

**BEFORE THE HON'BLE NATIONAL GREEN TRIBUNAL,  
SOUTHERN ZONE, CHENNAI**

**APPEAL No. 68 of 2021**

**BETWEEN**

1. M/s Sri Mahalakshmi Hatcheries  
Represented by its Proprietor  
Mr.D.Sagar Reddy

2. Mr. Pernati Shyam Prasad Reddy  
S/o Pernati ChenchuramaReddy

... Appellants

**VS**

State Environment Impact Assessment Authority (SEIAA)  
Represented by its Chairman & 2 others

... Respondents

**ADDITIONAL AFFADIVT & DOCUMENTS FILED BY THE APPELLANTS**

**Date:** 09.10.2023

**M/S. K.M. MRITHUNJAYAN**

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**COUNSEL FOR THE APPELLANT**

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It is certified that, all the documents specified in the above annexures are true copies.

**Date:** 09.10.2023

  
**COUNSEL FOR APPELLANTS**

1

**BEFORE THE HON'BLE NATIONAL GREEN TRIBUNAL,  
SOUTHERN ZONE, CHENNAI**

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**BETWEEN**

1. M/s Sri Mahalakshmi Hatcheries  
Represented by its Proprietor  
Mr.D.Sagar Reddy  
S/o D.Venkata Ramana Reddy  
Office at Srinivasa Satram, Kothapatnam Village,  
Kota Mandal, Sidavaram Post,  
Nellore – 524 411,  
Email: [sagar.duvvuru@gmail.com](mailto:sagar.duvvuru@gmail.com), Phone: +91 8978374567
2. Mr. Pernati Shyam Prasad Reddy  
S/o Pernati ChenchuramaReddy  
Residing at Allampadu Village, Molaganuru post,  
Kota Mandal, SPSR Nellore District  
Andhra Pradesh – 524 411  
Email: [syampernati@gmail.com](mailto:syampernati@gmail.com) ,Phone: -91 9440275554

... Appellants

**AND**

1. State Environment Impact Assessment Authority (SEIAA)  
Represented by its Chairman  
No. 33-26-14 D/2, Near Sunrise Hospital,  
Pushpa Hotel Centre, Chalamalavari Street,  
Kasturibaipet, Vijayawada – 520 010  
Email: [chairman@appcb.gov.in](mailto:chairman@appcb.gov.in) , Phone: 0866-2463200
2. Andhra Pradesh Pollution Control Board  
Represented by its Member Secretary  
No. 33-26-14 D/2, Near Sunrise Hospital,  
Pushpa Hotel Centre, Chalamalavari Street,  
Kasturibaipet, Vijayawada – 520 010  
Email: [membersecy@appcb.gov.in](mailto:membersecy@appcb.gov.in), Phone: 0866-2463200
3. M/s Divis Laboratories Limited  
Represented by its Managing Director  
303, DIVIs towers, Cyber Hills,  
Gachibowli, Hyderabad – 500 032.  
Email – [mail@divislaboratories.com](mailto:mail@divislaboratories.com), Phone: +91 40 23786300

... Respondents

**ADDITIONAL AFFIDAVIT FILED BY THE APPELLANTS**

We, (1) Mr.D.Sagar Reddy S/o D.Venkata Ramana Reddy, the proprietor for M/s Sri Mahalakshmi Hatcheries having office at Srinivasa Satram, Kothapatnam, Kota Mandal, SPSR Nellore – 524 411 & (2) Mr. Pernati Shyam Prasad Reddy, S/o Pernati Chenchurama Reddy , residing at Allampadu Village, Molaganuru post, Kota Mandal, SPSR Nellore District Andhra Pradesh – 524 411 both having

For SRI MAHALAKSHMI HATCHERIES



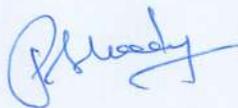
  
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temporarily come down to Chennai, do hereby solemnly affirm and sincerely state as follows:

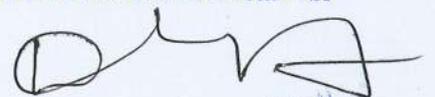
1. We humbly submit that, we are appellants in the present appeal and as such we are well acquainted with the facts and competent to swear this present affidavit.
2. We submit that, the present appeal is preferred against the order of the 1<sup>st</sup> Respondent granting Environmental clearance to the 3<sup>rd</sup> Respondent unit vide Order No. SEIAA/AP/VSP/IND/07/2020/1971/157.09/153.11-318 dated 28.06.2021.
3. We submit that, the present affidavit is filed pursuant to the orders of this Hon'ble Tribunal on 14.08.2023 whereby this Hon'ble Tribunal has directed us to furnish studies/ incidents on shrimp culture getting damaged due to marine discharge. The copy of the same is annexed herein as **ANNEXURE-1**.
4. In pursuance with the directions of this Hon'ble Tribunal, the appellant herein seeks to set out its submissions in this regard as below:

#### **WATER PARAMETERS FOR SHRIMP CULTURE**

5. It is submitted that a Hatchery is an indoor facility where Marine organisms viz. Fish, Crustaceans, Molluscs, Seaweed and other marine life forms are bred for Natural stock enhancement of the seas or for Aquaculture. Hatchery is completely an indoor unit comprising of source water treatment systems including various stages of filtration and UV treatment for purifying the source water to the highest level, water storage reservoirs, and production tanks made of concrete in which the matured adult shrimps are made to produce eggs under the controlled condition. These eggs are made to hatch out and reared in the larval and post larval tanks using sea water of oceanic quality to enable them to metamorphose through different stages of its life cycle.
6. A Hatchery requires pristine seawater of oceanic quality for the broodstock holding, maturation, larval and Juvenile rearing of all marine organisms. Hence, a Hatchery is essentially a Seafront activity requiring access to oceanic quality Seawater. Considering the indispensability for the requirement of oceanic quality Seawater and seafront access for a Hatchery, the CRZ regulations from the day came into existence in 1991 to this day, have consistently treated the Hatchery activity as a permitted activity in CRZ and



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excluded or exempted it from the prohibitions imposed by the CRZ Notification.

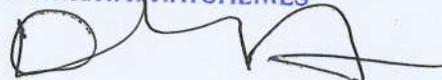
7. The Coastal Aquaculture and Hatcheries have been brought under the exclusive jurisdiction of Coastal Aquaculture Authority through the CAA Rules, Guidelines and regulations issued under the Coastal Aquaculture Authority Act 2005. As per the guidelines issued under Rule 3 of the Coastal Aquaculture rules, the Coastal Aquaculture Authority fixes the water quality parameters for hatcheries and shrimp farming units.
8. As per the guidelines in force as on date, the water quality parameters like pH, salinity, dissolved oxygen (DO) and the presence of toxicants/ pollutants should be ascertained. Low pH water will pose serious problems and similarly wide fluctuation in salinity will also be detrimental to the cultured species. The water source should be free from any industrial/ agricultural pollution. The presence of contaminants and their levels should be considered in the light of the tolerance and also sub-lethal effects on the species to be cultured.
9. The optimal levels including specified by the Coastal Aquaculture authority better survival and growth of shrimps are as follows

S.NO.	WATER QUALITY PARAMETERS	OPTIMAL LEVEL
1.0	Temperature (°C)	28 - 33
2.0	Transparency (cm)	25 - 45
3.0	pH	7.5 - 8.5
4.0	Dissolved oxygen (ppm)	5 - 7 (above 50% air saturation)
5.0	Salinity (ppt)	15 - 25
6.0	Total alkalinity (ppm)	200
7.0	Dissolved inorganic phosphate (ppm)	0.1 - 0.2
8.0	Nitrate - N (ppm)	< 0.03
9.0	Nitrite - N (ppm)	< 0.01
10.0	<b>Ammonia - N (ppm)</b>	<b>&lt; 0.01</b>
11.0	<b>Cadmium (ppm)</b>	<b>&lt; 0.01</b>
12.0	<b>Chromium (ppm)</b>	<b>&lt; 0.1</b>
13.0	<b>Copper (ppm)</b>	<b>&lt; 0.025</b>
14.0	<b>Lead (ppm)</b>	<b>&lt; 0.1</b>
15.0	<b>Mercury (ppm)</b>	<b>&lt; 0.0001</b>
16.0	<b>Zinc (ppm)</b>	<b>&lt; 0.1</b>

10. Moreover, the coastal aqua culture authority in its report dated 28.08.2021 in **O.A No.126/2020** (Sri Mahalakshmi Hatchery vs Union of India & 7 ors) annexed herewith as **ANNEXURE - 2**, categorically states as follows:

**Para 10.** "It is submitted that the quality of water available in the site has strong influence on the success of the coastal aquaculture farm Wide fluctuation

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in pH and salinity will be detrimental to the cultured species. The water source should be free from any industrial pollution. The optimal levels of various water quality parameters for survival and growth of shrimps.”

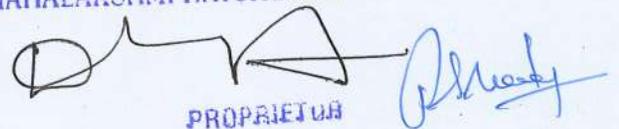
#### WATER PARAMETERS OF 3<sup>rd</sup> RESPONDENT (PROPOSED):

11. On the contrary, the marine discharge standards prescribed by the 2<sup>nd</sup> Respondent and proposed to achieved in its discharge by the 3<sup>rd</sup> Respondent (Project Proponent) is as stated hereunder:

#### COASTAL DISCHARGE STANDARDS:

PARAMETER	STANDARD
Suspended solids mg/l, Max.	100 mg/l
Particulate size of suspended solids	(a) Floatable solids, max. 3mm.
	(b) Settle able solids, max. 850 microns.
pH Value	5.5 to 9.0
Temperature	Shall not exceed 5°C above the receiving water temperature
Oil and grease	20 mg/l
Total residual chlorine	1.0 mg/l
Ammonical nitrogen (as N), mg/l Max.	50 mg/l
Total Kjeldahl Nitrogen(asNH <sub>3</sub> )	100 mg/l
Free ammonia(asNH <sub>3</sub> )	5.0 mg/l
Bio chemical Oxygen demand [3 days at 27°C]	100 mg/l
Chemical Oxygen Demand	250 mg/l
Arsenic (as As)	0.2 mg/l
Mercury (as Hg)	0.01 mg/l
Lead(as Pb)mg/l	2.0 mg/l
Cadmium (as Cd) mg/l	2.0 mg/l
Hexavalent Chromium (as Cr +6)	1.0 mg/l
Total chromium (as Cr.)	2.0 mg/l
Copper(as Cu)	3.0 mg/l
Zinc (As Zn.)	15 mg/l
Selenium (as Se.)	0.05 mg/l
Nickel (as Ni)	5.0 mg/l
Cyanide(as CN)	0.2 mg/l
Fluoride (as F)	15 mg/l
Sulphide (as S)mg/l Max.	5.0 mg/l
Phenoile compounds (as C <sub>6</sub> H <sub>5</sub> OH)mg/l, Max.	5.0 mg/l

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<b>Radioactive materials:</b>	
(a)Alphaemittermicro curie/ml.	10 <sup>-7</sup>
(b)Betaemittermicro curie/ml.	10 <sup>-6</sup>
Bio-assay test	90% survival of Fish after 96 hours in 100% effluent
Manganese (as Mn)	2mg/l
Iron(as Fe)	3mg/l
Vanadium (as V)	0.2mg/l
Nitrate Nitrogen	20 mg/l

### SCENARIO - I (DISCHARGE IN STRICT COMPLIANCE)

11. On analysing the comparison of the aforementioned Water parameters prescribed for Shrimp Hatcheries by the Coastal Aquaculture Authority and the 2<sup>nd</sup> Respondent (APPCB) in its report before this Hon'ble Tribunal dated 11.11.2022, the queries of this Hon'ble Tribunal can be answered evidently:

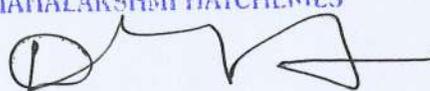
<b>CAA GUIDELINES</b>	
<b>WATER QUALITY PARAMETERS</b>	<b>OPTIMAL LEVEL (in PPM)</b>
Ammonia - N (ppm)	< 0.01
Cadmium (ppm)	< 0.01
Chromium (ppm)	< 0.1
Copper (ppm)	< 0.025
Lead (ppm)	< 0.1
Mercury (ppm)	< 0.0001
Zinc (ppm)	< 0.1

<b>PROPOSED DISCHARGE STANDARDS OF 3<sup>rd</sup> Respondent</b>	
<b>WATER QUALITY PARAMETERS</b>	<b>STANDARDS (in PPM)</b>
Free ammonia (asNH <sub>3</sub> )	5.0 ppm
Cadmium (as Cd)	2.0 ppm
Total chromium (as Cr.)	2.0 ppm
Copper(as Cu)	3.0 ppm
Lead (as Pb)	2.0 ppm
Mercury(as Hg)	0.01 ppm
Zinc (As Zn.)	15 ppm

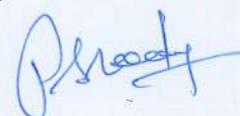
It can be evidently seen that from the above that, the coastal discharge standards prescribed for the marine outfall of the 3<sup>rd</sup> Respondent unit contains alarming levels of Ammonia, Cadmium, Copper, Lead, Mercury, Copper, Zinc etc., which directly affects the shrimp farm and not fit for shrimp culture/farming.

12. Also in addition to the above, it is pertinent to state that, the coastal discharge prescribed for the 3<sup>rd</sup> Respondent contains also includes other heavy metals, radioactive materials and other metabolites which are harmful for marine environment. The list of the same are stated hereunder

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Suspended solids mg/l, Max.	<b>Radioactive materials:</b>  <b>(a)Alphaemitter micro curie/ml.</b>  <b>(b)Betaemitter micro curie/ml.</b>  Manganese (as Mn) Iron(as Fe) Vanadium (as V) Nitrate Nitrogen Sulphide (as S)mg/l Max. Phenoile compounds (as C6H5OH)mg/l, Max.
Particulate size of suspended solids	
Oil and grease	
Total residual chlorine	
Bio chemical Oxygen demand	
Chemical Oxygen Demand	
Arsenic (as As)	
Selenium (as Se.)	
Nickel (as Ni)	
Cyanide(as CN)	
Fluoride (as F)	

13. Even assuming that, each and every discharge is in strict compliance with the above mentioned standards laid down by the 2<sup>nd</sup> Respondent, the water parameters per discharge are still in gross contrast and incompatible to the parameters/guidelines laid by the Coastal Aquaculture Authority for the shrimp hatcheries. Therefore, analysing **Scenario -1** to the present circumstances, evidently show that the coastal discharge standards for the marine outfall of the 3<sup>rd</sup> Respondent unit is in itself detrimental and harmful to the farming operations of the hatchery unit *per se*.

#### **SCENARIO - II (DISCHARGE IN ACTUAL)**

14. We once again reiterate the fact that, the 3<sup>rd</sup> Respondent has 2 functional units in Andhra Pradesh which adopts the following discharge mechanism

- Hyderabad (1<sup>st</sup> Unit) – Zero Liquid discharge
- Vishakapatnam (2<sup>nd</sup> Unit) – Coastal Discharge

15. It has been the stand of the 3<sup>rd</sup> Respondent that, they have been discharging only *NaCl* treated effluents in the streams. However, upon inferring the additional affidavit along with the typed set of papers filed by the 3<sup>rd</sup> Respondent before this Hon'ble Tribunal on 12.11.2022. The 3<sup>rd</sup> Respondent has furnished a "**monthly monitoring of Eco-toxicity of treated effluents June 2022**" sponsored by **Divis Laboratory Ltd, Vishakapatnam** from the CSIR - National Institute of Oceanography (NIO) which is once again annexed herewith as **ANNEXURE - 3** for the convenience of this Hon'ble Tribunal. Even as the study is sponsored by the 3<sup>rd</sup> Respondent's Vishakhapatnam unit, the extract of the trace elements concentrations in the treated effluents is given below for comparison with the standards prescribed by the CAA.

For SRI MAHALAKSHMI HATCHERIES



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TABLE No.1

CAA GUIDELINES	
WATER QUALITY PARAMETERS	OPTIMAL LEVEL (in PPM)
Ammonia - N (ppm)	< 0.01
Cadmium (ppm)	< 0.01
Chromium (ppm)	< 0.1
Copper (ppm)	< 0.025
Lead (ppm)	< 0.1
Mercury (ppm)	< 0.0001
Zinc (ppm)	< 0.1

TABLE No.2

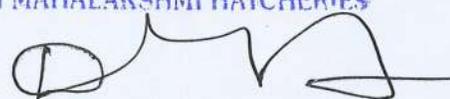
ACTUAL DISCHARGE STANDARDS OF DIVIS LAB	
ELEMENT	EFFLUENT CONCENTRATION (ppm)
Vanadium(V)	9.0
Chromium (Cr)	5.5
Manganese (Mn)	570.0
Iron (Fe)	80.7
Cobalt (Co)	4.1
Nickel (Ni)	22.9
Copper (Cu)	28.0
Zinc (Zn)	200.7
Arsenic (As)	1.6
Selenium (Se)	14.0
Cadmium (Cd)	1.0
Lead (Pb)	6.2

The aforesaid **Table No.2** depicts the actual trace elements concentration of the effluents discharged per **10L** from the 3<sup>rd</sup> Respondent in the month of June, 2022 which is submitted in their additional affidavit dated 12.11.2022. Therefore, it is visibly seen from the above that, the effluent discharge by the 3<sup>rd</sup> Respondent's unit in Vishakapatnam holds higher concentration levels of Lead, Chromium, Zinc, Copper alongside other non-compatible trace elements like Magnesium, Arsenic, Nickel, Selenium & cobalt in its treated effluent discharge.

16. Further with respect to the aforesaid report relied upon by the 3<sup>rd</sup> Respondent, there are three justifiable grounds on the impartiality of the report *per se*. *Firstly*, the report in itself sponsored by the Project Proponent. *Secondly*, the samples of the effluents were collected only from one guard pond i.e. Guard Pond No.9 which might not even be the guard pond for process residual discharge. *Thirdly*, the species used for bio-assay test was Zebra fish while Brine shrimp/Whiteleg shrimp was deliberately neglected while this issue was pending before this Hon'ble Tribunal.

17. Also an analytical experiment was executed to present detailed reports on the concentration of heavy metals (nickel, iron, zinc, manganese, chromium, lead, and cadmium) in farmed shrimp, ***Penaeus monodon*** and its concomitant human health risks upon consumption. A total of 147 farms from six sub-districts of Khulna, Bangladesh on the coast of Bay of Bengal were selected for sample collection and concentration of heavy metals were

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determined. The study revealed that the average concentrations of Fe, Mn, and Cr (in Rupsa and Paikgacha) in shrimps from Khulna were considerably higher than the maximum recommended limits. The copy of the study is annexed herewith as **ANNEXURE -4**.

#### **HUMAN RISK FACTOR**

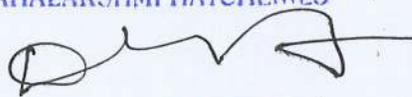
18. More so, the study also quoted that in aquatic ecosystems, food chain is considered as the main pathway of heavy metals accumulation and metals can create human health hazards upon consumption of these contaminated aquatic foods. Although a number of metals are essential for living organisms, some are highly toxic or become toxic at high concentration. Metals such as lead (Pb), tin (Sn), nickel (Ni), cadmium (Cd), and chromium (Cr) are not generally required for metabolic activities. Moreover, trace amount of these heavy metals can cause toxicities to animals. Besides their carcinogenic effects, heavy metals can cause serious problems, such as liver disorders, cardiovascular anomalies, kidney failure and death in case of extreme situation.
19. Therefore, it is pertinent to mention that, the actual treated discharge by the 3<sup>rd</sup> Respondent's unit in Vishakapatnam hereby analysed as **SCENARIO-II** still stands incompatible and detrimental to the guidelines issued by the Coastal Aquaculture Authority for shrimp farming. Further, even assuming that, the discharge of the 3<sup>rd</sup> Respondent's unit contains only NaCl, the fluctuations in salinity could make the shrimp more prone to diseases and reduce its success rate thereof. The extract of the guidelines stipulated in **Clause 6.3 "Water quality and its management"** is provided herewith for the convenience of this Tribunal

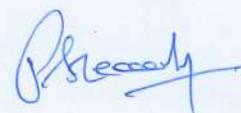
*"Use of freshwater to reduce the salinity of the culture water should be avoided for sustainability reasons; even though the shrimps can adapt and grow in a wide range of salinity, it is better to avoid salinity fluxes so as to avoid stress to the shrimps, which could make them more prone to diseases".*

#### **SCENARIO - III (DISCHARGE IN VIOLATION)**

20. It is an undeniable fact that, the 3<sup>rd</sup> Respondent's functional unit has a long standing chronicle of violating the discharge standards and also illegally discharging effluents into the sea. In order to highlight upon the incidents of violations committed by the 3<sup>rd</sup> Respondent a brief note on the date and

for **SRI MAHALAKSHMI HATCHERIES**

  
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incident is stated hereunder for the convenience of this Hon'ble Tribunal.

