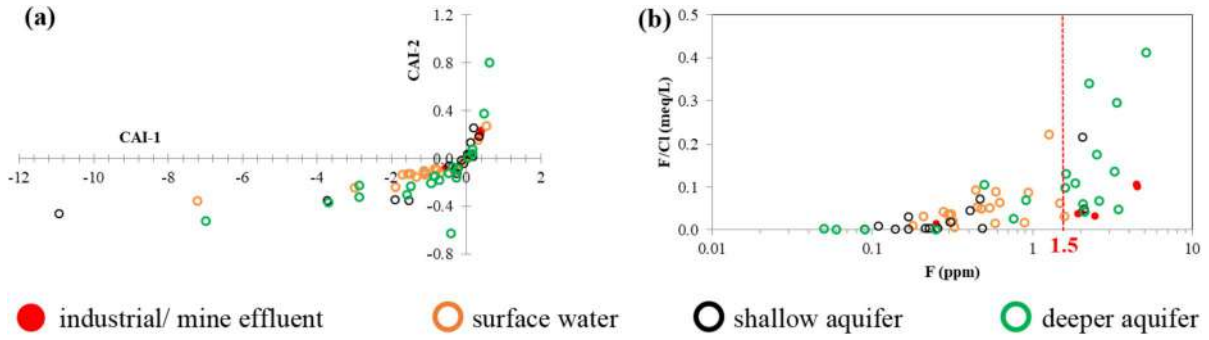


Fig. 4 Scatter plots of **a** Chloro-alkaline indices CAI-1 vs. CAI-2, and **b** F^- vs. F^-/Cl^- plot

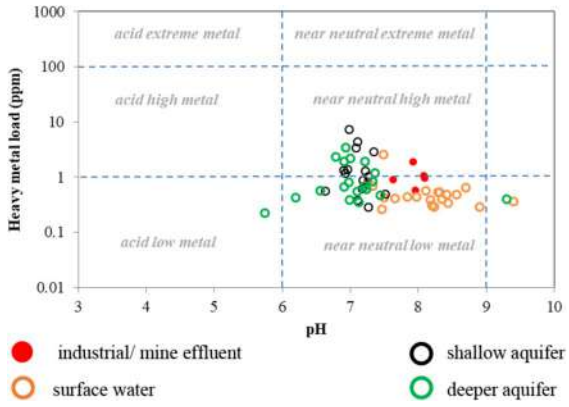


Fig. 5 Ficklin-Caboi diagram shows the classification based on total heavy metal load vs. pH of the surface and subsurface water

Table 3 Category and classification of water quality based on WQI, HMPI, and HMEI values

Indices	Class	Category	% of samples
WQI	< 25	Excellent	85.0
	25– < 50	Good	11.7
	50– < 75	Poor	1.70
	75– < 100	Very poor	0.00
	> 100	Unsuitable	1.70
HMPI	< 15	Low	78.3
	15–30	Medium	15.0
	> 30	High	6.70
HMEI	< 1.0	Fit	68.3
	> 1.0	Unfit	31.7

had negative values, which indicates a cation exchange reaction. Moreover, the samples from the ash ponds had a positive value, which indicates a reverse ion exchange process. Therefore, in the study area, cation exchange dominates the water chemistry with respect to reverse ion exchange.

As fluoride is a toxic element and hazardous for human health, therefore, to identify the origin of the F^- ion in water, the F versus F/Cl diagram (Jha et al., 2021; Olaka et al., 2016) was plotted and presented in Fig. 4b. This diagram reveals that the fluoride in industrial/ mine effluent water was of anthropogenic origin, whereas the fluoride found in deeper aquifers was of geogenic origin. Therefore, the high fluoride concentration in the aqueous media of Singrauli District was controlled by both anthropogenic and geogenic factors.

The precipitation and dissolution of heavy metals vary in accordance with the pH. Ficklin-Caboi diagram (Fig. 5) was used to interpret the water type based on the heavy metal concentration and pH. This diagram also helps to understand the mobility of heavy metals in an aqueous medium (Caboi et al., 1999; Ficklin et al., 1992). In the Singrauli area, heavy metal loads were distributed mainly in two fields, i.e., near neutral low metal and near neutral high metal. Under neutral pH, metals mostly remain in precipitated form, and hence the dissolved concentration was low, resulting in lower mobility of heavy metals in water samples. However, samples (subsurface water samples) showing a neutral to slightly acidic high metal load were on the verge of a hazard zone. Hence, a slight change in pH toward an acidic nature may enhance the mobility of metals in an aqueous medium.

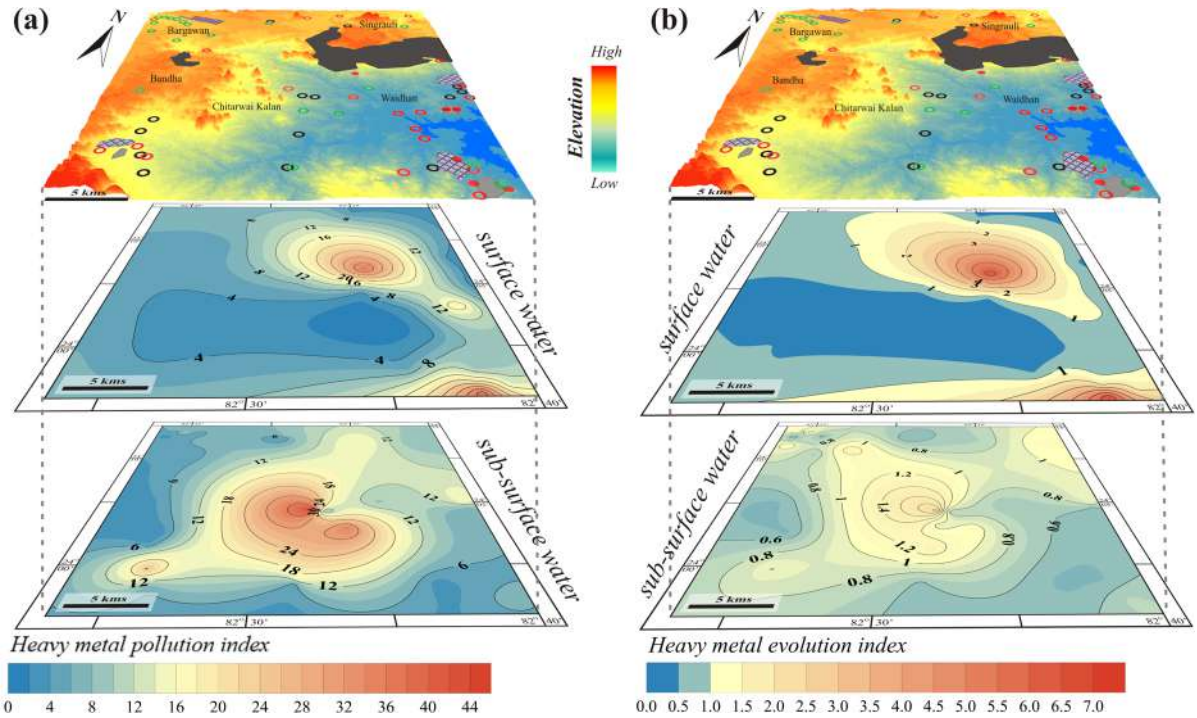


Fig. 6 Spatial distribution maps of **a** HMPI and **b** HMEI, projected on three-layer model with respect to elevation map, surface water and sub-surface water

Suitability of water quality

WQI was calculated by Eq. 1, as proposed by Tyagi et al. (2013). Calculated unit weights are given in Table 2. In WQI calculation, the most dominant unit weights were represented by Cd (0.5099), As (0.1530), and Pb (0.1530). For water quality rating, the index values were used to categorize the water samples as per the classification given by Sharmin et al. (2020) (Table 3). The value of WQI ranges from 3.18 to 168.57. Among the total samples, 85% were excellent, 11.7% were good, and 3.3% were categorized in the poor to unsuitable category. Although the 96.7% samples were cumulatively categorized as excellent and good, it also contains 3.5%, 36.2%, 84.5%, and 93.10% water samples with acidic pH, fluoride contaminated ($F \geq 1$ mg L^{-1}), high turbidity, and hard to very hard categories, respectively. Therefore, these samples, categorized within 96.7% of the total samples, also need to be discarded for drinking usage. The water samples categorized under the poor to unsuitable category were mainly surface water and the water collected from industrial/mine effluents. This water was not directly used for drinking purposes by the local inhabitants. However, this unsuitable water was mixing with other surface water in the downstream and down-flow directions, which may further degrade

Table 4 Correlation matrix among toxic elements, water quality and pollution indices

	WQI	HMPI	HMEI
WQI	1.00		
HMPI	0.56	1.00	
HMEI	0.45	**0.69**	1.00
Mn	0.32	**0.60**	**0.97**
Fe	0.13	0.45	0.01
Co	0.35	0.38	**0.66**
Ni	0.57	0.37	**0.60**
Cu	0.08	0.25	−0.03
Zn	−0.05	−0.08	−0.06
As	0.27	**0.79**	0.13
Sr	0.20	–	–
Mo	**0.63**	–	–
Cd	**0.64**	0.11	0.04
Pb	0.03	−0.02	−0.03
F	0.29	–	–

Values in **bold** are ≥ 0.60

their quality in the future. Water quality indices along with individual concentrations of various physicochemical parameters represent that the overall water quality of the Singrauli area is not suitable for direct consumption. Hence, proper filtration and purification of water are required before drinking.

In order to make the assessment based on heavy metals, HMPI was calculated, and the value of HMPI ranges from 3.14 to 43.55. Among all samples, 78.3% were in the low pollution category, and 21.7% were in the medium to high pollution category (Table 3). Singh et al. (2017) proposed HMEI to evaluate the overall quality and quantify the trend with respect to the permissible limit of the heavy metals. The HMEI values of all the samples vary from 0.47 to 6.82. Among which, 31.7% of samples were unfit and 68.3% of samples were fit for drinking purposes (Table 3). The water samples in the medium-to-high pollution category (as per HMPI) were also categorized as unfit (as per HMEI) for drinking usage. The spatial variation of HMPI and HMEI with respect to surface water and groundwater is given in Fig. 6.

In the correlation matrix (Table 4), WQI shows a positive correlation with Mo and Cd. HMPI had a strong positive relation with Mn and As. HMEI had a strong positive relation with Co, Ni, and Mn. Thus, it could be inferred that As, Mn, Cd, Mo, Co, and Ni were the major heavy metals that were responsible for contaminating the aqueous media of the Singrauli area.

Human health risk assessment

Potential health risk assessment

In this study, a health risk assessment was determined to estimate the degree of adverse effects of toxic elements on the inhabitants through the oral exposure pathway. The calculated ranges of CDI values for Mn,

Table 5 Summary of the carcinogenic and non-carcinogenic risk for the consumptions of toxic elements by adults and children through oral ingestion

	Non-carcinogenic risk							
	Adult				Children			
	CDI avg	HQ min	HQ max	HQ avg	CDI avg	HQ min	HQ max	HQ avg
Mn	4.03×10^{-3}	1.14×10^{-3}	4.67×10^{0}	2.88×10^{-1}	6.20×10^{-3}	1.91×10^{-3}	7.10×10^{0}	4.43×10^{-1}
Fe	3.56×10^{-3}	4.97×10^{-3}	7.93×10^{-3}	5.09×10^{-3}	5.47×10^{-3}	7.64×10^{-3}	1.22×10^{-2}	7.82×10^{-3}
Co	1.76×10^{-5}	5.80×10^{-4}	2.14×10^{-1}	5.86×10^{-3}	2.70×10^{-5}	8.91×10^{-4}	3.28×10^{-1}	9.02×10^{-3}
Ni	7.57×10^{-5}	1.74×10^{-3}	6.24×10^{-2}	3.79×10^{-3}	1.16×10^{-4}	2.67×10^{-3}	9.59×10^{-2}	5.82×10^{-3}
Cu	4.30×10^{-5}	4.69×10^{-4}	1.74×10^{-2}	1.16×10^{-3}	6.62×10^{-5}	7.21×10^{-4}	2.67×10^{-2}	1.78×10^{-3}
Zn	7.21×10^{-3}	6.73×10^{-3}	3.30×10^{-1}	2.40×10^{-2}	1.11×10^{-2}	1.04×10^{-2}	5.08×10^{-1}	3.69×10^{-2}
As	1.34×10^{-4}	1.16×10^{-1}	2.71×10^{0}	4.45×10^{-1}	2.05×10^{-4}	1.78×10^{-1}	4.16×10^{0}	6.84×10^{-1}
Sr	2.17×10^{-2}	1.91×10^{-3}	3.84×10^{-1}	3.61×10^{-2}	3.33×10^{-2}	2.94×10^{-3}	5.90×10^{-1}	5.55×10^{-2}
Mo	3.52×10^{-4}	3.48×10^{-3}	1.49×10^{0}	7.04×10^{-2}	5.41×10^{-4}	5.35×10^{-3}	2.30×10^{0}	1.08×10^{-1}
Cd	8.41×10^{-7}	3.48×10^{-4}	1.15×10^{-2}	8.41×10^{-4}	1.29×10^{-6}	5.35×10^{-4}	1.76×10^{-2}	1.29×10^{-3}
Pb	1.82×10^{-5}	4.97×10^{-3}	1.96×10^{-2}	5.21×10^{-3}	2.80×10^{-5}	7.64×10^{-3}	3.01×10^{-2}	8.01×10^{-3}
F	4.02×10^{-2}	4.02×10^{-2}	2.95×10^{0}	6.70×10^{-1}	6.18×10^{-2}	4.46×10^{-2}	4.54×10^{0}	1.03×10^{0}
Hazard Index		2.62×10^{-1}	5.90×10^{0}	1.56×10^{0}		4.03×10^{-1}	9.07×10^{0}	2.39×10^{0}
	Carcinogenic risk							
	Adult				Children			
	CR min	CR max	CR avg		CR min	CR max	CR avg	
As	5.22×10^{-5}	1.22×10^{-3}	2.00×10^{-4}		8.02×10^{-5}	1.87×10^{-3}	3.08×10^{-4}	
Cd	1.32×10^{-7}	4.36×10^{-6}	3.19×10^{-7}		2.03×10^{-7}	6.71×10^{-6}	4.91×10^{-7}	
Total Carcinogenic risk	5.23×10^{-5}	1.22×10^{-3}	2.01×10^{-4}		8.04×10^{-5}	1.87×10^{-3}	3.08×10^{-4}	

Fe, Co, Ni, Cu, Zn, As, Sr, Mo, Cd, Pb, and F with respect to adults and children are listed in Table 5. In non-carcinogenic risk assessment, for both adults and children, the maximum HQ values for Mn, As, Mo, and F were above 1. The mean HQ values for Mn, As, Mo, and F were 2.88×10^{-1}, 4.45×10^{-1}, 7.04×10^{-2}, and 6.70×10^{-1} for adults, and 4.43×10^{-1}, 6.84×10^{-1}, 1.08×10^{-1}, and 1.03×10^{0} for children, respectively. The statistical values of HI are also summarized in Table 5. The HI value for adults ranges from 2.62×10^{-1} to 5.90×10^{0} with a mean value of 1.56×10^{0}; and the HI value for children is within the range of 4.03×10^{-1} to 9.07×10^{0} with a mean value of 2.39×10^{0}. The spatial distribution of HI values for both adults and children is given in Fig. 7. In 55% and 70% of the total water samples, HI exceeded the safe limit (HI > 1) for adults and children, respectively. Therefore, it could be inferred that the unusual enrichment of toxic and heavy metals in the water of the concerned area makes it more likely to be hazardous to the health of both children and adults in the near future.

Potential carcinogenic risk assessments of the study area were estimated by considering As and Cd through oral ingestion for both adults and children. The maximum, minimum, and mean for the carcinogenic risk assessment with respect to As, Cd, and total CR are summarized and given in Table 5. According to the USEPA risk assessment recommendation level for carcinogenic risk, the values below 1×10^{-6} are not likely to pose a significant health hazard, the values between 1×10^{-6} and 1×10^{-4} are acceptable or tolerable, and the values above 1×10^{-4} are unacceptable and most harmful for human health (USEPA, 2012). As shown in Table 5, all the CR values of As for both adults and children were above 1×10^{-6}. Moreover, 43.3% and 38.3% of the samples for adults and children, respectively, were between 1×10^{-6} and 1×10^{-4}; and 56.7% and 61.7% of the samples from adults and children, respectively, were above 1×10^{-4} i.e., unacceptable and harmful for human health. Unlike As, all the CR values of Cd were less than 1×10^{-4}. Irrespective of age groups, only 6.7% of the samples were within the tolerable ranges, and the rest, 93.3%

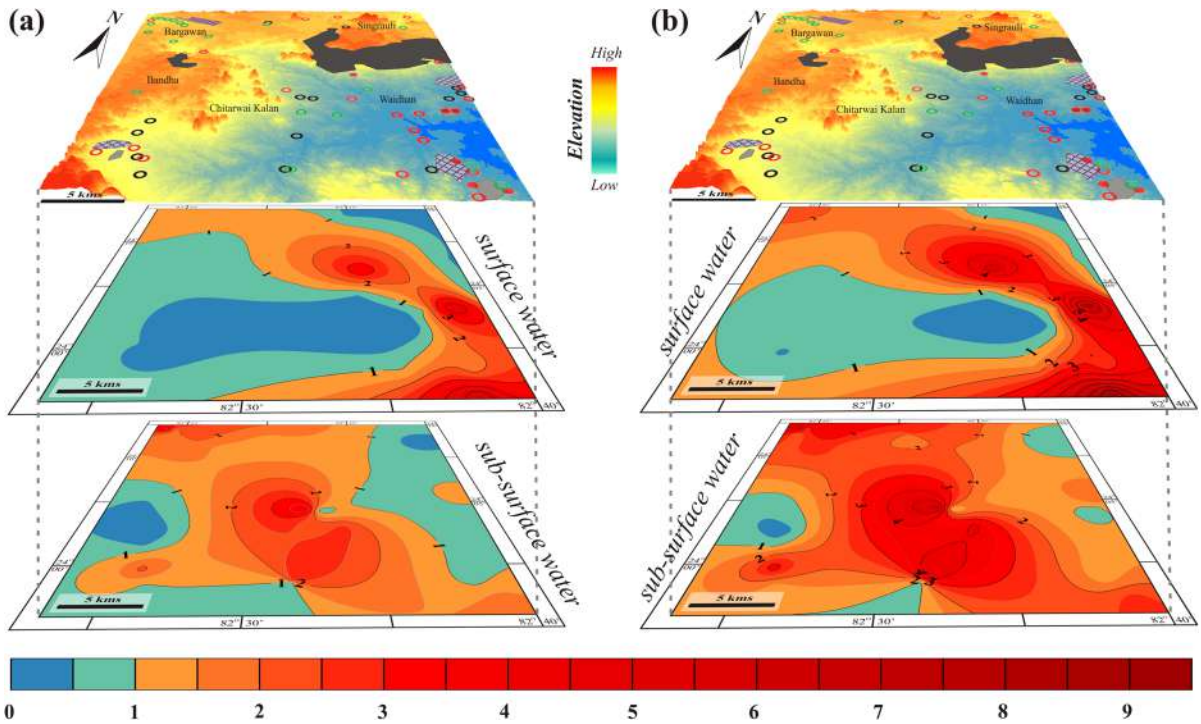


Fig. 7 Spatial distribution of Hazard Index (HI) through oral exposure pathway for **a** adults and **b** children, projected on three-layer model with respect to elevation map, surface water and sub-surface water

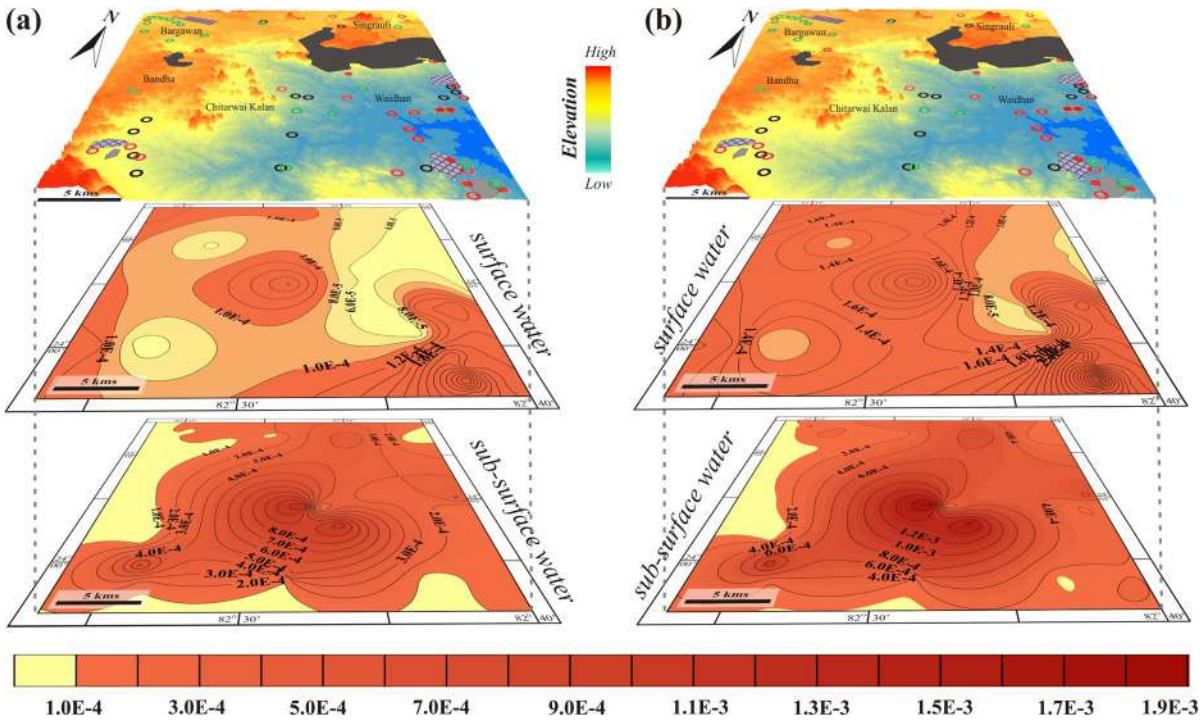


Fig. 8 Spatial distribution of total carcinogenic risk (CR) through oral routes for **a** adults and **b** children, projected on three-layer model with respect to elevation map, surface water and sub-surface water

of the samples were within the safe limit. Therefore, this research revealed that, in the Singrauli area, As posed a greater carcinogenic threat to human health than Cd. As a result, pollution of water from arsenic contamination needs more attention.

The spatial distribution map of HI and total CR values for oral ingestion of water with respect to surface water and subsurface water are given in Figs. 7 and 8, respectively. In Fig. 7, the intensity of the HI value was higher in the surface water compared to the sub-surface water. However, the spatial distribution of HI in groundwater was relatively more dispersed and scattered. On the other hand, both intensity and dispersion of total CR values were relatively higher in the groundwater than the surface water (Fig. 8). The surface water with higher values of HI and total CR was near the major coal mines, thermal power plants, and ash ponds. These polluted surface waters (collected from flowing streams, check dams, and industrial/mine effluents) were not directly consumed by the local human population; however, the same water was used for agricultural purposes. Therefore, the indirect consumption of the toxic elements present in the polluted surface water places the human health condition under significant threat. Further, this polluted surface water may percolate in the sub-surface aquifer and contaminate the groundwater. Additionally, it has already been discussed that the pH of surface water in this area was alkaline, and the groundwater was acidic to alkaline. Hence, the mobility of the heavy metals in the sub-surface aquifer was relatively enhanced than in the surface water. Therefore, pH also plays an important role in triggering the heavy metal contamination in water. The prolonged direct and indirect ingestion of the contaminated water by the local dwellers, without proper filtration or treatment, will severely harm human health in the near future. Therefore, proper maintenance of water quality and the supply of clean water are highly recommended in the Singrauli area.

Probabilistic health risk assessments

Figure 9 (for adults) and Fig. 10 (for children) show the probabilistic histograms for non-carcinogenic elements with the estimated 5% (5th percentile),

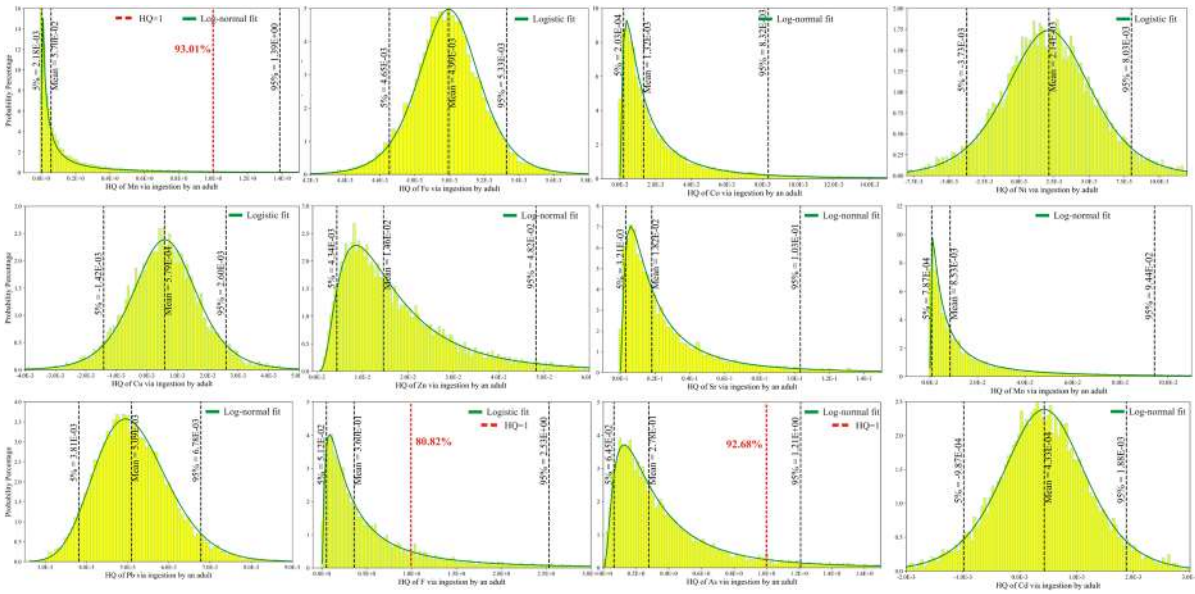


Fig. 9 Probabilistic estimates of HQ values for non-carcinogenic elements consumption by an adult through oral ingestion pathway

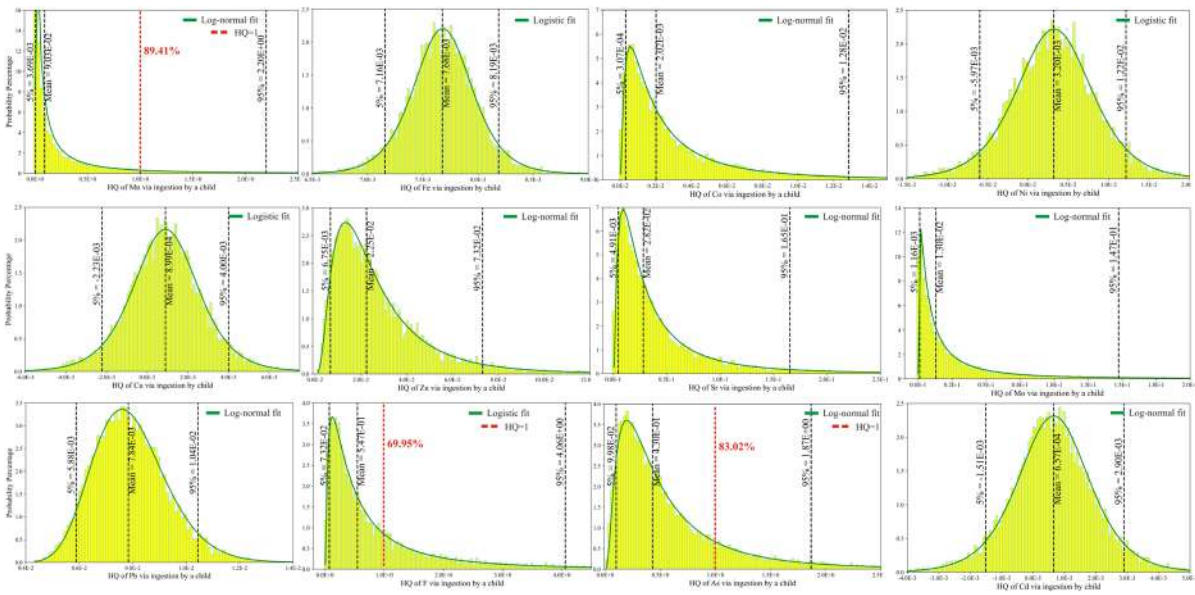


Fig. 10 Probabilistic estimates of HQ values for non-carcinogenic elements consumption by a child through oral ingestion pathway

mean, and 95% (95th percentile) values of HQ with distinct output fitting for individual toxic elements after 10,000 random simulations. After the analysis of the toxic elements by Anderson–Darling goodness-of-fit test, the probability distributions for Mn, Co, Zn, As, Sr, Mo, Pb, and F were fitted with log-normal distribution, and Fe, Ni, Cu, and Cd were fitted with logistic distribution. For non-carcinogenic risk assessment, an acceptable hazard quotient value less than 1 was considered (Bleam, 2016). In this

probabilistic simulation model, the simulated values at 5th percentile and 95th percentile were considered low- and high-end estimates for risk calculations (Saha et al., 2017), and the higher the output value, the greater its impact on the risk value (Tong & Yang, 2017). The mean value of the simulated HQ for children and adults was ranked as F > As > Mn > Sr > Zn > Mo > Pb > Fe > Ni > Co > Cu > Cd. For both the age groups, the highest and the least intense HQ were posed for F and Cd, respectively. In the figure for non-carcinogenic risk assessment (Figs. 9 and 10), the simulated values for F, Mn, and As at the 95th percentile were greater than 1. In the probabilistic assessment for adults, 6.9%, 7.3%, and 19.2% of the simulated values in Mn, As, and F, respectively, exceeded the safe limit (> 1). Similarly, 10.6%, 16.9%, and 30.1% values of Mn, As, and F, respectively, for children exceeded the safe limit. Additionally, to display the cumulative impact of all the toxic elements, the probabilistic estimates of HI for adults and children via ingestion through oral pathways were computed and given in Fig. 11. The mean and 95th percentile values of the simulated HI for both age groups had HI > 1. 56.2% and 75.2% of the simulated HI in adult and child, respectively, were above the safe limit. These values estimated the significant non-carcinogenic risk on human health of the local inhabitants in the study area due to ingestion of water through the oral pathway. More specifically, F, Mn, and As were responsible for the non-carcinogenic health risk, potentially resulting in a range of adverse health effects such as fluorosis, bronchopulmonary, and cardiovascular diseases. These diseases, along with the long-term health complications, were already reported by several researchers from this area (Bose & Leitmann, 1996; DDMP, 2012; Usham et al., 2018). Their findings have been corroborated with this research emphasizing the evidence of severe health risks associated with the polluted water of the study area.

