BEFORE THE NATIONAL GREEN TRIBUNAL
SOUTHERN ZONE BENCH AT CHENNAI
Original Application No. 131 of 2020 (SZ)

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…Applicants

Vs.

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8. M/s. Thirumalai Chemicals Limited
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Ranipet, Tamil Nadu – 632 403
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Email Id:- mail@thirumalaichemicals.com ...Respondents

INDEX TO TYPED SET

Dated at Chennai on this the 27th day of January, 2022.

COUNSEL FOR RESPONDENT NO.8

VIT®
Vellore Institute of Technology
(Deemed to be University under section 3 of UGC Act, 1956)

27-10-2021

To

Mr. N. R. Vijaya Kumar
Site Head
M/s. Thirumalai Chemicals Ltd. (TCL)
25 - B SIPCOT Industrial Complex,
Ranipet, 632 403.Tamil Nadu, India

Sub: Submission of Final Technical Report for the Consultancy Proposal titled, "*Hydro geological setup and geochemical status with respect to the surface and subsurface condition in the specified sub watershed area consisting Thirumalai Chemicals Ltd. (TCL), Ranipet*".

Ref: Work Order/Purchase Order No. 210461262 dated 30th November 2020.

Dear Sir,

With reference the above, please find herewith the Final Technical Report on "*Hydro geological setup and geochemical status with respect to the surface and subsurface condition in the specified sub watershed area consisting M/s. Thirumalai Chemicals Ltd. (TCL), Ranipet*".

This report is on the basis of survey conducted during December 2020 to April 2021 as per the following scopes mutually agreed and mentioned in the said Work Order.

1. Hydrogeological and geochemical exploration of the specified watershed.
2. Study of the natural drainage network and determination of flow direction.
3. Analysis of groundwater samples from the borewell/dug wells from the watershed area and determination of contamination profiling.
4. Determination of the soil contamination in the study area.

Kindly acknowledge after receiving the report.

Sincerely yours

Principle Investigator
Dr. Bhaskar Das

Dr. BHASKAR DAS
Associate Professor & Placement Co-ordinator
School of Civil Engineering (SCE)
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VIT - A place to learn ; A chance to grow

Hydro-geological setup and geochemical status with respect to the surface and subsurface condition in the specified sub watershed area consisting M/s. Thirumalai Chemicals Ltd. (TCL), Ranipet

Submitted to

M/s. Thirumalai Chemicals Ltd. (TCL)
25 - B SIPCOT Industrial Complex,
Ranipet- 632403
Tamil Nadu, India.

Submitted by

School of Civil Engineering (SCE)
Vellore Institute of Technology (VIT)
Vellore- 632014
Tamil Nadu, India.

VIT®
Vellore Institute of Technology
(Deemed to be University under section 3 of UGC Act, 1956)

October 2021

27/10/21

VIT®
Vellore Institute of Technology
(Deemed to be University under section 3 of UGC Act, 1956)

CERTIFICATE

Date: 27-10-2021

This is to certify that the present study titled, "**Hydro geological setup and geochemical status with respect to the surface and subsurface condition in the specified sub watershed area consisting M/s. Thirumalai Chemicals Ltd. (TCL), Ranipet**" conducted by Vellore Institute of Technology (VIT), Vellore, upon the request from M/s Thirumalai Chemicals Limited (TCL) on the basis of Work Order/Purchase Order No. 210461262 dated 30th November 2020.

The study was performed during December 2020 to April 2021, as per the scope mentioned below.

I. Hydrogeological and geochemical exploration of the specified watershed.

II. Study of the natural drainage network and determination of flow direction.

III. Analysis of groundwater samples from the bore well/dug wells from the watershed area and determination of contaminations.

IV. Determination of the soil contamination in the study area.

The finding of this study is based on the field visit, one time sampling and analysis of water and soil samples during the above said period. This final report submitted is the exact and unbiased technical representation of the finding from the study, which is to the best of our knowledge.

Principal Investigator
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Dr. BHASKAR DAS
Associate Professor & Placement Co-ordinator
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C

TABLE OF CONTENT

CONTENTS **PAGE NO.**

CERTIFICATION

LIST OF TABLES

LIST OF FIGURES

Executive Summary

Ranipet SIPCOT area is known for soil and water pollution since decades. Many scientific studies have been carried out by National Research Institutes like CSIR-NGRI, CSIR-NEERI, IIT and various Universities. Apart from chromium contamination from Tamilnadu Chromate & Chemicals(TCCL), the earlier research studies identified both soil & water pollution due to the various tanning & chemical industries in the entire SIPCOT area and its downstream up to Palar River.

Thirumalai Chemicals Limited (TCL) is a leading organic Manufacturing Company in India, situated in the south eastern side of SIPCOT. TCL uses O-Xylene and Maleic Anhydride as raw materials, and manufacture Phthalic Anhydride, Fumaric Acid and Malic Acid. Phthalic Anhydride is manufactured by the Oxidation of O Xylene with oxygen in the air and the off gases are scrubbed. Fumaric Acid is recovered from the scrubber solution through the catalyzed isomerization of Maleic Acid. Maleic Acid is manufactured mainly by the hydrolysis of Maleic Anhydride. TCL maintains a ZLD status from 2006 onwards.

The present study was conducted by VIT upon the request from Thirumalai Chemicals Limited (TCL) during December 2020 to April 2021 in order to investigate the pollution surrounding to TCL through geophysical and geochemical exploration.

In the present Sub-Watershed, an Integrated Scientific approach that included detailed Hydrogeological, Geophysical and Geochemical investigation of the Sub-Watershed where in Topographic survey using GPS, 1D & 2D mapping of the area to decipher the Resistivity and Thickness of the subsurface strata, soil and rock profiling, water level measurement and analysis of water and soil samples drawn from Auger holes for contamination of water, soil, weathered rock, and fractured rock were carried.

One objective of the study was to investigate the surface and subsurface drainage pattern of the existing sub-watershed and delineation of contaminated geological formation, if any. Another objective was to explore the geochemical status through the analysis of physio chemical parameters, heavy metals (Iron and Chromium), and organic acids (Formic Acid and Oxalic Acid) in water and soil samples surrounding to TCL.

Geologically the Sub-Watershed is a hard rock region beset with granites as country rock and quartzites intrusions. Just north of the TCL premises, one Dolerite Dyke runs East-West. The topographic contours obtained reveal that the major slope is from NW-SE and North –South. The Groundwater contour map obtained from the water level observation from the auger hole as

23/10/21

well as selected monitoring wells reveal that the subsurface flow direction follows the topography i.e. NW-SE and North to South. The groundwater velocity determined from the permeability test at selected location show that the predominant flow is NW-SE with a higher velocity followed by North to South due the presence of shallow water levels in the weathered and fractured subsurface layers as well as the steep terrain gradient. The flow direction is supported by the inferences obtained from geophysical investigations.

The Vertical Electrical Sounding (VES) was done in 26 locations around the study area with seven profile directions reveal the types of soil, hard and soft rock formations, and aquifers present under the study area. The zone ranging from 0 to 20 meters depth from the surface demonstrates that weathered and fractured rock conditions indicating possible contamination. The geographical contour explains the flow of ground water and surface drains from NW to SE of the study area. A total of 25 auger drills have been done and soil samples were collected from the maximum depth for chemical analysis. Totally 59 water samples were collected from natural drains, bore wells, industrial drains, river, lakes and ponds. The physiochemical analysis of water samples such as pH, turbidity, specific conductivity, hardness, total alkalinity, total chloride and sulphates revealed the presence of elevated concentrations compared to the CPCB discharge standards especially in the upstream of TCL.

From the physiochemical analysis of the samples it is revealed that the downstream industries in the south receive the pollution load due to their topographic location. The elevated level of total chromium and iron concentration are prevailing throughout the study area. The total and hexavalent chromium was found to be high in the soil and water surrounding to Tamil Nadu Chromate and Chemical Limited. The overlying of the drainage network with the respective concentration depicted that the contaminated wastewater was carried through the drains to the nearby waterbodies and finally Palar river at the South. The present study is based on one-time random sampling from the study area where the seasonal variation is not anticipated.

1. Background

Ranipet is an industrial hub in southern India mainly known for its production and export of raw and finished leather products. There are large medium & small-scale industries in Ranipet, mostly engaged in chemical, leather and steel fabrication. These industries are the major lifeline for the town. Most of these industries are falling under two major Industrial Park named SIPCOT (State Indus-tries Promotion Corporation of Tamil Nadu Limited) and SIDCO (Small Industries Development Corporation Limited). The SIPCOT (**Figure 1**) was formed in 1971 to promote industrial growth in the state and to advance term loans to medium and large industries.

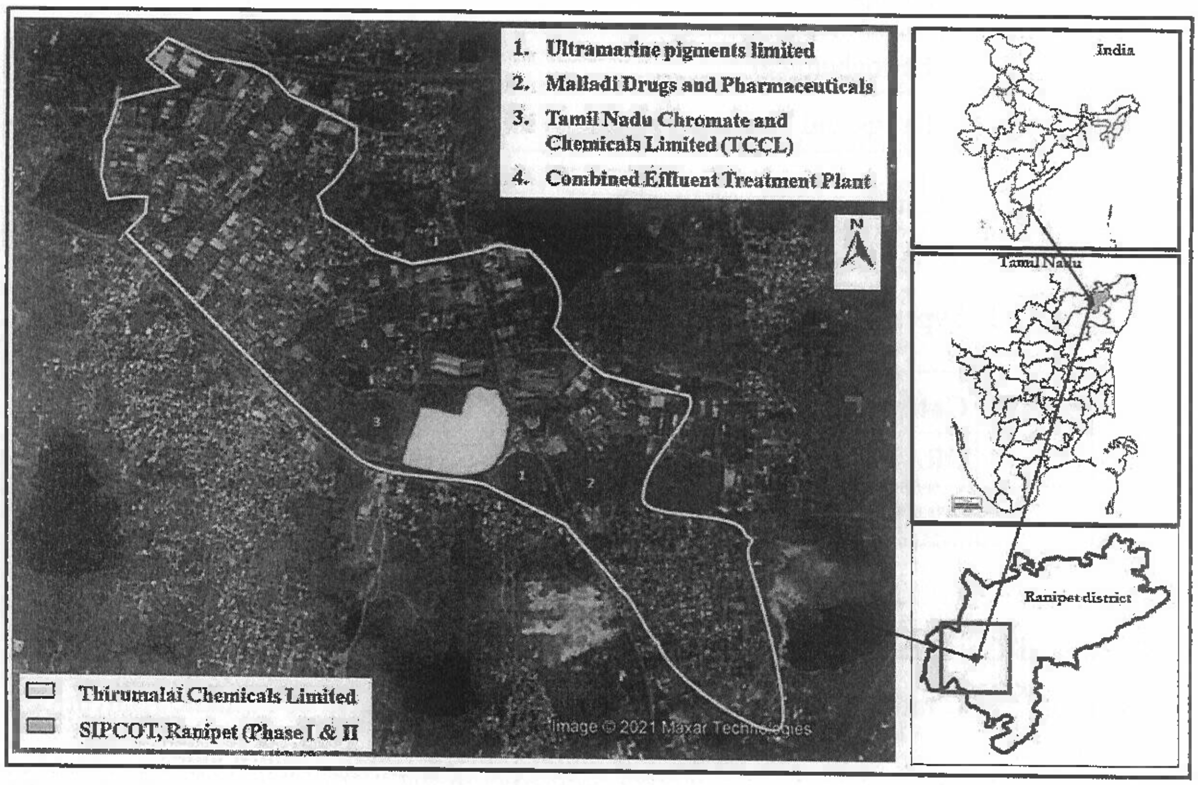

Figure 1: The study area along with SIPCOT boundary

The SIPCOT industrial complex, Ranipet was established during the year 1973.The industrial complex has Phase-I and Phase-II where Petro- chemical, Bulk drugs & Pharmaceuticals, Heavy Engineering, Foundry, Chemicals, Tanneries and miscellaneous industries are located. Ranipet SIPCOT Industrial Complex lies in the North-West of Ranipet town. According to TNPCB reports (TNPCB 2010 & TNPCB 2020) there are 18 numbers of Red Large/Medium categories of industries like Chemical, Heavy Engineering, Petrochemical, Pharmaceuticals and Common Effluent Treatment Plant (CETP) as mentioned in **Table 1.** There are 171 industries falling under Orange & Green category (**Table 2**). Most of them are tannery dry processing units and other few types of industries such as light engineering, pulverizing; plastic product, leather board, etc. are located at the critical area.

The Ranipet SIPCOT Industrial Complex is classified as Critically Polluted Industrial Area (CPA) based on the Comprehensive Environmental Pollution Index (CEPI) score assessed by CPCB during March 2018 for Air, Water and Land Environment (TNCPC 2020).

The CPCB has considered Total Ammoniacal (NH_4+NH_3) Nitrogen as Primary Pollutant and BOD, Total Chromium as secondary pollutants with respect to Surface Water Environmental Pollution Index (SWEPI) and individual score for the surface water environment is 75.0.

Table 1: Types of Red category industries in SIPCOT, Ranipet

Sl. No	Type of Industry	No of industries
1	Chemical	8
2	Heavy Engineering	4
3	CETP	2
4	Petrochemical	1
5	Drugs and Pharmaceuticals	3
	Total	**18**

Table 2: Types of Orange/Green category industries in SIPCOT, Ranipet

Sl. No.	Category	Large	Medium	Small	Total
1	ORANGE	8	19	118	145
2	GREEN	0	0	26	26

The Thirumalai Chemicals Limited (TCL) is a Chemical Manufacturing Company in India (TCL Website). TCL ranks among the largest producers in the world of Phthalic Anhydride, Malic Acid, and Fumaric Acid. The industry is situated in the South Eastern side of SIPCOT (**Figure 1**) and having approximate area and perimeter of 193403 m^2 (19.34 ha) and 1920 m respectively.

The present work is taken by VIT upon the request from TCL to investigate the local hydrogeological and geochemical condition surrounding to TCL premises and to determine the quality and flow pattern of the surface and subsurface flow. The work was started in December 2020 and continued till April 2021

2. Scope of the work

a. Hydrogeological and geochemical exploration of the specified watershed.

b. Study of the natural drainage network and determination of flow direction.

c. Analysis of groundwater samples from the bore well/dug wells from the watershed area and determination of contaminations.

d. Determination of the soil contamination in the study area.

3. Details of work elements

a. The hydrogeological study consists of the following activities

i. Topographical and Land Cover study –Satellite Image/Topo Sheet along with Google Earth Map are used for delineating the watershed area. The outcome of the work is in the form of Land Use Land Cover (LULC) map of the study area.

ii. Subsurface Geology and geophysical investigation – Study of subsurface geology is carried out on the study area in combination with geophysical surveying like Electrical Resistivity studies (Vertical Electrical Sounding). The information from the Piezo metric wells inside TCL are also considered in this study. The outcome of the study is the information regarding the groundwater table and soil strata on the basis of one time random sampling.

b. Natural drainage network and natural water bodies are analyzed from delineated LULC map. The drainage network is identified and the direction of the flow is determined on the basis of natural slope of the land.

c. Analysis of water samples consists of the following elements

i. The location of bore well/dug well samples are identified from the watershed map overlaid with Google Earth image. The five groundwater samples from the study area are collected and analyzed for physiochemical parameters, total Iron, total chromium and hexavalent chromium.

ii. Total 30 water samples are collected from the drains and surface water bodies from the sub watershed area and analyzed for same parameters as groundwater.

iii. Among the total 59 water samples collected from groundwater, surface water, drains and other sources, 10 water samples are analyzed for Oxalic Acid and Formic acid in VIT.

On the basis of the result analyses, contour maps are plotted depicting the concentration and distribution of the pollutants.

d. Analysis of soil samples consists of the following elements

i. Total 25 soil samples from the bottom layer of each auger hole are collected.

ii. The soil samples are digested and analyzed for total Iron, total Chromium and hexavalent chromium as mentioned before.

iv. In 20 soil samples, water soluble forms of oxalic acid and formic acid are analyzed in VIT.

v. On the basis of the result analyses, contour maps are plotted depicting the concentration and distribution of the pollutants.

4. Study area

4.1 Location

TCL is located in SIPCOT complex in Ranipet district adjacent to on Ranipet – Katpadi Highwayand is at distance of 4km from Ranipet town and District Head Quarters. The area of the SIPCOT Industrial Complex comprising of Phase I & II is 862.91 Acres. The site is accessible by road and the nearest railway station is Tiruvalam on Chennai- Bangalore B.G rail line. Ranipet district is one of 38 districts in Tamil Nadu, which is formed by trifurcating the district called Vellore. The Palar River flows through the Ranipet and Arcot border divisions. The geographical coordinates of the area are located between latitude 12.95520° and 12.95165° N and Longitude 79.31117° and 79.31205° E.

4.2 Physiography

The area is a sloping land with somewhat steep slope. The elevation in the north of the plant is 192 m M.S.L and towards south the elevation is 187 m above M.S.L. Thus, the there is a gradient of 5 m within 250 m. The general topographic slope of the watershed is NW to SE. The area falls under moderate to high rainfall zone, with average annual rainfall of 1,000 mm from southwest and northeast monsoons.

4.3 Geohydrology

The study area is just east of the confluence of Palar River with its tributary Ponnai River. A few lakes arelocated around the study area. Besides there are some minor streams running from NW to SE and joining Palar River. Palar River is running west to east and at the downstream of the industrial complex. The topographic slope is NW to SE as mentioned before.

Geologically the study area is covered by crystalline rock of Archaean granite with highly metamorphed gneissic complex as basement with secondary structures such as joints and fractures and intrusion of dolerite dykes and quartz Veins (*Sankaran et al 2010*). Presence of these formations generally controls the flow of groundwater and also influences the rate of recharge and discharge of the main aquifer units (*Bello and Makind 2007*). Soil cover is thin with thickness of 1 to 2m mostly alluvium consisting of fine to coarse sand and clay occurring in the area is of a fluviatile origin and restricted to the course of Palar river and major streams (*Subramanian and Selvan 2001*). Earlier study also reported the existence of a dolerite dyke just north of the study area and its direction of intrusion is across the strike of country rock (*Sankaran et al 2010*).

Hydro geologically, the area has good groundwater potential and the aquifers occur under both phreatic and semi confined conditions. The area is categorized ‘Semi-critical’ having groundwater development of 70- 90%. (CGWB 2020). The average annual rainfall of the study area is 938 mm.

4.4 Demarcation of the study area

In order to investigate the hydrogeological and geochemical properties surrounding to TCL, we have selected the sub watershed which consist of the specified industrial area (**Figure 2**) as, similar to the study carried out earlier by Sankaran et al 2010.

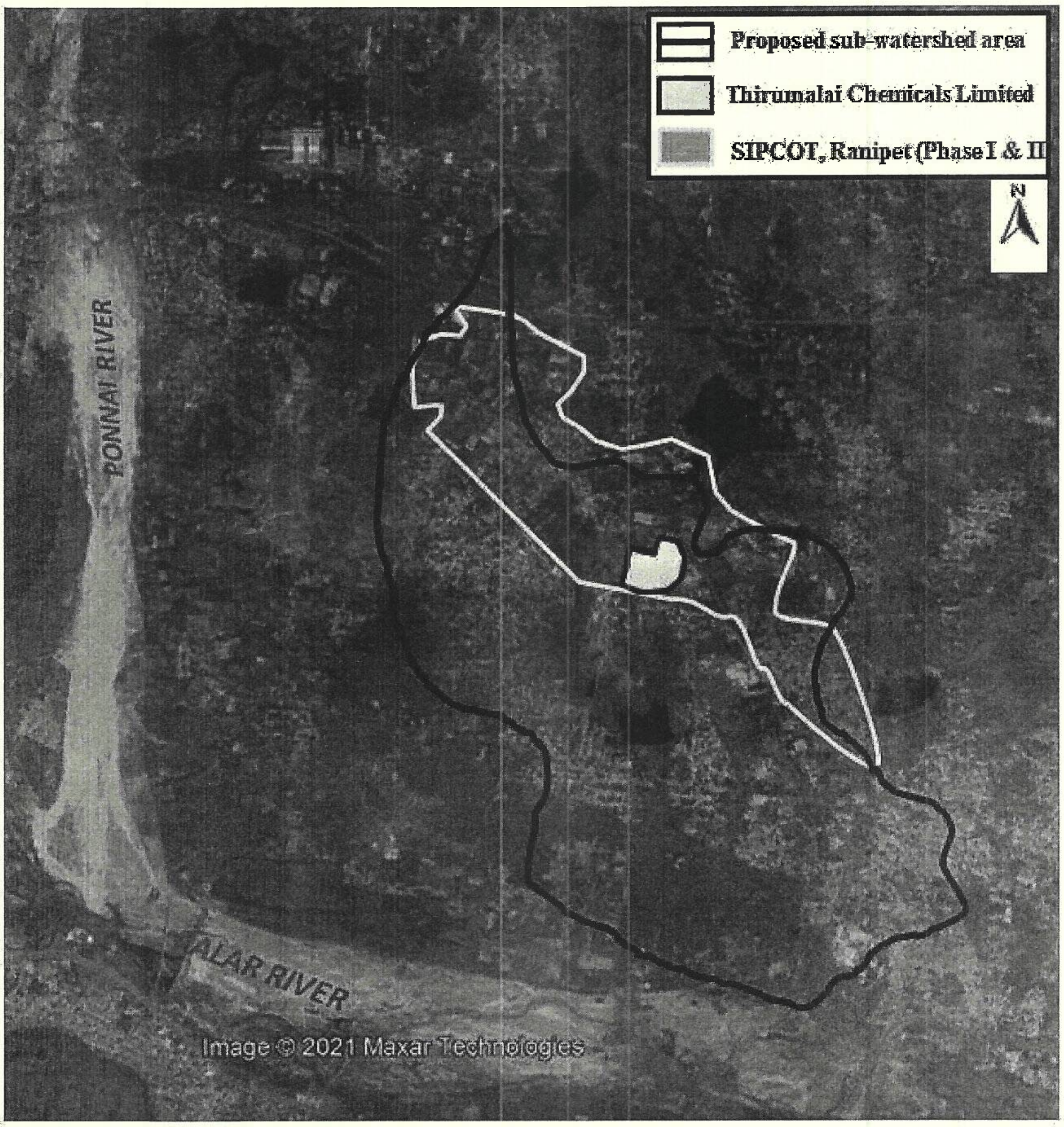

Figure 2: The proposed sub-watershed including SIPCOT area

The sub watershed is 17.3 sq. km, which fall under Ranipet district. A watershed is an area of land that contains a common set of streams and rivers that all drain into a single larger body of water, such as a larger river, a lake or an ocean. The study of watershed is essential for identifying the impact of the upstream on downstream side when developing and implementing water quality protection andrestoration actions.

This sub watershed area was further divided into 65 grids for sampling purpose (**Figure 3**). The approximate perimeter and area of each grid is 2 km and 0.25 km^2 respectively. The sub-watershed includes TCL and most of the SIPCOT area and having 41 big, medium and small industries. **Table 3** shows the industries situates in the study area along with their respective grid numbers.

Among the 65 grids the industries exist within 11 grids, the rest areas fall under other land use. This information was used while collection of the samples. We have concentrated those grids where numberof industries is more in upstream and downstream of TCL.

Table 3: Location of Industries with their Grid Numbers

Sl. No	List of Industries	Grid Number
1	Same Deutz-FAHR India	5
2	Greaves Cotton Limited, LEU II	5
3	Carborundum Universel Refractory Division	8
4	P A Footwear P Ltd., Tannery Division	8
5	Kaushik Leathers Pvt Limited	8
6	Sviss Labss Private Limited	8
7	Saroj Leathers (I) Pvt Ltd	8
8	ANS International	8
9	DMW CNC Solutions India Private Limited	8
10	Arjun Chemicals	8
11	Arasababu Associates	8
12	Kandha Enterprises	9
13	Hua Yao Moulds	9
14	Ram Leathers	9
15	BBK Shoes	9
16	Murugappa Morgan Thermal Ceramics Ltd	11
17	Surya Pelle Chemical & Mould (P) Ltd	12

Sl. No.	List of Industries	Grid Number
18	Lms Thamby & Co	12
19	Sarchem kimya Ranipet India	12
20	Karthik Steels	12
21	Bbk Leathers	12
22	Arrow Shoes Pvt Ltd	13
23	Maruthi Engg Works	13
24	Sun Paints	13
25	Alpa Lab Ranipet	13
26	Zeal Leathers	13
27	Balaji Oil Industries Pvt Ltd	13
28	Bluebird Overseas Pvt. Ltd	16
29	Chennai leather fashions	17
30	Shree Kamatchi fabrications	17
31	Tata International Limited (Bachi Shoes Division)	17
32	Ranipet SIDCO Finished Leather Effluent Treatment Company Ltd	17
33	Woodpack industries	17
34	Karas Polymer & Components	17
35	Astormueller Shoes (Pvt Ltd	18
36	United Foundries Private Limited	18
37	Cafoma Auto Parts	18
38	Thirumalai Chemicals Limited	23
39	Malladi drugs and pharmaceuticals	24
40	Ultramarine pigments limited	24
41	Euro Shoe Components Ltd	24

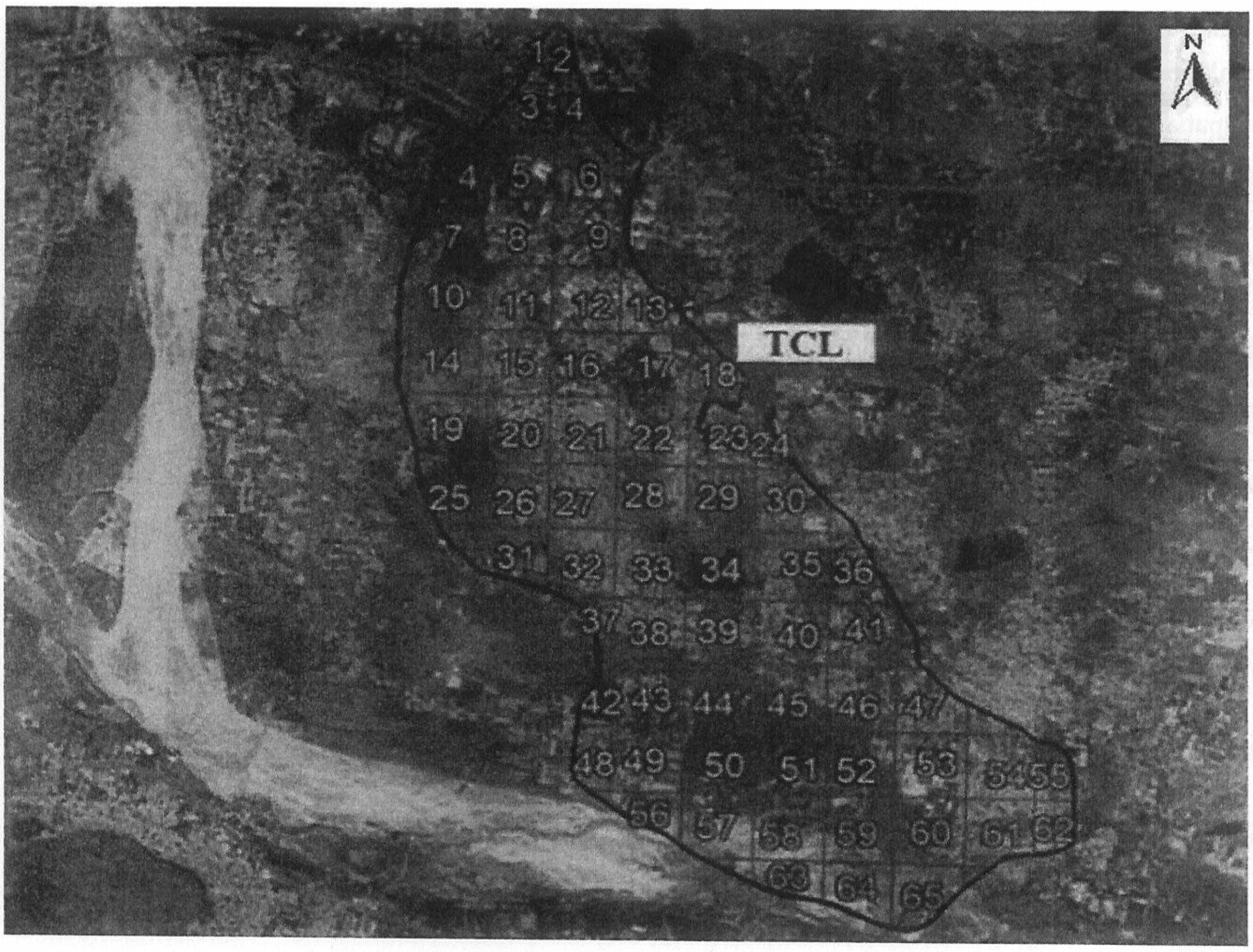

Figure 3: The specified watershed along with the grids

5. Methodology

5.1 Land Use Land Cover

The required images for the study of land use land cover changes of the location were obtained and downloaded from Bhuvan (https://bhuvan.nrsc.gov.in/home/index.php), the official site of NRSC for Geospatial analysis. The Sentinel – 2 image was downloaded of dated May, 2020 and 10 m resolution. During downloading as per standard protocol (*Vasconcelos et al., 2015*) the image was free of cloud cover for better clarity and applicability. Images were classified by visual interpretation. The initial land use land cover (LULC) types were classified into four basic and primary types which are settlements, vegetation, barren land and water bodies and the descriptions are shown in **Table 4**.

Table 4: Classification of Land use Land cover

Land use/Land cover types	**Description**
Settlements/Built up area	Residential, commercial and industrial services, transportation network, socio-economic infrastructure and urban and rural settlement.
Vegetation / Cultivated land	Agricultural area, crop fields, cultivated area and vegetable lands.
Barren land/ Uncultivatedland	Exposed soils, open fields, landfills, sand fill areas.
Water-bodies	River, lakes, ponds, perennial water bodies and reservoirs.

5.2 Contour and drainage flow

A contour map is a map illustrated with contour lines, for example a topographic map, which thus shows valleys and hills, and the steepness or gentleness of slopes. The contour interval of a contour map is the difference in elevation between successive contour lines. The contour map can be extracted from topographic map available from Geological Survey of India (GSI) or satellite image through Digital Elevation Model (DEM).

The drainage may be natural or man-made. Based on the geological position, natural drain flow takes places. There are two types of drainage i.e. Surface and sub-surface drainage. The surface drainage is categorized into natural drainage and man-made drainage. The surface drainage depends upon the slope of the ground which can be observed/ extracted from the topographic map. The drainage map can be plotted with the helpof satellite image in co-ordination with field investigation.

In the present study the base map was taken from Topo Sheet 57P5 which is overlaid on the drainage network identified from the field survey with the help of Global Positioning System (GAR-MIN ETrex 10) in Q-GIS.

5.3 Vertical Electrical Sounding

In order to understand the sub surface geological, geophysical and hydro-geological features surrounding to TCL, the Vellore Institute of Technology (VIT), Vellore conducted Vertical Electrical Sounding (VES) study in the specified sub-watershed area. This task was assigned to M/s Geonix, with the concurrence of TCL, Ranipet.

The primary objective is to study the variations and pattern of depth to base rock and its characteristics inside SIPCOT Industrial area, with special emphasis on TCL. More specific objective is to study the level of contamination and to assess the direction of flow of contaminant groundwater, if at all it is established.

The whole study is divided into three major components.

A. Geophysical investigation by Vertical Electrical Resistivity Sounding method to determine the spatial variations of electrical resistivity in the subsurface earth layers in order to infer hydrogeological and hydro-chemical characteristics.

B. Drilling auger holes manually using spiral/bucket auger till top of hard strata to obtain the soilsamples and to collect groundwater samples for further analysis in the laboratory.

C. Conducting in-situ permeability test using falling head method as per BIS procedure and with due modification to suit the geology and the water table.

The principle and methodology of the VES study is included in **ANNEXURE I**.

5.4 Auger drilling

The hand auger drilling process is one of the oldest and most fundamental ways of low-cost labor-intensive well drilling. Augers used for soil drilling are two types, one is helix or spiral auger and another bucket auger. Diameter of these will be 4 inches to 6 inches depending on the objective of drilling. The drilling operation in hand auguring is performed by manually turning a cutting blade or auger. When the drilling continues, the auger fills with soil and must be raised to the surface and drained on a regular basis. For thefirst few feet, this method of drilling is relatively fast. The number of drill rod parts that must be coupled and uncoupled each time the auger is brought to the surface after that significantly increases the drilling time. A hand auger rig's basic components are a support tripod, drill rod, auger handle, auger, sand bailer, temporary casing to case hole from caving soil, and drill bit to part ways hard soil and rock formations. Depending on the type of soil, the drilled hole will normally get retained without any support. However, in some highly sandy soils or if there is a pressure from water table, there is a likelihood of the drilled hole tocollapse. In such case a supporting casing is inserted during drilling and will be pushed further down as thedrill progresses. At the end of such drilling using a casing pipe, either the casing can be retained or pulled out.

In the present study total 25 points were considered for auger drilling with anticipated depth to be 2 to 4m using Hand auger Rigs. Soil samples were collected at 0.5 meter intervals based on the drilling depth at each location. The drilling procedure is repeated until the auger comes into contact with hard rock or weathered rock fragments.

5.5 Permeability testing

The rate of flow of water, under laminar flow conditions, through a unit cross sectional are of soil mass, under unit hydraulic gradient, is defined as coefficient of permeability. The coefficient of permeability is used to assess drainage characteristics of soil, rate of consolidation and to predict rate of settlement of soil bed.

The BIS Document for in-situ soil calculation in uncased wells is used to estimate permeability. The fundamental concept and methodology of the permeability test in included in **ANNEXURE II**.

This approach implies that the well is uncased, and that the region of concern is separated by placing a packer over it to prevent water from leaking into other areas. Via the packer, a smaller diameter intake pipe is inserted into the testing zone. Water is pumped into the well through the intake pipe until the head rises well above the average water level. The drop in water level is calculated using a time-based method, and the data is then analyzed using an algorithm.

Since an uncased structure will collapse if it is not supported by a covering, the test was conducted in a well with screens rather than an uncased structure in this case. Since the slotted pipes are used against the test site, it functions similarly to an uncased zone, allowing water to flow freely horizon-tally. Similarly, due to the restricted thickness of the trial region, the intake pipe was not used. The equation's necessary parameters are adjusted accordingly.

In the present study the horizontal in-situ soil permeability of the top soil zone between Ground Level to 1.70 m were determined in two points near TCL.

5.6 Collection and analysis of soil and water samples

5.6.1 Soil samples from Auger points

Approximately 500 g of soil samples were collected at 0.5 metre intervals based on the drilling depth at each auger points in 25 different locations. After the collection of the soil sample they were packed in a zip lock pouch, and given a tag and transferred to Environmental Engineering Laboratory in VIT. All the samples were air dried, homogenized with a pestle, passed through a 2.36mm sieve kept in zip lock pouches. Among the samples collected from different depths, the sample collected from the maximum depth from each auger location were considered for analysis. As a result, 25 soil samples were consideredfor analysis. The **Figure 4** shows the framework for the analyses of soil samples

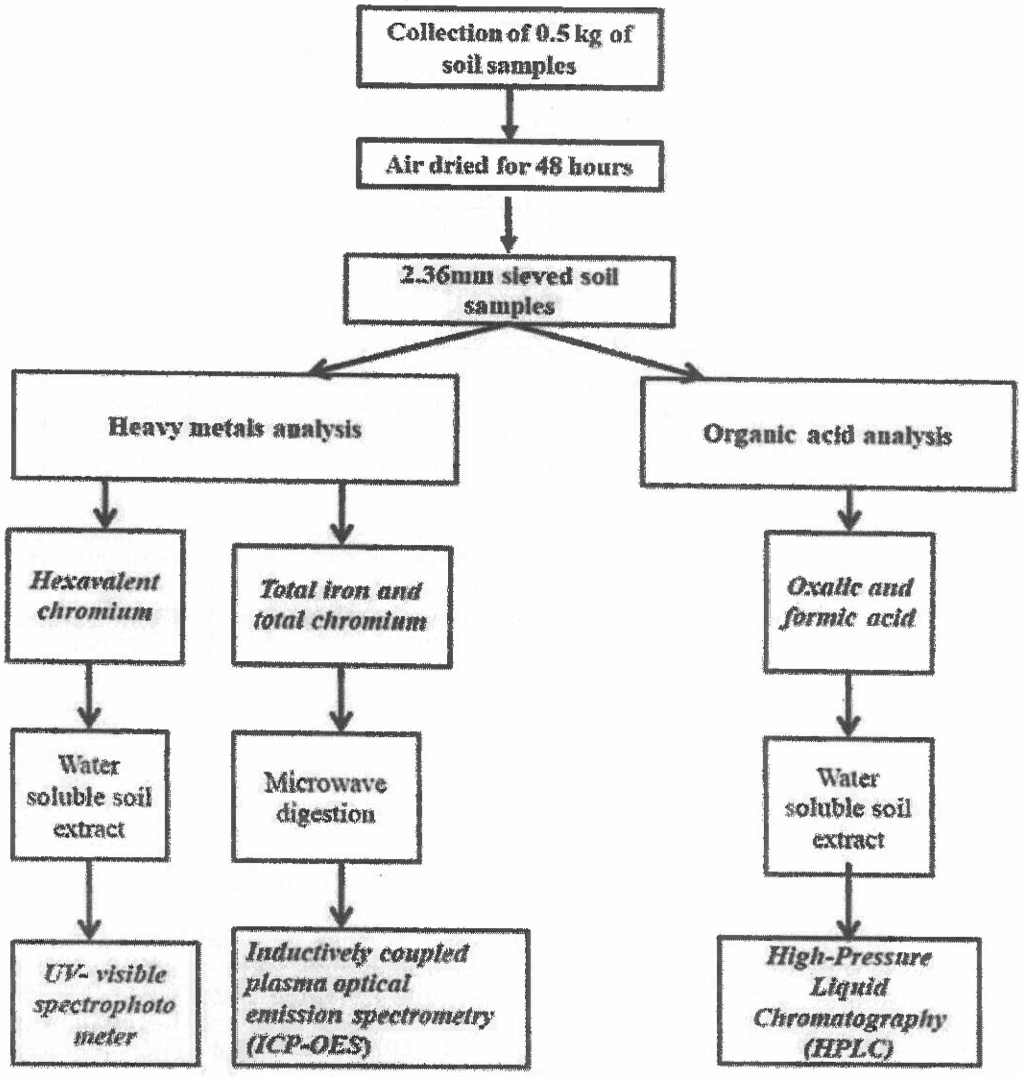

Figure 4: Framework for the analysis of soil samples

5.6.2 Collection of water samples

Water samples were collected from the study area for analyses of different physiochemical parameters (pH, Conductivity, Turbidity, Total alkalinity, Total Hardness, Chloride and Sulphate), total Cr, total Fe, hexavalent Cr, Oxalic acid and Formic acid. Properly cleaned, high-quality new plastic (polyethylene) containers were used for water collection and storage. All the available sources of water samples were considered for the sampling including auger holes, natural and artificial drains, surface water sources, borewell samples, and piezo metric wells inside TCL.

Various procedures and conditions were adopted for water analysis, depending on the criteria as-sessed which mentioned in (**Figure 5**). In terms of the parameters being investigated, samples were processed prior to preservation as mentioned in **ANNEXURE III**

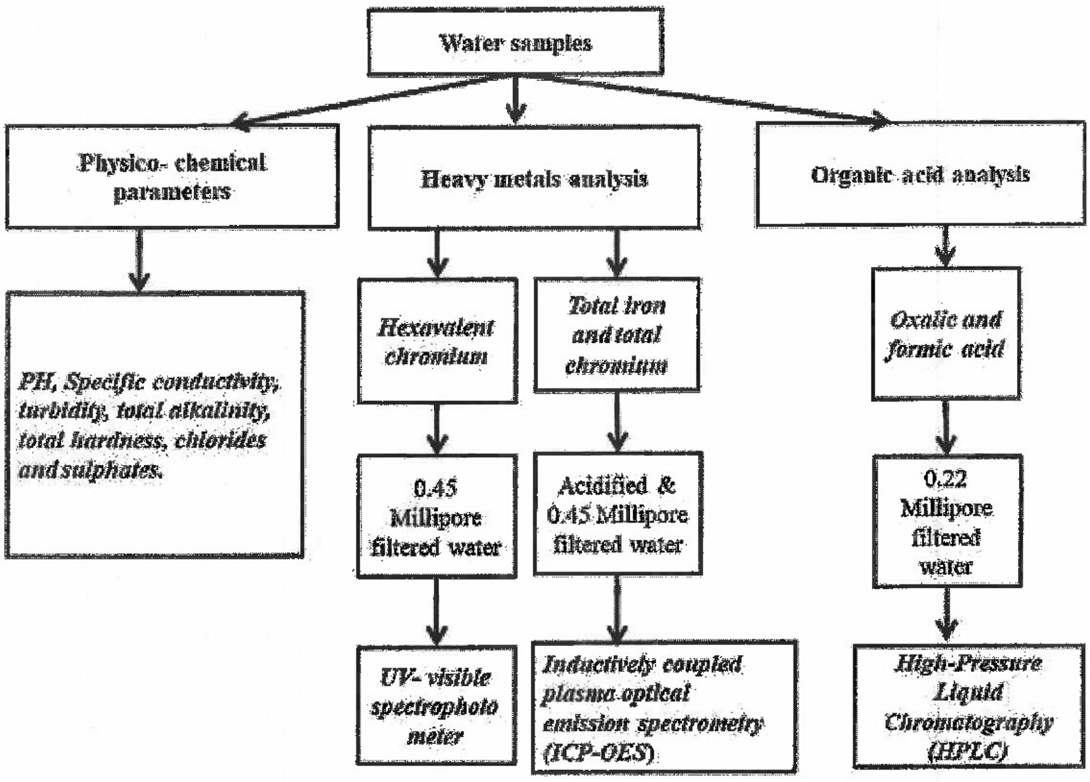

Figure 5: Framework for the analysis of water samples

5.6.3 Extraction of water- soluble fractions from the soil samples

This process of soil extraction is common for water soluble metals and organic acids (Lawongsa et al 1987; Wolf & Wilson 2010). Parameters such as oxalic, formic acid and hexavalent chromium are readily soluble in ultrapure water. At a ratio of 1:5 soil and ultrapure water was taken in a centrifuge tube. Initially the tubes kept in an orbital shaker at 30 RPM for 1 hour. Then the containers were subjected to centrifuge at 5000 RPM for 20 minutes. Finally, the centrifuge tubes were collected and the supernatants was filtered by 0.45 Millipore paper and refrigerated at 4⁰ C. Here the samples are ready for Hexavalent chromium and oxalic and formic acid analysis. The **ANNEXURE IV** shows theinstruments related to the extraction.

5.6.4 Hexavalent Chromium analysis (Cr^{6+})

Since Cr^{6+} is readily soluble in ultrapure water, the soil extracts are filtered and available for UV- Visible spectrophotometric analysis. Merck spectroquant Chromate test kit (ISO 8466-1) was usedfor the hexavalent chromium analysis in UV-Vis spectrophotometer. The method is analogous to APHA 3500-Cr D and DIN 38405-24. The reagents, procedure and analytical quality assurance is provided in **ANNEXURE V**.

5.6.5 Total Iron and Total Chromium analysis

Analysis of total chromium and iron in the soil samples have been done in Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES, Avio-200, Perkin Elmer) followed by microwave digestion (Multiwave Pro 24-HVT50, Anton Paar) as per USEPA 3051A method as mentioned below. Approximately 0.25 g of samples are transferred into Teflon vessels; 6 ml Hydrochloric acid and 2 ml Nitric acid was used as aqua-regia. The blanks and standard reference material (SQC-001, Sigma-Aldrich, Spain) were also subjected to same conditions for quality control. The conditions maintained in the digester are mentioned in the **ANNEXURE VI**. After digestion, Teflon vessels were carefully opened under fume hood, transferred to vacuum filtration unit, filtered through Millipore 0.45 µm filter paper; filtered samples were refrigerated at 4°C in sterile sample containers prior to analysis. The operational parameters of ICPOES are mentioned in the **ANNEXURE VI.** In the **ANNEXURE IV** the ICPOES is shown.

5.6.6 Oxalic and Formic acid analysis

The Oxalic acid and formic acid have been analyzed with C18 column with PDA detector (ACQUITY UPLC$^+$ H CLASS - WATERS). In the present study the oxalic and formic acids are extracted in UHPLC with Sep-pak C18 column and analysed with PDA detector. The method adopted is as per *Lawongsa et al 1987*. The soil extract obtained can be used to test for oxalic and formic acid in soil samples. Water samples and extracted water soluble samples was purified into a 0.22 µm syringe filter before being analysed in HPLC. The HPLC/MS grade standards for oxalic acid and formic acid were procured from Sigma Aldritch and Fisher Chemicals respectively to run for the initial standard peak observations (**ANNEXURE VII**). Mobile phase used for oxalic acid were 0.01N H_2SO_4 and ultrapure water for formic acid.

5.7 Quality Control

The quality control plays an important role for authenticating the result. We have ensured the quality of the analysis by the following ways,

a) For all the analysis purpose (preparation of standards and reagents, dilutions, extraction and digestion) ultrapure water has been used (Ultra-Pure Water System PALL CASCADA III.I).

b) All the instruments for the analysis of pH, conductivity meter, turbidity meter, UV Spectrometer were calibrated as per IS3025 prior to the analysis.

c) For the analysis of total alkalinity, total hardness, chloride, and sulphates, standard solutions are prepared for the standardization purpose as per IS3025.

d) All the samples for heavy metals in ICP-OES were measured in triplicates. Multi-elemental standards of Perkin Elmer were utilized for obtaining calibration. Two method blanks were also used for a batch of 24 samples. The accuracy in the analysis was assessed by using certified reference material (SQC-001, Sigma-Aldrich, Spain) (**ANNEXURE VII**) and the recovery rate was observed and reported.

e) At least two water and soil samples are sent to other reputed laboratories (NABL & IIT) with the aim of evaluating the extent of similarity in the results obtained by different laboratories using the same method. The parameters considered for this purpose were Total Cr, Total Fe, hexavalent chromium, Oxalic and Formic Acid.

6. Results & Discussions

6.1 Land Use Land Cover

The land use land cover (LULC) map of the study area shows (**Figure 6**) that the industrialization and occupational shift are to be the most influential drivers of LULC dynamics.

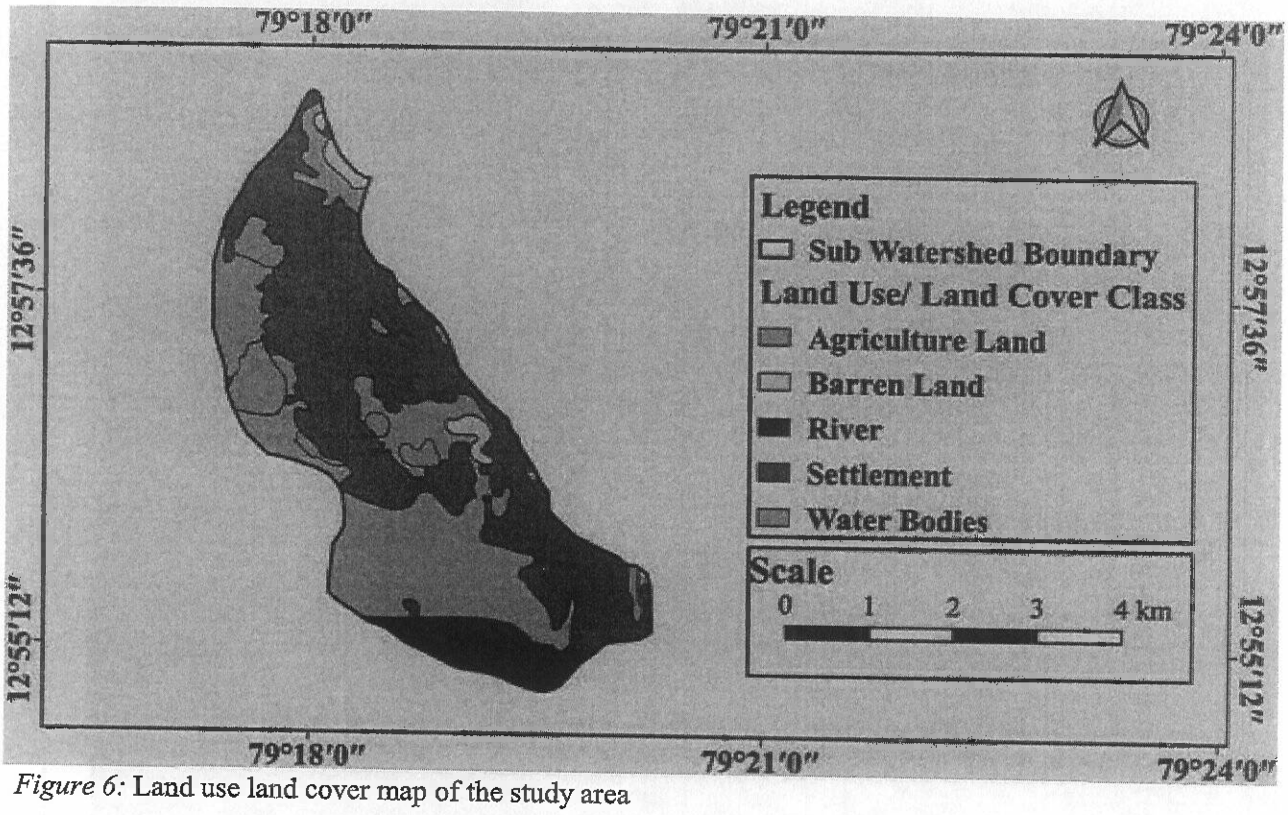

Figure 6: Land use land cover map of the study area

More than 50% of the area covers with settlement which includes industry and urban development. From the site investigation it has been observed that most of the industries are situated in the Northern side of the study area. This area is under SIPCOT.

6.2 Contour & Drainage Network

The contour map of the study area is shown in **Figure 7**. The figure clearly shows the slope of the land is ~~from.~~ NW to SE. Hence the flow in the drainage will be-in the same direction. During the preliminary investigation it has been observed that the most of the drainage are artificial and carries partially treated and untreated industrial effluent. They generally end up in the water bodies and Palar river basin in the south. The physiochemical analysis of water and soil samples have been done to identify the characteristics and magnitude of pollution caused by these surface flows to the surrounding area. **Figure 8 (a) & (b)** shows the direction of the natural and artificial drainage in the study area along with the locations of water samples.