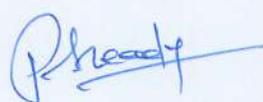
- a. **12<sup>th</sup> July 2012-** The APPCB through its Board Task Force committee had reviewed various Bulk Drug Industry and ordered closure of 12 Pharma Companies out of which Divis Lab, Vishakapatnam was also one amongst it. The copy of the same published in Financial Express, Delhi on 14.07.2012 currently available in Press Information Bureau is annexed herewith as **ANNEXURE -5.**
- b. **17.03.2020-** Based on several complaints by locals and observations by experts that Divi's Laboratories Limited at Choutuppal was allegedly causing groundwater pollution, the Telangana State Pollution Control Board (TSPCB) has directed the District Collector of Yadadri-Bhuvanagiri to constitute a multi-disciplinary committee to study the situation.
- c. **10.06.2020** - Application filed before this Hon'ble Tribunal regarding the pollution caused by the 3<sup>rd</sup> Respondent and other Pharmaceutical Companies situated in Yadadri, Bhuvanagiri District, State of Telengana. According to the applicant, these Pharmaceutical companies are not complying with the pollution laws. They are not properly maintaining the Effluent Treatment Systems and also pollution control mechanism which they are expected to maintain as per the directions of the Pollution Control Board
- d. **11.07.2020** - The 3<sup>rd</sup> Respondent unit at Vishakhapatnam had illegally discharged 850095 KL of effluent into the sea without the knowledge of the board between Sep 2019-2020 by annexing a parallel pipeline to the designated marine outfall. Report of the Joint chief environmental Engineer, APPCB dated 11.07.2020 is already annexed in additional typed set of papers filed by the Appellants between Pg Nos. 130-136.

21. It is humbly submitted that, the above incidents are some of the many which are known to us, the 3<sup>rd</sup> Respondent unit has committed gross breach of effluent discharge standards and illegally discharged effluents in violation to the norms. Drawing reference to one such incidents of violation which was reported by Joint chief environmental Engineer, APPCB dated 11.07.2020,

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the extract of the findings given by the Joint Chief Engineer is as follows:

*“VII- The LTDS treated effluent discharge mentioned in the above table had taken place under the supervision of Board officials. But the NaCl effluent & NaCl equipment washings quantity of 80095 KL was discharged into the sea illegally in violation of consent conditions without the knowledge of the Board. It is further submitted that the Board officials collected flow meter readings of different streams viz., NaCl, LTDS, Non Process and RO Rejects during the period from December 2019 to May”*

*“ VIII - The industry was directed to immediately remove the illegal pipeline and collect the so-called NaCl effluents in the guard ponds. It was observed during inspection on 24.06.2020 that the industry removed the pipeline. The representative of the industry informed that the NaCl effluents after neutralization were stored in the guard pond no. 6 and requested for permission to discharge into the sea. The samples from the guard pond no. 6 were collected on 24.06.2020 and 25.06.2020 and analysed”*

22. In pursuance with the above incident where the unit has discharge 80,095 KL of effluents, the parameters of the illegally discharged effluents cannot be traced and ascertained. In addition to the above, the discharged effluents cannot at all times adhere to the standards in strict sense, hence such violations are caused by the project proponents. On event of such violations if any caused by the 3<sup>rd</sup> Respondent unit, the Appellants herein cannot sustain their industry and the same might have drastic impact on the marine ecosystem as a whole.

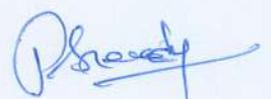
### **ZERO LIQUID DISCHARGE**

23. Further, in order to allay the fears of violations and fluctuating discharge standards of treated effluents, the Appellants herein have put forth a solution to adopt **Zero Liquid Discharge** mechanism for their proposed unit. However, the 3<sup>rd</sup> Respondent herein have raised few concerns pertaining to the adoption of ZLD mechanism for discharge of effluents. Zero liquid discharge (ZLD) is an ambitious wastewater management strategy that eliminates any liquid waste leaving the plant or facility boundary, with the majority of water being recovered for reuse. ZLD obviates the risk of pollution associated with wastewater discharge and maximizes water usage efficiency, thereby striking a balance between exploitation of freshwater resources and

For SRI MAHALAKSHMI HATCHERIES



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preservation of aquatic environments

24. Some of the notable concerns raised by the 3<sup>rd</sup> Respondent unit for adoption of ZLD are

- High Carbon Foot Print of ZLD Facility
- Additional Power and Fuel requirement

In response to the above concerns, it is noteworthy to point out that on issues concerning

a) **High Carbon Foot Print** - Studies have recommended that, Membrane Distillation is beneficial due to its ability to treat high salinity feed waters that cannot be desalinated by RO, and MD's potential to leverage low-grade thermal energy. When low-grade energy is available, MD achieves both cost saving and a reduced carbon footprint relative to electricity-driven desalination technologies. The copy of the same is annexed herewith as **ANNEXURE-6.**

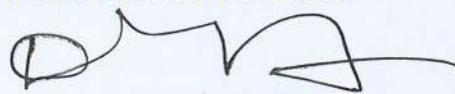
b) **Additional Power and Fuel requirement** - The sustainability of ZLD desalination systems can be further increased by using solar energy to fulfill their energy requirement. The copy of the review of such study along with economic options is annexed herewith as **ANNEXURE-7.**

25. It is humbly submitted that, on comparison of the ZLD trends all over the world, the

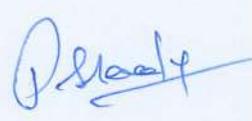
a. **United States:** The birth of ZLD dates back to the 1970s when the increased salinity of the Colorado River led to a regulatory mandate of ZLD for nearby power plants. The U.S. EPA recently completed its guidelines revising the existing regulations on wastewater discharge from thermal power plants. This new rule, which sets the first federal limits on the level of toxic metals and other harmful pollutants in waste water discharged from power plants, considers zero discharge as the preferred option for pollutants in fly ash transport water, bottom ash transport water, and wastewater from flue gas mercury control systems.

b. **China:** China generates another promising niche for ZLD application. The coal-to-chemicals industry, utilizing coal rather than oil or natural gas to produce raw materials for chemical

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production, is currently under pressure to reduce dependence on imported energy. As a consequence, ZLD is mandatory at coal-to-chemicals plants in those areas to preserve both local water resources and ecosystems. Several ZLD facilities are already installed or in the stage of design/construction at Chinese coal-to-chemicals plants, with a wide range of feed water salinities (2,000–16,000 mg/L of total dissolved salts, TDS) and treatment capacity (110–2300 m<sup>3</sup>/hour).

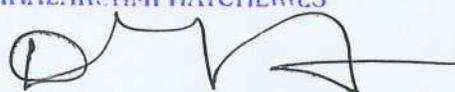
- c. **India:** India. Facing a situation similar to that in China, India is taking aggressive actions to curb severe water pollution, even in the holy river Ganga. The recent three-year target set by the Indian government, known as the “Clean Ganga” project, imposes stricter regulations on wastewater discharge and moves high-polluting industries toward ZLD. In 2015, the government issued a draft policy that requires all textile plants generating more than 25 m<sup>3</sup> of wastewater effluent per day to install ZLD facilities.

26. It is vital to note that, the United Nations (UN) has set out 17 Sustainable Development Goals (SDGs) that are a “blueprint to achieve a better and more sustainable future for all” and are intended to be achieved by 2030. Some of these goals are linked to the ‘3Rs’ principle i.e. Reduce, Reuse, and Recycle. Reduce waste generation, reuse the usable products or components, and recycle the waste for further use.

27. Zero Liquid Discharge (ZLD) is a pioneering technology designed on this principle and is used to recycle the entire wastewater from a process. The focus of ZLD is to produce clean water suitable for reuse, thereby saving money and benefitting the environment. ZLD Business (Evaporator) in India has grown exponentially in the recent past. Multiple factors are driving the adoption of this technology in India, such as:

- a. *Policy mandate for ZLD adoption in India:* Tamil Nadu is the first state in India to mandate ZLD in the textiles sector in 2008.
- b. *Stringent actions from Pollution Control Boards (PCBs):* In 2013, Andhra Pradesh Pollution Control Board (APCB) issued notices to Dr. Reddy Labs and other bulk drug manufacturing companies in the Hussain Sagar area to stop polluting the groundwater resources and achieve Zero Liquid Discharge.

MAHALAKSHMI HATCHERIES



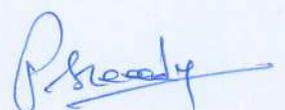
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- c. *Sector focus approach by Central Pollution Control Board (CPCB):* In 2015, ZLD guidelines were introduced for four industrial sectors in India – textile (wet processing), tanneries, distilleries, and pulp & paper.
- d. *Entry of several Indian and global companies into the Indian ZLD business:* Several Indian EPC companies, including Thermax, VA Tech Wabag, Triveni Engineering, and international companies like GEA, Suez, etc., have installed ZLD plants to tap the growing demand for ZLD compliance in India.
- e. Tamil Nadu Government and Central Government Scheme for a subsidy of Rs. 320 crore (interest free loan) to set up ZLDs in the state following the court order of 2006.
- f. Punjab Pollution Control Board mandated ZLD in 8 large electroplating industries in Ludhiana (2010).
- g. Punjab Pollution Control Board assisted 500+ small electroplating units in Ludhiana to set up a CETP with ZLD. (2010)
- h. Rajasthan Government declared a Capital Subsidy on ZLD based ETP equal to 20% of amount paid to the trader for the treatment plant excluding civil works, subjected to a maximum of Rs. 1.0 Crore (2014).
28. Also study a was conducted in a medium scale API (Active Pharmaceutical Ingredients) manufacturing industry where wastewater recycling through ZLD plant was analysed. The investigation shown that the plant was generated high quality water which was suitable to recycle in plant premises and which resulted in reduction of water consumption to 40KLD (Kilo Liter per Day). The copy of the study is annexed herewith as **ANNEXURE – 8**.
29. In fact, a sector wise survey of ZLD compatibility was analysed for all industries was conducted in an independent survey and the study concluded that, ZLD in Pharmaceutical sector was *achievable*. The extract of the study is as stated hereunder. The copy of the study is annexed herewith as **ANNEXURE – 9**.

For SRI MAHALAKSHMI HATCHERIES

  
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## Sector-wise treatment options for industries

PHARMACEUTICALS	<p><b>High COD, Low TDS Effluent treatment system</b>          Primary treatment+ Secondary treatment + tertiary chemical treatment to reduce TDS (Pressure sand filter, Activated Carbon filter and filter press for dewatering of sludge). RO system (permeate is utilized as cooling tower makeup water) + Multi effect evaporator/incinerators.</p> <p><b>High COD, High TDS Effluent treatment system</b>          Primary treatment + stripper to remove VOC + 3 stages Multi Effect Evaporator (forced circulation) Agitator Thin Film Drier (ATFD)+(MEE condensate is being taken along with Low TDS effluent for further treatment)+ MEE/incineration.</p>	ZLD ACHEIVABLE
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Therefore, the benefits of ZLD (Zero Liquid Discharge System) outweighs its challenges in implementation.

**OBJECTIONS TO ENVIRONMENTAL CLEARANCE**

30. We humbly submit that, this Hon'ble Tribunal had directed the 1<sup>st</sup> and the 2<sup>nd</sup> Respondent to furnish minutes of the meetings of SEIAA/SEAC for non-consideration of the objections given by the following authorities

- a. **MPEDA (Marine Products Export Development Authority)** vide Report dated 28.02.2020.
- b. **Joint Committee** comprised of the following officials vide report dated 07.03.2020
  - i. Joint Director, Fisheries, Nellore
  - ii. Dy. Director, District Industries Center, Nellore
  - iii. Dy. Inspector of Factories, Nellore
  - iv. Environmental Engineer, APPCB
  - v. Regional Officer, Nellore &
  - vi. Tahsildar, Kota Mandal.
- c. **Regional Officer, APPCB** vide verification report dated 29.09.2020
- d. **Coastal Aquaculture Authority** vide letter dated 20.11.2020
- e. **Commissioner of Fisheries, Andhra Pradesh** vide Letter dated 03.02.2021.

Upon careful examinations, the meeting submitted by the 1 & 2<sup>nd</sup> Respondent is silent on the above aspects and there is no discussion or agenda on the same.

for SRI MAHALAKSHMI HATCHERIES

  
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31. It is in fact vital to point out that, the 1<sup>st</sup> Appellant had preferred an Original Application vide **O.A No.126/2021** before this Hon'ble Tribunal seeking the following prayers

- a. Direct the respondents 1 to 6 to revoke/cancel all licenses/permissions granted to the 7<sup>th</sup> Respondent (now 3<sup>rd</sup> Respondent) to the unit at Survey Nos. 397 ,401 ,402, 403, 446, 676, 681, 682, 683, 700-709 , Kothapatnam (V), Kota (M) SPSR Nellore
- b. Pass an order of permanent injunction against the 7<sup>th</sup> Respondent (now 3<sup>rd</sup> Respondent) and also other third parties from carrying out any polluting activity detrimental to the environment and the hatcheries present surrounding the Krishnapatnam Industrial Area in Survey Nos. 397 ,401 ,402, 403, 446, 676, 681, 682, 683, 700-709 , Kothapatnam (V), Kota (M) SPSR Nellore.
- c. Pass an order directing the 7<sup>th</sup> Respondent(now 3<sup>rd</sup> Respondent) to relocate its Proposed unit from the Krishnapatnam Industrial Area in Survey Nos. 397 ,401 ,402, 403, 446, 676, 681, 682, 683, 700-709 , Kothapatnam (V), Kota (M) SPSR Nellore.
- d. Direct the Respondents 1-6 (MOEF/SEIAA) to notify the Krishnapatnam industrial area (KIA) and the areas within a radius of 10kms from the site as an eco-fragile area without any delay and permit only non-polluting industries to establish in the region.

The matter was admitted by this Hon'ble Tribunal and consequently came to be disposed of as Environmental Clearance was granted during the pendency of the said original application.

32. We, the Appellant herein are before this Hon'ble Tribunal under Precautionary Principle and the motto that "**Prevention is better than cure**". Shrimp Hatchery is a very sensitive industry wherein one speck of pollution can render the entire industry redundant.

33. Shrimp hatcheries require large quantity of seawater for their day-to-day operations. The water used in the hatchery and let out is likely to be contaminated with dissolved or suspended organic matter, nutrients,

for SRI MAHALAKSHMI HATCHERIES



PROPRIETOR



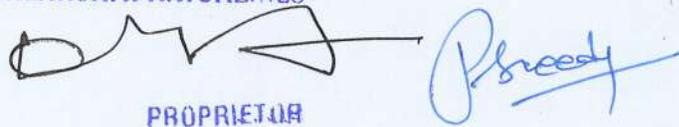
chemicals, antibiotics, etc. When contaminated water is discharged into open, it is likely to result in environmental pollution that could be detrimental to the hatchery operation itself, since intake and discharge points are nearby.

34. We humbly submit that, this Hon'ble Tribunal and the Hon'ble Supreme Court has stood a testament in invoking the Precautionary Principle Doctrine in various cases to protect the environment. Also, bulk drug industries like the 3<sup>rd</sup> Respondent if allowed to discharge would result in irreparable damage to the Appellants and other hatcheries operating in the vicinity. It is in fact pertinent to note that, these Bulk Drug industries will not mind causing environmental pollution and pay hefty environmental compensation thereof.

35. We commend the policy of the Government to reduce dependency of APIs from China, however at the same time we also require sustainable development goals (SDG) to meet the principles of 'live and let live' for every other businesses depending on seafront activity.

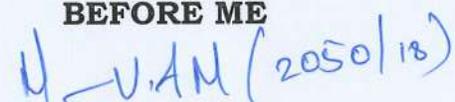
Under the circumstances, it is humbly prayed that, this Hon'ble Tribunal to take the above submissions on record and allow this appeal and pass such other orders as deems fit in the facts and circumstances of the case and thus render justice.

For SRI MAHALAKSHMI HATCHERIES

  
PROPRIETOR

Solemnly affirmed at Chennai }  
this the 10<sup>th</sup> day of October, 2023 }  
and signed his name in my presence;

BEFORE ME

  
ADVOCATE, CHENNAI  
No. 56/20, 1<sup>st</sup> Street  
Janakiram colony, Villivakkam  
Chennai - 49

**Item No.9:****BEFORE THE NATIONAL GREEN TRIBUNAL  
SOUTHERN ZONE, CHENNAI***(Through Video Conference)***Appeal No. 68 of 2021 (SZ)****IN THE MATTER OF:**

M/s. Sri Mahalakshmi Hatcheries,  
Rep. by its Proprietor  
Mr. D. Sagar Reddy,  
S/o. Venkata Ramana Reddy,  
Office at Srinivasa Satram, Kothapatnam Village,  
Kota Mandal, Sidavaram Post, Nellore and Anr.

... Appellant(s)

**Versus**

The State Environment Impact Assessment Authority (SEIAA)  
Represented by its Chairman,  
No.33-26-14 D/2, Near Sunrise Hospital,  
Pushpa Hotel Centre,  
Chalamalavari Street, Kasturibaipet,  
Vijayawada and Ors.

...Respondent(s)

**Date of hearing: 14.08.2023.****CORAM:****HON'BLE Smt. JUSTICE PUSHPA SATHYANARAYANA, JUDICIAL  
MEMBER****HON'BLE Dr. SATYAGOPAL KORLAPATI, EXPERT MEMBER**

For Appellant (s): Mr. K.M. Mrithunjayam.

For Respondent(s): Mr. Basu represented  
Mrs. Madhuri Donti Reddy for R1 & R2.  
Mr. Raghul Balaji for R3.

ORDER

1. The SEIAA - Andhra Pradesh (Respondent No.1) has produced a copy of the entire file relating to the grant of impugned EC.
2. When questioned whether the type book contains the Minutes of the Meeting of the SEIAA - Andhra Pradesh and SEAC - Andhra Pradesh, the learned counsel Mr. Basu representing the SEIAA - Andhra Pradesh said that it does not contain the Minutes of the Meeting.
3. Without the above referred Minutes of the Meeting, the entire file produced is of no use. Hence, the learned counsel appearing for the SEIAA - Andhra Pradesh is directed to produce the Minutes of the Meeting of both the SEIAA - Andhra Pradesh and SEAC - Andhra Pradesh from the date of application submitted by the Project Proponent till the date of issuance of the impugned EC.
4. The learned counsel appearing for the appellant is also directed to furnish the incidents of shrimp culture getting damaged due to marine discharge.
5. Post the matter on 11.09.2023.

Sd/-  
Smt. Justice Pushpa Sathyanarayana, JM

Sd/-  
Dr. Satyagopal Korlapati, EM

Appeal No.68/2021 (SZ),  
14<sup>th</sup> August 2023. Mn.