Beside non-carcinogenic risk assessment, carcinogenic risk for adults and children was also estimated utilizing the Monte Carlo simulation technique, but by considering two carcinogens, i.e., As and Cd. The histogram of the simulated CR values estimated for As and Cd ingestion by both age groups through oral route is given in Fig. 12. All the simulated CR values of As for both the concerned age groups were above 1×10^{-6}. Only 40.0% and 22.9% of the simulated samples for adults and children, respectively, were within the tolerable limit (1×10^{-6} to 1×10^{-4}); whereas the remaining 60% values for adults and 77.1% values for children exceeded the unacceptable limit ($>1\times10^{-4}$) for the ingestion through oral routes. Moreover, all the simulated CR values of Cd ingestion through oral routes by adults were within the safe limit (i.e., $<1\times10^{-6}$). Only 7% of the CR values of Cd ingestion through oral pathways by children were in the tolerable range. Therefore, it could be stated that the prolonged ingestion of As through the oral pathway by both age groups (especially children) leads to a significant risk of developing cancer. Moreover, the prolonged intake of Cd through the oral route by children has the potential to develop cancer in the future.

The degree of contribution of individual toxic elements to both non-carcinogenic and carcinogenic health hazards is given in Fig. 13. Irrespective of the

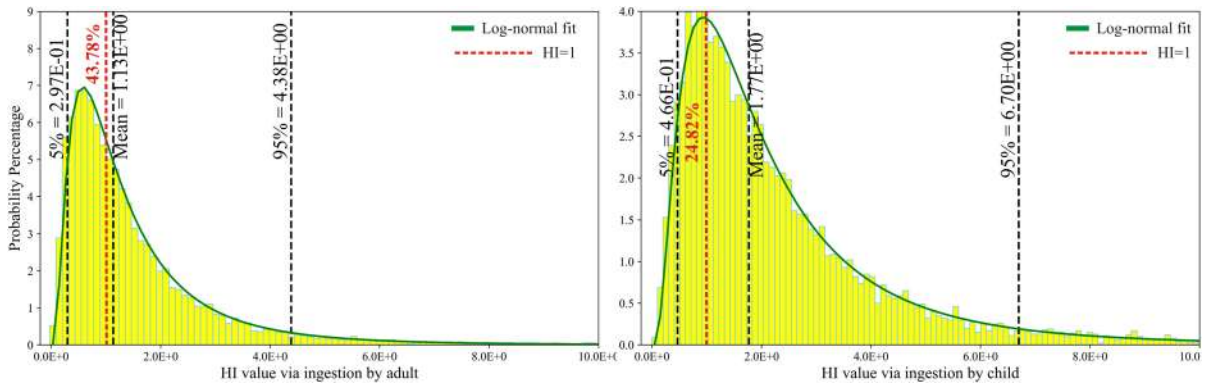


Fig. 11 Probabilistic estimates of HI values for consumption by an adult and child through oral ingestion pathway

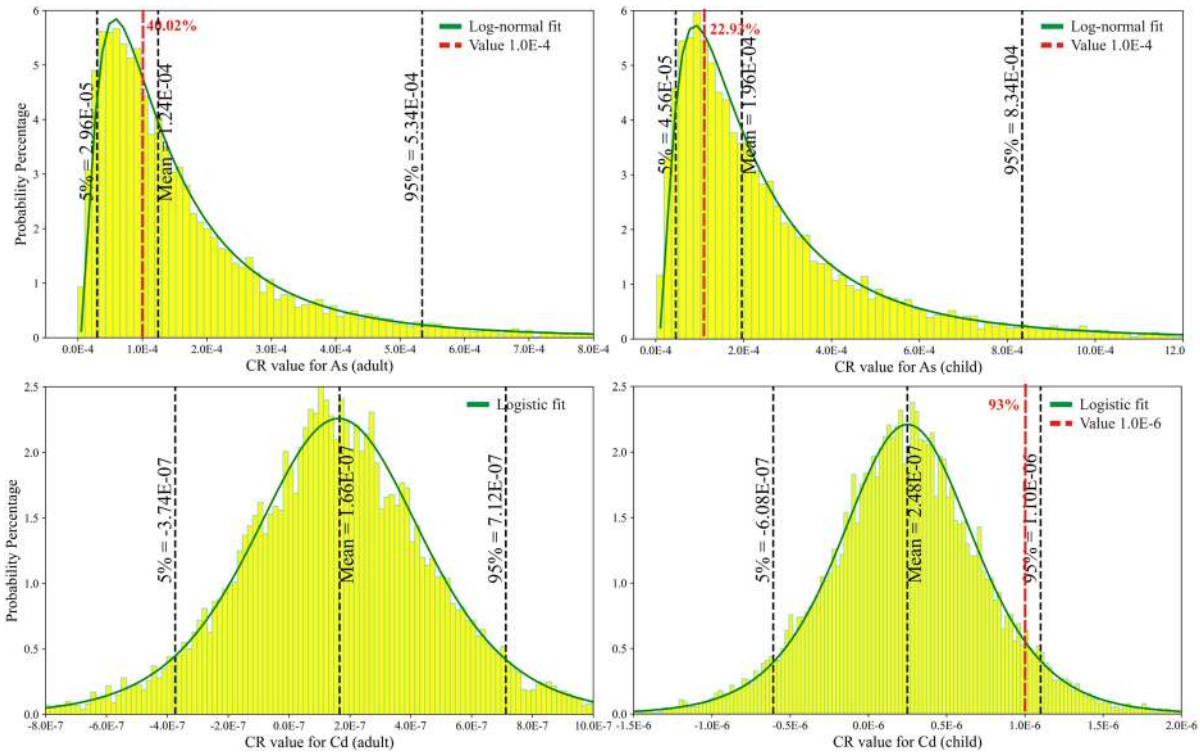


Fig. 12 Probabilistic estimates of CR values for carcinogenic elements consumption through oral ingestion pathway

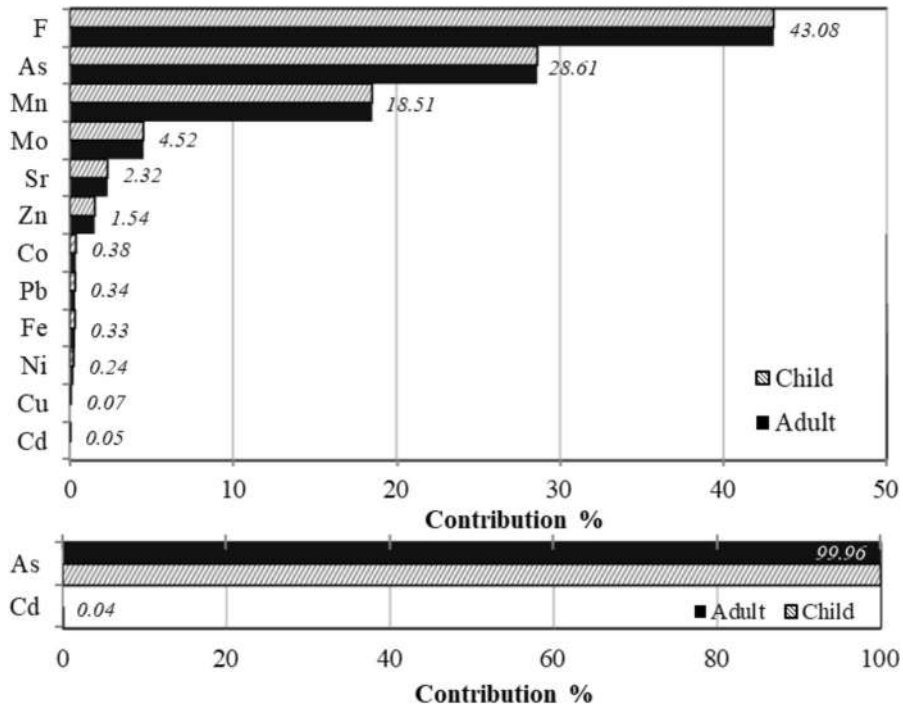


Fig. 13 Contribution percentage of the toxic elements for non-carcinogenic and carcinogenic risk in adult and child in the Singrauli area

age groups, the ranking of the toxic elements based on their contribution to the non-carcinogenic health hazard was F > As > Mn > Mo > Sr > Zn > Co > Pb > Fe > Ni > Cu > Cd. Similarly, for carcinogenic health hazards, irrespective of the age groups, the degree of contribution of As was 99.96% and Cd was 0.04% for both children and adults, respectively. Besides these individual contributions of the toxic elements, the cumulative contribution of multiple contaminants (both carcinogenic and non-carcinogenic) may trigger a significant hazardous risk to human health. Moreover, the similar outcome of the potential and probabilistic health risk assessment along with the degree of contribution additionally justified the previous occurrences of the health issues reported from the Singrauli area.

Multivariate statistical analysis

The overall KMO value of all datasets was 0.71, which was greater than 0.5, indicates that the component is significant (Kaiser & Rice, 1974). The calculated χ^2 value in Bartlett's sphericity test on the correlation matrix of the variables was 5042.39, which was about 174 times greater than the critical value of χ^2 distribution with 18 degrees of freedom and a 0.05 level of significance. It exhibits that PCA could be applied in this hydrochemical dataset to reduce the dimension of these variables (Aguirre et al., 2019).

PCA was applied to the correlation matrix of the hydrochemical dataset. A total of 5 components were considered, with eigenvalues > 1 (Cattell & Jaspers, 1967), representing 76.2% of the total variance of the dataset (Table 6). The distribution of eigenvalues with the component numbers is illustrated in a scree plot (Fig. 14a). In Table 6, the loading values above 0.75, 0.75–0.50, and 0.50–0.30 of the components with respect to the variables were categorized as strong, moderate, and weak, respectively (More et al., 2021). Principal component (PC) 1 was strongly associated with TDS, Cl^-, Ca^{2+}, total hardness, Na^+, NO^{-3}, As, and Sr, but with negative loading (Table 6). However, negative loading has no specific concern in PCA; it implies a lack of certain characteristics in a variable associated with the particular principal component (Burstyn, 2004). PC 2 had moderate positive loading associated with turbidity and SO_4 (Table 6). PC 3 had a negative loading with pH and CO_3. PC 5 was strongly associated with a single variable, i.e., Mn, whereas PC 4 was neither moderate nor strongly associated with any variables. Therefore, the first three principal components were considered to be the most significant, as mentioned in Table 6. The three-dimensional projection of the first three principal components is shown in Fig. 14b, which could represent the variable cluster for 63.29% of the total variance.

Table 6 Loadings of variables on principal components, eigen values and variances for water dataset (n = 60)

Variable	Principal components				
	PC 1	PC 2	PC 3	PC 4	PC 5
pH	0.41	−0.02	−0.72	−0.39	−0.04
TDS	−0.99	0.04	−0.05	−0.08	−0.01
T	0.04	0.71	0.07	0.00	−0.26
TH	−0.90	0.09	−0.03	−0.06	−0.13
A	−0.63	−0.49	0.28	−0.41	0.12
Ca	−0.94	0.06	−0.06	−0.02	0.06
Mg	−0.70	0.37	0.05	−0.31	0.05
Na	−0.84	−0.15	−0.08	−0.07	−0.14
K	0.03	0.40	0.12	0.30	−0.05
HCO_3	−0.66	−0.46	0.32	−0.39	0.11
CO_3	0.31	−0.17	−0.71	−0.34	−0.22
Cl	−0.92	0.05	−0.25	0.18	−0.11
F	0.16	0.48	0.23	−0.48	−0.41
NO_3	−0.75	−0.17	0.04	0.29	−0.08
SO_4	−0.64	0.61	−0.06	−0.15	0.15
Mn	−0.11	0.46	−0.09	−0.17	0.77
Zn	−0.02	0.06	0.46	−0.18	−0.34
As	−0.84	0.06	−0.33	0.21	−0.13
Sr	−0.77	−0.06	−0.21	0.23	−0.08
Eigen value	8.12	2.18	1.72	1.32	1.13
% variance	42.8	11.5	9.05	6.94	5.95
Cumulative %	42.8	54.2	63.3	70.2	76.2

Only two variables with positive loading of PC 1 were pH and CO_3, with lesser contribution to the variation of PC1. Moreover, the significant variables like TDS, Ca, Cl, total hardness, Na, As, and Sr have a strong contribution; whereas NO_3, Mg, HCO_3, SO_4, and alkalinity have a moderate contribution on PC1 with negative loading (Table 6). The coexistence of Na^+, Mg^{2+}, and Ca^{2+} is due to leaching from rocks (Sinha et al., 2023) and is common in naturally occurring groundwater and may also exist in landfill leachate (Nigro et al., 2017). The presence of Na^+,

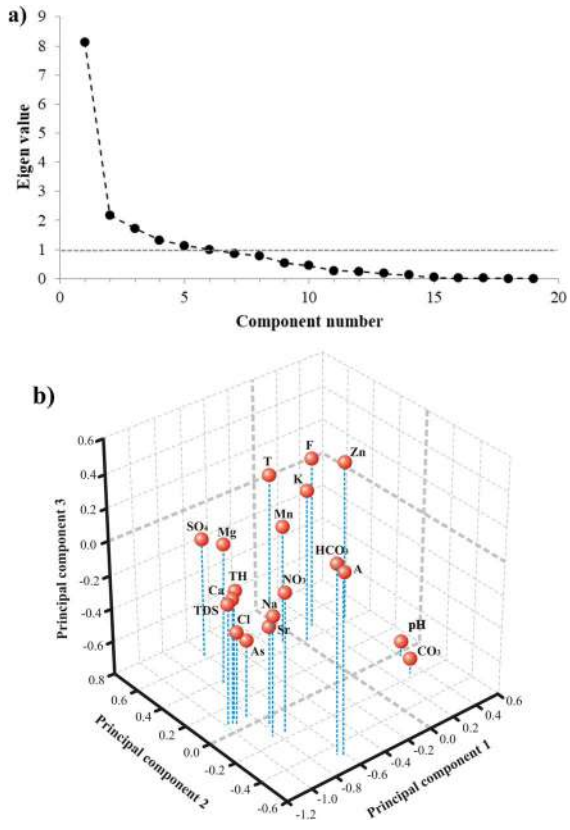


Fig. 14 **a** Scree plot of the eigen values **b** 3D image showing the graphical distribution of variables with respect to PC 1, PC 2, and PC 3

As, and TDS could originate from the effluents of coal mines and power plants. Cl^- and SO_4^{2-} were generally associated with sedimentary rocks (Battistel et al., 2016), and SO_4^{2-} was also found in the water of ash pond slurry as well (Gopinathan et al., 2022b). Therefore, due to rock-water interaction in the aquifer and the mixing of anthropogenic wastes (which include industrial wastes and leachates), the origin of such an assemblage of twelve variables could have their presence in the aquatic medium. The presence of different variables from diverse sources in the aquifer causes variations in electrical conductance and total dissolved solids. PC 2 typically originates from anthropogenic sources, which include mine waste and ash pond slurry waters. The waters from industrial and mine effluents were SO_4-dominated (Fig. 2), with high turbidity and a higher fluoride concentration. The suspected source of SO_4 in the effluents may be in the form of sulfosalts, and the further interaction of water with the ashes in the pond could enhance the dissolution and leaching of sulfate from the ashes generated from coal-based thermal power plants (Gopinathan et al., 2022c; Park et al., 2013). The variable assemblage in PC 3 was indicative of carbonate dissolution and weathering in the granitic terrain in the north-western and south-eastern parts of the selected area. As demonstrated in Fig. 2, the majority of water in the granitic terrain had mixed cation and bicarbonate-type water, with fluoride concentrations above the permissible limit. Despite the elevated fluoride concentration in the water samples, the influence of this toxic element on any principal components was inadequately significant. However, after PC2, the contribution of fluoride in PC3 was relatively more than the other three principal components. In PC3, pH and CO_3 had significant contributions with negative loading. Naturally, like any usual stream, alkaline pH and elevated CO_3 were observed in the surface water of this area, which is quite evident from the data given in Table 1. Therefore, considering the interpretation of Fig. 4b, it could be evidently stated that the fluoride in PC2 originated from industrial/mine effluents of anthropogenic origin, and the fluoride in PC3 was from the deeper aquifers in granitic terrain, representing geogenic origin. The factor PC 4 might be related to the leaching, dissolution, and percolation of anthropogenic waste material by surface run-off into the aquifer. The association of K^+ and NO_3^- loading indicates anthropogenic influence, specifically infiltrated waste effluent and the nitrogenous fertilizer KNO_3 (Dhakate et al., 2023; Fallatah & Khattab, 2023). The origin of As in PC 4 may be due to the infiltration of arsenic used in the fertilizer (Jayasumana et al., 2015), the impact of chemical fertilizer on arsenic mobilization in the sedimentary terrain (Islam & Mostafa, 2021), or the leaching of contaminated soils affected by coal combustion generated from thermal power plants (Dubey et al., 2012; and Mishra et al., 2014; Bhardwaj et al., 2020). Previous research had already reported the elevated concentration of As in soil and groundwater from the eastern side of the study area (Sonbhadra area) and interpreted it as both anthropogenic (Agrawal et al., 2011; Bhardwaj et al., 2020; Dubey et al., 2021) and geogenic origin (Dubey et al., 2021). Similarly, in this area, the association of As with K^+ and NO_3^- in this factor indicates the

mobilization of As from the As-bearing mineral present in the aquifer due to the influence of leached by-products generated from coal combustion and infiltrated chemical fertilizers. Moreover, Mn was solely responsible for influencing PC5 with strong positive loading. Additionally, the contamination of Mn (as per BIS, 2012) was witnessed in the water of ash pond slurry and decanted water, coal-mine outlet nala, nalas in and around the ash pond and coal mines, check dam, and water of sedimentary and granitic terrain as well. Mn-contaminated water was slightly acidic to neutral. According to Kimball et al. (1995) and Verplanck et al. (2000), Mn is more soluble in slightly acidic to neutral waters in comparison with many other transition metals, and it can remain in the neutralized acid drainage. Beside manganese, the coal-mine outlet water and the ash-pond water were contaminated with Ni and Mo (as per BIS, 2012), respectively.

Conclusions

This research was focused on a comprehensive hydrochemical assessment of surface and subsurface water collected from a typical coal-mine and industrial area of Singrauli with regard to toxic contaminants. Since drinking water is one of the routes of human exposure to several toxic elements, a health risk assessment in terms of both potential and probabilistic data processing methods was applied to achieve a more accurate outcome. A statistical approach was undertaken to identify the possible sources of the toxic contaminants. In this regard, the salient findings from this research are summarized below.

- Major hydrochemical facies were Ca–HCO_3, Ca–Mg–SO_4, Ca–Mg–HCO_3, and mixed types. Some groundwater and mostly industrial/mine effluents were Ca–Mg–SO_4 type water.
- F, As, Mn, Sr, Mo, Co, Ni, and Cd were the major toxic elements present in both surface water and groundwater. In addition to these toxic elements, turbidity, TDS, total hardness as $CaCO_3$, and total alkalinity exceeded the standardized permissible values.
- Fluoride concentrations were noticeably higher in 33.3% of the water samples. This includes the water samples that were collected from the granitic terrain, mines/industrial effluents, and the area in its vicinity, which indicates both geogenic and anthropogenic sources. Along with fluoride, 48.3% and 41.7% of the total samples had higher concentrations of Na^+ and Ca^{2+}, respectively, above the permissible limit.
- Quality indices represent that WQI, HMPI, and HMEI values were highly influenced by the toxic elements like As, Mn, Cd, Mo, Co, and Ni.
- In non-carcinogenic health risk assessment, HQ values for all age groups with respect to Mn, As, Mo, and F exceeded the safe limit. HI values in 55% and 70% of the total water samples exceeded the safe limit (HI > 1) for adults and children, respectively. Moreover, in probabilistic risk assessment, 56.2% and 75.2% of the simulated HI in adult and child, respectively, were above the safe limit.
- In carcinogenic health risk assessment, As posed a greater carcinogenic threat to human health than Cd. The CR values of As in 56.7% and 61.7% samples for adults and children, respectively, were above the unacceptable limit and harmful for human health. Moreover, in the probabilistic CR assessment of As, 60% values for adults and 77.1% values for children exceeded the unacceptable limit for the ingestion through oral routes.
- PCA revealed the presence of heavy metals in the groundwater of the study area affected by many factors, which include the influence of geogenic sources (salts and minerals present in the aquifer) and anthropogenic sources (like mining, industrial, and agricultural activities).
- The estimated health indices were indicative of significant carcinogenic and non-carcinogenic risk to the human health of the local inhabitants due to ingestion of polluted water through the oral pathway. Specifically, F, Mn, and As were responsible for the risk assessed, potentially resulting in a range of adverse health effects.
- The enrichment of heavy metal loads was noticed under neutral pH conditions. Furthermore, the health risk values were on the verge of an alarming level in the subsurface water, especially for children. Hence, a slight decrease in the pH of the aqueous medium may enhance the metal concentration. Therefore, appropriate maintenance of the water used for drinking/agriculture purposes

and regular health surveys for the children in the Singrauli District are recommended.

- Based on the outcome of this research, priority should be given to the pollution control of toxic elements like As, F, Mo, and Mn in terms of health concerns. Groundwater monitoring and management authorities should formulate appropriate control strategies. Regular monitoring of water quality and the supply of safe drinking water to the inhabitants are suggested.

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Data availability All data are generated or analyzed in this study are included in this article.

Declarations

Conflict of interest All the authors declare that they have no conflict of interest.

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Water Quality

District-Sone-bhadra

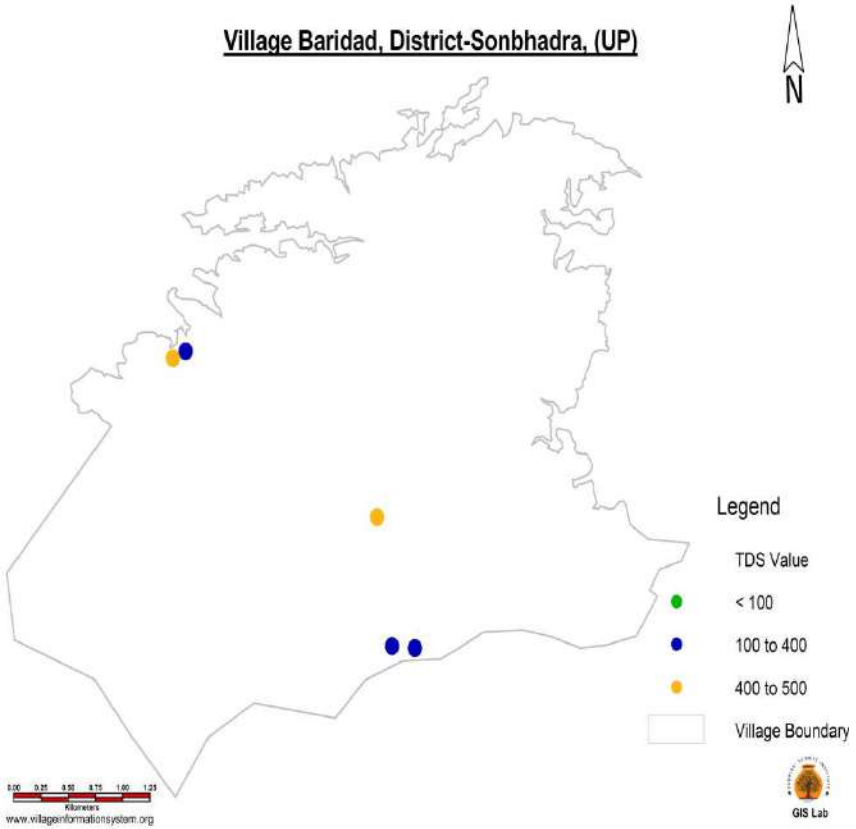
Village- Baraidar

S.N	Sample	Location	GPS POINT		Elevation (m)	Parameters			
			Longitude	Latitude		pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	BD-HP1	Yamuna Yadav-Pradhan	24°08'56.9"	082°57'59.2"	325	7	363	4.88	BDL
2	BD-W1	Dinesh Kumar	24°08'52.0"	082°57'59.8"	318	7.5	496	4.64	BDL
3	BD-W2	Vinod's House	24°09'07.1"	082°57'12.4"	306	8.2	284	4.9	BDL
4	BD-HP2	Primary School-Padri	24°09'12.9"	082°57'09.8"	313	7.6	485	4.53	1.9
5	BD-W3	Dinesh+Biren Kishwar	24°09'11.2"	082°57'03.8"	292	7.2	427	4.74	BDL
6	BD-HP3	Shiv Temple	24°08'50.8"	082°58'02.2"	315	7.4	533	9.94	BDL
7	BD-HP4	Kishan House	24°08'37.2"	082°58'16.4"	316	7.2	305	6.71	BDL
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

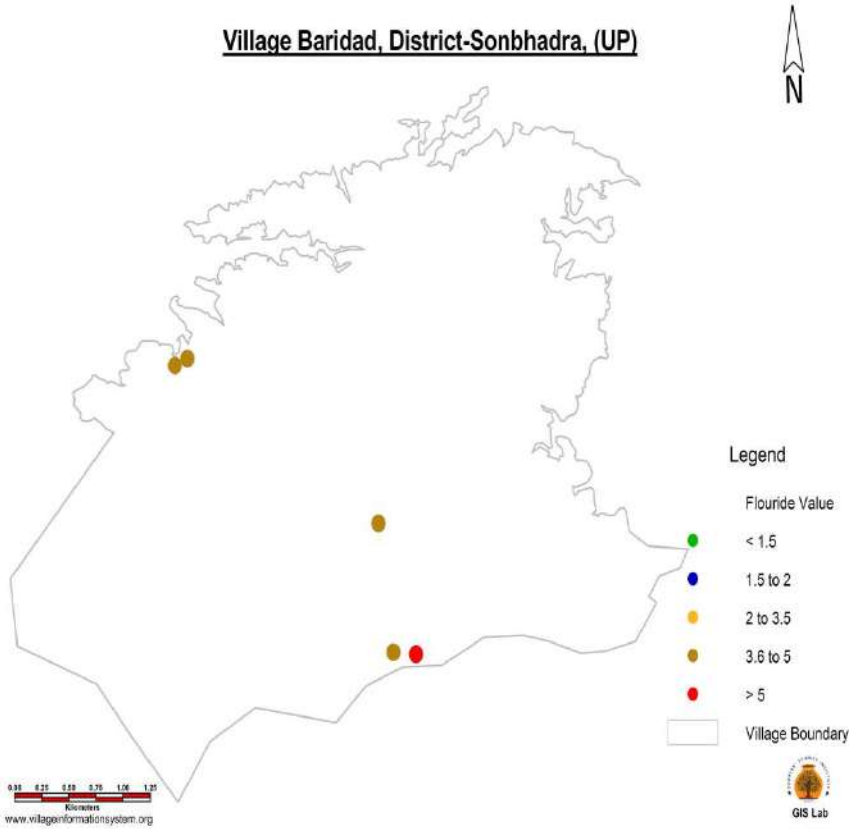
S.N	Composite Sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	BD-1 HP	Baraidar	7.6	455	5.62	0.6	3
2	BD-2 W	Baraidar	7.9	461	4.36	0.5	7
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village- Baraidar

TDS



Flouride



Village- Baraidar

- Total sample points:- 7

  Well:- 3

  Hand pump:- 4

WELL:-

- Out of 3 well,Vinod's Well show **lowest TDS(284ppm)** and Dinesh well show **highest TDS value(496ppm)** but was within the limit.
- **Fluoride** concentration measured between **4.6mg/l (Dinesh Well) to 4.9mg/l (Vinod well).**
- **Iron concentration** in all the well sources is **BDL(Below Detectable Limit).**

HANDPUMP:-

- Among Hand pump's , Shiv temple well show **high TDS (533ppm**)and Kishan HP show **lowest TDS (305ppm).**
- **Fluoride** concentration measured between **4.53mg/l (primary school)** to **9.94mg/l (Shiv temple).**
- Only one Hand **Pump(Primary School) show iron 1.9mg/l** (higher then the permissible limit).

Overall all the sources (well and Hand pump) show fluoride concentration more then the BIS permissible limit.