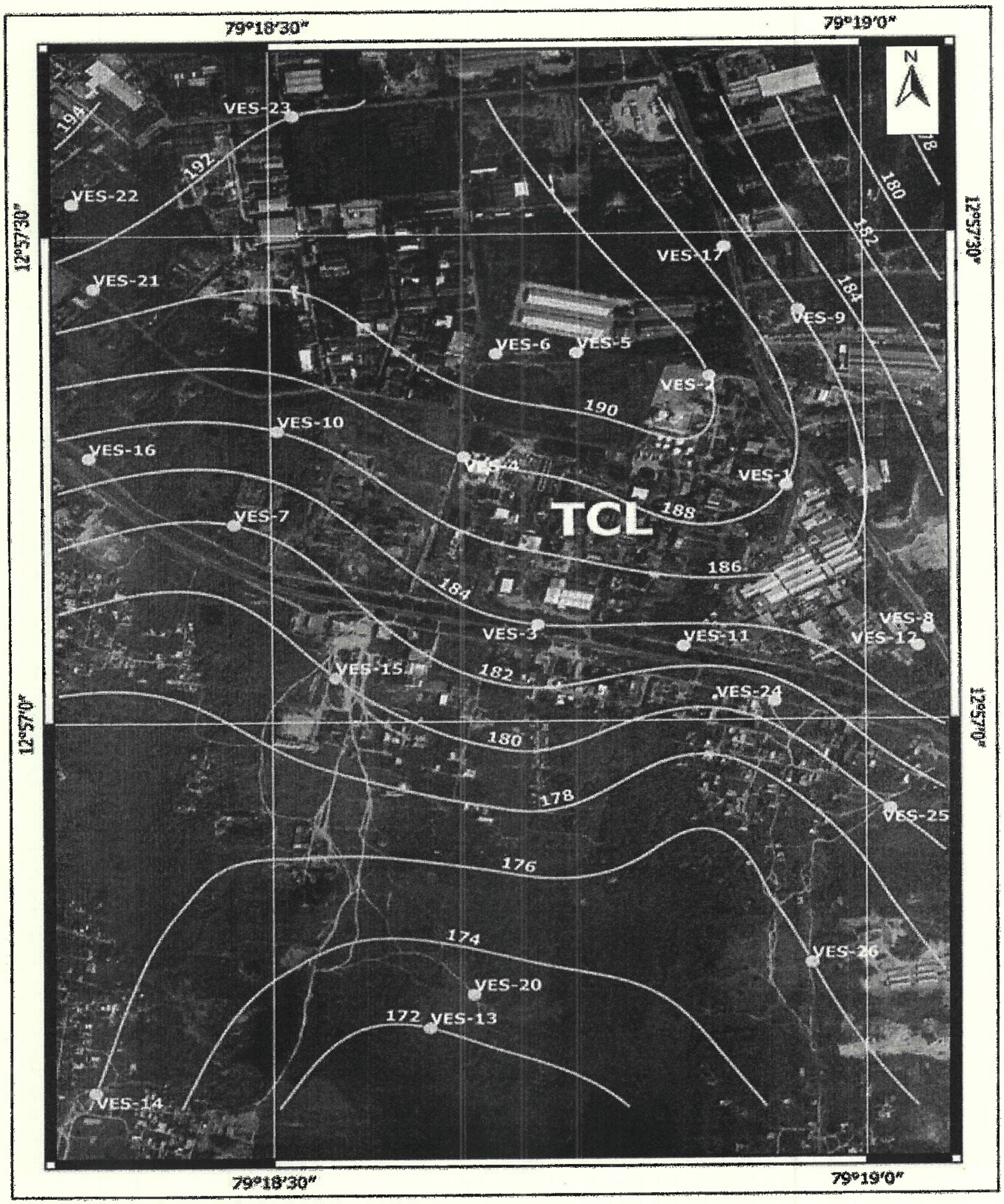

Figure 7: The elevation contour line of the study area

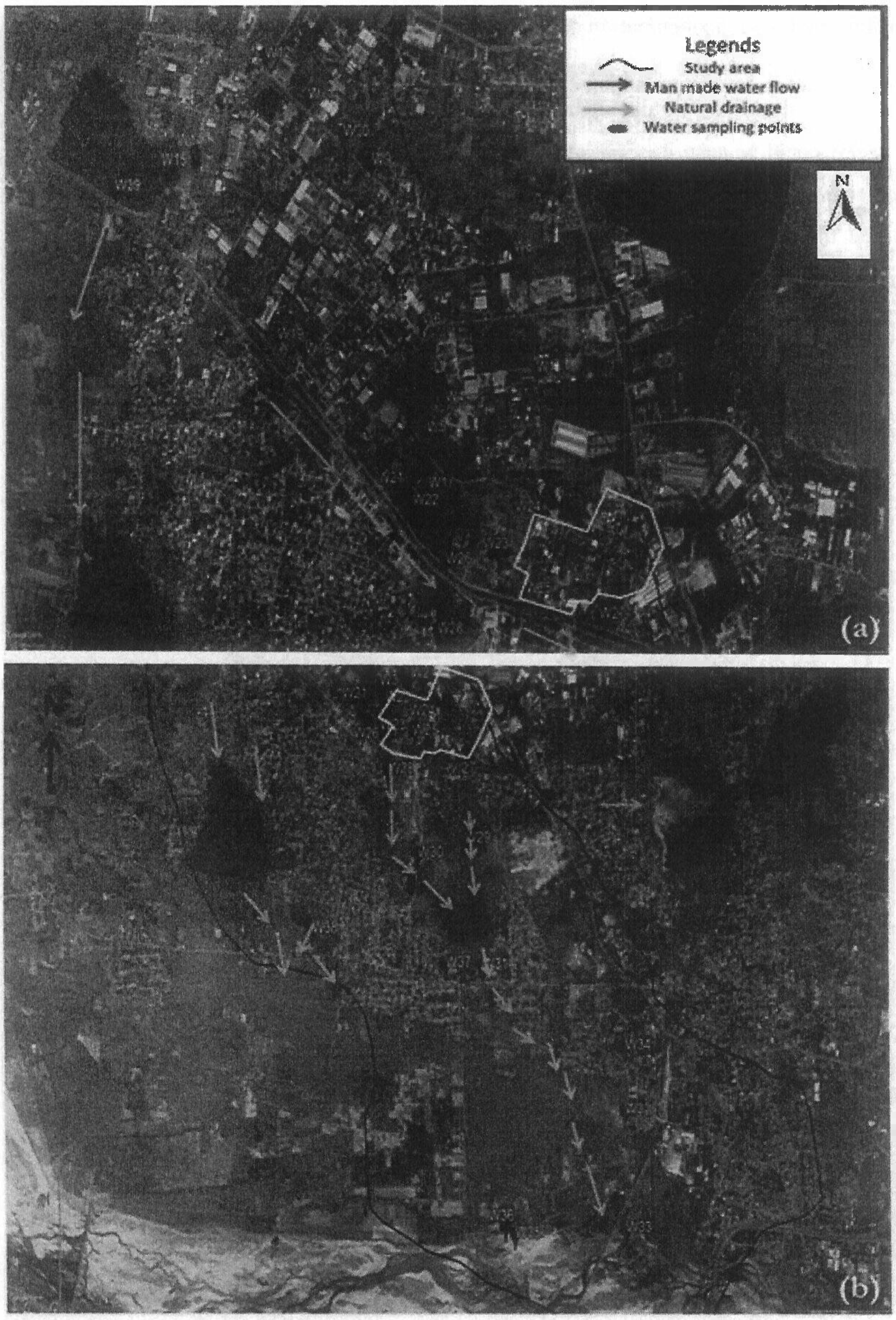

Figure 8: *The drainage direction and the locations of the water samples in the study area (a) SIPCOT area (b) Southern area*

6.3 Groundwater flow discussion:

6.3.1 Groundwater level information

Whenever information on contamination of groundwater is to be assessed, the groundwater levels in the area, and the groundwater flow direction shall be the two essential parameters besides the soil/rock characteristics like its permeability. Incidentally the study period being post monsoon and the water levels could be seen in some of the auger holes, where the soil thickness is more or the location of some holes is at lower terrain elevation. Water levels from BGL in such holes are measured and the levels are represented in a contour map which is presented in **Figure 9**. The direction of the flow is also approximately shown in the figure.

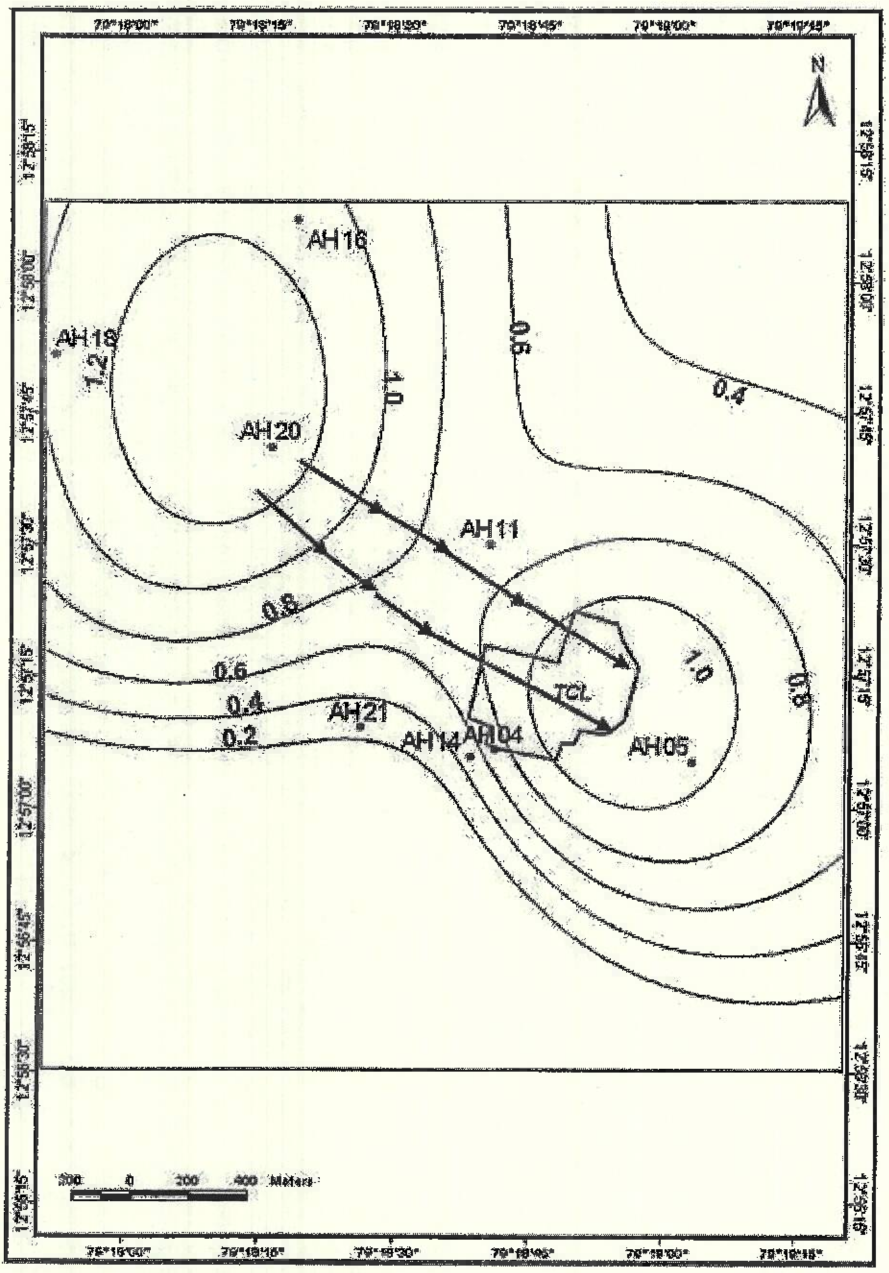

Figure 9: Groundwater level contours with reference to ground level

In order to obtain the water table data, the groundwater levels from ground level are reduced to a M.S.L valuesobtained using the google maps. In order to make the results more reliable and relevant, the groundwater levels obtained from eight monitoring wells of TCL are also considered. This integrated water level data from auger holes and monitoring wells is shown in **Table 5**.

Table 5: Water level data from auger holes and piezometers

WELL ID	LAT	LONG	W.L b.g.l (m)	DATE OF SAMPLING
AH-01	N 12.95576	E 79.30893	0.97m	28.01.2021
AH- 04	N 12.95173	E 79.31187	0.70m	28.01.2021
AH- 05	N 12.95144	E 79.31756	1.06m	28.01.2021
AH- 11	N 12.95833	E 79.31136	0.76m	29.01.2021
AH- 14	N 12.95160	E 79.31074	0.50m	30.01.2021
AH- 16	N 12.96857	E 79.30530	1.11m	30.01.2021
AH- 18	N 12.96433	E 79.29784	1.05m	31.01.2021
AH -21	N 12.95251	E 79.30729	0.26m	31.01.2021
US1	N 12.9539	E 79.31554	1.40m	25.01.2021
US2	N 12.9544	E 79.3137	1.40m	25.01.2021
US3	N 12.9549	E 79.31211	1.09m	25.01.2021
US4	N 12.9551	E 79.31133	0.46m	25.01.2021
DS2	N 12.95198	E 79.31131	2.88m	25.01.2021
DS3	N 12.95176	E 79.31232	1.78m	25.01.2021
DS4	N 12.95154	E 79.31316	2.23m	25.01.2021

The reduced groundwater level which is called water table is plotted in the form of contours on the map. The map is presented below. The groundwater flow direction as observed from this water table contour map is alsoshown with arrows (**Figure 10**).

The groundwater flow direction as derived from this map is from NW to SE and North to South.

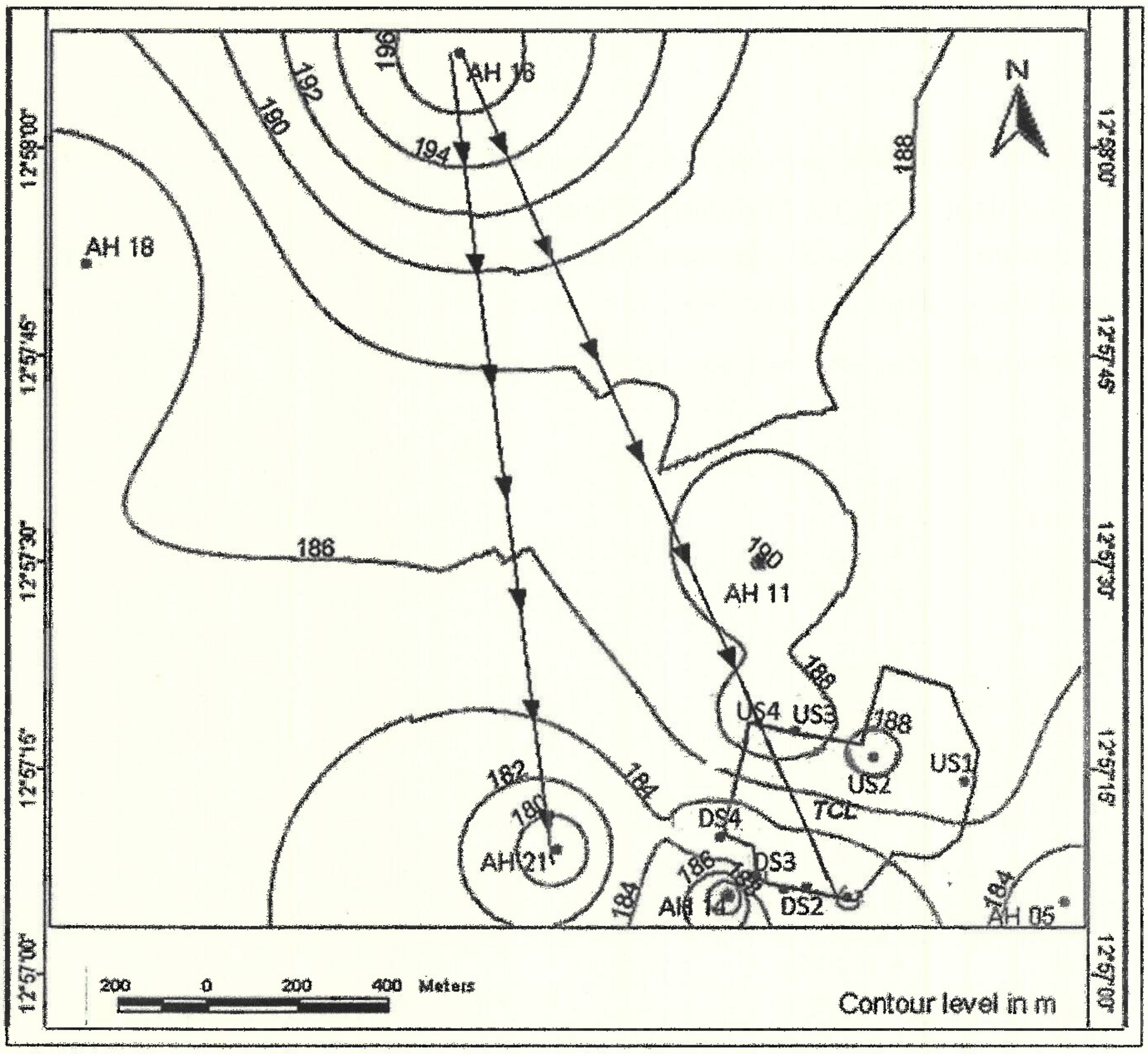

Figure 10: Groundwater level contours reduced to M.S.L

6.3.2. Groundwater velocity (Permeability Tests):

The permeability test is conducted in two points to estimate the groundwater flow and horizontal co-efficient ofsoil permeability of the top soil zone between Ground Level to 1.70m. The first point was AH1 (auger hole point 1) near the CETP pool and the second points was 2 m from AH 13 (auger hole point 13) inside TCL. The concept methodology and steps involved of the permeability test is mentioned in **ANNEXURE 2.**

In the following section the experimental data, result and inferences of the permeability values of the two pointsis being discussed.

Sample ID - PT01 (AH01)

Augar Hole Depth BGL:
2.30mStatic water level
BGL - 1.10m
Length of casing pipe below GL:
2.03mLemgth of plain casing: NIL
Length of screen pipe B.G.L:
2.03mStatic Water Level BGL:
0.97m
Pre Test Structure
Total casing pipe.
3m
Length of plain casing A.G.L: 0.97m
Diameter of casing pipe (both plain & Screen): 100mm Static WL (from T.O.C)
– 1.94mWL after filling (from T.O.C): 1.30m

Time since pumping started (min)	Depth of water level from measuring point (m)
0	1.30
0.36	1.50
1.30	1.60
2.52	1.70
5.10	1.80
9.26	1.90
17	1.95
30	1.98
40	1.99
50	2.00
60	2.00
70	2.01
80	2.01
90	2.01

From the above information the calculated Coefficient of permeability (K) =0.00508812 cm/minute =7.3268928 cm/day =0.073268928 m/day.

Sample ID -PT02 (Near AH13)

Augar Hole Depth BGL: 1.17m Static water level BGL – 0.64m Structure details

Length of casing pipe below GL : 1.17mLength of plain casing: NIL

Length of screen pipe B.G.L : 1.17mStatic Water Level BGL: 0.64m

Pre Test Structure

Total casing pipe. 2.17m

Length of plain casing A.G.L: 1.0m

Diameter of casing pipe (both plain & Screen): 100mm Static WL (from T.O.C) – 1.64mWL after filling water (from T.O.C): 1.24m

Time in minutes since pumping started	Depth of water level from measuring point in m.
0	1.24
1.01	1.50
2.30	1.55
9.40	1.60
15	1.61
20	1.62
30	1.63
40	1.63
50	1.65
60	1.67
95	1.64
120	1.64
125	1.64

From the above information the calculated Coefficient of permeability (K) =0.003837766 cm/minute =5.526382431 cm/day = .05526382431 m/day.

The calculation of both the analyses are shown in **ANNEXURE 2.**

The hydraulic conductivity of the present study area is measured to be at the range of 6.4 – 8.5 x 10-7 m/sec,which is high compared to other studies on fractured rock of 0.84 – 3.64 x 10-7 m/sec (Shahbazi et al 2019).

6.4. Geophysical investigation and interpretation of the subsurface strata through Vertical electrical Sounding (VES)

6.4.1 Objective

The chief objective is to study the variations and pattern of depth to base rock and its characteristics around the industrial units located in SIPCOT Industrial area, with special emphasis on Thirumalai Chemicals Ltd. More specific objective is to study the vertical variations in electrical resistivity of subsurface earth layers which in turn can be inferred in terms of their hydrogeological and hydro-chemical characteristics like possible contamination and to the direction of flow of contaminant groundwater, if at all it is established.

6.4.2. Procedure adopted in the present study

Totally 26 numbers of Vertical Electric Soundings (VES) were conducted covering theimmediate vicinity of the premises on all the directions in two phases within one month apart.Most of these sounding locations fall in the SIPCOT industrial area where there are several water-based industries from which movement of contaminant fluids can be suspected to flow downstream crossing the premises of TCL.

The locations of the 26 VES test sites located in the google map is shown in **Figure 11**. Sincethe depth requirements were less, the apparent resistivity data was analyzed using both by in- version technique using software IP WIN and also by Inverse Slope Method. However, the Geo-electric layer parameters like, thickness of layers and their resistivity values obtained from inversion technique were used for preparing the various maps. The geological inference drawn from the resistivity data through the interpretation using IPWIN are presented in **Table 6.**

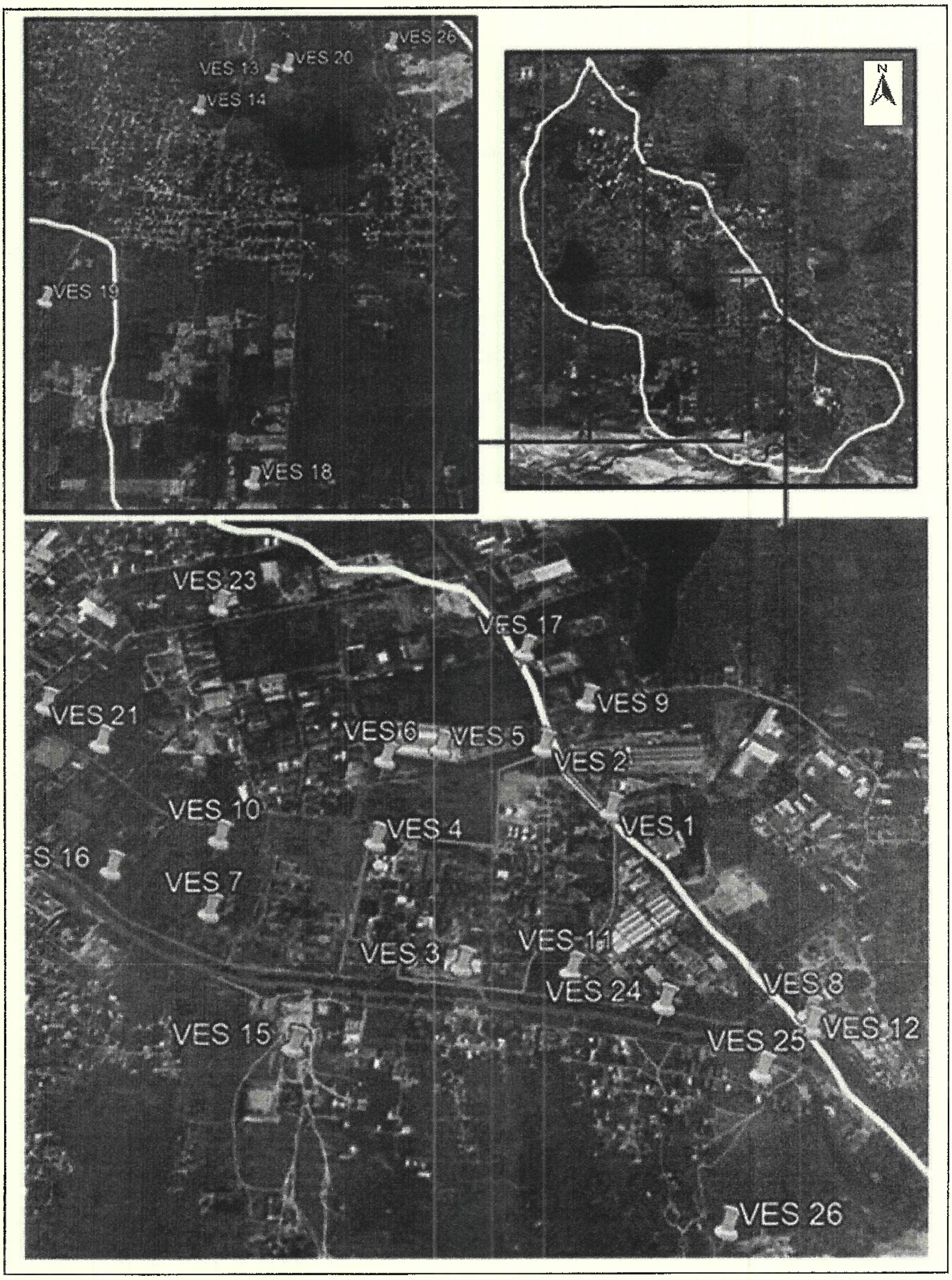

Figure 11: Locations of the VES points

Table 6: Geo-electric parameters and Lithological inferences from IP WIN interpretation

VES No.	Depth	Resistivity	Geological inference*	Grid/Location
1	0.75	9.52	Top Soil Contaminated	24/Western side of TCL
	2.19	4.2	Highly contaminated soil	
	19.30	51.4	Weathered rock contaminated	
		245	Fractured rock –May be contaminated	
2	0.75	6.14	Top Soil Contaminated	18/Northern side of TCL
	2.19	1.42	Highly contaminated soil	
		1788	Hard Rock-Compact	
3	0.75	67	Top Soil Sandy	23/Southern side of TCL
	2.12	30	Weathered rock contaminated	
	5.97	42.8	Weathered rock contaminated	
	16.90	28.5	Fractured rock- contaminated	
		42.6	Fractured rock –contaminated	
4	0.75	122	Top Soil –Transported	23/Southern side of TCL
	7.82	27.2	Weathered rock- Contaminated	
	25.30	3.52	Weathered rock- Contaminated	
		1491	Fractured Hard Rock	
5	0.75	827	Dry Sand	18/Northern side of TCL
	2.31	420	Hard rock Boulders?	
	7.14	806	Hard Rock less fractured	
	22.00	330	Fractured rock	
		455	Fractured rock	
6	2.68	518	Dry Sand	18/Northern side of TCL
	9.54	199	Weathered rock	
		607	Fractured rock	
7	0.78	92.3	Dry Sand	22/Western side of TCL
	1.04	27.3	Contaminant soil	
	11.40	87.2	Contaminant weathered rock	
		378	Fractured rock	
8	1.17	122	Top Soil Dry	24/Eastern side of TCL
	13.9	38.1	Contaminant soil or weathered rock	
		223	Fractured rock	

VES No.	Depth	Resistivity	Geological inference*	Grid/Location
9	0.88	2.89	Contaminant soil	18/Northern side of TCL
	9.68	19.2	Contaminant soil/W.R	
		7729	Had rock	
10	0.75	261	Dry top soil sandy	22/ Western side of TCL
	5.45	24.6	Contaminant soil/Weathered rock	
	33.30	72.6	Contaminant fractured rock	
		275	Fractured/Hard rock	
11	0.75	16.7	Contaminant soil	23/ Southern side of TCL
	19.40	41.7	Contaminant weathered rock	
		9265	Had Rock	
12	0.75	32.2	Contaminant soil	24/ Eastern side of TCL
	3.53	23.6	Contaminant soil/weathered rock	
	21.40	66.4	Contaminant weathered rock	
		278	Fractured rock	
13	1.64	89.1	Top Soil	29/Southern side of TCL
	6.21	49.4	Contaminant weathered rock	
	32.30	256	Fractured rock	
		12600	Hard rock	
14	2.48	60.7	Top Soil	33/South western side of TCL
	32.10	83.3	Fractured rock with impact of contamination	
		11910	Massive Hard rock	
15	0.75	116	Top Soil Sandy	22/Western side of TCL
	8.16	28.3	Contaminant soil/weathered rock	
		236	Fractured rock with certain degree of contamination	
16	0.75	71	Top Soil sandy	22/ Western side of TCL
	2.12	42	Weathered rock- Contaminated	
	16.9	52.6	Fractured rock contaminated	
	47.60	28.9	Fractured rock contaminated	
		351	Less fractured hard rock	
17	0.88	85.6	Sandy soil	18/ Northern side of TCL
	14.30	18.1	Weathered rock contaminated	
		4631	Compact hard rock	

VES No.	Depth	Resistivity	Geological inference*	Grid Number
18	0.75	101	Sandy soil	49/Southern side of TCL
	16.90	22.2	Fractured rock contaminated	
		288	Fractured rock	
19	0.75	4.66	Highly contaminant soil	42/South Western side of TCL
	2.12	0.982	Highly contaminant soil	
		567	Compact hard rock	
20	0.76	80.7	Sandy soil	29/Southern side of TCL
	9.31	40.3	Weathered rock- Contaminated	
		395	Fractured rock	
21	0.84	1045	Dry sand/Transported material	17/North Western side of TCL
	6.14	152	Fractured rock with certain degree of impact from contamination	
	16.00	22	Contaminant fractured rock	
		186	Fractured rock-Contaminant?	
22	0.75	89.4	Sandy soil	17/ North Western side of TCL
	18.70	29.3	Contaminant weathered rock	
		874	Hard rock with limited fractures	
23	0.88	318	Dry Sandy soil	13/ North Western side of TCL
	21.30	54.6	Weathered rock with certain degree of contamination	
		974	Hard rock with limited fractures	
24	2.12	22.2	Sandy soil	24/South Eastern side of TCL
	5.98	26.7	Weathered rock with contamination	
		378	Fractured rock	
25	0.77	71.6	Sandy soil	30/ South Eastern side of TCL
	26.10	30.7	Contaminant fractured rock	
		4846	Hard rock	
26	1.00	173	Dry Sandy soil	30/ South Eastern side of TCL
	5.17	99.9	Contaminant fractured rock	
		938	Hard rock	

* *The contamination with respect to different rock formation is mentioned inANNEXURE I*

On the basis of the above, the thickness soil, weathered rock, fractured rock and depth to hard rock where ever inferred is presented in the table below (**Table 7**). The probable zones of contamination are also arrived at and noted.

Table 7: Possible zones of contamination

VES No.	Soil thickness m	Bottom of Weathered rock bottom m	Bottom of Fractured rock/Top of hard rock m	Contaminant zones
1	2	17	Not inferred	S &W. R
2	2		2m and below	Soil
3	0.5	14	Not indicated	S, W.R & F. R
4	0.5	8	25.3m	W. R
5.	3	16	Not indicated	NIL
6	2.5	13	Not indicated	NIL
7	1.5	7	Not indicated	S & W. R
8	1.5	8	Not indicated	W.R
9	2	4	Below 4m	S & W. R
10	3	23	9.68	S, W.R, F. R
11	1.5	9	19.4	S & W. R
12	2	8	Not indicated	S, W.R
13	2	6	32.3	W.R
14	1.5	-	32.1	F.R
15	1.5	10	Not indicated	S,W.R, F.R
16	0.8	2	Not indicated	S,W.R,F.R
17	1.0	13	14.3	W.R
18	1.0	17	Not indicated	F.R
19	2.0	-	2m	S
20	0.8	9	Not indicated	W.R
21	0.8	7	Not indicated	F.R
22	0.8	18	18.7	W.R
23	0.8	4	21.3	W.R
24	2.1	6.0	Not indicated	W.R
25	0.75	-	26.1	F.R
26	1.0	5.0	5.0	F.R

Notation: *S-SOIL, W.R- WETHERED RROCK, F.R-FRACTURED ROCK, H.R- HARD COMPACT ROCK*

The field data mentioned in the previous tables for each VES locations have been interpreted to find the apparent resistivity (ρ_a) at different depth by Inverse Slope Method for each VES points is presented in **Table 8.**

Table 8: Geo-electric layer parameters from Inverse Slope method interpolation

SL.NO	VES 1		VES 2		VES 3		VES 4		VES 5		VES 6		VES 7	
	Layer Depth	$\rho_{a\text{-}ohm.m}$	Layer Depth	$\rho_{a\text{-}ohm.m}$	Layer Depth	$\rho_{a\text{-}ohm.m}$	Layer Depth	$\rho_{a\text{-}ohm.m}$	Layer Depth	$\rho_{a\text{-}ohm.m}$ -	Layer Depth	$\rho_{a\text{-}ohm.m}$	Layer Depth	$\rho_{a\text{-}ohm.m}$
1	1.3	7	1	4	1	51	1.3	52	1.3	606	0.9	588	1	77
2	1.3	8	1.3	2	1.3	31	2.7	25	2.7	500	1.3	385	1.3	49
3	2.7	11	2.7	3	2.7	33	4	22	4	392	2.7	385	2.7	88
4	4	63	4	339	4	34	5.3	15	5.3	714	4	247	4	120
5	5.3	192	5.3	9999	5.3	40	6.7	13	6.7	1333	5.3	196	5.3	92
6	6.7	77	6.7	1250	6.7	39	8	11	8	5000	6.7	211	6.7	101
7	8	87	8	120	13.3	30	10.3	8	9.3	1538	8	351	8	118
8	12	53	9.3	9999	20	36	12	7	10.7	526	9.3	426	9.3	75
9	13.3	31	10	9999	26.7	43	13.3	4	12	364	10.7	1111	10.7	294
10	16.7	261	13.3	9999	33.3	42	16.7	6	13.3	230	12	909	12	194
11	20	202	16.7	442	40	41	20	3	16.7	260	13.3	351	13.3	1176
12	23.3	120	20	9999		41	23.3	8	20	215	16.7	350	16.7	781
13	26.7	157	23.3	9999			26.7	8	23.3	321	20	538	20	9999
14	33.3	332	26.7	278			33.3	13	26.7	490	23.3	893	23.3	373
15	40	244	33.3	9999			40	86	33.3	694	26.7	505	26.7	197
16	46.7	385	40	9999			46.7	9999	40	926	30	455	23.3	340
17		140	46.7	9999			50	9999	46.7	448		4545	40	532
18				9999			56.7	9999	53.3	265				332
19								9999	60	578				
20										362				

	VES 8		VES 9		VES 10		VES 11		VES 12		VES 13		VES 14	
SL.NO	Layer Depth	$\rho_{a\text{-ohm.m}}$	Layer Depth	$\rho_{a\text{-ohm.m}}$	Layer Depth	$\rho_{a\text{-ohm.m}}$	Layer Depth	$\rho_{a\text{-ohm.m}}$	Layer Depth	$\rho_{a\text{-ohm.m}}$ -	Layer Depth	$\rho_{a\text{-ohm.m}}$	Layer Depth	$\rho_{a\text{-ohm.m}}$
1	1	104	1	4	1.3	72	1	22	1	29	1	86	1.3	62
2	1.3	64	1.3	14	1.3	22	1.3	41	1.3	19	1.3	71	2.7	73
3	2.7	40	2.7	31	2.7	21	2.7	49	2.7	32	2.7	62	4	71
4	4	33	4	21	4	28	4	63	4	49	4	58	5.3	100
5	5.3	32	5.3	26	5.3	39	5.3	53	5.3	51	5.3	83	6.7	79
6	6.7	37	6.7	20	6.7	66	6.7	45	6.7	71	6.7	150	8	101
7	8	79	8	21	8	52	8	34	8	60	8	149	9.3	87
8	9.3	136	9.3	9999	9.3	125	9.3	38	9.3	85	9.3	541	10.7	99
9	10.7	101	10.7	75	10.7	61	10.7	51	10.7	175	10.7	136	12	161
10	12	67	12	41	12	2222	12	112	12	79	12	9999	13.3	126
11	13.3	377	13.3	133	13.3	105	13.3	46	13.3	217	13.3	227	16.7	91
12	16.7	86	16.7	9999	16.7	81	16.7	9999	16.7	291	16.7	515	20	127
13	20	144	20	9999	20	168	20	160	20	101	20	331	26.7	263
14	23.3	110	23.3	9999	23.3	130	23.3	9999	23.3	106	26.7	613	33.3	752
15	26.7	231	26.7	9999	26.7	88	26.7	9999	26.7	145	33.3	2778	40	498
16	33.3	429	30	9999	33.3	128	33.3	9999	33.3	211	40	3030	46.7	1299
17	40	312	33.3	9999	40	216	40	9999	40	253	46.7	9999		826
18	46.7	302	40	9999	46.7	248	46.7	281		592		680		
19		214	46.7	552		485	53.3	9999						
20				9999			60	1031						
21								676						

	VES 15		VES 16		VES 17		VES 18		VES 19		VES 20		VES 21	
SL .NO	Layer Depth	$\rho_{a\text{-ohm.m}}$	Layer Depth	$\rho_{a\text{-ohm.m}}$	Layer Depth	$\rho_{a\text{-ohm.m}}$	Layer Depth	$\rho_{a\text{-ohm.m}}$	Layer Depth	$\rho_{a\text{-ohm.m}}$ -	Layer Depth	$\rho_{a\text{-ohm.m}}$	Layer Depth	$\rho_{a\text{-ohm.m}}$
1	1	74	1.3	54	1.3	45	1	62	1	3	1	64	1	652
2	1.3	31	1.3	46	1.3	52	1.3	23	1.3	2	1.3	38	1.3	250
3	2.7	24	2.7	45	2.7	14	2.7	19	2.7	2	2.7	40	2.7	119
4	4	33	4	48	4	17	4	23	4	25	4	41	4	92
5	5.3	46	5.3	44	5.3	19	5.3	21	5.3	9999	5.3	52	5.3	81
6	6.7	52	6.7	70	6.7	21	6.7	24	6.7	9999	6.7	65	6.7	58
7	8	89	8	49	8	26	8	23	8	303	8	102	8	43
8	9.3	154	9.3	55	9.3	31	9.3	29	9.3	9999	9.3	150	9.3	37
9	10.7	132	10.7	57	10.7	38	10.7	41	10.7	32	10.7	129	10.7	32
10	12	164	12	37	12	208	12	30	12	351	12	9999	12	35
11	13.3	97	13.3	32	13.3	177	13.3	34	13.3	23	13.3	194	13.3	26
12	16.7	847	16.7	53	16.7	9999	16.7	179	16.7	27	16.7	877	16.7	38
13	20	229	20	55	20	219	20	179	20	56	20	424	20	70
14	26.7	196	26.7	37	26.7	1299	26.7	313	26.7	67	26.7	413	23.3	407
15	33.3	781	33.3	33	33.3	9999	33.3	685	33.3	9999	33.3	347	26.7	1163
16	40	262	40	60	40	300	40	575	40	9999	40	1010	33.3	135
17		270		241	46.7	163		135		9999		304	40	166
18						1493							46.7	188
19														223

	VES 22		VES 23		VES 24		VES 25		VES 26	
SL.NO	Layer Depth	$\rho_{a\text{-ohm.m}}$	Layer Depth	$\rho_{a\text{-ohm.m}}$	Layer Depth	$\rho_{a\text{-ohm.m}}$	Layer Depth	$\rho_{a\text{-ohm.m}}$	Layer Depth	$\rho_{a\text{-ohm.m}}$
1	1.3	47	1	214	2	25	1	54	1	146
2	1.3	29	1.3	74	2	9999	2	26	2	132
3	2.7	28	2.7	51	3.3	40	3.3	29	3.3	102
4	4	27	4	46	6.7	48	6.7	30	6.7	303
5	5.3	26	5.3	37	10	120	10	37	10	4545
6	6.7	29	6.7	58	13.3	244	13.3	40	13.3	9999
7	10	41	10	88	16.7	9999	16.7	64	16.7	1163
8	13.3	64	13.3	88	20	2381	20	90	20	610
9	16.7	110	16.7	103	23.3	289	23.3	111	23.3	549
10	20	126	50	180	26.7	641	26.7	88	26.7	704
11	26.7	602	26.7	301	30	157	30	943	30	1667
12	33.3	268	33.3	2000	33.3	9999	33.3	282	33.3	685
13	40	9999	40	9999	36.3	202	36.7	201	36.7	794
14	46.7	392	46.7	422	40	633	40	427	40	735
15		385		1449	43.3	500	43.3	222	43.3	862
16						633	46.7	427	46.7	893
17								9999	50	962
18										1250

6.4.3. 2D Images

Considering the interpreted geo-electric parameters, the sounding data was classified into Seven (7) profiles covering most of the 26 VES locations in different directions which is shown in **Figure 12**. The 2D images for these nine profiles were drawn for the true resistivity values versus the depths. Since the IP WIN interpretation results in only limited depths and the corresponding resistivities, the geo-electric layer parameters obtained from INVERSE SLOPE interpretation were used for preparing these 2D sections. The 26 VES locations are classified into 7 profiles and vertical cross sections are prepared from each profiles.

In order to determine the geophysical characteristics across the individual profiles, graphs have been plotted considering the distance between the locations represented in X-axis kept as equal (not to scale) in view of large variations of distances between VES locations and the depth below ground surface is kept as y-axis. The absolute resistivity of the different layers "ρ" are used as Z-axis. These images are designated as the names of the profiles i.e., AA', BB', CC', DD', EE', FF', and GG' and presented below in sequential order (**Figure 13 - Figure 19**). Among these profiles, 4 profiles have bisected TCL which have shown in the respective figures. The higher order of resistivity depicted in these profiles indicates the basement and the lower values indicated contaminant zones. While considering the higher values, the highest value is limited to 500 ohm.m to avoid congestion of contours.

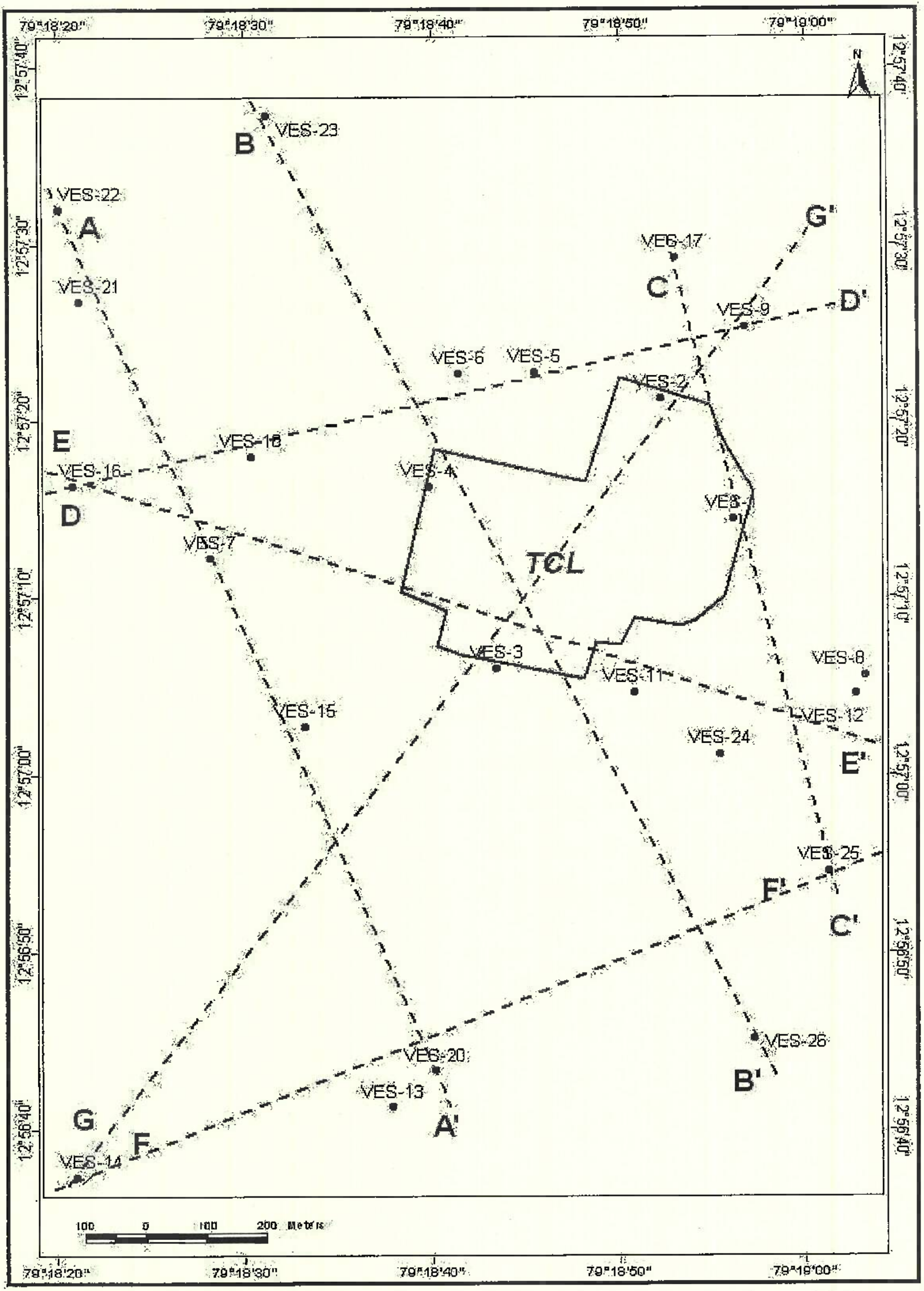

Figure 12: Geophysical traverse drawn from the VES points studied so far along with the profiles

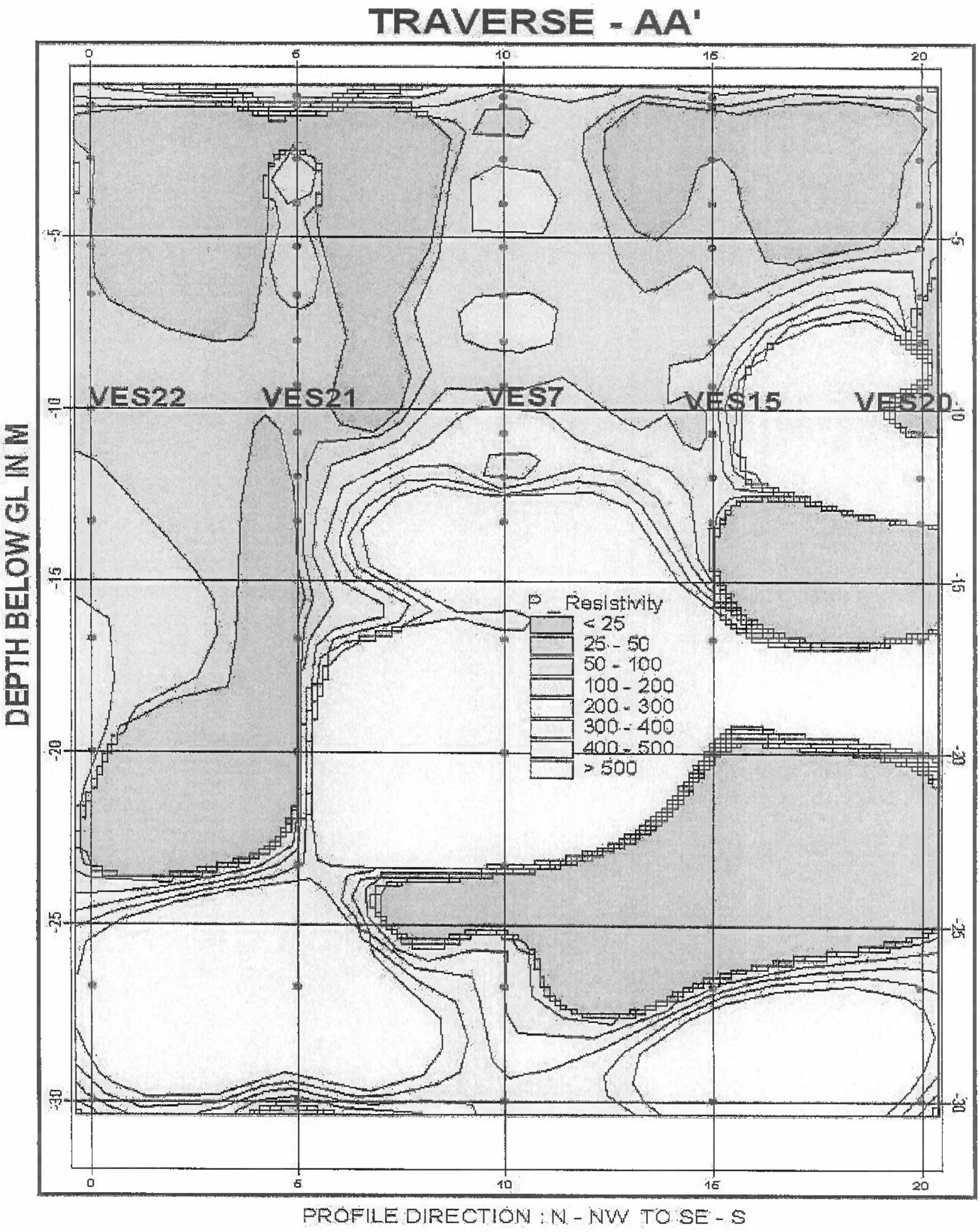

Figure 13: The absolute resistivity with respect to depth in traverse profile AA’

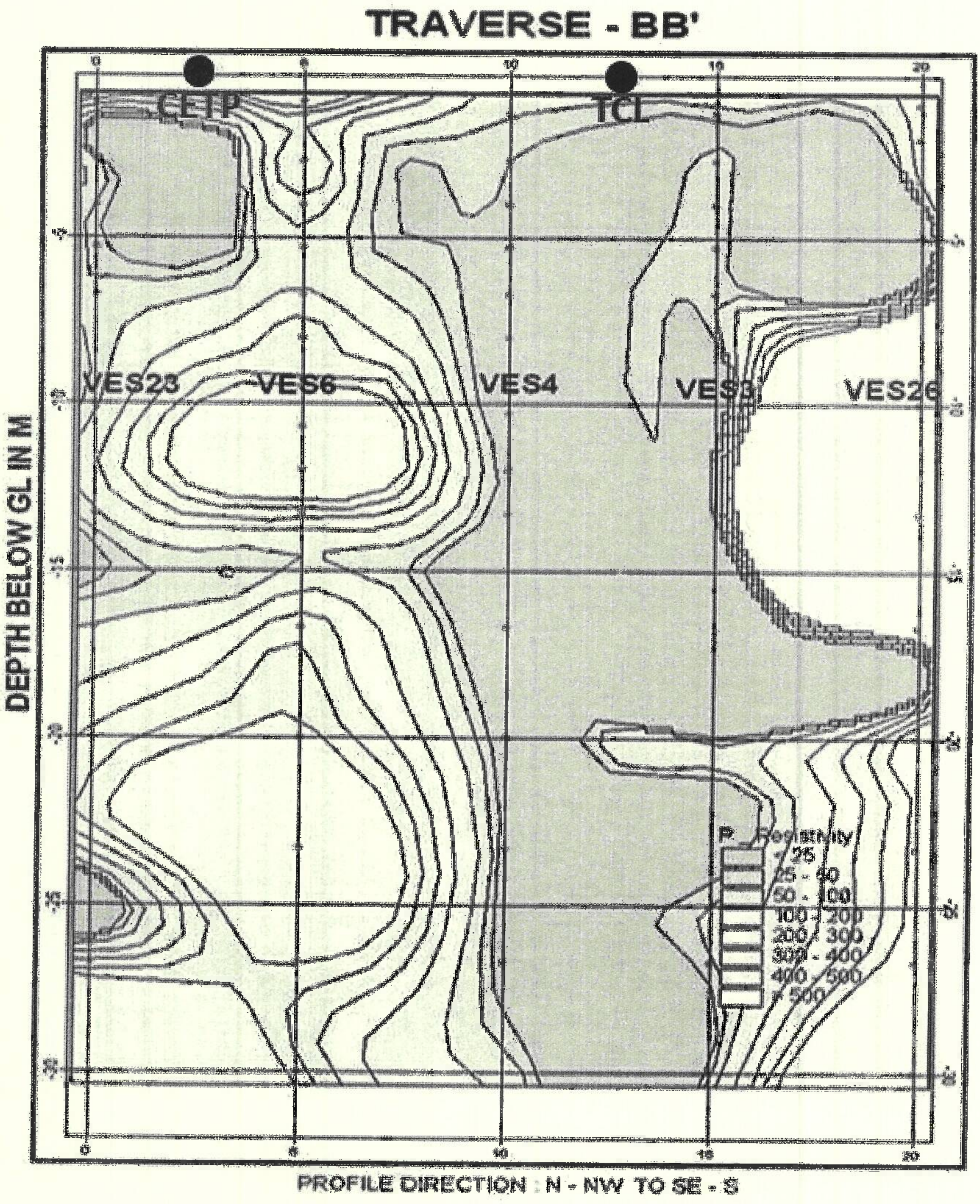

Figure 14: The absolute resistivity with respect to depth in traverse profile BB'

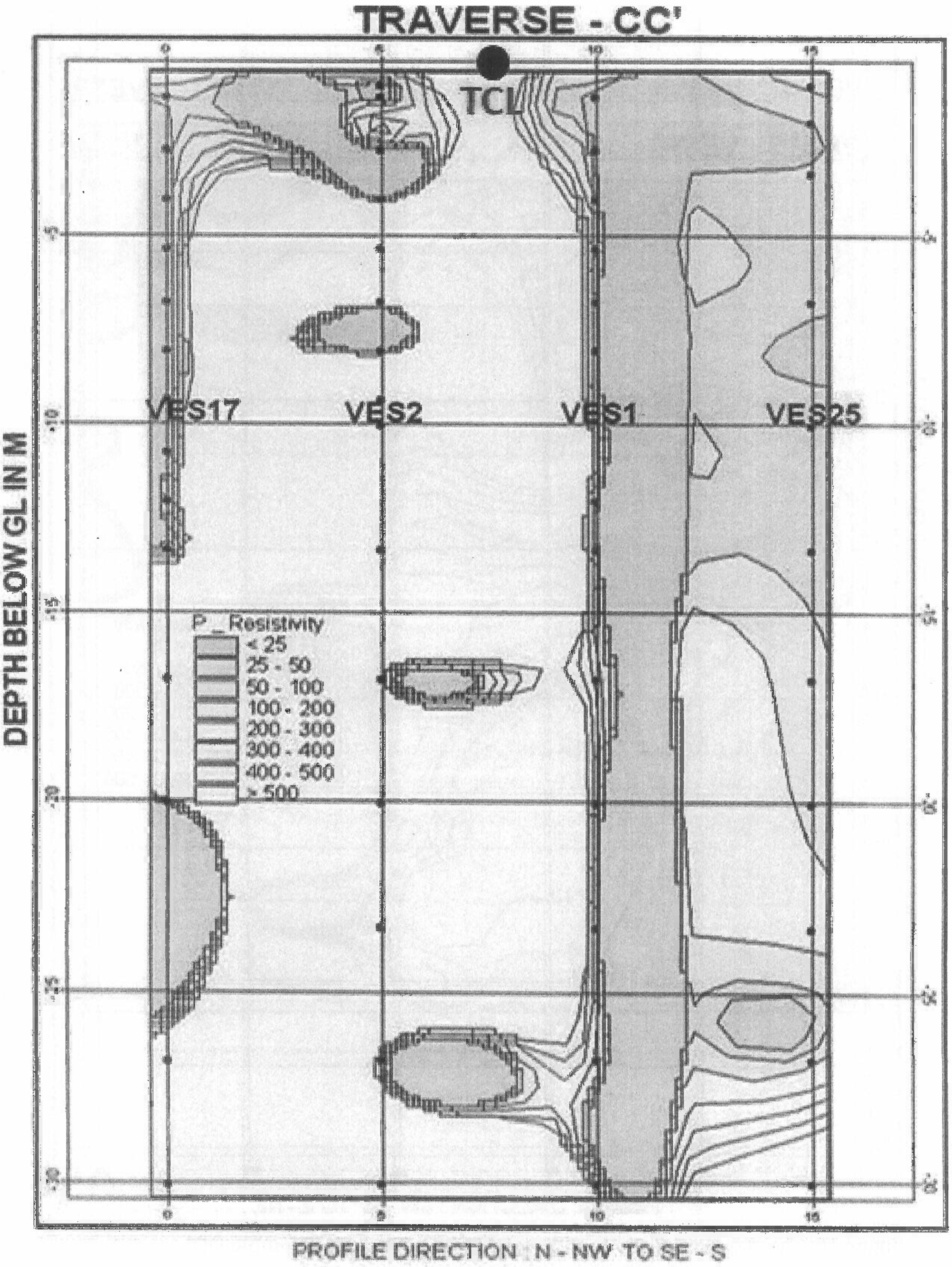

Figure 15: The absolute resistivity with respect to depth in traverse profile CC'