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**BEFORE THE HON'BLE NATIONAL GREEN TRIBUNAL**  
**SOUTHERN ZONE BENCH AT CHENNAI**  
**ORIGINAL APPLICATION NO. 126 OF 2021**

**IN THE MATTER OF:**

M/s. Sri Mahalakshmi Hatcheries  
 Represented by its Proprietor  
 Mr. D Sagar Reddy  
 S/o. Venkata Ramana Reddy  
 Office at Doruvukatta village, Kota Mandal  
 Sidavaram Post, Nellore – 524411.  
 Ph: +91 8978374567, Email: sagar.duvvuru@gmail.com

..... APPLICANT

-Vs-

**1. UNION OF INDIA**

Through the Secretary,  
 Ministry of Environment and Forests & Climate change,  
 JorBagh Road, Ali Ganj, Lodi Colony,  
 New Delhi – 110003.  
 Email: secy-moef@nic.in. Ph : 91-11-24621961

**2. STATE OF ANDHRA PRADESH**

Represented by its Chief Secretary,  
 1, 5th Floor, Interim Government Complex,  
 A.P. Secretariat, Valagapudi, Guntur,  
 Andhra Pradesh  
 Email: cs@ap.gov.in. Ph : +91 8632441024

**3. THE DISTRICT COLLECTOR**

Nellore District  
 Achari St. VRC Centre, Nellore,  
 Andhra Pradesh 524001  
 Email: collectornlr@ap.gov.in. Phone: 08612324374

**4. ANDHRA PRADESH COASTAL ZONE MANAGEMENT AUTHORITY**

Represented by its Member Secretary  
 D.No. 33-26-14 D/2. Near Sunrise Hospital  
 Pushpa Hotel Centre,  
 Chalamvaristreet, Kasturibaipet,  
 Vijayawada – 520010.  
 Email: membersecy@appcb.gov.in, Phone : 0866-2463200

1



#### 5. ANDHRA PRADWESH POLLUTION CONTROL BOARD

Represented by its Member secretary  
No. 33-26-14 D/2. Near Sunrise Hospital  
Pushpa Hotel Centre,  
Chalamvaristreet, Kasturibaipet,  
Vijayawada – 520010.  
Email: membersecy@appcb.gov.in, Phone : 0866-2463200

#### 6. COASTAL AQUACULTURE AUTHORITY

Represented by its Member Secretary  
5th Floor, Integrated Office Complex for  
Animal Husbandry and Fisheries Department, Nandanam,  
Chennai – 600035.  
Email: caaheadoffice@caa.gov.in, Phone : 04424353502

#### 7. M/S DIVIS LABORATORIES LIMITED

Represented by its Managing Director,  
303, DIVIS towers, Cyber Hills,  
Gachibowli,  
Hyderabad – 500032  
Email: mail@divislaboratories.com, Phone: +91 40 23786300

..... RESPONDENTS

I, Dr.V.Kripa Daughter of Shri Madhav Vasant Rao aged 59 years and working as Member Secretary, Coastal Aquaculture Authority do hereby solemnly affirm and sincerely state as follows:

1. I submit that I am the 6<sup>th</sup> respondent herein. I am well acquainted with the facts of the case on the basis of records available in my office. I read the affidavit filed in support of the Writ Petition. I deny all the averments made therein except those that are specifically admitted hereunder
2. India has an estimated potential brackish water area of 1.24 million ha along 8,129 kilometres of coastline available. India with huge aquatic resources has registered a phenomenal growth in fisheries production with 1.392 million tons (mt) in 2018-19 from mere 0.75 mt in 1950-51. India is the world's second largest fish producer (at 13.4 million tons) excluding seaweed cultivation and stands only next to China.



Fisheries contribute about US\$ 30 billion to the India's economy (1.0 percent of GVA in 2018-19 and in value terms nearly equals to rice production at US\$ 33 billion and much above wheat at US\$ 19 billion). Being one of the top fish producers and 2<sup>nd</sup> in aquaculture production in the world, India also has a thriving seafood export market (about 5 percent of the global sea food trade), earned about US\$ 6.73 billion / Rs. 46589.37 crore (2018-19) through exports. India has exported 6,52,253 MT of frozen shrimp in 2019-20 and earned US\$ 4,889.12 million/Rs.34,152 crore foreign exchange from export of cultured shrimp. Fish is the largest agriculture export commodity of India. India has shown continuous and sustained increments in shrimp production from the level of 75,000 MT during 2008-09 to the level of 7.5 lakh MT during the year 2019-20. It is obvious that, no other food production sector in the country has achieved such high growth rates as aquaculture in the past 10 years. Aquaculture and Fisheries has become an inevitable source of nutritional security for the human population with high quality of protein at cheaper cost. **The sea food export from India, though comprises of both captured and cultured aquatic food, the cultured shrimp with its 68.26% stake stands as the single largest commodity exported.**

3. It is submitted that the rural population, numbering about 16 million, comprising many poor and historically excluded people, are directly employed in fishing, and another about 30 million in associated activities especially coastal aquaculture which utilizes saline areas along the coastline, which are not suitable for other activities. Larger investment of public and private funds has also been made in the farming activity. If these farms are closed down, it may lead to unemployment of these large number of people. Hence, it was considered necessary to save the employment of the workers and also the investment already made in this economic activity and to provide for future growth of aquaculture farming in a manner, which is consistent with the requirement of safeguarding the environment. Therefore coastal aquaculture contributes significantly to the livelihood and development in the rural areas.
4. It is submitted that the Coastal Aquaculture Authority was established under the Coastal Aquaculture Authority Act, 2005 for regulating activities connected with coastal aquaculture in coastal areas (as provided under Clause (c) and Clause (d) of sub-section 1 of Section 2 of CAA Act, 2005 and Sub Para 7.1 of Para 7.0 in the Annexure-I to the CAA Rules, 2005) and for matters connected therewith or



incidental thereto to ensure that coastal aquaculture does not cause any detriment to the coastal environment and that the concept of responsible aquaculture is followed. The main objective of the Authority is to promote sustainable development without causing damage to the coastal environment following responsible coastal aquaculture practices and to protect the livelihood of various stakeholders living in the coastal area.

5. The Authority is empowered to make regulations for the construction and operation of aquaculture farms in coastal areas, inspection of farms and hatcheries for *L. vannamei* to ascertain their environmental impact, registration of aquaculture farms and hatcheries, removal or demolition of coastal aquaculture farms which cause pollution, fixing standards for all coastal aquaculture inputs, viz., seed, feed, growth supplements, chemicals, etc., used in coastal aquaculture and for the overall monitoring and regulation of coastal aquaculture activities in the country. Appropriate Rules, Regulations and Guidelines have been formulated and notified under the provisions of CAA Act, 2005 by the Govt. of India for this purpose. The CAA is entrusted with the responsibility to regulate the coastal aquaculture through Rules, Regulations and guidelines issued from time to time for the regulation aquaculture activities in coastal areas.
6. It is submitted that Clause (d) of sub-section 1 of Section 2 of CAA Act , 2005 defines 'coastal area' as an "Area of land within a distance of two kilometres from the High Tide Line (HTL) of seas, rivers, creeks and backwaters" as coastal aquaculture is essentially to be carried out in high quality sea water for sustainability of the sector.
7. The CRZ regulations from the day it came into existence in 1991 to this day, has consistently treated the Hatchery activity as a permitted activity in CRZ and excluded or exempted it from the prohibitions imposed by the CRZ Notification (Annexure 1), considering the indispensability for the requirement of oceanic quality Seawater and seafront access for a Hatchery. A Hatchery requires pristine seawater of oceanic quality for the broodstock holding, maturation, larval and Juvenile rearing of all marine organisms. Hence, a Hatchery is essentially a Seafront activity requiring access to oceanic quality Seawater as provided in Para 7.4 of Guidelines for Regulating Coastal Aquaculture issued as Annexure -I under Rule 3, Chapter 2 of CAA Rules 2005.



8. It is submitted that a Hatchery is an indoor facility where Marine organisms viz. Fish, Crustaceans, Molluscs, Seaweed and other marine life forms are bred for Natural stock enhancement of the seas or for Aquaculture. Hatchery is completely an indoor unit comprising of source water treatment systems for purifying the source water to the highest level, water storage reservoirs, and production tanks made of concrete in which the matured adult shrimps are made to produce eggs under the controlled condition. These eggs are made to hatch out and reared in the larval and post larval tanks using sea water of oceanic quality to enable them to metamorphose through different stages of its life cycle.
9. It is submitted that the microscopic shrimp eggs metamorphose through different life stages to reach the post larval stage and all these life stages are highly primitive and fragile in nature and they feed mainly natural food such as plankton. They are very sensitive to changes in the water quality as well as to strong chemicals. Hence, pesticides or chemicals which are harmful to the natural systems cannot be used in the hatcheries. It is submitted that the hatcheries do not discharge any chemical effluent and they are discharging only the water filtered and treated with high precision technologies used for the rearing of larval forms of Shrimp. Hence the water discharge from the Hatcheries contain planktons which are the natural food for all aquatic organisms and there is no source of contamination with any contaminants or pollutants in this water as they are detrimental to the (shrimps) organisms reared in these facilities. However, these discharges are mandatorily treated through the Effluent Treatment Systems as notified by this Authority and discharged into the sea. The entire facility being indoor and on concrete structure, the possibility of sea water seeping into the land is highly remote. Further all these hatcheries are established along the coast close to shore for the access of sea water and hence the majority of the areas in which they are established are saline in nature.
10. It is submitted that the quality of water available in the site has strong influence on the success of the coastal aquaculture farm. Wide fluctuation in pH and salinity will be detrimental to the cultured species. The water source should be free from any industrial pollution. The optimal levels of various water quality parameters for survival and growth of shrimps is provided under para 6.1 of Annexure -I of rule 3 of CAA Rules, 2005.



11. The use of antibiotics in coastal aquaculture is strictly prohibited as their use may result in development of pathogens resistant to such drugs and this resistance might get transferred to higher trophic levels in the food chain. 20 antibiotics/pharmacologically active substances are presently banned for use in aquaculture as provided under para 11.7 of Annexure -I of rule 3 of CAA Rules, 2005. Further, CAA is issuing certificates of compliance for the antibiotic free aquaculture inputs. All the coastal aquaculture farmers and hatchery operators are advised to use CAA certified aquaculture inputs to ensure that there is no possibility of accumulation of such antibiotic residue in the food chain and the environment.
12. It is submitted that the proper operation and viability of coastal aquaculture hatcheries depend on the availability of a continuous source of clean water, and proper treatment of their effluents before discharging to the surrounding environment, particularly in areas where several hatcheries may coexist. The treatment of the effluent from the hatcheries is inevitable for the survival of the hatcheries themselves and hence are to be followed scrupulously.

**The following extracts / excerpts from published scientific reports on the discharges from pharmaceutical manufacturing are submitted for the kind perusal**

13. It is submitted that there is scientific evidence that even low concentrations of pharmaceuticals in the environment have harmful effects on animal and plant life, with effects include including: renal failure in vultures, impairment of reproduction in fish, or inhibition of growth of certain aquatic species. Evidence shows that uncontrolled discharges from pharmaceutical manufacturing have devastating impacts on water systems as well as on people and animals coming into contact with the resulting resistant bacteria. This is especially true in India and China - where most Active Pharmaceutical Ingredients (APIs) for pharmaceutical products (including pharmaceuticals sold on the EU market) are manufactured. The production of APIs and finished dose antibiotics occurs in specific locations where point-source pollution results in incredibly high concentrations of APIs, encouraging the development of drug resistance. Recent studies from Hyderabad (India) reveal excessively high concentrations of pharmaceuticals exceeding maximum regulatory limits or safe exposure levels. Pharmaceutical manufacturing is a source of pharmaceutical pollution that is further exacerbated by poorly enforced



environmental legislation in countries such as India and China. Pharmaceutical pollution from drug manufacturing represents a global challenge that cannot be tackled without engaging the numerous stakeholders across supply chains. (Annexure 2)

14. Removal rates for pharmaceuticals in wastewater treatment plants (WWTPs) range from less than 10 to almost 100% in some cases for wastewater from pharmaceutical manufacturing. Pharmaceutical metabolites and transformation products can be more persistent and more toxic than the parent compound. (Annexure 3)
15. Several reports have confirmed the presence of pharmaceuticals in effluents of pharma industries and in municipal wastewaters and these have been recognized as a major source of drugs and pharmaceuticals in drinking water. The long term exposure of lower concentration of complex pharmaceutical mixtures on stream biota may result in acute and chronic damages, behavioral changes, and accumulation in tissues, reproductive damage and inhibition of cell proliferation. Several studies have demonstrated that fish exposed to wastewater effluents can exhibit reproductive abnormalities. Moreover, fish exposed to trace levels of birth control pharmaceuticals in the range of concentrations found in the environment show dramatic decreases in reproductive success, suggesting population level impacts are possible. Globally, the detection of waste pharmaceuticals in the environment creates the risks, which are associated with their introduction into human, aquatic life and wildlife and is becoming a serious problem equally for both regulators and the pharma industry. Significant success on this issue is simply not achievable with the currently limited state of knowledge on environmental transport, fate, and effects of pharmaceuticals. There is need to take into consideration the possible growing effects of different drugs affecting the same receptors<sup>12</sup>, Risk assessment of the pharma chemicals involves the detection of the inherent hazards at each stage and an estimation of the risks due to these hazards. (Annexure 4)
16. It is submitted that currently, pharmaceutical compounds are being discharged into the environment in extremely large quantities regularly and present system of regulations of their release is not able to control the untreated or partially treated



pharma effluents. These drugs are entering into and occurring in ecosystems, is causing impact on the biota and humans.

17. The negative impact of the production of pharmaceutical products on the natural environment is well known. However, this remains largely unregulated, meaning the extremely toxic impact it has on both animals and humans continues with no clear end in sight. Lord Jim O'Neill noted this trend in his 2016 UK government-funded independent Review on Antimicrobial Resistance. Although it is a global issue, like other environmental issues, pharma pollution more directly and seriously affects those living near production plants whose water and food sources are contaminated with waste pharma products. "The production of both active pharmaceutical ingredients (APIs) and finished dose antibiotics is concentrated in specific locations so the resulting point, source pollution, is in incredibly high concentrations and encourages the development of drug resistance," says HCWH Europe pharmaceuticals policy officer Dr Adela Maghear. "This practice has a detrimental impact on vulnerable populations living near manufacturing facilities and wastewater treatment plants in these countries." This grievous level of pharma pollution exists despite NGO, governmental and judicial pressure on companies operating in the area to clean up their act. In 2009, the Patancheru-Bollaram zone was classified in India's national pollution index as '**critically polluted**' and in 2016, **the country's Hon'ble Supreme Court ordered pharma companies to implement a zero liquid waste policy.** (Annexure 5)
  
18. Pharmaceutical plants are often incapable of filtering out all the chemical compounds used in their manufacturing process and as such, the chemicals will seep into the surrounding freshwater systems and eventually into the oceans, lakes, streams, and rivers. Wastewater from pharmaceutical manufacturers is also sometimes discharged into open fields and nearby water bodies, thereby increasing the pharmaceutical waste or their by-product load in the environment, landfills, or dumping areas. **All this is basically known as pharmaceutical pollution (Annexure 6)**
  
19. Pharmaceutical compounds are being used for several beneficial purposes in modern society but simultaneously pharma industries are releasing very toxic contaminants in the environment directly or after chemical modifications. Intermediates and raw



materials could be present in wastewater discharged from pharmaceutical industry. Traditional wastewater treatment methods, such as activated sludge, are not sufficient for the complete removal of active pharmaceutical ingredients and other wastewater constituents from these waters. Consequently, pharmaceuticals find their way into the aquatic environment, where they directly affect aquatic organisms and can be incorporated into food chains. In a recent study, the extraordinarily high levels (mg/L) of several drugs were found in the effluents from local wastewater treatment plant near Visakhapatnam in India. Moreover, higher concentrations of antibiotics can lead to change in microbial community structure and ultimately affect food chains. Many pharmaceutical industries are responsible to generate toxic effluent as a consequence of their operation. (Annexure 4). Further it is submitted that the US Food and Drug Administration (US FDA) has issued import alert on the Unit 2 facility of M/s. Divis Laboratories Limited at Visakhapatnam of Andhra Pradesh (Who is the 7th respondent in this case). It may be noted that a company cannot export products into the US from a site under import alert until the drug regulator reverses its action (Annexure 7)

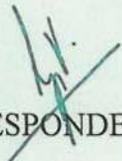
20. It is humbly submitted that a joint committee has been constituted by the District Collector, SPSR Nellore district, based on the representation made to the Hon'ble Chief Minister of Andhra Pradesh. The committee inspected the site on 07.03.2020 and reported that industrial discharge will settle residues of antibiotics and other harmful substances thus have strong influence on the agriculture, aquaculture and the hatchery activities in the area.
21. It is submitted that the said industry is proposed to be set up amidst the highly productive and sustainable coastal aquaculture farms falling under a declared Aquaculture Zone and food grain producing agricultural fields makes it a concern at large, though the above stated facts about the effluent treatment and the pharmaceuticals discharged into the open environment are universal for any pharma industry.
22. It is submitted that this authority believes from the above mentioned facts that the mechanism and the machinery used in the effluent treatment plants at such pharmaceutical industry do not efficiently remove the harmful substances from the



effluents they release into the environment. Therefore the Hon'ble NGT may constitute a larger committee which will thoroughly study the ETS and provide a report elaborating the aspects of effluent treatment process, components of the final discharge and their impact in the environment, the biology of the aquatic animals being cultured in the region and the agriculture sector.

23. Accordingly the following are submitted for the kind consideration of the Hon'ble NGT;

- I. The impact cause by pharmaceuticals, their metabolites and transformation products in the environment magnified many fold in this particular case since the location of the pharmaceutical manufacturing facility is in an area which has high dense production of aquatic organisms though coastal aquaculture and food grains through agriculture. It has a potential hazard to contaminate the food production from this area thus ultimately impacting a large number of human consumers from within the area and outside.
- II. Considering the presence of residual pharmaceuticals in the effluence and discharges of pharmaceutical industry, the Hon'ble Supreme Court of India issued orders to pharma companies to implement a zero liquid waste policy.
- III. Considering the sensitiveness of the location which mainly consists of Agricultural fields and Aquaculture farms involved in food production in which the pharmaceutical manufacturing facility is proposed to be established, implementation a zero liquid waste policy may be made mandatory for the pharmaceutical manufacturing facility to thwart the potential hazard from the residual pharmaceuticals
- IV. Considering the threat perception and perceived possibility of contamination of coastal aquaculture produces and agricultural produces by the pharmaceuticals which is expected to contaminate the surrounding environment around the proposed pharma manufacturing facility, it is submitted to consider constitution of a larger committee of domain experts from all sectors to assess the threats and propose appropriate mitigation measures before the commissioning of the project

  
RESPONDENT

10



डॉ. वी. कृष्ण / Dr. V. KRIPA  
सदस्य सचिव / Member Secretary  
भारत सरकार / GOVERNMENT OF INDIA  
मत्स्य पालन, पशुपालन व डेयरी उद्योग मंत्रालय  
Ministry of Fisheries, Animal Husbandry and Dairying  
तटीय मत्स्यपालन प्राधिकरण / Coastal Aquaculture Authority  
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## Annexure: I

**Exclusion or Exemption of Hatchery from CRZ Notifications****I. CRZ Notification 1991**

Sub para (i) & (iii) of Para 2 of the CRZ Notification 1991 excludes/exempts the hatchery activity from the prohibited activities in the CRZ. It provides for as under

## “2. Prohibited Activities :

The following activities are declared as prohibited within the Coastal Regulation Zone, namely :

- (i) setting up of new industries and expansion of existing industries, except those directly related to water front or directly needing foreshore facilities;
- (ii) Xxxx
- (iii) Setting up and expansion of fish processing units including warehouse (excluding hatchery and natural fish drying in permitted areas) ;”

**II. CRZ Notification 2011**

Sub para (i)a & (iii) of para 3 of the CRZ Notification 2011 excluded the hatcheries from the prohibited activities in CRZ. It provides as under:

## “3. Prohibited activities within CRZ,- The following are declared as prohibited activities within the CRZ,-

- (i) Setting up of new industries and expansion of existing industries except,-
  - (a) those directly related to waterfront or directly needing foreshore facilities;

*Explanation:* The expression “foreshore facilities” means those activities permissible under this notification and they require waterfront for their



operations such as ports and harbours, jetties, quays, wharves, erosion control measures, breakwaters, pipelines, lighthouses, navigational safety facilities, coastal police stations and the like.;

(ii) Xxx

(iii) Setting up and expansion of fish processing units including warehousing  
**except hatchery and natural fish drying in permitted areas.”**

### III. CRZ Notification 2019

Sub para 1.2(vii) of Para 5 of CRZ Notification 2019, under the regulation of permissible activities in CRZ, permits hatchery and natural fish drying in CRZ-I B – the inter tidal areas. It provides as under:

“5. **Regulation of permissible activities in CRZ:**

5.1 **CRZ-I**

5.1.1 **CRZ-IA:**

xxxx

5.1.2 **CRZ-IB- The inter tidal areas**

Activities shall be regulated or permissible in the CRZ-I B areas as under:-

(i) xxx

(ii) xxx

(iii) xxx

(iv) xxx

(v) xxx

(vi) xxx

(vii) Hatchery and Natural fish drying.”