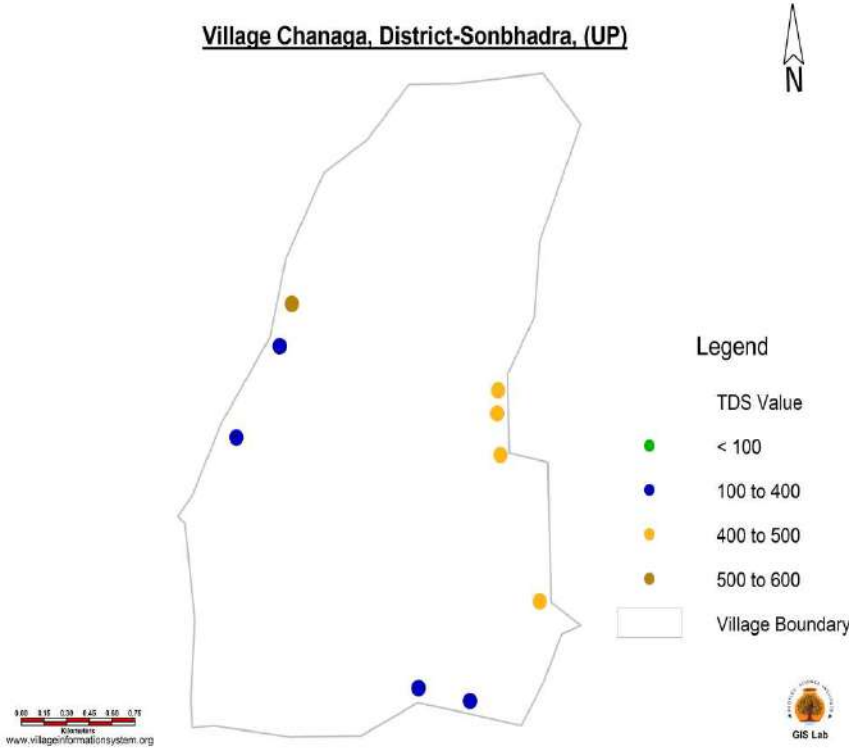
Village- Chanaga

SN	Sample	Location	GPS POINT		Elevation (m)	Parameters			
			Longitude	Latitude		pH	TDS (ppm)	F mg/l	Fe mg/l
1	HP(104)	Amarnath House(After Filter)	24^{0}03'.670"	083^{0}07'.444"	350	7.6	331	2.95	0.5
2	WELL (105)	Raamprasad House	24^{0}03'.641"	083^{0}07'.503"	351	7.9	395	1.95	0.4
3	HP(106)	Medium School-Chaga	24^{0}03'.662"	083^{0}07'.744"	347	7.8	526	6.85	0.3
4	HP(107)	Jailaal	24^{0}02'.439"	083^{0}08'.244"	366	7.2	220	4.73	0.5
5	HP(108)	Raamlagan	24^{0}02'.779"	083^{0}08'.250"	360	7.4	401	3.25	1.2
6	HP(109)	Amarsaah	24^{0}02'.688"	083^{0}08'.126"	358	7.4	277	3.25	BDL
7	HP(110)	Ramfal				7.5	331	3.81	0.2
8	HP(111)	Kailash Tola	24^{0}03'.364"	083^{0}08'.171"	348	7.8	474	6.76	0.5
9	HP(112)	Chanda	24^{0}03'.364"	083^{0}08'.172"	347	7..9	474	4.03	0.3
10	HP(113)	Shyamnarayan				7.8	296	4.5	BDL
11	HP(114)	Primary School	24^{0}03'.124"	083^{0}07'.803"	364	7.8	388	7.68	BDL
12	HP(115)	Ramdev Well	24^{0}03'.111"	083^{0}07'.930"	357	7.7	402	4.61	BDL
13	HP(116)	Hotilaal				7.4	485	2.71	
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

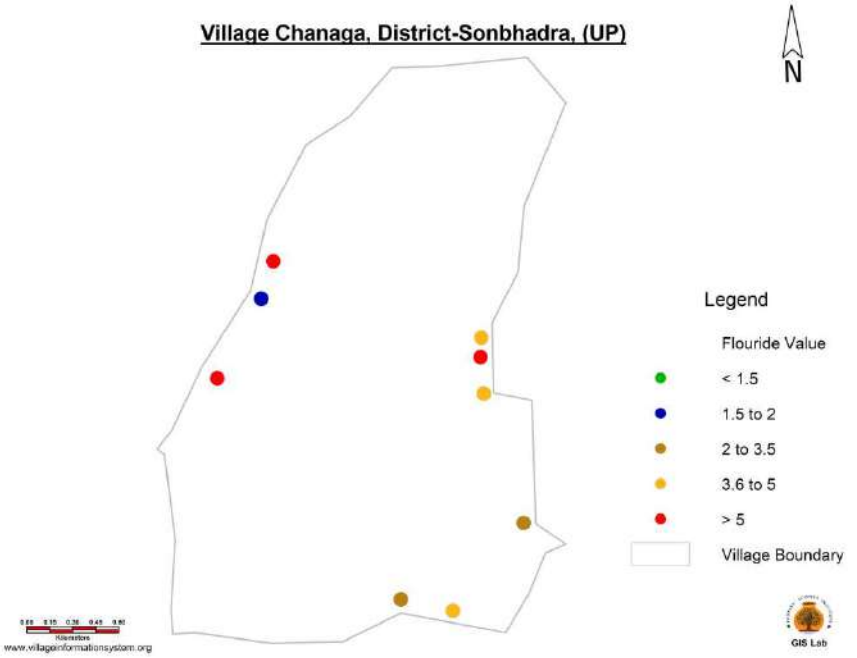
S.N	Composite sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	CG-1 HP	Chanaga	8	415	4.43	0.2	9
2	CG-2 W	Chanaga	8.3	441	3.07	1	15
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village- Chanaga

TDS



Flouride



Village- Chanaga

- Total sample points:13

  Hand pump:- 12

  Well:- 1

HAND PUMP:-

- Among all the 12 hand pump, lowest TDS measured was 220ppm(Jailaal)and highest TDS measured was 526ppm(Medium school).
- Fluoride concentration measured between 2.71mg/l (Hoti laal) to 7.68 mg/l (Primary School).
- Iron concentration measured was between O to 1.2mg/l (Raam Lagan's HP).

WELL:-

- TDS measured was 395ppm.
- Fluoride concentration was 1.95mg/l (Higher then the BIS permissible limit).
- Iron concentration was 0.4mg/l (Higher then BIS permissible limit).

Overall, it is seen that well water has less Fluoride concentration then Hand pump.

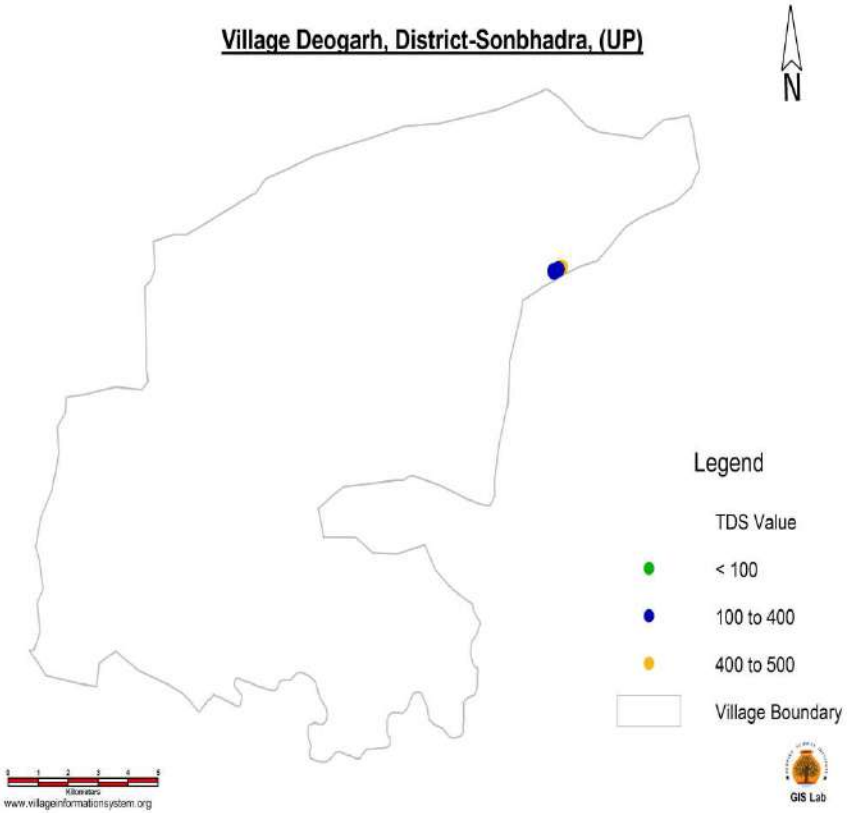
Village- Deoghar

SN	Sample	Location	GPS POINT		Elevation (m)	Parameters			
			Longitude	Latitude		pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	Hp(45)	Pradhan House	24^{0}31'.101"	082^{0}54'.545"	210	7.3	248	1.07	0.4
2	Hp(46)	Rajkumar House	24^{0}31'.604"	082^{0}55'.293"	214	7.5	283	0.825	0.4
3	Hp(47)	Raamroop Gond	24^{0}31'.585"	082^{0}55'.212"	219	7.3	264	0.73	
4	Hp(48)	Phunnu Gupta	24^{0}31'.765"	082^{0}55'.489"	214	7.2	322	0.73	0.1
5	Hp(49)	School	24^{0}31'.814"	082^{0}55'.502"	216	7.1	266	0.595	0.5
6	Hp(50)	Charku	24^{0}32'.327"	082^{0}54'.695"	224	7.3	427	0.575	0.1
7	Hp(51)	School	24^{0}32'.317"	082^{0}54'.625"	233	7.2	449	1.85	BDL
8	Hp(52)	Rangeela	24^{0}32'.176"	082^{0}54'.323"	221	6.3	480	0.859	0.8
9	Well(53)	Budhhu Gupta	24^{0}31'.752"	082^{0}55'.365"	216	7.1	163	0.673	BDL
10	Hp(54)	Gulab Harizan	24^{0}31'.524"	083^{0}54'.881"	212	7.2	402	0.664	0.2
11	Well(55)	Surendra Yadav	24^{0}31'.345"	083^{0}54'.805"	209	7.3	264	0.612	0.4
12	Hp(56)	Panchayat Bhawan	24^{0}31'.255"	083^{0}54'.795"	217	6.8	246	0.479	BDL
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

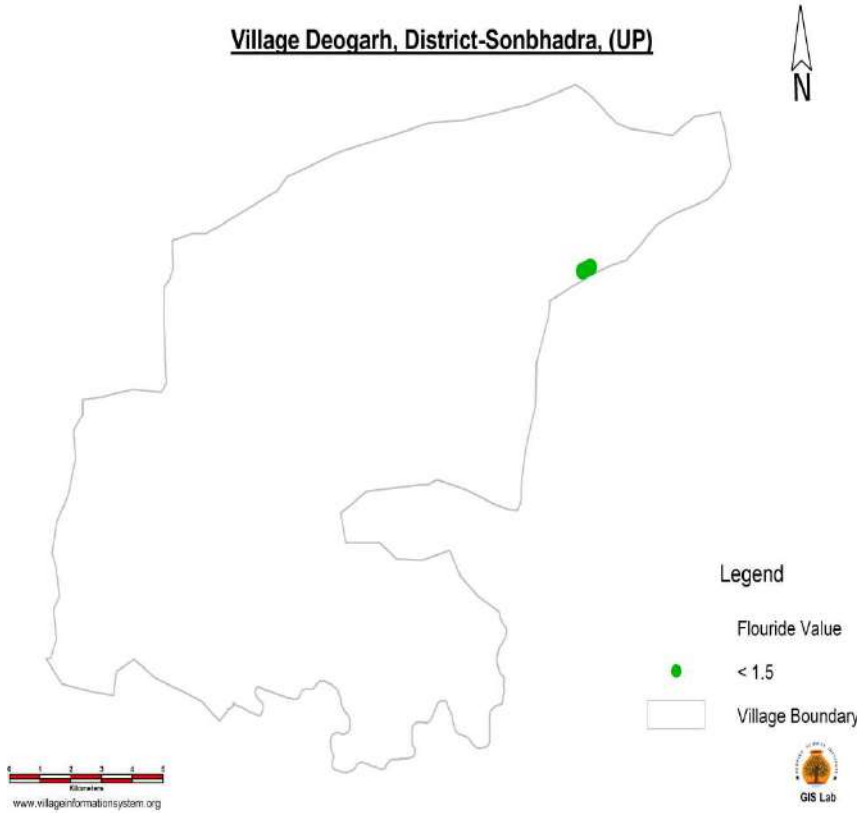
S.N	Composite Sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	DK-1 HP	Deoghar	7.7	339	0.395	0.9	11
2	DK-2 W	Deoghar	7.7	243	0.598	7	9
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village- Deoghar

TDS



Flouride



Village -Deoghar

- Total Sample Points:-12
- Hand pump:-10
- Well:-2

HAND PUMP:-

- Lowest TDS was measured in Panchayat Bawan (246ppm) and Highest TDS measured was measured in Rangeela (480ppm).
- Only one HP show fluoride concentration (higher then the permissible limit) 1.85mg/l(School) and other fluoride value were less then the limit.
- Out of 10 HP, 5 sources show iron below the permissible limit and other show iron more then the permissible limit. Highest Iron was measured in Rangeela (0.8mg/l).

WELL:-

- TDS of both the well was within the limit (163ppm and 264ppm).
- Fluoride concentration was also less then the limit(0.612mg/l and 0.673mg/l).
- One of the well(Surendra well) show iron content 0.4mg/l(higher then the permissible limit).

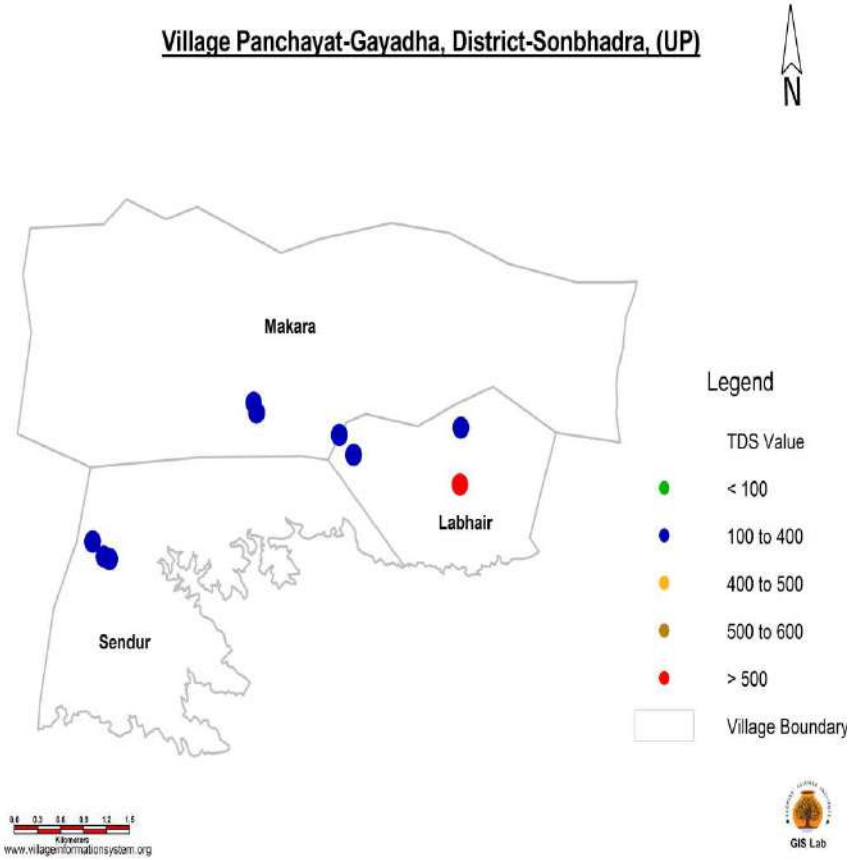
Village- Gaya dah

S.N	Sample	Location	GPS POINT		Elevation (m)	Parameters			
			Longitude	Latitude		pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	Well(81)	Raambriksha God	24^{0}12'.702"	082^{0}58'.924"	339	7.2	235	3.58	
2	Hp(82)	Primary School	24^{0}12'.566"	082^{0}58'.079"	326	6	250	2.98	
3	Well(83)	Ramdhari Srivastav	24^{0}12'.389"	082^{0}58'.908"	314	6.9	1280	2.53	
4	Bore Well(84)	Makra	24^{0}12'.482"	082^{0}58'.855"	324	6.4	1000	3.68	
5	Hp(85)	Pre-Medium School	24^{0}12'.684"	082^{0}57'.963"	328	7.2	280	1.59	
6	Pond (86)	Ramsevak Agrifield	24^{0}12'.870"	082^{0}57'.300"	300	9.1	260	2.95	0.4
7	Well(87)	Hardyal Gond	24^{0}12'.812"	082^{0}57'.319"	301	7.2	184	5.75	0.2
8	Hp(88)	Subhash Kewat	24^{0}12'.135"	082^{0}56'.022"	292	7.2	290	3.64	0.3
9	Hp(89)	Primary School-Myorpur	24^{0}12'.038"	082^{0}56'.150"	281	7.2	217	2.11	BDL
10	Well(90)	Kanhaiya laal	24^{0}12'.048"	082^{0}56'.110"	274	7.5	243	1.65	0.6
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

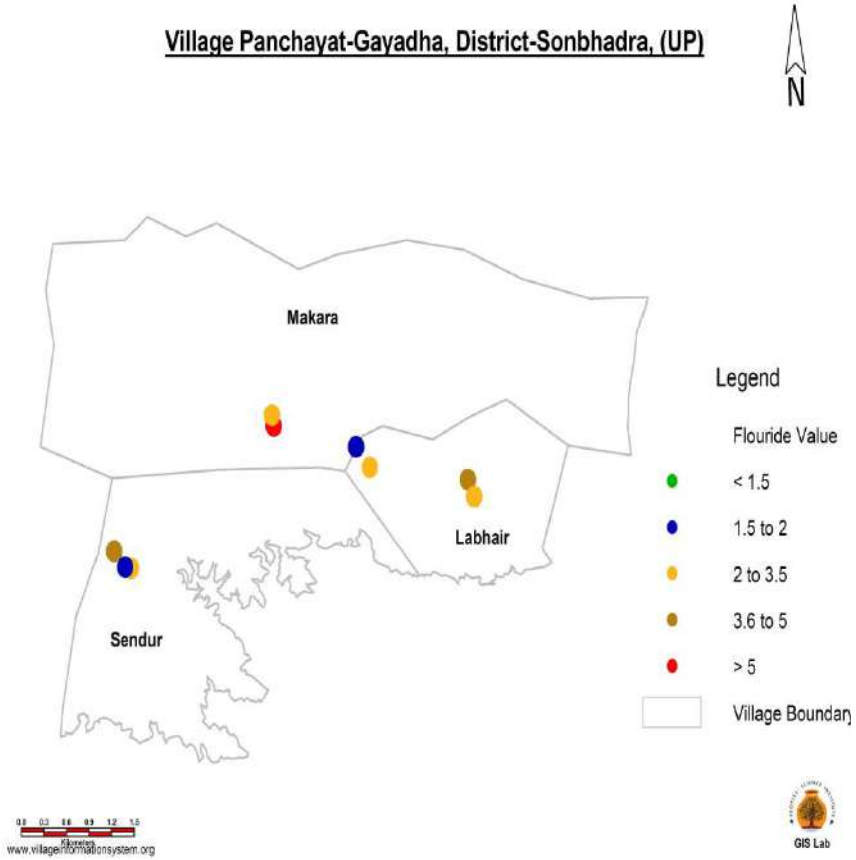
S.N	Composite sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	GH-1 HP	Gaya dah	6.9	325	1.54	0.9	6
2	GH-2 W	Gaya dah	7	731	1.31	2	6
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village- Gaya dah

TDS



Flouride



Village- Gaya dah

- Total sample points:- 10
- Hand Pump:-4
- Well-4
- Pond-1
- Bore-well-1

HAND PUMP:-

- TDS range of all the samples were less then the BIS limit as the variations seen were within 200ppm to 300ppm. Highest TDS was of Subhash's HP.
- Fluoride ranges from 1.59mg/l (Pre-medium school) to 3.64 mg/l(Shubhash's HP).
- Iron measured from 0 to 0.3mg/l (Subhash's HP).

WELL:-

- Highest TDS seen was 1280ppm (Ram dhari) and lowest was 184ppm.
- Fluoride concentration was between 1.65mg/l (Kanhaiya Laal) to 5.75mg/l(Hardyal).
- 0.6mg/l og the iron was measured in Kanhaiya laal well which is higher then the permissible limit.

BORE-WELL:-

- Both the TDS and Fluoride value of the bore well was higher then the BIS permissible limit i.e. TDS 1000ppm and Fluoride 3.64mg/l.

POND:-

- TDS was 260ppm but iron and fluoride was higher then the permissible limit as Fluoride was 2.95mg/l and Iron was 0.4mg/l.

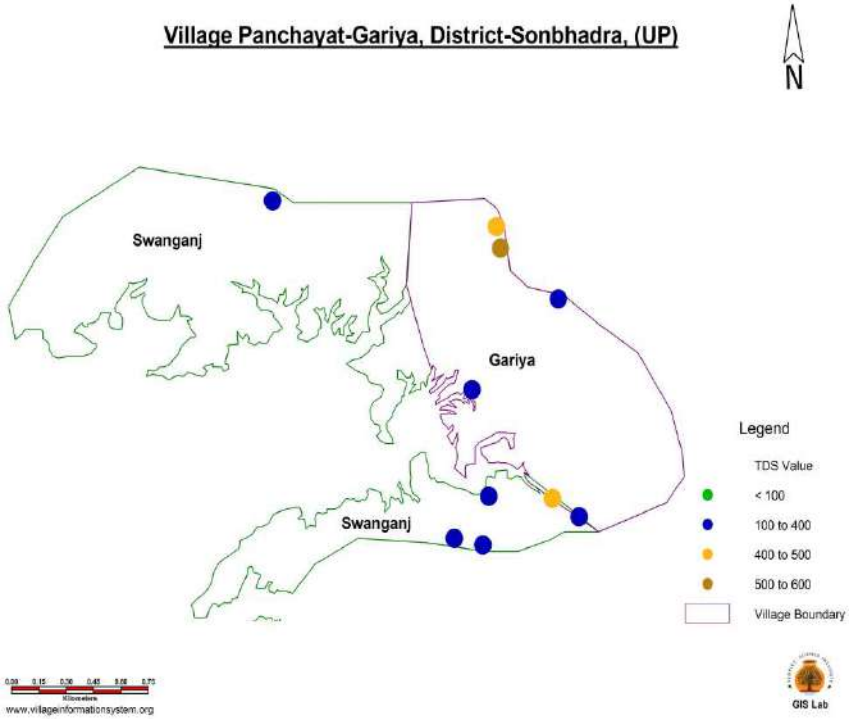
Gariya village

SN	Sample	Location	GPS POINT		Elevation (m)	Parameters			
			Longitude	Latitude		pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	GD-HP1	Pradhan House	24^{0}07'12.2"	082^{0}58'42.3"	266	7.4	451	4.93	BDL
2	GD-W1	Premchand Pradhan	24^{0}07'10.7"	082^{0}58'48.4"	268	8.9	303	2.83	BDL
3	GD-HP2	Awdhes's House	24^{0}07'07.8"	082^{0}58'31.1"	270	7.3	363	5.44	0.7
4	GD-W2	Near Sanjay Yadav House	24^{0}07'04.1"	082^{0}58'26.7"	272	7.7	354	7.79	0.1
5	GD-HP3	Primary School	24^{0}07'01.4"	082^{0}58'22.3"	279	7.3	344	4.85	BDL
6	GD-HP4	Panchayat House	24^{0}07'31.4"	082^{0}58'36.0"	264	6.9	192	3.56	3.4
7	GD-W3	Ram Swarat	24^{0}07'50.8"	082^{0}58'26.4"	267	7.5	517	5.65	0.1
8	GD-W4	Subhash House	24^{0}07'57.0"	082^{0}57'41.2"	266	8.7	235	3.19	BDL
9	GD-HP5	Munshiji House	24^{0}07'56.3"	082^{0}58'46.3"	266	7.7	363	2.81	BDL
10	GD-HP6	Dinesh House-Primary School	24^{0}07'55.4"	082^{0}51'36.4"	272	7.1	463	3.01	BDL
11	GD-RES	Reservoir Near Gadiya				8.8	75	0.972	BDL
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

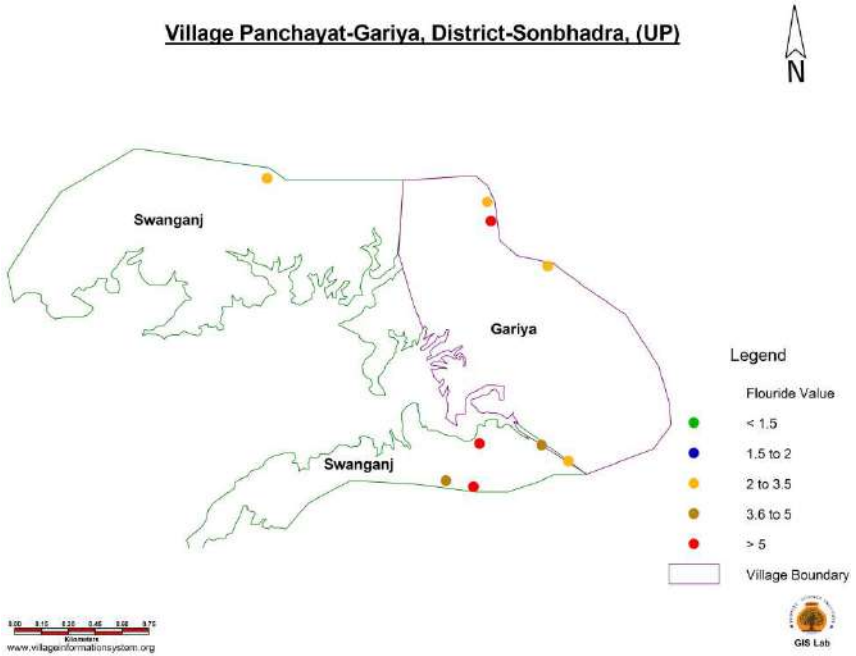
S.N	Composite Sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	GD-1 HP	Gariya	7.4	383	3.9	0.5	18
2	GD-2 W	Gariya	8.4	405	4.53	1	3
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village- Gariya

TDS



Flouride



Village- Gariya

- Total sample points:- 11

  Hand Pump:- 6

  Well:- 4

  Residential :- 1

HAND PUMP:-

- All the six sources show TDS within the limit. Lowest TDS is 192ppm (Panchayat House) and Highest TDS is 463 ppm (Dinesh house).
- Flouride concentration measured between 2.81 mg/l (Munshi ji) and 5.44 mg/l (Awdhesh's HP).
- Some sources do not show iron but some show very high iron concentration i.e. Upto 3.4mg/l in Panchayat House.

WELL:-

- Only one source show TDS above BIS limit i.e. Ram Swarat TDS 517ppm and other sources show TDS less then the BIS limit.Lowest TDS is 235 ppm.
- All the sources have high Flouride concentration ranges from 2.83mg/l to 7.79 mg/l.

RESIDENTIAL :-

- TDS ,iron and Flouride of the residential source is within the limit.

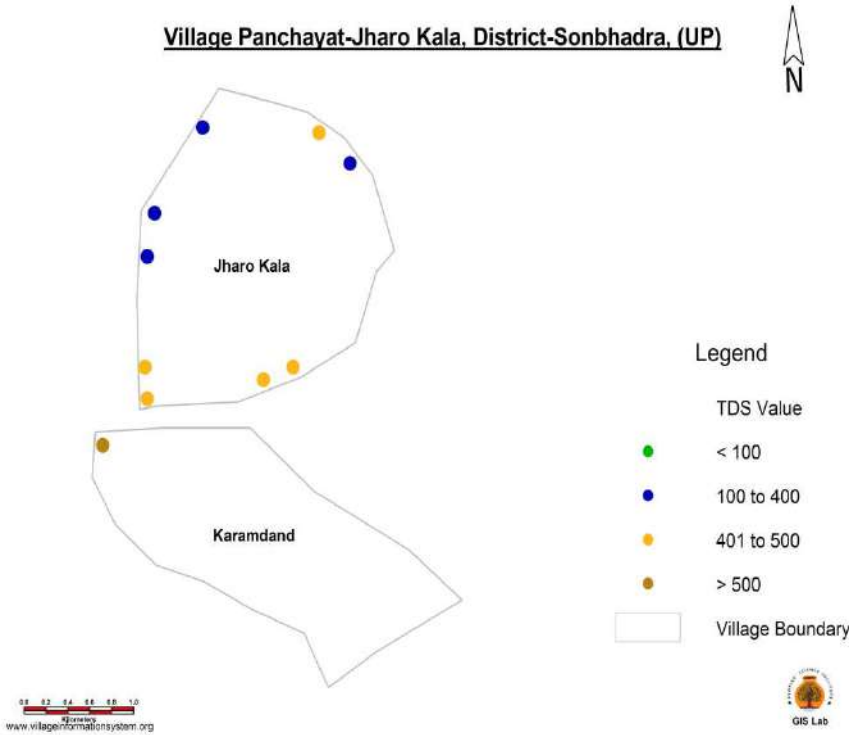
Village- Jharokala

S.N	Sample	Location	GPS POINT		Parameters				
			Longitude	Latitude	Elevation (m)	pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	WELL (1)	Ramvriksh	24^{0}11'37.0"	083^{0}09'14.6"	271	7.6	348	2.3	BDL
2	HP(2)	Raamsundar	24^{0}11'32.9"	083^{0}09'11."	270	7.1	403	3.3	BDL
3	HP(3)	Jaimangal	24^{0}11'33.4"	083^{0}08'11".9	269	7.5	241	2.78	0.6
4	WELL (4)	Kariraam	24^{0}11'28.2"	083^{0}08'56.5"	269	7.8	478	1.95	0.1
5	HP(5)	Ram Singh	24^{0}11'25.9"	083^{0}08'57.9"	270	7.5	262	2.42	0.2
6	HP(6)	Kishdhan (Dhaikar Basti)	24^{0}11'10.4"	083^{0}08'52.8"	278	7.8	502	3.32	BDL
7	DAM (7)	Jharo	24^{0}11'14.5"	083^{0}08'45.9"	269	9.7	235	2.93	BDL
8	HP(8)	Thakuritola-School	24^{0}11'47.3"	083^{0}08'41.7"	282	7.3	348	6.57	BDL
9	HP(9)	Jharokal-Primary School	24^{0}10'54.4"	083^{0}09'01.5	275	7.6	442	3.54	0.2
10	WELL (10)	Ramroop	24^{0}10'55.6"	083^{0}08'51.7	276	7	422	2.11	0.1
11	HP(11)	Upedra Doctor	24^{0}10'57.4"	083^{0}08'48.7	281	7.1	472	1.67	0.3
12	HP(12)	Jharokala-Panchayat	24^{0}10'50.0"	083^{0}08'33.2	286	7.4	507	3.87	0.2
13	HP(13)	Suraj Bali	24^{0}10'46.7"	083^{0}08'10.3	292	7	480	2.85	BDL
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

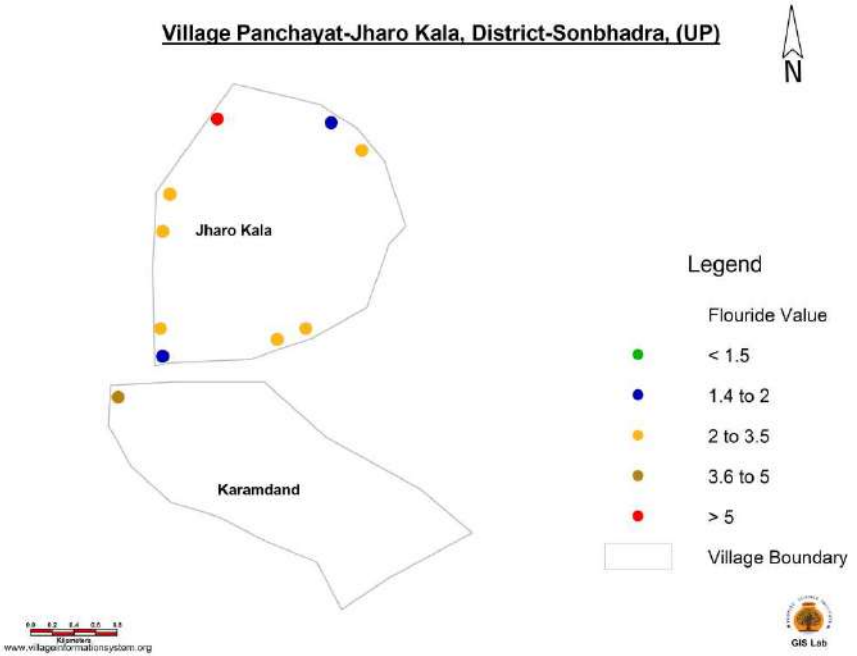
S.N	Composite sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	JH-1 HP	Jharokala	7.9	471	2.68	BDL	7
2	JH-2 W	Jharokala	8.2	407	1.43	BDL	5
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village- Jharo kala

TDS



Flouride



Village- Jharo Kala

- Sample points:- 13

Hand Pump:- 9

Well:- 3

Dam:- 1

WELL:-

- TDS of all the samples were within the permissible limit showing the variation within 348ppm(Ramvriksh) to 478 ppm(Kariraam).
- Fluoride conc. Was more then the BIS limit as lowest Fluoride was 1.95mg/l (Kariraam)and 2.3mg/l (Ram Vriksh)was highest.
- Iron conc. Was very less in all the well sources.