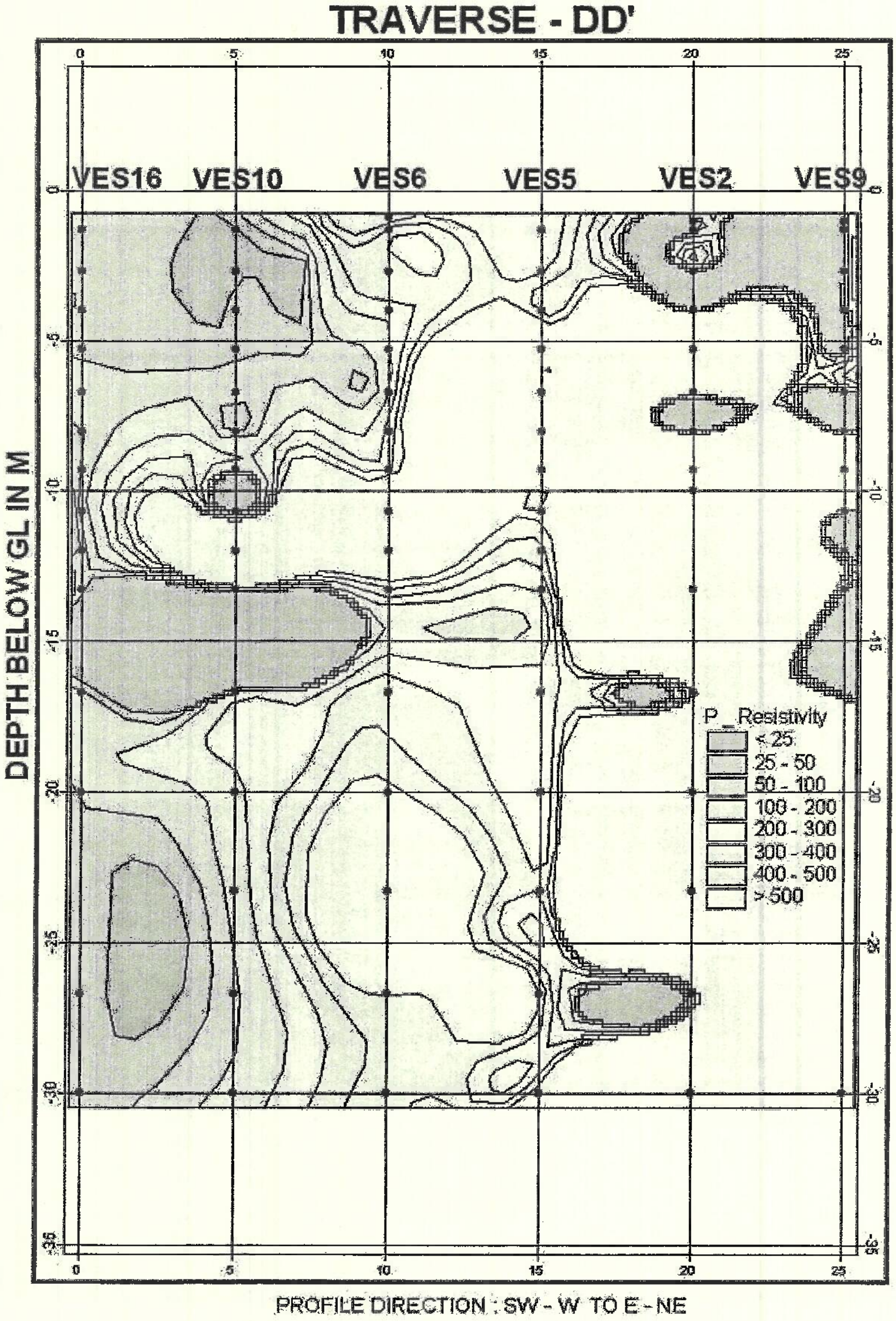

Figure 16: The absolute resistivity with respect to depth in traverse profile DD'

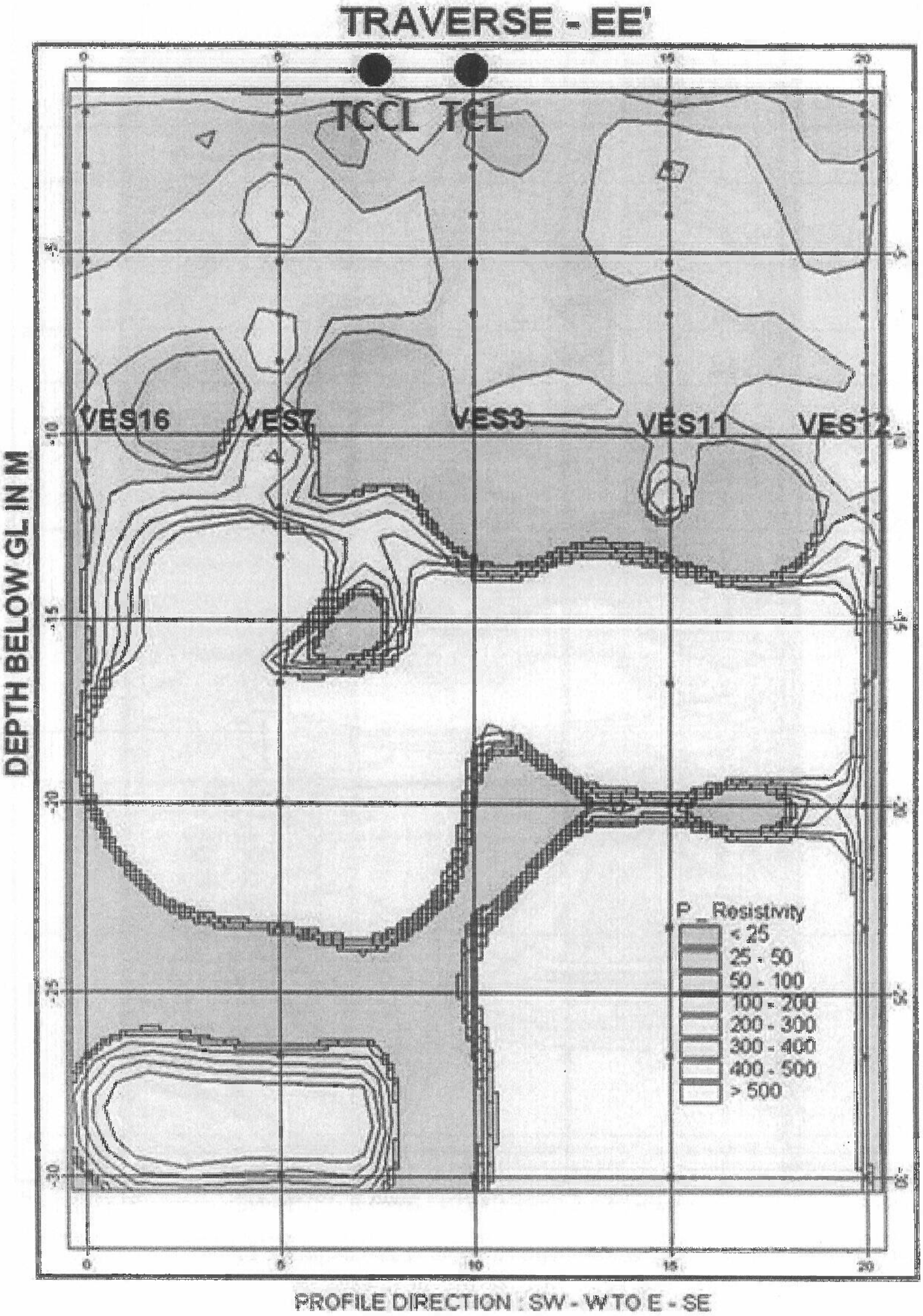

Figure 17: The absolute resistivity with respect to depth in traverse profile EE'

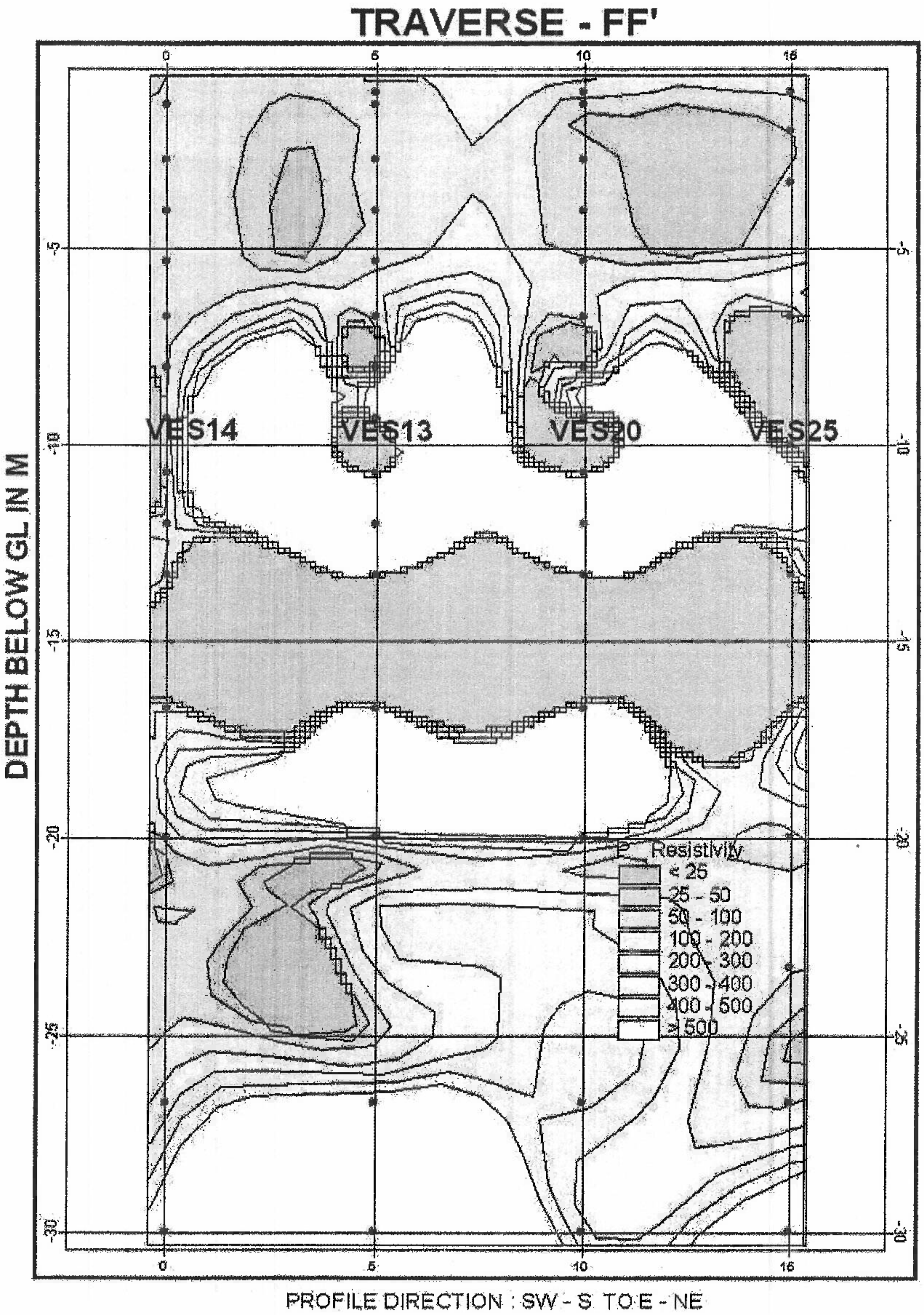

Figure 18: The absolute resistivity with respect to depth in traverse profile FF'

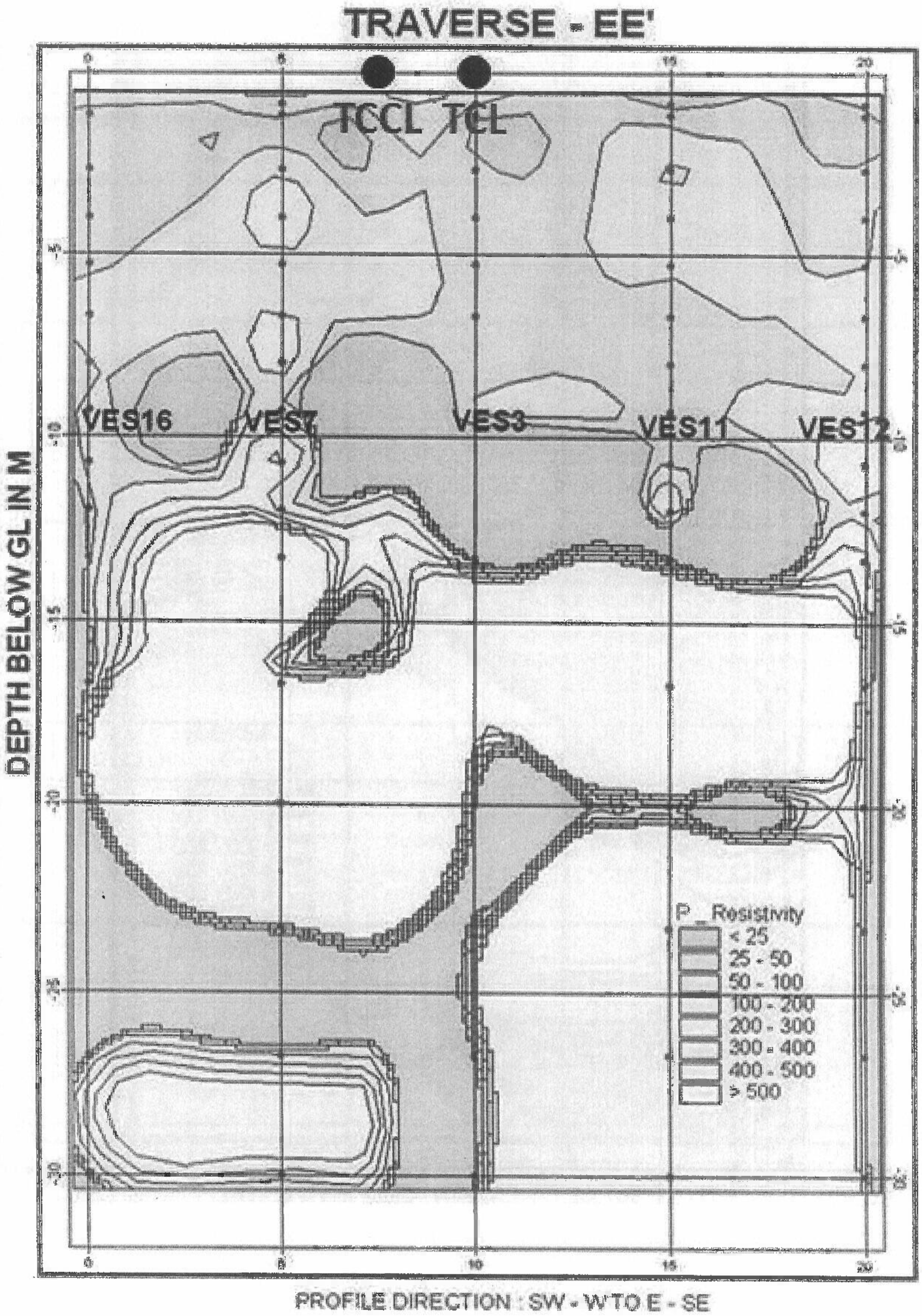

Figure 17: The absolute resistivity with respect to depth in traverse profile EE'

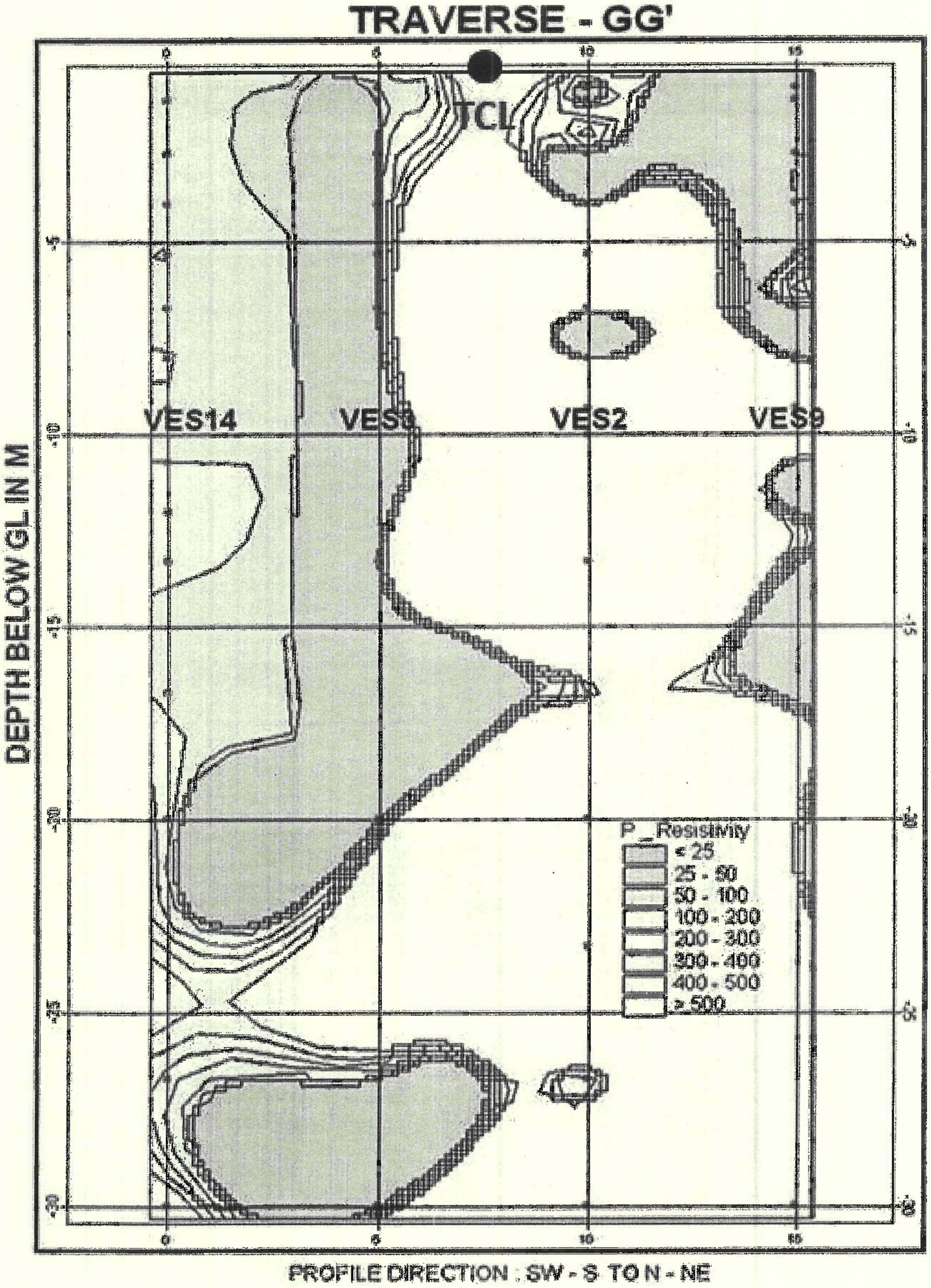

Figure 19: The absolute resistivity with respect to depth in traverse profile GG'

6.4.4. Discussion on Vertical sections

As indicated above the geo-electric layer parameters, ie., the thickness/depth of each layer and corresponding absolute resistivity were plotted to obtain vertical sections for all the 7 profiles AA' to GG' were represented in the form of seven vertical sections corresponding to each of the seven profiles. Three of the profiles AA' to CC' are in approximate N-S direction and the sections DD' to FF' are in approximate West- East direction and the last profile GG' is from South West to North East Direction.

Profile AA' running from NW to SE approximately represents a crucial line of data since his section covers the western part of TCL and open land south of the highway. From this section, the possibility of contamination is inferred till 10m in all the VES sites. In other locations like VES-21, VES-15, VES-7 and VES-20 the impact of contamination is inferred at deeper level say 25m.

Profile BB' is also is in the NW-SE direction and is parallel to AA'. This is crossing through middle of TCL. The middle area of this profile covering VES-3 and VES-4 which are abetting TCL boundary are impacted by possible contamination. The depth of such impact is more till about 25m.

The profile CC' is again parallel to AA' and BB" and running NW-SE. A part of this profile covers TCL on its eastern border. VES locations 1 and 25 exhibited the impact of possible contamination. The VES-1 falling close to eastern boundary of TCL and VES-25 falling in open land south of Highway are impacted by contamination. The VES-2 which is located just north of the TCL boundary did not exhibit any impact.

The fourth profile DD' runs approximately in west east direction. The VES locations 16 and 10 are impacted by possible contamination till about 25m while the eastern most location at VES 9 is impacted to a limited depth of 5m.

The fifth profile EE' runs a little NW-SE and passes through the southern boundary of TCL. All the locations in this profile exhibited the impact of possible contamination, of course with various degree of intensity.

The sixth profile FF' is running from SW corner of the region to mid-east of the region. This profile falls far south of TCL. Indication of contaminant soil/rock is exhibited till 7-8m in all the locations and again between 12 and 18m.

The seventh profile GG' runs from SW corner of the region to NE corner of the region and is passing through the middle of TCL. The region in the south west covering VES 24 and 20 and

NE portion covering VES 9 is impacted. The VES 2 area falling in just outside NE boundary of TCL is unaffected. This was observed in profile CC' also.

6.4.5. Thickness and Resistivity contours

Utilizing the results obtained from the geoelectric parameters obtained using IPWIN interpretation, namely the thickness (depths) of different layers and their respective absolute resistivity values inferred, contours are drawn and presented in **Figure 20** – **Figure 26**. This map coupled with the resistivity contours for the first layer will define to what extent the layer is impacted by possible contamination which is interpreted by IPWIN.

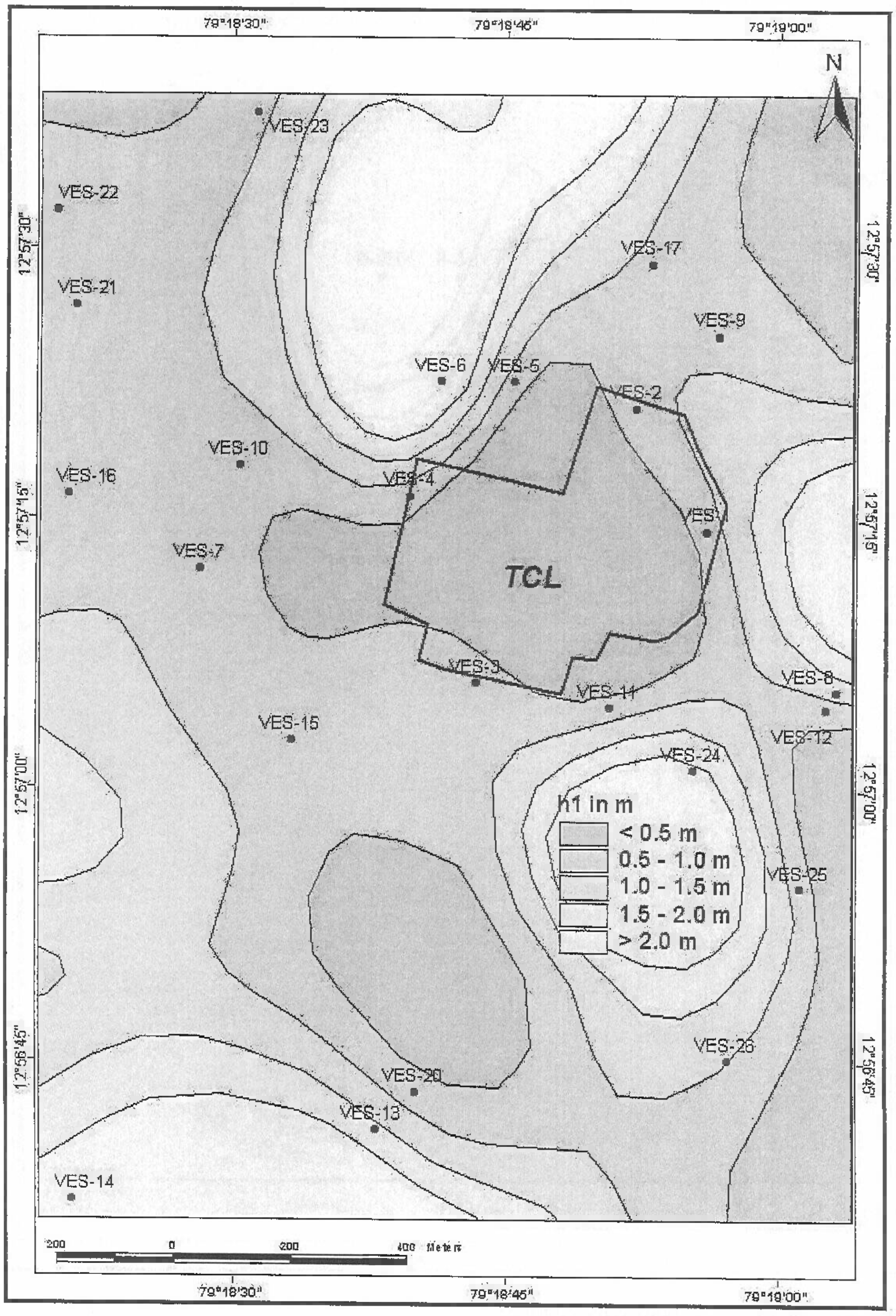

Figure 20: The first layer thickness contour

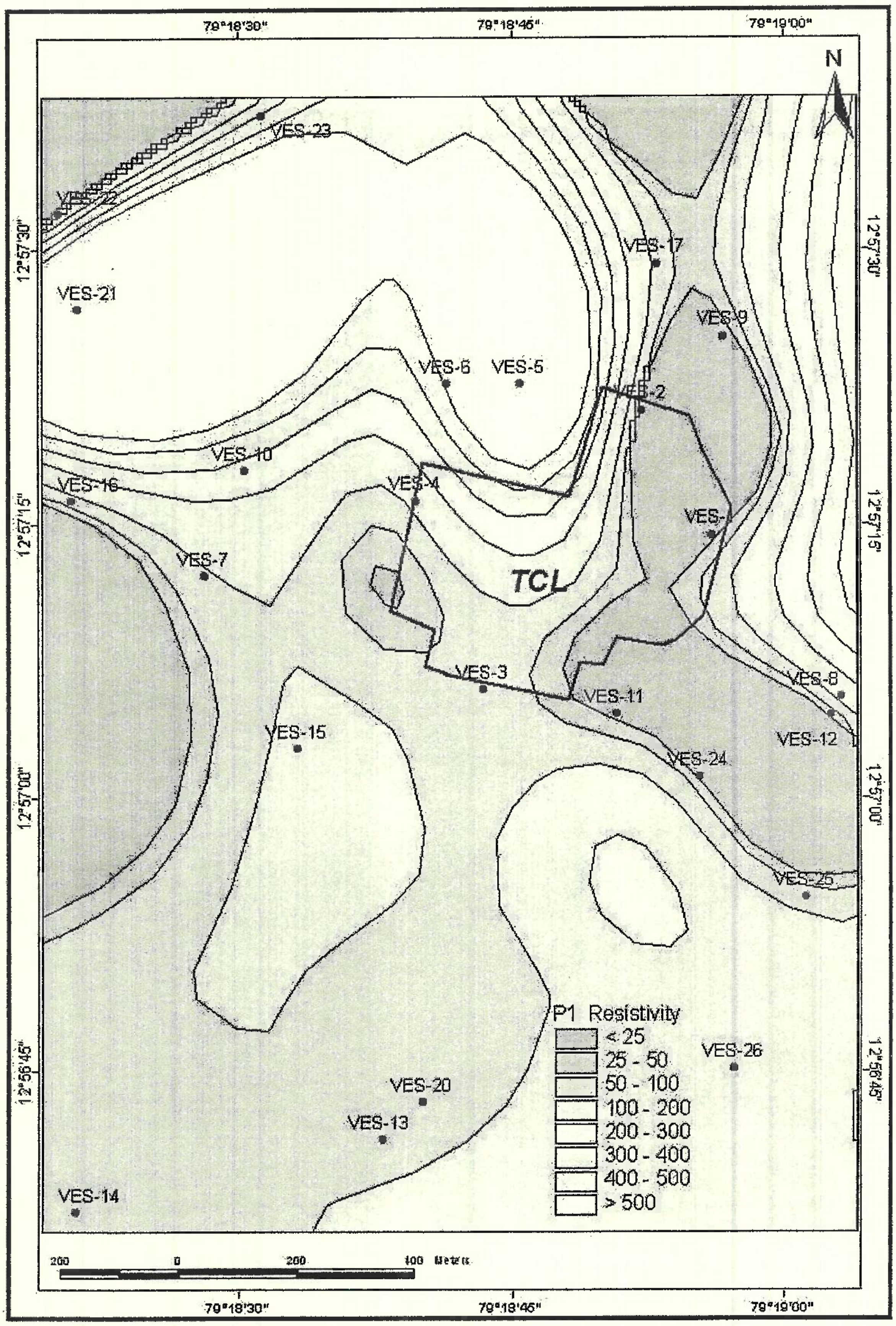

Figure 21: The first layer resistivity contour

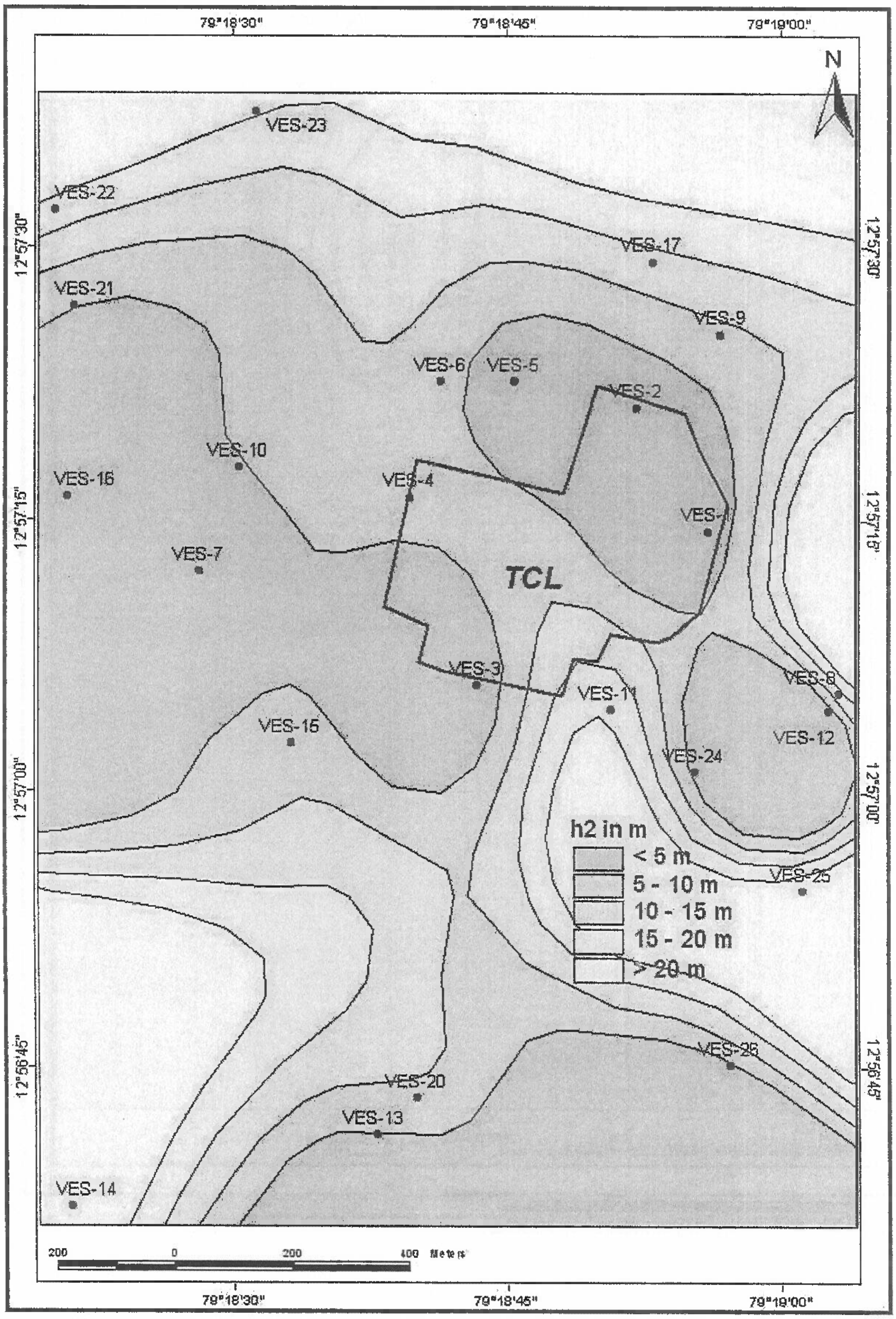

Figure 22: The second layer thickness contour

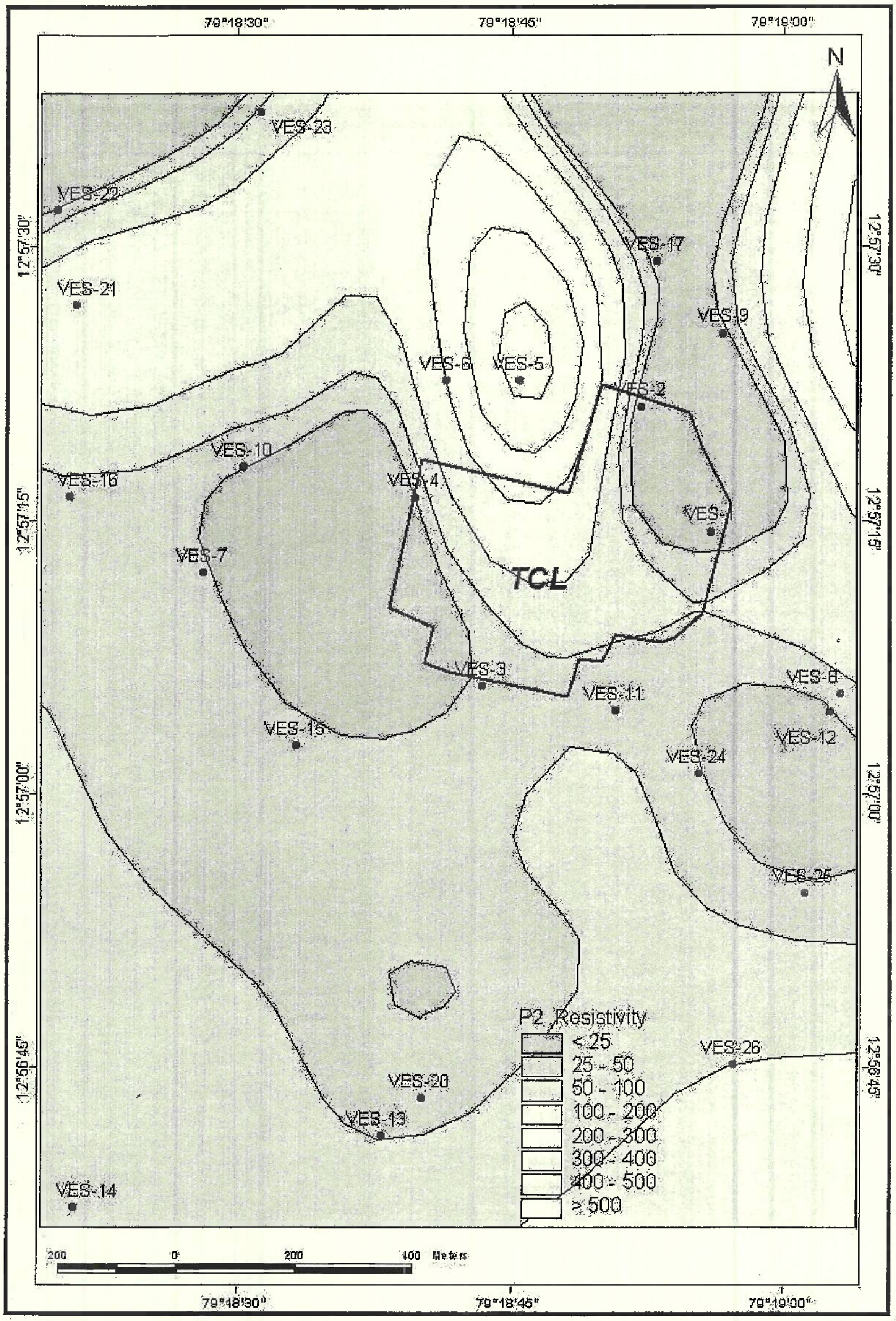

Figure 23: The second layer resistivity contour

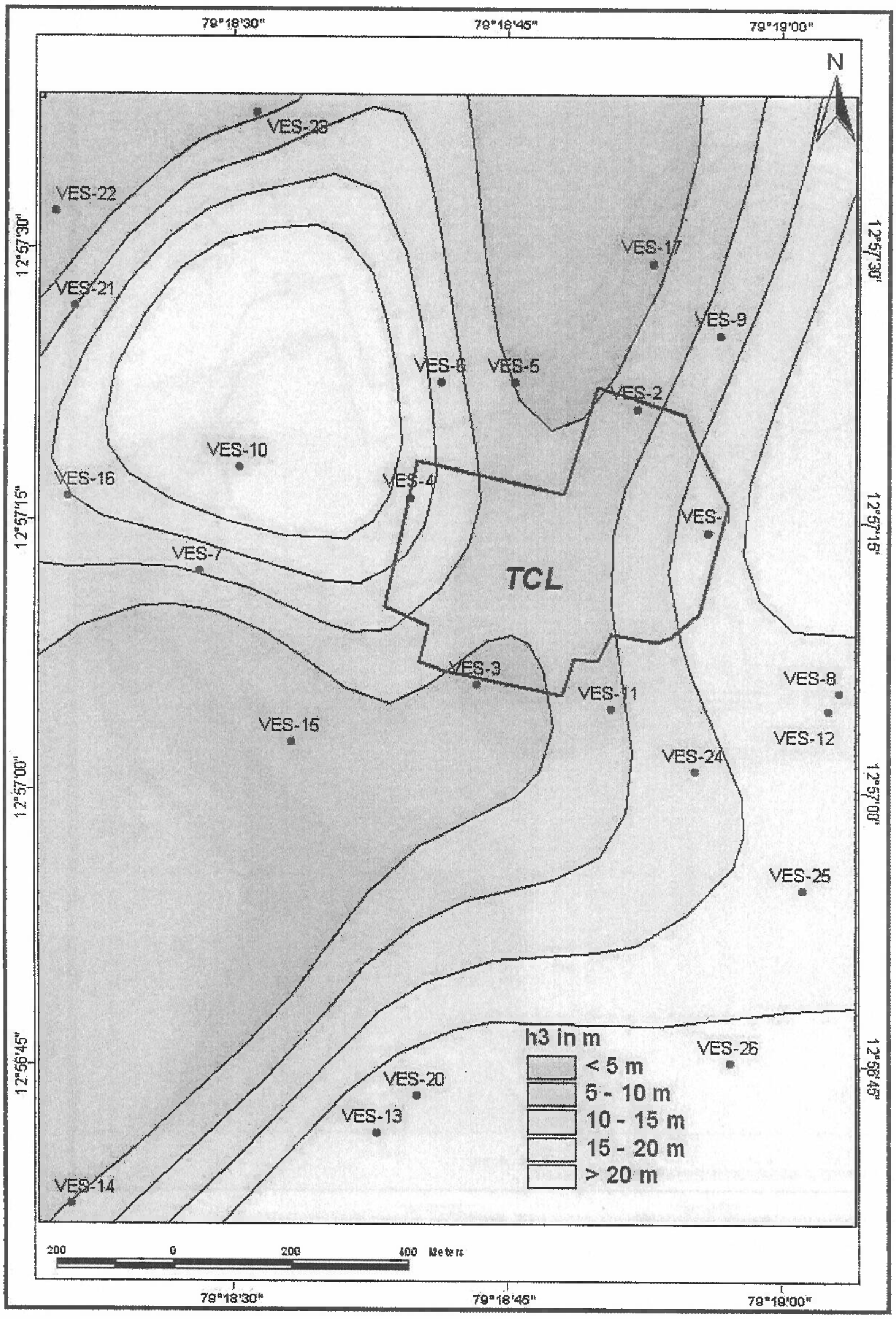

Figure 24: The third layer thickness contour

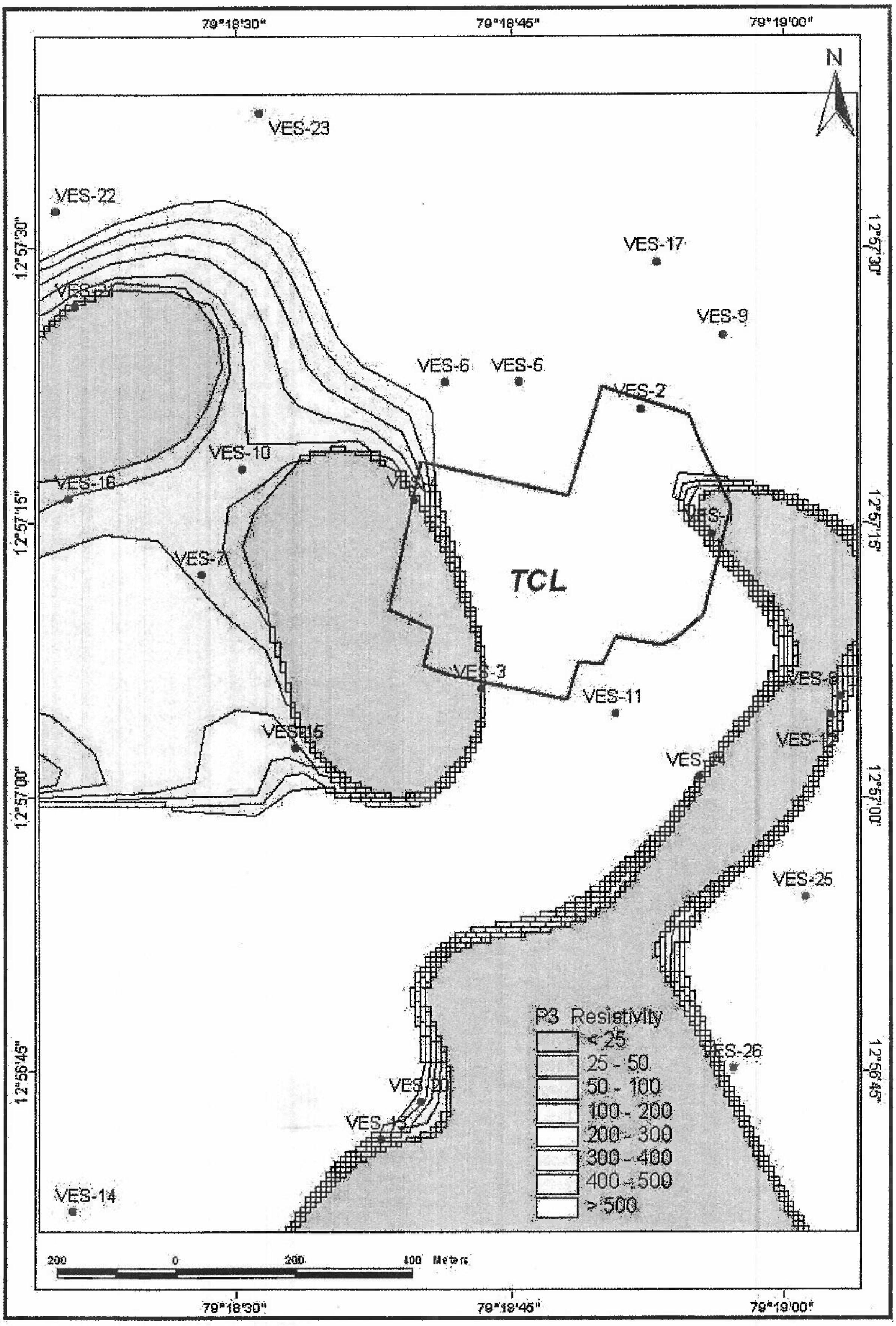

Figure 25: The third layer resistivity contour

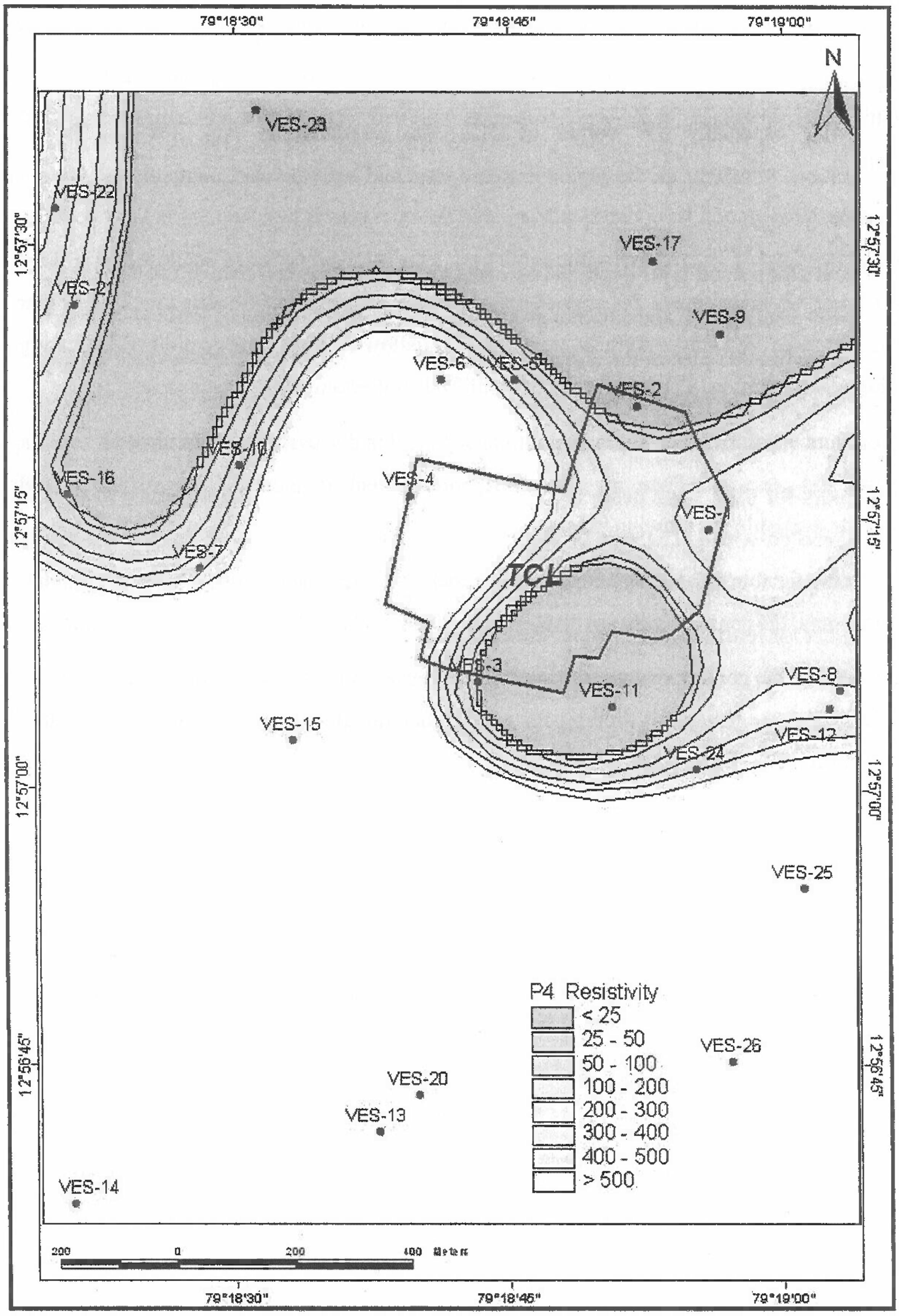

Figure 26: The fourth layer resistivity contour

6.4.6. Discussion on contour maps

The first layer which represents soil is very thin and it has a thickness ranging from 0.5 to 2.0m. Largest thickness of more than 2m is recorded in places just north west and east of TCL. The resistivities are generally high indicating dry sandy soil conditions. However, in the just western side especially SW corner of TCL, the resistivity is very low indicate the contamination. Similarly, in the region extreme west and extreme east, contamination of soil is possible.

The contours for second layer depth indicate that the thickness is less than 5m in three regions, West, North- East of TCL and extreme south east. This is an indication of shallow basement in these regions. In other places, the larger depths indicate occurrence of fractured rock till deeper levels. The resistivity values in these regions with shallow rock occurrence are low indicating possible contamination. The Western portion of TCL is predominantly contaminated.

The contours for third layer depth are not considered for discussion, though they have been pre-pared and presented. These maps may not represent realistic picture in view of the limited data points available for drawing contours.

The contours for fourth layer represent the hard rock/basement devoid of fractures. Again, due to limited data, the contours may not display clear picture of lateral variations of the subsurface.

On the basis of the geophysical survey results represented in the form of vertical cross sections and 2 D images, the final maps showing the area of contamination of groundwater are presented below (**Figure 27** – **Figure 29**).