# THE ENVIRONMENTAL IMPACT OF PHARMACEUTICAL MANUFACTURING:

How does industry address its own waste?



## INTRODUCTION

Pharmaceutical pollution is increasingly recognised as a threat to ecosystems and human health globally. Pharmaceuticals can enter the environment at all stages of their life cycle (production, use, and disposal), meaning they can ultimately end up in our drinking water as well as accumulate in vegetables and fish. Pharmaceutical residues have been detected in surface water, sewage effluents, groundwater, drinking water, manure, soil, and other environmental matrices globally.<sup>1,2</sup> There is scientific evidence that even low concentrations of pharmaceuticals in the environment have harmful effects on animal and plant life, with effects include including: renal failure in vultures, impairment of reproduction in fish, or inhibition of growth of certain aquatic species.<sup>3,4,5</sup>

Critically, the discharge of pharmaceuticals into the environment has also been linked to the development of antimicrobial resistance (AMR), which is recognised by UN Environment as one of the biggest global public health concerns that we face.<sup>6</sup> Evidence shows that uncontrolled discharges from pharmaceutical manufacturing have devastating impacts on water systems as well as on people and animals coming into contact with the resulting resistant bacteria. This is especially true in India and China - where most Active Pharmaceutical Ingredients (APIs) for pharmaceutical products (including pharmaceuticals sold on the EU market) are manufactured.<sup>7,8,9,10,11,12,13</sup>

The production of APIs and finished dose antibiotics occurs in specific locations where point-source pollution results in incredibly high concentrations of APIs, encouraging the development of drug resistance. Recent studies from Hyderabad (India) reveal excessively high concentrations of pharmaceuticals exceeding maximum regulatory limits or safe exposure levels.<sup>9</sup> Exposure to environmental sources of antimicrobial drugs is placing vulnerable populations, such as pregnant women from low-income backgrounds at a higher risk for community acquired AMR.<sup>14</sup> Contamination of water sources with antimicrobial drugs (combined with the mass misuse of antibiotics and poor sanitation) has grave consequences in India, where an estimated 58,000 new-borns die annually from multidrug-resistant infections.<sup>15</sup>

Pharmaceutical manufacturing is a source of pharmaceutical pollution that is further exacerbated by poorly enforced environmental legislation in countries such as India and China.<sup>16</sup> Several studies show that polluting factories breeding resistant bacteria are exporting to EU markets and directly selling drugs to EU-based healthcare providers and buyers (e.g. German insurance companies).<sup>17</sup>

Furthermore, European patients are often not fully informed about pharmaceutical supply chains - packaging labels almost always refer to the final stage in the supply chain (where medications are packaged) as the manufacturing location, instead of providing information about where the APIs or the finished doses were actually manufactured. To increase transparency, patients and health professionals should have access to accurate information regarding the origin of drugs they use so that they can make an informed decision - knowing more about suppliers allows users to find out more about the environmental and social conditions under which the drugs were manufactured.<sup>10</sup>

Recognising the problems highlighted above, Health Care Without Harm (HCWH) Europe conducted a survey to identify best practice and gather information about how pharmaceutical companies manage manufacturing waste throughout their supply chains.

The survey was sent to the top 50 pharmaceutical companies worldwide (according to Pharmaceutical Executive's annual ranking)<sup>18</sup> and covered aspects such as waste and pollution management, environmental sustainability, governance, and transparency (page opposite). Participating companies were evaluated according to their responses, as well as any publicly available information. A traffic light system was used as an assessment tool with the following performance indicators:

	<b>Red</b> - Low implementation/ no measures
	<b>Yellow</b> - Average implementation/ of measures
	<b>Green</b> - High implementation/ measures present

## ASSESSMENT AREAS

### A. ENVIRONMENTAL SUSTAINABILITY FRAMEWORK

- What are the company's environmental policies?
- How are these policies implemented?

### B. SUPPLIER ASSESSMENT

- Does the company require external suppliers to have environmental policies in place?
- How does the company verify that its suppliers' policies are being implemented?

### C. ENVIRONMENTAL GOVERNANCE

- Is there a department in the company in charge of reducing its environmental footprint?
- What are the company's commitments in terms of reducing its environmental footprint?

### D. TRANSPARENCY

- Does the company publicly report environmental monitoring data?
- Is the list of the company's external suppliers publicly available?



## RESULTS

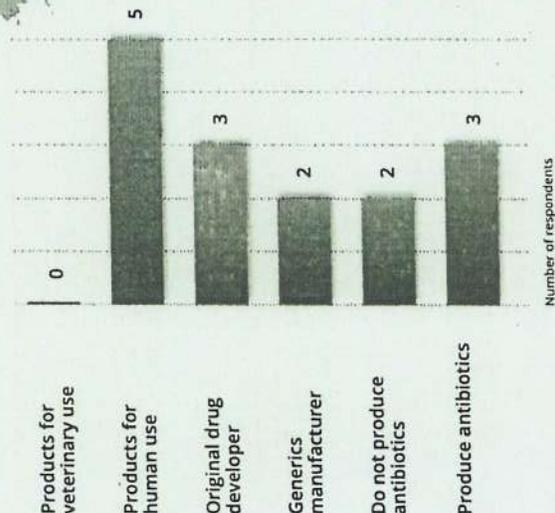
Five companies participated in the survey. Three directly responded to the survey as drafted by HCWH Europe:

- AstraZeneca (AZ)
- GlaxoSmithKline (GSK)
- F. Hoffmann-La Roche (Roche)

Others compiled answers in their own format covering the areas of interest in the survey:

- Mylan
- Teva

All the companies surveyed manufacture medicinal products for human use only, three develop original drugs, and three produce antibiotics.



All participating companies operate manufacturing sites in developed as well as emerging and developing countries (as defined by the IMF).<sup>19</sup> The UK, USA, Germany, Ireland, Canada, Australia, and Japan were the most frequently mentioned developed countries with manufacturing sites, whilst China, Brazil, India, Thailand, and Argentina were the most popular sites in emerging and developing countries.

### LOCATION OF PARTICIPANTS' MANUFACTURING SITES

Argentina	China	Italy	Puerto Rico	Thailand
Australia	Czech Republic	Japan	Romania	UK
Austria	Egypt	Kenya	Russia	USA
Belgium	France	Lithuania	Singapore	Zambia
Brazil	Germany	Mexico	Slovakia	Zimbabwe
Bulgaria	Greece	The Netherlands	South Africa	
Cameroon	Hungary	Nigeria	Spain	
Canada	India	Peru	Sweden	
Chile	Ireland	Poland	Switzerland	



### A. Environmental sustainability framework

All five companies indicated that they have implemented environmental policies or guidelines for managing and processing pharmaceutical manufacturing pollution. The comprehensiveness of these policies or guidelines, however, differs between the companies, as does their implementation.

Implementing widely recognised standards for manufacturing practice and environmental management is a common way for pharmaceutical companies to limit the negative environmental impacts of their manufacturing activities. One such example is the International Organization for Standardization's ISO 14001 certification, which requires an environmental management system to be in place and helps organisations improve their environmental performance.<sup>20</sup>

Among the study participants, two companies have all their sites ISO 14001 certified; the remaining three companies did not provide specific data for all of their manufacturing sites.

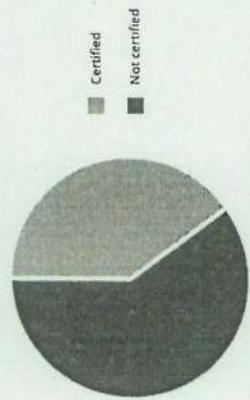
The ISO 14001 standard does not contain specific environmental performance criteria, but provides a framework for the holistic improvement of a company's environmental performance. Other measures are therefore usually taken (in place of or in addition to the ISO certification) to address the environmental impacts of manufacturing processes.

Examples of such measures listed by participating companies include:

- Written standards and procedures
- Environmental risk assessments
- Internal and quality audits
- Air emissions, water, and soil contamination controls

### ENVIRONMENTAL SUSTAINABILITY

ISO 14001 certification of all manufacturing sites (5 respondent companies)



- Safe discharge programmes
- Waste management programmes
- Training of staff and suppliers

### Waste and pollution management

Responsible environmental management requires controlling the amount of APIs entering the environment. In terms of waste and pollution management practices, all participants indicated having implemented hazardous substance management programmes, aimed at reducing hazardous waste.

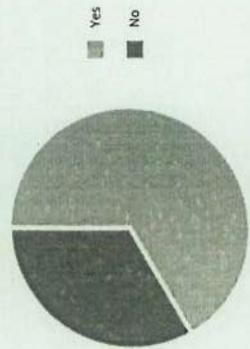
To determine the potential environmental impact of APIs, all the participating companies monitor their facilities and evaluate the discharge of wastewater to surface waters.

Three companies make use of Common Effluent Treatment Plants, which also collect and treat domestic sewage, and are not designed to specifically treat effluent from pharmaceutical manufacturing sites.<sup>21</sup> Notably, three companies indicated that they implement zero liquid discharge wastewater treatment systems at either their own sites or at their suppliers' sites. These systems have the potential to limit the discharge of liquid waste into the environment.<sup>22</sup>

Emissions to the air from manufacturing operations are also assessed at all five companies, but only two companies provided information about detailed measures taken to reduce air pollution at their facilities. These measures include containment and local exhaust ventilation, as well as the use of other air cleaning equipment (e.g. HEPA filtration, electrostatic precipitation, and/or carbon beds).

Finally, two of the three companies producing antibiotics confirmed that they take measures to limit their discharge, including discharge limits and specific wastewater treatment methods.

Companies producing antibiotics that take measures to limit their discharge (3 respondent companies)



### B. Supplier assessment

The majority of responding pharmaceutical companies outsource their API production. Two companies provided responses showing that 10% and 40% of their APIs are produced in emerging and developing countries. Two further companies indicated that they use APIs produced in emerging countries, but no specific percentages were provided.

All five companies require external suppliers to have environmental policies for hazardous waste management, wastewater discharge, or air emissions as part of their Supplier Code of Conduct. In order to ensure environmentally responsible operations at supplier sites, all surveyed companies undertake inspections verifying compliance with environmental standards and examine appropriate authorisations on a regular basis. Three respondents specified how many audits/inspections take place at their or their suppliers' sites per year, and the other two companies indicated the number of audits that took place in 2017.

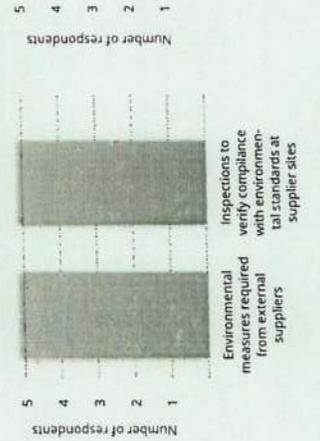
### C. Environmental governance

All companies reported having internal governance structures overseeing activities related to environmental sustainability at their manufacturing sites. These most commonly comprised safety, health, and environment departments, as well as sustainability and social responsibility divisions.

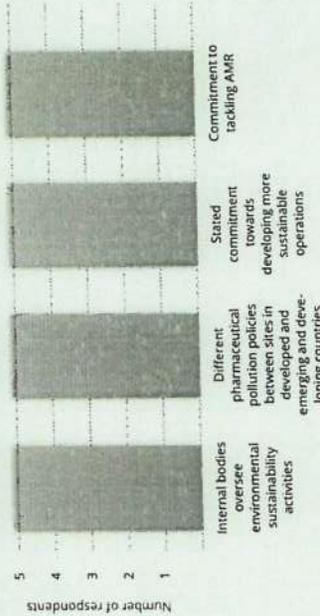
Examining governance practices in different parts of the world, participating companies indicated that their pharmaceutical pollution policies do not differ between manufacturing sites located in developed countries versus those in emerging and developing countries. Furthermore, aware of the environmental impacts of manufacturing activities, all surveyed companies have established specific goals and targets towards more sustainable operations. Some examples relevant to this study include: goals related to the quality of effluent discharge, safe discharge limits, the minimisation of waste, and unintended releases. Only two companies explicitly mentioned that they require external suppliers to follow their sustainability commitments.

Finally, all five companies recognise the threat posed by AMR; they fund relevant research (e.g. to develop new antibiotics and detection methods) and support measures to reduce pharmaceutical pollution. All surveyed companies are also signatories of the 2016 Davos Declaration, mobilising the pharmaceutical industry to accelerate efforts to reduce the development of antimicrobial resistance<sup>23</sup> and are also part of the AMR Industry Alliance - a coalition initiated to provide sustainable solutions to curb AMR.<sup>24</sup>

### ENVIRONMENTAL GOVERNANCE OF SUPPLIERS



### ENVIRONMENTAL GOVERNANCE FOR OWN-OPERATED SITES



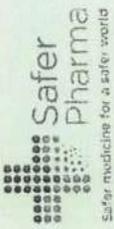
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manufacturing, or imposing stronger rules on Environmental Risk Assessments as part of market authorisations for pharmaceutical products, are imperative to curb the negative impacts of pharmaceutical manufacturing.

The problems associated with pharmaceutical pollution, however, seem to be neglected by key actors, including the industry and European legislators. For example, the Strategic Approach to Pharmaceuticals in the Environment is already three years overdue - it was originally scheduled for release in 2015. It is hoped that its publication will trigger more action from Member States and pharmaceutical manufacturers.

In the absence of action from regulators and manufacturers, it is imperative that civil society and the public continue to highlight this important issue and the need for appropriate action. To this end, HCWH Europe is committed to repeating this study in the future, in order to increase transparency and highlight gaps in both knowledge and legislation.



This study is part of HCWH Europe's Safer Pharma campaign, initiated to protect the environment from pharmaceutical pollution at all stages of their lifecycle. The campaign seeks to challenge the pharmaceutical industry to clean-up its production and raise awareness within the healthcare sector about the impact of pharmaceuticals in the environment, encouraging rational prescription practices. It also aims to raise awareness amongst citizens about the impact of pharmaceuticals in the environment and the steps they can take to tackle the problem. For more information, please visit [www.saferpharma.org](http://www.saferpharma.org).

**CONCLUSIONS**

Through its operations, the pharmaceutical industry has a substantial impact on the environment. Not only do pharmaceutical manufacturers have a critical role to play in addressing these issues, they also have a responsibility to foster environmental sustainability and reduce pharmaceutical pollution at source, throughout their supply chains.

With such a small sample size, and little publicly available information from pharmaceutical manufacturers, this study provides only a general introduction to the subject and is not intended to offer a representative sample or showcase best practices.

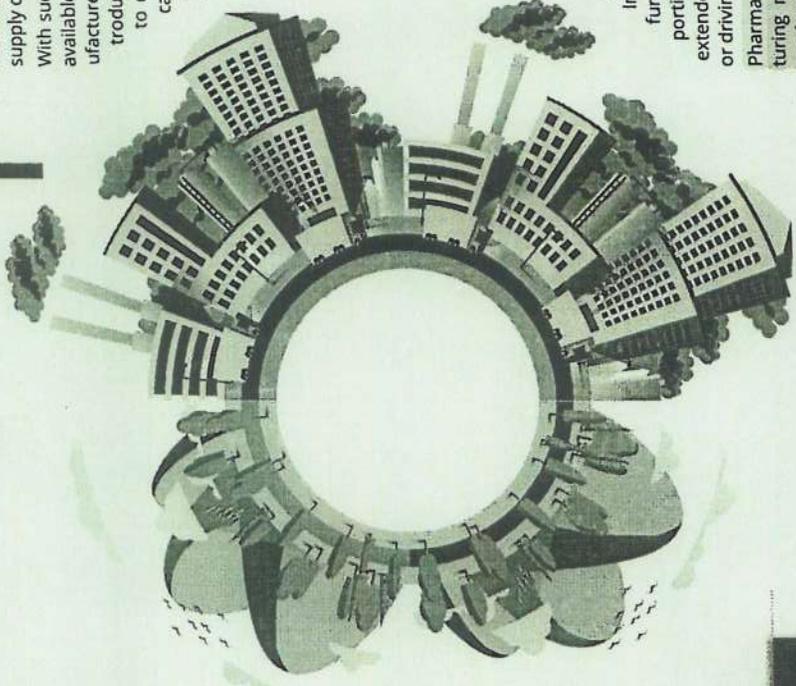
The limited response, however, demonstrates an industry-wide lack of transparency and reluctance to acknowledge the industry's responsibilities in terms of manufacturing to protect the environment from pharmaceutical pollution.

The results of this study show that although these companies frequently disclose general data related to environmental sustainability and governance, detailed information relating to specific measures taken to prevent pharmaceutical pollution at own-operated and supplier facilities remain unavailable to the public. There is a need for greater transparency from the industry in this regard.

Increased transparency could encourage further responsible practices such as reporting environmental incidents, promoting extended environmental risk assessment, and/or driving technology investments.

Pharmaceutical pollution from drug manufacturing represents a global challenge that cannot be tackled without engaging the numerous stakeholders across supply chains. The EU has an important role to play in proposing ambitious legislation to deal with pharmaceutical pollution, including the global threat of AMR.

For example, the long-awaited Strategic Approach to Pharmaceuticals in the Environment<sup>25</sup> from the European Commission (which should have been published in September 2015 but has yet to be finalised) should call for the Environmental Risk Assessment (ERA) to be considered in the market authorisation process.<sup>26</sup> Further measures, such as broadening the Good Manufacturing Practices (GMP) framework to cover environmental impacts of pharmaceutical



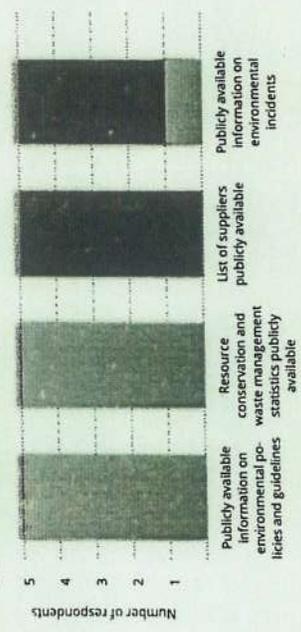
**D. Transparency**  
All surveyed companies make general information about their environmental policies and guidelines publicly available through their websites and relevant corporate documents (e.g. annual and sustainability reports).

All five companies also publish general statistics on their resource conservation (greenhouse gas emissions, and energy and water consumption), waste management (both hazardous and non-hazardous), as well as appropriate reduction or increase trends.

No company, however, provides site-specific information and none of the participating companies make their list of suppliers publicly available.

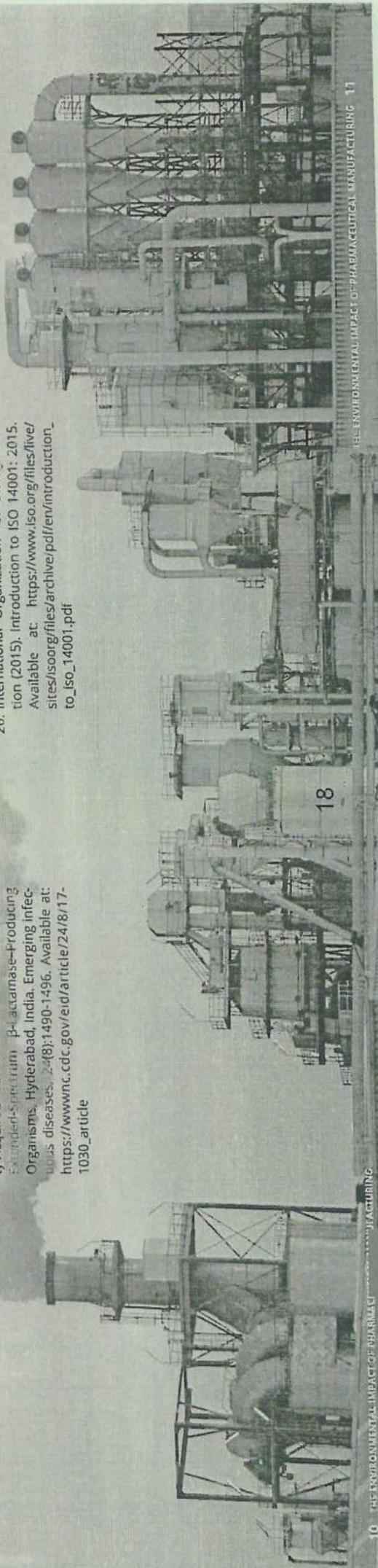
Only one company indicated that they publicly disclose information related to environmental incidents occurring at its manufacturing sites and the appropriate remediation.