HAND PUMP:-

- Out of 9 sources of only two sources show high TDS value then BIS limit. Highest TDS was seen in Panchyat house(507ppm).
- All the sources have high fluoride value value range from 1.67 mg/l (Upendra doctor) to 6.57mg/l(Thakri tola school).
- Except Jai Mangal, all the other sources have iron within the BIS limit. Jai Mangal has 0.6mg/l of the Iron concentration.

DAM:-

- TDS of sample is within the limit but Fluoride concentration is 2.93mg/l which is higher then the BIS permissible limit.

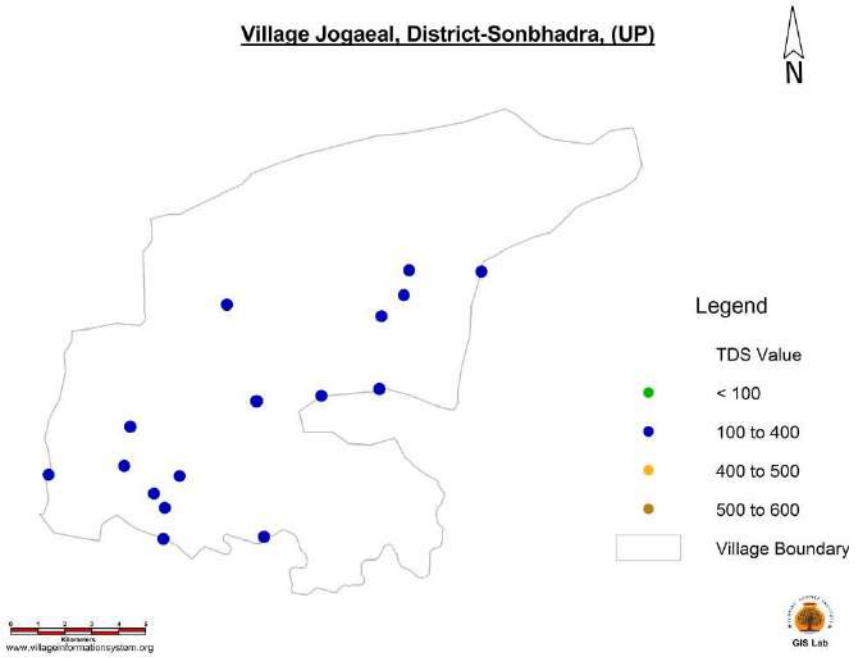
Village- Jogaeal

S.N	Sample	Location	GPS POINT		Elevation (m)	pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
			LONGITUDE	LATITUDE					
1	HP(57)	Pradhan House	24°27'.092"	082°47'.017"	272	6.4	303	0.633	0.4
2	HP(58)	Parmanand House	24°26'.738"	082°46'.434"	292	6.4	258	0.476	0.3
3	HP(59)	School-Semra	24°26'.003"	082°46'.578"	285	7	245	1.45	0.1
4	WELL(60)	Judawan	24°26'.445"	084°46'.665"	268	7.2	184	1.01	BDL
5	HP(61)	Jaggan Gurjar	24°27'.323"	082°45'.780'	298	6.7	223	0.73	0.9
6	WELL(62	Raamdas-Mahuvariya	24°28'.117"	082°45'.928"	312	7.6	298	1.62	0.4
7	Pond-patwa Tola(63)		24°28'.128"	082°47'.986"	302	8.6	744	4.41	6.9
8	HP(64)	Ajodhya/Bachha Laal	24°27'.062"	082°44'.324"	305	7.1	274	0.977	0.2
9	WELL(65)	Komal Singh Butti	24°26'.973"	082°48'.662"	262	7.1	227	1.18	0.1
10	HP(66)	Mohan Singh	24°28'.596"	082°48'.743"	294	7.3	236	1.26	
11	WELL(67)	Janakdhari Gond House	24°28'.594"	082°48'.774"	295	8	233	1.26	0.3
12	HP(68)	Raamcharan	24°28'.542"	082°50'.357"	248	6.9	157	0.906	BDL
13	WELL(69)	Kailash Prajapati	24°28'.630"	082°51'.597"	228	6.5	135	0.749	BDL
14	WELL(70)	Rattu Kharwar-Sidhwa Daand	24°30'.287"	082°51'.221"	222	7.3	186	0.875	0.1
15	HP(71)	Near Sbi Bank	24°30'.382"	082°51'.137"	233	6.7	171	0.026	1.5
16	HP(72)	Gram Panchayat Jugail	24°30'.576"	082°48'.625"	266	6.7	349	1.41	BDL
17	HP(73)	Kasturba Gandhi School	24°30'.750"	082°48'.065"	272	6.6	601	1.03	0.2
18	HP(74)	Ashram-Employee	24°30'.695"	082°52'.105"	237	6.6	289	1.73	0.1
19	HP(75)	Raamdayal House	24°31'.217"	082°52'.238"	226	6.2	226	1.03	0.4
20	HP(76)	Laalbahadur House	24°31'.171"	082°53'.489"	216	6	217	0.726	BDL
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

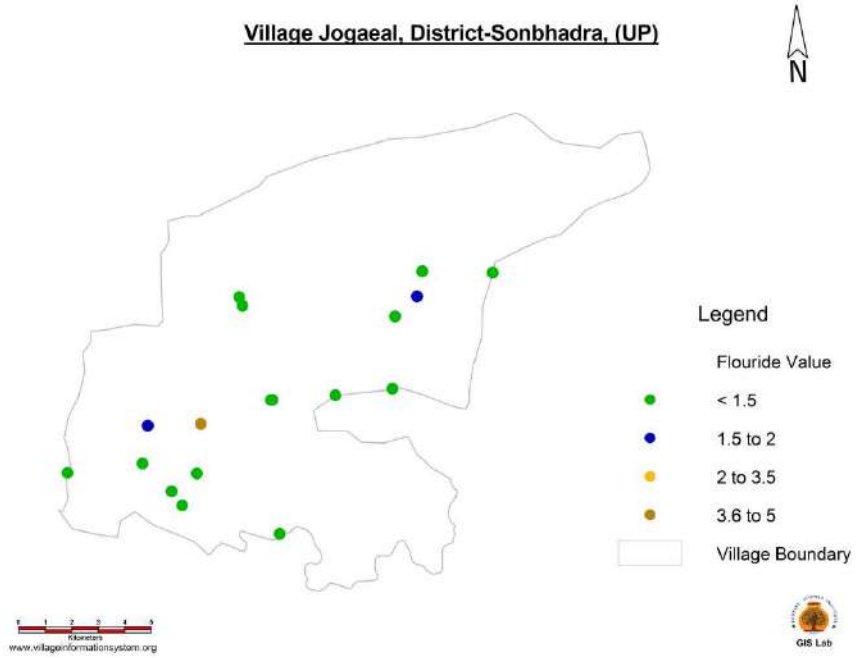
S.N	Composite sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	JG-1 HP	Jogaeal	7.4	285	0.809	2	10
2	JG-2 W	Jogaeal	7.7	322	0.871	60	2
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village- Jogaeal

TDS



Flouride



Village- Jogaeal

- Total Sample points:- 20

  Hand pump:- 13

  Well:- 6

  Ponds:- 1

HAND PUMP:-

- TDS ranges from 216ppm(Lal bahadur) to 305ppm (Ajodhya).
- Except Ashram(1.73mg/l), all the other HP sources show fluoride range within the limit, showing variation from 0.026 mg/l to 1.5mg/l.
- Out of all the HP, only 4 sources have crossed BIS limit. HP near SBI bank have the highest iron concentration of 1.5mg/l.

WELL:-

- TDS is within the BIS limit showing variation within 100 to 300 ppm.
- Only Ramdas well have high fluoride concentration of 1.62mg/l.
- 0.4mg/l of the iron was measured in Ramdas well. Other have less iron content.

POND:-

- Only TDS range is within the limit but Fluoride and iron have very high value i.e. Fluoride 4.41mg/l and iron 6.9mg/l.

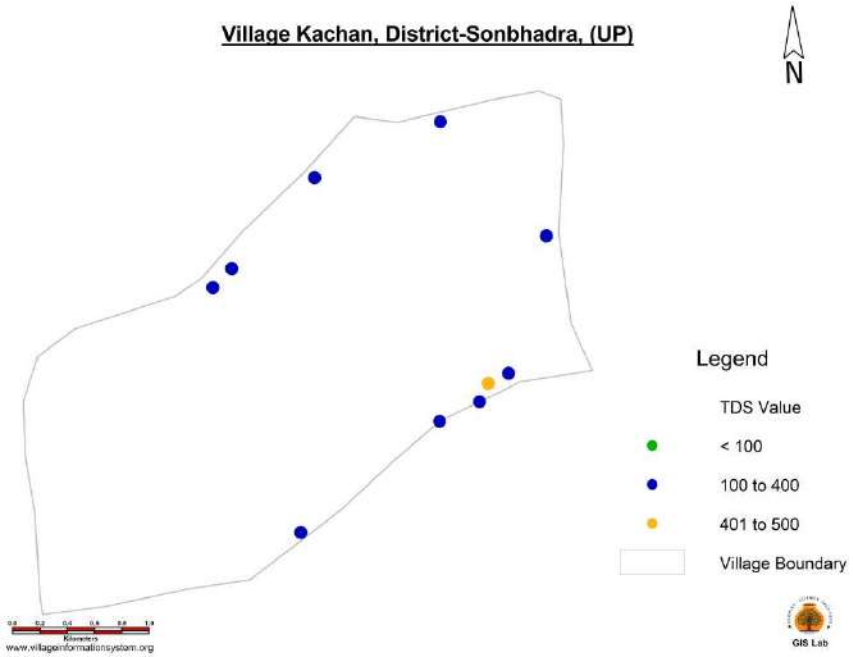
Village- Kachan

S.N	Sample	Location	GPS POINT		Elevation (m)	Parameters			
			Longitude	Latitude		pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	HP(16)	Panchayat Bhawan	24°04'41.9"	083°01'36.8	352	7.2	251	1.38	0.1
2	HP(17)	Near Mosque	24°04'50.7"	083°01'38.0	344	7.4	183	1.45	0.1
3	WELL (18)	Jagmohan	24°04'49.8"	083°01'50.2	342	6.9	123	1.2	2.1
4	HP(19)	Near School	24°04'28.1"	083°01'49.0	340	6.6	408	1.18	0.5
5	HP(20)	Jagat Sahani	24°04'16.4"	083°01'35.3	349	7.7	251	3.54	0.6
6	HP(21)	Chet Singh	24°04'26.0"	083°00'54.2	352	7	162	1.96	0.1
7	HP(22)	Primary School	24°04'10.2"	083°00'40.1	357	7.1	328	1.41	1.9
8	HP(23)	Bholadas House	24°04'37.6"	083°00'58.5	350	6.8	186	1.1	0.2
9	HP(24)	Amrud Daad-Maksud Daroga	24°05'00.1"	083°01'11.7	337	7.1	198	1.71	BDL
10	HP(25)	School	24°05'12.3"	083°01'39.9	349	7	289	1.24	0.2
11	HP(26)	Kripashankar	24°04'21.9"	083°01'59.2	354	7.5	189	1.29	0.9
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

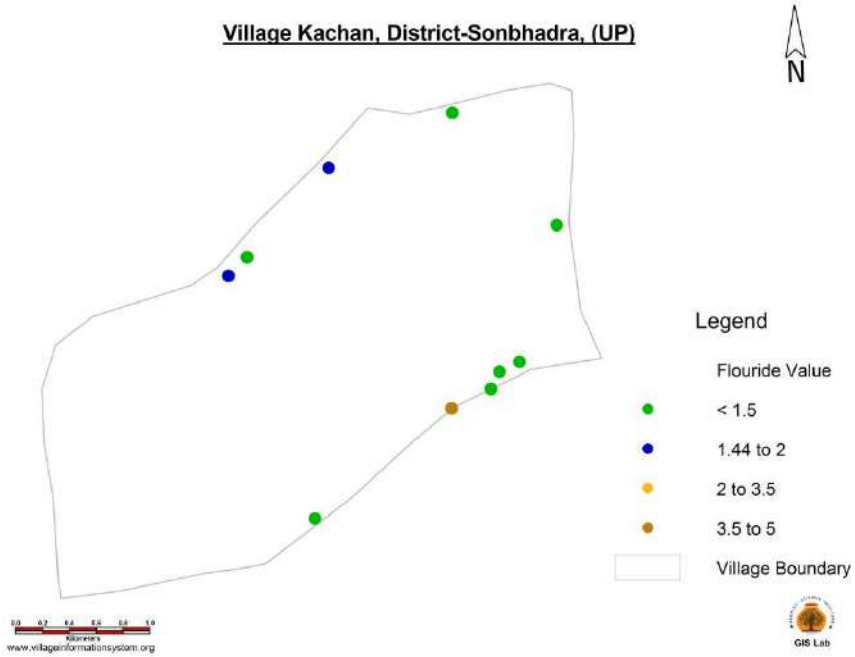
S.N	Composite Sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	KHN-1 HP	Kachan	7.8	274	1.38	0.7	8
2	KHN-2 W	Kachan	7.6	134	1.03	BDL	4
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village-Kachan

TDS



Flouride



Village- Kachan

- Total Sample points:- 11
- Hand pump:- 10
- Well:- 1

HAND PUMP:-

- TDS was within the limit (from 162ppm(Chet Singh) to 408ppm(near School)).
- Out of 10 HP, 8 HP show less flouride(between 1.1mg/l to 1.45mg/l) and 2 HP show high flouride between (1.96mg/l to 3.54mg/l).
- Iron concentration was from 0 to 1.9mg/l(HP near primary school).

WELL:-

- TDS (123ppm) and fluoride (1.2mg/l) were within the limit but iron contents(2.1mg/l) was higher then the permissible limit.

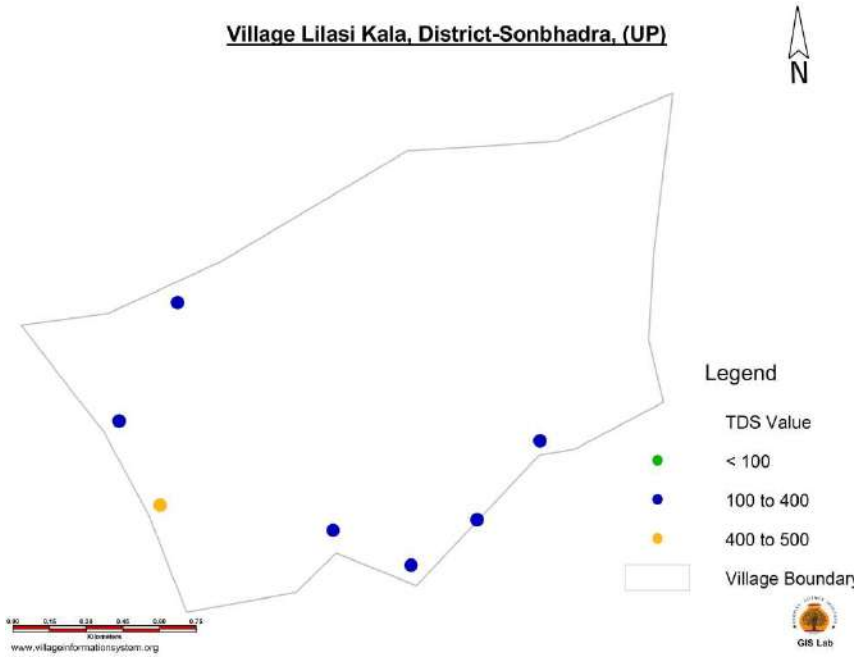
Village- Lilasi Kala

S.N	Sample	Location	GPS POINT		Elevation (m)	Parameters			
			Longitude	Latitude		pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	HP (117)	Ramprasad	24°04'.887"	083°09'.023"	334	7.3	322	1.66	0.2
2	HP (118)	Shobhnath	24°05'.087"	083°09'.402"	324	7.2	211	1.52	BDL
3	RIVER (119)	Katauli Lilasi	24°05'.013"	083°09'.702"	318	8.2	219	3.24	
4	HP(120)	Raamsevak-purva Pradhan	24°05'.318"	083°09'.393"	319	7.5	446	1.94	BDL
5	BW(121)	Pradhan House	24°05'.390"	083°09'.190"	318	7.1	393	1.38	BDL
6	HP(122)	Anil House	24°05'.390"	083°09'.190"	318	6.9	284	1.34	BDL
7	HP(123)	Kamlesh Kumar	24°05'.288"	083°08'.748"	321	7.6	375	1.81	0.2
8	DAM (124)	Lilasi-lilmarwa Pond	24°05'.107"	083°08'.902"	343	9.4	166	4.61	
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

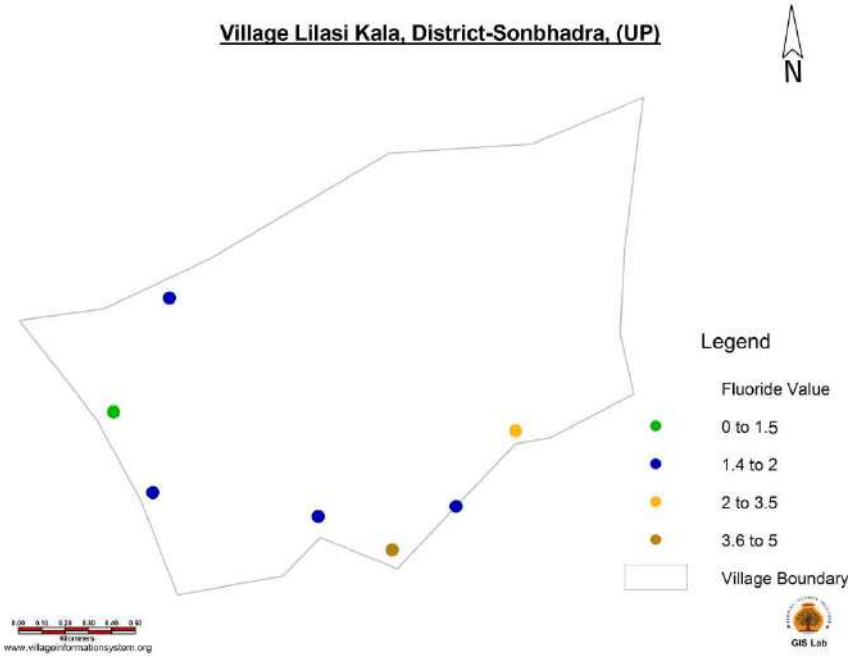
S.N	Composite sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	LS-1 HP	Lilasi	7.4	375	1.59	1	11
2	LS-2 R	Lilasi	8.7	198	2.29	2	26
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village- Lilasi Kala

TDS



Flouride



Village :- Lilasi Kala

- Total sample points:- 8
- Hand pump:- 5
- River:- 1
- Dam:-1

HAND PUMP:-

- TDS range is within the limit of all the HP ranging from 211ppm to 446ppm(Ram sewak).
- Except Anil's HP(1.34mg/l), all the other have fluoride higher then the permissible limit(1.52mg/l to 1.94mg/l).
- Iron in all the HP sources was within the limit.

BORE-WELL:-

- TDS,Fluoride and Iron are all within the BIS permissible limit.

RIVER AND DAM:-

- Except fluoride (River=3.24mg/l and Dam=4.61mg/l), TDS and Iron were within the limit.

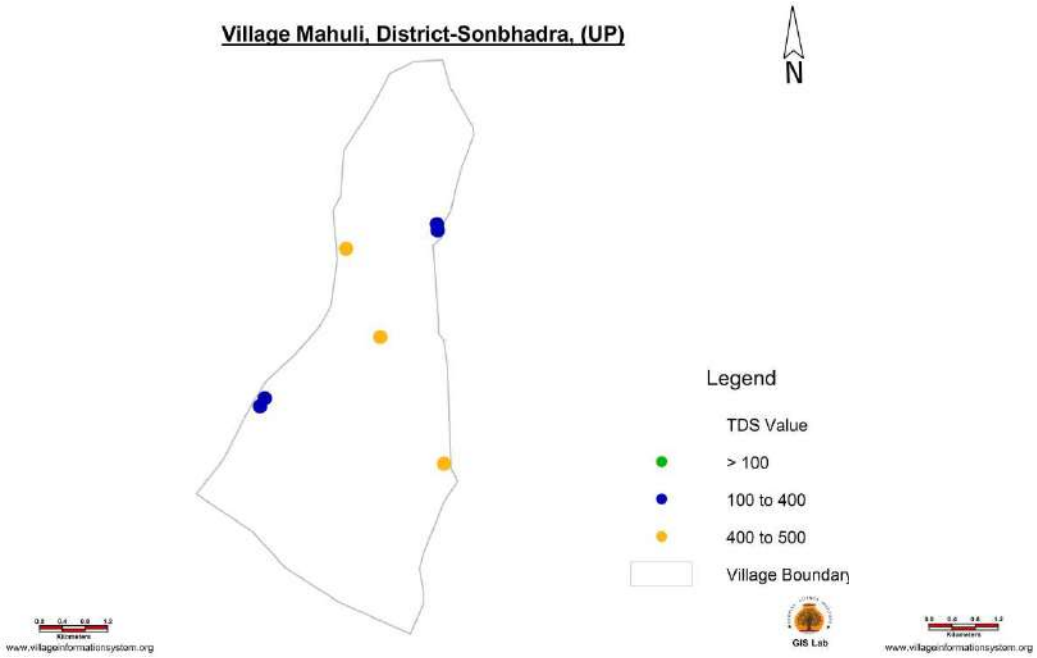
Village- Mahuli

S.N	Sample	Location	GPS POINT		Elevation (m)	Parameters			
			Longitude	Latitude		pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	MHHP-1	Near Primary School	23°56'38.9"	082°54'21.9"	380	6.9	332	3.5	0.5
2	MHW-1	Pradhan Raamkishun House	23°56'46.8"	082°54'23.0"	370	7.2	463	2.75	BDL
3	MHW-2	Mahendra Singh House-Lakhar	23°58'05.9"	082°54'48.9"	334	7.3	341	2.02	BDL
4	MHHP-2	Near Primary School-Lakhar	23°58'02.4"	082°54'47.6"	339	6.8	352	1.54	BDL
5	MHW-3	Jhamman Singh House-Rehta Daad	23°57'44.8"	082°54'12.6"	349	7.3	476	1.36	BDL
6	MHHP-3	Jogindar Singh House-Rehtadaad	23°57'42.9"	082°54'04.3"	353	6.8	389	2.63	BDL
7	MHW-4	Devnarayan House	23°55'27.3"	082°54'54.1"	401	7.2	435	2.35	BDL
8	MHHP-4	Sriraam Jal House-Jaliyatola	23°55'57.3"	082°53'40.9"	383	6.8	201	2.09	0.9
9	MHW-5	Anjani House	23°55'51.3"	082°53'34.4"	371	7.1	180	2.98	BDL
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

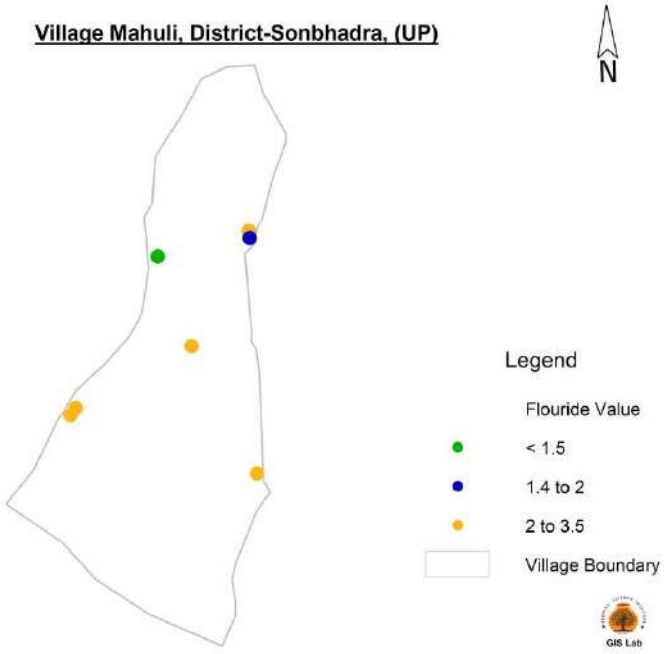
S.N	Composite sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	MH-1 HP	Mahuli	8.1	362	2.79	0.3	7
2	MH-2 W	Mahuli	7.6	262	2.83	BDL	3
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village- Mahuli

TDS



Flouride



Village:- Mahuli

- Total sample points:- 9
- Hand pump:- 4
- Well:- 5

HAND PUMP:-

- TDS range is within the limit (201ppm to 389ppm).
- All the HP sources have fluoride concentration more then the BIS limit(1.54 mg/l to 3.5mg/l).
- Only two HP have iron content (0.5mg/l and 0.9mg/l).

WELL:-

- Well shows variation in TDS between (180ppm to 476ppm).
- Except Jhamman's well(1.36mg/l), all the other well show high fluoride content upto 2.98mg/l.
- Iron is absent in all the well.

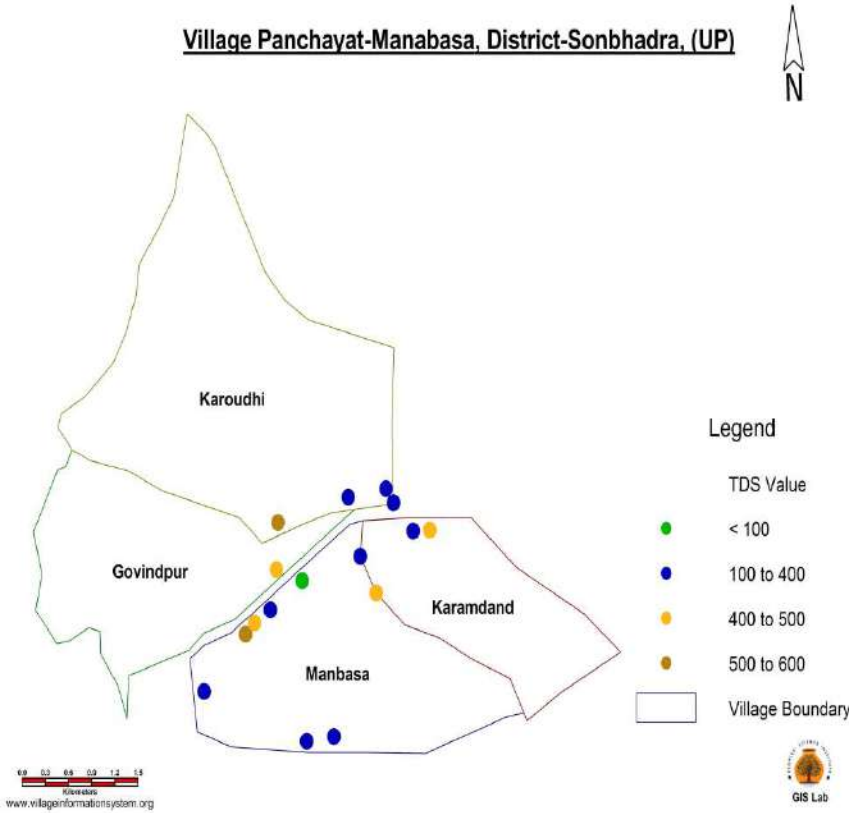
Village- Manabasa

S.N	Sample	Location	GPS POINT		Elevation (m)	Parameters			
			Longitude	Latitude		pH	TDS (ppm)	F (mg/ l)	Fe (mg /l)
1	HP (27)	Market-kodu Raam	24°10'.390"	083°07'.319"	288	6.9	510	2.19	1.5
2	HP (28)	Jiyaul Rehman	24°10'.229"	083°07'.616"	283	7.4	285	2.32	0.1
3	HP (29)	Rajaram House	24°10'.230"	083°07'.785"	274	7.5	301	4	0.6
4	WELL (30)	Maheep				8	322	3.51	
5	HP (31)	Hotilaal	24°10'.167"	083°08'.374"	287	7.1	375	1.46	0.4
6	WELL (32)	Motilaal S/0 Lallu	24°10'.137"	083°08'.480"	286	7.7	281	1.73	
7	HP (33)	Primary School	24°10'.227"	083°08'.530"	284	7.5	285	1.38	BDL
8	HP (34)	Sudama Maurya	24°10'355"	083°08'350"	276	7	380	1.22	0.2
9	WELL (35)	Raam Singh	24°10'.338"	083°08'.408"	275	7.8	443	5.3	0.3
10	HP (36)	Sohan House	24°10'.234"	083°07'.319"	288	7.6	406	3.24	0.2
11	HP (37)	Raghu House	24°09'.927"	083°07'.819"	286	7.4	441	3.47	BDL
12	HP (38)	Primary School	24°09'.650"	083°07'.704"	292	7.4	375	3.68	BDL
13	HP (39)	Harikrishnan Kewat	24°09'.456"	083°07'.342"	304	8.2	325	3.28	BDL
14	TW (40)	Ro-filter Plant	24°09'.963"	083°07'.401"	302	8.1	85	0.95	BDL
15	HP (41)	Jivanshal-manbasa=ashram School	24°09'979"	083°07'.298"	296	7.5	336	5.59	
16	HP (42)	Laalchand	24°09'.794"	083°07'.135"	294	7.4	449	1.87	0.5
17	HP (43)	Raamavatar	24°09'.950"	083°06'.982"	306	7.5	519	5.07	0.1
18	HP (44)	Vijaypal Houses	24°09'.646"	083°06'.687"	313	7.5	367	2.57	BDL
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

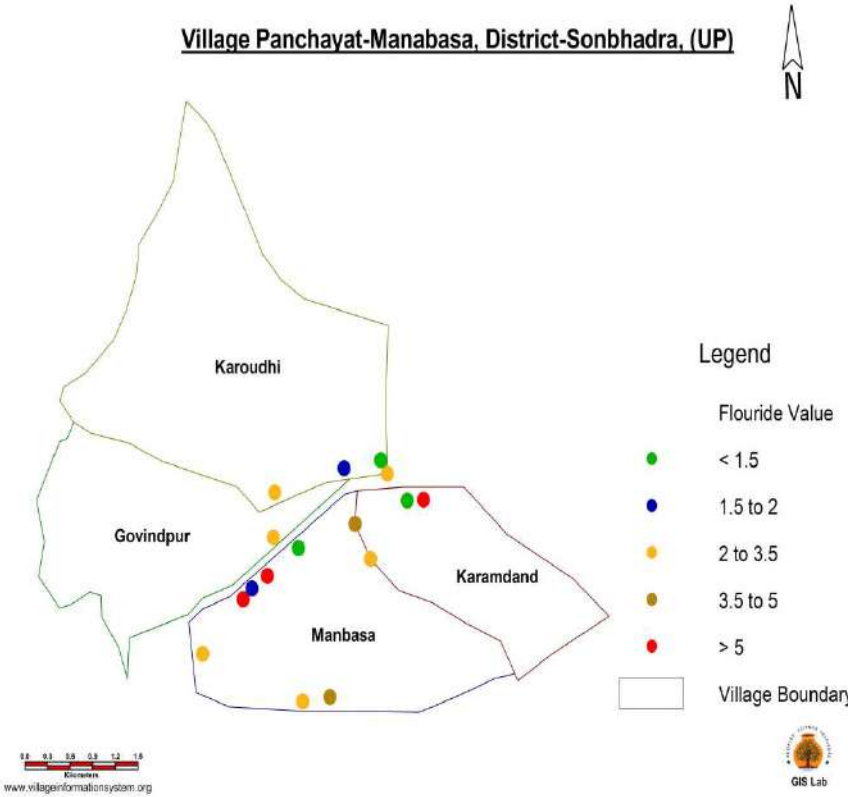
S.N	Composite sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	MSH-1 HP	Manbasa	7.7	396	2.74	1	8
2	MSH-2 W	Manbasa	8	366	3.84	BDL	28
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village- Manabasa

TDS



Flouride



Village- Manabasa

- Sample points:- 18
- Hand pump:- 14
- Well:- 3
- Tube well:- 1

HAND PUMP:-

- Only two sources have TDS Higher then the limit. Highest TDS 519ppm(Ram Vatar) and lowest TDS is 285ppm.
- Out of 14 HP, only 3 HP have less Fluoride content. Highest Fluoride seen was 5.59mg/l in Jivanshal near Ashram School.
- 4 HP sources have high iron. Highest Iron measured was 1.5mg/l.