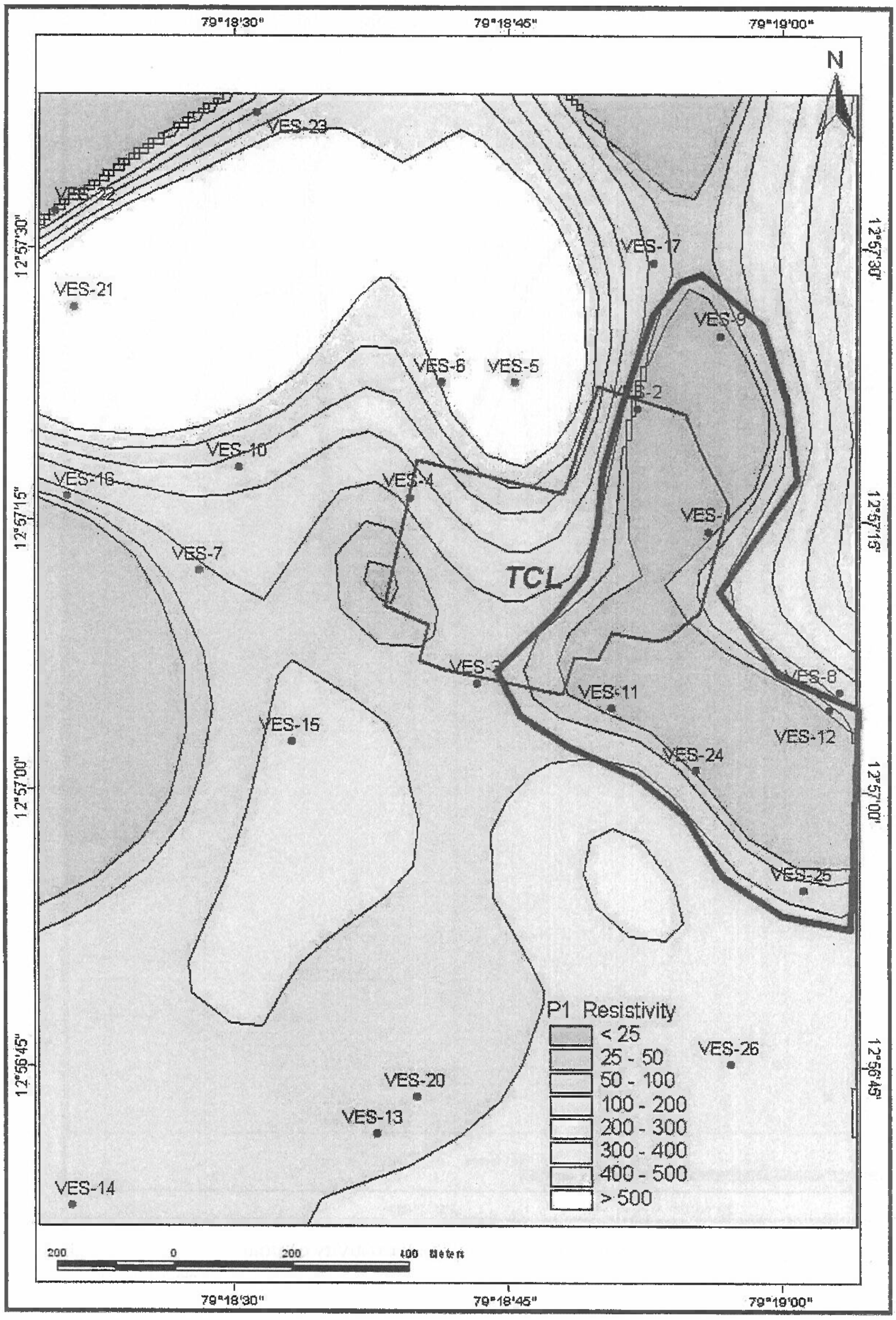

Figure 27: The possible contamination in the first layer resistivity contour

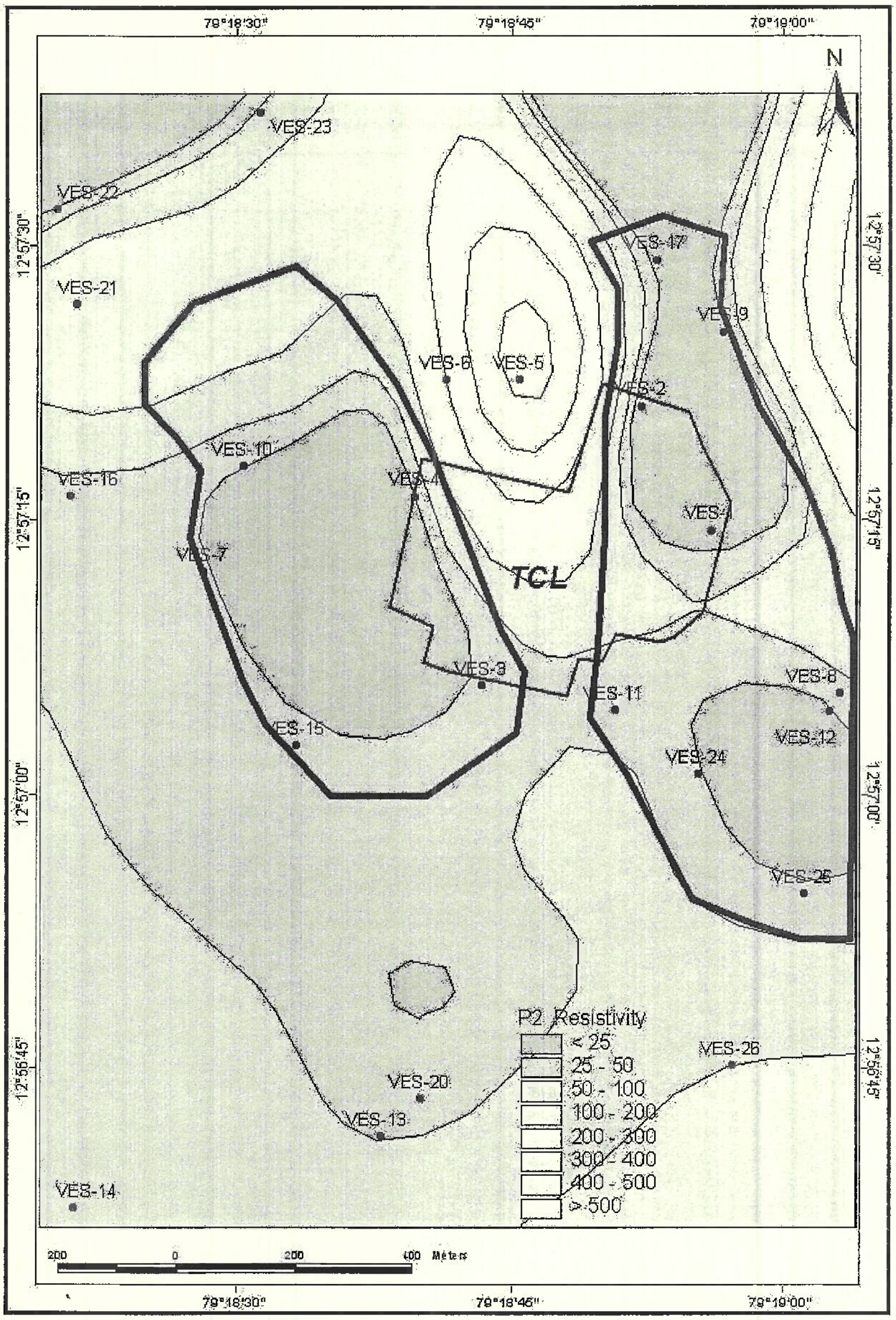

Figure 28: The possible contamination in the second layer resistivity contour

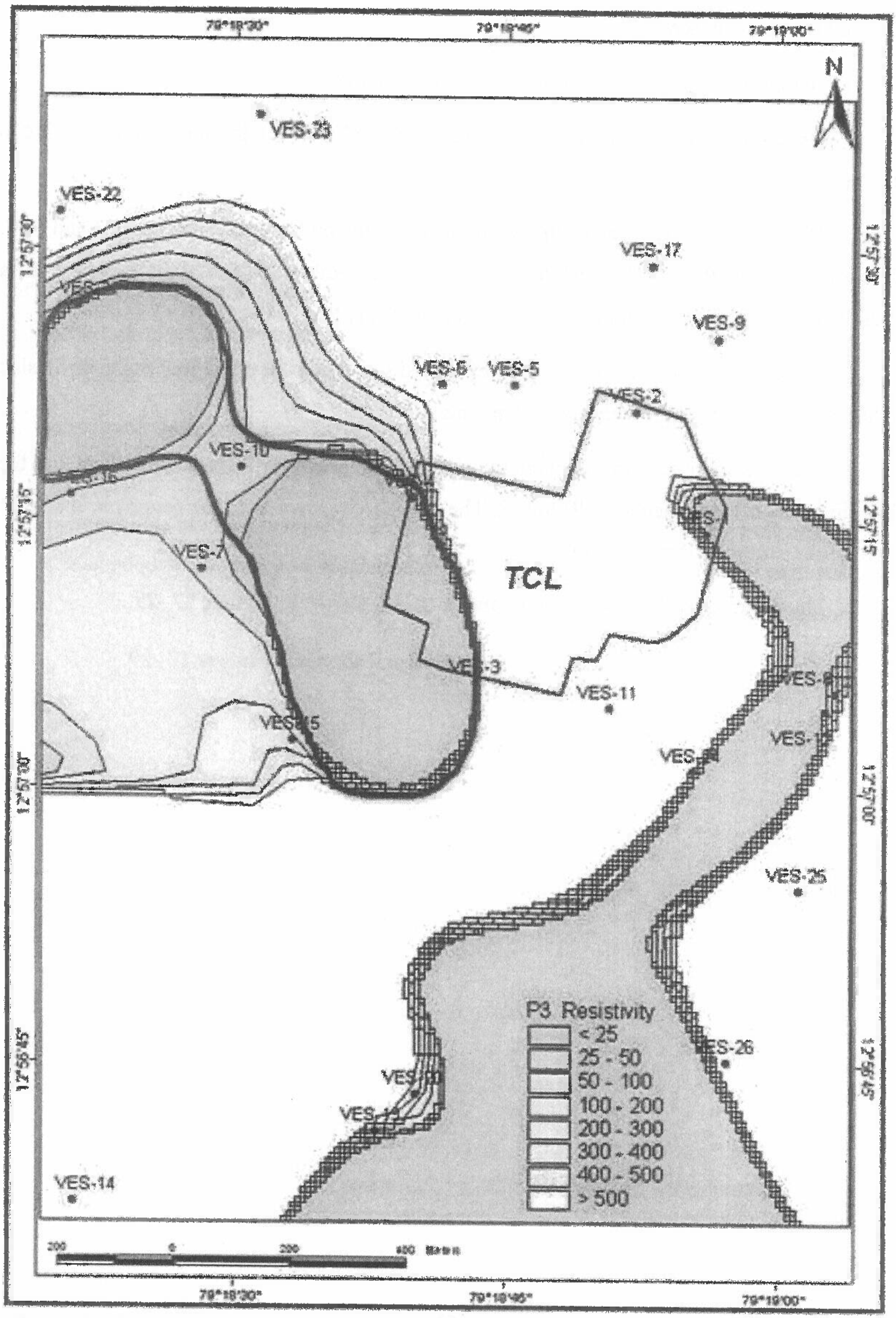

Figure 29: The possible contamination in the third layer resistivity contour

6.4.7.Summary of Geophysical survey

A combination of results as obtained from the vertical cross sections provided a picture of vertical variations in the possible contamination and the resistivity contours provided a lateral picture of the subsurface.

A combination of these two types of images concludes that

1. The indication of contamination of soil, weathered rock and fractured rock is visible in the region.

2. The most impacted part of the region is a) the region between profiles AA' and BB'. This region covers the CETP, western part of TCL and southern part of highway which is an open land. The VES sites falling in this region are 22, 21, 10,7, 15, 4, 3, 20,13 and 26.

3. The eastern part of the region also exhibited soil/rock contamination. Some of outside industries may be the source of this contamination.

4. The flow direction was assessed by using a VLF Magneto Telluric equipment and the flow direction is confirmed as N.W to S.E. The inferences drawn from the geophysical studies corroborate with the flow direction

5. The inferred polluted areas are demarcated and shown in Figures 27 -29.

6.5. Auger Drilling

In the present study, auger boring was conducted in 25 locations. The hand auger was used to dig below the ground till 2.0 m or the presence of groundwater, whichever is less. The main objectives of the auger boring were a) determine groundwater level, if it is occurring within 2 m, b) investigate the shallow soil profile and c) collect the soil and water samples. The results of drilling and sampling from auger holes are presented in **Table 9**. The distribution of the auger boring points in the study area is shown in Most of the auger points were concentrated surrounding to TCL in **Figure 30**.

Table 9: Information collected from the auger holes

Auger Hole No.	Coordinates	Location	Depth Range	Soil Profile	Water level BGL in m
1	12.95575 N 79.30893 E	CETP Pool	0.5m	Filled up soil	0.97m
			1.0m	Greyish black color, fine to medium sand with weathered rocks	
			1.5m	Brown silty, Fine to medium sand	
			2.0m	Fine to medium sand with weathered rocks	
			2.35m	Greyish fine to medium sand with major weathered rocks	
2	12.95468 N 79.30832 E	Backside of intercontinental leather	0.5m	Brownish silty very fine-medium sand	Not Available
			1.0m	Greyish brown weathered rocks	
			1.30m	Soft rock particles	
3	12.95631 N 79.91145 E	TCCL Open land	0.5m	Brown fine to medium sand	Not Available
			1.0m	Brown fine to medium sand with weathered rocks	
			1.2m	Soft weathered rocks with quartz	
4	12.95174 N 79.91145 E	TCL loading gate	0.5m	Greyish fine to medium sand	0.7
			1.0m	Greyish fine to medium sand with soft weathered rocks	

Auger Hole No.	Coordinates	Location	Depth Range	Soil Profile	Water level BGL in m
5	12.95144 N 79.31756 E	UPL East side	0.5m 1.0m 1.50m	Brown fine to medium sand Brown silty fine to medium sand with weathered rocks Brownish fine to medium sand with weathered rocks	1.06m
6	12.96222 N 79.31008 E	South West of Euro shoes	0.5m	Hard weathered rocks	Not Available
7	12.95666 N 79.30692 E	South West of CETP Pool	0.5m 1.0m 1.10m	Grey silty fine to medium sand Grey fine to medium sand with weathered rocks Hard weathered rocks	Not Available
8	12.95942 N 79.30625 E	Ranipet Fire Station	0.5m 1.0m 1.3m	Weathered rocks with coarse sand Medium coarse sand Hard weathered rocks	Not Available
9	12.9583 N 79.3016 E	Opp To Lakshmi Industries	0.50m 1.0m	Grey fine to medium sand Grey weather rock with soft rock pieces	Not Available
10	12.96342 N 79.30559 E	Opp to Rahaman Leathers	0.5m 0.75m	Brownish Coarse sand with weathered rocks Hard rock particles	Not Available
11	12.9583 N 79.3114 E	North west Boundary of tamil nadu warehouse	0.5m 0.97m	Brown coarse sand with weathered rocks Soft weathered rocks with water	0.73m
12	12.9555 N 79.3105 E	Behind TCCL North boundary wall	0.5m 1.0m	Brown fine to medium sand Grey fine to medium sand with small weathered rock pieces	Not Available
13	12.9529 N 79.3105 E	Between TCL and TCCL	0.5m 1.0m	Greyish medium sand Greyish medium sand with hard weathered rocks	Not Available
14	12.9516 N 79.3107 E	Opp to Maruthi Suzuki	0.5m 0.90m	Grey fine sand Hard rock particles	0.5m

Figure 30: The map showing the locations of the auger holes

Compiling the above results, the thickness of soil /depth to top of rock in each auger drilling locationis assessed and tabulated in **Table 10.**

Table 10: Summary of soil- rock profile from auger holes

Sl. No	**Auger Holes No**	**Elevation**	**Thickness of soil**	**Water level BGL**
1	AH1	196m	2.35 m	0.97
2	AH2	190m	1.30m	Not Available
3	AH3	196m	1.20m	Not Available
4	AH4	191m	1.0m	0.70m
5	AH5	187m	1.50m	1.06m
6	AH6	190m	0.50m	Not Available
7	AH7	191m	1.10m	Not Available
8	AH8	198m	1.3m	Not Available
9	AH9	192m	1.0m	Not Available
10	AH10	199m	0.75m	Not Available
11	AH11	196m	0.97m	0.73m
12	AH12	196m	1.0m	Not Available
13	AH13	188m	1.0m	Not Available

Sl. No	Auger Holes No	Elevation	Thickness of soil	Water level BGL
14	AH14	180m	0.9m	0.50m
15	AH15	194m	1.8m	Not Available
16	AH16	194m	1.3m	1.11m
17	AH17	199m	1.2m	Not Available
18	AH18	188m	1.5m	1.05m
19	AH19	198m	1.0m	Not Available
20	AH20	201m	1.3m	Not Available
21	AH21	180m	1.2m	0.26m
22	AH22	175m	0.5m	Not Available
23	AH23	175m	1.0m	Not Available
24	AH24	190m	1.5m	Not Available
25	AH25	185m	1.0m	Not Available

The above data are used for preparing a contour map showing the thickness of soil. The map is presented in **Figure 31**.

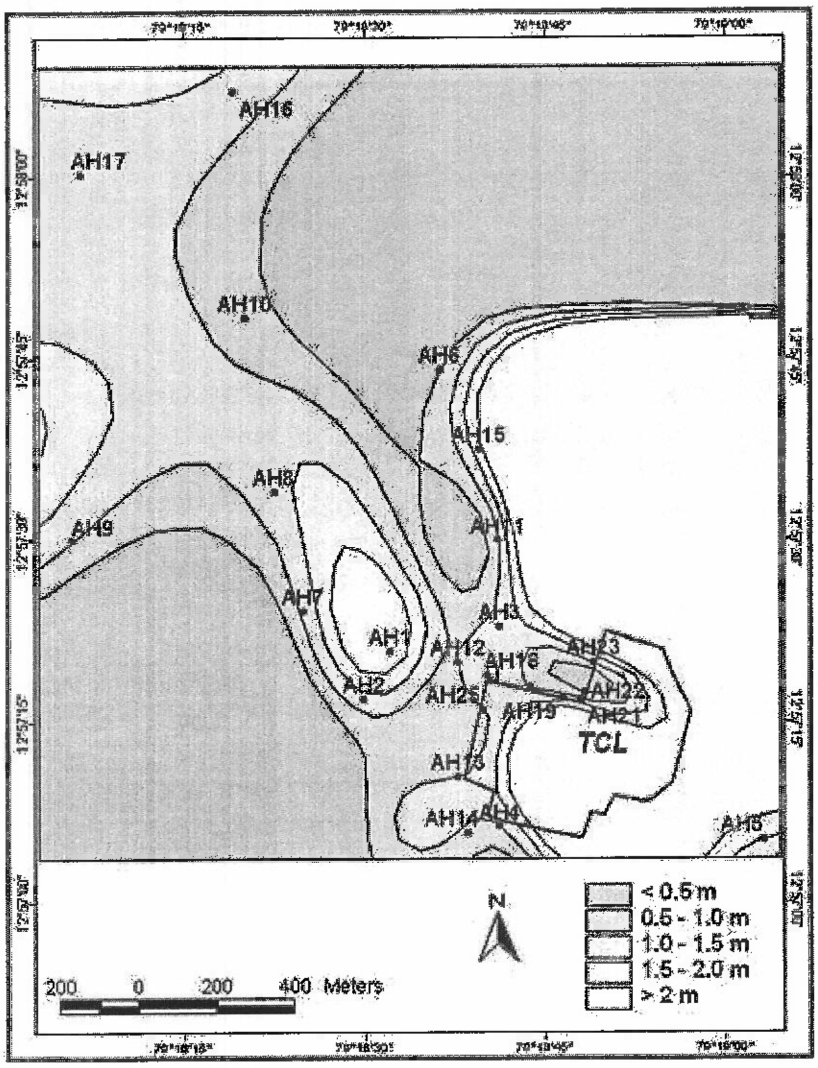

Figure 31: Map showing the lateral variations of soil thickness /top of rock

6.6. Analysis of soil samples:

The soil samples collected from the bottom portion of the each of 25 auger boring points were considered for analysis of heavy metals (total Cr, total Fe) and hexavalent Cr. Among them 20 samples were analyzed for Oxalic acid and Formic acid. The procedure for the analysis is mentioned in the previous section. The location of the soil samples is same as the auger boring location was shown in **Figure 30.** The location and depth of the soil samples collected are included in **Table 11.**

Table 11: The detail of the soil samples collected from the auger boring points

Sl. No.	Soil Sample ID	Latitude	Longitude	Depth of sample	Location
1	AH1	12.95575 N	79.30893 E	2.35 m	CETP Pool
2	AH2	12.95468 N	79.30832 E	1.30m	Backside of intercontinental leather
3	AH3	12.95631 N	79.91145 E	1.20m	TCCL Open land
4	AH4	12.95174 N	79.91145 E	1.0m	TCL loading gate
5	AH5	12.95144 N	79.31756 E	1.50m	UPL East side
6	AH6	12.96222 N	79.31008 E	0.50m	South west of Euro shoes
7	AH7	12.95666 N	79.30692 E	1.10m	South West of CETP Pool
8	AH8	12.95942 N	79.30625 E	1.3m	Ranipet Fire Station
9	AH9	12.95830 N	79.3016 E	1.0m	Opp To Lakshmi Industries
10	AH10	12.96342 N	79.30559 E	0.75m	Opp to Rahaman Leathers
11	AH11	12.9583 N	79.3114 E	0.97m	North west Boundary of Tamil Nadu warehouse
12	AH12	12.9555 N	79.3105 E	1.0m	Behind TCCL North boundary wall
13	AH13	12.9529 N	79.3105 E	1.0m	Between TCL and TCCL
14	AH14	12.9516 N	79.3107 E	0.9m	Opp to Maruthi Suzuki
15	AH15	12.9604 N	79.31097 E	1.8m	North East to warehouse
16	AH16	12.9686 N	79.3053 E	1.3m	North side of BBK shoes
17	AH17	12.9667 N	79.3018 E	1.2m	Opp to BBK leathers behind Arjun chemicals
18	AH18	12.9552 N	79.31117 E	1.5m	Puliyanthangal graveyard
19	AH19	12.95493 N	79.31215 E	1.0m	Murugappa side road
20	AH20	12.95472 N	79.31293 E	1.3m	Opp to annai marketing
21	AH21	12.95466 N	79.31332 E	1.2m	Near Reliance petrol bunk
22	AH22	12.95483 N	79.31342 E	0.5m	Karai lake
23	AH23	12.95551 N	79.31363 E	1.0m	Puliankannu lake
24	AH24	12.95509 N	79.31125 E	1.5m	TCL near QA lab
25	AH25	12.95443 N	79.31107 E	1.0m	Veterinary hospital water tank

The soil samples prior to the analyses are air dried for 48 hours and preserved in zip pouch with proper labelling. In the first stage the samples were dried inside the zip pouches until they are dried enough to be taken out of the pouch. After that they are dried on open space for two days. **Figure 32** shows the air drying of the samples with proper labelling.

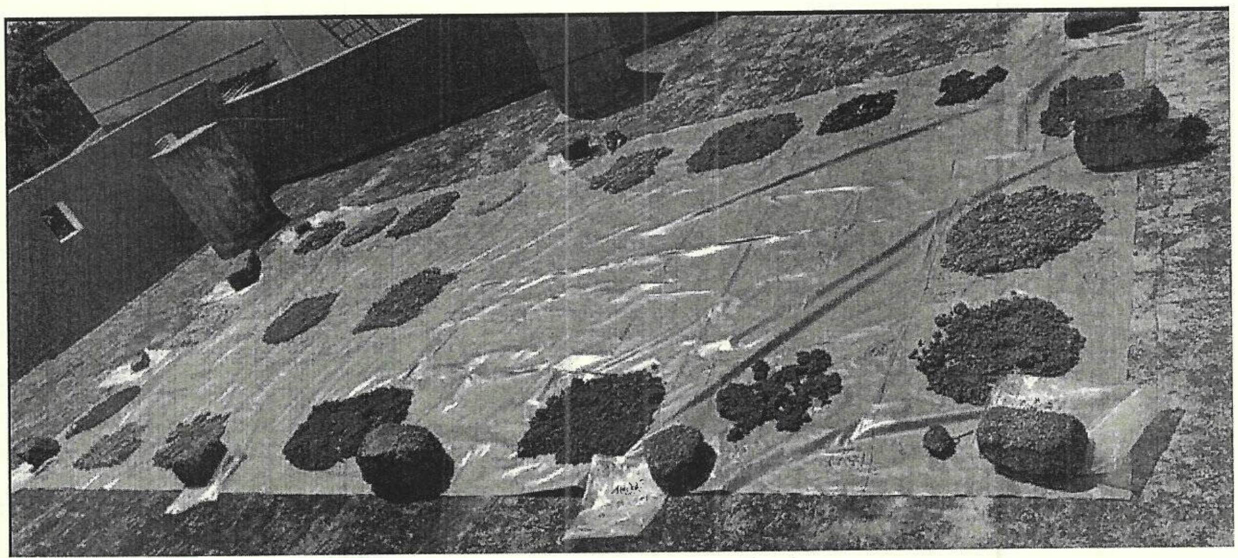

Figure 32: Air drying of the soil samples collected from auger boring

The soils were digested in microwave digester and analyzed for total iron and chromium in ICP-OES. The water soluble hexavalent chromium is analyzed in UV-Spectrophotometer as per the standard procedure mentioned before. The analysis result of these three parameters are tabulated below (**Table 12).**

Table 12: Result of the heavy metals concentration in the soil samples

Sl. No.	Sample ID	Total Chromium (mg/kg)	Total Iron (mg/kg)	Hexavalent Chromium (mg/kg)
1	AH01	372.65	11035	ND
2	AH02	104.76	27138	ND
3	AH03	9.13	6951	ND
4	AH04	18.87	14494	ND
5	AH05	10.62	18214	ND
6	AH06	8.99	12537	ND
7	AH07	39.99	26165	ND
8	AH08	39.39	6939	0.425
9	AH09	30.14	10574	ND
10	AH10	27.53	11637	ND
11	AH11	6.37	5389	ND
12	AH12	285.67	8598	ND
13	AH13	321.29	45637	7.25
14	AH14	1503	8184	ND
15	AH15	107.91	38442	ND
16	AH16	19.61	12331	ND
Sl. No.	**Sample ID**	**Total Chromium**	**Total Iron (mg/kg)**	**Hexavalent Chromium**

		(mg/kg)		(mg/kg)
17	AH17	70.50	25679	ND
18	AH18	71.44	17605	ND
19	AH19	70.62	27449	ND
20	AH20	71.47	17890	ND
21	AH21	54.51	4981	0.343
22	AH22	111.14	6601	ND
23	AH23	83.13	13195	ND
24	AH24	22.25	17493	ND
25	AH25	13.63	8618	0.217

ND = Not Detected

The distribution of the heavy metals concentration of the soil from the study area is plotted in QGIS as shown in **Figure 33 (a-c)**

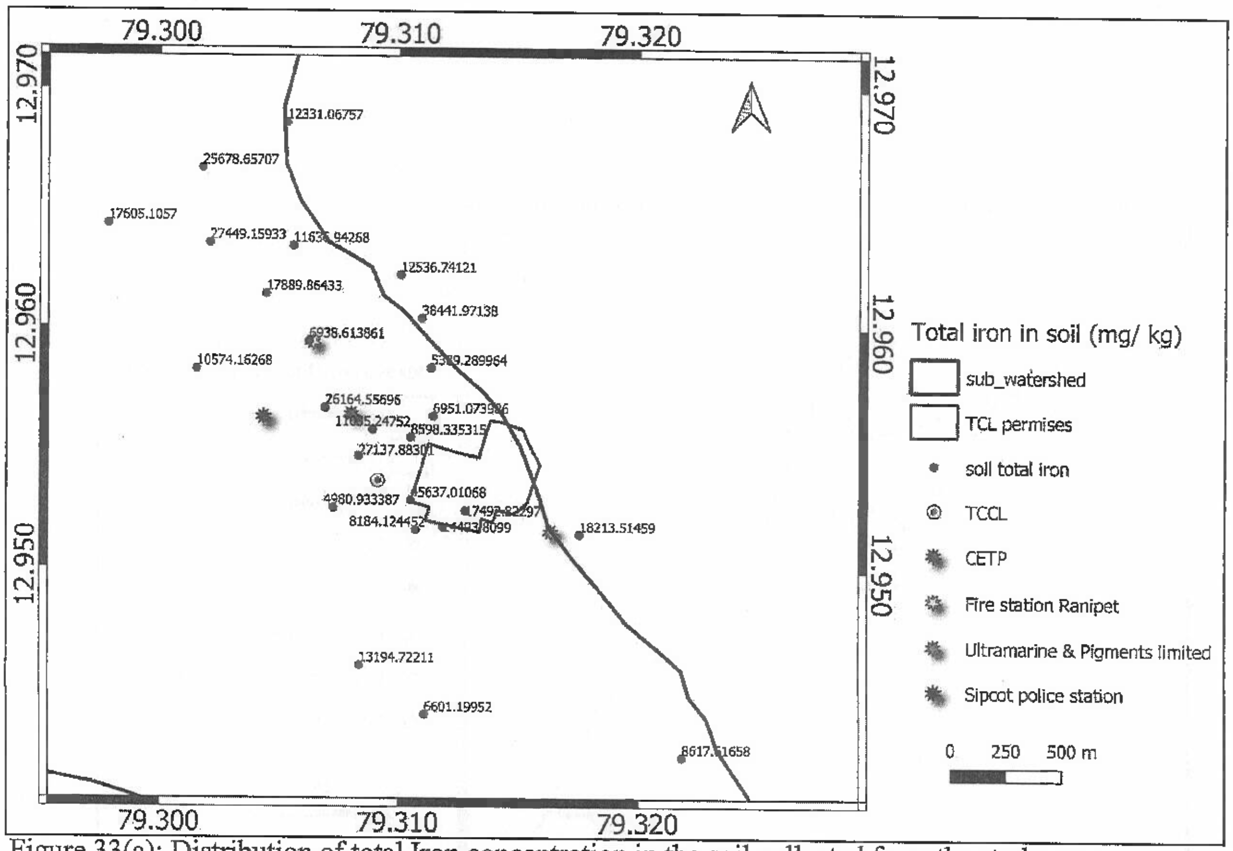

Figure 33(a): Distribution of total Iron concentration in the soil collected from the study area

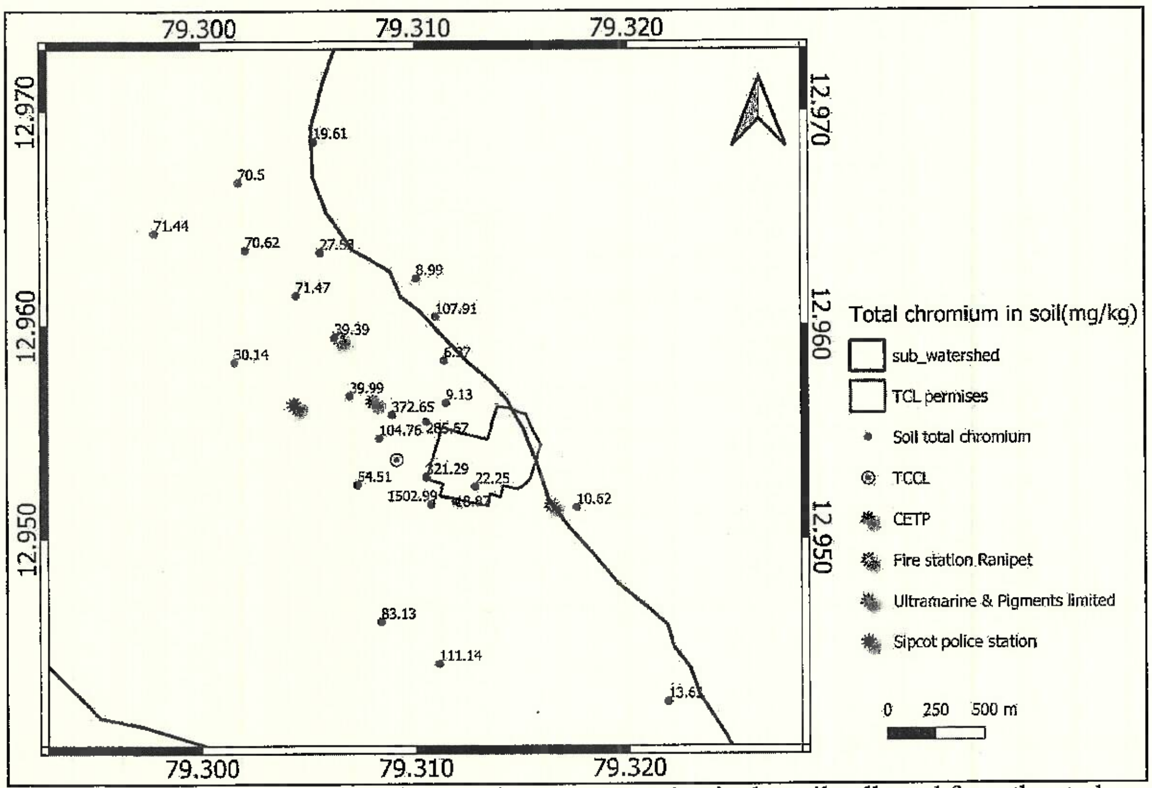

Figure 33(b): Distribution of total Chromium concentration in the soil collected from the study area

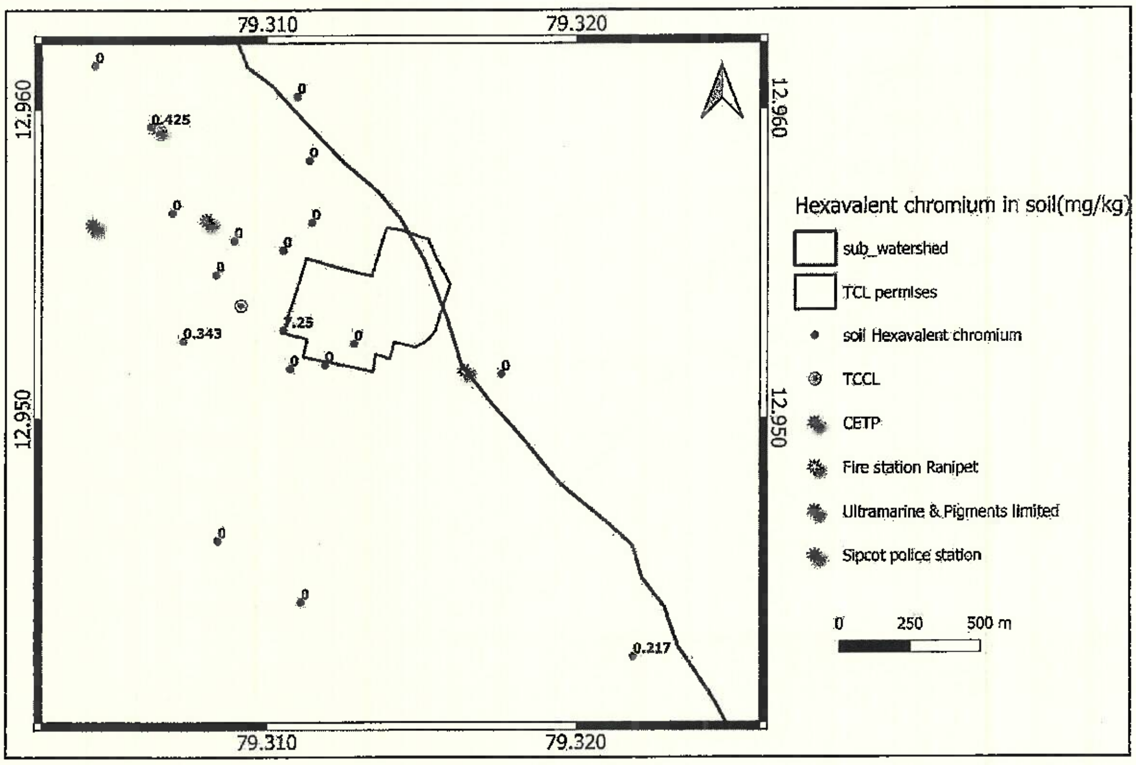

Figure 33(c): Distribution of Hexavalent Chromium concentration in the soil collected from the study area

Chromium is a non-biodegradable element and exists in nature in two oxidation states, trivalent and Hexavalent. The soil samples taken from the bottom of the 25 Auger holes were analyzed for total chromium. The values are expressed in mg/kg of soil. The concentrations are marked on the map at the sample points of Auger holes. The concentration profiles appear like waves propagated in a pond. The center point of origin with the maximum concentration 372 mg of Cr/kg of soil is the chromium dump at Tamilnadu Chromates Limited. The propagating waves confirm the flow paths of North to South, and NW to SE. The profile pattern confirms and is in agreement with the pattern of ground water flow estimated by hydro-geophysical tests and instrumental analytical results. TCL is located in one of the waves of propagation.

Formic acid and Oxalic Acid:

Among the 20 soil samples analysed none of the samples showed the presence of water soluble Formic Acid. None of the samples Formic Acid was present. The result of the samples is shown in **Table 13** and the spatial distribution and contour of Oxalic acid is shown in **Figure 34**.

Table 13: Concentration of Formic acid and Oxalic acid in the soil samples

Sl. No.	Sample ID	Formic Acid (gm/kg)	Oxalic Acid (mg/kg)
1	AH01	ND	ND
2	AH02	ND	115
3	AH03	ND	89
4	AH04	ND	234
5	AH05	ND	156
6	AH07	ND	614
7	AH08	ND	133
8	AH11	ND	136
9	AH12	ND	113
10	AH13	ND	106
11	AH14	ND	120
12	AH15	ND	127
13	AH18	ND	131
14	AH19	ND	110
15	AH20	ND	303
16	AH21	ND	205
17	AH22	ND	129
18	AH23	ND	124
19	AH24	ND	189
20	AH25	ND	174

ND = Not Detected

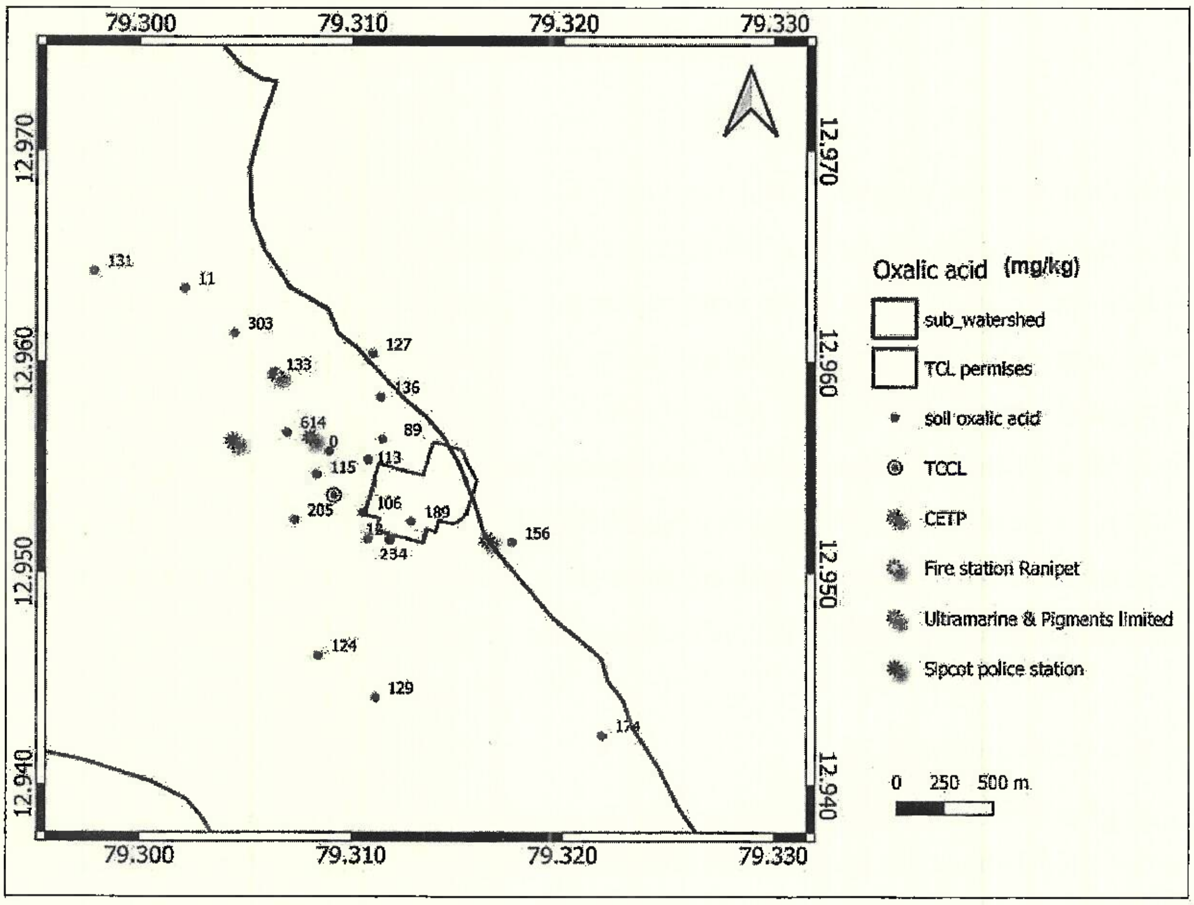

Figure 34: Spatial distribution of Oxalic Acid in soil samples

Oxalic acid is an organic acid. It is extensively used in various stages of leather processing. It is soluble in water. The used Oxalic acid finds its way into the process waste waters. Oxalic acid is biodegradable, both in water and soil. Oxalic acid is toxic, non-potable. A single oral dose toxicity test with 5% aqueous solution of Oxalic acid, an LD50 of 9.5 mL/Kg (475 mg/kg bw) was determined in male rats, and an 7.5 mL/Kg (375 mg/kg bw) was determined in female rats. (Vernot et al 1977).

The presence of Oxalic acid in soil samples show that there is a continuous ingress of Oxalic acid into the land, such that in spite of the bio degradability, a residual Oxalic Acid is existing.

The concentration of Oxalic acid in each sample is marked on the map, at the sample points of Auger holes; The concentration profiles of oxalic acid in the soil show two major sources of high concentration, Auger Hole -20 and Auger Hole -07. The concentration profiles super imposed with the ground water flow, estimated by hydro geophysical studies show the following patterns

Oxalic acid originates from AH-07, mixes in the ground water flowing in the direction of North to South. The concentration of Oxalic acid gets reduced both by dilution and biodegradation.

Oxalic acid originating from AH-20 takes similar pattern, but at a lesser concentration. The direction of depletion of concentration follows a ground water flow in the direction of NW to SE. The direction of ground water flow estimated by depletion of concentration – NW to SE is in agreement with the ground water flow estimated by hydrogeo physical tests and instrumental analytical results. The pattern of less rate of depletion in the concentration can be attributed to the shorter distance between the sample points.

TCL do not use or produce Oxalic acid. Because of the neighboring industrial activity, the plume of Oxalic acid passes through TCL, by virtue of already established flow paths and proceeds downstream further.

6.7. Analysis of water samples

6.7.1. Overall analysis and sample distribution

In order to evaluate the contamination status of surface and ground water, total 59 water samples were collected from the study area. The types of samples and their respective numbers are given in below **Table 14**. The **Figure 35** shows some photographs taken during the water sampling from different locations.

During the drilling of the auger holes water was found in 8 out of 25 locations of 1, 4, 5, 11, 14, 16, 18, and 21. Water samples from these locations were collected for analyses. The same locations were investigated after 19 days for available water. It was found that in 3 locations 4, 11, and 16 water was absent. Hence water samples from the other 5 locations were collected again for analyses. Apart from water samples from auger holes, water samples were collected from various sources throughout the study area. A total of 59 water samples were taken for study, with 13 from auger holes, 7 from the Piezo metric wells within TCL, and 39 from the drains, man-made water flow, bore wells, and river water.

During the collection of the water samples GPS location long with the location information was also collected, which is shown in **ANNEXURE 8**. The location of the water samples corresponding to the grids in mentioned in **Table 15** and is shown in **Figure 36**.

Table 14: Types of water samples collected from the study area

Sl. No.	**Sample Code**	**Samples Type**	**Number of samples**
1	WAH	Auger hole water collected on 28-01-2021	8
2	RWAH	Resampling Auger hole water collected on 17-02-2021	5
3	DS/DS	Downstream/Upstream Piezo metric well	7
4	DR	Drain water	24
5	SW	Lake/River	6
6	GW	Borewells	5
7	OT	Others	4
Total			59

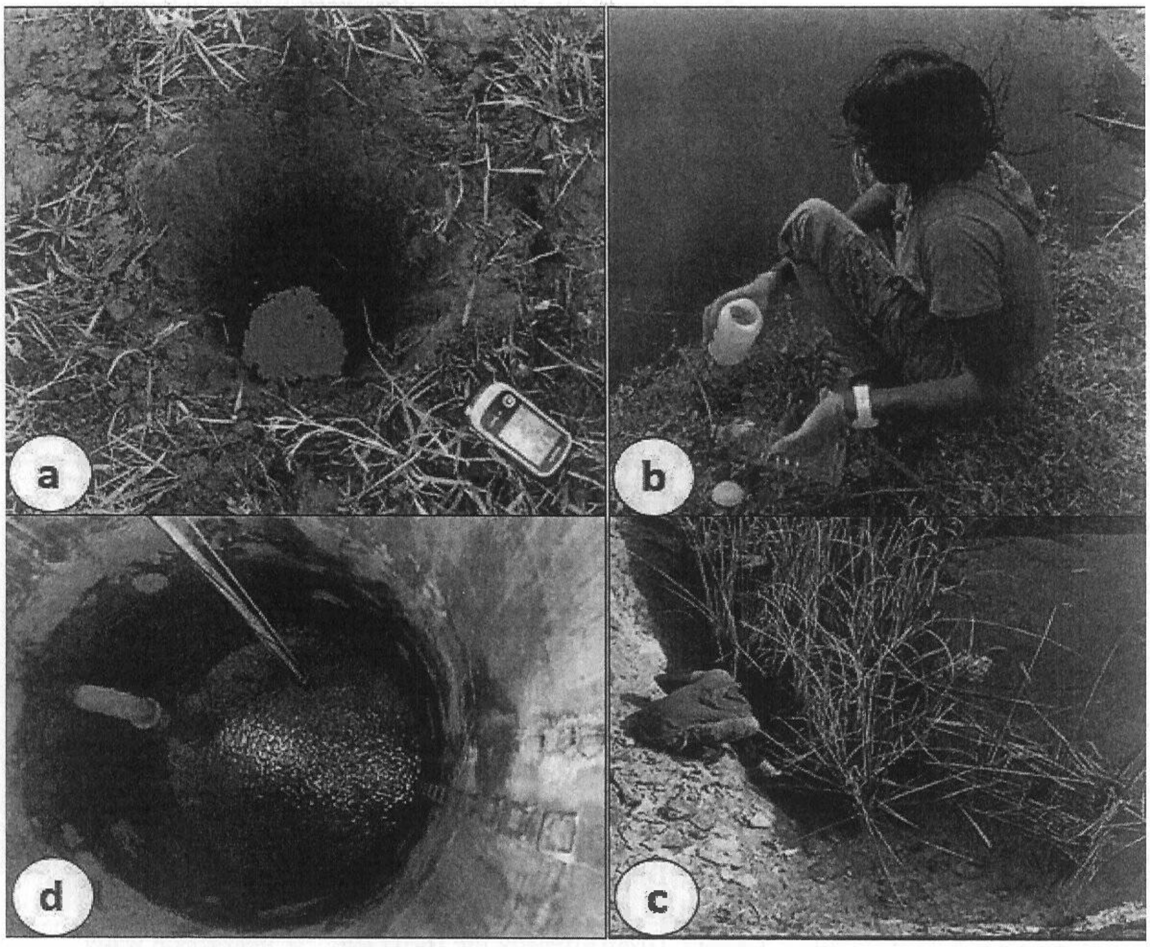

Figure 35: Water sampling from a) auger hole, b) pond, c) pool, and d) Govt. bore well tank

Table 15: Location and details of the water samples

Sl. No.	Sample ID	Gridno.	Location	Sample type
1	WAH 01	17	Back side of Intercontinental Leathers (CETP Pool)	Auger hole water
2	WAH 04	23	TCL PA3 Main Gate - Behind Raw water collection tank	Auger hole water
3	WAH 05	24	UPL (Main Gate) Ponnai highway	Auger hole water
4	WAH 11	18	NW Boundary of TN Warehouse - Near TATA international	Auger hole water
5	WAH 14	13	Opposite to Maruthi Suzuki (Emerald road)	Auger hole water
6	WAH 16	9	Opposite To BBK Shoes - Near Balaji Oil company	Auger hole water
7	WAH 18	11	Near puliyanthangal Lake Crematorium land	Auger hole water
8	WAH 21	22	West to Reliance petrol bunk	Auger hole water
9	RWAH 01	17	Back side of Intercontinental Leathers. (CETP Pool)	Resampling Auger hole water

Sl. No.	Sample ID	Gridno.	Location	Sample type
10	RWAH 05	24	UPL (Main Gate) Road Side	Resampling Auger hole water
11	RWAH 14	13	Opposite to Maruthi Suzuki (Emerald road)	Resampling Auger hole water
12	RWAH 18	11	Crematorium Near Puliyanthangal Lake	Resampling Auger hole water
13	RWAH 21	22	West side of Reliance petrol bunk	Resampling Auger hole water
14	DS2	23	Downstream Piezo metric well inside TCL No. 2	Piezometric well
15	DS3	23	Downstream Piezo metric well inside TCL No 3	Piezometric well
16	DS4	23	Downstream Piezo metric well inside TCL No 4	Piezometric well
17	US1	23	Upstream Piezo metric well inside TCL No 1	Piezometric well
18	US2	23	Upstream Piezo metric well inside TCL No 2	Piezometric well
19	US3	23	Upstream Piezo metric well inside TCL No 3	Piezometric well
20	US4	24	Upstream Piezo metric well inside TCL No 4	Piezometric well
21	DR01	18	Opposite to TATA International	man-made water flow
22	DR02	18	Opposite to Hi-Tech Engineering (Behind TCCL)	man-made water flow
23	DR03	17	Near Rich Marks Leathers (Behind TCCL)	man-made water flow
24	DR04	17	CETP Drain starting Point 7th Cross Street	man-made water flow
25	DR05	17	CETP Drain crossing the road (7th Cross Street)	man-made water flow
26	DR06	17	Opposite to KM Weigh Bridge	man-made water flow
27	DR07	13	Opposite to MS Overseas Leathers	man-made water flow
28	DR08	13	Near Euro Shoes	man-made water flow
29	DR09	12	Opposite to ALFA Leathers	man-made water flow
30	DR10	9	Near Balaji Oil Company	man-made water flow
31	DR11	9	Opposite to BBK Leather	man-made water flow
32	DR12	9	Opposite to Arjun Chemicals	man-made water flow
33	DR13	8	Opposite To Jothy Leathers	man-made water flow

Sl. No.	Sample ID	Gridno.	Location	Sample type
34	DR14	11	Drain towards Puliyanthagal Lake	man-made water flow
35	DR15	12	Near Kowshik Leathers	man-made water flow
36	DR16	17	Drain CETP Culvert	man-made water flow
37	DR17	16	Near AP Exports	man-made water flow
38	DR18	16	Near Arul Leathers	man-made water flow
39	DR19	9	Near BBK Shoes	man-made water flow
40	DR20	22	Near SOPCOT Police Station	man-made water flow
41	DR21	23	Near TCCL Culvert	man-made water flow
42	DR22	22	Near Reliance Culvert	man-made water flow
43	DR23	23	TCL ATM Outlet	man-made water flow
44	DR24	22	Drain to Maniampattu Lake MGR Nagar, SIPCOT	man-made water flow
45	SW01	28	Drain towards Karai from Maniampattu Lake	lake water
46	SW02	39	Drain From Karai Lake to Paalar River	lake water
47	SW03	59	At Paalar River Downstream	river water
48	SW04	57	Paalar River Upstream Near the Kaarai village Pump House	river water
49	SW05	10	Pulliyanthangal Lake	lake water
50	SW06	54	Small water body Karai to Paalar River	water flows from lake to river
51	GW01	46	Borewell in Karai Village Cotton Bazzar Street	borewell
52	GW02	57	Bore well pump at the Paalar River (GWD 2402)	borewell
53	GW03	39	Maniamattu Bore well	borewell
54	GW04	11	Bore well Near Puliyanthangal Lake	borewell
55	GW05	31	Agriculture Land	pump borewell
56	OT01	29	Near Drain Dug Well above Karai Lake	gutter flowing water
57	OT02	22	Inside Intercontinental Leathers	pool sample
58	OT03	22	TCCL Inside Pit	pit sample
59	OT04	23	TCCL Backside Pool	pool sample

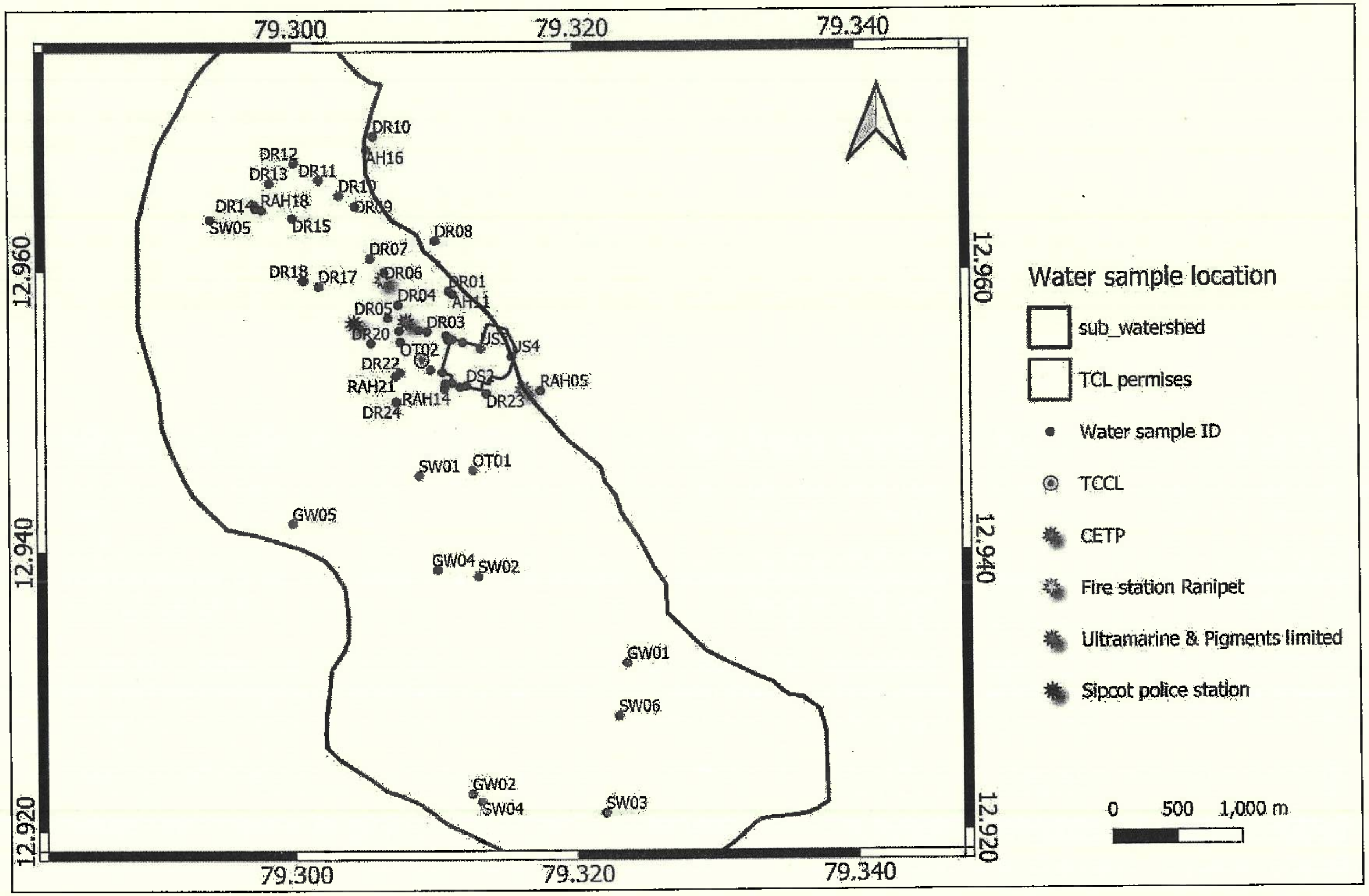

Figure 36: Location of different types of water samples in the study area.

The physiochemical parameters for all the water sample as mentioned in the previous section have been analysis which is tabulated in **Table 16**. Due to presence of color in few samples, which caused interference in the result, we could not analyze Turbidity, Total alkalinity, Total hardness, Sulphate and Chloride. These samples are mostly artificial drain samples near to tanneries and other industries.