**TRANSPARENCY**



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10 THE ENVIRONMENTAL IMPACT OF PHARMACEUTICAL MANUFACTURING

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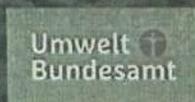
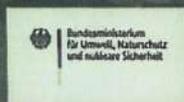
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**Sources, impacts and trends of pharmaceuticals in the marine and coastal environment**

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## Review

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# Sources, impacts and trends of pharmaceuticals in the marine and coastal environment

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There has been a significant investment in research to define exposures and potential hazards of pharmaceuticals in freshwater and terrestrial ecosystems. A substantial number of integrated environmental risk assessments have been developed in Europe, North America and many other regions for these situations. In contrast, comparatively few empirical studies have been conducted for human and veterinary pharmaceuticals that are likely to enter coastal and marine ecosystems. This is a critical knowledge gap given the significant increase in coastal human populations around the globe and the growth of coastal megacities, together with the increasing importance of coastal aquaculture around the world. There is increasing evidence that pharmaceuticals are present and are impacting on marine and coastal environments. This paper reviews the sources, impacts and concentrations of pharmaceuticals in marine and coastal environments to identify knowledge gaps and suggests focused case studies as a priority for future research.

## 1. Introduction

Over the last 15 years increasing attention has been paid to understanding the presence and impacts of pharmaceuticals entering or detected in freshwater ecosystems [1]. By contrast, significantly less attention has been paid to understanding releases of pharmaceuticals from sewage and other routes into coastal environments and their potential marine impacts. There is now widespread recognition of the need for a cradle-to-grave stewardship of medicines for minimizing environmental exposure while promoting human and animal health [2]. Large centres of human population are often found in coastal areas and pharmaceutical releases via municipal effluent discharges are probable. For example, Martínez *et al.* [3] reported that based on 2003 data, over 2.3 billion people live within coastal limits (representing 41% of world global population) and more than 50% of coastal countries have 80–100% of their total population within 100 km of the coastline. Twenty-one of the world's 33 megacities (cities with more than 8 million inhabitants) are on the coast and face a range of environmental management issues [4]. Global demographic trends towards coastal conurbations suggest increasing numbers of people living along coastlines, while waste management from coastal megacities is increasingly recognized as a major challenge [3,5,6]. These trends suggest the potential for increasing inputs of human pharmaceuticals into coastal environments and therefore the need to address potential exposure scenarios and implications for marine risk assessments of drug residues and their transformation products [7–9]. Marine risk assessments for pharmaceuticals are also relevant to veterinary medicines used in aquaculture [10–12].

More broadly, if releases of pharmaceuticals into coastal ecosystems are high enough to induce biological impacts, they may act as additional stressors on marine ecosystems already impacted by climate change, eutrophication and over-fishing [13]. It is estimated that 49% of marine ecosystems worldwide are strongly impacted by anthropogenic stressors with significant economic implications [3,14]. If unmanaged, multiple anthropogenic impacts on marine



ecosystems may also affect coastal fisheries and aquaculture. For example, human health concerns linked to aquaculture include exposure to pharmaceuticals through consumption of seafood and the induction and spread of antibiotic resistance [15,16]. This paper reviews the sources, concentrations and potential impacts of human and veterinary pharmaceuticals in coastal environments to support risk assessments and to identify key knowledge gaps as priorities for future research. The scope of the review has been limited to human pharmaceuticals and antibiotics used as veterinary medicines.

## 2. Sources of pharmaceuticals in marine environments

### (a) Sewage

Sewage effluent is recognized as a major source of multiple pharmaceuticals, including their metabolites, entering aquatic environments. Removal rates for pharmaceuticals in wastewater treatment plants (WWTPs) range from less than 10 to almost 100% and depend on the physico-chemical characteristics of the pharmaceutical and type of treatment technology [17]. Sources of human pharmaceuticals in sewage include patient use in the community, discharges from hospitals and, in some cases, wastewater from pharmaceutical manufacturing [18]. Sewage can be discharged into marine environments through coastal and ocean outfalls for WWTPs combined sewer overflows and via rivers receiving WWTP effluents [19,20]. For example, the Yangtze River in China transports sewage from 400 million people out to sea and releases an estimated 152 tonnes of pharmaceuticals annually [21]. Sewage may also be discharged into the marine environment from boats. Ships, including cruise liners, may discharge (under Annex IV of MARPOL 73/78 ships) treated sewage into the sea 4 nautical miles from the nearest land and 12 nautical miles for untreated sewage [22]. The volumes of sewage discharged can be significant as cruise liners can have passenger numbers equivalent to populations found in small towns. Sewage effluents from small boats, on the other hand, may not receive any treatment prior to being discharged. Typhoon shelters for small boats were a point source of antibiotics in Victoria Harbour, Hong Kong [23]. As discussed by Kookana *et al.* [24] in this issue, many large cities in Asia still rely on septic tanks with poorly managed septage which can contaminate surface and groundwaters with pharmaceuticals and ultimately be discharged into coastal areas.

Sewage impacted groundwater can also be a source of pharmaceuticals entering coastal waters. Pharmaceuticals have been detected in a coastal aquifer on the Yucatan Peninsula, Mexico injected with municipal sewage discharges [25]. Reuse of treated domestic wastewater for irrigation contributed to pharmaceutical contamination in groundwater on Mallorca [26]. Throughout the world rural and peri-urban areas including popular coastal holiday areas are reliant on septic tanks or small decentralized systems for sewage treatment disposal [27]. Depending on their treatment efficiency and the capacity of the local soils, these systems are a potential source of pharmaceuticals in coastal waters via leakage to ground and surface waters [28,29].

### (b) Aquaculture

Globally the production of seafood through aquaculture is rapidly increasing with over 90% of aquaculture based in

Asia [30]. A range of veterinary medicines including antibiotics, also registered for human use, is used prophylactically and to control disease outbreaks in marine aquaculture. Up to 75% of the administered dietary dose of a veterinary medicine can be lost to the surrounding environment. The loss mechanisms include dispersal of non-ingested pellets, gill and renal excretion of the unprocessed drug, and renal and faecal excretion of drug metabolites [31]. Other marine organisms in the vicinity including wild fish feed on leftover food and faecal material from marine aquaculture potentially further spreading pharmaceuticals and their transformation products. Pond-based farms located in coastal areas are also a source of antibiotics entering coastal waters through leaks and discharge of wastewaters which can contain elevated concentrations of pharmaceuticals. Extremely high antibiotic concentrations of up to  $2.5 \text{ mg l}^{-1}$  were measured in water samples from shrimp ponds in Vietnamese mangroves [32]. The ancient practice of wastewater- (human and animal) fed aquaculture, although declining, still occurs in some parts of Asia [30]. Aquaculture practices including the use of antibiotics vary greatly between countries [33].

### (c) Animal husbandry and horticulture

Animal husbandry and horticulture along rivers and in coastal areas may also contribute to loadings of pharmaceuticals entering coastal waterways [17,34]. Antibiotics are added to animal feeds and in some cases drinking water to treat disease particularly in feedlots housing large numbers of animals [35]. The use of low doses of antibiotics in feed as growth promoters still occurs in some regions of the world despite being banned in Europe [36]. Some countries permit the use of antibiotics including oxytetracycline and streptomycin on horticultural crops [17]. Application of municipal biosolids to farmland as fertilizer is a further source of pharmaceuticals entering agricultural systems [37].

### (d) Waste disposal

Waste disposal in coastal areas is a further source of pharmaceuticals entering the marine environment. Leachate from coastal landfills and seafills may be a pathway for pharmaceuticals disposed of in household and clinical wastes to enter coastal waters. Landfill leachate on the island of Mallorca contained up to  $27\,000 \text{ ng l}^{-1}$  total concentration of pharmaceuticals [26]. Historically, in some regions drug manufacturing waste, sewage sludge and animal manure were dumped at sea [38,39].

### (e) Environmental fate of pharmaceuticals in marine environments

Once discharged into aquatic environments, pharmaceuticals and their metabolites can undergo biotic and abiotic transformation (degradation) and sorb to suspended particulate matter (SPM) and sediments, and in some cases accumulate in the tissues of aquatic organisms [40]. Existing data for the environmental fate of pharmaceuticals generated for freshwater environments may not necessarily be transferable to marine environments. The differences in physico-chemical conditions including salinity, pH and organic matter between freshwater and seawater can impact on the environmental fate of pharmaceuticals [41]. The environmental fate of ionizable pharmaceuticals may be altered by the increased pH of seawater. Photodegradation may be a less important removal



mechanism in coastal waters compared with more shallow freshwater environments due to light attenuation. Indirect photodegradation mechanisms may differ to those occurring in freshwater due to differences in water composition [42,43]. There is some evidence to suggest that the environmental fate of pharmaceuticals can differ between fresh and saline environments. The transformation behaviour of ibuprofen differed between freshwater and seawater [44] and prochlorperazine was more stable in seawater than freshwater [43].

### 3. Current state of knowledge of pharmaceutical concentrations in marine environments

#### (a) Seawater

The assessment of the concentrations of pharmaceuticals in coastal environments has been limited. Forty-nine studies have reported concentrations for individual pharmaceuticals and metabolites detected in estuarine and coastal waters. Only studies published since 2000 are considered. Seventy per cent of these studies have been published since 2010. The geographical breakdown for the studies is Europe (20), Asia (21), North America (6), South America (1) and Oceania (1). The studies included those investigating the presence of 30 or more pharmaceuticals over a wide spatial area [45] studies targeting specific classes of compounds, for example, sulfonamide antibiotics [34] and method validation studies screening only a limited number of 'real' samples [46].

To date, 113 pharmaceuticals and pharmaceutical metabolites have been detected in coastal waters at concentrations ranging from 0.01 to 6800 ng l<sup>-1</sup> with the maximum concentrations for 69 of these compounds exceeding the European Medicines Agency threshold for predicted environmental concentrations for surface waters of 0.01 µg l<sup>-1</sup> [47] (electronic supplementary material, tables S1–S3). Data were most frequently reported for antibiotics (41 compounds) followed by non-steroidal anti-inflammatories (8) and analgesics (8). Twenty compounds were reported in five or more studies (table 1) including acetaminophen, atenolol, carbamazepine, clarithromycin, diclofenac, 17α-ethinyloestradiol, erythromycin-H<sub>2</sub>O, gemfibrozil, ibuprofen, ketoprofen, naproxen, norfloxacin, oxafloxacin, propranolol, roxithromycin, sulfadiazine, sulfadimidine, sulfamethoxazole, tetracycline and trimethoprim. The higher frequency of reporting for concentrations of antibiotics and painkillers for the marine environment are consistent with Hughes *et al.* [1] synthesis of pharmaceutical data for freshwater environments.

Current methodologies targeting the dissolved fraction of pharmaceuticals may be underestimating the environmental concentrations and the potential impacts on aquatic ecosystems [49]. The majority of the studies published to date have reported pharmaceutical concentrations in seawater for the dissolved fraction only with filtering being the first step in sample extraction methods. Two studies have investigated pharmaceutical concentrations in SPM. Mean concentrations of pharmaceuticals in SPM (more than 0.7 µm) from the Long Island Sound Estuary ranged from 7 to 44 ng g<sup>-1</sup>. The pharmaceuticals detected in the SPM were either hydrophobic, for example, tamoxifen, or positively charged, for example, clarithromycin, and up to 47% of the total concentration was sorbed to the SPM [19]. Yang *et al.* [19] compared concentrations of pharmaceuticals in the sediment, SPM and the

colloidal and soluble phases in the Yangtze River Estuary and adjacent coastal areas. SPM concentrations were up to 5 times higher than that in the sediments. The colloidal phase had sorption affinities of 2–4 orders magnitude greater for pharmaceuticals than the SPM and contributed up to 45% of the target pharmaceuticals in the Yangtze system.

Pharmaceutical metabolites and transformation products can be more persistent and more toxic than the parent compound [50]. Twenty-one studies reported data for pharmaceutical transformation products in coastal waters with erythromycin-H<sub>2</sub>O the most commonly reported transformation product. Transformation products can be present in WWTP effluents and surface waters at concentrations equivalent to or exceeding the parent compound. For example, concentrations of metabolites of carbamazepine (carbamazepine epoxide), diclofenac (4'- and 5-hydroxy diclofenac) and atorvastatin (*o*- and *p*-hydroxy atorvastatin) in wastewater discharged into the Oslofjord were present at higher concentrations than the parent compounds [51]. Similarly the concentrations of sulfonamide metabolites measured in Liaodong Bay, China were comparable to those of the parent compounds [34].

Pharmaceuticals have been detected significant distances from their source(s). Pharmaceuticals were detected at a reference site approximately 9 km downstream from the WWTP outfall in Halifax Estuary [52]. Similarly, pharmaceuticals in the Baltic Sea were detected 17 km downstream of WWTP outfalls [53]. Zhang *et al.* [54] detected antibiotics including erythromycin-H<sub>2</sub>O, sulfamethoxazole and trimethoprim (0.1–16.7 ng l<sup>-1</sup>) 400 km offshore of the coast of China.

#### (i) Seasonal trends

Identifying seasonal trends for pharmaceutical concentrations in marine and coastal waters is crucial for determining time periods during which sensitive ecosystems may be at greater risk from exposure [55,56]. To date only a handful of studies have investigated seasonal trends for pharmaceutical concentrations in the marine environment. Pharmaceutical concentrations in the Yangtze River and Pearl River Estuary were higher in the dry season than in the wet season [57]. Similarly, heavy rainfall events reduced pharmaceutical concentrations in Jamaica Bay, a wastewater impacted estuary [20]. Conversely, Zheng *et al.* [58] and Qi *et al.* [21] reported increased river water concentrations of antibiotics in China during the wet season and attributed the increased concentrations to increased runoff of veterinary medicines and decreased efficiency of WWTPs due to increased wastewater flow. Temporal trends in pharmaceutical concentrations were not observed in Southern California coastal waters with relatively constant year-round temperatures [59]. By contrast, Hedgespeth *et al.* [55] reported higher probability of detecting acetaminophen in seawater from Charleston Harbor, South Carolina during winter. Pharmaceuticals were transported further downstream when the Aura River (Finland) was covered by snow and ice with the spring snowmelt increasing the speed of transport [60].

Seasonal trends in WWTP effluent pharmaceutical concentrations have also been reported which will in turn influence seawater concentrations. For example, total concentrations of NSAID drugs and bezafibrate were 3–5 times higher in effluent in winter than in summer [60]. Reduced removal rates in WWTPs and in surface seawaters can occur during colder months due to lower temperatures and



Table 1. Summary of seawater and biota concentrations and marine ecotoxicology data for the human and veterinary pharmaceuticals most frequently detected in seawater (ww, wet weight; dw, dry weight).

pharmaceutical	class <sup>a</sup>	seawater		marine biota		marine ecotoxicology data		most sensitive endpoint reported [ $\mu\text{g L}^{-1}$ ]
		no. studies	concentration range [ $\text{ng L}^{-1}$ ]	no. studies	concentration range [ $\text{ng g}^{-1}$ ]	no. studies	organisms tested	
acetaminophen	analgesic	7	1.9–1952	1	65–115	1	mussels	feeding rate LOEC = 23
ibuprofen	analgesic	18	0.01–2370			2	algae mussels	biochemical responses 0.25
carbamazepine	anticonvulsant	18	0.4–1400	4	1.3–11	2	algae amphipods	21d <sup>b</sup> growth, NOEC = 1
erythromycin-H <sub>2</sub> O	antibiotic metabolite	9	0.1–1900	2	0.1–2			
clarithromycin	antibiotic	8	0.3–17.6					
norfloxacin	antibiotic	8	2.3–6800	3	370			
ofloxacin	antibiotic	7	3.5–5100	3	5–242			
roxithromycin	antibiotic	8	0.1–630					
sulfadiazine	antibiotic	10	0.4–71.8	3	2.7			
sulfadimidine	antibiotic	9	0.2–219	3	29.8–430			
sulfamethoxazole	antibiotic	18	0.6–765	2	20.1			
tetracycline	antibiotic	7	2.4–313	1	1.9	1	bacteria diatom	growth EC50 = 16000
trimethoprim	antibiotic	20	0.2–870	1	<4–9			
atenolol	anti-hypertensive agent	5	3.8–293	2	0.3–13			Feeding rate NOEC = 11
propranolol	anti-hypertensive agent	5	0.3–142	1	19–52	3	mussels	
gemfibrozil	hypolipidemic agent	11	1–758					
diclofenac	NSAID	11	0.6–843			7	algae amphipods copepods decapods diatoms mussels	biochemical responses 0.25
ketoprofen	NSAID	7	0.6–805					
naproxen	NSAID	8	1.1–130					
17 $\alpha$ -ethinyloestradiol	SERM	9	0.1–38	2	7.2–38	2	copepod echinoderm	development EC50 = 30.3

<sup>a</sup>Class descriptors as used in DrugBank (<http://www.drugbank.ca/>; [48]).

<sup>b</sup>Units are  $\text{ng g}^{-1}$  lipid.



resulting in lower rates of biological activity enhancing the persistence of pharmaceuticals in marine ecosystems [43]. Reduced sunlight levels during winter can inhibit removal of pharmaceuticals susceptible to photodegradation [60]. Snowmelt reduced pharmaceutical concentrations in effluent in Norway [61]. Seasonal trends in pharmaceutical usage should also be considered [62]. Antibiotic use patterns can be influenced by a number of factors. High antibiotic use in winter can be due to the inappropriate use for treating respiratory tract infections including the common cold and viral infections [63]. Anti-allergenic medicines may also have a seasonal profile. Wastewater concentrations of over-the-counter anti-allergenic cetirizine peaked in summer and followed the pollen season [64]. Certain disease-specific pharmaceuticals, such as antiviral drugs, will peak during disease outbreaks, as has been demonstrated for oseltamivir (Tamiflu) during the recent influenza A(H1N1)pdm09 outbreak in Europe [65].

### (b) Sediment data

Sediments are a reservoir for the accumulation of pharmaceuticals in marine ecosystems and can act as a secondary pollution source from which pharmaceuticals can be released by changes in environmental conditions such as salinity and pH [57]. Sediments can be resuspended during tidal changes and during storm events exposing marine biota to sorbed pharmaceuticals. Twenty-two studies reporting sediment concentrations of pharmaceuticals for estuarine and marine environments have been published since 2000. In total, 62 pharmaceuticals and transformation products have been detected in marine sediments at concentrations up to 2 615 000 ng g<sup>-1</sup> wet weight (electronic supplementary material, tables S4 and S5). Excluding the extremely high concentrations of antimicrobials measured in marine shrimp aquaculture pond sediments [32], 17 $\alpha$ -ethinyloestradiol was the pharmaceutical measured in sediment at the highest concentration (129.8 ng g<sup>-1</sup>). 17 $\alpha$ -ethinyloestradiol was also the pharmaceutical most frequently detected with sediment concentrations reported for nine studies. All other pharmaceutical compounds were reported in a maximum of three studies. Data were most frequently reported for antibiotics (26 compounds) followed by anti-hypertensive agents (6). Marine sediment data for pharmaceutical transformation products and metabolites are currently almost non-existent with only four studies reporting concentrations of pharmaceutical metabolites in marine sediments. Langford & Thomas [51] reported concentrations of  $\alpha$ -hydroxy metoprolol (1–3 ng g<sup>-1</sup>) and simvastatin hydroxy carboxylic acid (2–4 ng g<sup>-1</sup>) in sediments collected from Oslofjord in Norway. Erythromycin-H<sub>2</sub>O was reported in San Francisco Bay (3.4 ng g<sup>-1</sup> dw) [66] and in the Pearl River Estuary, China (0.7–14 ng g<sup>-1</sup> dw) [57]. Only nine of the 22 studies analysed both seawater and sediment samples.