WELL:-

- Except fluoride(1.7mg/l to 5.3mg/l), TDS and Iron were withi the limit.

TUBE WELL:-

- TDS, Fluoride and Iron all were within the limit.

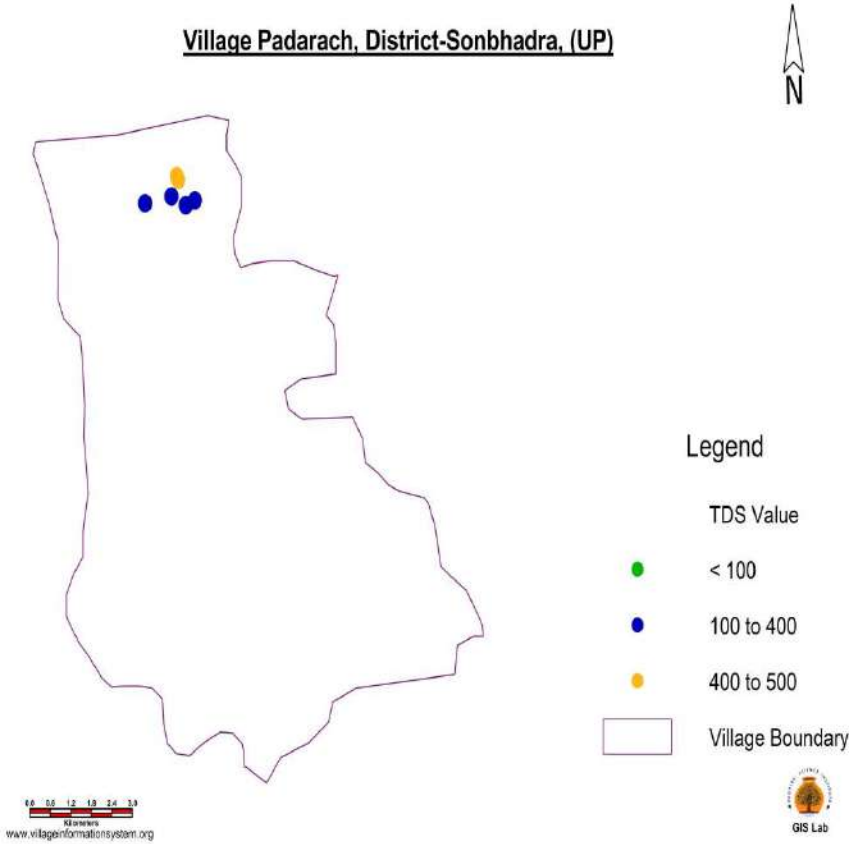
Village- Nai Basti

S.N	Sample	Location	GPS POINT		Elevation (m)	Parameters			
			Longitude	Latitude		pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	JRDHP-1	Raamgovind House	24°26'56.8"	083°10'32.2"	183	7.2	353	4.38	BDL
2	NBHP-1	Krishnapatel House	24°27'01.6"	083°11'0.4"	185	7.2	283	7.35	BDL
3	NBHP-2	Vindhyachal House	24°27'16.4"	083°11'05.8"	174	7.1	453	4.29	0.3
4	NBHP-3	Shiv Temple	24°27'13.3"	083°11'07.3"	176	7.4	427	11.7	BDL
5	NBHP-4	Dakshinanchal Maa Sharda Inter College	24°26'54.3"	083°11'15.5"	198	7.8	296	4.3	0.3
6	NBHP-5	Vijay K. Sharma	24°26'58.0"	083°11'24.8"	183	7.1	229	4.26	BDL
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

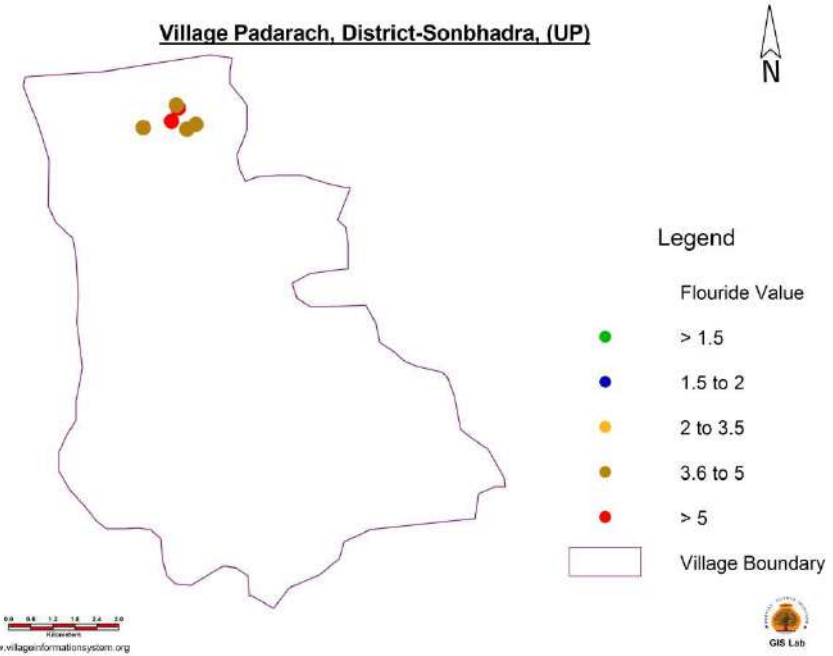
S.N	Composite Sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	NB-1 HP	Nai Basti	7.7	392.0	6.17	12	15
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village- Nai Basti

TDS



Flouride



Village:- Nai Basti

Sample points:- 6 (Hand pump)

- TDS value is within the limit(229 ppm(Vijay K sharma) to 453ppm(Vindhyachal)).
- Iron value is within within the limit.
- Variation in Fluoride was seen 4.26 mg/l to 11.7mg/l.

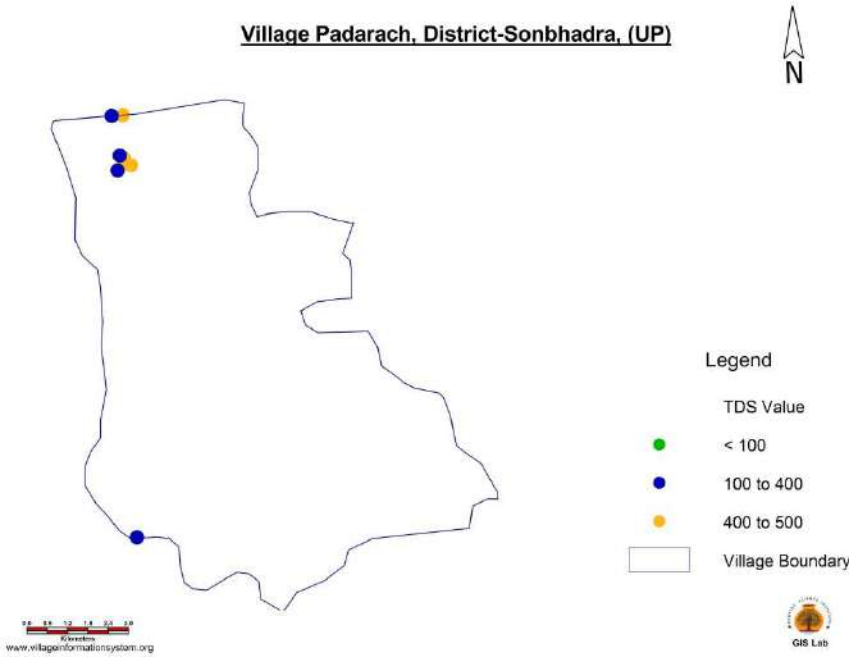
Village-Piprawaha

S. N	Sample	Location	GPS POINT		Elevation (m)	Parameters			
			Longitude	Latitude		pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	PPRHP-1	Rameshwar Prasad House	24°26'54.7"	083°09'44.3"	176	7.5	328	6.16	
2	PPRW-1	Babulaal House	24°27'06.7"	083°09'50.9"	175	7.4	439	6.18	BDL
3	PPRHP-2	Brijmohan House	24°27'08.7"	083°09'46.9"	171	7.3	271	2.84	BDL
4	PPRW-2	Jawahar House	24°27'15.0"	083°09'41.0"	170	7.4	352	4	BDL
5	PPRHP-3	Near Primary School/Munnilal House	24°27'70.7"	083°09'37.9"	178	7.2	358	3.53	BDL
6	PPRHP (A)4	Tulasidas House(Before Filter)	24°26'59.2"	083°09'58.8"	187	7	488	3.18	BDL
	PPRHP (B)-4	Tulasidas House(After Filter)	24°26'59.2"	083°09'58.8"	187	7	464	0.44	BDL
7	PPRW-3	Kamla House	24°21'14.3"	083°10'0.4"	174	7.7	334	1.58	BDL
8	PPRHP-5	Loknath House	24°27'17.6"	083°09'57.1"	173	7.3	436	3.11	BDL
9	PPRBW-1	Rameshwar Prasad House	24°26'55.3"	083°09'44.9"	176	7.8	415	6.39	BDL
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

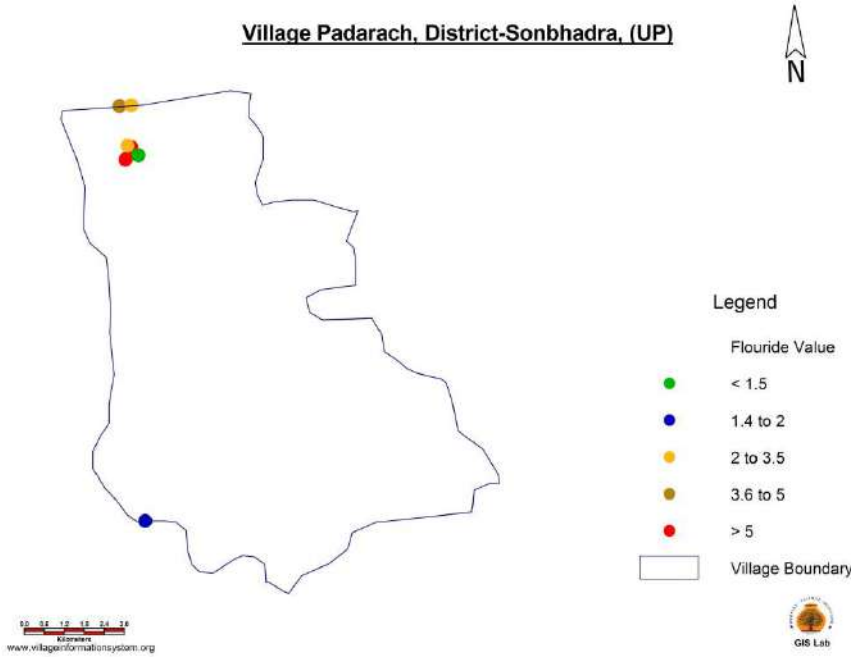
S.N	Composite sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	PPR-1 HP	Piprahawan	8.5	526	1.885	5	14
2	PPR-2 W	Piprahawan	8	433	4.23	1	13
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village-Piprawaha

TDS



Flouride



Village-Piprawaha

- Total Sample points:- 9

  Well:- 4

  Hand pump:- 5

WELL:-

- TDS value ranges from 334ppm (Kamla) to 439ppm (Babulal).
- Fluoride concentration is from 1.58mg/l to 6.39mg/l(Ramesh war).
- Iron is not present in the well sources.

HAND PUMP:-

- TDS value ranges from 271 ppm(Brij Mohan) to 488 ppm (Tula sidar).
- No iron content but high Fluoride concentration was seen in all the HP samples ranging from 1.58 mg/l to 6.39mg/l.

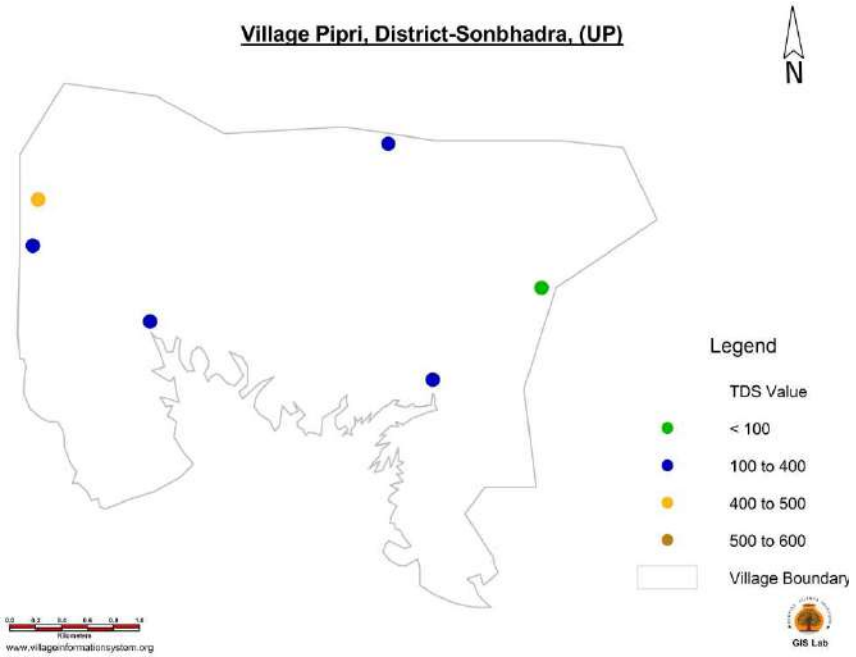
Village- Pipari

S.N	Sample	Location	GPS POINT		Elevation (m)	Parameters			
			Longitude	Latitude		pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	TW(92)	Ro-Mayaram House(After Filter)	24°12'.084"	082°51'.855"	293	7.5	68	2.56	0.2
2	TW(93)	Ro-Mayaram House(Before Filter)	24°12'.084"	082°51'.855"		7.5	262	1.82	
3	HP(94)	Brahmnarayan Singh	24°12'.037"	082°51'.611"	291	7.2	262	2.86	
4	HP(95)	Mandhari House	24°12'.002"	082°51'.122"	276	7.3	361	1.37	
5	HP(96)	Pradhan House	24°12'.309"	082°50'.511"	282	7.4	345	3.86	
6	HP(97)	High Primary School	24°12'.210"	082°49'.975"	283	7.4	342	1.58	
7	HP(98)	Arjun	24°12'.321"	082°49'.823"	300	6.8	213	4.12	
8	RO(99)	Ro Plant-Tw	24°12'.357"	082°49'.300"	277	7.4	115	4.8	
9	HP(100)	Babuli-Raasamen	24°12'.215"	082°49'.578"	276	7.5	395	4.12	
10	WELL (101)	Rajkumar	24°12'.483"	082°49'.418"	282	7.4	467	1.96	
11	HP(102)	Mahadev	24°12'.518"	082°49'.346"	282	7	537	2.18	
12	WELL (103)	Mahavir	24°12'.494"	082°49'.342"	281	7.5	464	1.59	
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

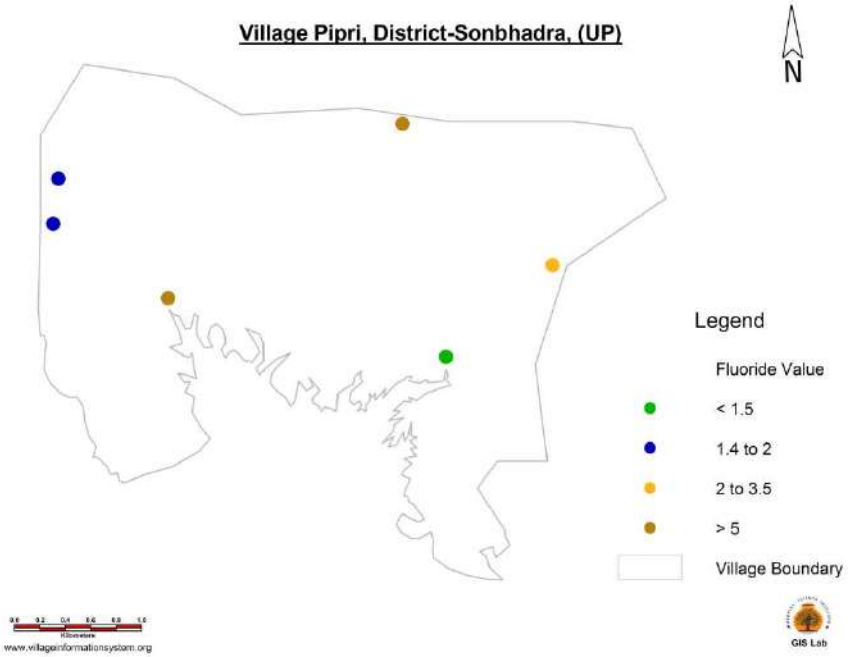
S.N	Composite Sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	PS-1 HP	Pipari	7.2	348	2.81	1	18
2	PS-2 W	Pipari	7.6	543	3.92	1	26
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village-Pipari

TDS



Flouride



Village- Pipari

- Sample points:-12

Tube well:- 2

Hand Pump:- 7

Well:- 2

RO:-1

TUBE WELL:-

- TDS of both the sources is within the limit(68ppm to 262ppm).
- No iron but fluoride was found (1.82mg/l to 2.56mg/l).

HAND PUMP:-

- Between 115ppm to 537 ppm, TDS was seen.
- Except Mandhari (1.37mg/l),all the other sources have high flouride content(4.12mg/l).
- No iron concentration was found.

WELL:-

- High flouride (1.96mg/l) but low TDS(467ppm) was found.

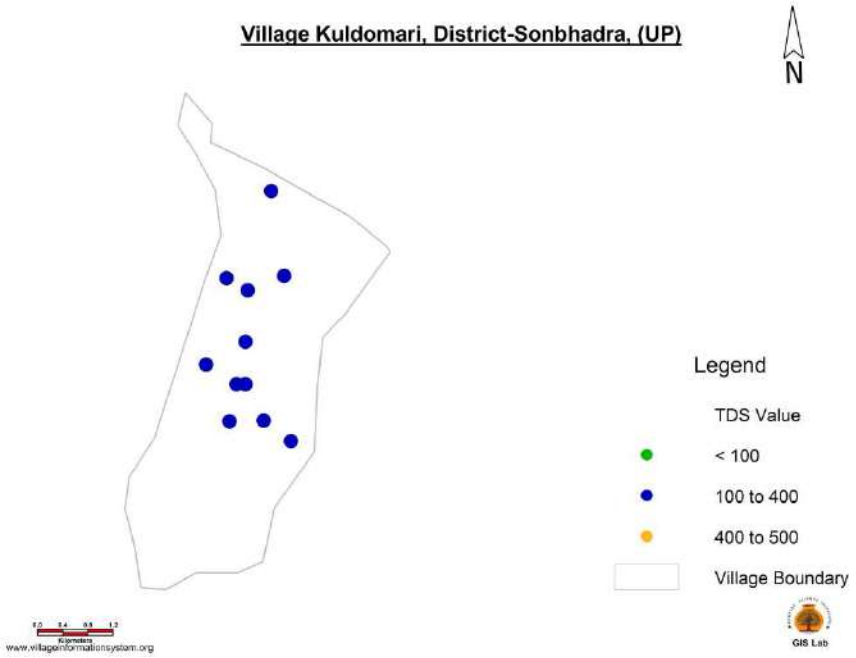
Village-Randhore

S.N	Sample	LOCATION	GPS POINT		Elevation (m)	pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
			Longitude	Latitude					
1	HP(124)	Basudev Tiwari	24°16'.029"	082°46'.553"	342	6.7	130	0.779	3.7
2	HP(125)	Vishwakarma	24°16'.487"	082°46'.623"	343	6.7	171	0.759	BDL
3	HP(126)	Devlal Kol	24°16'.350"	082°46'.709"	343	6.7	185	0.566	0.7
4	HP(127)	Budhi Temple	24°16'.350"	082°46'.709"	343	7.3	339	1.22	7.7
5	WELL (128)	Dayaram Well	24°16'.032"	082°46'.876"	341	7.5	250	1.18	
6	HP(129)	Ramlallu Baiga	24°15'.849"	082°47'.132"	354	7.3	307	0.96	0.3
7	WELL (130)	Ajay Kumar	24°16'.533"	082°46'.337"	344	7.9	262	0.792	0.2
8	HP(131)	Dasrath Kharwar	24°16'.533"	082°46'.337"		7.1	153	0.805	0.2
9	HP(132)	Ramji-Near School	24°16'.724"	082°46'.723"	339	7.1	200	0.585	BDL
10	HP(133)	Mirch-Kole House	24°17'.176"	082°46'.754"	340	7.6	260	0.596	BDL
11	WELL (134)	Rambhog Well	24°17'.286"	082°46'.554"	325	7.7	371	0.757	5.2
12	HP(135)	Kapil Dev House	24°17'.294"	082°47'.104"	325	7.4	248	0.419	2.8
13	HP(136)	Highr Secondary School	24°18'.035"	082°46'.994"	338	7.4	193	0.435	0.4
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

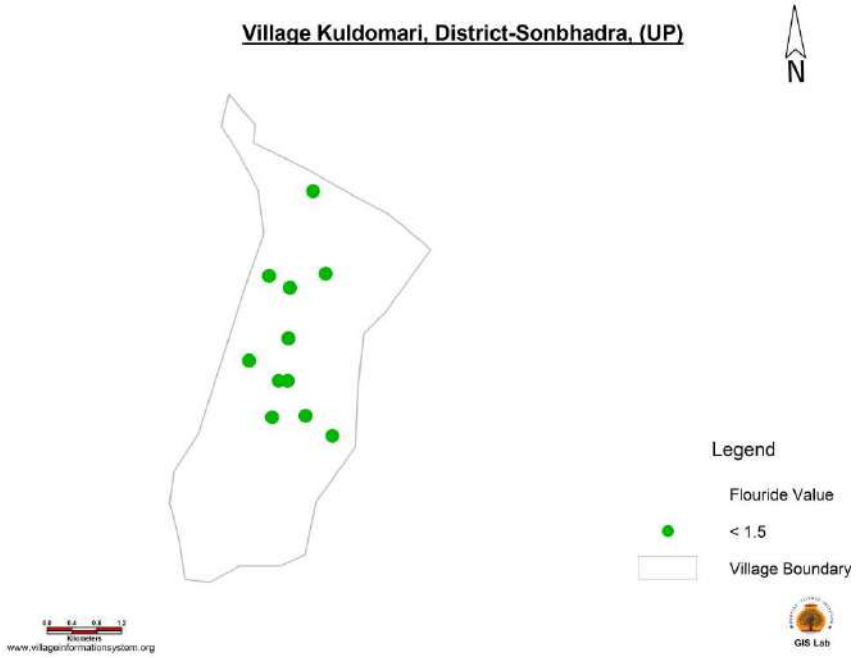
S.N	Composite Sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	RD-1 HP	Radhore	7.5	255	0.749	0.8	11
2	RD-2 W	Radhore	7.9	319	0.492	0.9	15
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village-Randhore

TDS



Flouride



Village:- Randhore

- Sample points:- 13
- Hand pump:- 10
- Well:- 3

HAND PUMP:-

- TDS ranges from 130ppm(Basudev) to 339ppm(Budhi temple).
- No or very less fluoride concentration.
- 7.7 mg/l (budhi temple) iron conc. Was seen.

WELL:-

- TDS ranges from 250ppm(Daya ram) to 371ppm(Ram bhog).
- Less fluoride and but high iron concentration was seen .
- Iron found upto 5.2mg/l(Ram bhog).

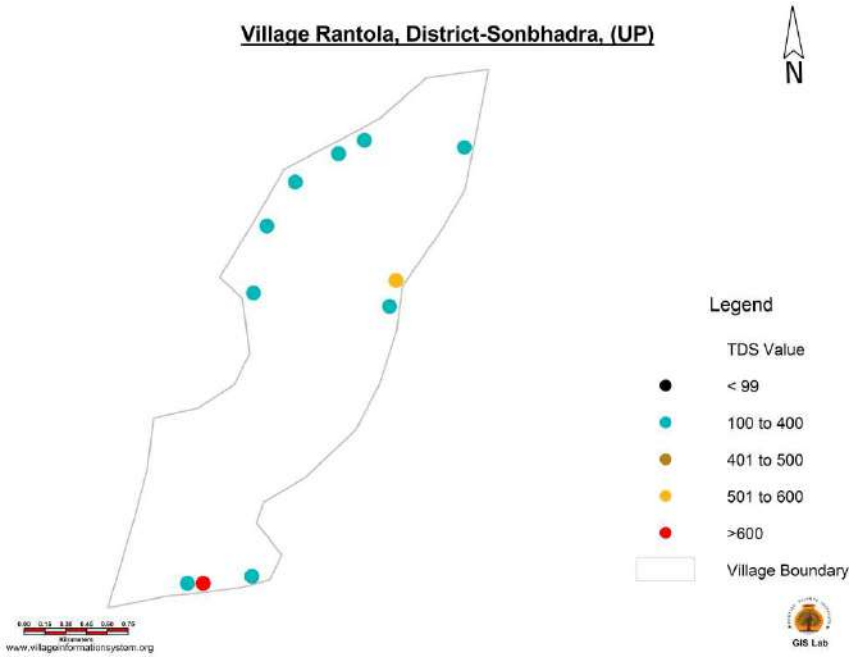
Village-Rantola

S.N	Sample	Location	GPS POINT		Elevation (m)	Parameters			
			LONGITUDE	LATITUDE		pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	HP	Ashram Mod	24°10'48.5"	083°05'19.8"	344	6.7	800	1.16	0.3
2	WELL	Under Rantola Gate	24°10'48.2"	083°05'17.8"	333	DRY			
3	HP	Near The Well	24°10'48.6"	083°05'17.1"	336	7	716	1.45	0.1
4	HP	In School(Middle)	24°12'23.3"	083°06'00.2"	320	6.3	317	1.26	BDL
5	HP	Near Pond	24°12'21.2"	083°06'02.6"	317	6..8	225	2.26	0.3
6	WELL	Near Bifal House	24°12'33.6"	083°06'05.6"	316	6.6	182	1.11	BDL
7	TW	Babulaal	24°12'36.1"	083°06'22.8"	316	6.9	212	1.28	BDL
8	HP	Near Raamsundar House	24°12'37.3"	083°06'24.5"	321	6.5	281	1.56	1.3
9	WELL	Heeralaal House	24°12'26.2"	083°05'57.1"	315	6.9	221	1.25	BDL
10	Tw(filter Plant)	Katauli Tiraha	24°12'27.8"	083°05'40.2"	329	6.4	206	0.902	BDL
11	HP	Near Sunil House	24°12'14.8"	083°05'35.3"	311	6.7	280	1.5	BDL
12	HP	Near Shri Goving House	24°12'06.0"	083°05'36.1"	295	7.2	367	1.31	BDL
13	HP	Near Lakshandhari House	24°12'05.1"	083°05'58.2"	315	7	531	1.39	BDL
14	HP	Near Chhannuraam House	24°11'58.4"	083°05'56.2"	319	6.7	251	0.962	0.2
15	HP+TW	In Pradhan House	24°10'49.6"	083°305'15.9"	317	7.1	397	2.52	0.4
16	HP	Myorpur-Manrahvan Tola	24°10'56.4"	083°04'50.0"	325	7	395	1.1	0.2
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

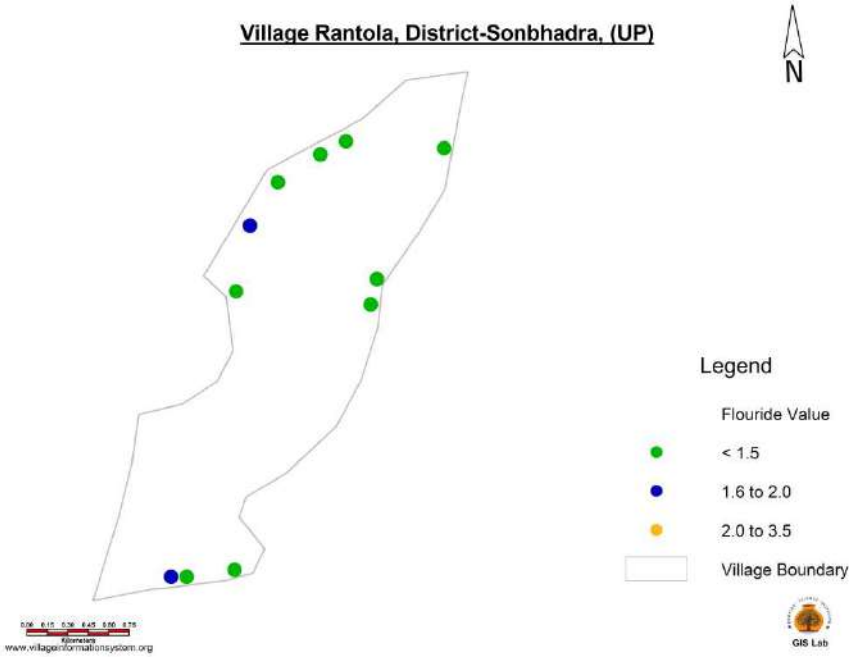
S.N	Composite sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	RT-1 HP	Rantola	7.6	719	1.75	1.3	15
2	RT-2 WELL	Rantola	7.6	302	1.62	1.4	7
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village- Rantola

TDS



Flouride



Village - Rantola

- Sample points:- 16
- Well:- 3
- Hand pump:- 11
- Tube well: 2

WELL:-

- Variation is TDS is Seen between 182 to 221 ppm.
- Flouride and Iron were within the limit

HAND PUMP:-

- In 3 HP, high TDS was seen(highest seen is 800ppm Ashram Mod) and others show TDS less the the limit.
- 7 hand pump has fluoride less then the lim9t but other four has flouride more then the ,limit upto 2.52mg/l.
- In two HP, iron was more then the limit. Highest Iron content was 1.3mg/l in Ram under House).