Table 16: Physiochemical parameters of the water samples collected from the study area

Sl. No.	Sample ID	PH	Sp Cond (µS/cm)	Turbidity (NTU)	Total Alkalinity (mg/L)	Total Hardness (mg/L)	Chloride (mg/L)	Sulphate (mg/L)
1	WAH01	8.43	2400	12.3	330	690	425	135
2	WAH04	7.57	3900	6.4	550	915	1142	38
3	WAH05	8.29	2900	9	535	625	537	100
4	WAH11	7.92	1713	23.8	260	475	400	73
5	WAH14	8.34	428	12.4	175	185	82	32
6	WAH16	8.13	1468	18	440	815	217	64
7	WAH18	8.23	700	21.6	140	215	110	79
8	WAH21	8.06	4200	1	490	550	950	225
9	RWAH01	8	2700	12.7	410	715	495	131
10	RWAH05	8.13	3600	9.6	580	925	700	158
11	RWAH14	7.94	669	5.2	280	320	60	51
12	RWAH18	8.05	1942	12.2	325	550	237	156
13	RWAH21	7.91	5100	1.9	750	750	1015	191
14	DS2	7.63	3100	31.8	435	600	587	114
15	DS3	7.64	3100	25.8	850	625	517	74
16	DS4	7.97	1495	1.5	300	450	235	52
17	US1	8.01	1927	0	525	230	265	57
18	US2	7.52	8300	5.3	1075	950	2249	57
19	US3	7.73	16700	17.3	770	1525	5361	168
20	US4	7.59	14400	16.4	530	3775	4249	181
21	DR01	7.48	2100	5.8	415	675	400	69
22	DR02	8.86	817	60.9	245	275	137	25
23	DR03	8.2	6500	9.5	2050	450	1142	31
24	DR04	7.89	4900	0	470	700	945	233
25	DR05	7.62	5400	0	340	900	1125	308
26	DR06	8.26	2500	6.2	580	600	380	65
27	DR07	8.15	2700	15.6	530	575	412	61
28	DR08	7.6	3100	0.5	310	475	532	156
29	DR09	7.62	3800	**COULD NOT ANALYSED DUE TO COLOUR**				
30	DR10	8.8	2500	5.6	110	325	450	168

	SampleID	PH	Sp Cond (µS/cm)	Turbidity (NTU)	Total Alkalinity (mg/L)	Total Hardness (mg/L)	Chloride (mg/L)	Sulphate (mg/L)
31	DR11	7.4	5100	**COULD NOT ANALYSED DUE TO COLOUR**				
32	DR12	7.86	4700	**COULD NOT ANALYSED DUE TO COLOUR**				
33	DR13	8.66	1909	0	390	295	310	80
34	DR14	8.08	5700	**COULD NOT ANALYSED DUE TO COLOUR**				
35	DR15	7.54	1245	8	235	295	262	36
36	DR16	7.83	5100	0	455	795	1100	271
37	DR17	6.71	11400	13.3	215	2365	2974	577
38	DR18	7.45	8200	**COULD NOT ANALYSED DUE TO COLOUR**				
39	DR19	7.89	659	2.5	200	225	112	35
40	DR20	7.8	1400	6.5	365	610	375	61
41	DR21	10.18	1900	0	360	70	330	94
42	DR22	7.42	3800	0	305	305	800	206
43	DR23	7.43	6500	9.6	835	725	1475	328
44	DR24	7.38	3900	0	340	345	812	209
45	SW01	7.7	3700	0	435	410	762	196
46	SW02	7.66	2400	6	325	465	612	116
47	SW03	8.86	1200	25.1	175	265	332	37
48	SW04	8.52	1000	7.1	290	285	237	41
49	SW05	8.09	1900	5.7	210	500	442	120
50	SW06	7.08	2200	12.5	450	525	550	81
51	GW01	7.6	955	0.7	365	345	150	36
52	GW02	7.74	1200	0	295	300	287	43
53	GW03	7.49	1400	0.4	415	550	232	58
54	GW04	7.45	2400	0	400	930	437	94
55	GW05	7.67	1000	1.4	370	425	180	43
56	OT01	7.3	805	9.4	290	225	125	40
57	OT02	7.95	10200	8.1	360	1015	2424	565
58	OT03	10.86	2700	8.6	975	75	120	120
59	OT04	7.68	1400	8.3	250	375	262	110

The **Figure 37 (a-g)** shows the distribution of different physiochemical parameters of all the water samples collected from the study area.

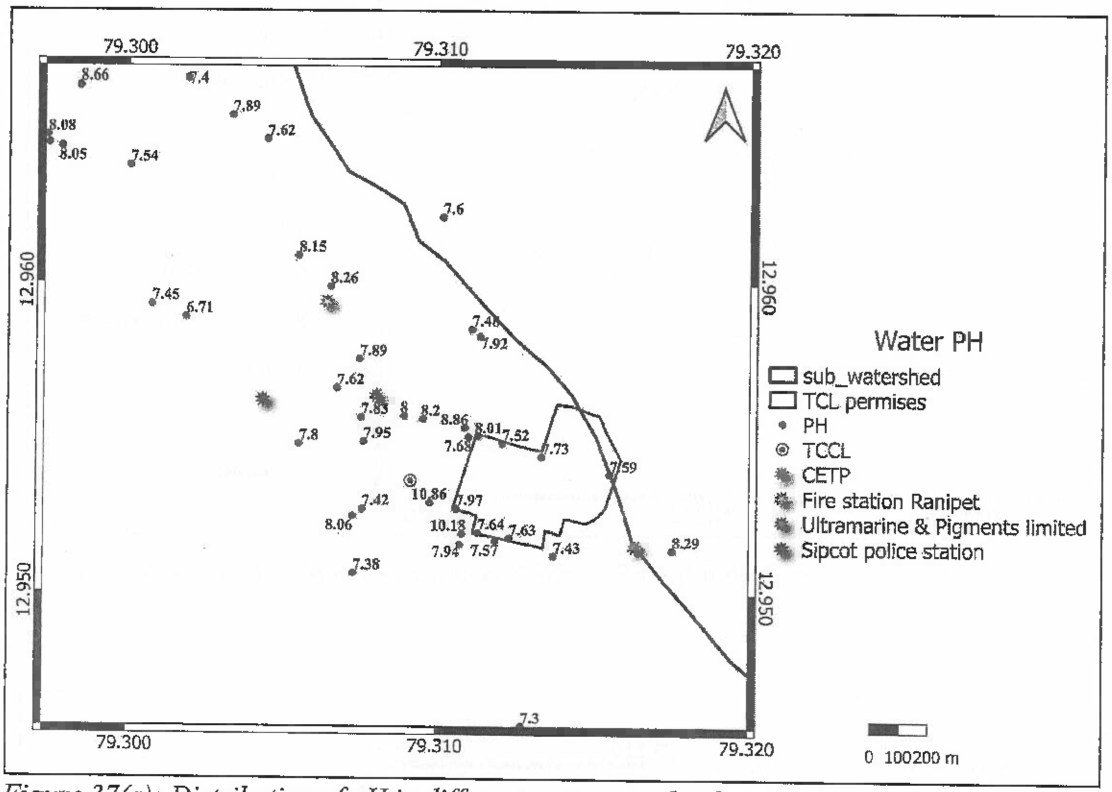

Figure 37(a): Distribution of pH in different water samples from the study area.

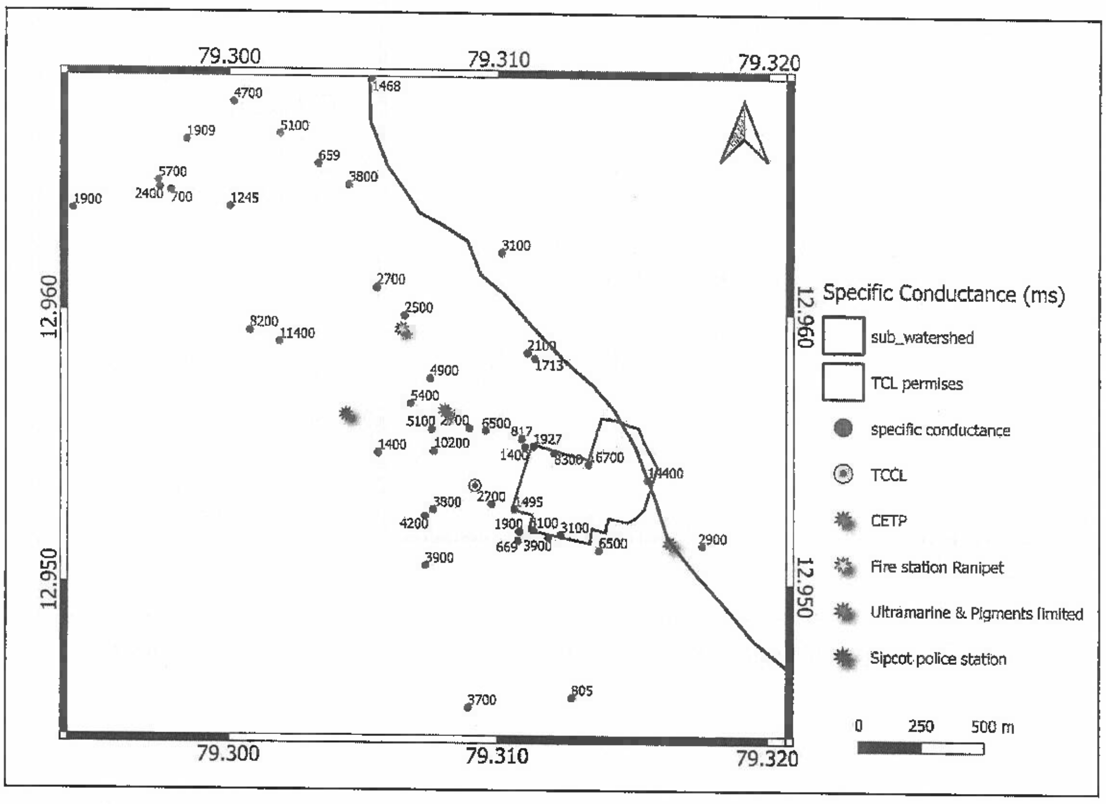

Figure 37(b): Distribution of Specific conductivity in different water samples from the study area.

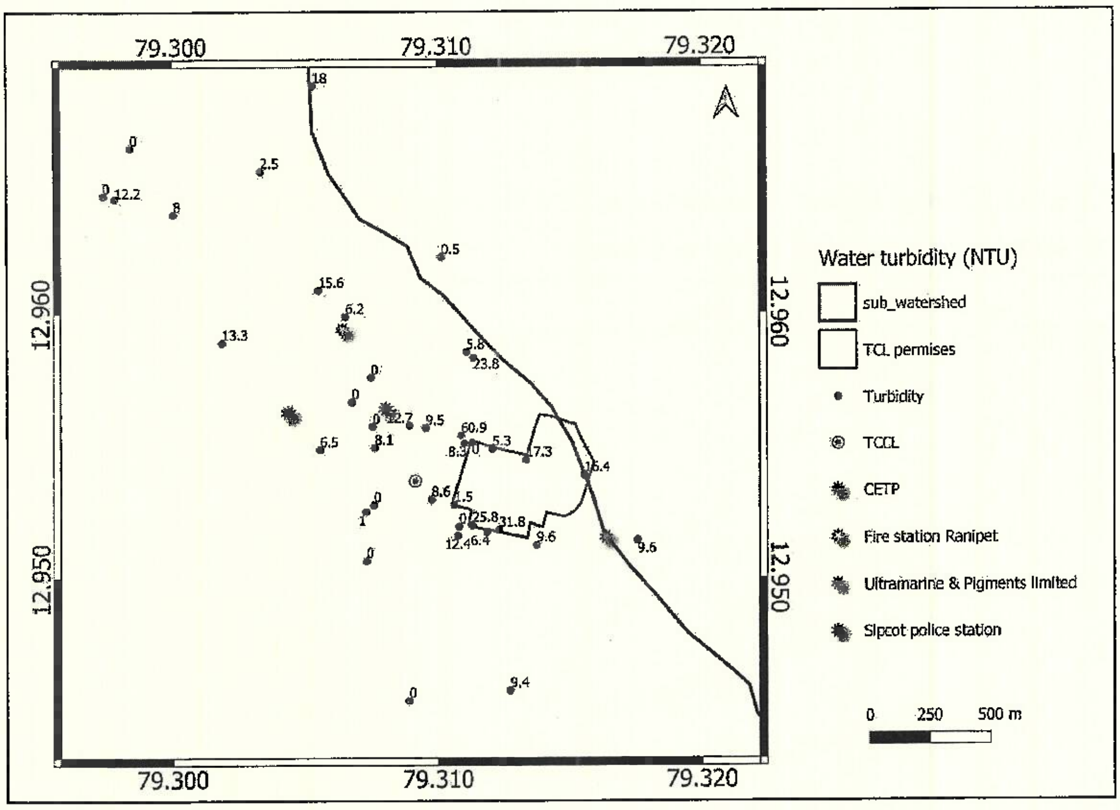

Figure 37 (c): Distribution of Turbidity (NTU) in different water samples in the study area

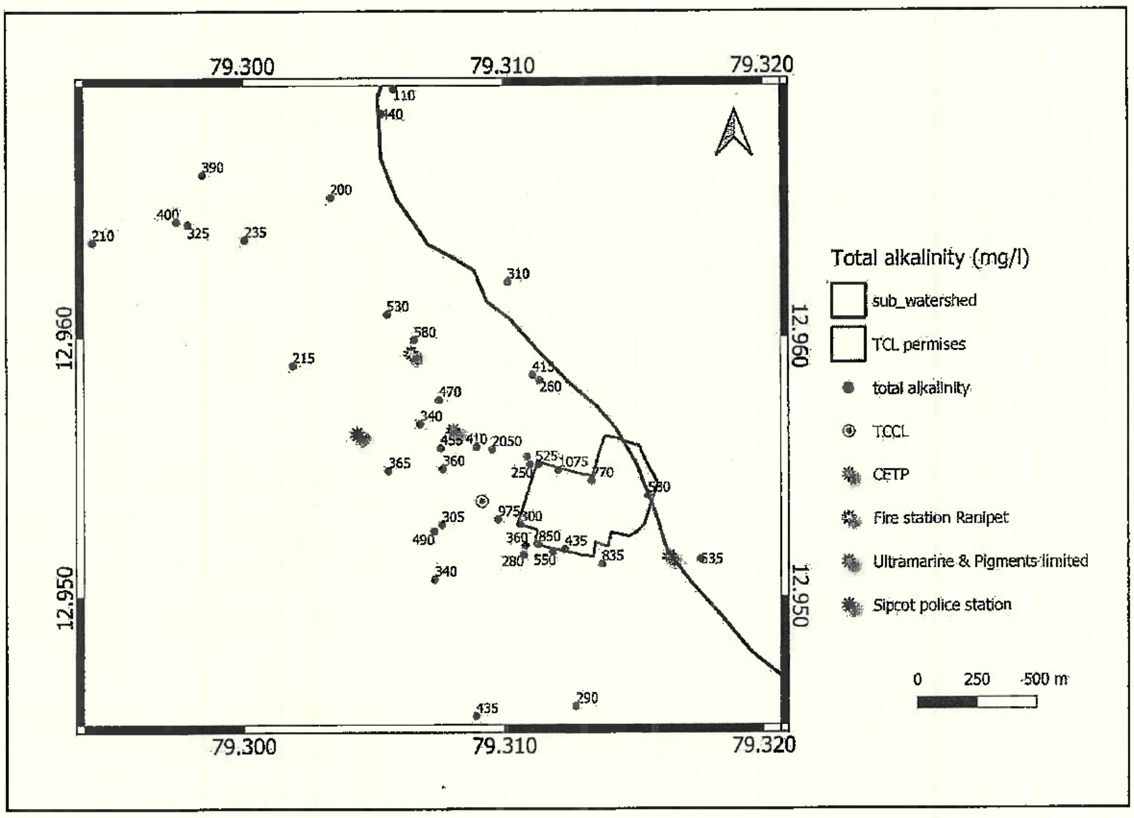

Figure 37 (d): Distribution of Total alkalinity in different water samples in the study area

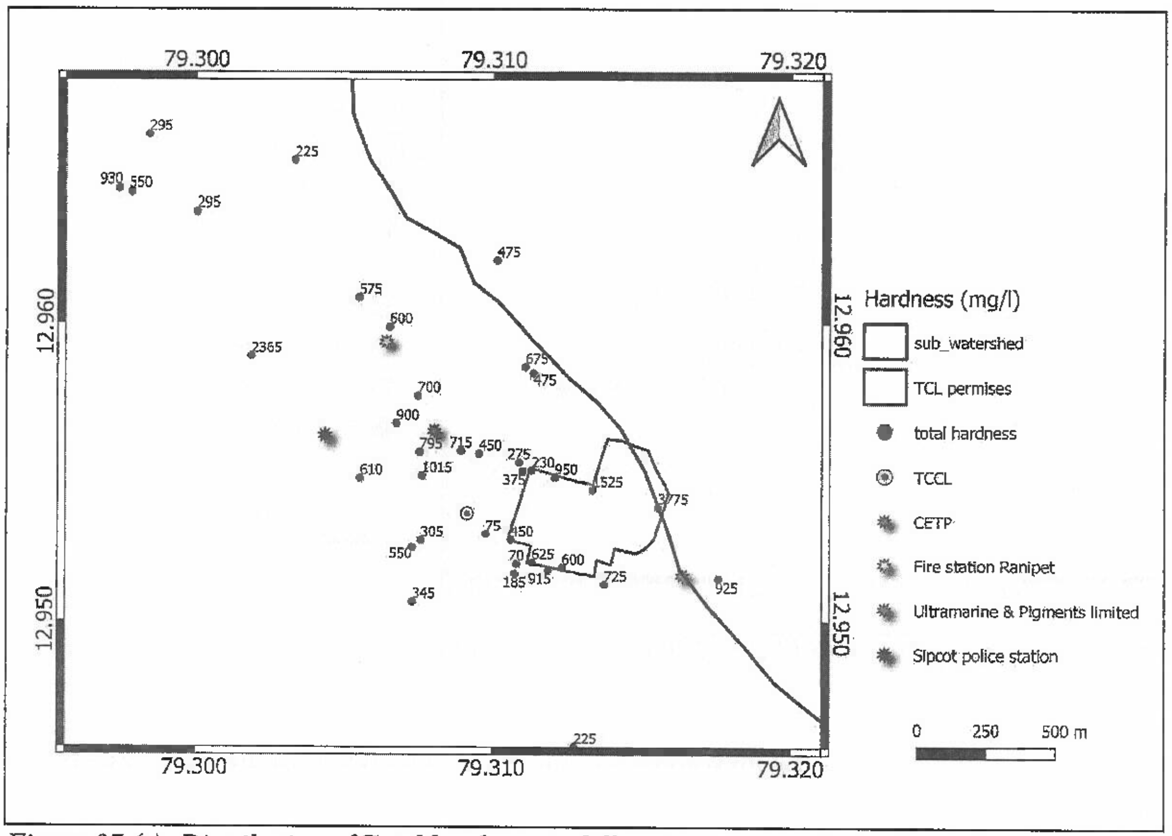

Figure 37 (e): Distribution of Total hardness in different water samples in the study area

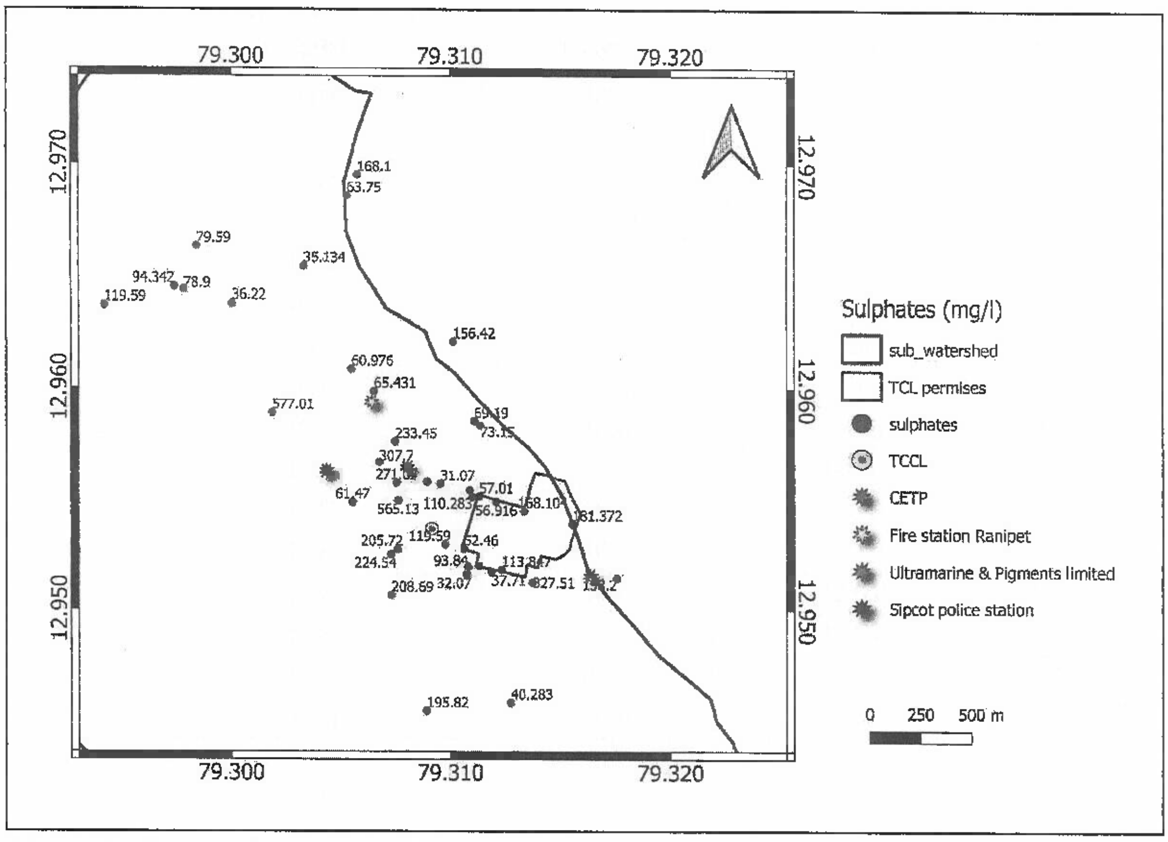

Figure 37 (f): Distribution of Sulphate in different water samples in the study area

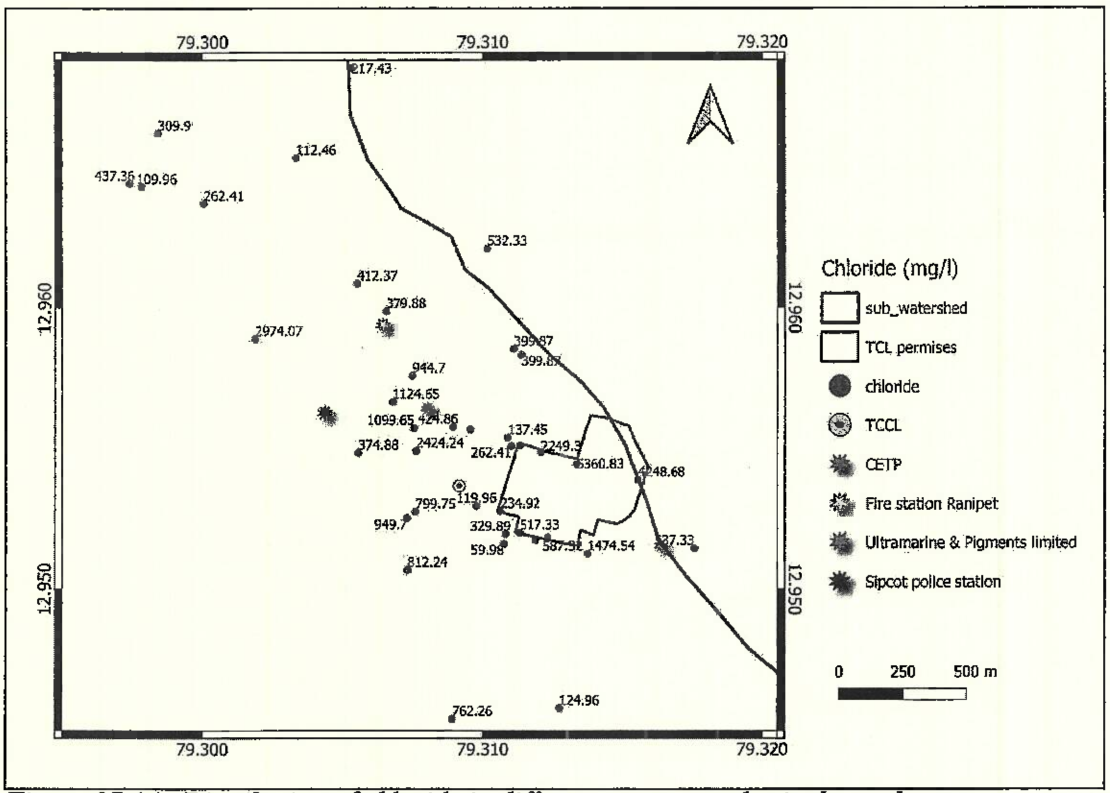

Figure 37 (g): Distribution of chloride in different water samples in the study area

The total Cr, Fe and hexavalent Cr concentration in the water samples from the study area is presented in **Table 17**.

Table 17: Heavy metal concentration of the water samples collected from the study area

Sl. No.	Sample ID	Total Chromium (mg/L)*	Total Iron (mg/L)*	Hexavalent Chromium (mg/L)#
1	AH01	0.007	BDL	BDL
2	AH04	BDL	BDL	BDL
3	AH05	BDL	BDL	BDL
4	AH11	0.046	0.163	BDL
5	AH14	BDL	BDL	BDL
6	AH16	0.297	1.669	BDL
7	AH18	BDL	BDL	BDL
8	AH21	BDL	0.859	BDL
9	RAH01	BDL	BDL	BDL
10	RAH05	0.044	0.046	BDL
11	RAH14	BDL	BDL	BDL
12	RAH18	BDL	BDL	BDL
13	RAH21	0.022	BDL	BDL
14	DS2	0.017	0.155	BDL
15	DS3	6.701	8.29	BDL
16	DS4	24.41	BDL	10.95

Sl. No.	Sample ID	Total Chromium (mg/L)*	Total Iron (mg/L)*	Hexavalent Chromium (mg/L)#
17	US1	15.72	0.098	9.15
18	US2	0.029	0.039	BDL
19	US3	BDL	0.303	BDL
20	US4	0.088	0.864	BDL
21	DR01	0.124	3.319	BDL
22	DR02	0.163	0.802	BDL
23	DR03	13.30	42.19	BDL
24	DR04	0.278	2.052	BDL
25	DR05	0.315	1.301	BDL
26	DR06	0.167	0.373	BDL
27	DR07	0.007	0.003	BDL
28	DR08	0.049	0.042	BDL
29	DR09	1.874	0.501	BDL
30	DR10	0.025	0.634	BDL
31	DR11	9.059	0.752	BDL
32	DR12	2.938	0.783	BDL
33	DR13	4.868	17.58	ND
34	DR14	2.012	7.046	BDL
35	DR15	0.133	1.018	BDL
36	DR16	0.557	2.668	BDL
37	DR17	6.675	3.273	BDL
38	DR18	50.36	13.47	BDL
39	DR19	1.034	0.067	BDL
40	DR20	0.695	1.721	BDL
41	DR21	44.50	5.701	28.2
42	DR22	0.351	0.511	BDL
43	DR23	0.059	3.707	BDL
44	DR24	0.219	0.07	BDL
45	SW01	0.764	2.411	BDL
46	SW02	0.656	2.922	BDL
47	SW03	0.05	0.266	BDL
48	SW04	BDL	BDL	BDL
49	SW05	BDL	BDL	BDL
50	SW06	BDL	1.802	BDL
51	GW01	0.405	BDL	BDL
52	GW02	0.05	1.23	BDL
53	GW03	BDL	BDL	BDL
54	GW04	1.486	4.695	BDL
55	GW05	BDL	BDL	BDL
56	OT01	1.424	0.276	BDL
57	OT02	0.496	2.614	BDL
58	OT03	144.78	1.069	0.23
59	OT04	1.721	0.882	1.37

The **Figure 38 (a-c)** shows the distribution of heavy metal of all the water samples collected from the study area

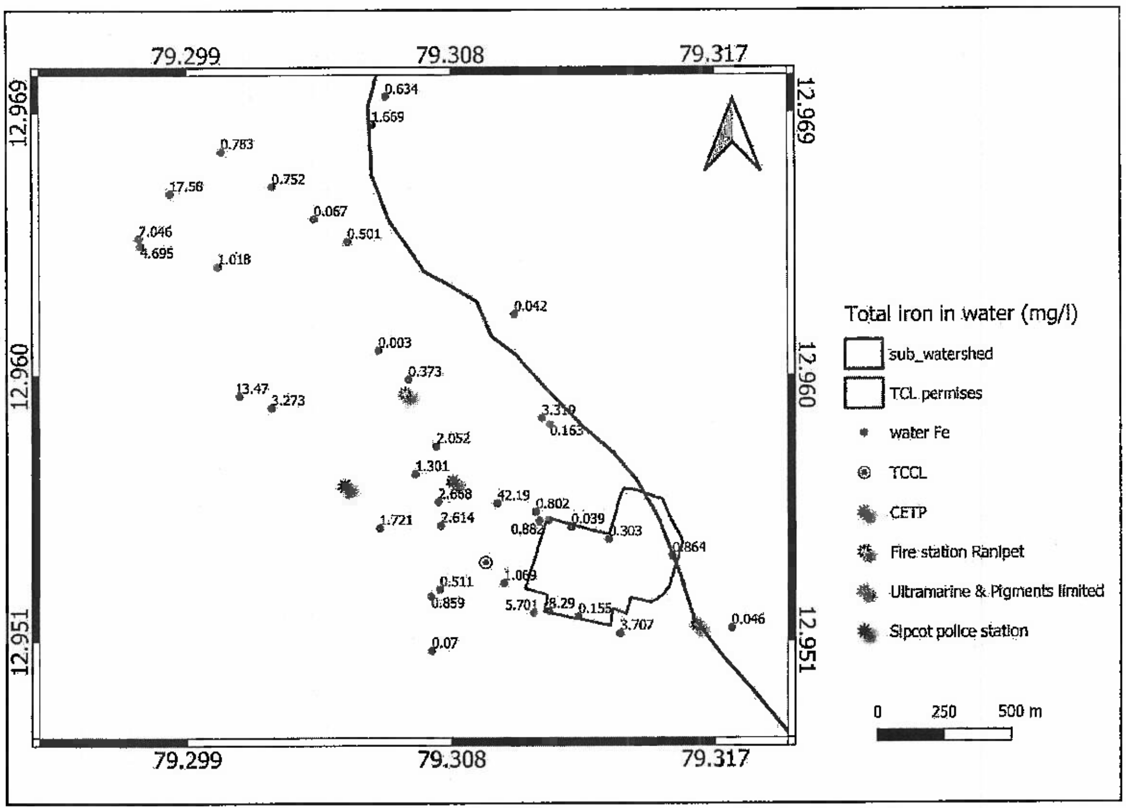

Figure 38(a): Distribution of total iron in different water samples in the study area

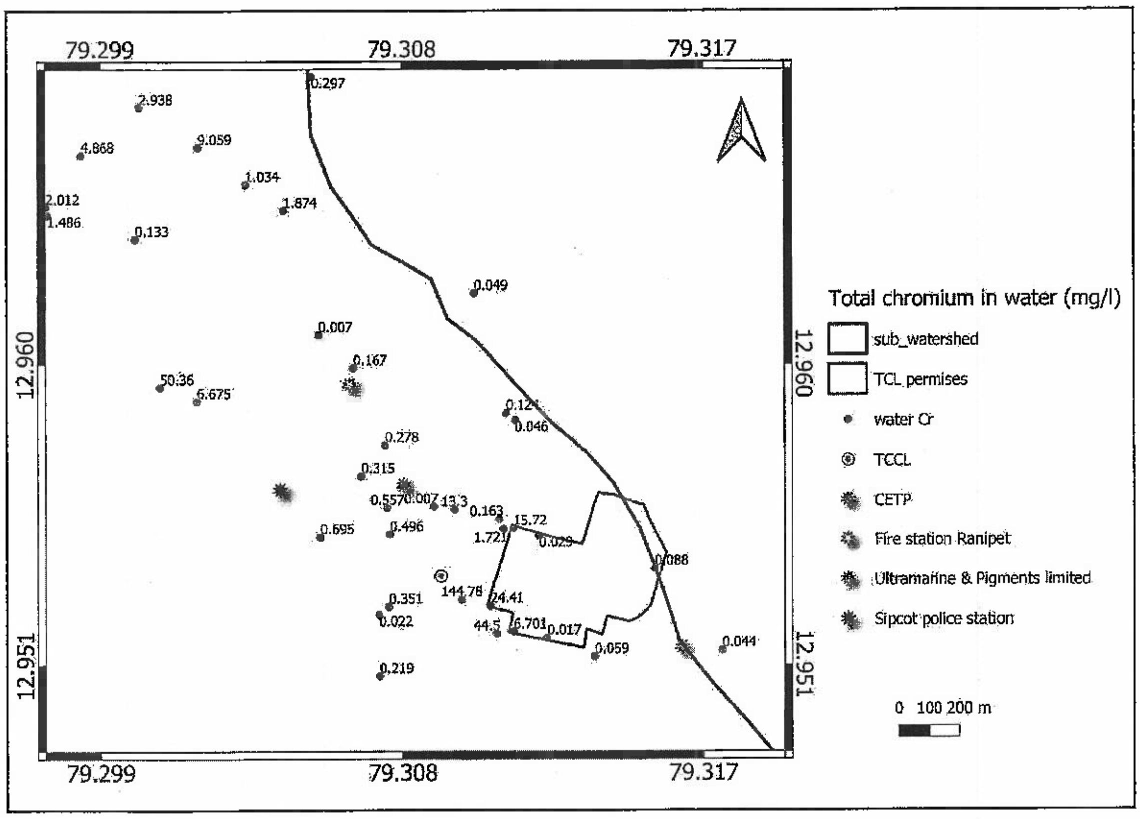

Figure 38(b): Distribution of total chromium in different water samples in the study area

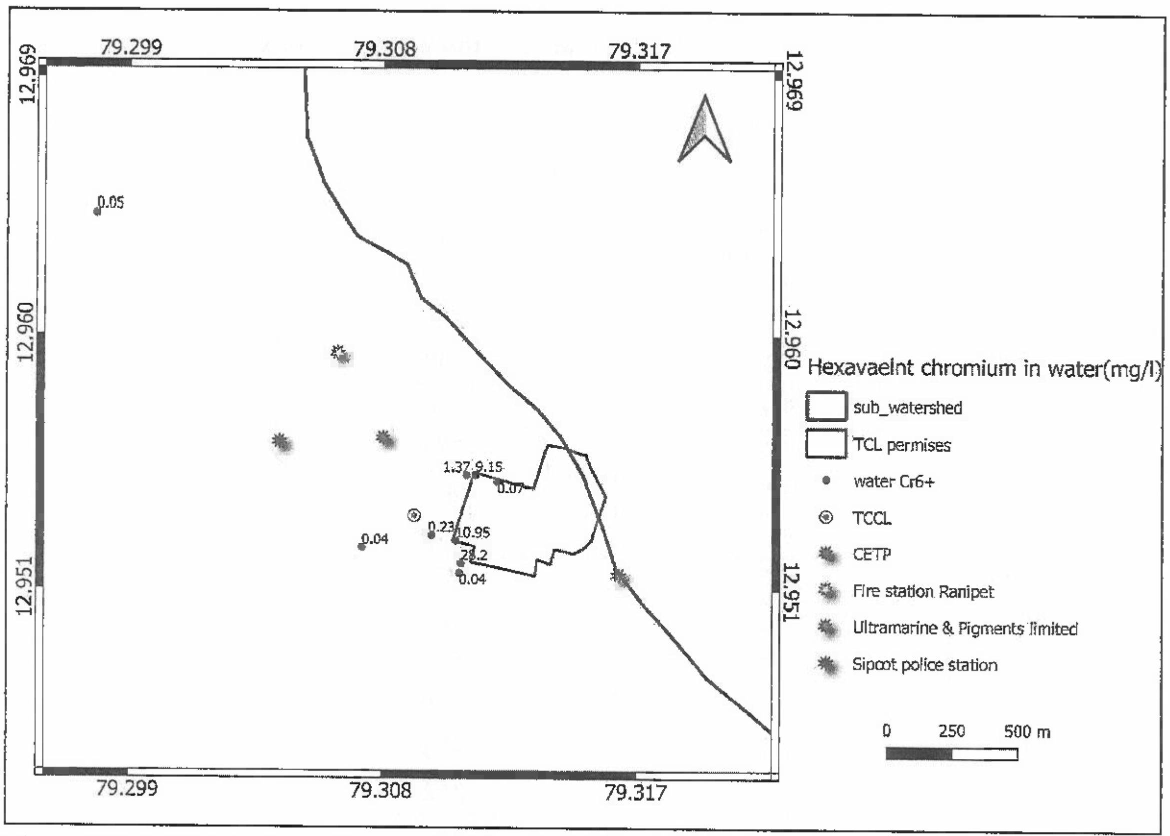

Figure 38(c): Distribution of hexavalent iron in different water samples in the study area

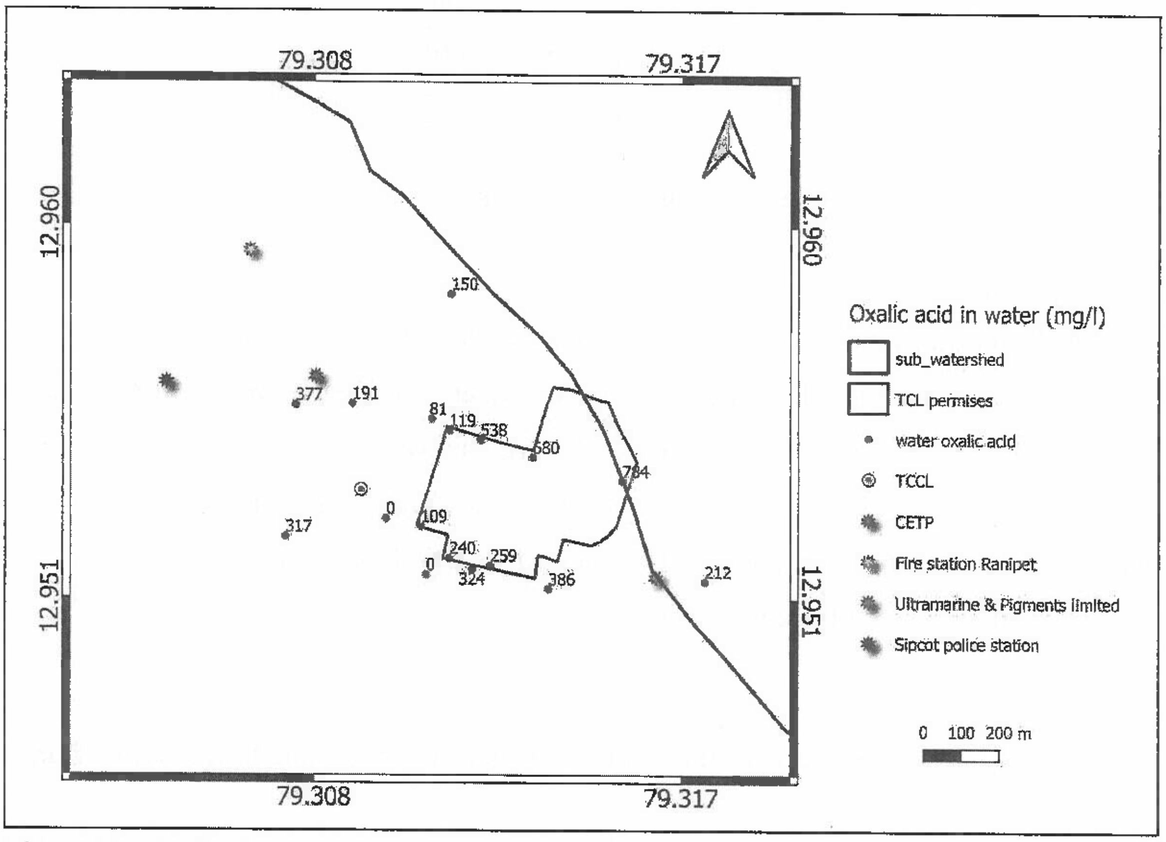

Figure 39: Distribution of Oxalic acid in water samples in the study area

The analysis of Formic Acid and Oxalic acid in the water samples is shown in **Figure 39** and **Table 18**. Interpretation of the results is given at the end of section.

Table 18: Concentration of Formic acid and Oxalic acid in the water samples

Sl. No.	Sample ID	Formic Acid (gm/L)	Oxalic Acid (mg/L)
1	US01	ND	119
2	US02	ND	538
3	US03	ND	680
4	US04	ND	784
5	DS04	ND	109
6	DS03	ND	240
7	DS02	ND	259
8	OT03	ND	46
9	DR23	ND	386
10	DR16	ND	377
11	DR02	ND	81
12	SW04	ND	117
13	WAH1	ND	191
14	WAH4	ND	324
15	WAH5	ND	212
16	WAH11	ND	150
17	WAH14	ND	24
18	WAH16	ND	105
19	WAH18	ND	110
20	WAH21	ND	317

6.8. Interpretation of Results of analysis of water samples

1. pH:

The average pH concentration of all the samples is 8.0 and all of the samples are between 6.71 and 8.86, except two samples. It indicates no acidic water was present in the open surface flowing water bodies. The samples W23 and W25 are having high pH of 10.86 and 10.18 respectively. These two manmade streams have surface flowing leachate from the chromium sludge dump at Tamilnadu Chromates and Chemicals Limited (TCCL). In general, there were sporadic values of pH10, and there is no value below 5.0.

2. HARDNESS:

The average hardness concentration of the water samples is 622 mg/L and having range from

70 mg/L to 3777 mg/L. Since, this parameter is influenced equally by both the domestic and industrial activities their concentration values cannot be interpreted as a source of pollution.

3. CHLORIDE & SULFATE:

The chloride and sulphate concentration of the water samples are having the range of 60-5360mg/L and 25-577 mg/L. The elevated chloride and sulphate concentration was found in the drains upstream of TCL. The chloride and sulphate content of freshwater (surface and groundwater) are in the range of 150-442 mg/L and 36-120 mg/L respectively. Since these parameters are highly influenced equally by the domestic and industrial activities, their concentration values cannot be interpreted as a source of pollution. Hence these analytical values are of less importance with respect to industrial activity.

4. IRON:

Iron is the second most abundant metal in the earth's crust. Therefore, it will be present in mostof the water samples and does not signify any substantial source of pollution. However the presence of iron consistently in elevated concentration in the drain samples compared to borewell samples indicate in contribution from industrial sources.

5. CHROMIUM

The presence of total chromium was identified in all the types of samples from the study area. Many drain water contain high level of chromium concentration indicate the possible sources from the surrounding industries. The groundwater samples also found to be chromium contaminated. Even the presence of chromium was found in the natural drains in the southernportion of the study area far from the industries indicate the wide prevalence of contamination. The presence of hexavalent chromium was found only in the samples surrounding to the abandoned site of Tamil Nadu Chromate and Chemicals Limited (TCCL) which is located adjacent to TCCL.

5. FORMIC ACID & OXALIC ACID

Among the 20 samples analyzed for Oxalic acid and Formic acid none of the samples have the Formic Acid. However, 18 of the samples have Oxalic acid concentration are in the range of 81 to 283 mg/L. The average Oxalic acid concentration of the three upstream monitoring wells is 531 mg/L and downstream is 203mg/L which clearly indicates the oxalic acid presence maybe from the outside sources.

The overall concentration of the water samples collected is indicative and gives very preliminary idea of the contamination status of the study area. In order to identify the contamination sources, the parametric concentration of the different water sources has been investigated in the following section.

6.8.1. Auger bore water samples

Among the 25 auger boring points, in only 8 points, as mentioned before, water was present. In the remaining points, the bedrock was there. The location of the samples is given in **Table 14** and **Figure 36**. The physiochemical parameters analyzed in these samples are shown in **Table 15**. There is no specific trend of their concentration towards the direction of the flow. The heavy metal analyses of the samples showed no presence of hexavalent chromium. The total chromium and iron concentration of the samples is shown in the **Figure 40** and **Figure 41.**

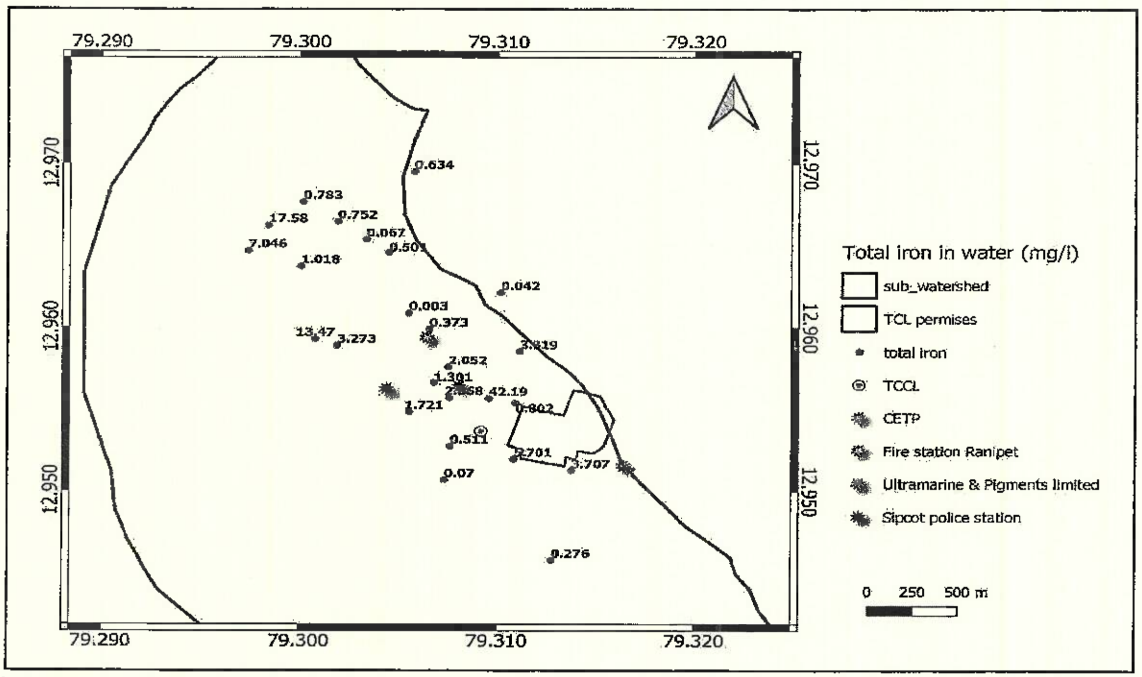

Figure 40: Distribution of total iron in the water samples collected from auger boring

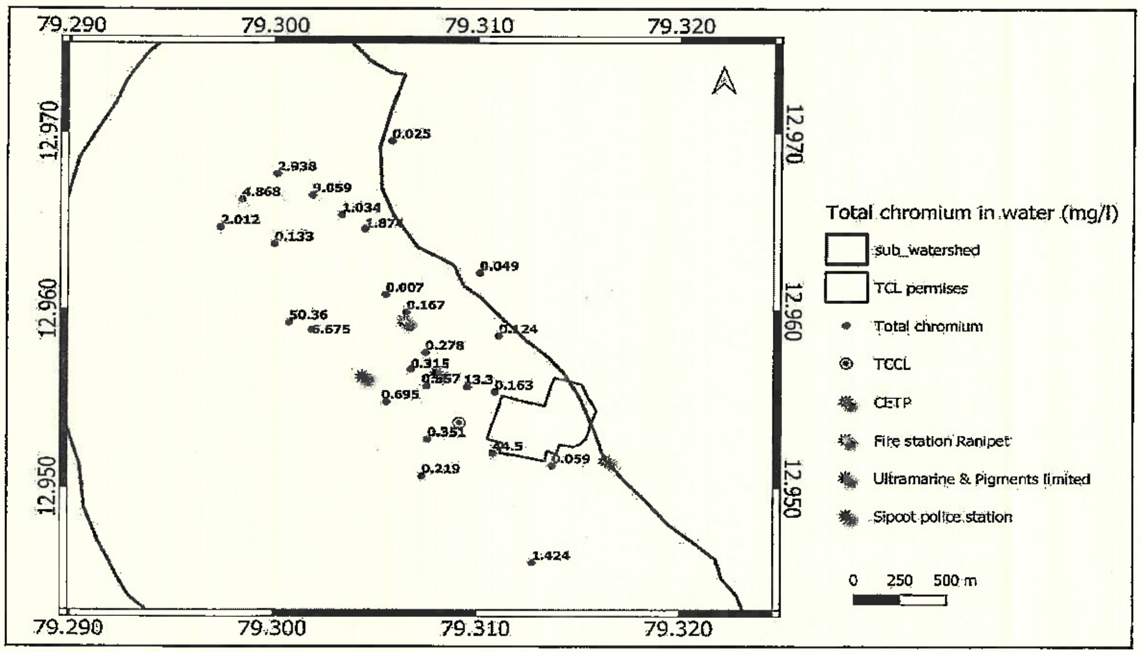

Figure 41: Distribution of total chromium in the water samples collected from auger boring

There is no formic acid present in the water samples. The oxalic acid was analyzed in 8 water samples collected and found to be in the range of 24 – 324 mg/L. The result has mentioned been tabulated in Table 18.

6.8.1. Auger bore water samples

Among the 25 auger boring points, in only 8 points, as mentioned before, water was present. In the remaining points, the bedrock was there. The location of the samples is given in **Table 14** and **Figure 36**. The physiochemical parameters analyzed in these samples are shown in **Table 15**. There is no specific trend of their concentration towards the direction of the flow. The heavy metal analyses of the samples showed no presence of hexavalent chromium. The total chromium and iron concentration of the samples is shown in the **Figure 40** and **Figure 41**. There is no formic acid present in the water samples. The oxalic acid was analyzed in 8 water samples collected and found to be in the range of 24 – 324 mg/L. The result has mentioned been tabulated in **Table 17**.

6.8.2. Piezo metric well water samples

Water samples were collected from the seven peizometric wells located inside TCL. The depthof the piezo metric wells range from 20-30 m hence the water samples collected from these well representing the subsurface water at these depth. The location of the wells is shown in **Figure 42**.

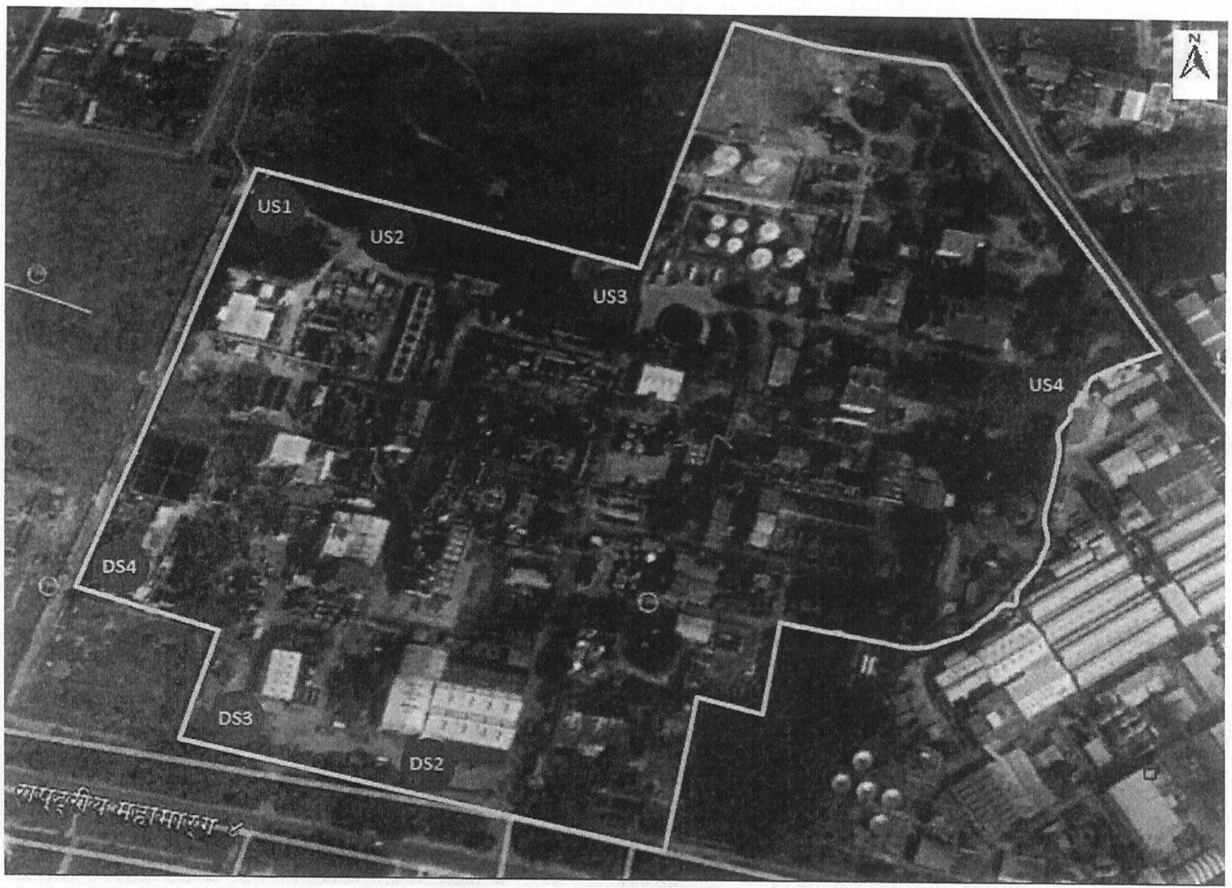

Figure 42: The location of Piezo metric wells inside TCL

From the heavy metal analysis of the samples shown in **Table 16**, it source of chromium is identified to be somewhere upstream to TCL in NW direction. The presence of hexavalent chromium was also found in US1 and US4 which are adjunct to TCCL. **Table 17** shows the presence of oxalic acid in all the samples in the range of 109 – 784 mg/L.