### (c) Factors influencing pharmaceutical concentrations in seawater and sediment

Factors reported to increase concentrations of pharmaceuticals in seawater and sediment include proximity to WWTP outfalls [67,68], higher effluent outflows [69], size of the urban area and population [11,70,71], the number of rivers discharging into coastal waters [70], the type of wastewater treatment [19], low mixing and dilution rates for WWTP

effluents [72], the hydrodynamic flushing and residence time for confined water bodies [61,73,74], the type, scale and density of animal husbandry [34,58] and proximity to aquaculture [74,75]. Higher concentrations of pharmaceuticals have been measured in estuaries during low and incoming tides [76]. Re-suspension of sediments during weather events including monsoons and during incoming tides can increase surface water concentrations of pharmaceuticals. Stratification of pharmaceuticals in the water column with higher concentrations being measured at the surface has been reported in the Long Island Sound Estuary [19] and in Victoria Harbour, Hong Kong [77]. Local conditions may inhibit wastewater treatment resulting in higher surface water concentrations. For example, Arctic permafrost conditions reduce the efficiency of WWTPs [78].

### (d) Marine biota

Data for accumulation of pharmaceuticals in marine biota are scant most probably because of the lack of reliable analytical methods for these challenging analytical matrices [66]. Fourteen studies were identified reporting data for concentrations of pharmaceuticals in finfish, crustaceans and shellfish (electronic supplementary material, table S6). Ten of these studies reported results for filter-feeding marine shellfish and five for marine finfish. Tissue concentrations of 60 pharmaceuticals and seven metabolites have been reported with antibiotics being the most frequent class reported (38) followed by anti-hypertensive agents (6). Carbamazepine, ciprofloxacin and enrofloxacin were the most frequently reported compounds each being reported in four studies. Only three studies reported concentrations for pharmaceutical transformation products including erythromycin-H<sub>2</sub>O, salicylic acid and metabolites of venlafaxine [62,66,79]. Higher concentrations of venlafaxine metabolites than parent compound were detected in mussels (*Mytilus galloprovincialis*). As some marine organisms also metabolize pharmaceuticals [80], a wide range of metabolites could potentially be present.

Marine organisms can be exposed to pharmaceuticals over widespread geographical areas. The anti-depressant sertraline was detected at 43 of 68 mussels sampling stations along the California Coast [81]. Antibiotics were detected in 142 out of 190 mollusc samples collected from nine cities along the Bohai Sea in China [82]. Detectable concentrations of pharmaceuticals were measured in wild seafood samples purchased from Czech supermarkets including squid caught in the Eastern Central Pacific, herring from the Atlantic Northeast and shark from the Eastern Central Atlantic [83].

Pharmaceuticals have been detected in marine organisms despite not being detected in water or sediment. Ranitidine, sertraline and enalapril were detected in mussels from San Francisco Bay but not in seawater [66]. Diazepam was detected in all liver samples of hornyhead turbot but only infrequently detected in sediments near wastewater outfalls in the Southern Californian Bight [84]. Fluoroquinolone antibiotics were detected less frequently in water than in fish from six sampling sites in two marine aquaculture regions of the Pearl River Delta, China [74].

Pharmaceutical uptake in marine organisms is compound, species and body-tissue specific. Oxytetracycline preferentially accumulated in the viscera and oxolinic acid in the gills of *Mytilus edulis* [85]. Concentrations of fluoroquinolones antibiotics in fish from marine aquaculture regions of the Pearl River Delta were higher in liver tissue than in muscle tissue

[74]. Fluoxetine tissue concentrations in *Mytilus galloprovincialis* followed the order digestive gland > gills > mantle/gonads [86]. Li *et al.* [82] reported differences in uptake of antibiotics between mollusc species harvested from the Bohai Sea, China. In some situations, gender may also influence uptake of pharmaceuticals by marine organisms. Higher concentrations of diazepam were measured in male than female *Pleuronichthys verticalis* (hornyhead turbot) [84]. These preferential uptakes have implications for ecotoxicological impacts and human exposure to pharmaceuticals via consumption of seafood.

Field data for bioaccumulation of pharmaceuticals in marine organisms is limited. Field-derived bioaccumulation factors (BAFs) for pharmaceuticals in mussels from San Francisco Bay included dehydronifedipine (290–764), carbamazepine (90–322), diphenhydramine (118–218), triamterene (57–71) and erythromycin-H<sub>2</sub>O (11–54). The BAFs varied between sites by up to a factor of 7 [66]. Bioconcentration factors (BCFs) ranged from 1300 to 1500 for uptake of 17 $\alpha$ -ethinyloestradiol by mussels (*M. galloprovincialis*) harvested from Venice Lagoon, Italy [87]. Field-derived BAFs for antibiotics ranged from 0 to 11 000 in shellfish collected from the coastal environment of Dalian in China. Based on the average BAFs, the authors concluded that sulfamethazine, sulfamethiazole, sulfamonomethoxine and doxycycline are potentially bioaccumulative and that sulfadiazine, sulfamer, sulfamethoxypyridazine and chloramphenicol are bioaccumulative in shellfish [88].

The uptake of pharmaceuticals by marine bivalves has been investigated using laboratory assays. Maximum BCF values in mussels of 100 were reported for tetrazepam and 51 for diazepam [89] and ranged from 200 to 800 for fluoxetine [86]. BAFs for diclofenac and propranolol in mussels (*Mytilus edulis*) ranged between 10 and 180 [90] and from 0.12 to 2 for oxytetracycline and from 0.27 to 0.55 for oxolinic acid [85]. No studies could be found reporting BCFs or BAFs for the uptake of pharmaceuticals by marine finfish.

Only one study has reported pharmaceutical concentrations in higher trophic level marine organisms. Federova *et al.* [83] reported a flumequine concentration of 2.9 ng g<sup>-1</sup> in an Eastern Central Atlantic shark sample. It is probable that trophic transfer of pharmaceuticals to top level predators including sharks, dolphins and whales is occurring in coastal ecosystems. Six anti-depressants and ethinyloestradiol were measured at trace concentrations (below quantitative limit to 4 ng ml<sup>-1</sup>) in plasma from bull sharks (*Carcharhinus leucas*) caught in the Caloosahatchee River, a wastewater impacted freshwater tributary of Florida's Charlotte Harbour [91]. The personal care product triclosan has been detected in plasma from wild Atlantic bottlenose dolphins (*Tursiops truncatus*) [92] and UV filters have been detected in Franciscana dolphins (*Pontoporia blainvillei*) [93]. Coastal avian species that feed on fish and shellfish may also be chronically exposed to pharmaceuticals.

## 4. Biological impacts in marine organisms

### (a) Marine ecotoxicology studies

While the body of work on the aquatic ecotoxicology of both human and veterinary pharmaceuticals is steadily growing, there is currently minimal data on the toxicity of pharmaceuticals to marine organisms. Only one study reporting field ecotoxicity data for marine organisms could be found. Exposure of benthic microalgal communities in the North Inlet Estuary (USA) to the antimicrobial tylosin in sediments

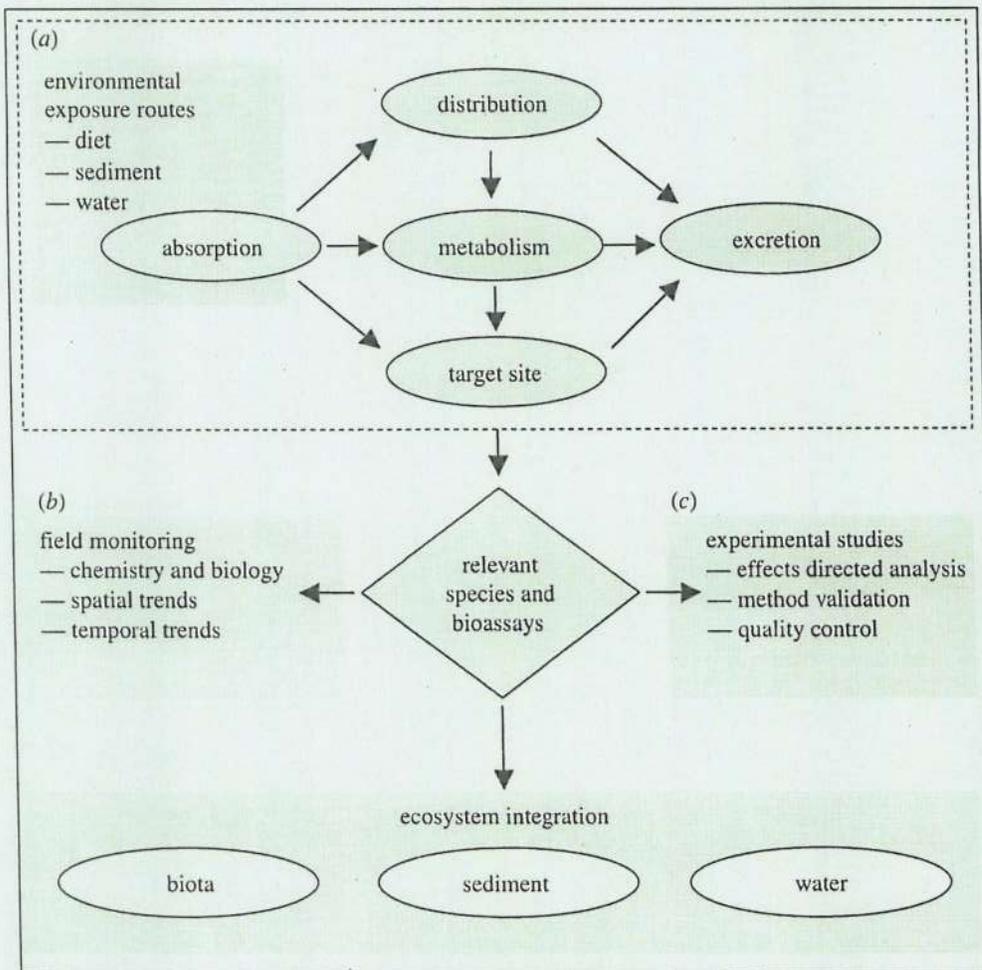
resulted in reduction of microalgal biomass and primary productivity and retarded diatom growth [94]. Laboratory ecotoxicity data could be found for 22 compounds and for the majority of compounds only one or two studies have been undertaken using marine organisms (electronic supplementary material, table S7). Fluoxetine was the exception, with marine ecotoxicity data reported in seven studies. Marine ecotoxicity laboratory data could be found for only seven of the 20 pharmaceuticals most frequently reported in seawater highlighting the current gap between researchers focusing on environmental presence and researchers focusing on ecotoxicity (table 1). Only one of these studies investigated the toxicity to sediment dwelling organisms [95]. A limited range of marine organisms have been tested to date including primary producers (e.g. microalgae and diatoms), primary consumers (e.g. bivalve molluscs and copepods) and consumers (e.g. crustaceans and fish). It is of great concern that in most studies nominal rather than measured pharmaceutical exposure concentrations were used.

Despite the limited number of studies, a wide variety of adverse effects have been reported for marine organisms with the effects being both test species and pharmaceutical specific. Examples of reported adverse effects for analgesics include reduced feeding rates [96], impacts on survival [97], reduced mussel byssus strength [90] and changes in immune response [96] and biochemical markers [98]. Studies have tended to focus on endpoints related to the therapeutic mode of action of the pharmaceutical. For example, reduced survival and developmental effects have been reported for anti-cancer drugs whereas studies on anti-depressant drugs have focused on neurobehavioural endpoints and spawning [99,100]. The reported no observable effect concentrations (NOECs) and lowest observable effect concentrations (LOECs) ranged from several orders of magnitude above environmental concentrations to comparable to reported environmental concentrations. For example, despite the NOECs for diclofenac for effects on byssus strength and oxidative stress in mussels of 1000  $\mu\text{g l}^{-1}$  [101], transient tissue-specific changes were reported after a 7 day exposure to 0.25  $\mu\text{g l}^{-1}$  diclofenac [98], a concentration well within the range reported in seawater (table 1).

Pharmaceuticals are present in marine ecosystems as mixtures complicating risk assessments. These complex mixtures may contain a wide variety of pharmaceuticals and other contaminants as well as a number of compounds from the same class (e.g. quinolone antibiotics) or with similar modes of action (e.g. non-steroidal anti-inflammatories) [102]. Additive effects have been reported for mixtures of pharmaceuticals on marine organisms. DeLorenzo & Fleming [103] investigated the toxicity of six pharmaceuticals and personal care products to the marine phytoplankton species *Dunaliella tertiolecta* both singly and in binary mixtures and reported additive toxicity for a mixture containing simvastatin and clofibrac acid. As mixture toxicity effects including synergistic effects have also been reported for freshwater organisms and cell lines [104,105], NOECs and LOECs derived from single substance testing may not be sufficient for deriving environmental quality standards [106].

There is a need to assess the impacts of pharmaceuticals on marine food webs. Marine food webs could either be directly affected through bioaccumulation of pharmaceuticals in the food chain to toxic levels or indirectly through the loss of a key species particularly sensitive to pharmaceuticals. The impacts of pharmaceuticals on primary producers such as phytoplankton is a key concern for marine ecosystems due





**Figure 1.** Adverse outcome pathways of chemicals fundamentally reflect patterns of absorption, distribution, metabolism, excretion and target sites in either acute or chronic exposure scenarios pertinent to marine contaminant monitoring. (Adapted from Hutchinson *et al.* [113].)

to the potential follow on effects on nutrient cycling and availability of food for other organisms [103]. Similarly, endocrine disrupting compounds which impact growth and reproduction in fish have the potential to affect predator and prey species [107].

### (b) Antibiotic resistance

Exposure of microorganisms to sub-lethal concentrations of antimicrobial compounds including antibiotics can induce antibiotic resistance. The rapid development of antibiotic resistance in bacteria is considered to be a global health security emergency and attention is being focused on mechanisms of transfer of antibiotic-resistant bacteria between species and identifying aquatic environmental reservoirs [108]. As high rates of horizontal gene transfer have been reported for marine bacteria [109], the contribution of contaminants in the marine environment to induction of antibiotic resistance and pathways for dispersal of clinically relevant antibiotic-resistant pathogens warrant further investigation. The development of antibiotic resistance in marine bacteria has been linked with wastewater discharges and the use of antibiotics in aquaculture [33,58]. Widespread antibiotic resistance has been reported in fish, marine mammals and seabirds living in coastal waters including in the North Eastern United States [110]. Higher prevalence of antibiotic-resistant strains of bacteria has been reported for marine wildlife populations exposed to sewage [111] and there is evidence to suggest that the antibiotic-resistant bacteria present in seabirds are of human origin [112]. The presence of antibiotic resistance

genes in marine ecosystems may be an indicator of ecological shifts occurring due to the presence of pharmaceuticals [113].

## 5. Data gaps and priorities for future research

This review has highlighted that human and veterinary pharmaceuticals and their transformation products (including metabolites) are present in coastal ecosystems. Occurrence data for the marine environment are only available for a tiny fraction of the large number of pharmaceuticals currently in global use. There are extremely limited laboratory ecotoxicology data for the impacts of pharmaceuticals on marine organisms and a marked lack of field data. As for other ecosystems, a forward-looking prioritization approach is needed for the marine risk assessment of both generic and novel prescription pharmaceuticals. For example, such an approach has been successfully used for Tamiflu that involved defining both the predicted exposure concentration ( $PEC_{\text{marine}}$ ) and predicted no-effect concentrations ( $PNEC_{\text{marine}}$ ) to provide a prospective risk assessment [8]. For the  $PNEC_{\text{marine}}$  to be reliable, it is important to consider the mode of action of the pharmaceutical, for instance, through the evaluation of Adverse Outcome Pathways in freshwater organisms and to extrapolate this to marine species [114] (figure 1). An Adverse Outcome Pathway is a conceptual framework for the link between exposure, the interaction of a contaminant at the molecular level within a cell and an adverse outcome or toxicological endpoint at the individual or community level.

Mechanisms for the increased sharing of data also need to be developed and a number of schemes have been developed in Europe (see the Swedish scheme [www.fass.se](http://www.fass.se) and <http://www.lif.se/default.aspx?id=29916> and the Norman network's EMPODAT Database [www.norman-network.net/empodat](http://www.norman-network.net/empodat)) and by individual companies through their Material Safety Data Sheets for specific pharmaceuticals. More widely, Daughton [56] recently proposed the development of a database on pharmaceutical occurrence in the environment, contributed to and curated by the wider science community.

The monitoring of prioritized pharmaceuticals and relevant metabolites in coastal environments should be considered as complementary to prospective risk assessments and include both dissolved and particulate fractions. In Europe, the Water Framework Directive (WFD; Directive 2000/60/EC) covers both freshwaters and transitional waters (the estuarine and coastal area up to one nautical mile, or 1.85 km, from the shore). Two hormones (17 $\alpha$ -ethinyloestradiol and 17 $\beta$ -oestradiol) and diclofenac have been placed on a watch list for emerging pollutants under the WFD. In a global context, it would be prudent to develop a monitoring suite of priority pharmaceuticals and transformation products that can be used in conjunction with biological assays to identify marine environments at risk from major centres of pharmaceutical inputs (e.g. WWTPs from megacities, intensive areas of aquaculture and pharmaceutical manufacturing industries).

As highlighted in reviews for pharmaceutical concentrations in freshwater [1] there is a marked absence of data for pharmaceuticals in marine environments in many regions (notably Africa, South America and small island nations in Oceania). These data gaps could easily be overcome by collaboration between well-resourced groups, with access to appropriate technology and validated analytical methods in developed countries, and local scientists in developing countries, at the same time providing valuable scientific and technical training.

The majority of data reported to date for pharmaceutical concentrations in marine organisms are for antibiotics used in aquaculture. In contrast, there are limited data for the accumulation of other classes of pharmaceuticals, their metabolites and transformation products in marine organisms. Further research is required to identify appropriate analytical methods for risk assessments for fish and shellfish to ensure that potentially reversible pharmaceutical metabolite conjugates are accounted for.

There are insufficient data on the potential for impacts on higher trophic levels, either through trophic transfer of pharmaceuticals or indirect effects, such as limited availability of food, due to impacts on lower trophic levels including algae. For high priority pharmaceuticals, it would be desirable to extend the environmental assessment to include fish-eating birds and mammals as recently illustrated by Murray Smith *et al.* [115].

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## IMPACT OF PHARMACEUTICAL WASTES ON HUMAN LIFE AND ENVIRONMENT

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### ABSTRACT

Now days, concerns about the occurrence and fate of active pharmaceutical ingredients, solvents, Intermediates and raw materials that could be present in water and wastewater including pharmaceutical industry waste water have gained increasing attention. Traditional wastewater treatment methods, such as activated sludge, are not sufficient for the complete removal of active pharmaceutical ingredients and other wastewater constituents from these waters. Environment and health are directly or indirectly affected by pharmaceutical effluents especially in the vicinity of pharma industrial zones. Though untreated or partially treated effluents released by pharma industries, drinking water sources are being polluted. Different classes of pharmaceutical compounds like analgesic, antidepressant, antihypertensive, contraceptive, antibiotic, steroids and hormones etc. have been detected in water samples from mg/L to µg/L range. Though the detected amounts are very minute but highly toxic for human, animal and aquatic lives. There is a need of regular monitoring of concentration of pharmaceutical compounds in pharmaceutical effluents entering into drinking water sources in order to save environment as well as living form of lives from health hazards. The present paper highlights such toxicity, health risk and assessment of environmental hazards due to pharmaceutical pollutants.

**Key words:** Pharmaceutical effluent, Industrial wastewater, Health Hazards.

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### INTRODUCTION

Pharmaceutical compounds are being used for several beneficial purposes in modern society but simultaneously pharma industries are releasing very toxic contaminants in the environment directly or after chemical modifications.<sup>1</sup> Moreover, pharmaceutical compounds may enter the environment by different routes such as discharge of treated wastewater, seepage from landfills sites, sewer lines, runoff from animal wastes etc.<sup>2,3</sup> Even though various physical and biological processes occurring in aquatic ecosystem may cause reduction of many pharmaceutical compounds, trace concentrations of human and veterinary pharmaceutical compounds as well as their metabolites have been detected in different water bodies like surface water, groundwater and drinking water sources.<sup>4-6</sup> The pharmaceutical industry in India is the world's third-largest in terms of volume and stands 14th rank in terms of value. It is growing at about 8 to 9 percent annually and is estimated to be worth 4.5 billion dollar. Different industries including pharmaceuticals, chemicals, paints etc. are speedily growing in India which disposes off their effluents into the streams either directly or after partial treatment.<sup>7</sup> It has been found that the pharmaceutical compounds reach the environment and can be considered as environmental pollutants. Several pharmaceutical production facilities were found to be sources of much higher environmental concentrations than those caused by the applications of drugs.<sup>8</sup> Generally, pharmaceutical industries generate a huge quantity of wastes during manufacturing and maintenance operations. Pharmaceuticals have been detected in wastewater treatment plant effluents and drinking water sources. Trace amount of pharmaceuticals in drinking water for longer duration may cause considerable adverse effects to human health and aquatic life, though concentrations of pharmaceuticals detected in drinking water (in nano gram per liter range) are several orders of lower magnitude than the minimum therapeutic dose.<sup>9</sup> There is currently no Bureau of Indian Standards (BIS)/ regulations limiting the levels of pharmaceuticals in wastewater or drinking water. However, the United States Environmental Protection Agency<sup>10</sup> has added four pharmaceutical compounds, which extensively used by human, to the most recent contaminant



candidate list (CCL 3) including three birth control substances and one antibiotic. The present paper highlights and reviews the impact of pharmaceutical effluents on nearby drinking water sources.