TUBE WELL:-

- All were within the limit.

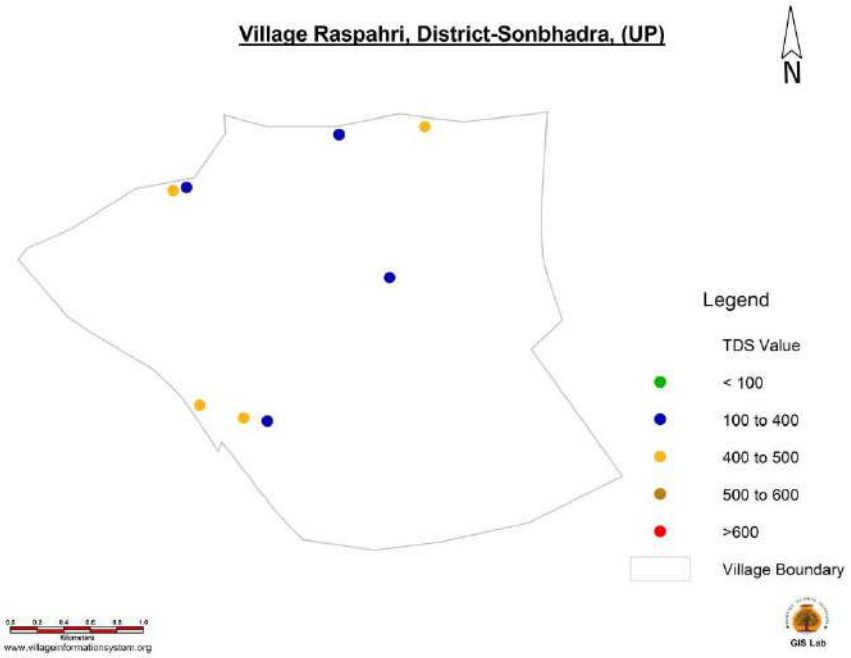
Village-Rashphari

S.N	Sample	Location	GPS POINT		Elevation (m)	Parameters			
			Longitude	Latitude		pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	RSP-HP1	Bodhan's House	24°09'36.3"	083°03'19.7"	330	6.7	445	1.71	BDL
2	RSP-W1	Arjun Singh	24°09'39.5"	083°03'21.04"	328	7.4	396	3.15	0.2
3	RSP-HP2	Jansor Khadhan Tola	24°09'01.4"	083°03'25.4"	352	7.1	402	2.81	BDL
4	RSP-W2		24°09'02.1"	083°03'31.8"	343	7.2	442	1.52	BDL
5	RSP-HP3	Panchayat Bhawan	24°09'13.3"	083°03'49.6"	338	7.4	395	5.77	0.1
6	RSP-W3(KOCHA)	Rajman's House	24°09'15.9"	083°03'48.0"	335	7.6	421	1.83	BDL
7	RSP-HP4	Near Shivdas House	24°09'35.4"	083°04'06.5"	339	7.5	364	1.87	0.4
8	RSP-HP5	Harishankar Mishra	24°09'28.1"	083°04'13.8"	339	6.9	324	1.85	BDL
9	RSP-HP6	Budhai House	24°09'46.1"	083°04'26.1"	316	6.8	483	1.08	BDL
10	RSP-HP7	Ramkishore House	24°09'50.5"	083°04'01.5"	328	7	778	1.47	BDL
11	RSP-W4	Shiv Prasad	24°09'50.3"	083°03'58.5"	320	7.3	664	1.7	BDL
12	RSP-HP8		24°09'58.9"	083°04'14.9"	313	6.9	477	1.37	0.2
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

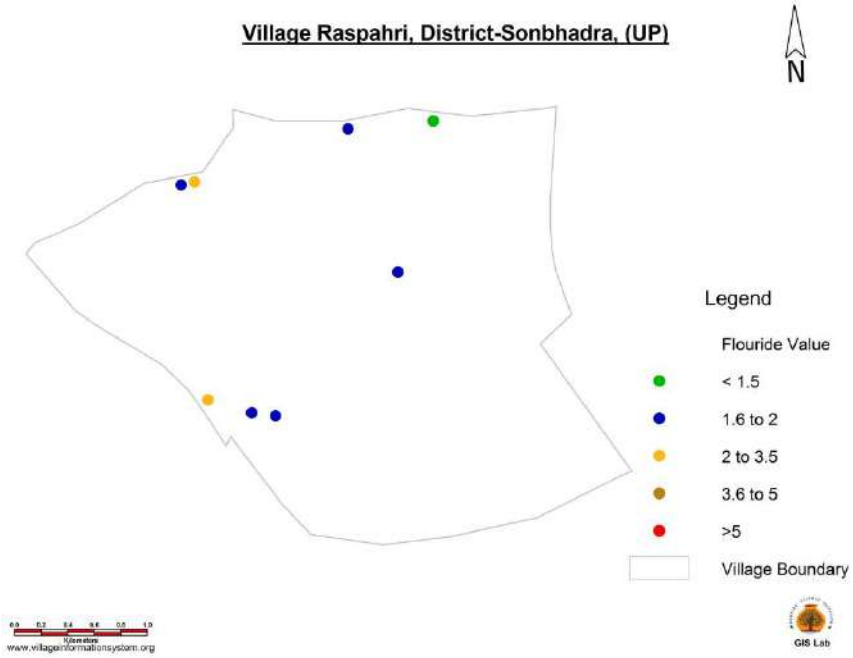
S.N	Composite sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	RP-1 HP	Raspahari	7.7	532	2.56	4.5	16
2	RP-2 W	Raspahari	7.4	500	1.96	0.9	13
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village- Raspahari

TDS



Flouride



Village- Rashphari

- Sample points:- 12

Hand pump:- 8

Well:- 4

HAND PUMP:-

- Variation in TDS was seen between 324ppm to 778 ppm (Ram kishore).
- Fluoride in 3 sources were within limit but other sources have high Fluoride up to 5.77mg/l .
- No iron content is seen.

WELL:-

- TDS value is from 396 ppm to 664ppm(Shiv prasad).
- All the well water have high fluoride ranging from 1.52 mg/l to 3.15 mg/l(Arjun).
- Iron is not present.

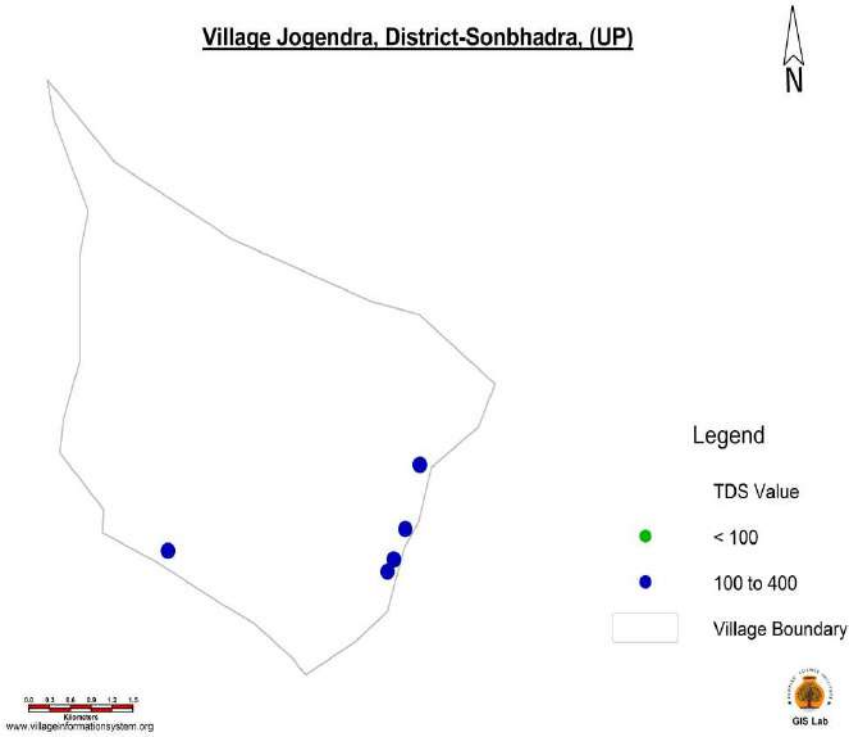
Village-Jogendra

S.N	Sample	Location	GPS POINT		Elevation (m)	Parameters			
			Longitude	Latitude		pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	HP(137)	Gagan Yadav	24°18'.253"	082°46'.984"	339	7.2	178	0.409	0.2
2	HP(138)	Primary School				7	180	0.33	0.5
3	WELL(139)	Rajwanti Bahan Well	24°18'.838"	082°49'.357"	315	7.6	313	0.428	BDL
4	WELL(140)	Hardev House	24°18'.856"	082°49'.239"	321	8.3	231	0.744	1.6
5	HP(141)	Parsari Tola				7.5	342	1.06	5.2
6	HP(142)	High School	24°18'.581"	082°48'.919"	338	7.3	332	0.715	0.2
7	WELL(143)	Darbari	24°18'.196"	082°48'.559"	325	7.5	393	0.814	0.2
8	HP(144)	Raamjiyavan	24°18'.262"	082°48'.717"	339	7.3	328	0.751	BDL
9	HP(145)	Forest Chauki				7.4	286	0.892	0.7
BIS:10500						**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

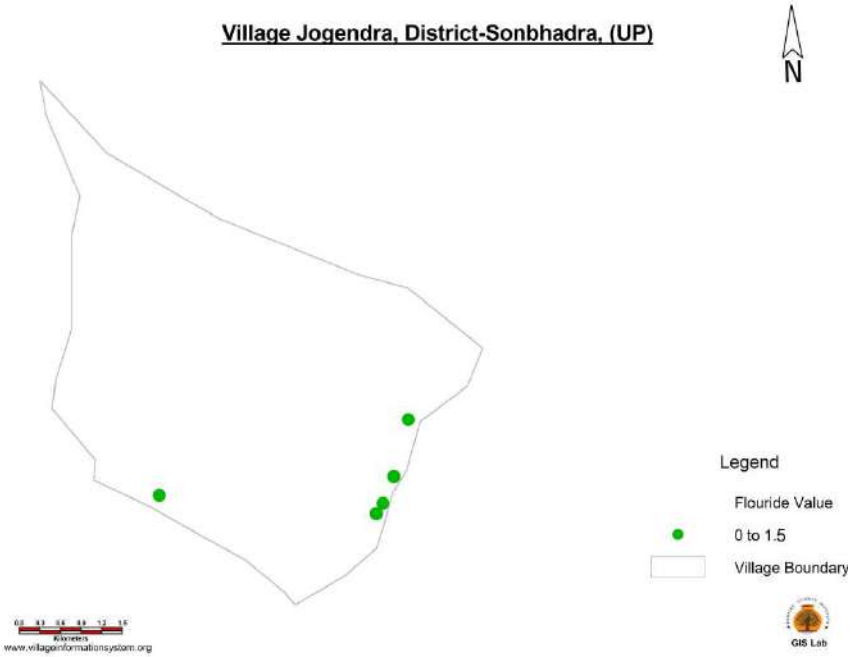
S.N	Composite sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	YOG-1 HP	Jogendra	7.7	289	0.574	1.8	13
2	YOG-2 W	Jogendra	8	349	0.499	0.8	14
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village-Jogendra

TDS



Flouride



Village-Jogendra

- Sample:- 9

Hand pump:- 6

Well:- 3

WELL:-

- TDS was from 231ppm to 393 ppm(Darbari).
- Fluoride is less then the limit.
- Iron is 0 to 1.6mg/l.

HAND PUMP:-

- TDS was within the limit from 180ppm to 342 ppm.
- Fluoride is also within the limit.
- Iron value ranging from 0 to 5.2mg/l.

Village- Ahirbudwa

S.N	Sample	Location	GPS POINT		Parameters			
			Longitude	Latitude	pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	ABHP-1	Dhanushdhari House			6.8	358	2.03	BDL
2	ABHP-2	Raamdhani Chairo			7.3	381	2.81	BDL
3	ABHP-3	Baijnath House			7.2	448	1.7	BDL
4	ABHP-4	Near School			7.3	403	1.13	BDL
5	ABHP-5	Suresh's House	24°01'26.8"	083°16'03.2"	7.4	417	1.59	BDL
6	ABHP-6	Hanslaal House			7.2	457	2.5	BDL
7	ABW-1	Sugriv House			7.4	309	1.94	BDL
8	ABHP-7	Manrutola School			7.4	345	2.96	0.2
9	ABW-2	Chandrakesh House			7.7	359	2	BDL
10	ABW-3	Raampati Dharkar			7.1	342	2.35	BDL
11	ABHP-8	Raampratap Bharti House			7.3	344	2.54	0.9
BIS:10500					**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

S.N	Composite Sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	AB-1 HP	Ahirbudva	8.3	549	2.29	40	2
2	AB-2 W	Ahirbudva	8.5	322	2.79	0.2	BDL
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village- Ahirbudwa

- Sample points:- 11

Hand pump:- 8

Well:- 3

HAND PUMP:-

- TDS is measured between 344ppm to 457ppm.
- Fluoride, in all except one(1.13mg/l in near school), is higher then the permissible limit up to 2.96mg/l(Manrutola school).
- Iron found up to 0.9mg/l.

WELL:-

- TDS is measured between 309ppm to 359ppm.
- No iron was found .
- Fluoride was higher then the limit from 1.94mg/l to 2.35mg/l.

Village- Deohar Purab

S.N	Sample	Location	pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	DPHP-1	Near Primary School	7.4	364	2.11	0.6
2	DPW-1	Raamlaxman Agri Field	10.7	208	1.82	BDL
3	DPHP-2	Sheshpal Home	7.5	472	2.31	0.1
4	DPW-2	Raajbali Agri Field	7.5	774	1.68	BDL
5	DPW-3	Raghuvir Agri Field	7.5	397	2.02	BDL
6	DPHP-3	Ghanshyam Home	7.6	404	3.15	BDL
7	DPW-4	Kamsha Agri Field	7.7	587	3.45	BDL
8	DPHP-4	Muneshwar House	7.2	463	2.59	BDL
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

S.N	Composite sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	DP-1 HP	Deohar Purab	7.9	435	3.19	ND	13
2	DP-2 W	Deohar Purab	8.3	483	2.9	0.8	5
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village- Deohar Purab

- Total sample:- 8

Hand pump:- 4

Well:- 4

HAND PUMP:-

- TDS is within the limit from 4.4ppm to 472ppm.
- Fluoride is higher then the permissible limit(2.11mg/l to 3.15mg/l).

WELL:-

- Variation in TDS was seen from 208ppm to 774ppm.
- Fluoride was higher then the limit(1.68mg/l to 3.45mg/l).

Village- Pharipan

S.N	Sample	Location	pH	TDS (ppm)	F (mg/l)	Fe (mg/l)
1	PPW-1	Ramchandra House	7.6	582	1.55	BDL
2	PPHP-1	Raamchandra House	7.2	583	1.9	0.1
3	PPHP-2	Raamprasad House	7.4	491	1.125	BDL
4	PPW-2	Raamkhelawan House	8.3	411	3.1	BDL
5	PPW-3	Haricharan House	7.4	464	1.85	BDL
6	PPHP-3	Raamprasad House	7	425	1.52	BDL
7	PPW-4	Bhagwan Daas	7.5	715	1.52	BDL
8	PPHP-4	Shyamsundar House	7.2	587	1.36	0.1
9	PPW-5	Sitaram House	7.7	514	1.57	BDL
10	PPHP-5	Sitaram House	7.3	537	1.59	0.2
11	PPHP-6	Jagatji House	7.4	338	1.13	BDL
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**0.3 mg/l**

S.N	Composite Sample	Village	pH	TDS (ppm)	F (mg/l)	Hg (µg/l)	As (µg/l)
1	PP-1 HP	Pharipan	8.4	716	1.5	3	11
2	PP-2 W	Pharipan	8.5	526	1.85	1	13
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

Village- Pharipan

- Sample points:- 11

Hand pump:- 6

Well:- 5

HAND PUMP:-

- In 3 sources High TDS was seen (highest 587mg/l). Lowest TDS seen was 425ppm.
- In 3 sources, fluoride conc. was less then the permissible limit but in 3 sources, fluoride was high up to 1.9mg/l.

WELL:-

- In 3 sources, TDS was higher then the limit. Highest was 715ppm(Bhagwan das).
- Fluoride conc. Was high from 1.52mg/l to 3.1mg/l.

Iron is less then the permissible limit in all the sources.

District level Study

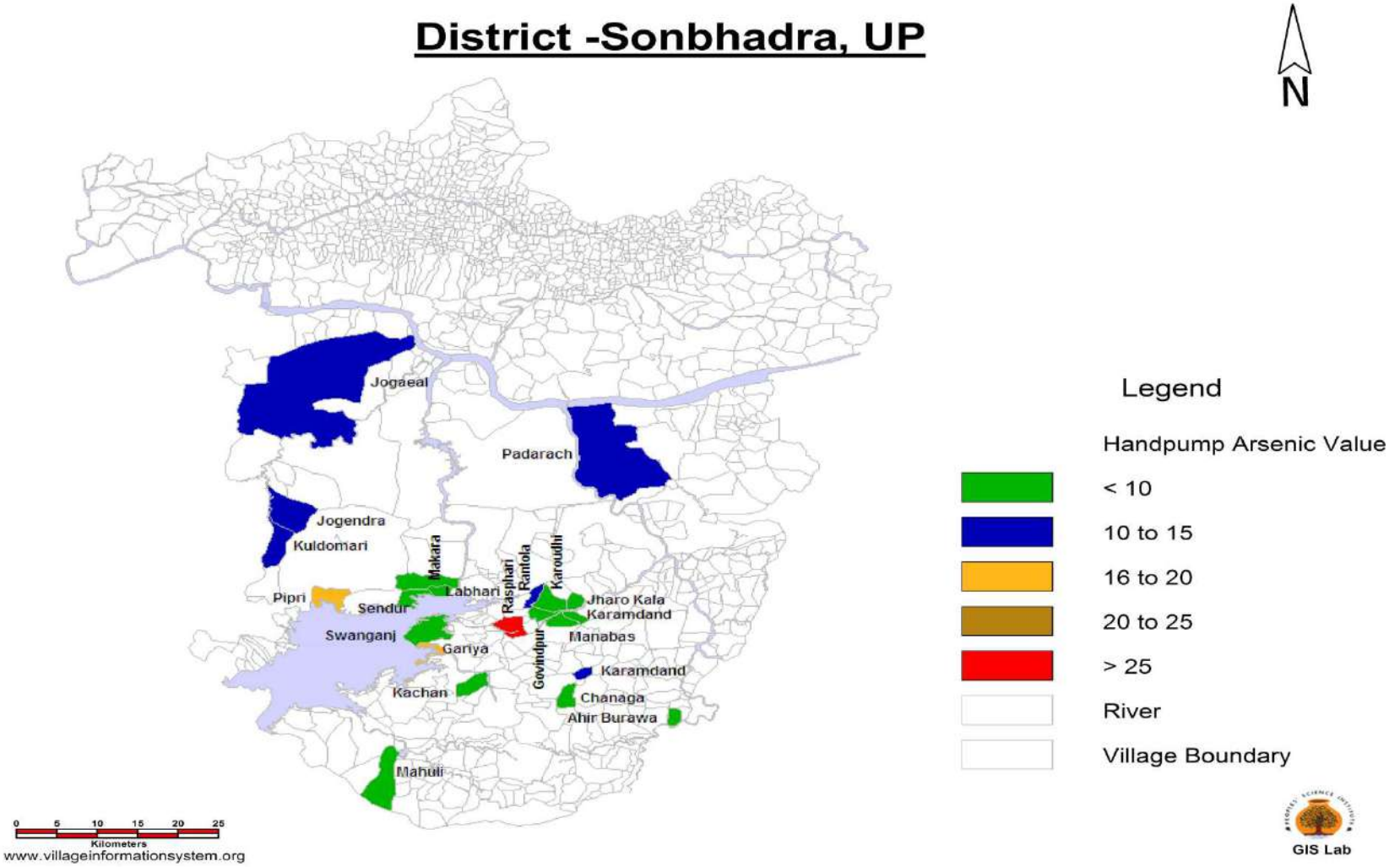
Composite Samples

S.NO	COMPOSITE SAMPLES	VILLAGE	pH	TDS	Fluoride(mg/l)	Mercury(µg/l)	Arsenic(µg/l)
1	RT-1 HP	RANTOLA	7.6	719	1.75	1.3	15
2	RT-2 WELL	RANTOLA	7.6	302	1.62	1.4	7
3	RP-1 HP	RASPAHARI	7.7	532	2.56	4.5	16
4	RP-2 W	RASPAHARI	7.4	500	1.96	0.9	13
5	GD-1 HP	GADIYA	7.4	383	3.9	0.5	18
6	GD-2 W	GADIYA	8.4	405	4.53	1	3
7	BD-1 HP	BARAIDAD	7.6	455	5.62	0.6	3
8	BD-2 W	BARAIDAD	7.9	461	4.36	0.5	7
9	PP-1 HP	PHARIPAN	8.4	716	1.5	3	11
10	PP-2 W	PHARIPAN	8.5	526	1.85	1	13
11	DP-1 HP	DEVHAR POORVI	7.9	435	3.19	ND	13
12	DP-2 W	DEVHAR POORVI	8.3	483	2.9	0.8	5
13	AB-1 HP	AHIRBUDVA	8.3	549	2.29	40	2
14	AB-2 W	AHIRBUDVA	8.5	322	2.79	0.2	ND
15	MH-1 HP	MAHULI	8.1	362	2.79	0.3	7
16	MH-2 W	MAHULI	7.6	262	2.83	ND	3
17	PPR-1 HP	PIPRAHAWA	8.5	526	1.885	5	14
18	PPR-2 W	PIPRAHAWA	8	433	4.23	1	13
19	NB-1 HP	NAI BASTI	7.7	392.0	6.17	12	15
20	JH-1 HP	JHAROKALA	7.9	471	2.68	ND	7
21	JH-2 W	JHAROKALA	8.2	407	1.43	ND	5
22	KHN-1 HP	KACHAN	7.8	274	1.38	0.7	8
23	KHN-2 W	KACHAN	7.6	134	1.03	ND	4
24	MSH-1 HP	MANBASA	7.7	396	2.74	1	8
25	MSH-2 W	MANBASA	8	366	3.84	ND	28
26	DK-1 HP	DEVKHAR	7.7	339	0.395	0.9	11
27	DK-2 W	DEVKHAR	7.7	243	0.598	7	9
28	JG-1 HP	JUGAIL	7.4	285	0.809	2	10
29	JG-2 W	JUGAIL	7.7	322	0.871	60	2
30	GH-1 HP	GADHA	6.9	325	1.54	0.9	6
31	GH-2 W	GADHA	7	731	1.31	2	6
32	PS-1 HP	PIPARI	7.2	348	2.81	1	18
33	PS-2 W	PIPARI	7.6	543	3.92	1	26
34	CG-1 HP	CHAGA	8	415	4.43	0.2	9
35	CG-2 W	CHAGA	8.3	441	3.07	1	15
36	LS-1 HP	LILASI	7.4	375	1.59	1	11
37	LS-2 R	LILASI	8.7	198	2.29	2	26
38	YOG-1 HP	YOGINDRA	7.7	289	0.574	1.8	13
39	YOG-2 W	YOGINDRA	8	349	0.499	0.8	14
40	RD-1 HP	RADHORE	7.5	255	0.749	0.8	11
41	RD-2 W	RADHORE	7.9	319	0.492	0.9	15
BIS:10500			**6.5-8.5**	**500 ppm**	**1.5 mg/l**	**1 µg/l**	**10 µg/l**

HP (Composite sample)

S.NO	COMPOSITE SAMPLES	VILLAGE	pH	TDS	Fluoride(mg/l)	Mercury(µg/l)	Arsenic(µg/l)
1	RT-1 HP	RANTOLA	7.6	719	1.75	1.3	15
2	RP-1 HP	RASPAHARI	7.7	532	2.56	4.5	16
3	GD-1 HP	GADIYA	7.4	383	3.9	0.5	18
4	BD-1 HP	BARAIDAD	7.6	455	5.62	0.6	3
5	PP-1 HP	PHARIPAN	8.4	716	1.5	3	11
6	DP-1 HP	DEVHAR POORVI	7.9	435	3.19	ND	13
7	AB-1 HP	AHIRBUDVA	8.3	549	2.29	40	2
8	MH-1 HP	MAHULI	8.1	362	2.79	0.3	7
9	PPR-1 HP	PIPRAHAWA	8.5	526	1.885	5	14
10	NB-1 HP	NAI BASTI	7.7	392.0	6.17	12	15
11	JH-1 HP	JHAROKALA	7.9	471	2.68	ND	7
12	KHN-1 HP	KACHAN	7.8	274	1.38	0.7	8
13	MSH-1 HP	MANBASA	7.7	396	2.74	1	8
14	DK-1 HP	DEVKHAR	7.7	339	0.395	0.9	11
15	JG-1 HP	JUGAIL	7.4	285	0.809	2	10
16	GH-1 HP	GADHA	6.9	325	1.54	0.9	6
17	PS-1 HP	PIPARI	7.2	348	2.81	1	18
18	CG-1 HP	CHAGA	8	415	4.43	0.2	9
19	LS-1 HP	LILASI	7.4	375	1.59	1	11
20	YOG-1 HP	YOGINDRA	7.7	289	0.574	1.8	13
21	RD-1 HP	RADHORE	7.5	255	0.749	0.8	11

Arsenic (Hand pump)

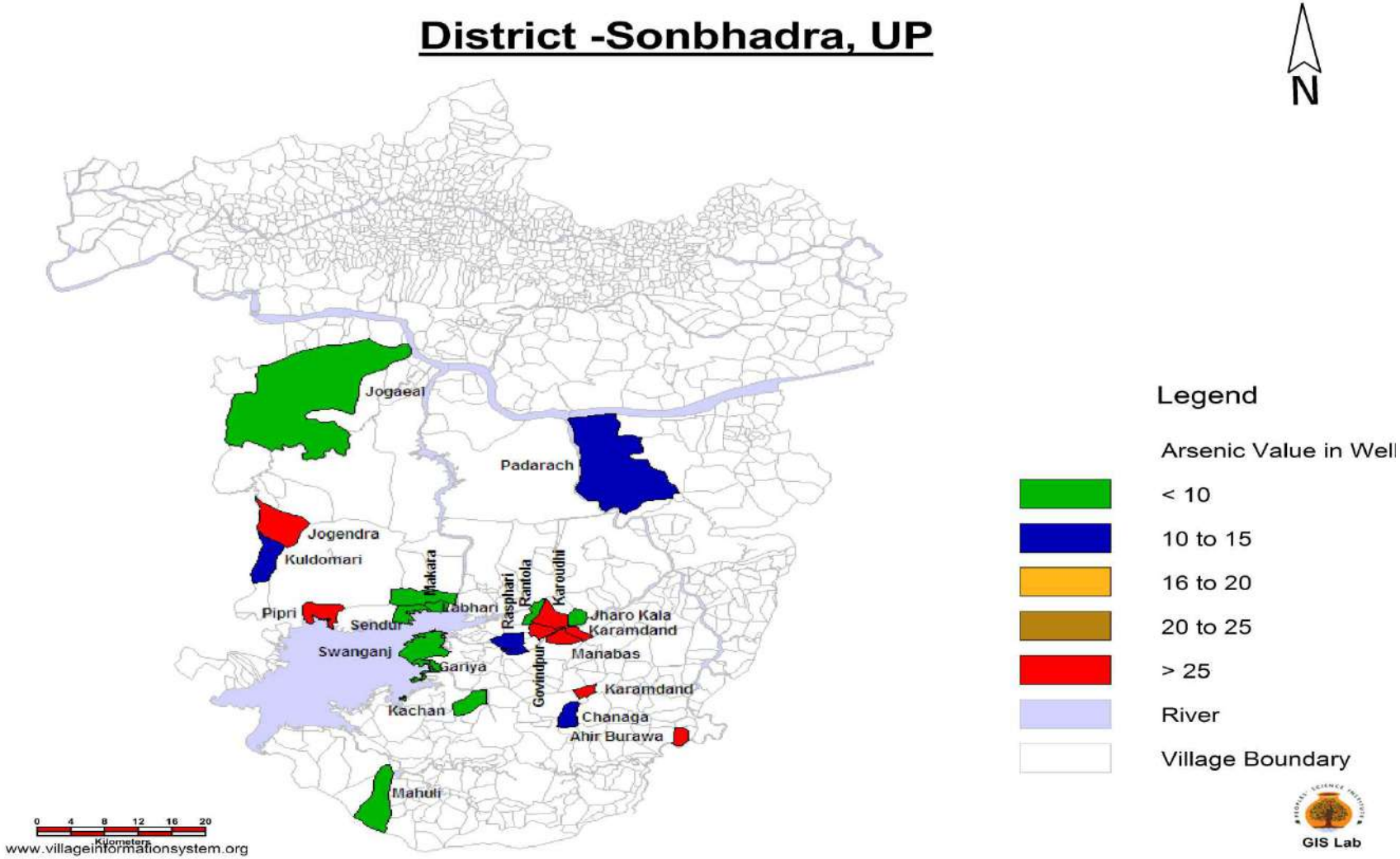


Arsenic in HP

- Baraidar, Ahribudwa, Mahuli, Jharo kala, Kachan, Manabasa, Gaya dah, Chanaga, Jogaeal show less arsenic content in HP.
- Highest is 18microgram/lit in Gariya.