6.8.3. Drain water samples

Within SIPCOT area there are many artificial drains for conveying the industrial effluent. Total24 drain water samples were collected from the study area. During our survey we found manywater in the drain are black and turbid. **Table 15**, shows the physiochemical analyses of the drain water samples. It should be noted that 5 drain water samples were so turbid and coloured we could not analyze for physiochemical parameters. These samples are DR09, DR11, DR12, DR14, and DR18. The total chromium concentration for these samples shows in the range of 1.874 – 50.360 mg/L (**Table 16**). The highest concentration is in DR18, which is 50.36 mg/L. Physical survey indicated many tanneries nearby hence the possibility of the tannery effluent for the elevated level of total chromium concentration cannot be ruled out. The sample DR21 is the drain which is flowing between TCCL and TCL, shows also high concentration of total chromium of 40.55 mg/L. This is also the samples of highest hexavalent chromium concentration from the study area, i.e., 28.2 mg/L. It should be also noted that the water samples from piezo metric wells in the eastern side (TCCL side), i.e., DS4 and US1, which are also very close from this drain samples, also having high hexavalent chromium concentration of 10.95 mg/L and 9.15 mg/L respectively. Inflow of water carrying Chromium Compounds into the premises of TCL is confirmed by this. Hexavalent chromium is considered to be 100 timesmore toxic than the trivalent chromium, hence it's present in water reveal high risk on the available water resources in the surrounding area. Though there was no presence of Formic acid in the drain water samples, we found trace amount of oxalic acid upstream and downstreampiezo metric wells of TCL (**Table 17**). The concentration is significant and represent treat to human as well as environment (Vernot et al 1977). The presence of Oxalic acid in all the downstream and upstream piezo metric wells confirm the infiltration of effluents from neighbouring leather processing industries into TCL land.

In order to investigate the source of the contamination in the drain water samples, we overlaid the drainage network on the spatial distribution of the heavy metals in **Figure 43(a)** and **Figure 43(b)**. In the figure blue lines represents the natural drainage and red line are artificial drainage. The map was drawn in combination with the google image with physical survey in the field. It has been observed that at the US to TCL most of the natural drainage was dried up and no water was available for sampling hence the artificial drains were considered for sampling due as water flow was there. The result shows multiples points of heavy metal concentration in the upstream of TCL. One of them is near Puliyanthangal Lake, where many tanneries and other industries are present and the other one at the northern side of TCL. The samples DR18 and DR21 having extremely high concentration of total chromium of 50.36 and 44.50 mg/L respectively. The DR21 sample, which is collected from the drain flowing from Tamil Nadu Chromate and Chemicals Limited (TCCL) through the SW cornet of TCL is also the only drainsamples having hexavalent chromium of 28.2 mg/L.

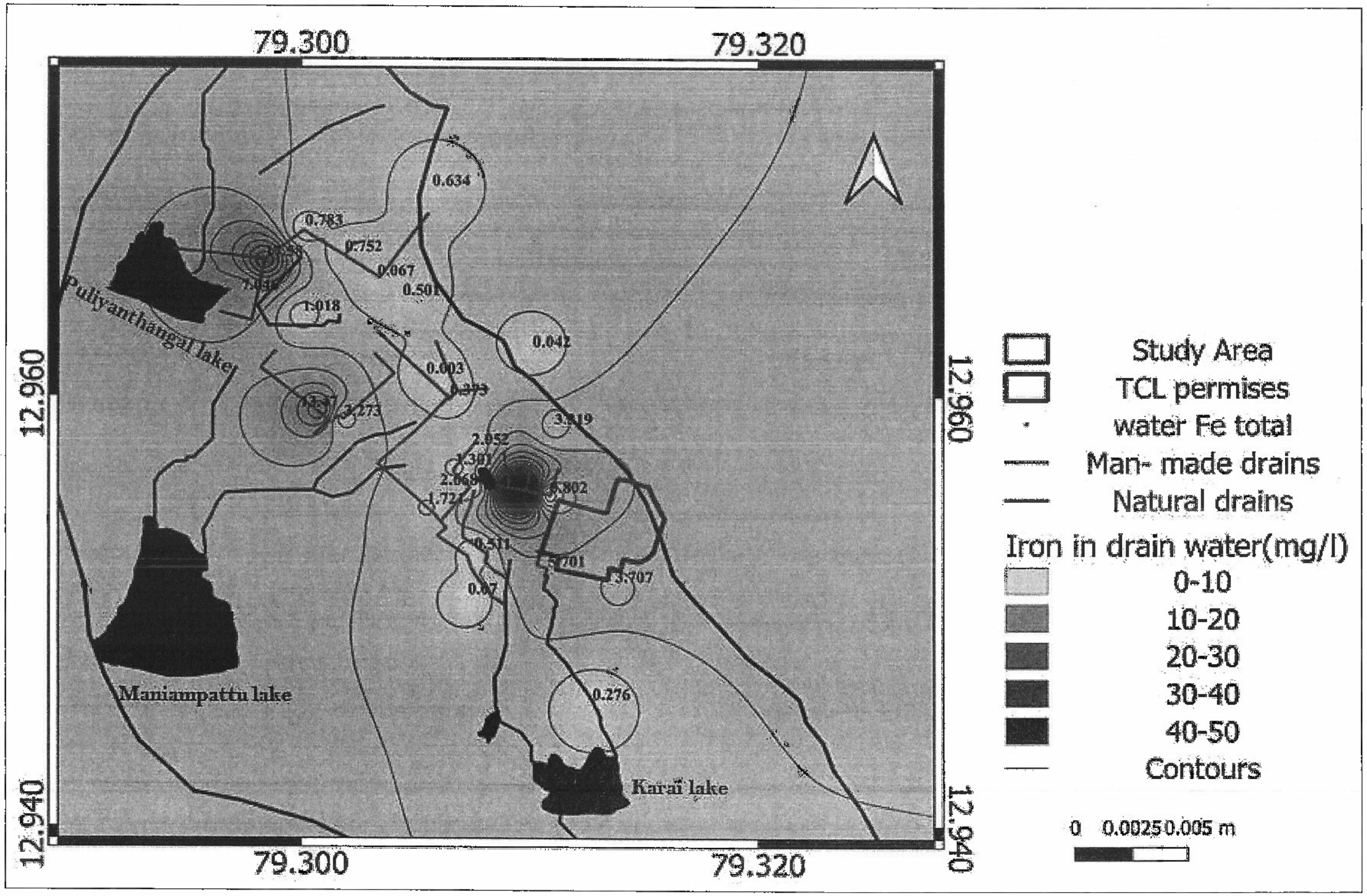

Figure 43(a): Distribution of total iron in drain water samples in the study area

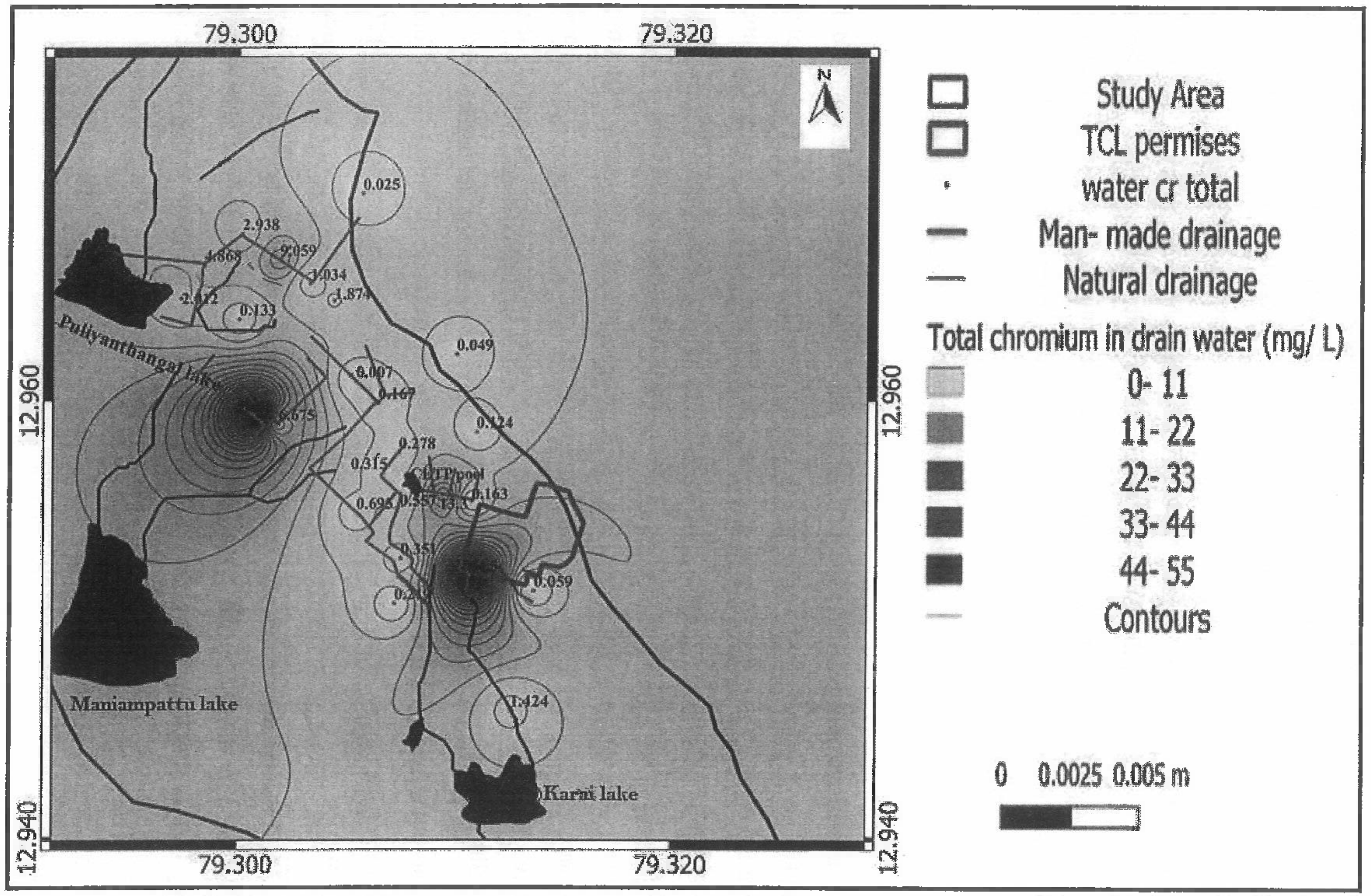

Figure 43(b): Distribution of total chromium in drain water samples in the study area

6.8.4. Groundwater samples

Five groundwater samples were collected from the existing bore wells study area mentioned and shown in **Table 15 and Figure 36.** The **Figure 37** illustrate the result of physiochemical parameters of these samples. All these samples are open borewell generally used for irrigationpurpose and located near to the lakes and Palar River. Though the quality of these samples arenot conforming IS10500:2014, they are moderately polluted and can be used for drinking purpose after treatment.

The **Figure 38** and **Table 17** illustrate the heavy metal concentration in the borewell samples along with other samples. Among the five samples 2 samples, GW01 and GW04, are having total chromium >0.05 mg/L (Requirement/Acceptable Limit as per 1S10500:2012). The GW04is located near Puliyanthangal Lake and borewell is not used for drinking purpose but for irrigation. The concentration of 1.49 mg/L which is high enough to induce food chain contamination and need to be taken care of. The other sample, i.e., GW02 is the borewell installed at Karai Village Cotton Bazzar Street. This borewell also used for irrigation purposeand having total Chromium concentration of 0.405 mg/L. Another samples GW02, which was collected from the borewell from the Palaar Rver bed shown 0.05 mg/L of total chromium concentration. Though the sample concentration is moderate, this indicate the possible contamination of river bed sediment.

6.8.5. Surface water samples

In order to investigate the existing surface water quality, water samples were collected from the surrounding lakes and Palar River as mentioned in **Table 15** and shown in **Figure 36.** Mostof the drains which carries industrial effluent end up in these waterbodies. Similarly, the surfacewater pollution, if any can be traced back to the influent canals. **Figure 37** and **Table 16** depictsthe physiochemical result of these samples. All the samples are having one or more parametersmore than IS10500:2012. Comparing the groundwater samples discussed before, the surface water samples are found to be more polluted. Among the samples analyzed, SW04, which is the down-stream sample collected from Palar river very high turbidity and pH, which is abnormal. Apart from that other parameters are nominal. The reason of this abnormality is notclear but it is worth mentioning.

Figure 38 shows the heavy metal analysis of these samples. No hexavalent chromium was found but in two samples total Chromium is ten times Requirement/Acceptable Limit as per 1S10500:2012. The SW01 and SW02 are the natural drainage connecting two lakes. Presenceof heavy metals indicate that either they are used for direct disposal of industrial effluent or having connectivity with artificial canals which carry industrial effluent. Elevated total Iron concentration in these drains substantiate these finding.

6.8.6. Other water samples

Random water samples were collected from local pools, and pits. These samples are mostly stagnant and been stored for some purpose in the past but present of no use. The reason to collect and analyze these samples are, (a) to understand the extent of contamination in the past, and (b) the present risk associated to its disposal. In the present study four samples were collected from the SIPCOT area surrounding to TCL as mentioned in **Table 15** and **Figure 36.**The physiochemical parameters and heavy metals concentration of these samples is shown in **Figure 37** and **Figure 38** as well as tabulated in **Table 16** and **17.** The result shows elevated concentration of all the parameters. The OT03 samples shows extremely high concentration oftotal chromium, which is collected from TCCL pool. However most of the Chromium seems to be trivalent, i.e., less toxic.

6. 9. Quality control

a) For the parameters like pH, Turbidity, Sp. Conductivity, the instrument was calibrated as per IS3025/APHA recommended methods. **Table 19** shows the summary of the calibration. These standards were used prior to operating the instrument by setting the instrument values as per the theoretical standards.

b) The standard solution was prepared for quality checking of Total Alkalinity, Total Hardness, Chloride and Sulphate **Table 19**, gives the calibration details. These standards were analyzed as unknown samples and their percentage of deviation from the theoretical values were calculated and found to be less than ±10.

Table 19: The calibration detail for pH, Turbidity and Sp. Conductivity

Parameter	**Reagent/Standards**	**Concentration**
pH	Buffer Tablet	4.0, 7.0, and 9.2
Turbidity	Formazine Solution (Hydrazine Sulphate + Hexamethylene Tetramine)	40 NTU
Conductivity	Potassium Chloride solution	1408 µS/cm
Total alkalinity	Standard Sulphuric Acid Solution	0.02 N
Total Hardness	Standard EDTA Solution	0.01 M
Chloride	Standard Sodium Chloride Solution	0.0141 N
Sulphate	Standard Sulphate solution from Sodium Sulphate	5, 10, 20, 40, and 100 mg/L

c) The total Iron and Chromium in water were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES, Model Avio-200, Perkin Elmer). The operational parameters of ICPOES are mentioned in **ANNEXURE VI.** Multi-elemental standards of Perkin Elmer were uti-lized for obtaining calibration; by serial dilution of 100mg/L. **Figure 44** shows the result of the calibration for total Iron and Chromium. The calculated R2 value of the graph is >0.99, which is accepted.

d) The accuracy in the heavy metal analysis was assessed by using certified reference material (SQC-001, Sigma-Aldrich, Spain) (**ANNEXURE VII**). The table below (**Table 20**) shows the preparation, dilution and recovery rate. Comparing the result with Certificate of Analysis (**ANNEXURE IX**). The result show recovery >90%.

e) Soil and water samples were sent to three different labs for heavy metals and one lab for Oxalic and Formic Acid. The comparison result is given in **Table 21**. The % of deviation of the heavy metals with respect to other labs are within 9 – 12% of variation. The result of the analysis from external labs is included in **ANNEXURE X.**

Element	**Intensity**	**0**	**0.1**	**0.5**	**1**	**5**
Cr	Corrected intensity	4985.7	111739	645757.4	979705.7	4937045.5
Fe	Corrected intensity	5115.8	128380	844209.9	884147	4397693.9

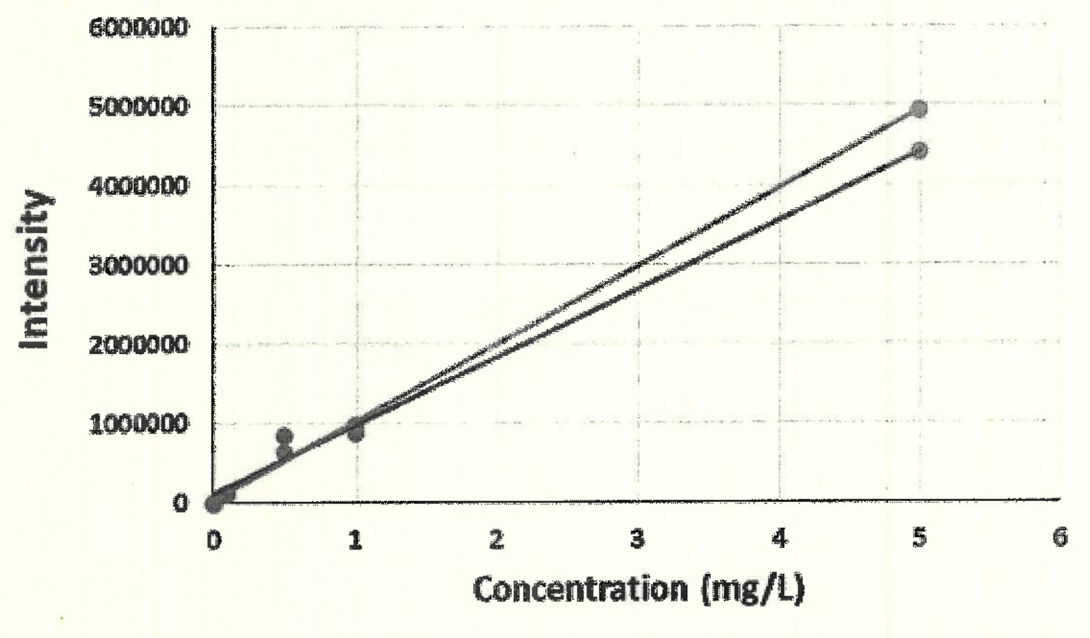

Figure 44: Calibration for Total Fe and Cr by serial dilution in ICP-OES

Table 20: Accuracy in the heavy metal analysis

Parameters	Measured Concentration (mg/L)	Dilution Factor	Volume after digestion (ml)	Wt of CRM taken (gm)	Calculated concentration (mg/kg)	Certified Value (mg/kg)	Recovery %	Average Recovery %
Fe	31.2	15	15	0.5008	14017.57	12923 ± 296	91.53	90.92
	15.95	30	15	0.5008	14332.07	12923 ± 296	89.10	
	62.56	15	15	1.0005	14068.97	12923 ± 296	91.13	
	31.05	30	15	1.0005	13965.52	12923 ± 296	91.93	
Cr	0.75	15	15	0.5008	336.96	299 ± 4	87.30	91.38
	0.37	30	15	0.5008	332.47	299 ± 4	88.81	
	1.38	15	15	1.0005	310.34	299 ± 4	96.21	
	0.71	30	15	1.0005	319.34	299 ± 4	93.20	

Table 21: External laboratory comparison of heavy metal and organic acid results

Sample ID	Type of Sample	**Total Iron**				
		VIT	IITB	ITC	ECOTECH	% of variation*
AH-13 (mg/kg)	Soil	45637	56317	41800		-7.5
AH-14 (mg/kg)		8184		9900	8600	-13.03
DS4 (mg/l)	Water	<0.005	0.193	0.121	0.22	NA
US1 (mg/l)		0.098		0.092	0.12	-8.16
					Average % of variation	**-8.73**

* (VIT result - average of all results)*100/(VIT result)

Sample ID	Tyoe of sample	**Total Chromium**				
		VIT	IITB	ITC	ECOTECH	% of variation*
AH-13 (mg/kg)	Soil	321.3	307.9	333		0.18
AH-14 (mg/kg)		1503.0	1112	2200.0	1728.0	-8.84
DS4 (mg/l)	Water	24.4	30.8	27.03	29.6	-14.80
US1 (mg/l)		15.7	19.5	16.5	18.9	-12.35
					Average % of variation	**-8.95**

* (VIT result - average of all results)*100/(VIT result)

Sample ID	Type of Sample	**Hexavalent Chromium**			
		VIT	ITC	ECOTECH	% of variation*
AH-14 (mg/kg)	Soil	<0.25	0.08	<1.0	NA
DS4 (mg/kg)	Water	10.95	14.8	13.42	-19.2
W25 (mg/l)		28.2	31.8	24	1.06
				Average % of variation	**-9.09**

* (VIT result - average of all results)*100/(VIT result)

Sample ID	Formic Acid		Oxalic Acid		
	VIT	IITB	VIT	IITB	% of variation*
SAH07 (gm/kg)	ND	ND	0.614	0.451	26.55
SAH03 (gm/kg)	ND	ND	0.089	ND	NA
US04 (g/l)	ND	ND	0.784	0.732	6.63
US02 (g/l)	ND	ND	0.538	0.500	7.10
				Average % of variation	**13.43**
* (VIT result - IIT result)*100/(VIT result)					

7. Summary of the findings and Overall Conclusion

Widespread pollution of soil and water in SIPCOT areas in Ranipet have been confirmed many times before, by scientific studies that were carried out by national research institutes like CSIR-NGRI, CSIR-NEERI, IIT and various Universities. Apart from Chromium contamination from Tamilnadu Chromate & Chemicals Limited, the earlier and contemporary research identified both soil & water pollution due to the various tanning & chemical industries in the entire SIPCOT area and its downstream up to Palar River. The present study is concentrated on Thirumalai Chemicals Limited (TCL), which is located in the downstream side of the SIPCOT area. The objective of this project is to study the hydrogeological set up and to explore the geochemical condition and evaluate the effects of surrounding pollution, if any, in and around the area of Thirumalai Chemicals Limited.

In the present sub-watershed, an integrated scientific approach that included detailed hydrogeological, geophysical and geochemical investigation where in topographic survey using GPS, 1D & 2D mapping of the area to decipher the resistivity and thickness of the subsurface strata, soil and rock profiling. The permeability study, water level measurement and analysis of water and soil samples drawn from Auger holes were also carried out. On the basis of above study, the major findings and conclusions are mentioned below.

1) Geologically the sub-watershed is a hard rock region beset with granites as country rock and quartzites intrusions. Just north of the TCL premises, one dolerite dike runs east-west.

2) The overall terrain elevation varies from 192 m in the north in SIPCOT area to 172 m in the south near Karai Lake above M.S.L within a distance of 2 km only. The topographic contours obtained reveal that the major slope is from NW-SE (**Figure 7**).

3) The groundwater contour map obtained from the water level observation from the auger hole as well as selected monitoring wells reveal that the subsurface flow direction follows the Topography i.e., NW-SE (**Figure 10**).

4) The soil thickness varies from 0.5 to 2.5 m below which weathered granite or quartzite is occurring. Fractured rocks are also present below this weathered zone.

5) The hydraulic conductivity of the present study area is measured to be in the range of 6.4 – 8.5 x 10^{-7} m/sec, which is high compared to fractured rock as reported in earlier studies.

6) The water levels were also shallow during the study period and were mostly in the soil portion itself. The lowest water level was found to be 0.26 m BGL.

7) Due to shallow water level in post monsoon season combined with the relatively high hydraulic conductivity of the weathered and fractured rocks and steep gradient of the terrain, the velocity of flow of groundwater which is from NW to SE direction is high.

8) The groundwater flow direction was assessed from the depth of water level in auger holes and piezometric wells inside TCL. The direction of the flow as shown in **Figure 10** is from N.W to S.E. The inferences drawn from the geophysical studies corroborate with the flow direction.

9) The 2D vertical cross section study along the seven VES profiles revealed the possible contamination in at least two profiles AA' and BB'. This region covers the CETP, western part of TCL, TCCL, and southern part of highway which is an open land.

10) The observations from the vertical cross section study with resistivity contour reveals the occurrence of possible contamination in soil, weathered rock as well as fractured rock in the region.

11) The eastern part of the region also exhibited possible contamination in the soil/rock.

12) The physiochemical investigation of water and soil samples indicates several sources of pollution in the upstream of TCL. This is further established by the identified artificial canals having connectivity to the natural drainages. In the absence of detailed source apportionment studies, the responsibility for pollution cannot be fixed.

13) The physiochemical study of the drain water samples indicates the elevated level of total chromium concentration (**Figure 43**). The man made drain from the TCCL (passing close to TCL South Western boundary), carry the Chromate seepage (hexavalent chromium of 28.2

mg/L) to join with the natural drain leading to Karai Lake.

14) There is evidence of freshwater (borewell and surface) contamination from chromium in the study area which implies the possible human health risk.

15) The presence of iron in the drain samples is much higher than the borewell samples, speculates industrial contribution as there are many steel fabrication units in SIPCOT area.

16) The presence of Oxalic Acid was found in both soil and water samples. From the concentration profile of Oxalic acid shown in **Figure 34** and **Figure 39** the source can be identified in the NW side of TCL. Oxalic Acid is an organic acid which is soluble in water and also biodegradable. It is used for laundry rinse, wood-bleaching, calcium removal and tanning operation, hence the possibility of industrial discharge of Oxalic Acid in SIPCOT area cannotbe ruled out.

17) After examination and analysis of soil and water samples collected from the study area in and around Thirumalai Chemicals limited, contamination by Chromium and Oxalic acid is seen in the samples.

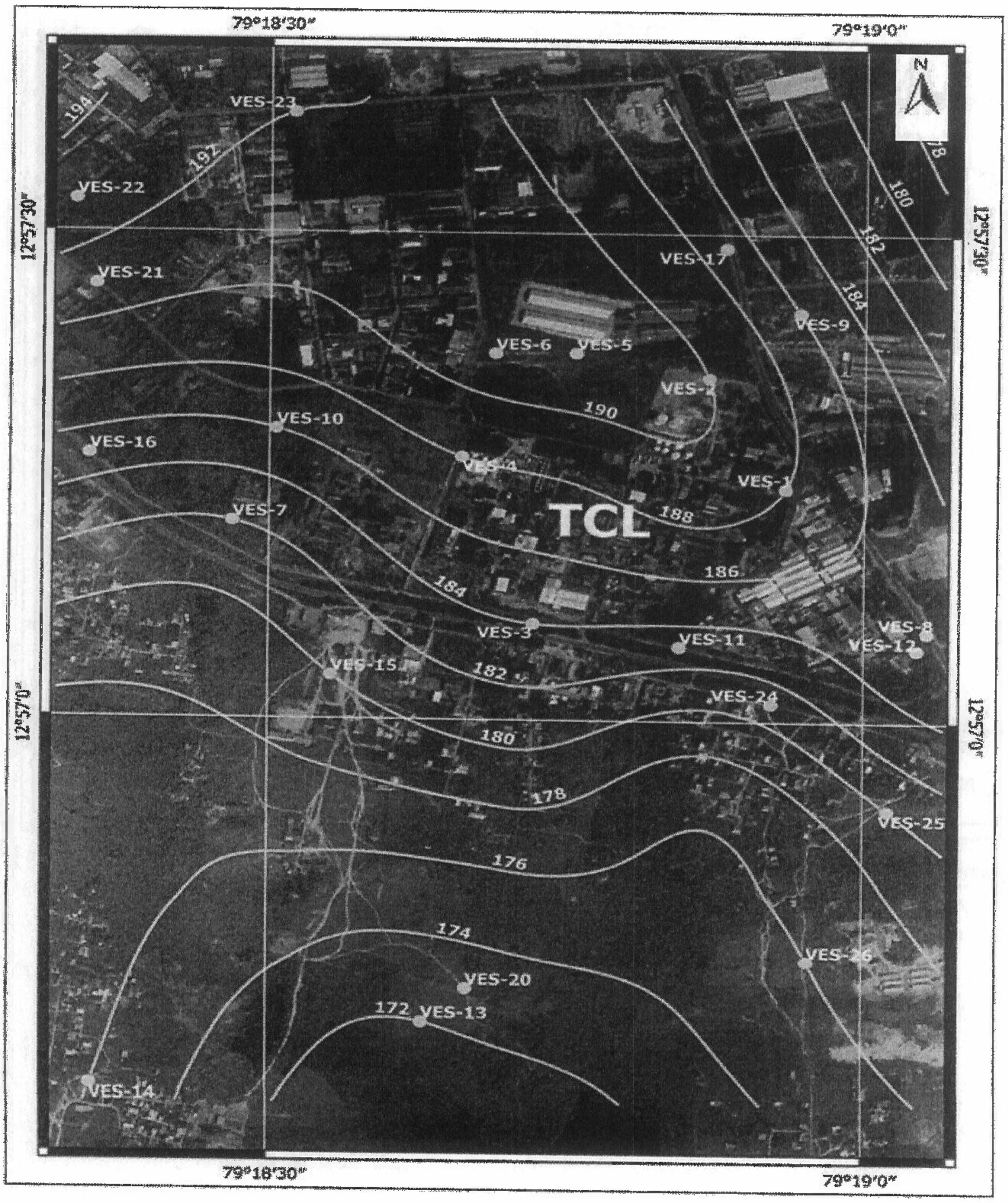

Figure 7: The elevation contour line of the study area

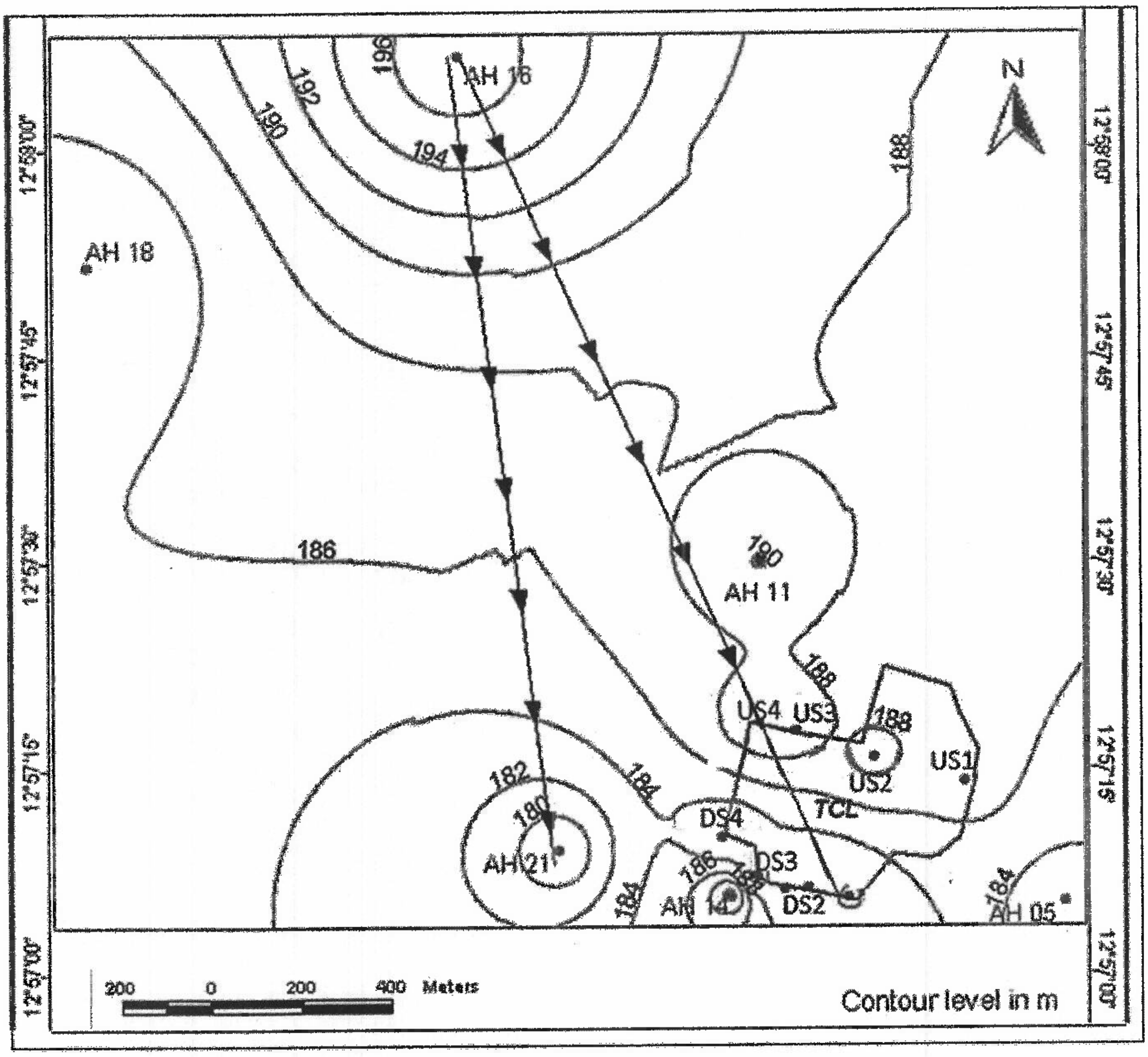

Figure 10: Groundwater level contours reduced to M.S.L

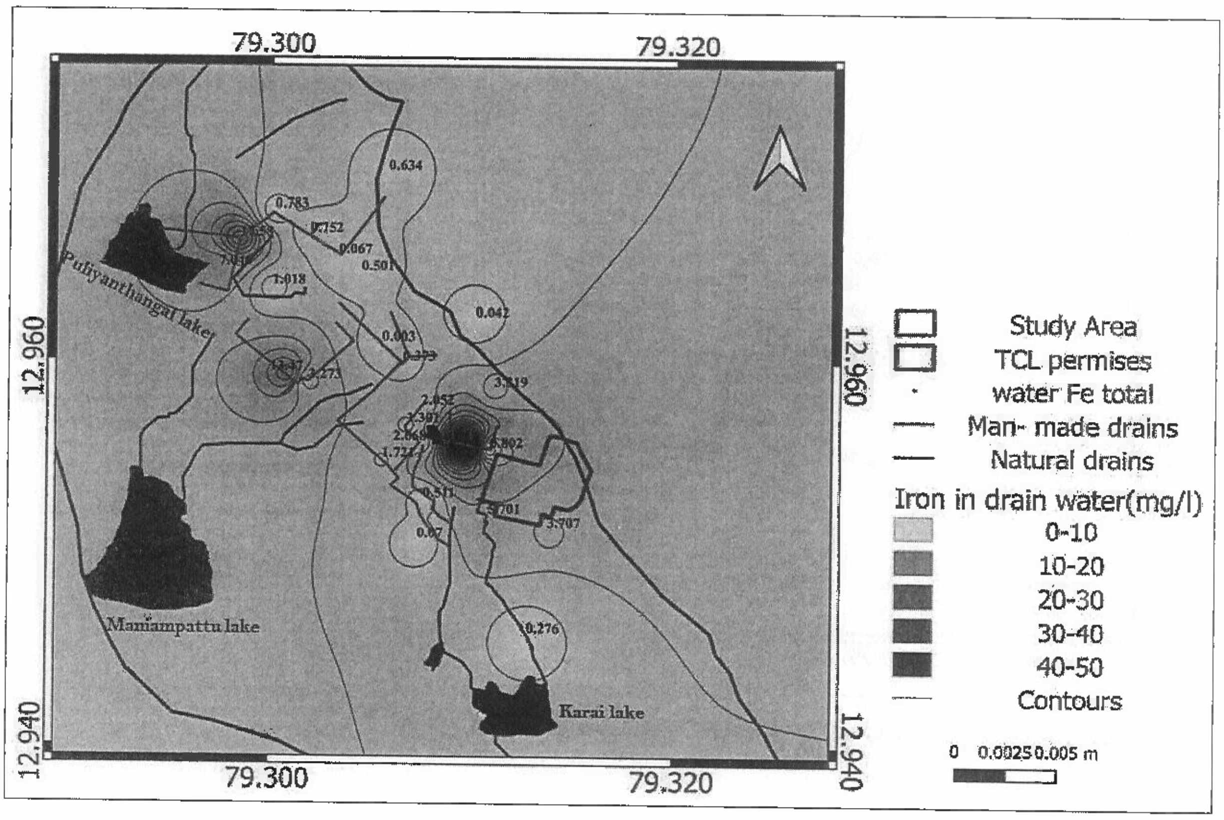

Figure 43(a): Distribution of total iron in drain water samples in the study area

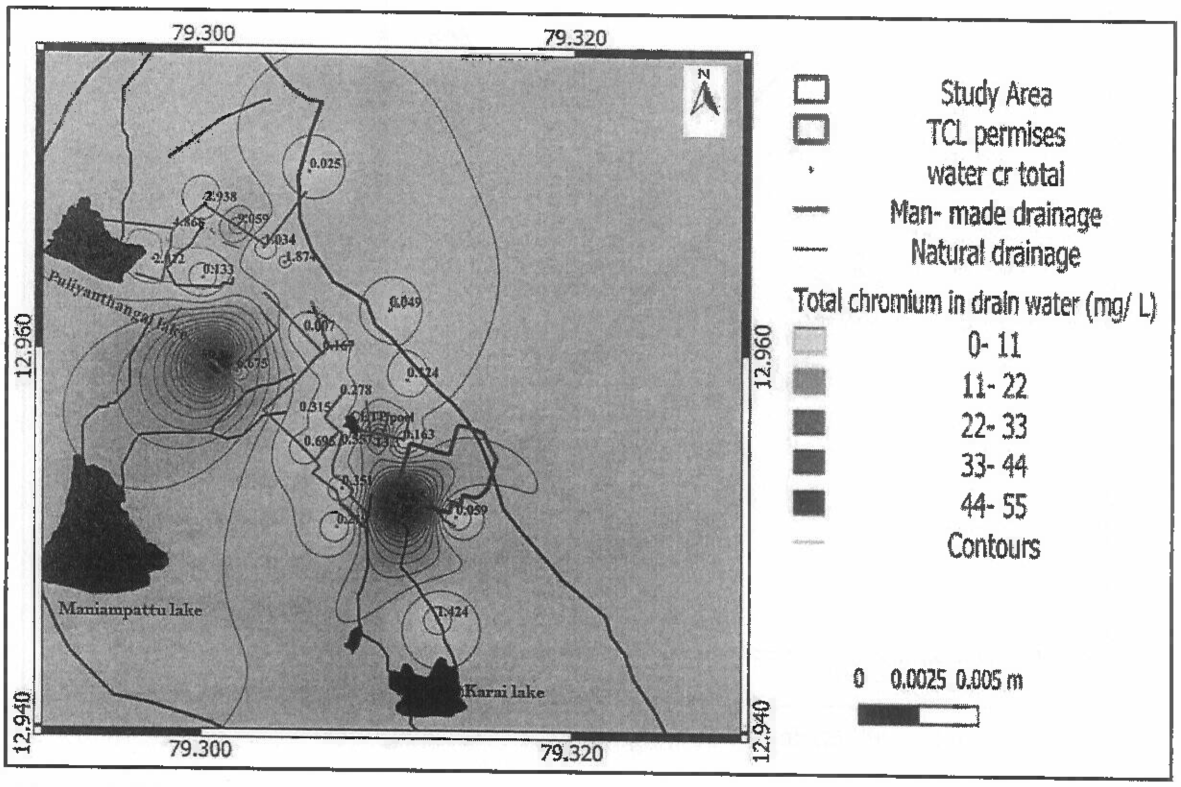

Figure 43(b): Distribution of total chromium in drain water samples in the study area

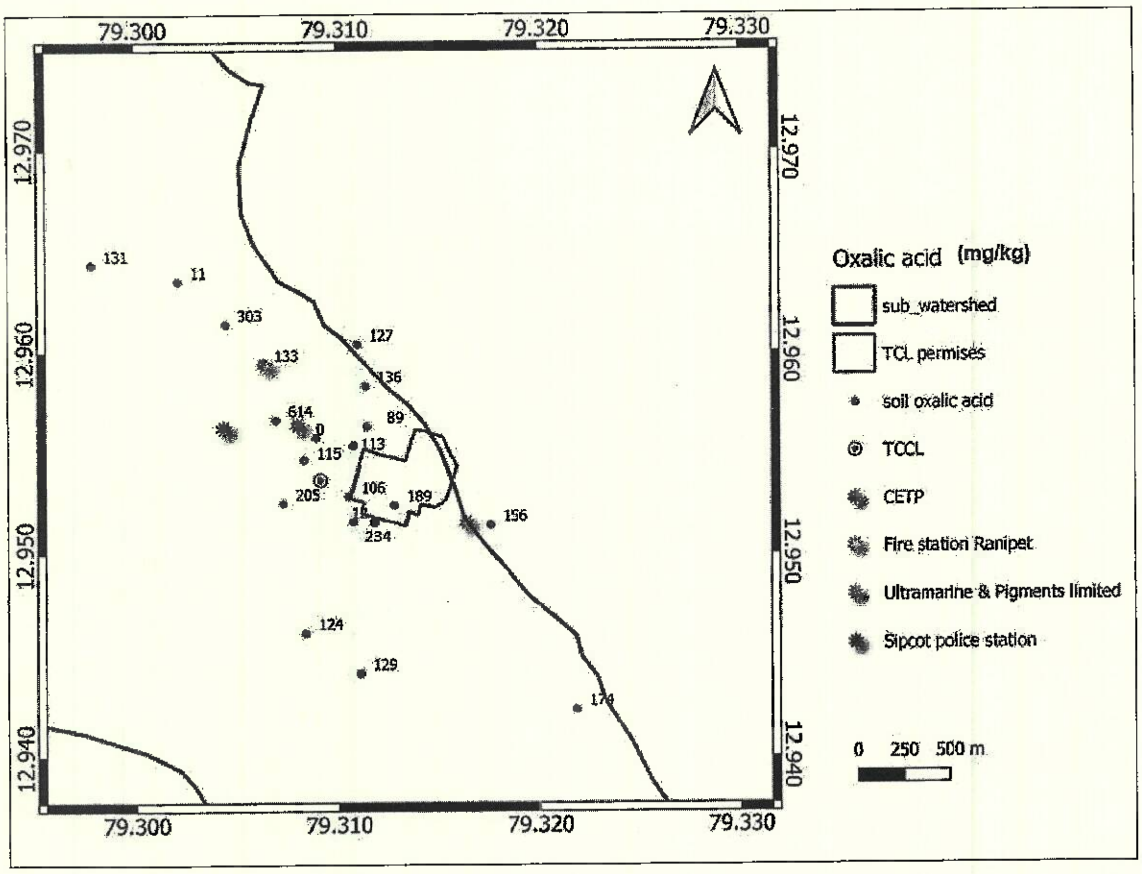

Figure 34: Spatial distribution of Oxalic Acid in soil samples

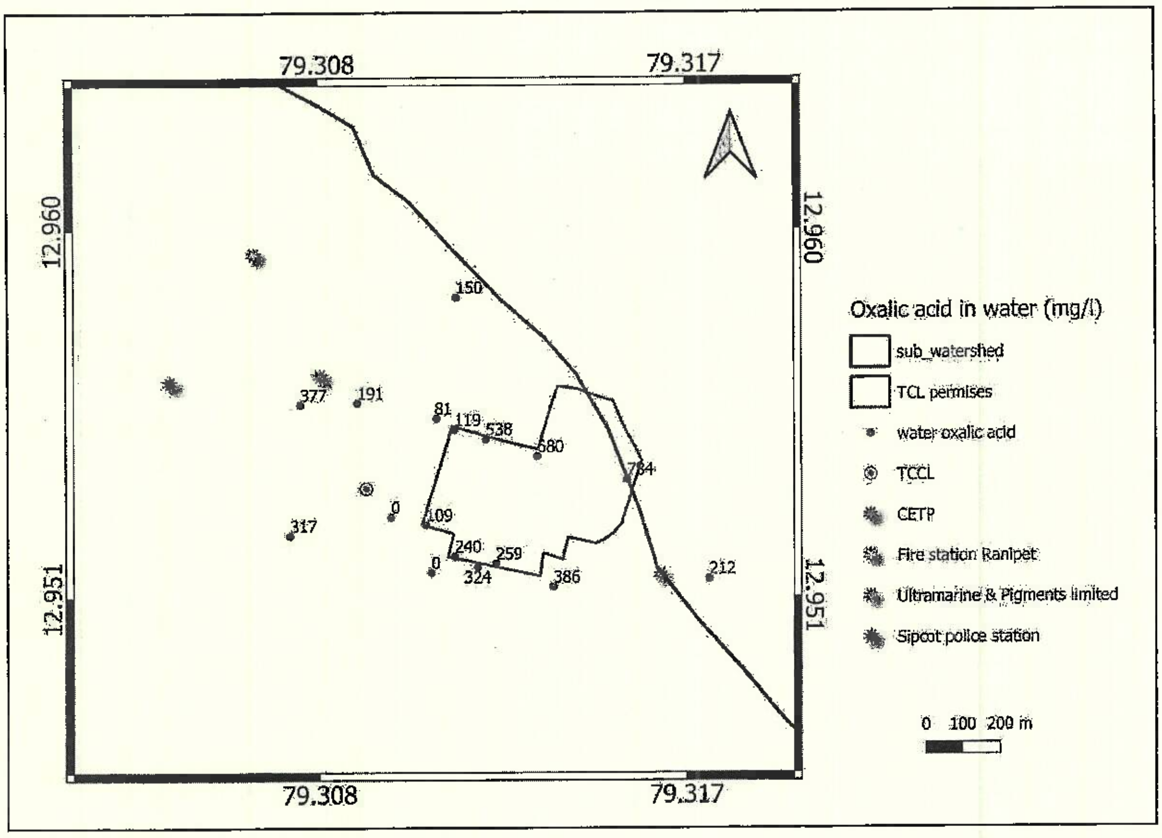

Figure 39: Distribution of Oxalic acid in water samples in the study area

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End of main report.

27/10/21.

ANNEXURE 1

Principle of Electrical Methods

Electrical Resistivity Method is one of the Geophysical techniques used to investigate the nature of the subsurface formations. In the Electrical Resistivity methods current sent into the ground through a pair of electrodes, called current electrodes, and resulting potential difference across the ground is measured with the help of another pair of electrodes, called potential electrodes.

The ratio between the potential difference (ΔV) and the current (I) gives the apparent resistance, which depends on the electrode arrangement and on the resistivity's of the subsurface formations. There are several types of electrode arrangements (configurations) of which Werner and Schlumberger configurations are more popular.

In Werner Configuration all the four electrodes are kept along a line at equal distances called electrode separation 'a'. For each measurement all the electrodes are moved simultaneously keeping the inter electrode spacing's same. The current is sent normally through outer electrodes and potential difference is measured across the inner electrodes. The resistance is multiplied by the configuration factor $2\ \pi a\ R$, Where $R=\Delta V/ I$

In Schlumberger Configuration all the four electrodes are kept in a line similar to that of Werner but the outer electrode spacing is kept large compared to the inner electrode spacing, usually more than 5 times. For each measurement only current electrodes are moved keeping the potential electrodes at the same locations. The potential electrodes are moved only when the signal becomes too weak to be measured. The apparent resistivity for this configuration is computed with the formula;

$\rho_{as} = \pi\ [(AM*AN)/MN]\ *R$ where AB is the distance between two outer current electrodes and MN is the distance between the two inner potential electrodes. The point "O" will be the midpoint of the eleztrode system

There are two types of procedures for making resistivity observation, namely Resistivity Sounding (also called Vertical Electrical Sounding, VES) and Resistivity Profiling (Horizontal Electrical Profiling). Resistivity profiling is employed to determine the lateral variations in the resistivity's thereby establishing the existence of vertical bodies like dykes, fracture zones, geological contacts etc. The Vertical Electrical Sounding is used to estimate the resistivities and thickness of various subsurface layers at a given location and is mainly employed in groundwater exploration to determine the disposition of the aquifers.

Vertical Electrical Sounding (VES):

In this approach, the centre of the configuration is kept fixed and the measurements are made by successively increasing electrode spacing's. The apparent resistivity values obtained with increasing values of electrode separations are used to estimate the thicknesses and resistivity's of the subsurface formations. A few photographs depicting the survey procedures are presented below.

Data processing

Over the last 60 years several developments have taken place in the data processing techniques. Initially empirical and semi empirical methods were used besides the curve matching technique. After the advent of fast computers, inversion programmes were made available to arrive at the geo-electrical parameters like thickness of layers h1, h2, h3---etc., and their corresponding absolute resistivity values ρ_1, ρ_2 ρ_3 --- etc. from the sounding curves. One such programme is IP WIN software, which is compatible with WINDOWS.

Conventional Method

Conventionally the plot between apparent resistivity and electrode separation (a) in case of Werner configuration and between apparent resistivity and half current electrode separation (AB/2), in case of Schlumberger configuration on double logarithmic scale is used for analysis of thicknesses and resistivity's of the subsurface layers. The data density is between 6-8 per log cycle of electrode separation.

The field curve is first compared with the theoretical curves for obtaining a preliminary model and this model is modified and refined with computer inversion programs, incorporating the geological information of the area. However, the resistivity sounding technique (in the present form) has the following inherent disadvantages:

The resolving power of this method is poor and is particularly true for deeper boundaries. Due to the principle of suppression, a middle layer with resistivity intermediate between enclosing beds will have practically no influence on the resistivity curve as long as its thickness is small in comparison to its depth. Hence the layers with small thickness cannot be recognized.

Due to principle of equivalence (i) a conductive layer sandwiched between two layers of higher resistivity's will have the same influence on the curve as long as the ratio of its thickness to resistivity (h/p) remains the same and similarly (ii) a resistive layer sandwiched between two conducting layers will have the same influence on the curve as long as the product of its resistivity and thickness.

Hence the thicknesses and resistivities of sandwiched layers of small thickness cannot be determined uniquely.

Added to this disadvantage of ambiguity in interpretation by established conventional approach by Curve matching and inversion techniques, the resolution of the conventional approach is poor and thin layers buried at depths more than 5-times their thickness cannot be identified because of the logarithmic plotting.

Imagine 3 aquifers of each 10 meters thickness existing between depths 10-20, 50-60 and 90-100 m. When they are represented on a linear scale they look real and when the same aquifers are represented on a logarithmic scale, they look very thin and the third layer between 90-100 m depths simply looks like an interface. In such conditions, it is difficult to identify the last two layers if the data is plotted on a logarithmic scale. This suggests that linear plotting of the data and analysing will be able to decipher thin layers even if they are buried at great depths, provided the data density is adequate enough to get the signals from the target layers.

Inverse Slope method

Taking lead from this concept, Dr.KRR Chary of IGIS has invented an innovative to interpret the vertical electrical sounding data with Werner configuration. According to this approach, the inverse of resistance measured (1/R) is plotted against the Werner electrode separation '*a*' on a linear graph. The plotted data points and align themselves on discrete line segments and are joined by straight lines. Each line segment represents a layer and the intersections of the line segments correspond to the depths of the particular layers. The resistivity of the layers are obtained by the inverse slope of the particular line segment multiplied with '2π'.

Originally, the Inverse Slope method was proposed for interpretation of Werner sounding data. However, this method can also be used for Schlumberger data with a minor modification. For Schlumberger sounding the linear plot has to be prepared between (AB/2) on X-axis and $\{(AB/2)/\rho_a\}$ on Y-axis. You should not use (1/R) for plotting since R depends on both AB/2 and MN/2. While the inverse slope of the line segments directly gives the true resistivity of the layers, the intersections of the line segments have to be multiplied with (2/3) to get the depths to the interfaces. Two very important things to keep in mind:

1. The detectability of thin layers at deeper levels depends on density of data. More the data density better is the detectability.
2. More the resolution of the resistivity meter better is the possibility of detecting thin layers at depths.

Interpretation and inferences

The results of interpretation of VES data gives rise to Geo-electric Sections at each of the test. These will be in the form of Thickness/Depth to different geological layers and their absolute resistivities. Now it is for the geophysicist to make the inference from these absolute resistivities in terms of the corresponding soils, rocks, their texture, the saturation with water, and water quality. This is a subjective matter since the theoretical values attributed to rocks or soils provide a very high range. Further these vary from place to place because the earth is quite heterogeneous with overburden deposits formed at different geological eras and are saturated with water of different compositions. The table below provides a glance of resistivity ranges of soils and rocks in general. While this table is reproduced from the source mentioned, different books on Geophysics show different ranges.