### General Environmental Pollutants i.e. Pharmaceutical Compounds

Pharmaceutical drugs being used for human as well as veterinary medicines are emerging as environmental pollutants. Different pharmaceuticals have been classified as Analgesics, Antibiotics, Antiepileptic, Antiseptics, Beta-blockers, Antihypertensive, Hormones, Contraceptives, Psychotherapeutics and Anti Virals.<sup>11</sup>

### Pharmaceuticals in the Environment

The environmental exposure routes of pharmaceuticals into the environment are manufacturing units and hospital effluents, land applications (e.g., bio solids and water reuse) etc.<sup>12</sup> However; sewage treatment services are not always successful in removing the active chemicals from waste-water. Consequently, pharmaceuticals find their way into the aquatic environment, where they directly affect aquatic organisms and can be incorporated into food chains. In a recent study, the extraordinarily high levels (mg/L) of several drugs were found in the effluents from local wastewater treatment plant near Visakhapatnam in India.

### Toxicity due to Some Pharmaceutical Compounds

Studies on antibiotics have shown that up to 95% of antibiotic compounds can be released unaltered into the sewage system. Moreover, higher concentrations of antibiotics can lead to change in microbial community structure and ultimately affect food chains. Non-steroidal anti-inflammatory drugs (NSAIDs), like ibuprofen, naproxen and diclofenac are widely being used and consequently are frequently detected in sewage, surface water and may be found in ground water system. Ibuprofen, ketoprofen, naproxen, indomethacin, diclofenac, acetyl salicylic acid and phenazone have been found in surface water system. However, diclofenac, ibuprofen and propyphenazone are the most commonly found drugs in the water bodies after clofibrac acid. Moreover, diclofenac has been proven to be highly toxic for vultures and cattle's.<sup>13</sup> NSAIDs like ibuprofen, naproxen and aspirin are the most commonly used drugs, which are usually found in effective quantities in municipal effluents.<sup>14,15</sup>

### Properties of Pharmaceutical Effluents

Many pharmaceutical industries are responsible to generate toxic effluent as a consequence of their operation. The waste water generated from these industries possess solids, biodegradable and non degradable organic compounds etc. Pharmaceutical effluents offer basic information about the reliability of the aquatic habitat in rivers and streams, into which they are discharged. The physico-chemical analysis of the effluents should indicate that most of these industries obey the standard guidelines of Federal Environmental Protection Agency (FEPA).<sup>10</sup> An important pollution index of industrial wastewaters is the oxygen content in chemical oxygen demand (COD) and biological oxygen demand (BOD), where the nutrients status are measured in terms of amount of nitrogen and phosphorus in waste water. Besides this, other significant water quality parameters include pH, temperature and total suspended solids (TSS).<sup>16</sup> However; pharmaceutical effluents are also categorized by their unusual turbidity, conductivity, COD, TSS and total hardness.

### Pharmaceuticals Analysis in Drinking Water

The mystery of pharmaceutical occurrence in drinking water has particularly concerned the public health. While unpleasant human health results from the existing levels of drugs and pharmaceuticals in drinking water are highly unlikely, the resulting impacts to aquatic ecosystems are more dangerous. Moreover, pharmaceuticals have been detected in waters for more than four decades. In the past decade, the number of papers on the analysis of drugs or pharmaceuticals in drinking water sources has increased considerably.<sup>2-5</sup>



In a monitoring study, out of fourteen pharmaceutical drugs analyzed, some pharmaceuticals like acetaminophen (detection frequency 0.32%), codeine (0.16%), p-xanthine (0.08%), sulfamethoxazole (0.41%), caffeine (0.24%), carbamazepine (1.5%) and trimethoprim (0.08%) have been detected at concentrations more than or equal to detection limits of selected methods. Besides, detection frequencies of pesticides (33%) and trihalomethanes (28%) in the same sources were reported considerably higher<sup>17</sup>. The pharmaceuticals have been identified in water cycle at trace levels by advanced analytical techniques and instrumentation. Several reports have confirmed the presence of pharmaceuticals in effluents of pharma industries and in municipal wastewaters and these have been recognized as a major source of drugs and pharmaceuticals in drinking water. Most of the research work has been performed on the analysis and detection of pharmaceutical in drinking water samples in developed countries including USA, Japan, the Republic of Korea and some countries in Europe.<sup>9</sup>

#### Health Risk of Pharmaceutical Effluents

The long term exposure of lower concentration of complex pharmaceutical mixtures on stream biota may result in acute and chronic damages<sup>18,19</sup>, behavioral changes<sup>20,21</sup>, accumulation in tissues<sup>22</sup>, reproductive damage<sup>23</sup> and inhibition of cell proliferation.<sup>24</sup> Several studies have demonstrated that fish exposed to wastewater effluents can exhibit reproductive abnormalities. Moreover, fish exposed to trace levels of birth control pharmaceuticals in the range of concentrations found in the environment show dramatic decreases in reproductive success, suggesting population level impacts are possible.<sup>25</sup>

#### Assessment of Environmental Hazard

Globally, the detection of waste pharmaceuticals in the environment creates the risks, which are associated with their introduction into human, aquatic life and wildlife and is becoming a serious problem equally for both regulators and the pharma industry. Significant success on this issue is simply not achievable with the currently limited state of knowledge on environmental transport, fate, and effects of pharmaceuticals. There is need to take into consideration the possible growing effects of different drugs affecting the same receptors<sup>12</sup>. Risk assessment of the pharma chemicals involves the detection of the inherent hazards at each stage and an estimation of the risks due to these hazards.

#### CONCLUSION

Currently, pharmaceutical compounds are being merged into the environment in extremely large quantities regularly and present system of regulations of their release is not able to control the untreated or partially treated pharma effluents. The impacts of drugs are entering into and occurring on ecosystems, biota and humans. The side effects on human, aquatic and animal health need to be investigated through thorough safety and toxicological studies. Sincere efforts are required to reduce the problem along with some adequate regulations to monitor or to control them. Water quality guidelines enforced in India needs to include analysis of most commonly used pharmaceutical compounds in drinking water sources. Moreover, the latest remedial measures need to be adopted at large in effluent treatment plants of pharmaceutical industrial units to check long term environmental and health hazards.

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ANALYSIS

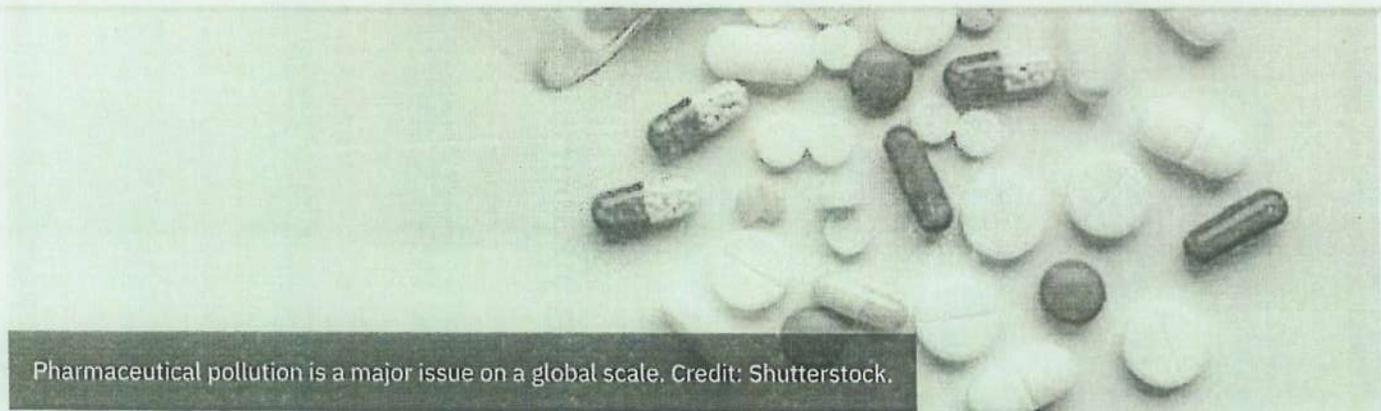
# Pharma and the environment: pollution continues despite public pressure

By Allie Nawrat | 02 Oct 2018 (Last Updated January 27th, 2020 05:10)

The negative impact of the production of pharmaceutical products on the natural environment is well known. However, this remains largely unregulated, meaning the extremely toxic impact it has on both animals and humans continues with no clear end in sight.



## PHARMACEUTICAL TECHNOLOGY



Pharmaceutical pollution is a major issue on a global scale. Credit: Shutterstock.



Over the past 30 years, international organisations and the pharmaceutical industry have begun to notice that the detrimental impact pharma products have on the environment on a global scale.



Pharmaceutical products enter the environment at various stages of their life-cycle, but particularly during the production phase. One of the main threats is that discharging antibiotics into the environment can promote the natural development of antibiotic-resistant pathogens that are harder to treat. Lord Jim O'Neill noted this trend in his 2016 UK government-funded independent Review on Antimicrobial Resistance.

Although it is a global issue, like other environmental issues, pharma pollution more directly and seriously affects those living near production plants whose water and food sources are contaminated with waste pharma products.



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Health Care Without Harm (HCWH) Europe runs the Safer Pharma campaign to raise awareness of the negative relationship between pharma and the environment and challenge the healthcare industry to clean up its production.

“The production of both active pharmaceutical ingredients (APIs) and finished dose antibiotics is concentrated in specific locations so the resulting point, source pollution, is in incredibly high concentrations and encourages the development of drug resistance,” says HCWH Europe pharmaceuticals policy officer Dr Adela Maghear. “This practice has a detrimental impact on vulnerable populations living near manufacturing facilities and wastewater treatment plants in these countries.”



The pollution of pharma products into the environment also adversely affects animals, particularly fish living in contaminated water. For example, a report published in science journal Nature in 2009 noted that 'many of Europe's rivers are home to male fish that are 'intersex' and so display female sexual characteristics, including female reproductive anatomy. Some males also produce vitellogenin, a protein normally found in eggs that can be induced in males by hormone exposure'.

Another large study of this problem in 2004 by the UK government's Environment Agency found that 86% of male fish sampled at 51 sites around the country were intersex." This phenomenon is blamed upon pollution of the contraceptive pill and its API, ethynyl oestradiol.

## Reforming the relationship between pharma and the environment

This awareness has led to a number of initiatives to try to better understand the consequences of pharma production on the environment and how this can be mitigated.



Poll |

**In your opinion, which of the following is a potential barrier to widespread adoption of sustainability principles in tourism activities?**

*Please rank, with 1 being the most and 5 being the least relevant factor*

	1- Most relevant factor	2	3	4	5- Least relevant factor
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Consumer preferences	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
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Lack of regulation	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
Awareness	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>

Next

An early initiative was the European Commission's environmental risk assessment of pharma products (ERAPharm). Between 2004 and 2007, ERAPharm tracked the fate and effect of pharma products in the environment in order to educate and inform legislators. It primarily focused on three compounds: the  $\beta$ -blocker atenolol, fluoxetine, an anti-depressant, and the veterinary parasiticide ivermectin.

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# &A: SmartSense Sales Director Josh Griggs

08 Jun 2021

Backed by global internet of things (IoT) leader Digi International, SmartSense delivers IoT solutions for leaders in the retail pharmaceutical

In Europe, this was followed by, among others, commitments by the European Federation of Pharmaceutical Industries and Associations (EFPIA) to reduce the presence of pharmaceuticals in the environment.

Must Read



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Unfortunately EFPIA’s primary course of action seems to be to push the burden of responsible pharma disposal to patients, according to Maghear, ‘This moves focus away from the fact that pharmaceutical companies should be cleaning up their own production and supply chains and investing in biodegradable pharmaceuticals’.

She believes: “Solely focusing on one pathway, as the EFPIA declaration suggests, will not ensure long-term



protection of the environment.”

However, despite recognition of the destructive impact the pharma industry has on the environment, the US Food and Drug Administration and European Medicines Agency have not moved to include environmental standards in their good manufacturing practices guidelines.

In addition, there is a lack of legislation and regulation on a local, regional and global level focusing on reducing the negative impact of the pharmaceutical industry on the environment; for example, Maghear explains there is no legislation requiring pharma companies to report environmental incidents.

Non-governmental organisation (NGO) Changing Markets, which has organised awareness campaigns on the issue of pharmaceuticals in the environment agreed, telling The Bureau of Investigative Journalism in January: “There is a crying lack of transparency about pharmaceutical supply chains which means that we know practically nothing about where our drugs are made. This is a scandal and pharmaceutical companies will face increasing calls to do something about it.”

The main role of HCWH Europe’s Safer Pharma campaign, according to Maghear, is ‘to push the EU to be the first region to legislate on pharmaceutical pollution – leveraging health professionals’ leadership role in tackling this issue’. They have made some progress, however, there is a long way to go and environmental breaches continue to occur across the world.

## Case study: contaminated water in Hyderabad, India

In November 2016, German scientists found that all of the specimens collected from sampling sites in the direct environment of bulk drug manufacturing facilities in



Hyderabad and nearby villages, known as the Patancheru-Bollaram zone, India, were contaminated with antimicrobials.

They also found 95% contained worryingly high levels of bacteria and fungi resistant to antibiotic drugs.

These findings led the researchers to conclude: "Insufficient wastewater management by bulk drug manufacturing facilities leads to unprecedented contamination of water resources with antimicrobial pharmaceuticals, which seems to be associated with the selection and dissemination of carbapenemase-producing pathogens." The findings were published in the *Infection* journal in August 2017.

Hyderabad is where 50% of India's drug exports are produced – there are approximately 170 companies operating in the area – and India is the world's fifth largest producer of generic drugs.

A contributor to the study, German media company NDR, found that 19 companies operating in the area were suppliers of antibiotics to the European market.

This grievous level of pharma pollution exists despite NGO, governmental and judicial pressure on companies operating in the area to clean up their act. In 2009, the Patancheru-Bollaram zone was classified in India's national pollution index as 'critically polluted' and in 2016, the country's Supreme Court ordered pharma companies to implement a zero liquid waste policy.

Safer Pharma notes that 'contamination of water sources with antimicrobial drugs (combined with mass misuse of antibiotics and poor sanitation) has had grave consequences in India, where an estimated 58,000 newborns die from multidrug-resistant infections every year'. These figures are based on a research project by



Laximnarayan, Duse, Wattal et al published in The Lancet in November 2013.

The immense scale of the pollution problem from drug manufacturing has pushed Indian public health professionals, campaign groups and local people to call on the European Union (EU) to revise good manufacturing practices and include these considerations during factory inspections. The letter follows the EU's announcement that it had scrapped plans to clampdown on pharma pollution.

Campaigners hope that pressure from local groups directly affected by the pharma industry's pollution will persuade the EU to reverse its earlier decision and, along with the industry and other governments, fulfill its unmet promises to mitigate the environmental consequences of drug manufacturing.

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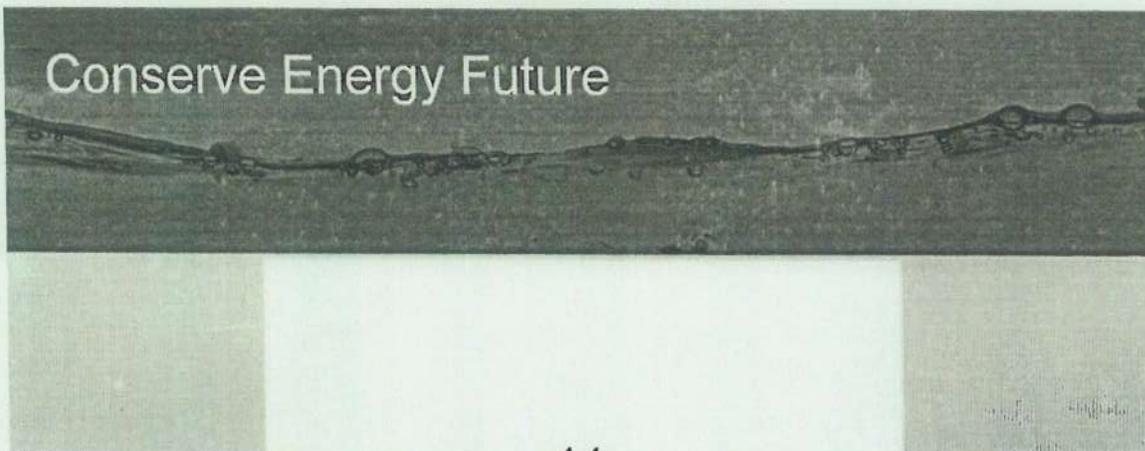
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## What is Pharmaceutical Pollution?

As the world's population continues to expand, pharmaceutical products – generally drugs and chemical-based care products have continued to become more prevalent. Their significance in modern life cannot be underestimated, but then again, their use and disposal is bringing about massive concerns in regard to environmental pollution.

A great example is the pollution of water systems, where pharmaceuticals are released into the environment and reach aquatic systems such as lakes, oceans, rivers, and groundwater. Pharmaceutical plants are often incapable of filtering out all the chemical compounds used in their manufacturing process and as such, the chemicals will seep into the surrounding freshwater systems and eventually into the oceans, lakes, streams, and rivers.



64

# SOURCES AND EFFECTS OF WATER POLLUTION



Many urban and rural sources of groundwater, although clean and pure enough to drink, for example, contain trace amounts of pharmaceutical ingredients, from birth control pills, antidepressants, painkillers, shampoos, anti-epileptics, caffeine, and many other pharma products.

Wastewater from pharmaceutical manufacturers is also sometimes discharged into open fields and nearby water bodies, thereby increasing the pharmaceutical waste or their by-product load in the environment, landfills, or dumping areas. **All this is basically known as pharmaceutical pollution, and this article looks at the causes, effects, and solutions to pharmaceutical pollution.**

[Contents \[show\]](#)

## Causes of Pharmaceutical Pollution

### 1. The Drugs We Use and How They are Ingested and Expelled!

Our bodies metabolize only a fraction of the majority of the drugs we swallow. The remaining part can be sweated out, but the large part is excreted from the body through urine or fecal matter, meaning the excreta will be part of the wastewater and eventually will be in the environment.



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## 2. Healthcare Institutions

Hospitals and nursing homes also contribute to pharmaceutical pollution. Hospitals, in particular, might be less of a problem as they have on-site pharmacies with arrangements to return the unused drugs to the manufacturers for credit or disposal.

Nursing homes, on the other hand, are particularly guilty of flushing medications down the toilet or drain, especially if a patient dies or is transferred to another facility, mainly because in most cases, they do not have a similar return policy with drug manufacturers as hospitals.

**See also** [Various Types and Serious Effects of Pollution You Can't Afford](#)

To Miss



The rule of getting rid of the opioid painkillers is to flush them down the drain as it is an acceptable option, encouraging them to flush down all their leftover medications.



### 3. Di

Altho Il guilty of  
contributing to pharmaceutical pollution. Some will dispose of the drugs  
in a landfill, and some will flush them, among many other ways of  
disposing of the drugs.

A US Geological Survey study revealed contamination levels downstream  
from two drug manufacturing plants in the state of New York, which were  
between ten and 1,000 times higher than those at comparable facilities in  
the country.

### 4. Agriculture and Agro-products

Like humans, not all the drugs fed to domesticated animals are  
metabolized by their bodies. For this reason, they excrete parts of the  
drugs that remain undigested. About 2 trillion pounds of animal waste,  
which is generated by large-scale poultry and livestock operations in the  
United States, was found to be laced with hormones and antibiotics fed to  
animals.

The drugs and hormones  
grow faster as well  
inevitably some of

ock and poultry  
s such, and  
leach into



groundwater or get into waterways and contribute to pharmaceutical pollution.