Arsenic (Well)

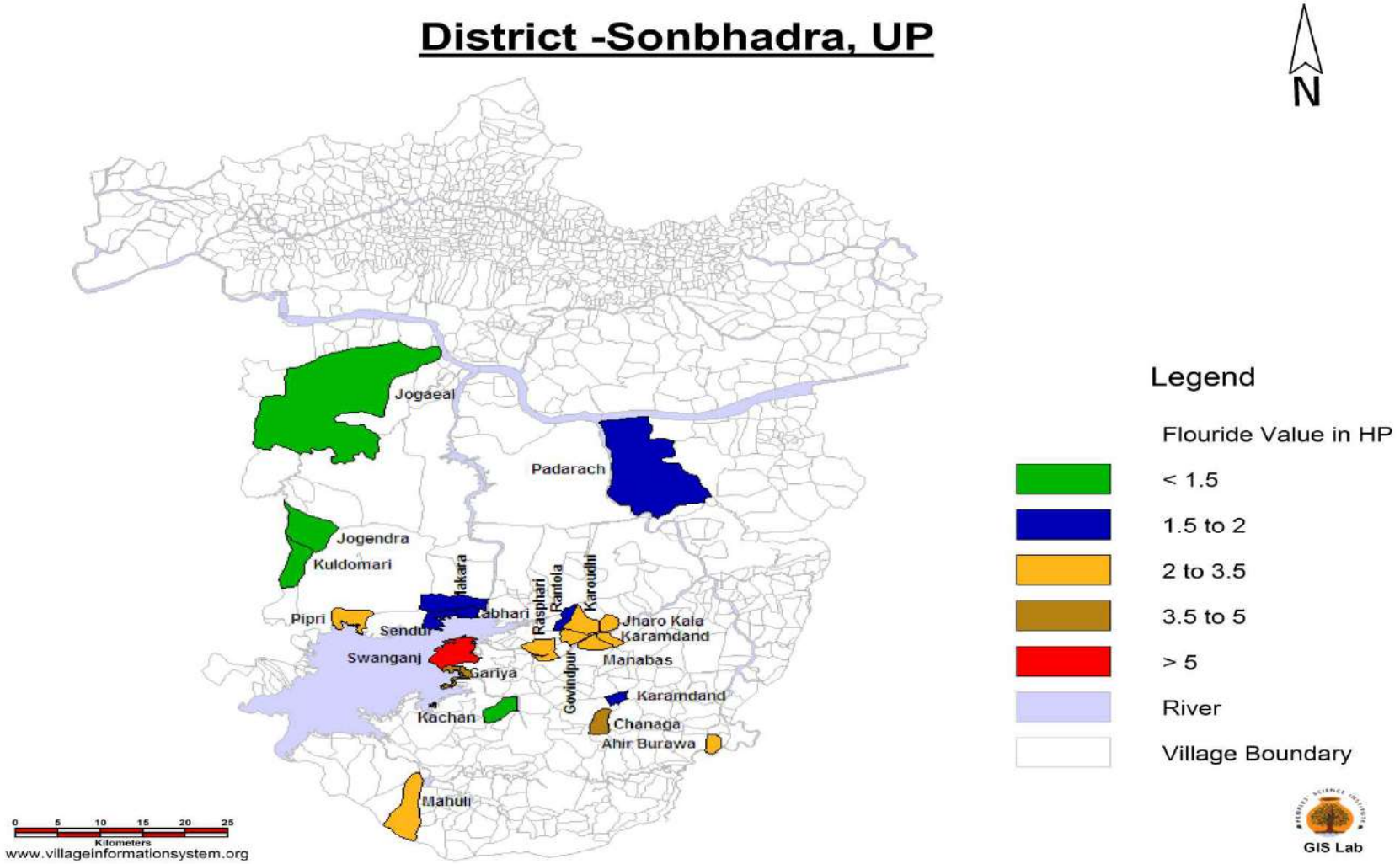
District -Sonbhadra, UP



Arsenic in well

- Rantola, Gariya, Baraidar, Devharpurvi, Ahirbudwa, Mahuli, Jharokala, Kachan, Deoghar, Jogaeal, ang jogendra have less arsenic.
- High arsenic value seen in Manabasa i.e 28 microgram/lit.

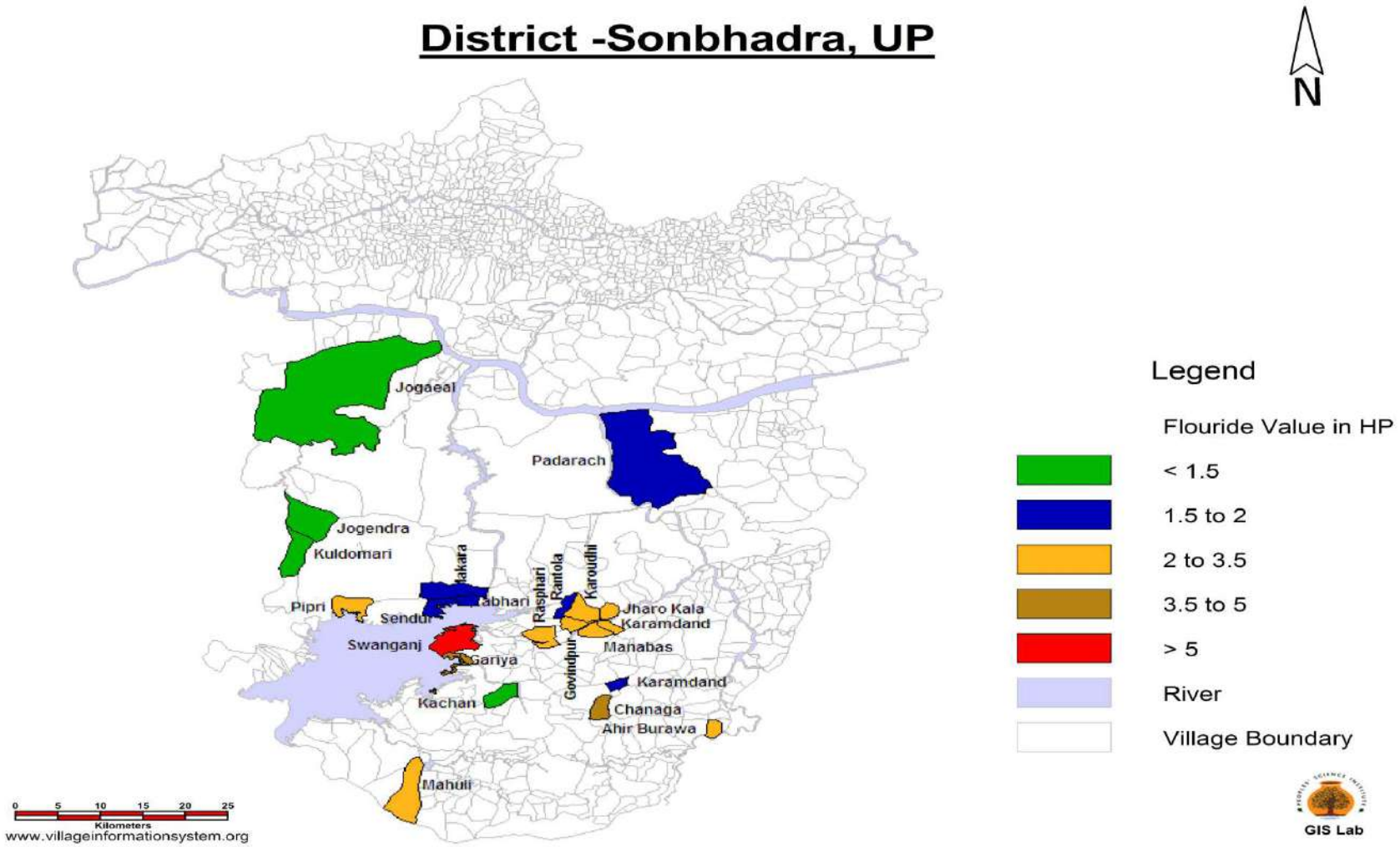
Flouride(Hand pump)



Flouride in HP

- Kachan, Devkhar, Jogaeal, Jogendra, Radhore has high Flouride content.
- Nai basti have high flouride i.e. 6.17mg/l

Flouride (Well)

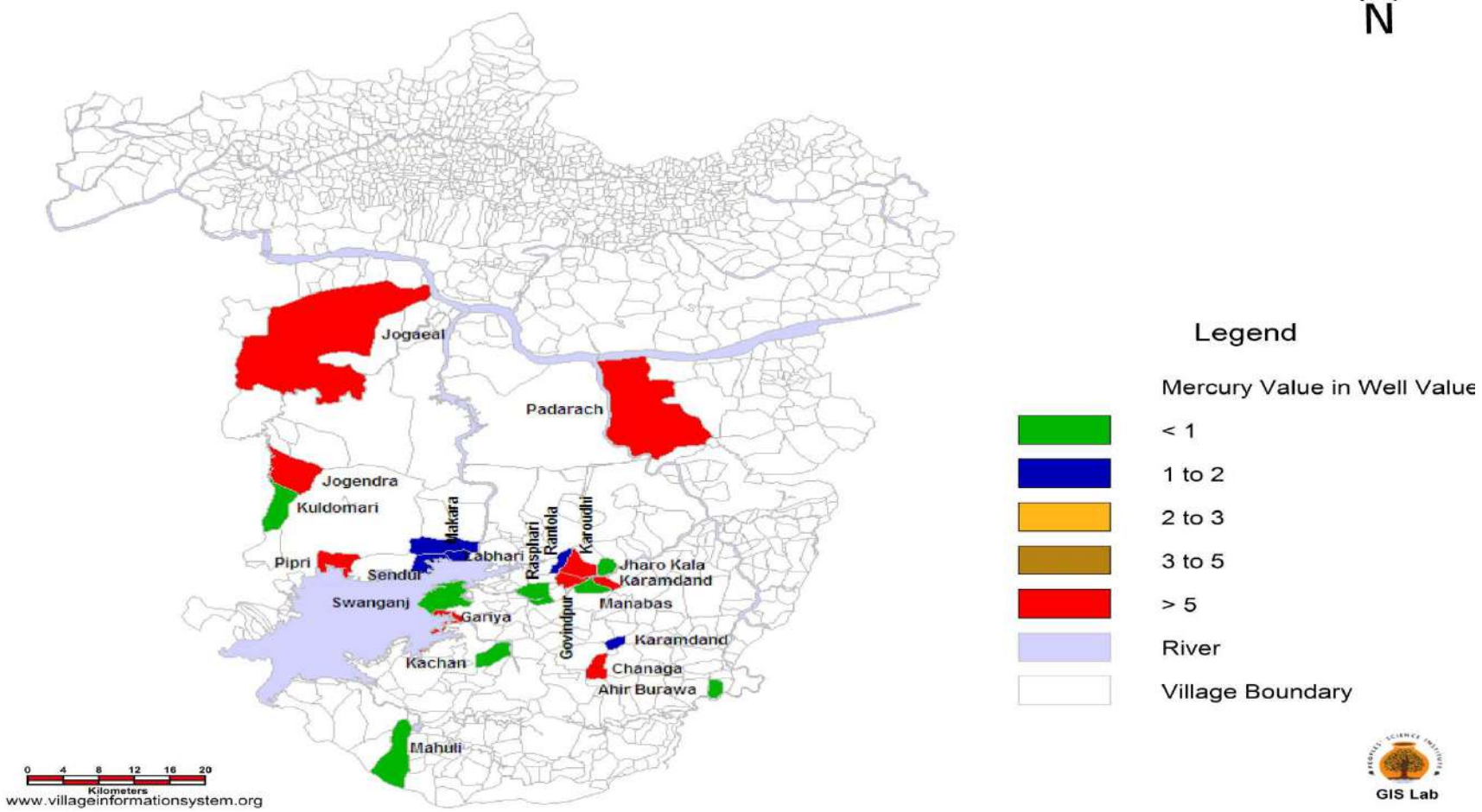


Flouride in well

- Jharo kala, Kachan, Deoghar, Jogaeal, Gaya dah, Jogendra, and Randhore have less Flouride .
- Gariya have highest flouride i.e 4.53mg/l.

Mercury (well)

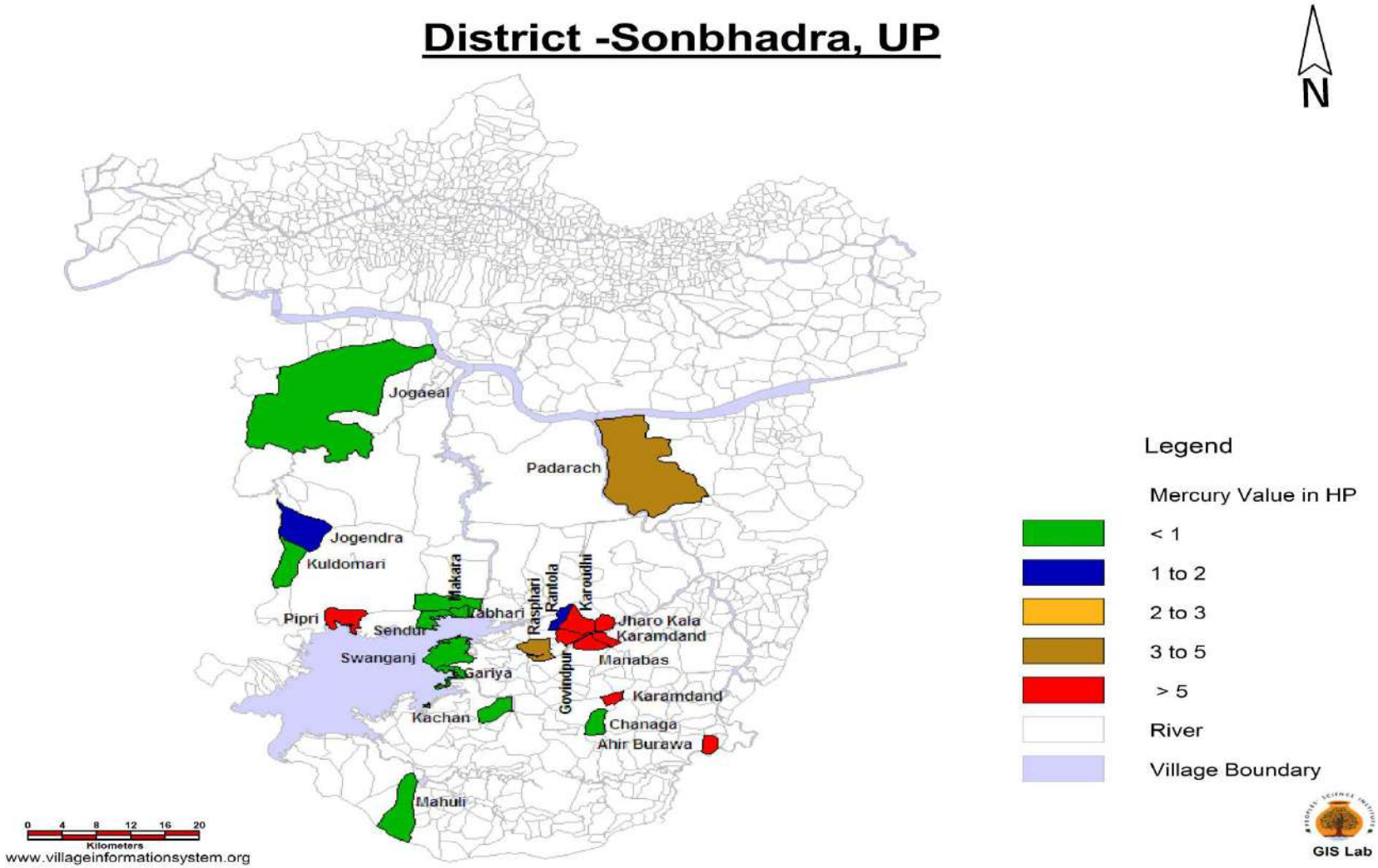
District -Sonbhadra, UP



Mercury in well

- Rantola, Deoghar, Jogaeal,Gaya dah, and lilasi kala have high mercury content.
- Jogaeal have 60 microgram/lit.

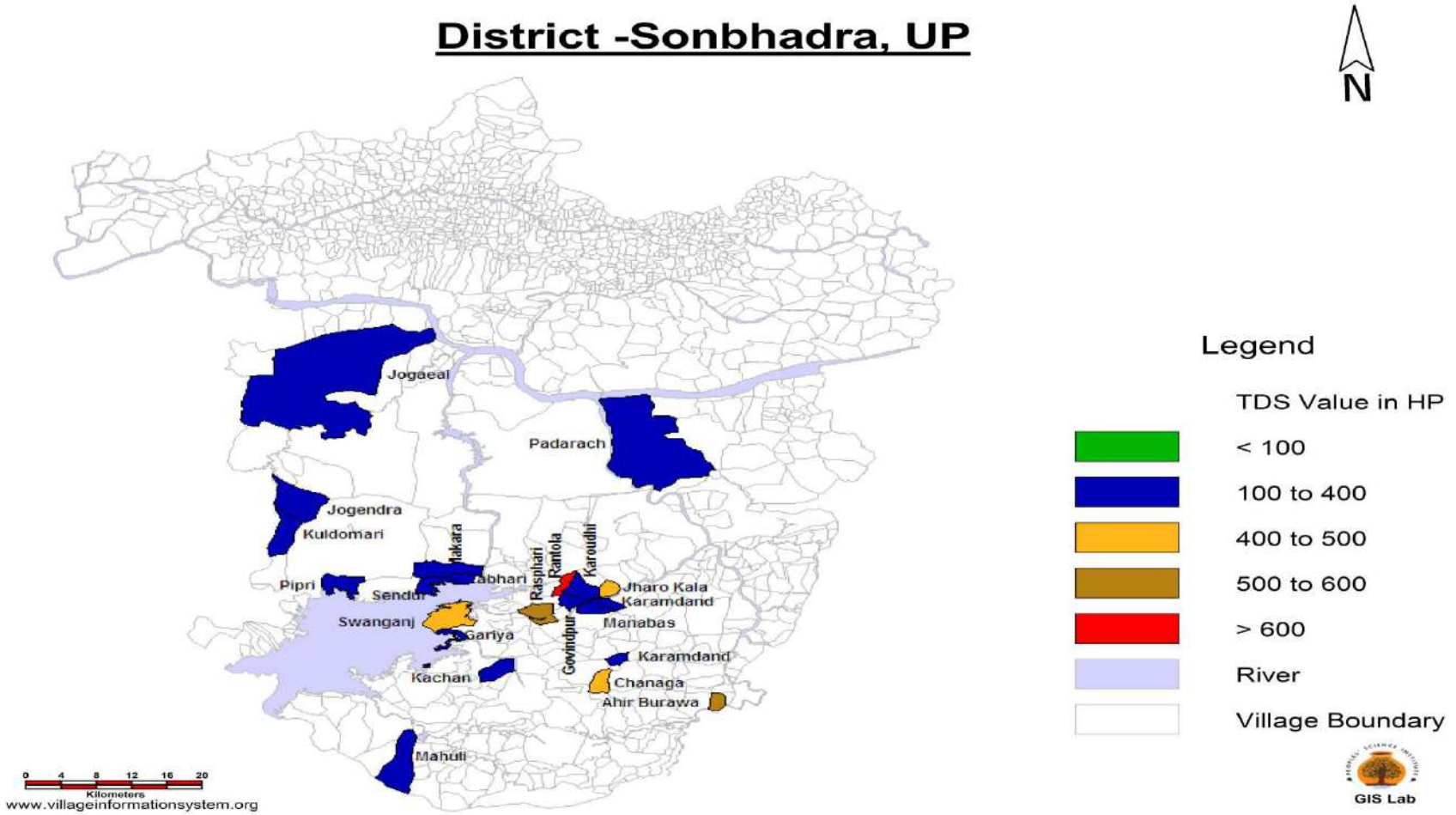
Mercury (Hand Pump)



Mercury in HP

- Gariya, Baraidar, Devhar poorvi, Mahuli, Jharo khala, Kachan, Manabasa, Devkhar, Gayadah, Pipari, Chanaga, Lilasi and Randhore have less mercury then the permissible limit.

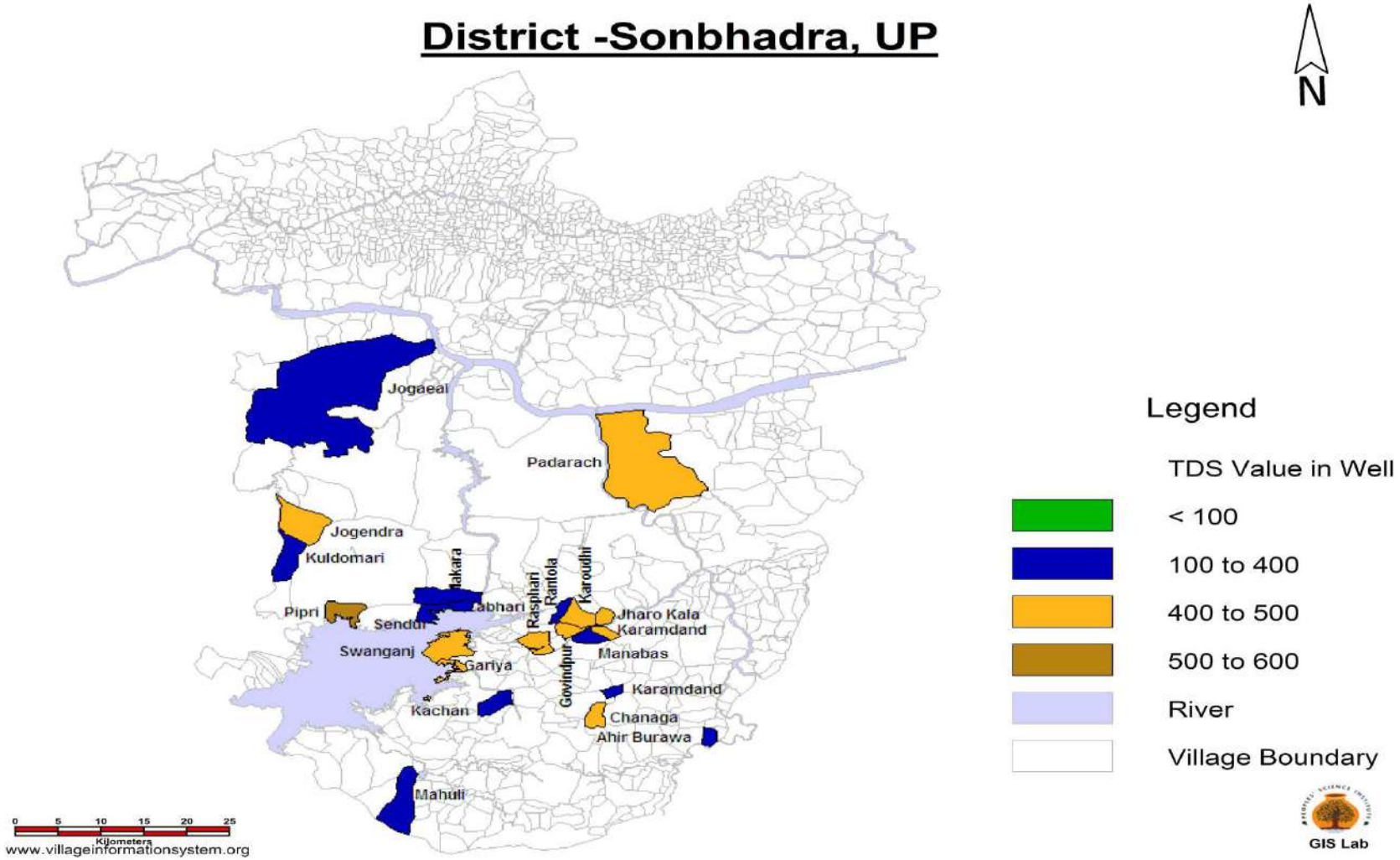
TDS (Hand pump)



TDS in HP

- Rantola, rashpahari, Phari phan, Ahir budwa, and Piprawaha have less TDS then the permissible limit.

TDS(Well)


District -Sonbhadra, UP
N
Jogaeal
Padarach
Jogendra
Kuldomari
Pipri
Sendur
Swanganj
Gariya
Kachan
Mahuli
Jharo Kala
Karamdand
Manabas
Karamdand
Chanaga
Ahir Burawa
Legend
TDS Value in Well
< 100
100 to 400
400 to 500
500 to 600
River
Village Boundary
0 5 10 15 20 25
Kilometers
www.villageinformationsystem.org
GIS Lab

TDS in Well

- Pariphan , gaya dah, and pipari have high TDS content.
- Highest TDS seen in Gaya dal village i.e 731ppm.

Atmospheric deposition as a possible source of surface water pollution

(Preliminary results of the project, part 1 — heavy metals)

SILVIE SEMERÁDOVÁ, JULIE SUCHAROVÁ, TOMÁŠ MIČANÍK, FRANTIŠEK SÝKORA, LUCIE JAŠÍKOVÁ

Keywords: atmospheric deposition — surface water — pollution sources

SUMMARY

Concentrations of selected heavy metals in collected atmospheric precipitation and surface water were monitored at pilot sites in the Jizera Mountains, Moravian-Silesian Beskydy Mountains, and Bohemian-Moravian Uplands (Czechia) over the course of one year to determine the significance of the impact of precipitation on surface water quality in an otherwise relatively low anthropogenically influenced environment. The measurements show that, for some metals, atmospheric deposition in heavily loaded areas can cause significant inputs to surface water. The resulting balance of substance load is strongly influenced by the environment and its load in the past.

INTRODUCTION

The Water Framework Directive (2000/60/EC) [1] requires EU member states to assess the state of groundwater and surface water in regular six-year cycles. In cases of failure to achieve good chemical and/or ecological status, it is necessary to determine the fundamental influences causing this situation and propose measures for its improvement. The assessment of the state of surface water bodies, which has been carried out in the Czech Republic since 2009 in accordance with Czech legislation in three-year cycles, repeatedly shows a high proportion of water bodies not achieving good chemical status in the case of certain priority substances according to Government Regulation No. 401/2015 Coll., and good ecological status in the case of some specific hazardous substances [2, 3]. Failure to achieve good status for some groups of substances is also recorded in water bodies where most of the potential anthropogenic influences can be excluded, and for which the possible main influence is the transfer of pollution to the aquatic environment from the air through atmospheric deposition. These groups mainly include heavy metals and polycyclic aromatic hydrocarbons (PAHs).

The TA CR project SS01010231 "*Dopady atmosférické depozice na vodní prostředí se zohledněním klimatických podmínek* (*Impacts of atmospheric deposition on the aquatic environment with consideration of climatic conditions*)" deals with this topic. The project builds on the methodology [4] which, among other things, based on available data, proposes procedures for assessing the danger for surface water bodies from the point of view of atmospheric deposition. The main problem with this part of the methodology was the unavailability of current and comprehensive data, as well as unverified procedures for their use. The aim of the project is to at least partially supplement these missing data and procedures. Part of the project solution is the quantification of pollution in various environmental components using field monitoring in selected pilot forest catchments. The aim of this activity is to verify the extent to which individual substances can affect the situation in the real environment, and to identify other factors increasing the risk of contamination entering the aquatic environment.

Due to the breadth of the topic and the number of results, it was not possible to process all the findings in one contribution. This article presents the results of the representation of selected heavy metals in the matrices of surface water and precipitation water, which were collected as throughfall and bulk deposition. Additional separate articles will deal with PAHs, a more detailed assessment of the relationships between the load of individual environmental components, and the use of biological materials as an indicator of anthropogenic influences.

HEAVY METALS IN THE ENVIRONMENT

Due to their toxic effects, heavy metals represent a significant source of surface water pollution [5–7]. There are three decisive properties for determining the environmental hazard of metals: resistance, bioaccumulation, and toxicity. Heavy metals that are both persistent and bioaccumulative are more dangerous because they can accumulate in organisms and be transported from one environment to another [8]. Metals that occur most often in surface water and pose a risk to the environment are in particular: mercury (Hg), lead (Pb), cadmium (Cd), nickel (Ni), and arsenic (As), [9, 10]. In addition to natural causes, anthropogenic activities are also responsible for their occurrence in the environment, especially the burning of fossil fuels, industrial activities (metallurgy, surface treatment of metals and enamelling), the use of paints and pigments, and agriculture [11, 12]. Through emissions, heavy metals enter the atmosphere and from the air they subsequently deposit into water and soil [13]. Metal compounds occur in the atmosphere in the form of particles that are sorbed onto aerosol particles. The amount of metals in the aerosol varies throughout the year [14]. Other factors that influence the amount of metals in the atmosphere are: meteorological conditions, site location, possibilities of long-distance transport, and amount of emissions [15]. Long-distance transport of particles can take place in the atmosphere due to air masses, therefore high levels of heavy metal pollution can be found even in places without a direct source of pollution [16, 17]. From the atmosphere, heavy metals are transported to the Earth's surface by deposition, which is driven

Photo: 123RF.com

by gravity and can occur through two mechanisms: dry and wet deposition. Dry deposition is slower and does not depend on precipitation, while wet deposition is faster and is affected by the amount of precipitation and the rate of capture of particles on the droplet surface [18].

METHODS USED

As part of the project, substances that cause poor water quality and at the same time are expected to be significantly transmitted through the air were examined and evaluated. Thus, the heavy metals As, Cd, Hg, Ni, and Pb were selected. From the point of view of the categorization of substances harmful to the aquatic environment, it should be mentioned that As is a specific pollutant, the other metals addressed in the project are priority substances, and Cd and Hg are priority dangerous substances.

To compare the presence of selected elements in different components of the environment, sampling of the following matrices was carried out in the model catchments:

- bulk deposition (monthly*),
- throughfall deposition (monthly*),
- surface water (monthly),
- river sediment (twice during the year),
- humus – a biologically stable humification layer (H, Oh horizon), after removal of litter layer (Ol) and fermentation horizon (Of) in the overburden (1x – samples represent a longer period of time),
- moss (1x – samples represent a longer period).

Note*: To determine the pollutants of interest in atmospheric deposition, it was necessary to obtain a sufficient volume of samples. In cases of insufficient rainfall, samples were taken after two months of exposure.

Fig. 1. Location of pilot areas

In water matrices, the total concentration of As, Cd, Hg, Ni, and Pb was determined by mass spectrometry and AAS-Hg methods. Spot samples of surface water were evaluated in the first part of the project by the ETA-AAS method for metals and AMA 254 for Hg. This is also the reason for higher detection limits for some of the results (for surface water in the first six months of monitoring).