Source: *Andrade, Rolland. (2011). Intervention Of Electrical Resistance Tomography (ERT) In Resolving Hydrological Problems of a Semi-Arid Granite Terrain of Southern India. Journal of Geological Society of India. 78. 337-344. 10.1007/s12594-011-0100-x.*

Table 1. Resistivity range of different rock types, soil and chemicals

Material	Resistivity (Ohm–m)	Conductivity (Siemen/m)
Igneous and Metamorphic Rocks		
Granites	$5 \times 10^{2} - 10^{3}$	$10^{-6} - 2 \times 10^{-4}$
Basalt	$10^{3} - 10^{6}$	$10^{-6} - 10^{-3}$
Slate	$6 \times 10^{2} - 4 \times 10^{7}$	$2.5 \times 10^{-8} - 1.7 \times 10^{-3}$
Marble	$10^{2} - 2.5 \times 10^{8}$	$4 \times 10^{-9} - 10^{-2}$
Quartzite	$10^{2} - 2 \times 10^{8}$	$5 \times 10^{-9} - 10^{-2}$
Sedimentary Rocks		
Sandstone	$8 - 4 \times 10^{3}$	$2.5 \times 10^{-4} - 0.125$
Shale	$20 - 2 \times 10^{3}$	$5 \times 10^{-4} - 0.05$
Limestone	$50 - 4 \times 10^{2}$	$2.5 \times 10^{-3} - 0.02$
Soils and Waters		
Clay	1 –100	0.01 – 1
Alluvium	10 – 800	1.25 x 10 – 0.1
Groundwater(Fresh)	10 – 100	0.01 – 0.1
Salt Water	0.2	5
Chemicals		
Iron	9.074×10^{-8}	1.102×10^{7}
0.01M Potassium Chloride	0.708	1.413
0.01M Sodium Chloride	0.843	1.185
0.01M acetic acid	6.13	0.163
Xylene	6.998×10^{16}	1.429×10^{-17}

Now coming to the interpretation cum inferences in the present area, it should be noted that it is an established fact that this is an industrial area with a number of polluting industries like, chemicals, leather, metals etc. From the very visual view itself it is obvious that the surface and subsurface of the terrain are contaminated in terms of soil and groundwater. This is the basic point to be noted. Further the rocks below the permeable overburden are less weathered but more of jointed and fractured. Such geologically disturbed rocks have secondary porosity facilitating the downward as well as horizontal movement of groundwater. These are granites and quartzites, which have no geogenic salinities unlike the calcareous rocks. Obviously, any poor quality of groundwater is the result of non-natural induced contamination. With this background the resistivity ranges obtained from the geo-electric section are inferred into whether they are fresh or contaminated. It can be seen that in some cases no contamination is derived for the same type of rocks depending on their location, the resistivity values etc. In respect of overburden soil also, this principle applies. For example, it is noticed from auger holes that the soil is coarse sand and no clay. Naturally a resistivity value of 3-5 ohm.m for over burden soil in such case reflects only highly contaminated sand. Similarly, a 50-80 ohm.m fractured rock reflects its contaminated nature because this value is very low compared to normal resistivity values of about 300-500 ohm.m or more for a fractured rock. As already mentioned, the interpretations and inferences are subjective and the efficacy of the same depends on the experience of the geophysicists and the knowledge of local geology. At the end of it, all the geophysical inferences which are exploratory in nature need to be test by trial drilling to match the reality in case of any doubts.

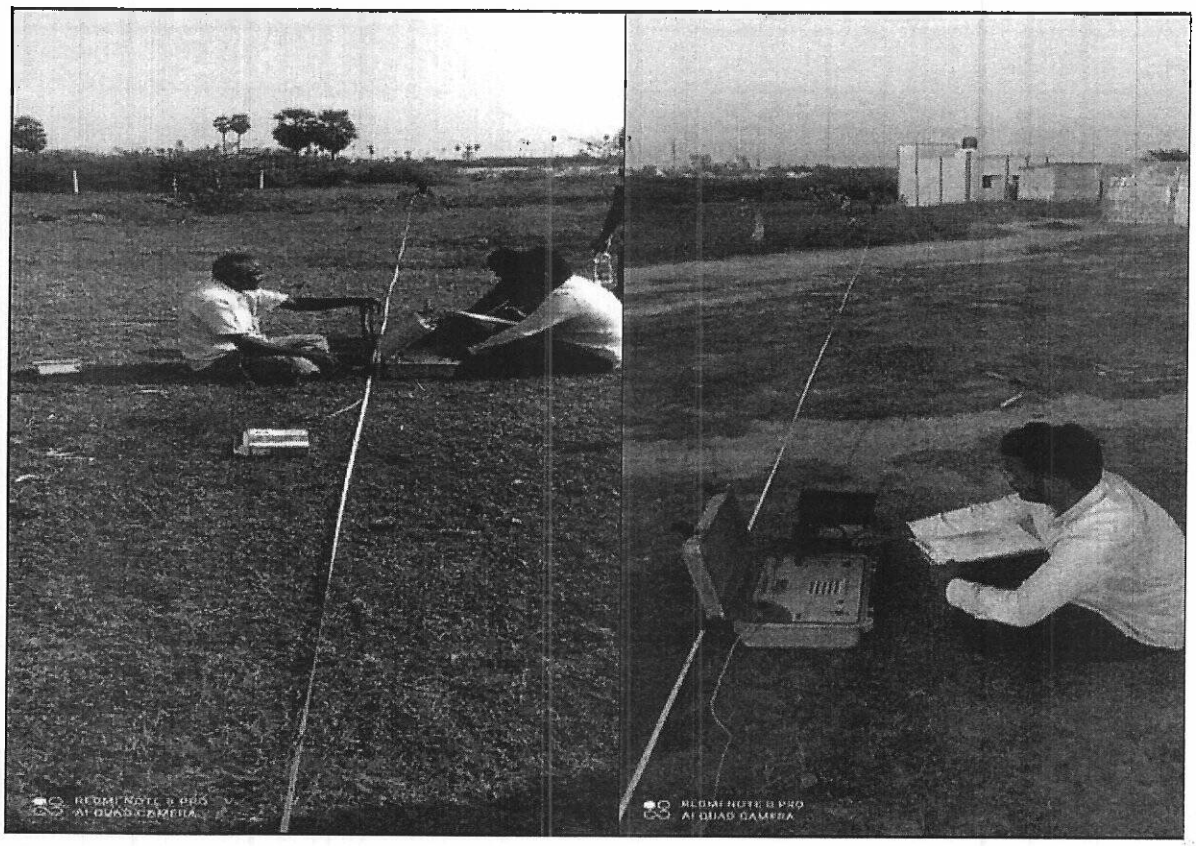


Figure 1: Photographs of Geophysical Survey

ANNEXURE 2

Permeability Test

1.1 Objectives

The objective of the permeability tests is to measure the horizontal in-situ soil permeability of the top soil zone between Ground Level to 1.70m.

1.2 Activities accomplished

The investigations comprised of measuring the in–situ soil permeability (hydraulic gradient) in one well, constructed in the auger holes. The coordinate of the test hole are 12.96715, 79.29266. The test procedure adopted is as per CODE OF PRACTICE FOR *IN-SITU* PERMEABILITY TESTS, PART 1 TESTS IN OVERBURDEN

(*Second revision*).Doc 05 (450) May 2007 described under section 3.3 for measuring in-situ permeability of soils using Falling Head Method.

1.3 Limitations

The well, used for testing is not a full-fledged structure. Its depth is limited to 1.70m. Normally these tests are conducted in wells with sufficient thickness of aquifer zone. Such test zone occurs in between other upper and lower layers. In order to ensure that the water passes through the specific zone selected for testing, packers are inflated above and below the zone of testing. In the present case only 1.7 meter of soil is available for testing. This soil layer is resting on hard/weathered rock. Hence the casing pipe is dummied at the bottom to arrest downward flow of water.

Also, as per the document, an intake pipe is to be inserted in the main pipe and water levels are to be measured in the standpipe. In the present case, this arrangement was not followed because the structure used for testing is not a perfectly constructed tube well and the thickness of testing zone is very small and occurring from ground level itself.

1.4 Details of structure.

As mentioned earlier, the structure used for testing is an auger hole drilled for collection of soil and water samples. After collection of these samples, a slotted casing pipe of 4 inches diameter was inserted in the hole. The total length of the slotted pipe was 1.70m extending from ground level to the top of rock. The bottom of the slotted pipe was sealed with an end cap. In order to facilitate adding water into the structure, additional plain casing pipe of same diameter and 1m length was added at the top of the slotted pipe using a coupler. The top of this extended pipe is kept open.

1.5 Test procedure

The estimation of permeability is made using the BIS Document for in-situ measurement of soils in uncased wells. This method assumes that the well is uncased and the zone of testing is isolated by fixing a packer above the zone of interest so that water will not leak through other zones. An intake pipe of smaller diameter is inserted into the zone of testing through the packer. Water is poured into the well through the intake pipe till the head raises much above the normal water level in the hole. The fall in water level is measured with reference to time and the data is processed through an equation.

In the present case, the test was conducted in a well with screens, instead of an uncased structure because the uncased structure will collapse if not supported by a casing. Since the slotted pipes are used against the test zone, it is more or less equivalent to an uncased zone and allows free flow of water horizontally. Similarly, the intake pipe was not used because of limited thickness of testing zone. The parameters required in the equation are modified accordingly.

$$K = \frac{d^2}{8L}(\log_e \frac{L}{R})\frac{\log_e h_1 / h_2}{t_2 - t_1}$$

where

K = coefficient of permeability,
d = diameter of intake pipe (stand pipe),
L = length of test zone,
h_1 = head of water in the stand pipe at time t_1 above piezometeric surface,
h_2 = head of water in the stand pipe at the time t_2 above piezometeric surface, and
R = radius of hole.

The formula is based on the following assumptions:

a) The soil stratum is homogeneous and the permeability of soil is equal in all directions, and

b) The soil stratum in which the intake point is placed is of infinite thickness and that artesian conditions do not prevail.

The head ratio *ht/ho (where ht*= head of water in the stand pipe at any time t and *ho* = depth of static water level at time *to*) versus time curve should be plotted on the semi-log plot as shown in Figure below. The curve shows pronounced initial curvature whereas after a time lag of about 20 minutes, the curve is straight. A straight line through the origin and parallel to the straight portion of the curve should be drawn to represent a steady state of flow into the test strata. The value of *h1/ho* and *h2/ho* corresponding to time *t1*, and *t2* respectively is read from the graph. The value *h1/h2* corresponding to time *t1* and *t2* is calculated and substituted in equation (2) to obtain the coefficient of permeability.

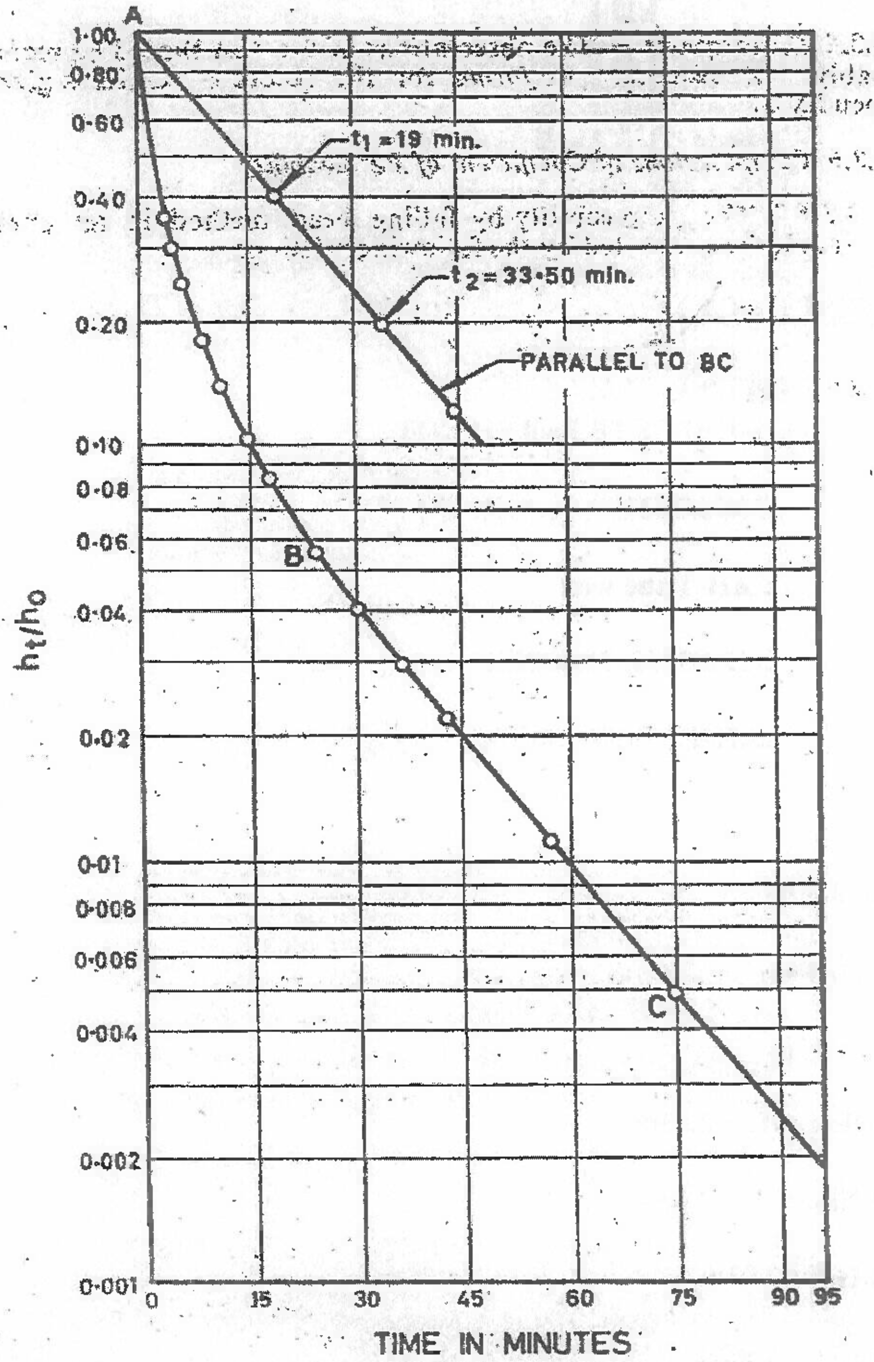


FIG. 6 SEMI-LOG PLOT OF HEAD RATIO VERSUS TIME OF TEST
(FALLING HEAD METHOD)

The design for the measuring system as provided in the document is as shown below.

Doc. WRD 05(450)
May 2007

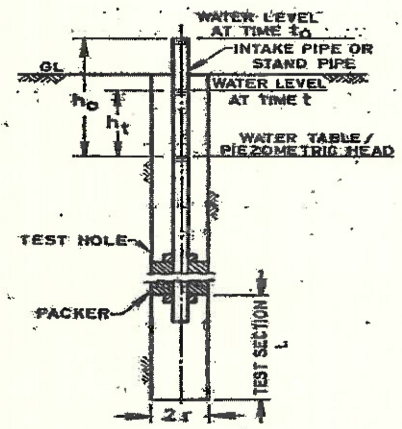


FIG. 5 SET UP FOR FALLING HEAD METHOD

1.6 PERMEABILITY TEST DATA 1

Location : **S-E of CETP Pool SIPCOT**

Date of Test :**30/01/2021**

Type of Well : **AH-Tube well**

Coordinates :**(12.95575, 79.30893)**

Well Id :**AH-1**

RAW Hole Details

Augar Hole Depth BGL: 2.30m

Static water level BGL - 1.10m

Structure details

Length of casing pipe below GL : 2.03m

Lemgth of plain casing: NIL

Length of screen pipe B.G.L : 2.03m

Static Water Level BGL: 0.97m

Pre Test Structure

Total casing pipe. 3m

Length of plain casing A.G.L: 0.97m

Diameter of casing pipe (both plain & Screen): 100mm

Static WL (from T.O.C) – 1.94m

WL after filling (from T.O.C): 1.30m

Time in minutes since pumping started	Depth of water level from measuring point in m
0	1.30
0.36	1.50
1.30	1.60
2.52	1.70
5.10	1.80
9.26	1.90
17	1.95
30	1.98
40	1.99
50	2.00
60	2.00
70	2.01
80	2.01
90	2.01

1.6.1 Results - Well AH 1

Using the above data, the permeability of the zone between G.L and 2.03m is computed for Well AH1 as shown below.

Diameter of intake pipe (d)= 100mm

Length of test zone (L) = 2.03m or 203cm

h_1/h_0 =0.5 from the graph at time t_1=30minutes

h_2/h_0 = 0.4 from graph at time t_2= 40minutes

Radius of hole = 50mm = 5 cm

t_2-t_1= 40-30=10 minutes

$d^2 = (10)^2 = 100\ cm^2$

L/R= 203/5= 40.6

$\log_e (L/R)=\log_e (40.6) = 3.703768$

h_1/h_2 =0.5/0.4= 1.25

$\log_e (h_1/h_2)=\log e(1.25)= 0.2231$

$$k= \frac{d^2}{8L} \left(\log_e (L/R)\right) \frac{\log_e(h_1/h_2)}{(t_2-t_1)}$$

=100*[(3.703768*0.2231)/ 8*203*10]

= (82.63106408/16240)

=0.00508812

K=0.00508812 cm/minute

=7.3268928 cm/day

=0.073268928 m/day

1.7 PERMEABILITY TEST DATA II

Location : Inside TCL

Date of Test :30/01/2021

Type of Well : AH- Tube Well

Coordinates : (12.95443, 79.31107)

Well Id : AH-8

RAW Hole Details

Augar Hole Depth BGL: 1.17m

Static water level BGL – 0.64m

Structure details

Length of casing pipe below GL : 1.17m

Length of plain casing: NIL

Length of screen pipe B.G.L : 1.17m

Static Water Level BGL: 0.64m

Pre Test Structure

Total casing pipe. 2.17m

Length of plain casing A.G.L: 1.0m

Diameter of casing pipe (both plain & Screen): 100mm

Static WL (from T.O.C) – 1.64m

WL after filling water (from T.O.C): 1.24m

Time in minutes since pumping started	Depth of water level from measuring point in m.
0	1.24
1.01	1.50
2.30	1.55
9.40	1.60
15	1.61
20	1.62
30	1.63
40	1.63
50	1.635
60	1.637
95	1.64
120	1.64
125	1.64

1.7.1 Results - Well AH 8

Using the above data, the permeability of the zone between G.L and 1.17m is computed for Well AH 8 as shown below.

Diameter of intake pipe (d)= 100mm

Length of test zone (L) = 1.17m or 117cm

h_1/h_0 =0.6 from the graph at time t_1=44 minutes

h_2/h_0 = 0.5 from graph at time t_2= 60 minutes

Radius of hole = 50mm = 5 cm

t_2-t_1= 60-44=16 minutes

$d^2 = (10)^2 = 100\ cm^2$

L/R= 117/5= 23.4

$\log_e (L/R)=\log_e (23.4) = 3.152736$

h_1/h_2 =0.6/0.5= 1.20

$\log_e (h_1/h_2)=\log e(1.20)=0.1823$

$$k= \frac{d^2}{8L} (\log_e (L/R)) \ \frac{\log_e(h_1/h_2)}{(t_2-t_1)}$$

=100*[(3.152736*0.1823)/ 8*117*16]

=57.47437728/14976

K=0.003837766 cm/minute

=5.526382431 cm/day

=0.05526382431 m/day

1.8 Field standards

Several literatures have been referred for understanding the permeability/hydraulic conductivity values of various soil types with different structure. Some of these data are presented below.

Table-1

Grain size classification	K (10^3m/year
Clay	< 0.0001
Silt clayey	0.1-0.4 **(0.2739-1.09 m/day)**
Silt slightly sandy	0.5
Silt moderately sandy	0.8-0.9
Silt very sandy	1.0-1.2
Sandy silt	1.2
Silty sand	1.4

Source: EPA 1986

Table-2

Material	Intrinsic Permeability (darcy)	Hydraulic conductivity(cm/sec)
Clay	10^{-6}-10^{-3}	10^{-9}-10^{-6}
Silt, sandy silts, clayey sands, till	10^{-3}-10^{-1}	10^{-6}-10^{-4}
Silty sands,fine	10^{-2}-1	10^{-5}-10^{-3}
Sands well sorted, Sands, glacial outwash	1- 10^{2}	10^{-3}-10^{-1}
Well sorted gravel	10-10^{3}	10^{-2}-1

Source: HSIN-YU- SHAN, Department of Civil Engg, National Chiao University

Table-3

K Value range by soil texture (Ritzema 2006)

Texture	Hydraulic Conductivity K (m/day)
Gravelly coarse sand	10-50
Medium sand	1-5
Sandy loam, fine dsand	1-3
Loam, clay loam, clay	0.5-0.2
Very fine sandy loam(well structured)	0-2-0.5
Clay loam, clay (poorly structured)	0.002-0.2
Dense clay (no cracks,pores	< 0.002

Table-4

Hydraulic Conductivity of different soils (Ramakrishnan 1998)

Soil type	Hydraulic Conductivity m/day
Clayey soils	0.01-0.20
Deep clay deposits	10^{-8}-10^{-2}
Loam soils	0.1-1.0
Fine Sand	1-5
Medium sand	5-20
Coarse sand	20-100
Gravel	100-1000
Sand and gravel mix	5-100
Clay, sand and gravel mix	0.001-0.1

Figure 1: Photographs of Permeability Testing

ANNEXURE 3

TABLE 1060:I. SUMMARY OF SPECIAL SAMPLING AND HANDLING REQUIREMENTS*

Determination	Container†	Minimum Sample Size *mL*	Sample Type‡	Preservation§	Maximum Storage	
					Recommended	Regulatory‖
Acidity	P, G(B)	100	g	Refrigerate	24 h	14 d
Alkalinity	P, G	200	g	Refrigerate	24 h	14 d
BOD	P, G	1000	g, c	Refrigerate	6 h	48 h
Boron	P (PTFE) or quartz	1000	g, c	HNO_3 to pH <2	28 d	6 months
Bromide	P, G	100	g, c	None required	28 d	28 d
Carbon, organic, total	G (B)	100	g, c	Analyze immediately; or refrigerate and add HCl, H_3PO_4, or H_2SO_4 to pH <2	7 d	28 d
Carbon dioxide	P, G	100	g	Analyze immediately	0.25 h	N.S.
COD	P, G	100	g, c	Analyze as soon as possible, or add H_2SO_4 to pH <2; refrigerate	7 d	28 d
Chloride	P, G	50	g, c	None required	N.S.	28 d
Chlorine, total, residual	P, G	500	g	Analyze immediately	0.25 h	0.25 h
Chlorine dioxide	P, G	500	g	Analyze immediately	0.25 h	N.S.
Chlorophyll	P, G	500	g	Unfiltered, dark, 4°C Filtered, dark, −20°C (Do not store in frost-free freezer)	24–48 h 28 d	
Color	P, G	500	g, c	Refrigerate	48 h	48 h
Specific conductance	P, G	500	g, c	Refrigerate	28 d	28 d
Cyanide						
Total	P, G	1000	g, c	Add NaOH to pH >12, refrigerate in dark#	24 h	14 d; 24 h if sulfide present
Amenable to chlorination	P, G	1000	g, c	Add 0.6 g ascorbic acid if chlorine is present and refrigerate	stat	14 d; 24 h if sulfide present
Fluoride	P	100	g, c	None required	28 d	28 d
Hardness	P, G	100	g, c	Add HNO_3 or H_2SO_4 to pH <2	6 months	6 months
Iodine	P, G	500	g	Analyze immediately	0.25 h	N.S.
Metals, general	P(A), G(A)	1000	g, c	For dissolved metals filter immediately, add HNO_3 to pH <2	6 months	6 months
Chromium VI	P(A), G(A)	1000	g	Refrigerate	24 h	24 h
Copper by colorimetry*			g, c			
Mercury	P(A), G(A)	1000	g, c	Add HNO_3 to pH <2, 4°C, refrigerate	28 d	28 d
Nitrogen						
Ammonia	P, G	500	g, c	Analyze as soon as possible or add H_2SO_4 to pH <2, refrigerate	7 d	28 d
Nitrate	P, G	100	g, c	Analyze as soon as possible; refrigerate	48 h	48 h (28 d for chlorinated samples)
Nitrate + nitrite	P, G	200	g, c	Add H_2SO_4 to pH <2, refrigerate	1–2 d	28 d
Nitrite	P, G	100	g, c	Analyze as soon as possible; refrigerate	none	48 h
Organic, Kjeldahl*	P, G	500	g, c	Refrigerate, add H_2SO_4 to pH <2	7 d	28 d
Odor	G	500	g	Analyze as soon as possible; refrigerate	6 h	N.S.
Oil and grease	G, wide-mouth calibrated	1000	g	Add HCl or H_2SO_4 to pH <2, refrigerate	28 d	28 d
Organic compounds						
MBAs	P, G	250	g, c	Refrigerate	48 h	N.S.
Pesticides*	G(S), PTFE-lined cap	1000	g, c	Refrigerate, add 1000 mg ascorbic acid/L if residual chlorine present	7 d	7 d until extraction; 40 d after extraction
Phenols	P, G, PTFE-lined cap	500	g, c	Refrigerate, add H_2SO_4 to pH <2	*	28 d until extraction
Purgeables* by purge and trap	G, PTFE-lined cap	2 × 40	g	Refrigerate; add HCl to pH <2; add 1000 mg ascorbic acid/L if residual chlorine present	7 d	14 d

TABLE 1060:I. CONT.

Determination	Container†	Minimum Sample Size *mL*	Sample Type‡	Preservation§	Maximum Storage Recommended	Maximum Storage Regulatory‖
Base/neutrals & acids	G(S) amber	1000	g, c	Refrigerate	7 d	7 d until extraction; 40 d after extraction
Oxygen, dissolved	G, BOD bottle	300	g			
Electrode				Analyze immediately	0.25 h	0.25 h
Winkler				Titration may be delayed after acidification	8 h	8 h
Ozone	G	1000	g	Analyze immediately	0.25 h	N.S.
pH	P, G	50	g	Analyze immediately	0.25 h	0.25 h
Phosphate	G(A)	100	g	For dissolved phosphate filter immediately; refrigerate	48 h	N.S.
Phosphorus, total	P, G	100	g, c	Add H_2SO_4 to pH <2 and refrigerate	28 d	
Salinity	G, wax seal	240	g	Analyze immediately or use wax seal	6 months	N.S.
Silica	P (PTFE) or quartz	200	g, c	Refrigerate, do not freeze	28 d	28 d
Sludge digester gas	G, gas bottle	—	g	—	N.S.	
Solids[9]	P, G	200	g, c	Refrigerate	7 d	2–7 d; see cited reference
Sulfate	P, G	100	g, c	Refrigerate	28 d	28 d
Sulfide	P, G	100	g, c	Refrigerate; add 4 drops 2*N* zinc acetate/100 mL; add NaOH to pH >9	28 d	7 d
Temperature	P, G	—	g	Analyze immediately	0.25 h	0.25 h
Turbidity	P, G	100	g, c	Analyze same day; store in dark up to 24 h, refrigerate	24 h	48 h

* For determinations not listed, use glass or plastic containers; preferably refrigerate during storage and analyze as soon as possible.

† P = plastic (polyethylene or equivalent); G = glass; G(A) or P(A) = rinsed with 1 + 1 HNO_3; G(B) = glass, borosilicate; G(S) = glass, rinsed with organic solvents or baked.

‡ g = grab; c = composite.

§ Refrigerate = storage at 4°C ± 2°C; in the dark; analyze immediately = analyze usually within 15 min of sample collection.

‖ See citation[10] for possible differences regarding container and preservation requirements. N.S. = not stated in cited reference; stat = no storage allowed; analyze immediately.

\# If sample is chlorinated, see text for pretreatment.

9. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1996. 40 CFR Part 136, Table II.
10. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1992. Rules and Regulations. 40 CFR Parts 100-149.

1060 C. Sample Storage and Preservation

Complete and unequivocal preservation of samples, whether domestic wastewater, industrial wastes, or natural waters, is a practical impossibility because complete stability for every constituent never can be achieved. At best, preservation techniques only retard chemical and biological changes that inevitably continue after sample collection.

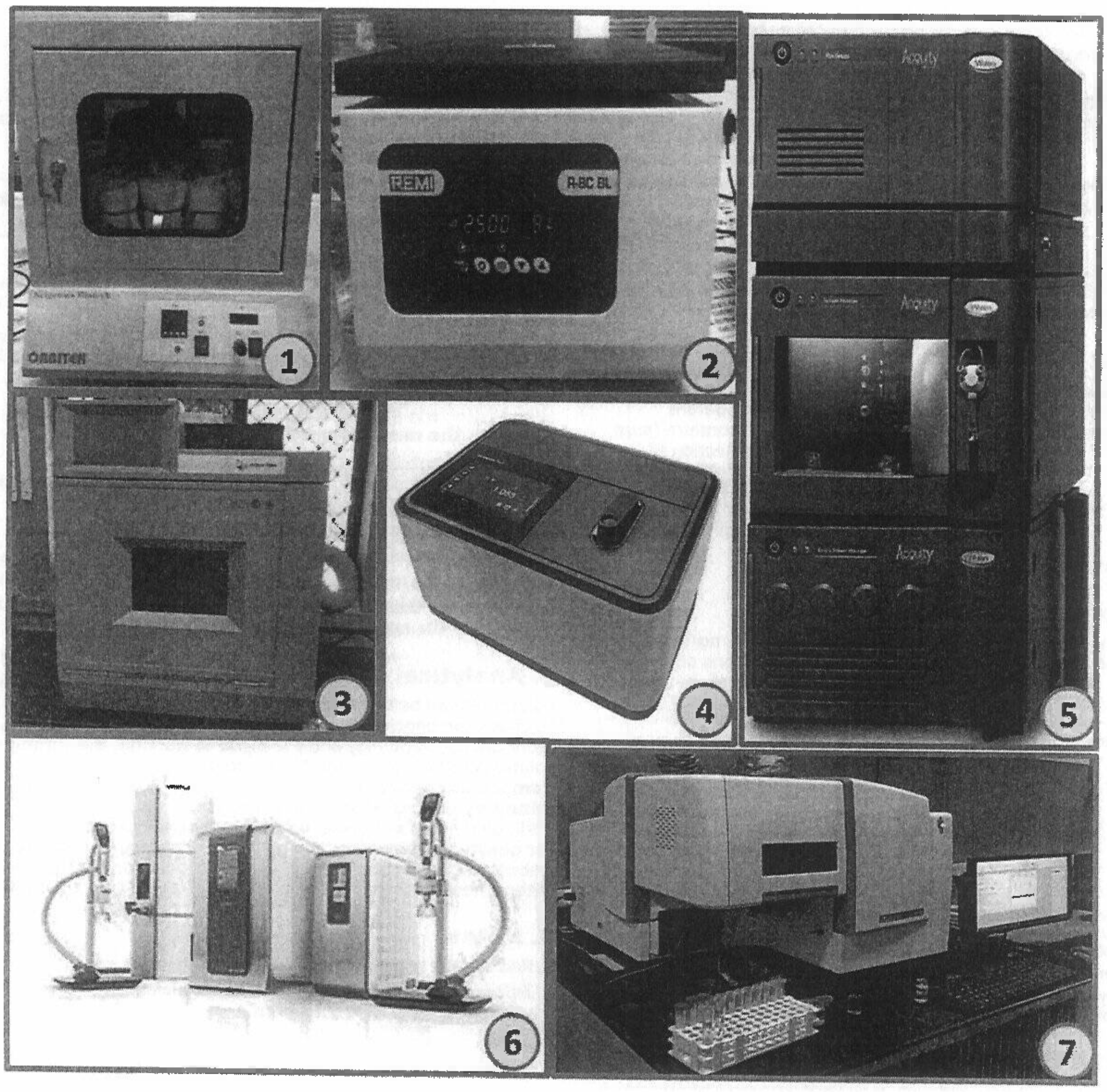
1. Sample Storage before Analysis

a. Nature of sample changes: Some determinations are more affected by sample storage than others. Certain cations are subject to loss by adsorption on, or ion exchange with, the walls of glass containers. These include aluminum, cadmium, chromium, copper, iron, lead, manganese, silver, and zinc, which are best collected in a separate clean bottle and acidified with nitric acid to a pH below 2.0 to minimize precipitation and adsorption on container walls. Also, some organics may be subject to loss by adsorption to the walls of glass containers.

Temperature changes quickly; pH may change significantly in a matter of minutes; dissolved gases (oxygen, carbon dioxide) may be lost. Because changes in such basic water quality properties may occur so quickly, determine temperature, reduction-oxidation potential, and dissolved gases in situ and pH, specific conductance, turbidity, and alkalinity immediately after sample collection. Many organic compounds are sensitive to changes in pH and/or temperature resulting in reduced concentrations during storage.

ANNEXURE 4

MAJOR INSTRUMENTS USED IN THE PRESENT STUDY



1: Incubator orbital shaker ORBITEK – LT – *Extraction of water soluble fractions*

2: Laboratory Centrifuge – REMI- R-8C BL - *Extraction of water soluble fractions*

3: Microwave Reaction System-Multiwave PRO- 24HVT50 – AntonPaar – *Digestion of soil samples for total heavy metal analysis*

4: Prove 100 Spectroquant®, UV/Vis spectroscopy – *Analysis of Hexavalent Chromium*

5: UHPLC – Waters – *Analysis of Oxalic Acid and Formic Acid*

6: ULTRA PURE WATER SYSTEM PALL CASCADA III.I – *For the preparation of standards and reagents, dilutions, extraction and digestion*

7: ICP-OES – AVIO200, Perkin Elmer – *Analysis of total heavy metals (Cr & Fe)*

1.14758.0001

Spectroquant®

Chromate Test

Cr

for the determination of chromium(VI)

1. Method

In weakly phosphoric solution chromium(VI) ions react with diphenylcarbazide to form chromium(III) and diphenylcarbazone, which form a red-violet complex. This complex is determined photometrically.
The method is analogous to APHA 3500-Cr D and DIN 38405-24.

2. Measuring range and number of determinations

Cell mm	Measuring range mg/l Cr	 mg/l CrO_4^{2-}	Number of determinations
50	**0.010** - 0.600	**0.02** - 1.34	250
20	0.03 - 1.50	0.07 - 3.35	
10	0.05 - **3.00**	0.11 - **6.69**	

For programming data for selected photometers / spectrophotometers see www.service-test-kits.com.

3. Applications

This test measures chromium(VI) present in the sample as chromate or dichromate ions. Samples must be decomposed by digestion before complex-bound chromium(III) occuring in waters or total chromium (sum of chromium(VI) and chromium(III)) can be measured (see section 6).

Sample material:
Groundwater, surface water, and seawater
Drinking water
Industrial water
Wastewater and percolating water

4. Influence of foreign substances

This was checked individually in solutions containing 1 and 0 mg/l Cr. The determination is not yet interfered with up to the concentrations of foreign substances given in the table. Cumulative effects were not checked; such effects can, however, not be excluded.

Concentrations of foreign substances in mg/l or %							
Al^{3+}	1000	Fe^{3+}	100	**Pb^{2+}**	**10**	**EDTA**	**0.1 %**
Ca^{2+}	1000	Hg^{2+}	1000	PO_4^{3-}	1000	Surfactants[2]	1 %
Cd^{2+}	1000	Mg^{2+}	1000	SiO_3^{2-}	1000	**~~Na-acetate~~**	**0.1 %**
CN^-	100	Mn^{2+}	1000	Zn^{2+}	100	NaCl	10 %[3]
Cr^{3+}	100[1]	NH_4^+	1000			$NaNO_3$	10 %
Cu^{2+}	**10**	Ni^{2+}	1000			Na_2SO_4	10 %
F^-	1000	NO_2^-	100				

[1] when determined without digestion
[2] tested with nonionic, cationic, and anionic surfactants
[3] for determination of total chromium only 1 %

Reducing agents interfere with the determination.

High COD values may impair the efficacy of the digestion mixture in the determination of total chromium and thus result in false-low readings.

5. Reagents and auxiliaries

The test reagents are stable up to the date stated on the pack when stored closed at +15 to +25 °C.

Package contents:
1 bottle of reagent Cr-1
1 bottle of reagent Cr-2
1 AutoSelector

Other reagents and accessories:
Spectroquant® Crack Set 10C, Cat. No. 114688
+ thermoreactor
or
Spectroquant® Crack Set 10, Cat. No. 114687
+ empty cells 16 mm with screw caps (25 pcs), Cat. No. 114724
+ thermoreactor

MQuant® Chromate Test, Cat. No. 110012,
measuring range 3 - 100 mg/l CrO_4^{2-} (1.3 - 45 mg/l Cr)
MQuant® Universal indicator strips pH 0 - 14, Cat. No. 109535
Sodium hydroxide solution 1 mol/l Titripur®, Cat. No. 109137
Sulfuric acid 0.5 mol/l Titripur®, Cat. No. 109072
Chromium standard solution CRM, 0.050 mg/l Cr^{6+}, Cat. No. 133012
Chromium standard solution CRM, 1.00 mg/l Cr^{6+}, Cat. No. 133013

Pipette for a pipetting volume of 5.0 ml
Rectangular cells 10, 20, and 50 mm (2 of each), Cat. Nos. 114946, 114947, and 114944
Semi-microcells 50 mm (2 pcs), Cat. No. 173502

6. Preparation

- Analyze immediately after sampling.
- Total chromium can be determined after pretreatment of the sample using one of the Spectroquant® Crack Sets.
- Check the chromate content with the MQuant® Chromate Test. Samples containing more than 3.00 mg/l Cr must be diluted with distilled water **prior to** digestion.
- **The pH must be within the range 1 - 9.**
  Adjust, if necessary, with sodium hydroxide solution or sulfuric acid.
- Filter turbid samples.

7. Procedure

Reagent Cr-1	1 level grey microspoon (in the cap of the Cr-1 bottle)	Place into a dry test tube.
Reagent Cr-2	6 drops[1]	Add and shake **vigorously until the reagent is completely dissolved.**
Pretreated sample **(15 - 35 °C)**	5.0 ml	Add with pipette and mix.
Leave to stand for 1 min (reaction time), then fill the sample into the cell, and measure in the photometer.		

[1] **Hold the bottle vertically while adding the reagent!**

For measurement in the **50-mm cell** both the sample volume as well as the quantities of reagents Cr-1 and Cr-2 must be doubled. Alternatively, the semi-microcell Cat. No. 173502 can be used.
When using the 50-mm cell is recommended to measure against an own prepared blank sample (preparation as per measurement sample, but with distilled water instead of sample) to increase the accuracy.
Configure the photometer for blank measurement.

Notes on the measurement:

- **Certain photometers may require a blank** (preparation as per measurement sample, but with distilled water instead of sample).
- For photometric measurement the cells must be clean.
  Wipe, if necessary, with a clean dry cloth.
- Measurement of turbid solutions yields false-high readings.
- The pH of the measurement solution must be within the range 1.0 - 3.0.
- The color of the measurement solution remains stable for at least 60 min after the end of the reaction time stated above.

8. Analytical quality assurance

recommended before each measurement series
To check the photometric measurement system (test reagent, measurement device, handling) and the mode of working, the chromium standard solutions CRM (see section 5) can be used.
Sample-dependent interferences (matrix effects) can be determined by means of standard addition.
Additional notes see under **www.qa-test-kits.com**.
For quality and batch certificates for Spectroquant® test kits see the website, where you will find all data in production control, that are determined in accordance with ISO 8466-1 and DIN 38402 A51.

9. Notes

- Reclose the reagent bottles immediately after use.
- **Information on disposal can be obtained at www.disposal-test-kits.com.**

Merck KGaA, 64271 Darmstadt, Germany,
Tel. +49(0)6151 72-2440
www.analytical-test-kits.com
EMD Millipore Corporation, 400 Summit Drive
Burlington MA 01803, USA, Tel. +1-978-715-4321

ANNEXURE 6

INSTRUMENTATION PARAMETERS AND OPERATIONAL CONDITIONS OF ICP-OES AND MICROWAVE DIGESTION

Table 1: ICP-OES instrumental parameters for the analysis of metals

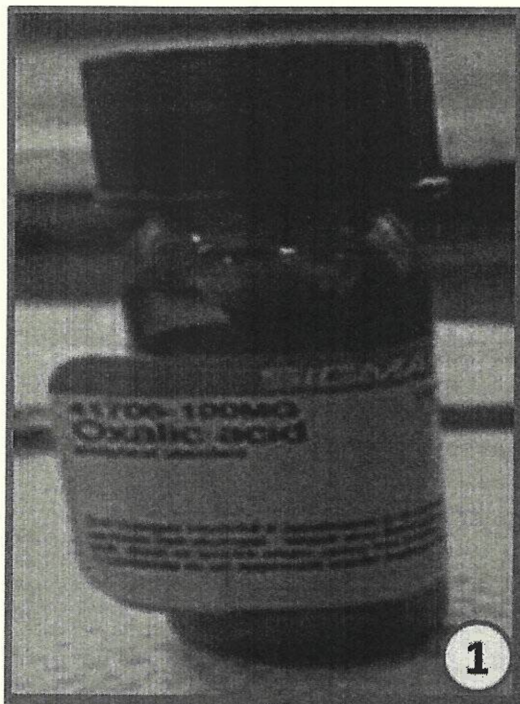
Parameter	Value	Parameter	Value
Nebuliser type	Cross-flow	Processing mode	Area
Spray chamber type	Scott-type	Read delay	45 s
RF power	1450 W	Calibration type	Linear
Plasma gas flow	10 L min^{-1}	Purge	Normal
Auxiliary gas flow	0.2 L min^{-1}	Rinse	20 s
Plasma viewing	Axial/radial	Replicates	3
Sample flow rate	1 mL min^{-1}	Carrier solution	Aqua regia
Nebuliser gas flow	0.7 L min^{-1}	Rinse solution	5 % HNO_3

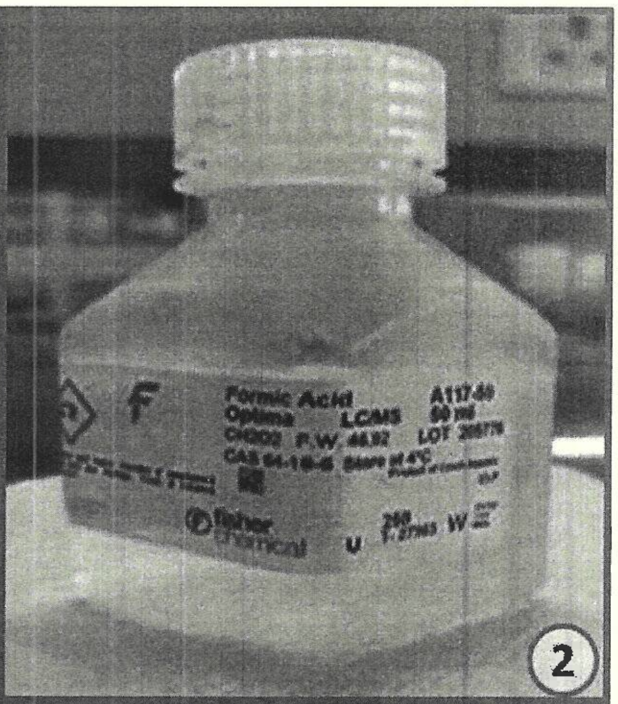
Table 2. Power conditions for Microwave digestion (Chand and Prasad 2013)

Step	Power (Watt)	Hold time	Fan speed
1	200	5	1
2	500	5	1
3	1000	15	1
4	0	15	2

ANNEXURE 7

THE STANDARDS AND CERTIFIED REFERENCE MATERIAL





1: OXALIC ACID ANALYTICAL STANDARD 41706-100MG – SIGMA ALDRITCH – *Preparation of Oxalic Acid standard for UHPLC analysis*

2: FORMIC ACID FOR LC-MS LICHROPUR 00940-20ML – FISHER CHEMICALS – *Preparation of Formic Acid standard for UHPLC analysis*

3: CERTIFIED REFERENCE MATERIAL SQC001-30G– SIGMA ALDRITCH – *Validation of accuracy in the heavy metals analysis of the soil samples*

ANNEXURE 8

Geographical co-ordinations of the water samples location

Sl. No.	Sample ID	Date of Collection	Latitude	Longitude
1	AH01	28.01.2021	12.95576	79.30893
2	AH04	28.01.2021	12.95173	79.31187
3	AH05	28.01.2021	12.95144	79.31756
4	AH11	29.01.2021	12.95833	79.31136
5	AH14	29.01.2021	12.9516	79.31074
6	AH16	29.01.2021	12.96857	79.3053
7	AH18	30.01.2021	12.96433	79.29784
8	AH21	30.01.2021	12.95251	79.30729
9	RAH01	17.02.2021	12.95576	79.30893
10	RAH05	17.02.2021	12.95144	79.31756
11	RAH14	17.02.2021	12.9516	79.31074
12	RAH18	17.02.2021	12.96433	79.29784
13	RAH21	17.02.2021	12.95251	79.30729
14	DS2	18.02.2021	12.95182	79.31232
15	DS3	18.02.2021	12.952	79.31131
16	DS4	18.02.2021	12.95277	79.31061
17	US1	18.02.2021	12.9551	79.31131
18	US2	18.02.2021	12.95487	79.31208
19	US3	18.02.2021	12.95445	79.31335
20	US4	18.02.2021	12.95388	79.31554
21	W1	18.02.2021	12.95854	79.31109
22	W2	18.02.2021	12.95538	79.31088
23	W3	18.02.2021	12.95567	79.30954
24	W4	18.02.2021	12.95759	79.30748
25	W5	18.02.2021	12.95666	79.30676
26	W6	18.02.2021	12.95988	79.30653
27	W7	18.02.2021	12.96087	79.3055
28	W8	18.02.2021	12.96211	79.31014
29	W9	18.02.2021	12.96458	79.30446
30	W10	18.02.2021	12.96953	79.30577
31	W11	18.02.2021	12.96647	79.3019
32	W12	18.02.2021	12.96767	79.30016
33	W13	18.02.2021	12.96624	79.29842
34	W14	18.02.2021	12.96469	79.29737
35	W15	18.02.2021	12.96444	79.29742
36	W16	18.02.2021	12.96373	79.30004
37	W17	19.02.2021	12.95572	79.30754
38	W18	19.02.2021	12.9589	79.30187
39	W19	19.02.2021	12.95931	79.30077
40	W20	19.02.2021	12.96536	79.30333
41	W21	19.02.2021	12.95484	79.30554

42	W22	19.02.2021	12.95492	79.30762
43	W23	19.02.2021	12.95296	79.30976
44	W24	19.02.2021	12.95508	79.311
45	W25	19.02.2021	12.95195	79.3108
46	W26	19.02.2021	12.95275	79.30759
47	W27	19.02.2021	12.95125	79.31374
48	W28	19.02.2021	12.95067	79.30731
49	W29	19.02.2021	12.94578	79.31274
50	W30	19.02.2021	12.9454	79.30891
51	W31	19.02.2021	12.93822	79.31308
52	W32	19.02.2021	12.92822	79.32299
53	W33	19.02.2021	12.92123	79.32201
54	W34	19.02.2021	12.93202	79.32359
55	W35	19.02.2021	12.92207	79.31322
56	W36	19.02.2021	12.92261	79.31255
57	W37	19.02.2021	12.93869	79.31017
58	W38	19.02.2021	12.94202	79.29994
59	W39	19.02.2021	12.96363	79.2942

ANNEXURE 9

Certificate of Analysis

Certified Reference Material

Description

Product ID SQC001-30G
Lot LRAC6625
Expiration Date April 2024
Manufacturing Date April 2020
Storage Conditions Room Temperature
Solvent/Matrix LOAMY CLAY

Certified Values

Analyte	*Units*	*Certified*[1,4] *Value*
Aluminum, Al	mg/Kg	11450 ± 619
Antimony, Sb	mg/Kg	42.0 ± 4.1
Arsenic, As	mg/Kg	43.1 ± 0.7
Barium, Ba	mg/Kg	597 ± 9
Beryllium, Be	mg/Kg	117 ± 2
Boron, B	mg/Kg	230 ± 6
Cadmium, Cd	mg/Kg	118 ± 2
Calcium, Ca	mg/Kg	4272 ± 66
Chromium, Cr (total)	mg/Kg	299 ± 4
Cobalt, Co	mg/Kg	114 ± 2
Copper, Cu	mg/Kg	330 ± 4
Iron, Fe	mg/Kg	12923 ± 296
Lead, Pb	mg/Kg	144 ± 2
Lithium, Li	mg/Kg	103 ± 6
Magnesium, Mg	mg/Kg	1827 ± 43
Manganese, Mn	mg/Kg	1065 ± 19
Mercury, Hg	mg/Kg	2.86 ± 0.1
Molybdenum, Mo	mg/Kg	60.2 ± 1.4
Nickel, Ni	mg/Kg	171 ± 3
PHOSPHORUS AS P, TOTAL	mg/Kg	294 ± 26
Potassium, K	mg/Kg	6087 ± 141
Selenium, Se	mg/Kg	154 ± 3
Silver, Ag	mg/Kg	73.5 ± 1.6
Sodium, Na	mg/Kg	1417 ± 28
Strontium, Sr	mg/Kg	369 ± 10
Tin, Sn	mg/Kg	215 ± 8

ANAB ACCREDITED
ISO 17034
REFERENCE MATERIAL PRODUCER

Description

Lot	LRAC6625
Expiration Date	April 2024
Manufacturing Date	April 2020
Storage Conditions	Room Temperature
Solvent/Matrix	LOAMY CLAY

Vanadium, V	mg/Kg	259 ± 4
Zinc, Zn	mg/Kg	874 ± 11

Informational Values

Analyte	*Units*	*Suggested Acceptance Windows*	*Standard Deviation*
Aluminum, Al	mg/Kg	0 to 23308	3964
Antimony, Sb	mg/Kg	0 to 126	27.3
Arsenic, As	mg/Kg	27.3 to 58.8	5.26
Barium, Ba	mg/Kg	390 to 797	67.9
Beryllium, Be	mg/Kg	75.2 to 161	14.3
Boron, B	mg/Kg	125 to 337	35.3
Cadmium, Cd	mg/Kg	81.7 to 153	11.9
Calcium, Ca	mg/Kg	3031 to 5542	418
Chromium, Cr (total)	mg/Kg	202 to 391	31.4
Cobalt, Co	mg/Kg	79.6 to 147	11.2
Copper, Cu	mg/Kg	240 to 419	29.9
Iron, Fe	mg/Kg	6994 to 18874	1980
Lead, Pb	mg/Kg	99.1 to 187	14.6
Lithium, Li	mg/Kg	25.0 to 189	27.3
Magnesium, Mg	mg/Kg	1005 to 2680	279
Manganese, Mn	mg/Kg	670 to 1456	131
Mercury, Hg	mg/Kg	1.47 to 4.20	0.455
Molybdenum, Mo	mg/Kg	31.2 to 89.5	9.72
Nickel, Ni	mg/Kg	112 to 225	18.9
PHOSPHORUS AS P, TOTAL	mg/Kg	0.00 to 589	98.3
Potassium, K	mg/Kg	3285 to 8622	889
Selenium, Se	mg/Kg	80.2 to 226	24.3
Silver, Ag	mg/Kg	39.7 to 106	11.0
Sodium, Na	mg/Kg	877 to 1972	182
Strontium, Sr	mg/Kg	186 to 552	60.9
Tin, Sn	mg/Kg	96.5 to 337	40.1
Vanadium, V	mg/Kg	167 to 353	31.0
Zinc, Zn	mg/Kg	625 to 1125	83.3

Additional Information:

DESCRIPTION

A total sample size of 30g is provided.
The sample has been heat sterilized.
This sample should be digested using USEPA method 3050, 3051 or equivilent methods.

Certificate of Analysis

Certified Reference Material

Description

Product ID	SQC001-30G
Lot	LRAC6625
Expiration Date	April 2024
Manufacturing Date	April 2020
Storage Conditions	Room Temperature
Solvent/Matrix	LOAMY CLAY

SAMPLE PREPARATION

Perform the sample digestion on an appropriate amount of sample according to the selected digestion procedure. The recommended minimum sampling size is 0.5 grams.

Determination of the percent moisture content of the material is required.

All results are reported on a dry weight basis.

It is recommended that approximately one gram of the soil be digested.

---

1 **Metrological traceability:** Traceable to the SI and higher order standards from NIST through an unbroken chain of comparisons. The balance used to weigh raw materials is accurate to +/-0.0001 g and calibrated regularly using mass standards traceable to NIST. All dilutions were performed gravimetrically. Additionally, individual analytes are traceable to NIST SRMs where available and specified above.

4 Ucrm - Uncertainty values in this document are expressed as Expanded Uncertainty (Ucrm) corresponding to the 95% confidence interval. Ucrm is derived from the combined standard uncertainty multiplied by the coverage factor k, which is obtained from a *t*-distribution and degrees of freedom. K=2 unless specified. The components of combined standard uncertainty include the uncertainties due to characterization, homogeneity, long term stability, and short term stability (transport). The components due to stability are generally considered to be negligible unless otherwise indicated by stability studies. The mathematical representation of the Ucrm calculation is as follows:

$$u_{CRM} = \sqrt{u_{char}^{2} + u_{\mathrm{hom}\ ogeneity}^{2} + u_{stability}^{2}}$$

k: Coverage factor derived from a t-distribution table, based on the degrees of freedom of the data set. Assume 2.0 for a **Confidence interval = 95%**

6 Analytical Value- For QC verification of the certified value only- not to be used in calculations. Represents the analytical data obtained by comparison to a standard as analyzed by the method described in the CoA or another acceptable method. The result may differ from the certified value and UCRM based on method uncertainty as well as the uncertainty associated with the standard used for comparison.

Traceability: The standard was manufactured under an ISO/IEC 17025:2017 certified quality system. The balance used to weigh raw materials is accurate to +/- 0.0001g and calibrated regularly using mass standards traceable to NIST. All dilutions were preformed gravimetrically. Additionally, individual analytes are traceable to NIST SRMs where available and specified above.

Homogeneity: Homogeneity was assessed in accordance with ISO 17034:2016. Completed units were sampled using a random stratified sampling protocol. The results of chemical analysis were then compared using a one-way analysis of variance approach as described by TNI EL-V3-2009 Appendix A.2. See Instructions for minimum sub-sample size.

Expiration is at end of month given on certificate and label.

MSDS reports for components comprising greater than 1.0% of the solution or 0.1% for components known to be carcinogens are available upon request.