For the project, model forest micro-catchments were selected, which were suitable for the monitoring of all the above-mentioned matrices and where, apart from the influence of the actual atmospheric deposition, other anthropogenic sources of pollution were not present.

The following catchments were selected as pilot areas:

- The area east of the Ostrava and Třinec agglomerations, which due to the prevailing air flow is heavily loaded with PAHs and heavy metals from the local power stations and industry, but at the same time it is a mountainous and forested area with no direct discharges into the watercourse. The model upper part of the Suchý stream basin in the eastern part of the cadastral territory of Bystřice has an area of 0.462 km^2 up to the sampling point. Suchý

Fig. 2. Precipitation sampling in Bystřice pilot area

stream is part of the catchment area of the HOD_750 – Hluchová water body from the source to the mouth of Olše, which in the third planning cycle does not reach good status due to the presence of PAHs. No other violations of Environmental Quality Standard (EQS) were detected. In the resulting tables, the catchment area is labelled Bystřice (BY), based on the nearest municipality.

— The area of the Bohemian-Moravian Highlands, which is considered to be an area with clean air, mainly influenced only by local heaters. In addition, areas with significant logging are currently expanding in this site after the bark beetle outbreak. It is therefore possible to monitor how deforestation and logging contribute to the leaching of hazardous substances. In contrast, it was necessary to avoid places with current and past mining of mineral resources. The model basin of the Lesní stream, a tributary of the Anenský stream on the north-eastern edge of the cadastral area of the Košetice municipality and the nearby meteorological station of the same name, has an area of 0.292 km^2 up to the sampling point. The stream is part of the catchment area of the DVL_0440 Martinický stream water body, which achieved good chemical status in the second and third cycles and EQS for selected substances were not exceeded. In the resulting tables, the catchment area is labelled Košetice (KO), based on the nearest municipality.

The area of the Jizera Mountains, which in the past was particularly affected by emissions of Cd and other metals from the nearby glass industry, and possibly from coal-fired power stations on the Polish side of the Jizera Mountains (in recent years, however, the air quality has improved). The model catchment of the Hřebový (sometimes also Hřebenový) stream, which is a left-hand tributary of the Souš reservoir in the municipality of Desná and Kořenov, has an area of 1,029 km^2 up to the sampling point. The stream is located in the catchment of the HSL_1896_J – Souš reservoir water body on the Černá Desná stream, which in the second planning cycle did not reach good chemical status due to exceeding EQS for Cd, and was not classified in the third cycle. In the resulting tables, the catchment area is labelled Desná (DE), based on the nearest municipality.

In these sites, rain gauges were placed near the watercourse, and a mixed sample of precipitation (collected over the entire period of one or two months) was always taken at the end of the given period. For the throughfall exposure, conifers (spruce in all three locations) were chosen because precipitation was also collected in winter. In the snow-free period, the upper part of the rain gauges was equipped with a protective net, so that the coarse solid particles and insects did not get into the collected water phase. The volume of collected precipitation was measured. Each collection campaign was photographically documented. Together with the precipitation collection, point sampling of surface water from the watercourse was carried out near the rain gauge station. The installation of rain gauges for the first sampling campaign took place on 6 October 2020 (BY), 7 October 2020 (KO), and 8 October 2020 (DE).

Data on the amount of precipitation obtained from the Czech Hydrometeorolo gical Institute (CHMI) and confirmed by the actual measurements in the sites were attached to the individual campaigns. The flow rate in the watercourse at the time

Fig. 3. Hřebový stream in Desná

Fig. 4. Bulk precipitation sampling at Košetice pilot site (left: 6 November 2020, right: 7 January 2021)

Tab. 1. Monthly precipitation amounts and flow rates at the time of measurement at individual sites

Campaign	Date		Precipitation [mm]			Flow rate [$m^3.s^{-1}$]		
	DE, BY	KO	BY	DE	KO	BY	DE	KO
1	5. 11. 2020	6. 11. 2020	190.8	176.6	55.9	0.19	0.021	0.0008
2	7. 12. 2020	8. 12. 2020	22	35.1	9.2	0.003	0.033	0.0005
3	6. 1. 2021	7. 1. 2021	51	58.7	27.1	0.007	0.009	0.0004
4	5. 2. 2021	6. 2. 2021	122.2	124.3	65.1	0.018	0.118	0.0024
5	5. 3. 2021	8. 3. 2021	90.1	24.8	10	0.017	0.201	0.0014
6	6. 4. 2021	7. 4. 2021	89.6	73.9	21.2	0.012	0.026	0.0008
7	6. 5. 2021	7. 5. 2021	151.8	89.1	42.2	0.008	0.096	0.0008
8	7. 6. 2021	8. 6. 2021	179.2	88	86.8	0.005	0.182	0.0008
9	7. 7. 2021	8. 7. 2021	75.5	100.6	69.1	0.001	0.014	0.0015
10	6. 8. 2021	9. 8. 2021	192.1	164.2	126.9	0.001	0.016	0.001
11	6. 9. 2021	7. 9. 2021	224.8	144.6	19.9	0.017	0.011	0.0004
12	6. 10. 2021	7. 10. 2021	83.2	74.4	31.9	0.025	0.066	0.0004
Total precipitation [mm]	-	-	1,472.3	1,154.3	565.3	-	-	-
Average flow rate [$m^3.s^{-1}$]	-	-	-	-	-	0.025	0.066	0.0009

of sampling was estimated, by analogy with the flow rates at the nearest CHMI gauging stations. The ratio of the flow rate at the observed point of the experimental site and at the nearest gauging station was equal to the ratio of the area of the point catchments. The exception was the site in Košetice, where data was taken from regular measurements carried out by CHMI.

Based on the amount of precipitation and the detected concentrations of monitored pollution parameters in precipitation, an estimate of the total deposition for the given experimental basin was calculated according to the following formula:

$$RS = \sum Sx * Cx$$

where RS is annual deposition in the given catchment
Sx amount of precipitation in the given month per area of the catchment
Cx concentration of the pollutant in the throughfall sample of the given month

An estimate of the annual substance load of watercourses for a given pollutant was calculated on the basis of the calculated flow rate and the detected concentrations according to the following formula:

$$LOD = \sum Qx * Cx * d$$

where LOD is substance load
Qx instantaneous flow rate at the time of withdrawal
Cx concentration of the substance in the point sample
d length of the period to which the value refers, in this case one month

Values below the limit of determination were not included in the average; for the purpose of calculating the substance load, instead of concentrations below the limit of determination, the average of actually measured values was used if this was lower than the limit of determination, and the limit of determination if the average of the other values was higher. The usual procedure of using half the limit of determination was not used because comparison of the results of both methods of determination shows a large relative error of this procedure.

RESULTS

Due to the different properties of the monitored substances, the results for each metal are presented separately. For informational purposes, the limit of good surface water status based on Directive 39/2013/EU [19] in the case of priority substances Ni, Cd, Pb, and Hg and from the methodology for evaluating the ecological status of surface waters [20] in the case of As is given for comparison. The EQS value means, as already mentioned, the Environmental Quality Standard, AA EQS value the annual average and the MAC EQS value the maximum acceptable concentration. The number of surface water bodies for which the limit for good status was exceeded during the evaluation for the second and third basin plans is also given. The total number of surface water bodies is 1 121 and 1 118 in the second and third planning cycles, respectively. The number of non-compliant water bodies indicates the importance of the substance from the point of view of the assessment of the surface water status. Significant differences between the evaluation in the second and third cycles for Ni and Pb are caused, among other things, by changes in evaluation methodologies, i.e. the use of determining the bioavailability of metals in the evaluation of the chemical status for the third planning cycle. Methodologies and results of status evaluation are discussed in more detail in [3]. In *Tab. 2–6*, values that are higher than the values of EQS for good surface water status are marked in red. Simultaneously, it must be emphasized that the EQS in the case of Ni, Cd, and Hg are set for the dissolved form of metals, while their total concentration was monitored as part of the project, the marking of values above EQS is therefore only indicative. The average annual value is compared with the value of AA EQS, measurements in individual months with the value of MAC EQS.

Tab. 2. Lead concentrations in surface and precipitation water

Pb [µg.l^{-1}]	Bystřice			Desná			Košetice		
Campaign	**flow**	**bulk**	**throughfall**	**flow**	**bulk**	**throughfall**	**flow**	**bulk**	**throughfall**
1	1.11	0.584	1.503	< 1.0	0.153	0.991	< 1.0	0.775	0.307
2	< 1.0	1.712	2.094	< 1.0	0.237	1.388	< 1.0	-	-
3	< 1.0	0.828	2.627	< 1.0	0.398	1.702	4.85	0.315	0.381
4	< 1.0	1.832	1.893	< 1.0	0.506	0.913	2.74	0.688	0.695
5	< 1.0	2.33	4.35	< 1.0	0.376	1.22	< 1	-	-
6	< 1.0	1.839	4.711	< 1.0	0.525	2.846	< 1	0.584	0.640
7	< 1.0	0.620	2.302	1.63	0.292	1.764	1.87	0.591	1.141
8	1.934	0.555	2.020	0.664	0.252	2.819	0.501	0.374	0.865
9	0.114	0.745	2.959	1.098	0.285	1.899	0.509	0.136	0.319
10	1.85	0.692	6.11	2.41	0.194	1.39	0.528	0.154	0.632
11	0.512	0.495	0.841	1.03	0.152	1.59	1.38	0.725	0.272
12	0.013	0.065	0.076	1.434	0.194	0.868	0.059	0.083	0.136
Average	0.922	1.025	2.624	1.378	0.297	1.616	1.554	0.444	0.534

Tab. 3. Nickel concentrations in surface and precipitation water

Ni [µg.l^{-1}]	Bystřice			Desná			Košetice		
Campaign	**flow**	**bulk**	**throughfall**	**flow**	**bulk**	**throughfall**	**flow**	**bulk**	**throughfall**
1	< 2.0	0.562	2.808	< 2.0	0.032	0.474	5.59	0.933	0.972
2	< 2.0	0.217	1.334	< 2.0	0.117	1.187	2.7	-	-
3	< 2.0	0.0789	0.0861	< 2.0	0.0861	1.2917	12.2	0.1461	0.9165
4	< 2.0	0.180	0.537	< 2.0	0.223	0.286	7.41	0.376	0.668
5	< 2.0	0.249	1.625	< 2.0	0.132	0.781	8.09	-	-
6	< 2.0	0.262	1.105	< 2.0	0.467	1.682	5.19	0.911	0.723
7	< 2.0	0.269	0.560	< 2.0	0.141	0.610	4.1	0.306	1.243
8	1.04	0.184	0.560	0.342	0.493	2.814	6.77	0.197	0.905
9	0.536	0.344	1.053	0.333	0.180	1.704	7.63	0.353	0.852
10	0.822	0.294	0.825	0.570	0.169	0.999	6.653	0.215	0.993
11	0.238	0.067	0.371	0.346	0.055	1.142	8.624	1.469	1.455
12	0.207	0.086	0.201	0.271	0.157	1.522	4.156	0.347	1.696
Average	0.569	0.233	0.922	0.372	0.188	1.208	6.593	0.526	1.005

Tab. 4. Arsenic concentrations in surface and precipitation water

As [µg.l^{-1}]	Bystřice			Desná			Košetice		
Campaign	**flow**	**bulk**	**throughfall**	**flow**	**bulk**	**throughfall**	**flow**	**bulk**	**throughfall**
1	< 1.0	0.107	0.218	< 1.0	0.085	0.371	< 1.0	0.122	0.205
2	< 1.0	0.322	0.705	< 1.0	0.082	0.715	1.1	-	-
3	< 1.0	0.119	0.487	< 1.0	0.092	1.958	1.29	0.104	0.098
4	< 1.0	0.319	0.455	1.03	0.191	0.313	< 1.0	0.124	0.165
5	< 1.0	0.449	0.888	1.03	0.210	0.352	< 1.0	-	-
6	< 1.0	0.457	1.077	< 1.0	0.228	0.758	< 1.0	1.033	0.385
7	< 1.0	0.173	0.422	1.02	0.078	0.425	< 1.0	0.185	0.410
8	0.265	0.166	0.318	0.701	0.108	0.863	0.425	0.111	0.210
9	0.212	0.121	0.605	1.075	0.089	0.931	0.491	0.081	0.150
10	0.301	0.109	0.308	1.597	0.058	0.376	0.476	0.050	0.129
11	0.194	0.046	0.141	0.821	0.034	0.551	0.585	0.102	0.224
12	0.393	0.113	0.136	1.089	0.067	0.530	0.377	0.089	0.328
Průměr	0.273	0.208	0.480	1.045	0.110	0.678	0.607	0.262	0.232

Tab. 5. Cadmium concentrations in surface and precipitation water (the colour marking of values above EQS is based on the limit for hardness class 1, i.e. soft to very soft water)

Cd [µg.l^{-1}]	Bystřice			Desná			Košetice		
Campaign	**flow**	**bulk**	**throughfall**	**flow**	**bulk**	**throughfall**	**flow**	**bulk**	**throughfall**
1	< 0.1	0.035	0.0467	0.23	0.033	0.072	< 0.1	0.045	0.035
2	< 0.1	0.088	0.208	0.23	0.027	0.344	< 0.1	-	-
3	< 0.1	0.021	0.268	< 0.1	0.025	0.477	< 0.1	0.019	0.025
4	< 0.1	0.045	0.135	0.21	0.041	0.107	< 0.1	0.049	0.047
5	< 0.1	0.121	0.504	0.19	0.033	0.170	-	-	-
6	< 0.1	0.235	0.712	0.2	0.033	0.204	< 0.1	0.081	0.036
7	< 0.1	0.073	0.200	0.16	0.020	0.251	< 0.1	0.075	0.113
8	0.108	0.039	0.113	0.103	0.026	0.300	0.037	0.026	0.046
9	0.034	0.050	0.194	0.107	0.021	0.202	0.041	0.072	0.040
10	0.091	0.105	0.134	0.272	0.041	0.110	0.036	0.095	0.059
11	0.037	0.048	0.023	0.122	0.010	0.129	0.038	0.039	0.014
12	0.056	0.0679	0.012	0.256	0.018	0.129	0.020	0.0164	0.027
Average	0.065	0.077	0.213	0.189	0.027	0.208	0.034	0.051	0.042

Lead

The main source of Pb in water is primarily industry, and previously also transport, while a significant means of its penetration into the aquatic environment is transmission through the air. After the ban on the use of leaded fuels in 2001, Pb also enters the water through leaching from contaminated soil.

Limits of good status for surface waters: AA EQS = 1.2 μg.l^{-1}, MAC EQS = 14 μg.l^{-1}. Number of surface water bodies not meeting EQS in the Czech Republic in the second/third planning cycle: 43/4.

Nickel

Ni occurs naturally in the Earth's crust and is also present in soil. It can be emitted by volcanic activity. In industry, it is often used in the manufacture of batteries, in metallurgy and in the manufacture of electronics. Ni is mainly found in the air as a result of the burning of fossil fuels. It gets into the water mainly by leaching from rocks and sediments.

Limits of good status for surface waters: AA EQS = 4 μg.l^{-1}, MAC EQS = 34 μg.l^{-1}. Number of surface water bodies not meeting EQS in the Czech Republic in the second/third planning cycle: 175/5.

Arsenic

As occurs naturally in the earth's crust, it can also be present in ore deposits of coal. It can get into water from mine waters, and into the air by burning some types of coal.

Limit of good status for surface waters: AA EQS = 11 μg.l^{-1}.Number of surface water bodies not meeting EQS in the Czech Republic in the second/third planning cycle: 8/13.

Cadmium

Cd is a relatively rare element in nature. It can enter the atmosphere through volcanic activity, during fires, or with dust particles during wind erosion and the burning of fossil fuels. In industry, it is used to a limited extent in the production of batteries, ceramics, electronics, and textile products. It enters surface waters mainly as part of industrial discharges and waters from the mining of non-ferrous metals or by transfer from the air.

Limits of good status for surface water depending on its hardness classes: AA EQS = ≤ 0.08 (class 1), 0.08 (class 2), 0.09 (class 3), 0.15 (class 4), 0.25 (class 5), MAC EQS = ≤ 0.45 (class 1), 0.45 (class 2), 0.6 (class 3), 0.9 (class 4), and 1.5 (class 5) μg.l^{-1}.

Number of surface water bodies not meeting EQS in the Czech Republic in the second/third planning cycle: 56/26.

Tab. 6. Mercury concentrations in surface and precipitation water

Hg [μg/l]	Bystřice			Desná			Košetice		
Campaign	flow	bulk	throughfall	flow	bulk	throughfall	flow	bulk	throughfall
1	< 0.05	< 0.006	< 0.006	< 0.05	< 0.006	< 0.006	< 0.05	0.175	0.036
2	< 0.05	0.153	0.23	< 0.05	0.29	0.305	< 0.05	-	-
3	< 0.05	< 0.006	0.04	< 0.05	< 0.006	0.07	< 0.05	< 0.006	< 0.006
4	< 0.05	< 0.006	< 0.006	< 0.05	< 0.006	< 0.006	< 0.05	< 0.006	< 0.006
5	< 0.05	280	27.5	< 0.05	15	13.8	< 0.05	-	-
6	< 0.05	< 0.006	< 0.006	< 0.05	< 0.006	< 0.006	< 0.05	0.35	< 0.006
7	< 0.05	< 0.006	< 0.006	< 0.05	< 0.006	< 0.006	< 0.05	< 0.006	< 0.006
8	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006
9	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006
10	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006
11	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006
12	< 0.006	< 0.006	< 0.006	0.067	0.087	< 0.006	< 0.006	< 0.006	< 0.006

Tab. 7. Indicative comparison of concentrations of selected metals in other monitored matrices

[mg.kg^{-1}]	Stream sediment			Moss			Humus		
	BY	DE	KO	BY	DE	KO	BY	DE	KO
As	6.07	17.00	10.82	0.19	0.15	0.14	8.35	10.53	5.86
Cd	0.66	0.30	0.59	0.74	0.28	0.13	1.23	0.80	0.37
Hg	< 0.2	< 0.2	< 0.2	0.05	0.03	0.03	0.39	0.37	0.37
Ni	16.05	8.21	62.33	0.85	0.83	0.98	8.72	7.65	7.41
Pb	30.25	42.50	29.77	8.39	2.56	1.48	127.00	74.87	45.07

Tab. 8. Calculation of atmospheric deposition and substance load in pilot areas

Substance	As			Pb			Cd			Ni		
Site	BY	DE	KO	BY	DE	KO	BY	DE	KO	BY	DE	KO
Atmospheric deposition [g.year^{-1}]	269	718	34	1,763	1,849	97	116	207	8	649	1,334	161
Atmospheric deposition per area unit [g.km^{-2}. year^{-1}]	583	697	115	3,817	1,797	331	250	201	27	1,404	1,296	553
CHMI 2020 total deposition [Ni only bulk]	-	-	-	600–1,300	600–1,000	100–400	55–70	200–400	15–35	1,000–1,500	3,000–5,000	750–1,000
Substance load [g/year]	219	1,982	17	752	2,191	40	50	364	1	417	739	195
Substance load per area unit [g.km^{-2}year^{-1}]	474	1,926	57	1,628	2,129	138	108	354	3	903	718	667
Ratio of load and deposition [%]	81	276	49	43	118	42	43	176	13	64	55	121

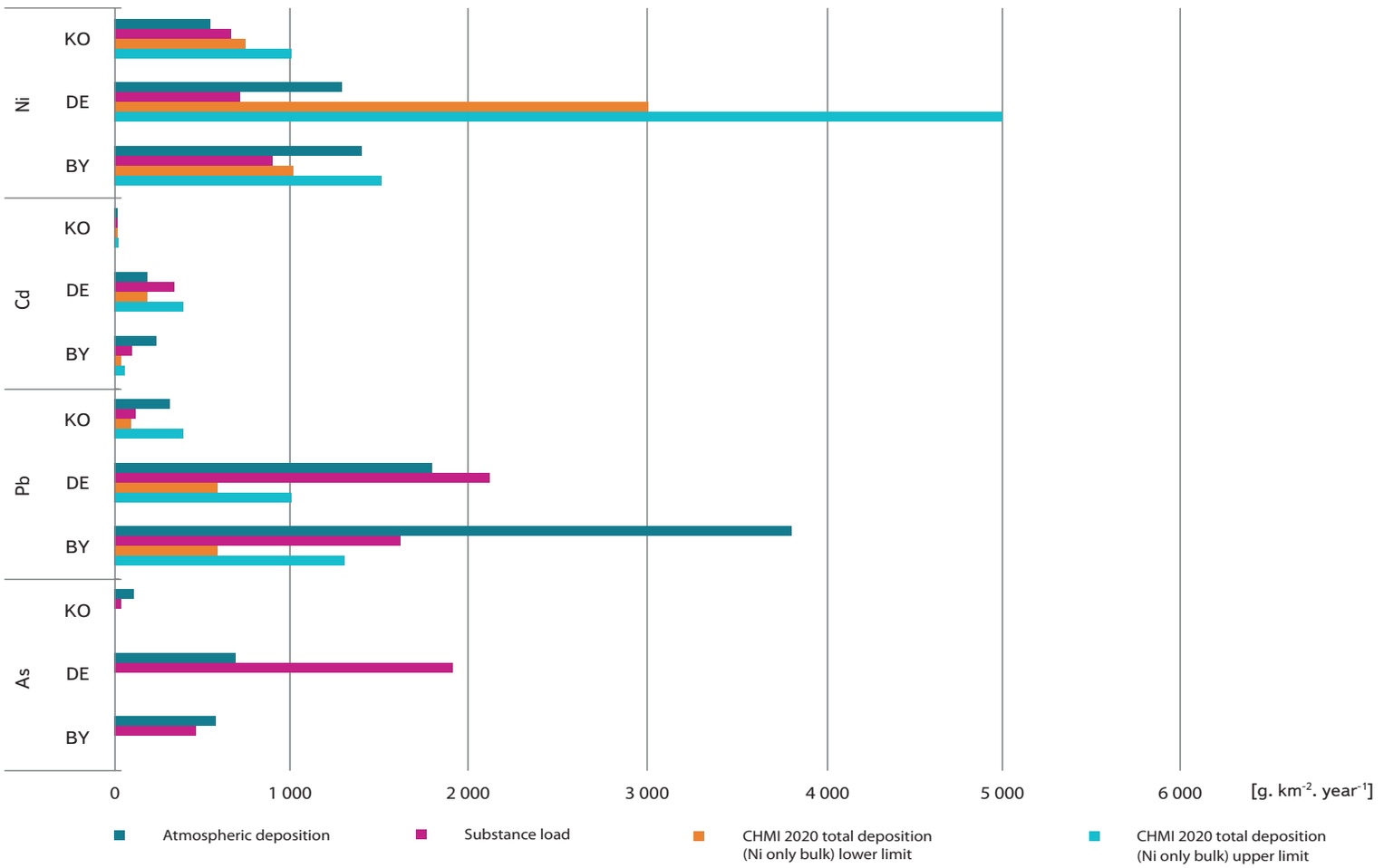


Fig. 5. Calculation of atmospheric deposition and substance load per area unit

Mercury

Hg occurs naturally in rocks and soils. From a global perspective, the increased Hg content of the recent zone reflects recent and past tectonic and volcanic activity.

An increased concentration of Hg in natural waters is usually the result of anthropogenic pollution. Hg compounds can be contained in waste water from some types of industrial production, it can get into the air by burning fossil fuels and by wind drift during surface mining.

Hg has a high accumulation potential, especially in sediments and in aquatic flora and fauna.

Limit of good status for surface water: MAC EQS = 0.07 $\mu g.l^{-1}$.

The number of surface water bodies not meeting EQS in the Czech Republic in the second/third planning cycle: 75/95.

Tab. 7 shows a comparison of the values measured in the other monitored matrices. These are average values from two to three measurements in the case of stream sediment and from three sites in each catchment in the case of moss and humus. The methodology and more detailed results will be published in the following article; however, even the summary data indicate an increased deposition level for Pb and Cd in the industrial sites of Desná and Bystřice, and, in contrast, a relatively uniform level of deposition for Ni, As, and Hg.

Tab. 8 and *Fig. 5* provide an overview of the calculated atmospheric deposition and substance load, both absolutely and relatively per area unit in the experimental sites, and compare them with the values reported by CHMI [21].

The comparison of the calculated relative values shows that the highest values of both deposition and substance load are achieved by concentrations of Pb or Ni, while the lowest values were confirmed for Cd.

The order of concentrations of individual substances in relative atmospheric deposition is Pb > Ni > As > Cd, with the exception of Košetice, where Ni is in first place (Ni > Pb > As > Cd). The order of magnitude of the substance load varies in each site; the lowest values remain common in the case of Cd.

Košetice Ni >> Pb > As >> Cd
Desná Pb > As > Ni > Cd
Bystřice Pb > Ni > As > Cd

DISCUSSION

The measurements carried out confirm that, in the case of some metals, precipitation pollution is comparable to surface water pollution. In the case of metals, no significant seasonality was noted for the pollution of precipitation and surface water. It should be noted that for surface water the result is affected by the high limit of determination in the first half of annual monitoring. The calculated atmospheric deposition is comparable to the calculated substance load in the given basin, although both calculations are burdened with a considerable degree of uncertainty. As expected, higher substance load than deposition was recorded at the Desná site, where a higher load of selected metals in the past is assumed. Closer connections will be possible to evaluate with the involvement of evaluation of other monitored matrices in experimental sites.

Specific assessments for individual metals:

Lead

Pb concentrations are decreasing in the long term [22], both in the air and in surface water. The calculated atmospheric deposition can be compared with the values determined within other projects, e.g. [7] reports deposition of 5.8 or 9.3 $kg.km^{-2}.year^{-1}$ in two sites in Krkonoše mountains. By comparison with the value of the calculated deposition at the Desná site of 1 797 $kg.km^{-2}.year^{-1}$, this indicates that there has been a significant reduction in Pb deposition in the past 17 years.

The Pb concentration in precipitation is comparable to its concentration in surface water, but it can be even higher in sites affected by industry (especially metallurgical processing of non-ferrous metals). The concentrations in throughfall precipitation alone can then reach EQS levels, which would pose a risk in the case of an impact on water surface or in the case where precipitation waters are discharged into surface waters without interaction with the environment, if it were a dissolved form of Pb in precipitation water.

The calculated deposition corresponds to the values reported by CHMI for 2020 in the Košetice site; in other sites it is higher, which may be due to local conditions (e.g. in the Bystřice site, a particularly exposed site was chosen; CHMI, on the other hand, works with a modelled network with a step of 1 km), or with a time shift (CHMI year 2020, measurement within the project 10/2020–9/2021).

Nickel

Increased concentrations of Ni in precipitation were not detected in the monitored sites. In the pilot basin of Košetice, higher Ni concentrations were detected in surface water; significant input of Ni to the site from precipitation was not confirmed. It can therefore be assumed that surface water pollution in the Košetice site comes from a different source than the current atmospheric deposition, which is also consistent with the evaluation of other matrices.

The calculated deposition corresponds to the values given by CHMI in the Bystřice site; in the Desná and Košetice sites the values calculated from the data obtained as part of the project were lower.

Arsenic

Precipitation values in all sites including those affected by coal mining and burning are higher, but well below the EQS value for surface water. The highest values in surface water were recorded at Desná, where a higher load can be assumed in the past.

Cadmium

As expected, the lowest concentrations in both precipitation and surface water were measured in the lightly loaded Košetice basin, which served as a reference site for the other two. Higher concentrations in precipitation were measured in Bystřice and Desná, i.e. sites affected by industry and coal burning. These detected concentrations are higher than the EQS values for surface water, if we do not consider the limit values determined for the highest hardness class and the validity of the EQS values for the dissolved form of cadmium. While in the Bystřice site, the highest deposition was recorded, but lower substance load, in Desná, the substance load by the Hřebový stream was, on the contrary, higher. The cause is probably a higher load of cadmium in the given area in the past from nearby sources of air pollution (glass industry) with the accumulation of this pollution in the upper soil layers.

The calculated deposition corresponds to the values reported by CHMI, with the exception of the Bystřice site, where it is significantly higher.

Mercury

Due to the frequent values below the detection limit, it was not possible to determine the atmospheric deposition and substance load. Hg occurred in the surface water of the model areas only once (Desná) in a concentration just below the EQS limit. In the precipitation, we could observe two episodes

when Hg was measurable, even in several sites simultaneously. The campaign at the beginning of November 2020 ended with a question mark when there was an increased concentration of Hg in the Košetice site. In the other two areas, increased concentrations did not occur until the December campaign; however, we must consider that the campaigns in Košetice were always concluded one day later than in the other two sites. In the March campaign, on the other hand, increased Hg concentrations in Košetice occurred later and at lower values; however, due to the lack of precipitation, this is a sample taken after a two-month exposure. These increased concentrations of Hg are correlated with the passage of dust from the Sahara Desert through the territory of the Czech Republic, while it is confirmed in literature [23] that areas regularly exposed to these phenomena are also more loaded with Hg. The occurrence of Hg in surface water is sporadic. Nevertheless, due to its high bioaccumulation potential, it is significantly represented in biota, accompanied by the failure to achieve good chemical status of surface waters. However, this problem is not specific only to the Czech Republic; due to the physical-chemical properties of Hg and its behaviour in the environment, it is a worldwide issue.

CONCLUSION

The project confirmed that air pollution can have a significant effect on surface water quality through atmospheric deposition. Environmental characteristics, including historical deposition, also play a significant role. This risk is particularly evident for Pb and Cd. In the case of As and Ni, on the other hand, atmospheric deposition does not appear to pose a threat to surface water quality in the selected sites. Hg is characterized by special properties which, in addition to requiring more complex laboratory processing, also shows much more significant fluctuations in values. In precipitation in particular, the amount of Hg can change significantly, apparently also in connection with distant external influences.

We will provide a more detailed description of the representation of metals in the monitored matrices within the framework of this project and the links between the pollution of individual components of the environment in one of the following articles. All outputs to date are available on the project website [24].

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Service of Applicant - Rejoinder to the CPCB report dated 10.9.2024 on behalf of Applicant in Original Application No. 240/2024[Singrauli Pradooshan Mukti Vahini & Ors. vs. Union of India & Ors.]

1 message

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Dear sir/ ma'am

I am writing on behalf of Ms. Srishti Agnihotri, Advocate for the Applicant in the above-titled matter. Please find attached a copy of the rejoinder to the CPCB report dated 10.9.2024 that the Applicant will be filing today. Kindly treat this as due service of the same.

Best regards
Shivani Sagar Kalra
Advocate

Rejoinder Final.pdf