THIS PRODUCT WAS DESIGNED, PRODUCED AND VERIFIED FOR ACCURACY AND STABILITY IN ACCORDANCE WITH **ISO/IEC 17025:2017 (ANAB Cert AT-1467)** and **ISO 17034:2016 (ANAB Cert AR-1470).**

Andy Ommen - QC Manager

Mark Pooler - QA Supervisor

Certification Date	November 06, 2020
Version	0-1162020

ANAB ACCREDITED REFERENCE MATERIAL PRODUCER

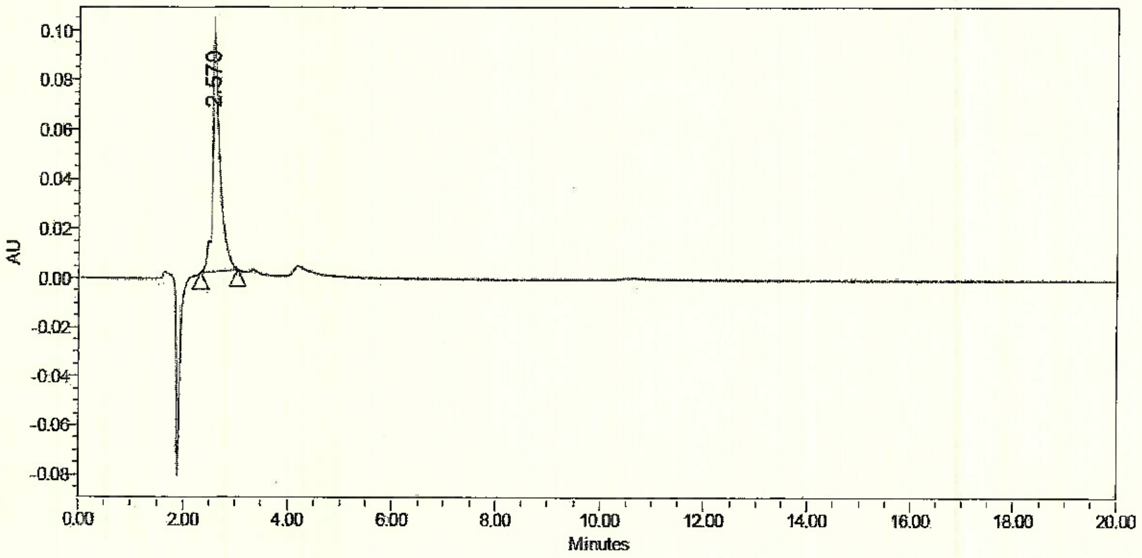
ANNEXURE 10

OXALIC ACID CALCULATION FROM HPLC RESULTS in VIT:

Standard calibration

Sample Name:	STD OXALIC ACID	Acquired By:	System
Sample Type:	Standard	Sample Set Name:	dass
Vial:	1:A,2	Acq. Method Set:	VIT HPLC EXT 2
Injection #:	4	Processing Method:	vit1
Injection Volume:	20.00 ul	Channel Name:	190.2nm
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 190.2 nm (PDA Spectrum (190-400)nm)
Date Acquired:	10-04-2021 04:03:10 IST		
Date Processed:	12-04-2021 15:06:46 IST		

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height	Amount	Units
1		2.570	964044	97598		

Standard area = 964044

Volume injected = 20 μL

Total Volume of the sample = 315 ml

Mass added in total volume = 6.3 mg (equivalent to 20 mg/L)

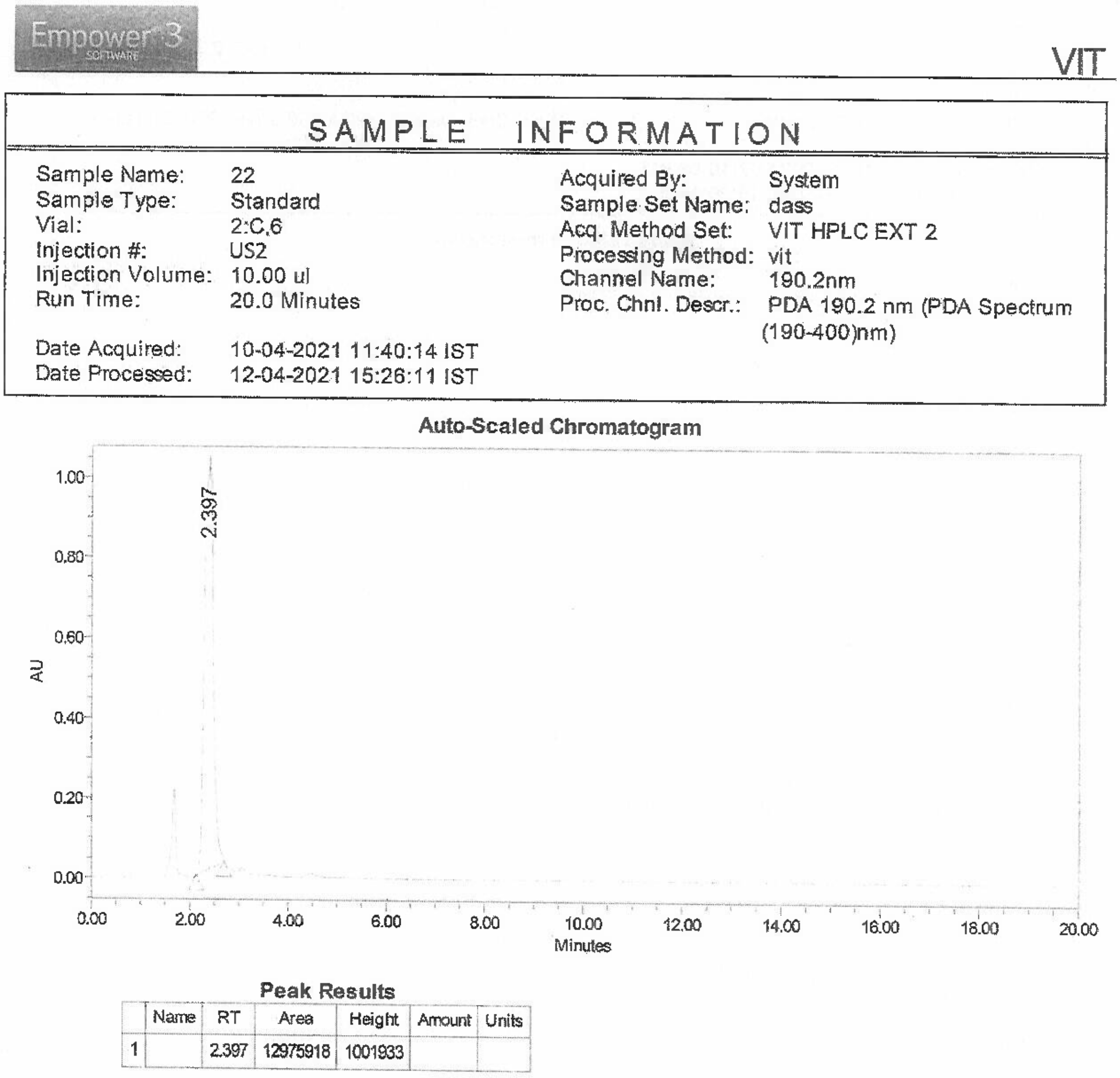
Molecular wt of Oxalic Acid = 90 gm

Mole in total volume = $\frac{6.3\times10^{-3}}{90}$ = 0.00007 mole

Mole injected = $\frac{0.00007\times20\times10^{-3}}{315}$ = 4.44 x 10^{-09} mole

Area per mole = $\frac{964044}{4.44\times10^{-09}}$ = **2.169 x 10^{14}**

Calculation of US2 sample (water):



Empower 3 SOFTWARE

VIT

SAMPLE INFORMATION

Sample Name:	22	Acquired By:	System
Sample Type:	Standard	Sample Set Name:	dass
Vial:	2:C,6	Acq. Method Set:	VIT HPLC EXT 2
Injection #:	US2	Processing Method:	vit
Injection Volume:	10.00 ul	Channel Name:	190.2nm
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 190.2 nm (PDA Spectrum (190-400)nm)
Date Acquired:	10-04-2021 11:40:14 IST		
Date Processed:	12-04-2021 15:26:11 IST		

Auto-Scaled Chromatogram

Peak Results

	Name	RT	Area	Height	Amount	Units
1		2.397	12975918	1001933		

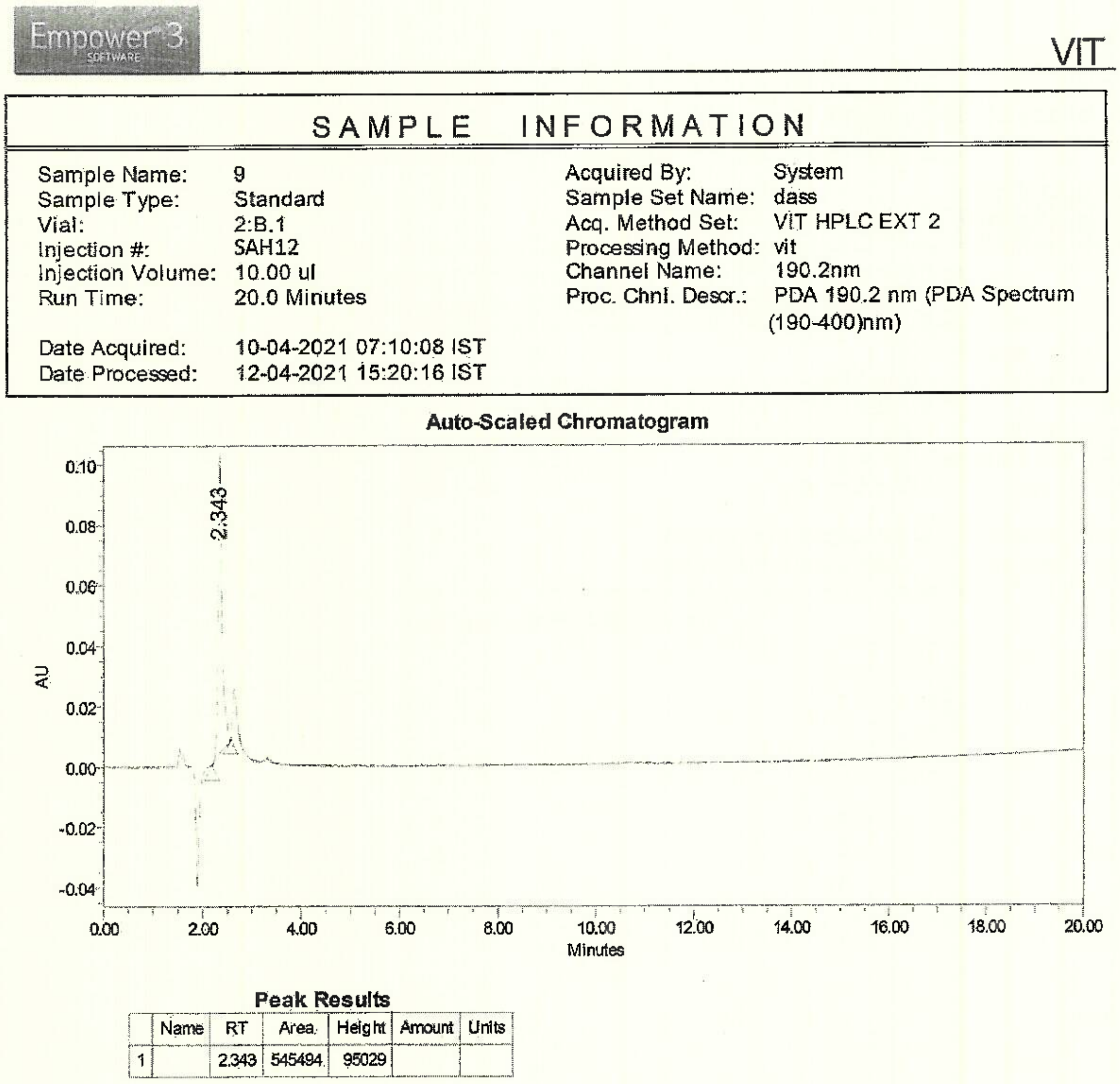
Area = 12975918

Mole = $\frac{12975918}{2.169 \times 10^{14}} = 5.98 \times 10^{-08}$

Mole injected = 10 µL

Mole/L = $\frac{5.98 \times 10^{-08} \times 10^{06}}{10}$ = 0.00598 Mole/L = 0.00598 x 90 = **0.5382 gm/L**

Calculation of SAH12 sample (soil):



Empower 3 SOFTWARE

VIT

SAMPLE INFORMATION

Sample Name:	9	Acquired By:	System
Sample Type:	Standard	Sample Set Name:	dass
Vial:	2:B.1	Acq. Method Set:	VIT HPLC EXT 2
Injection #:	SAH12	Processing Method:	vit
Injection Volume:	10.00 ul	Channel Name:	190.2nm
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 190.2 nm (PDA Spectrum (190-400)nm)
Date Acquired:	10-04-2021 07:10:08 IST		
Date Processed:	12-04-2021 15:20:16 IST		

Auto-Scaled Chromatogram

Peak Results

	Name	RT	Area	Height	Amount	Units
1		2.343	545494	95029		

Area = 545494

Mole = $\frac{545494}{2.169 \times 10^{14}}$ = 2.51 x 10^{-09}

Mole injected = 10 µL

Mole/L = $\frac{2.51 \times 10^{-09} \times 10^{06}}{10}$ = 0.000251484 Mole/L = 0.00598 x 90 = **0.02263 gm/L**

The soil was mixed with water in 1:5 ratio as mentioned in the methodology.

Hence, soil concentration = 0.02263 x 5 = 0.113 gm/kg

OXALIC ACID CALCULATIONS IN IIT IS ATTACHED IN THE FOLLOWING PAGES [soil: water = 1:2]

Qualitative Analysis Report

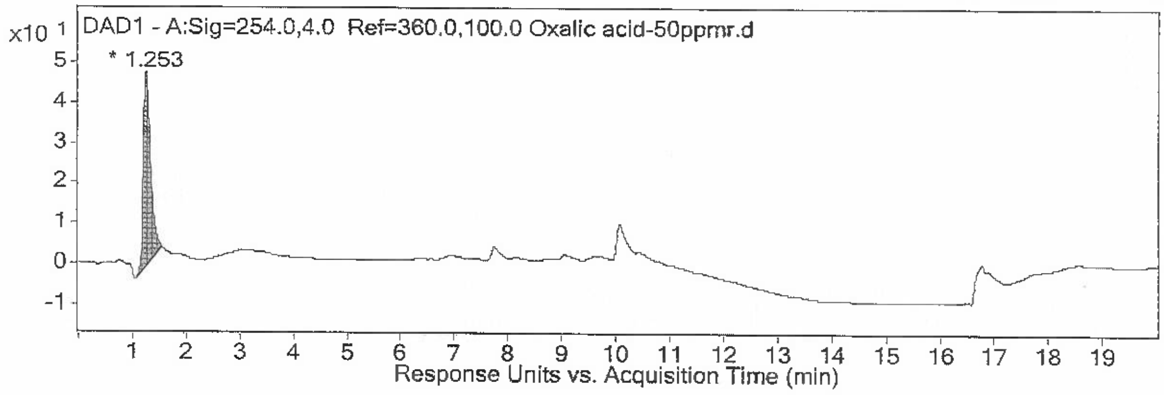
Data Filename	Oxalic acid-50ppmr.d	**Sample Name**	Oxalic acid-50ppm
Sample Type	Sample	**Position**	P1-F8
Instrument Name	QTOF	**User Name**	
Acq Method	30min_+esi_14072021_MSMS.m	**Acquired Time**	7/15/2021 1:01:34 PM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

Sample Group **Info.**

Acquisition SW 6200 series TOF/6500 series

Version Q-TOF B.05.01 (B5125.3)

User Chromatograms



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	1.093	1.253	1.553	48.38	465.44	100

--- End Of Report ---

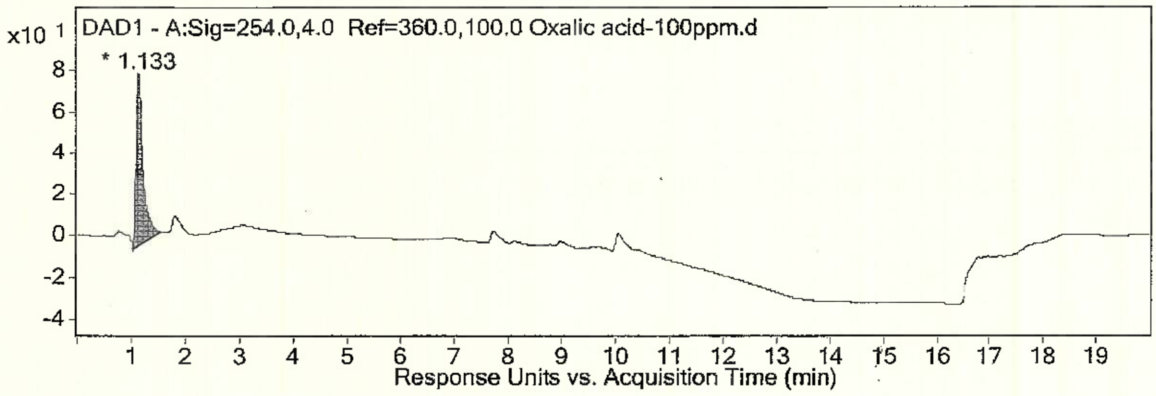
Qualitative Analysis Report

Data Filename	Oxalic acid-100ppm.d	**Sample Name**	Oxalic acid-100ppm
Sample Type	Sample	**Position**	P1-F2
Instrument Name	QTOF	**User Name**	
Acq Method	30min_+esi_14072021_MSMS.m	**Acquired Time**	7/14/2021 5:43:40 PM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

Sample Group **Info.**

Acquisition SW Version 6200 series TOF/6500 series Q-TOF B.05.01 (B5125.3)

User Chromatograms



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	1.037	1.133	1.553	83.71	770.55	100

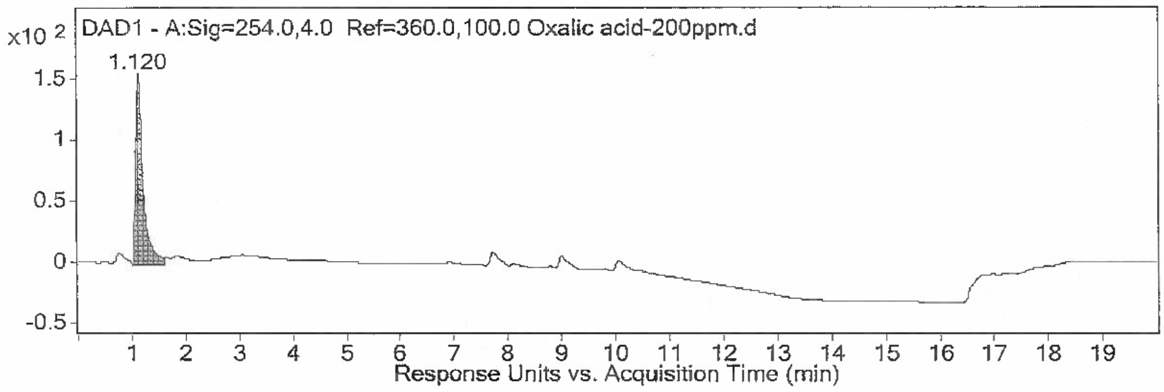
--- End Of Report ---

Qualitative Analysis Report

Data Filename	Oxalic acid-200ppm.d	**Sample Name**	Oxalic acid-200ppm
Sample Type	Sample	**Position**	P1-F3
Instrument Name	QTOF	**User Name**	
Acq Method	30min_+esi_14072021_MSMS.m	**Acquired Time**	7/14/2021 6:04:49 PM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

Sample Group		**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.3)	

User Chromatograms



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	1.019	1.12	1.607	157.57	1564.86	100

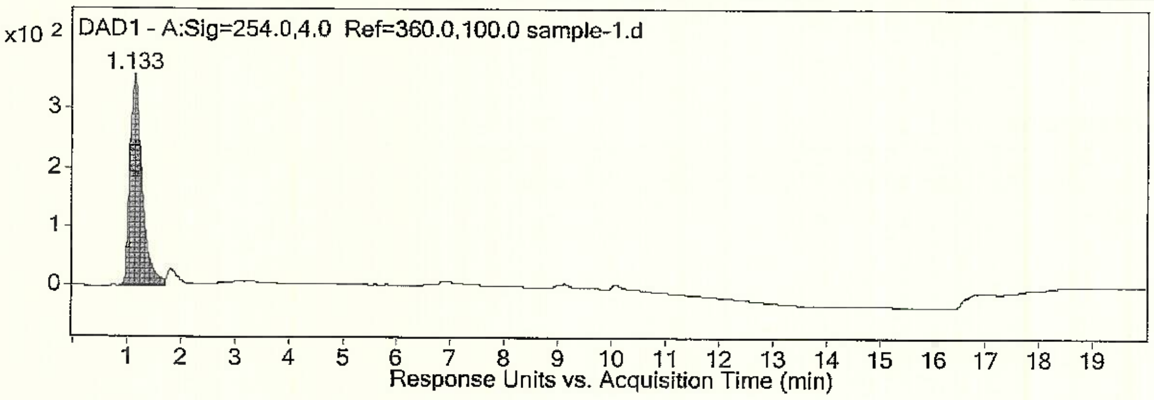
--- End Of Report ---

Qualitative Analysis Report

Data Filename	sample-1.d	**Sample Name**	sample-1
Sample Type	Sample	**Position**	P1-F4
Instrument Name	QTOF	**User Name**	
Acq Method	30min_+esi_14072021_MSMS.m	**Acquired Time**	7/14/2021 6:46:26 PM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

Sample Group		**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.3)	

User Chromatograms



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	0.86	1.133	1.707	357.84	5758.98	100

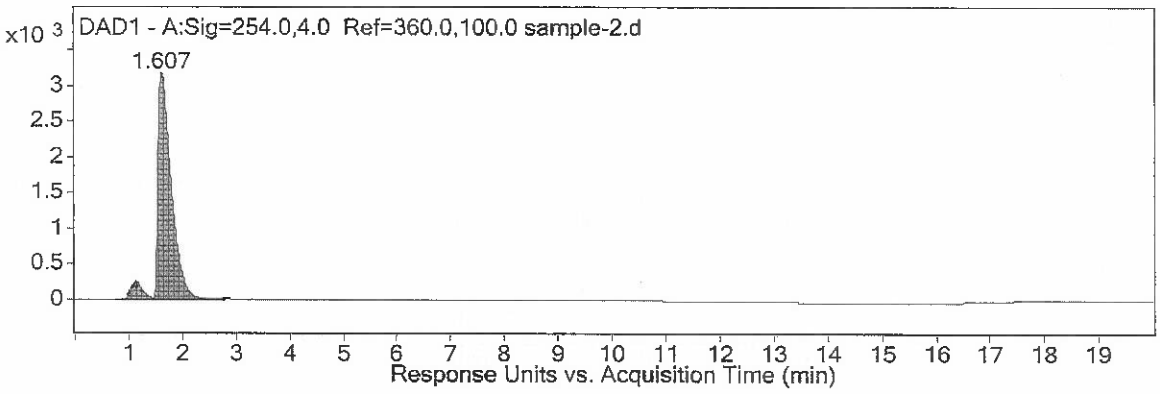
--- End Of Report ---

Qualitative Analysis Report

Data Filename	sample-2.d	**Sample Name**	sample-2
Sample Type	Sample	**Position**	P1-F5
Instrument Name	QTOF	**User Name**	
Acq Method	30min_+esi_14072021_MSMS.m	**Acquired Time**	7/14/2021 7:27:59 PM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

Sample Group		**Info.**
Acquisition SW	6200 series TOF/6500 series	
Version	Q-TOF B.05.01 (B5125.3)	

User Chromatograms



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	0.864	1.133	1.46	255.26	3933.32	7.07
2	1.46	1.607	2.773	3183.16	55622.06	100

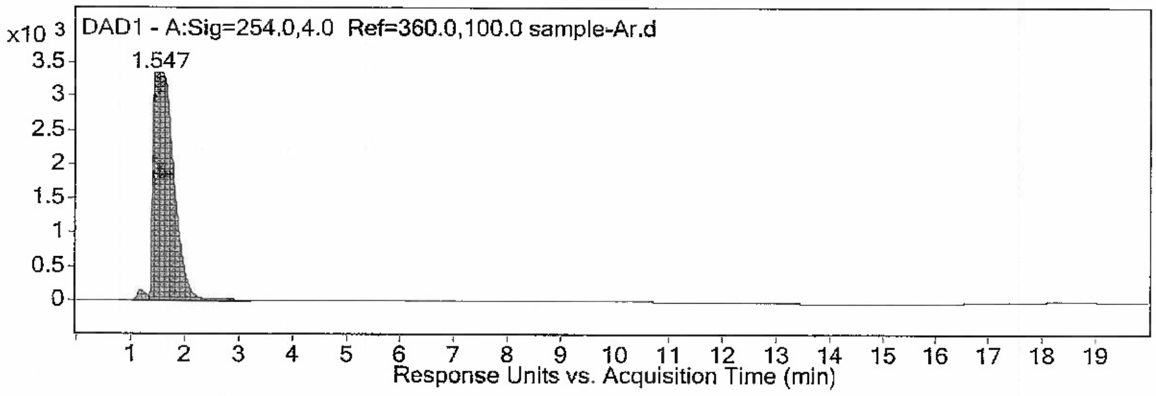
--- End Of Report ---

Qualitative Analysis Report

Data Filename	sample-Ar.d	**Sample Name**	sample-A
Sample Type	Sample	**Position**	P1-F6
Instrument Name	QTOF	**User Name**	
Acq Method	30min_+esi_14072021_MSMS.m	**Acquired Time**	7/15/2021 11:49:13 AM
IRM Calibration Status	[redacted]	**DA Method**	Default.m
Comment			

Sample Group		**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.3)	

User Chromatograms



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	1.021	1.193	1.353	158.5	1778.79	1.99
2	1.353	1.547	3.233	3352.04	89366	100

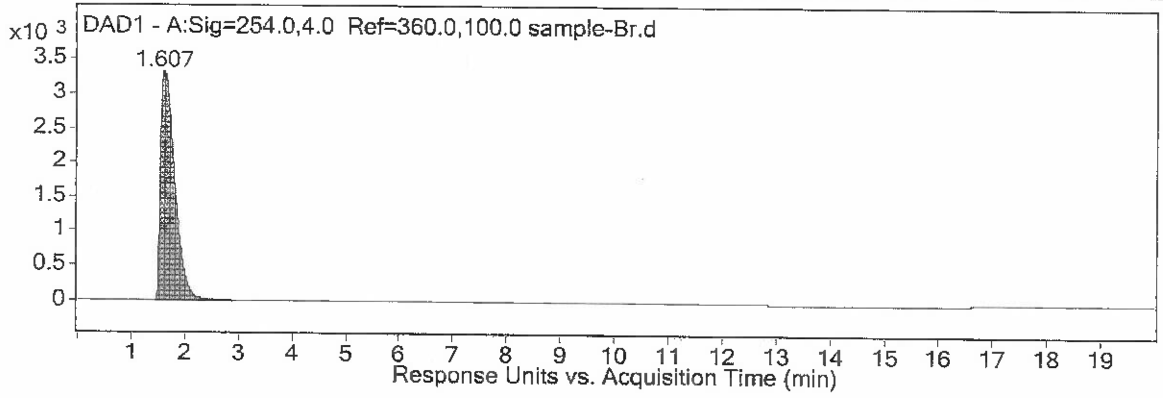
--- End Of Report ---

Qualitative Analysis Report

Data Filename	sample-Br.d	**Sample Name**	sample-B
Sample Type	Sample	**Position**	P1-F7
Instrument Name	QTOF	**User Name**	
Acq Method	30min_+esi_14072021_MSMS.m	**Acquired Time**	7/15/2021 12:10:21 PM
IRM Calibration Status	[redacted]	**DA Method**	Default.m
Comment			

Sample Group		**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.3)	

User Chromatograms



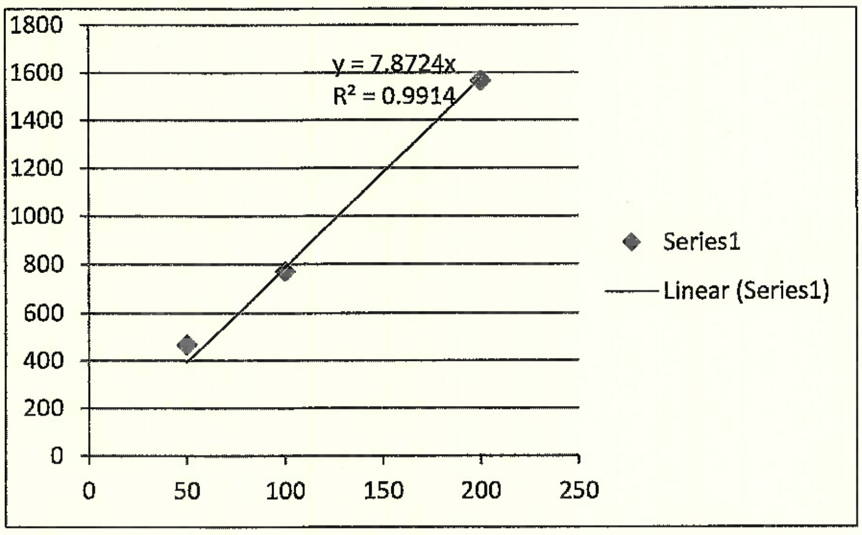
Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	1.447	1.607	2.893	3325.5	62251.8	100

--- End Of Report ---

QXALIC ACID Std in (ppm)	Area
50	465.44
100	770.55
200	1564.86

sample details		
sample name	Area	concentration in ppm
sample-1	5758.98	731.5405721
sample-2	3933.32	499.6341649
sample-A	1778.79	225.9526955
sample-B	ND	ND



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Phone : 8144115515, Email : info@ecotechlabs.in / lab@ecotechlabs.in, Website : www.ecotechlabs.in

Accredited by NABL ISO/IEC 17025 : 2017, Quality Council of India

TEST REPORT

Report No : TC593721000001303F	Report Date: 26.04.2021	Page 1 of 1

Name of the Client : **Dr. Baskar Doss**
Address of the Client : **VIT university, Vellore-632014**

Sample Name	: Soil	Sample Description	: Soil-B
Sample Code	:ETL0421289	Sample Condition	: Good
Sample Drawn By	: Client	Sampling date	: -
Sampling Procedure	: -	Received date	: 20.04.2021
Sample Location	:-	Commenced on	: 20.04.2021
Customer Reference	: Test Requested on 20.04.2021	Completed on	: 24.04.2021

S.No	Parameters	Test Method	Result	Units
1	Total Chromium	IS 3025 (P-53)2017	1728	mg/kg
2	Iron	IS 3025 (P-52)2017	0.86	%

End of Report

ECO TECH LABS PRIVATE LIMITED
CHENNAI 600 100

Authorised Signatory - Chemical

S. Kokila
Lab Manager

Eco Tech Labs Pvt Ltd

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TEST REPORT

Report No : TC593721000001296F   Report Date: 26.04.2021   Page 1 of 1

Name of the Client : Dr. Baskar Doss
Address of the Client : VIT university, Vellore-632014

Sample Name : Water
Sample Code :ETL0421282
Sample Drawn By : Client
Sampling Procedure : -
Sample Location :-
Customer Reference : Test Requested on 20.04.2021

Sample Description : Water Soluble - A
Sample Condition : Good
Sampling date : -
Received date : 20.04.2021
Commenced on : 20.04.2021
Completed on : 24.04.2021

S.No	Parameters	Test Method	Result	Units
1	Hexavalent Chromium	IS 3025 (P-52)2003	13.42	mg/L

End of Report

ECO TECH LABS PRIVATE LIMITED
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Authorised Signatory - Chemical

S. Kokila
Lab Manager

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TEST REPORT

Report No : TC593721000001300F	Report Date: 26.04.2021	Page 1 of 1

Name of the Client : Dr. Baskar Doss
Address of the Client : VIT university, Vellore-632014

Sample Name : Water
Sample Code :ETL0421286
Sample Drawn By : Client
Sampling Procedure : -
Sample Location :-
Customer Reference : Test Requested on 20.04.2021

Sample Description : HNO3 Acidfied-1
Sample Condition : Good
Sampling date : -
Received date : 20.04.2021
Commenced on : 20.04.2021
Completed on : 24.04.2021

S.No	Parameters	Test Method	Result	Units
1	Total Chromium	IS 3025 (P-53)2017	29.6	mg/L
2	Iron	IS 3025 (P-52)2017	0.22	mg/L

End of Report

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Authorised Signatory - Chemical
S. Kokila
Lab Manager

---

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3. The test results relate only to the test items.

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TEST REPORT

Report No : TC593721000001301F	Report Date: 26.04.2021	**Page 1 of 1**

Name of the Client : **Dr. Baskar Doss**
Address of the Client : **VIT university, Vellore-632014**

Sample Name	: Water	Sample Description	: HNO3 Acidfied-2
Sample Code	:ETL0421287	Sample Condition	: Good
Sample Drawn By	: Client	Sampling date	: -
Sampling Procedure	: -	Received date	: 20.04.2021
Sample Location	:-	Commenced on	: 20.04.2021
Customer Reference	: Test Requested on 20.04.2021	Completed on	: 24.04.2021

S.No	Parameters	Test Method	Result	Units
1	Total Chromium	IS 3025 (P-53)2017	18.9	mg/L
2	Iron	IS 3025 (P-52)2017	0.12	mg/L

End of Report

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Lab Manager

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TEST REPORT

Report No : TC593721000001298F Report Date: 26.04.2021 Page 1 of 1

Name of the Client : Dr. Baskar Doss
Address of the Client : VIT university, Vellore-632014

Sample Name : Water
Sample Code :ETL0421284
Sample Drawn By : Client
Sampling Procedure : -
Sample Location :-
Customer Reference : Test Requested on 20.04.2021

Sample Description : Water -1
Sample Condition : Good
Sampling date : -
Received date : 20.04.2021
Commenced on : 20.04.2021
Completed on : 24.04.2021

S.No	Parameters	Test Method	Result	Units
1	Hexavalent Chromium	IS 3025 (P-52)2003	24	mg/L

End of Report

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Authorised Signatory - Chemical

S. Kokila
Lab Manager

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ORIGINAL
Page 1 of 1

TEST REPORT

Test Report No. : ICE-2106250367
NABL ULR No. : TC695221100002971F

TC-6952

Issued To
Dr. Bhaskar Das
Vellore Institute of Technology
Vellore

Sample Registration No. : E02-2104200282
Sample Name# : Soil Sample
Sample Condition : Good
Sample details (if any) :-
Sample Quantity# : 10g X 1 No
Batch No.# : Sample - A
Sample Submission Type : Courier
Customer Reference# : Test Request Form/20.04.2021
Test Report as per : NA

Received On : 20-04-2021
Commenced On : 25-06-2021
Completed On : 25-06-2021
Date of Report : 25-06-2021

Description	
Description	Brown coloured sample

S.No.	Parameters	Instrument	Method	Result
	Discipline : Chemical			
	Group : Pollution and Environment			
1.	**Heavy Metals**			
a.	Iron as Fe,(% by Mass)	ICPOES	USEPA 6010 D	4.18
b.	Chromium as Cr,(mg/kg)	ICPOES	USEPA 6010 D	333

'#' represents Customer Defined Fields

NOTE : BLQ : Below limit of Quantification, LOQ : limit of Quantification

REMARKS : All parameters are analysed as dry basis

*****End Of Report*****

Verified by **Authorised by**

C. DILLIBABU
Lab Head
Head Technical

Interstellar Testing Centre Pvt. Ltd.
Plot No. 2,S.No.12/2A, Industrial Estate,
Perungudi, Sholinganallur Taluk, Chennai - 600 096.
Ph : 044 - 24962512
Email : itclabs.chennai@itclabs.com
Website : www.itclabs.com

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TEST REPORT

Test Report No. : ICE-2106250372

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Page 1 of 1

Issued To

Dr. Bhaskar Das
Vellore Institute of Technology
Vellore

Sample Registration No.	:	E02-2104200287			
Sample Name#	:	Water Sample	Received On	:	20-04-2021
Sample Condition	:	Good	Commenced On	:	25-06-2021
Sample details (if any)	:-		Completed On	:	25-06-2021
Sample Quantity#	:	20ml X 1 No	Date of Report	:	25-06-2021
Batch No.#	:	B			
Sample Submission Type	:	Courier			
Customer Reference#	:	Test Request Form/20.04.2021			
Test Report as per	:	NA			

Description				
Description		Colourless liquid		
S.No.	***Parameters**	**Instrument**	**Method**	**Result**
	Discipline : Chemical			
	Group : Water			
1.	**General Parameters**			
a.	Chromium (as Cr^{6+}),(mg/l)	UV- Spectrophotometer	IS 3025 (Part 52)	0.016

'*' represents categories/test parameters not covered under NABL | '**' represents outsource sample | '#' represents Customer Defined Fields

NOTE : BLQ : Below limit of Quantification, LOQ : limit of Quantification

REMARKS :Not Applicable

*****End Of Report*****

Verified by

Authorised by

S. DILLIBABU
Lab Head
Head Technical

Interstellar Testing Centre Pvt. Ltd.

TEST REPORT

Test Report No. : ICL-2106250368
NABL ULR No. : TC695221100002972F

TC-6952

ORIGINAL
Page 1 of 1

Issued To
Dr. Bhaskar Das
Vellore Institute of Technology
Vellore

Sample Registration No.	:	E02-2104200283			
Sample Name#	:	Soil Sample	Received On	:	20-04-2021
Sample Condition	:	Good	Commenced On	:	25-06-2021
Sample details (if any)	:-		Completed On	:	25-06-2021
Sample Quantity#	:	10g X 1 No	Date of Report	:	25-06-2021
Batch No.#	:	Sample B			
Sample Submission Type	:	Courier			
Customer Reference#	:	Test Request Form/20.04.2021			
Test Report as per	:	NA			

Description	
Description	Brown coloured sample

S.No.	Parameters	Instrument	Method	Result
	Discipline : Chemical			
	Group : Pollution and Environment			
1.	**Heavy Metals**			
a.	Iron as Fe,(% by weight)	ICPOES	USEPA 6010 D	0.99
b.	Chromium as Cr,(% by weight)	ICPOES	USEPA 6010 D	0.22

'#' represents Customer Defined Fields

NOTE : BLQ : Below limit of Quantification, LOQ : limit of Quantification

REMARKS : All parameters are analysed as dry basis

*****End Of Report*****

Verified by

Authorised by

S. DILLIBAB
Lab Head
Head Technical

Since 1988
ITC Labs
Assuring Integrity, Trust & Confidence

Interstellar Testing Centre Pvt. Ltd.

TEST REPORT

Test Report No. : ICE-2106250371

ORIGINAL
Page 1 of 1

Issued To

Dr. Bhaskar Das
Vellore Institute of Technology
Vellore

Sample Registration No.	: E02-2104200286			
Sample Name#	: Water Sample	Received On	:	20-04-2021
Sample Condition	: Good	Commenced On	:	25-06-2021
Sample details (if any)	:-	Completed On	:	25-06-2021
Sample Quantity#	: 20ml X 1 No	Date of Report	:	25-06-2021
Batch No.#	: A			
Sample Submission Type	: Courier			
Customer Reference#	: Test Request Form/20.04.2021			
Test Report as per	: NA			

Description				
Description	Colourless liquid			
S.No.	***Parameters**	**Instrument**	**Method**	**Result**
	Discipline : Chemical			
	Group : Water			
1.	**General Parameters**			
a.	Chromium (as Cr^{6+}),(mg/l)	UV- Spectrophotometer	IS 3025 (Part 52)	14.8

'*' represents categories/test parameters not covered under NABL | '**' represents outsource sample | '#' represents Customer Defined Fields

NOTE : BLQ : Below limit of Quantification, LOQ : limit of Quantification

REMARKS : Not Applicable

*****End Of Report*****

Verified by

Authorised by

S. DILLIBABU
Lab Head
Head Technical

Since 1988
ITC Labs
Assuring Integrity, Trust & Confidence

Interstellar Testing Centre Pvt. Ltd.

TEST REPORT

ORIGINAL
Page 1 of 1

Test Report No. : ICE-2106250369

Issued To

Dr. Bhaskar Das
Vellore Institute of Technology
Vellore

Sample Registration No.	: E02-2104200284			
Sample Name#	: Water sample (Acidified)	Received On	:	20-04-2021
Sample Condition	: Good	Commenced On	:	25-06-2021
Sample details (if any)	:-	Completed On	:	25-06-2021
Sample Quantity#	: 20ml X 1 No	Date of Report	:	25-06-2021
Batch No.#	: I			
Sample Submission Type	: Courier			
Customer Reference#	: Test Request Form/20.04.2021			
Test Report as per	: NA			

Description				
Description	Colourless liquid			
S.No.	***Parameters**	**Instrument**	**Method**	**Result**
	Discipline : Chemical			
	Group : Water			
I.	**General Parameters**			
a.	Iron as Fe, (mg/L)	ICPOES	ITC/CHN/FD/STP/020	0.121
b.	Total Chromium as Cr, (mg/L)	ICPOES	ITC/CHN/FD/STP/020	27.03

'*' represents categories/test parameters not covered under NABL | '**' represents outsource sample | '#' represents Customer Defined Fields

NOTE : BLQ : Below limit of Quantification, LOQ : limit of Quantification

REMARKS : Not Applicable

*****End Of Report*****

Verified by

Authorised by

S. DILLIBABU
Lab Head
Head Technical

Since 1988
ITC Labs
Assuring Integrity, Trust & Confidence

Interstellar Testing Centre Pvt. Ltd.

TEST REPORT

ORIGINAL
Page 1 of 1

Test Report No. : ICE-2106250370

Issued To

Dr. Bhaskar Das
Vellore Institute of Technology
Vellore

Sample Registration No.	: E02-2104200285			
Sample Name#	: Water sample (Acidified)	Received On	:	20-04-2021
Sample Condition	: Good	Commenced On	:	25-06-2021
Sample details (if any)	:-	Completed On	:	25-06-2021
Sample Quantity#	: 20ml X 1 No	Date of Report	:	25-06-2021
Batch No.#	: 2			
Sample Submission Type	: Courier			
Customer Reference#	: Test Request Form/20.04.2021			
Test Report as per	: NA			

Description	
Description	Colourless liquid

S.No.	*Parameters	Instrument	Method	Result
	Discipline : Chemical			
	Group : Water			
1.	**General Parameters**			
a.	Iron as Fe, (mg/L)	ICPOES	ITC/CHN/FD/STP/020	0.092
b.	Total Chromium as Cr, (mg/L)	ICPOES	ITC/CHN/FD/STP/020	16.5

'*' represents categories/test parameters not covered under NABL | '**' represents outsource sample | '#' represents Customer Defined Fields

NOTE : BLQ : Below limit of Quantification, LOQ : limit of Quantification

REMARKS : Not Applicable

*****End Of Report*****

M.
Verified by

Authorised by

S. DILLIBABU
Lab Head
Head Technical

Interstellar Testing Centre Pvt. Ltd.

Since 1988
ITC Labs
Assuring Integrity, Trust & Confidence

TEST REPORT

Test Report No. : ICE-2106250373

ORIGINAL
Page 1 of 1

Issued To

Dr. Bhaskar Das
Vellore Institute of Technology
Vellore

Sample Registration No. : E02-2104200288
Sample Name# : Water Sample
Sample Condition : Good
Sample details (if any) :-
Sample Quantity# : 20ml X 1 No
Batch No.# : 1
Sample Submission Type : Courier
Customer Reference# : Test Request Form/20.04.2021
Test Report as per : NA

Received On : 20-04-2021
Commenced On : 25-06-2021
Completed On : 25-06-2021
Date of Report : 25-06-2021

Description	
Description	Colourless liquid

S.No.	*Parameters	Instrument	Method	Result
	Discipline : Chemical			
	Group : Water			
1.	**General Parameters**			
a.	Chromium (as Cr^{6+}),(mg/l)	UV- Spectrophotometer	IS 3025 (Part 52)	31.8

'*' represents categories/test parameters not covered under NABL | '**' represents outsource sample | '#' represents Customer Defined Fields

NOTE : BLQ : Below limit of Quantification, LOQ : limit of Quantification

REMARKS :Not Applicable

*****End Of Report*****

Verified by

Authorised by

S. DILLIBABU
Lab Head
Head Technical

Interstellar Testing Centre Pvt. Ltd.
Plot No. 2,S.No.12/2A, Industrial Estate,
Perungudi, Sholinganallur Taluk, Chennai - 600 096.
Ph : 044 - 24962512
Email : itclabs.chennai@itclabs.com
Website : www.itclabs.com

Ref: -ICP-AES-10
Date: 18/05/2021

Analytical report of the samples submitted by **Dr. Bhaskar Das, Vellore Institute of Technology, Vellore-632014,** using Inductively Coupled Plasma Atomic Emission Spectroscopy.

Sample	Cr	Fe
	ppm	ppm
1-HNO3 ACIDIFIED WATER	30.783	0.193
2-HNO3 ACIDIFIED WATER	19.523	
A	307.851	56317.231
B	1112.234	

ND MEANS LESS THAN 0.01PPM

Note: Content of this report is meant for your information only and should not be quoted as certificate to third party for advertisement, evidence or litigation.

To,
Dr. Bhaskar Das,
Associate Professor,
Vellore Institute of Technology (VIT),
Vellore-632014

——— X ——— X ——— X ———

End of Complete report

27/10/21

Envis Centre, Ministry of Environment & Forest, Govt. of India

Printed Date: Thursday, January 27, 2022

Notification 26th December 2019 - G.S.R. 952(E)

रजिस्ट्री सं० डी० एल०-33004/99 REGD. NO. D. L.-33004/99

सत्यमेव जयते

भारत का राजपत्र
The Gazette of India

असाधारण
EXTRAORDINARY
भाग II—खण्ड 3—उप-खण्ड (i)
PART II—Section 3—Sub-section (i)
प्राधिकार से प्रकाशित
PUBLISHED BY AUTHORITY

सं. 745] नई दिल्ली, बृहस्पतिवार, दिसम्बर 26, 2019/पौष 5, 1941
No. 745] NEW DELHI, THURSDAY, DECEMBER 26, 2019/PAUSHA 5, 1941

पर्यावरण, वन और जलवायु परिवर्तन मंत्रालय

अधिसूचना

नई दिल्ली, 26 दिसम्बर, 2019

सा.का.नि. 952(अ).—कतिपय प्रारूप नियम अर्थात् पर्यावरण (संरक्षण) संशोधन नियम, 2018, पर्यावरण (संरक्षण) नियम, 1986 के नियम 5 के उपनियम (3) की अपेक्षानुसार भारत के राजपत्र, असाधारण, में भारत सरकार के पर्यावरण, वन और जलवायु परिवर्तन मंत्रालय की अधिसूचना संख्यांक सा.का.नि. 1173(अ), तारीख 5 दिसंबर, 2018 द्वारा प्रकाशित किए गए थे, जिसमें उन सभी व्यक्तियों से, जिनके उससे प्रभावित होने की संभावना है, एतद्वारा सूचित किया जाता है कि उक्त प्रारूप अधिसूचना पर उस तारीख से, जिसको इस अधिसूचना को अंतर्विष्ट करने वाले भारत के राजपत्र की प्रतियां जनसाधारण को उपलब्ध करा दी जाती हैं, साठ दिन की अवधि की समाप्ति पर या उसके पश्चात् विचार किया जाएगा;

और उपरोक्त अधिसूचना में अंतर्विष्ट राजपत्र की प्रतियां जन साधारण के लिए 5 दिसंबर, 2018 तक उपलब्ध थी ;

और, केंद्रीय सरकार द्वारा, पणधारियों और सभी व्यक्तियों से आक्षेप और सुझाव प्राप्त कर उपरोक्त अधिसूचना की प्रतिक्रया पर सम्यक् रूप से विचार किया गया;

अत:, अब, केंद्रीय सरकार पर्यावरण (संरक्षण) नियम, 1986 के नियम 5 के उपनियम (3) सपठित पर्यावरण (संरक्षण) अधिनियम, 1986 (1986 का 29) की धारा 6 और धारा 25 द्वारा प्रदत्त शक्तियों का प्रयोग करते हुए, पर्यावरण (संरक्षण) नियम, 1986 में निम्नलिखित और संशोधन करती है, अर्थात्:—

1. संक्षिप्त नाम और प्रारंभ—(1) इन नियमों का संक्षिप्त नाम पर्यावरण (संरक्षण) दूसरा संशोधन नियम, 2019 है।

(2) ये राजपत्र में उनके प्रकाशन की तारीख से प्रवत्त होंगे।

2. पर्यावरण (संरक्षण) नियम, 1986 की अनुसूची-I में, क्रम संख्यांक 113 और उससे संबंधित प्रविष्टियों के पश्चात्

निम्नलिखित अंत:स्थापित किया जाएगा, अर्थात्:—

क्रम सं.	उद्योग	मानदंड	मानक
(1)	(2)	(3)	(4)
“114	आटोमोबाइल सेवा स्टेशन, बस डिपो या कर्मशाला	(सांद्रता निर्धारण से अधिक नहीं होगी, पीएच के लिए सांद्रता को छोड़कर मि.ग्रा./ली में)	
		अंतर्देशीय सतही जल/सिंचाई के लिए भूमि/सार्वजनिक सीवर	
		पीएच	6.5-8.5
		कुल निलंबित ठोस	50
		केमिकल आक्सीजन डिमांड	150
		तेल और ग्रीस	10”

टिप्पण :

(i) सर्विस स्टेशन, बस डिपो और धातु पूर्व-शोधन सुविधाओं से युक्त कर्मशालाओं के लिए, घुले हुए फॉस्फेट (पी के रूप में) 5 मि.ग्रा./ली और जस्ते की 5 मि.ग्रा./ली. की सीमा भी लागू होगी ।

(ii) ठोस अपशिष्ट/परिसंकटमय अपशिष्ट, यदि कोई हो, को ठोस प्रबंध नियम, 2016 और परिसंकटमय और अन्य अपशिष्ट (प्रबंधन और सीमापार संचलन) नियम, 2016 के अनुसार निपटान किया जाएगा ।”।

[फा. सं. क्यू-15017/6/2010-सीपीडब्ल्यू]

जिगमेत टक्पा, संयुक्त सचिव

टिप्पण: मूल नियम भारत के राजपत्र, असाधारण, भाग II, खंड 3, उपखंड (i) का.आ. संख्यांक 844(अ), तारीख 19 नवंबर, 1986 द्वारा और अंतिम संशोधन अधिसूचना संख्यांक सा.का.नि. 5(अ), तारीख 3 जनवरी, 2019 द्वारा किया गया था ।

MINISTRY OF ENVIRONMENT, FOREST AND CLIMATE CHANGE

NOTIFICATION

New Delhi, the 26th December, 2019

G.S.R. 952(E).—Whereas, certain draft rules, namely the Environment (Protection) Amendment Rules, 2018 were published in the Gazette of India, Extraordinary, as required under sub-rule (3) of rule 5 of the Environment (Protection) Rules,1986, vide notification of the Government of India in the Ministry of Environment, Forest and Climate Change, number G.S.R 1173 (E), dated 5th December, 2018 inviting objections and suggestions from all persons likely to be affected thereby within a period of sixty days from the dated on which copies of the Gazette containing the said notification were made available to the public;

And Whereas, copies of the Gazette containing the aforesaid notification were made available to the public on the 5th December, 2018;

And Whereas, objections and suggestions received from all persons and stakeholders in response to the aforesaid notification have been duly considered by the Central Government;

Now, therefore, in exercise of the powers conferred by sections 6 and 25 of the Environment (Protection) Act, 1986 (29 of 1986) read with sub-rule (3) of rule 5 of the Environment (Protection) Rules, 1986, the Central Government hereby makes the following rules further to amend the Environment (Protection) Rules, 1986, namely:-

1. **Short title and commencement.**-(1) These rules may be called the Environment (Protection) Second Amendment Rules, 2019.

(2) They shall come into force on the date of their publication in the Official Gazette.

2. In the Environment (Protection) Rules, 1986, in Schedule-I, after serial number 113 and the entries relating thereto, the following shall be inserted, namely:-

S. No.	Industry	Parameter	Standard
(1)	(2)	(3)	(4)
“114	Automobile Service Station, Bus Depot or Workshop	**Effluent Standard** (Concentration not to exceed, in mg/l except for pH)	
		Inland Surface water/land for irrigation/Public Sewer	
		pH	6.5-8.5
		Total Suspended Solids	50
		Chemical Oxygen	150

		Demand	
		Oil and Grease	10”

Note :

(i) For Service Stations, Bus Depots and Workshops with metal pre-treatment facilities, limit of 5 mg/l of dissolved phosphates (as P) and 5 mg/l of zinc shall also apply.

(ii) Solid Wastes/ Hazardous Waste, if any, shall be disposed off as per the Solid Waste Management Rules 2016 and the Hazardous and Other Waste (Management and Trans-boundary Movement) Rules, 2016.”.

[F. No. Q-15017/6/2010-CPW]

JIGMET TAKPA, Jt. Secy.

Note: The principle rules were published in the Gazette of India, Extraordinary, Part II, Section 3, Sub-section (i) vide number S.O.844 (E), dated the 19th November, 1986 and last amended vide notification number G.S.R. 5 (E), dated the 3rd January 2019.

Notification 26th December 2019 - G.S.R. 952(E)

BEFORE THE NATIONAL
GREEN TRIBUNAL SOUTH ZONE

O.A 131 OF 2020

M.Jayachandran and Anr
....Applicants

Vs

MoEFCC and Ors

.. Respondents

Typed set of papers

Counsel for Respondent No.8

M/s. Tanushree Arvind
Madhupreetha Elango