## 5. Human Domestic Drug Use and Disposal Behavior

We as consumers are responsible for a significant amount of the pharmaceutical and personal care products that end up in streams, groundwater, lakes, and rivers. It is not uncommon to find a home cabinet full of unused and expired drugs. The problem is that out of all these drugs, only a fraction is disposed of properly.

For instance, data collected in 2007 from a medication collection program in California, suggested that only about 50% of all medications, prescription and over-the-counter, were discarded properly. Even if that figure is a huge estimate, and the real proportion could be lower, the conclusion is that there is a lot of unused and mostly expired medication that potentially gets into the water systems.



A number of studies have indicated that Oestrogen and chemicals that behave like it, have a feminizing effect on male fish and can alter female-to-male ratios. Such Oestrogen can be found in birth control pills and postmenopausal hormone treatments.

The Potomac River, in the United States, is known to have several intersex fish, which are fish with both male and female characteristics, mainly because of the pollution of the river in different sections.

Because of the higher Oestrogen levels in the downstream water from the river, there are more female and intersex fish downstream from the plants that pollute it. Popular antidepressant medications have also been found concentrated in the brain tissue of fish downstream from wastewater treatment plants.

## 2. Disrupting the Normal Operations of the Sewerage Process

Antibiotics are wide  
that can disrupt the

contain material  
microbial ecology



of surface water. Antibiotics present in the sewage treatment systems can, therefore, inhibit the activities of the sewage bacteria, and therefore seriously affect the organic matter decomposition. Antibiotics can also be toxic to nitrifying bacteria in the wastewater treatment process.

See also Causes, Effects and Solutions of Agricultural Pollution on Our Environment 

### 3. Effect on Drinking Water

The chemicals present in these pharmaceuticals, find a way into waterways, after being excreted from the body or after being flushed down the toilet. Most municipal sewage treatment facilities do not remove these pharmaceutical compounds from your drinking water and as such, we end up consuming the same compounds.

They are found in very minimal concentration in rivers and streams as compared to the normal dose, but there is a growing concern that chronic exposure to these compounds could result in serious health issues. It is

also speculated that

could eventually cause



For instance, endocrine disruptors, which come from agricultural, domestic and industrial sources such as pharmaceuticals, disrupt biological processes like growth, development and reproduction, which are regulated by hormones. Also according to a 2006 research by Italian researchers, a combination of pharmaceutical compounds inhibits the growth of embryonic kidney cells in laboratory tests.

Researchers first identified trace amounts of pharmaceutical drugs in surface water and groundwater in the early 1990s, sounding alarm bells ever since.

#### 4. Long-term Effects on the Environment

Some pharmaceutical compounds last a long time in the environment and in water supplies. Once the concentration reaches a certain level, usually around one part per million, the chemicals begin to affect the environment. Some drugs, like antiepileptics, are persistent, with some being pseudo-persistent, meaning, they degrade eventually, but after quite some time.

This means they do not  
disappear after they are  
disposed of. Some

do not disappear after they are  
disposed of, meaning they can



bioaccumulate, enter a cell and move up food chains, becoming more concentrated in the process.

Surveys in Europe and the US, have found hundreds of these compounds in groundwater, sewage, surface water, wastewater from treatment plants and of course tap water. Polluted water from streams, lakes, rivers and other sources, will therefore eventually make its way into our bodies

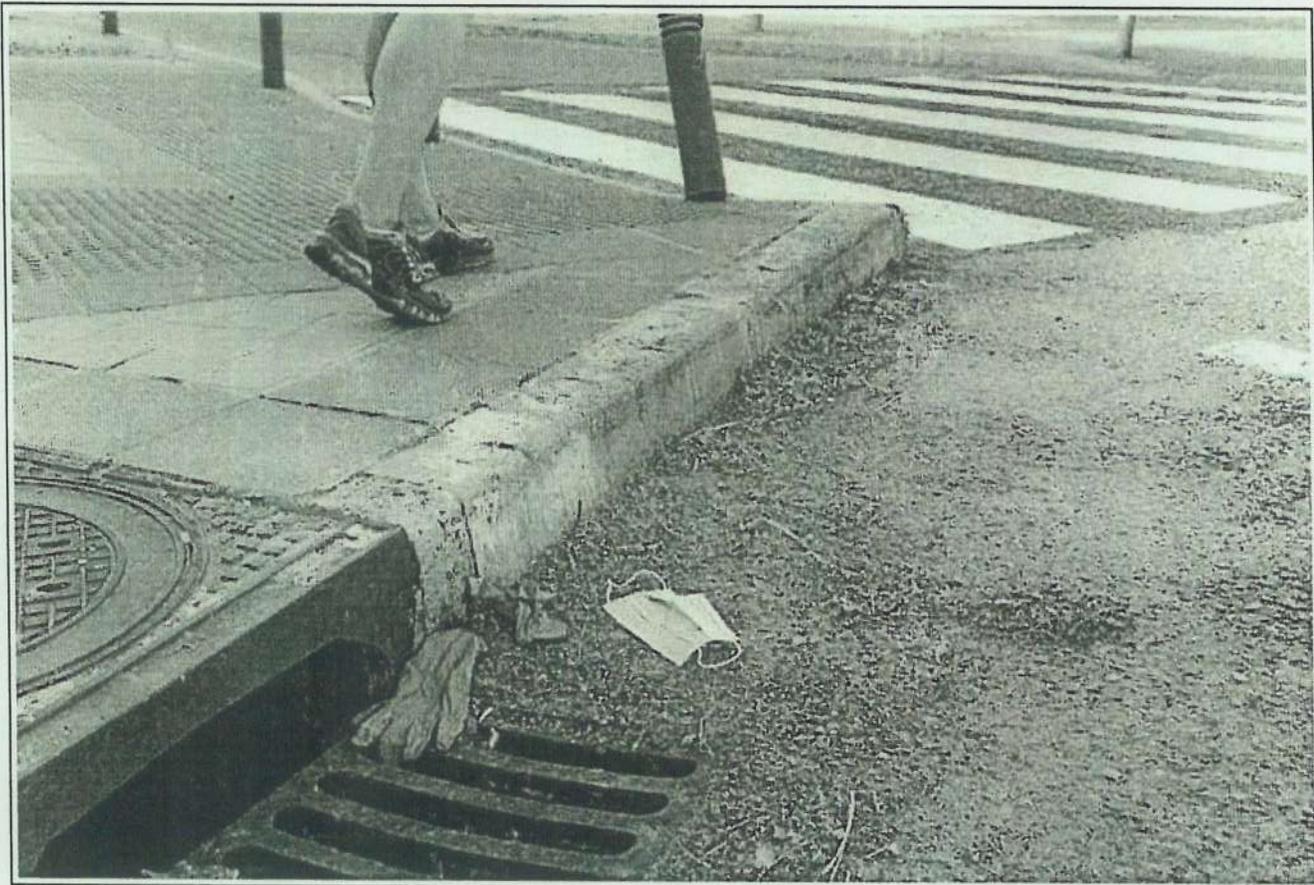


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### 5. AI

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Howe' used by drug  
manufacturing pollution. This is the conclusion drawn from studies in 2016  
and 2017, focused on antibiotic manufacturing pollution in India and  
China.

### 6. Effects on Wildlife

Pharmaceuticals, flushed into the environment by humans, or through the  
sewage are also affecting wildlife. These animals are consuming water that  
contains these particles, or are preying on fish which swim in such waters.

Studies on the effects of pharmaceuticals on wildlife are little and have not  
led to conclusive results, but it is believed that these effects will soon  
affect the natural world massively. The little known results have shown  
that antidepressants reduce feeding in starlings and a contraceptive drug  
is decreasing fish populations in lakes.



[See also](#) Air Quality Index: Categories and Types of Air Pollutants



## Solutions to Pharmaceutical Pollution

### 1. Proper Drug Disposal

The easiest, cheapest, and most effective solution to pharmaceutical pollution is keeping the drugs from reaching the waterways in the first place. We should invest in public education on the proper disposal of drugs, as part of the drug take-back programs.

This way, people will know how to properly get rid of old or expired medicine without contributing to pharmaceutical pollution. awareness can also create initiatives that mitigate the effects already caused by pharmaceuticals on the environment.

### 2. Tougher Regulations

If tougher regulations are in place, they would help limit large-scale medicine flushing in hospitals, nursing homes and other healthcare institutions. Tougher regulations can be installed by the nation or state's department of health, or by the national body that handles health matters.



The institutions would restrict themselves from disposing of the drugs without proper procedure and would also ensure their relationship with drug manufacturers is in a way that they can return the drugs if they are expired.

### 3. Additional Research Pertaining to the Potential Dangers of Pharmaceutical Pollution

More research is desperately required to assess the potential human effects of pharmaceutical pollution. It will also address the best methods for removing the compounds at treatment plants in a way that is not hazardous or dangerous to the environment in general. If a significant long-term risk to public health is identified, more aggressive efforts can then be taken to control the problem as required.

### 4. Limit Bulk Purchases

Another solution is to limit the bulk purchases of pharmaceuticals. The majority of institutions and individuals purchase them in bulk since large volumes attract discounts, which makes the overall price more attractive.

However, it gives rise to a situation where there are large bottles of unused pills which ultimately end up being flushed or disposed of in the wrong way. Limiting bulk purchases will ensure only the required amount is supplied and therefore, less pharma pollution.



## 5. Trashing is Better Than Flushing

Throwing unused medication into the trash leads to them being incinerated or buried in landfills. It is a better way of disposing them than flushing or pouring them down the drain. However, if you are to trash them, do it properly. Remove them from their packaging, crush them, and seal them in a plastic bag with water.

More to that, add sawdust, coffee grounds, or cat litter or any other material that is unappealing. Although this is not for environmental reasons, it cuts down the chances that a child or animal might ingest the contents.

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### About Rinkesh

A true environmentalist by heart ❤️. Founded Conserve Energy Future with the sole motto of providing helpful information related to our rapidly depleting environment. Unless you strongly believe in Elon Musk's idea of making Mars as another habitable planet, do remember that there really is no



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In a big setback to Hyderabad-based active pharmaceutical ingredients (APIs) maker Divi's Laboratories Limited, the US Food and Drug Administration (USFDA) has issued an import alert on the company's Unit 2 facility at Visakhapatnam, Andhra Pradesh, though with certain exemptions.

The latest action comes after Divi's management had submitted a 700-page response in the light of Form 483 observations issued by the US drug regulator in December 2016. On December 7, 2016, the USFDA inspection team issued a Form 483 with five observations citing lack of proper control ...

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June, 2022

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## ***Foreword***

Andhra Pradesh Pollution Control Board (APPCB), zonal office, Visakhapatnam has issued a notice (No. 2313/PCB/ZO-VSP/NIO/2022) on 27<sup>th</sup> May 2022 to all the marine discharge industries and CETPs to conduct monthly eco-toxicology tests on treated effluent, and trace metals and major organic compounds present in the treated effluent by CSIR-National Institute of Oceanography (NIO), Visakhapatnam. In this connection, M/s Divis Laboratories Limited has contacted CSIR-NIO, Regional Centre, Visakhapatnam to take up a study on monthly assessment of the eco-toxicity (bio-assay), trace metals and major organic compounds of the treated effluent from the guard ponds of M/s Divis Laboratories Limited to fulfil the specific condition of APPCB. After considering the proposal, CSIR-NIO has agreed to carry out the study on monthly assessment of the treated effluent for the above-mentioned investigations. CSIR-NIO has conducted first field campaign for the month of June on 25<sup>th</sup> June 2022 and treated effluent was collected from the guard pond No. 9. This report is the compilation of the data obtained for various investigations conducted on the treated effluent.

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## ***Executive Summary***

---

As part of the continuous monthly studies on the assessment of the quality of treated effluent of M/s Divis Laboratories Limited, the treated effluent was collected from the guard pond No. 9 in the Divis Laboratories Limited on 25<sup>th</sup> June 2022. This treated effluent was tested for its eco-toxicity, levels of trace metals and major organic compounds. A 4-day (96 hours) bio-assay experiment was conducted on the treated effluent using zebra fish following the method IS: 6582-1971 (Re-affirmed, 2003) as suggested by the CPCB. The results of the bio-assay experiment revealed that the eco-toxicity levels of the treated effluent collected from M/s Divis Laboratories Limited meet the CPCB standard of '90% survival after 96 hours in the 100% effluent' as the mortality of the zebra fish in 100% effluent after 96 hours is only 9.99%. Based on the survival rate of zebra fish at different concentrations of effluent, the median lethal concentration (LC50) is . Trace metal concentrations determined in the treated effluent are within the limits prescribed by CPCB for treated effluent of sea discharge. These results suggest that the treated effluent collected from the guard pond No. 9 on 25<sup>th</sup> June 2022 meets the CPCB norms for release in to the sea.

## 1. Introduction

Some of the coast-based industries discharge their treated effluent in to the sea through a designated marine outfall point after fulfilling the criterion set up by the central pollution control board (CPCB) and Andhra Pradesh state pollution control board (APPCB) for the treated effluent. APPCB has established a lock and key system for the guard ponds to release of treated effluent into the sea. There are 7 pharmaceutical industries (Andhra Organics Ltd., Aurobino Pharma Ltd., Lantech Pharmaceuticals Ltd., SMS Pharmaceuticals Ltd., Divis Laboratories Ltd., Hetero Drugs Ltd., Deccan Fine Chemicals India Pvt. Ltd.) and one text tile industry (Brandix India Apparel City Pvt Ltd) processing their effluent in the ETP (effluent treatment plant) and discharge the treated effluent in to the coastal waters of north Andhra coast (between Pydibhimavaram and Kesavaram). In addition, two CETPs (common effluent treatment plant), namely, Visakha Pharmacy Ltd. and Achyutapuram SEZ Ltd process the effluents received from various pharmaceutical industries in the CETP and discharge the treated effluent in to the sea. National Thermal Power Corporation and Rastriya Ispat Nigam Ltd. draw seawater for the cooling purpose the discharge the warm and high salinity water back to the sea.

Andhra Pradesh Pollution Control Board (APPCB), Visakhapatnam has issued a notice (No. 2313/PCB/ZO-VSP/NIO/2022) to all sea discharge industries on 27<sup>th</sup> May, 2022 and instructed to assess the quality of treated effluent on monthly time scales for a period of one year through the bio-assay experiments and the levels of trace metals and major organic compounds in the treated effluent by the CSIR-National Institute of Oceanography, Visakhapatnam. With reference to this, M/s Divis Laboratories Limited has approached CSIR-NIO, Visakhapatnam to carry out the above-mentioned studies on their treated effluent for the period of one year (from June 2022 to May 2023) on monthly time intervals. In this connection, CSIR-NIO has collected the treated effluent from the guard pond No. 9 M/s Divis

Laboratories Limited on 25<sup>th</sup> June 2022 and to carryout bio-assay experiment for four days using zebra fish and to determine the concentration levels of trace metals and major organic compounds present in the treated effluent.

### ***1.2 Objective:***

The main objective of this study is to assess the quality of treated effluent of M/s Divis Laboratories Limited through bio-assay test and concentration levels of trace metals and organic constituents present in the treated effluent, and to compare the results with the CPCB standards for compliance/non-compliance.

### ***1.3 Sample collection:***

A Niskin water sampler (10L, plate. 1.1) was used to treated effluent sample from guard pond No.9 of M/s Divis Laboratories Limited on 25<sup>th</sup> June, 2022 for dissolved oxygen (DO), biochemical oxygen demand for five days (BOD<sub>5</sub>), pH, dissolved inorganic nutrients and microbial community studies. Water samples were collected in pre-cleaned in white jerry cans (20L) for bio-assay studies and for filtration of samples for chlorophyll-a and total suspended matter.

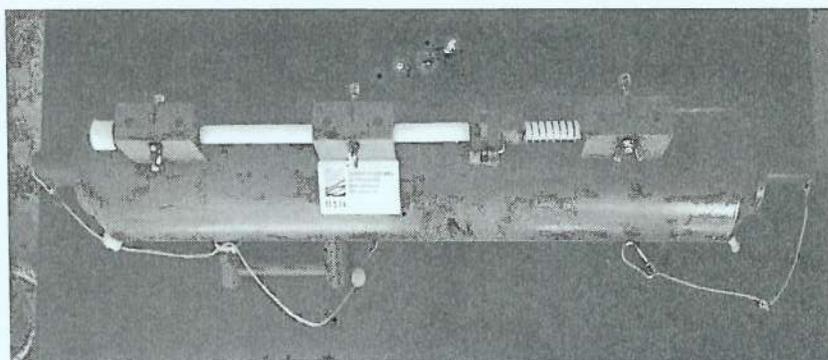


Plate 1.1: Niskin sampler (10L) used for collection of water samples

#### *1.4 Methodology*

The Physico-chemical parameters were analysed through the standard procedures following Carrit and Carpenter (1966), Grashoff (1974), Suzuki and Ishimaru (1990) and Grasso et al. (1992). The detailed methodology of each parameter is given below.

##### a) pH

pH of the treated effluent sample collected in air-tight glass bottle (60ml) was measured using Metrohm pH analyzer (Titrand 865). Standard buffer solutions (Merck, Germany) were used for calibration of the instrument. Based on the repeated analysis of aliquots of standards and samples, the precision of the analysis for pH is 0.002 units.

##### b) Dissolved Oxygen (DO)

Winkler's method was adopted for the determination of DO concentrations. A measured volume of effluent sample was fixed immediately after collection with the reagents Winkler's A (manganous chloride) and Winkler's B (alkaline potassium iodide). Standard titration with sodium thiosulphate was adopted for the analysis purpose. Concentration of DO was expressed in mg/l. The precision of analysis, expressed as standard deviation with this method was  $\pm 0.07\%$ .

##### c) Biochemical Oxygen Demand (BOD)

Samples for the determination of biochemical oxygen demand were collected in triplicate. The dissolved oxygen concentration was immediately determined using one of the triplicate samples according to Winkler's method. The remaining bottles were left for five days at 20°C in the BOD incubator. Dissolved oxygen in these samples was determined after fixing the samples on completion of five days incubation. BOD<sub>5</sub> was computed from the initial DO concentrations and expressed in mg/l.

d) Ammonium - Nitrogen ( $\text{NH}_4^+$  - $\text{N}_2$ )

Ammonical - Nitrogen in treated effluent sample was determined with the indophenol blue method using trione. Care was taken for the analysis of ammonium and ammonia free distilled water was used for analysis to avoid any contamination as ammonia is highly soluble in water. The absorbance of the coloured complex was measured at 630 nm in Spectrophotometer against a standard.  $\text{NH}_4$  - N is expressed in  $\mu\text{mol/l}$  and the precision of analysis, in terms of standard deviation, is  $\pm 0.02 \mu\text{mol/l}$

e) Nitrite - Nitrogen ( $\text{NO}_2^-$  - $\text{N}_2$ )

Nitrite was determined by the method of Bend Schneider and Robinson whereby the nitrite in water sample was diazotised with sulphanilamide and coupling with N-1-Naphthyl ethylene diamine dihydrochloride. The absorbance of the resultant azo-dye was measured at 543 nm against a standard solution. Concentrations of  $\text{NO}_2^-$  - N in seawater is expressed in  $\mu\text{mol/l}$ .

f) Nitrate - Nitrogen ( $\text{NO}_3^-$  - $\text{N}_2$ )

Nitrate in effluent sample was first reduced to nitrite using heterogeneous reduction by passing the buffered samples through an amalgamated cadmium column and the resultant nitrite was determined as above. The measured absorbance was due to initial nitrite present in the sample and nitrite obtained by reduction of nitrate in the sample. Necessary correction was therefore applied for any nitrite initially present in the sample. Concentrations of  $\text{NO}_3^-$  - N in seawater were expressed in  $\mu\text{mol/l}$ . The precision of analysis for both nitrite and nitrate, in terms of standard deviation, is  $\pm 0.02 \mu\text{mol/l}$

g) Phosphate - Phosphorus ( $\text{PO}_4^{3-}$  -P)

Inorganic phosphate was measured by the method of Murphy and Riley in which the samples were made to react with acidified molybdate reagent and then reduced using ascorbic acid. The absorbance of the resultant phosphorous molybdenum blue complex was measured at 880

nm against a standard. Concentrations of  $\text{PO}_4^{3-}$  - P in effluent samples were expressed in  $\mu\text{mol/l}$ . The precision of analysis, in terms of standard deviation, is  $\pm 0.01 \mu\text{mol/l}$

**h) Silicate - Silicon ( $\text{SiO}_4^{2-}$  - Si)**

Silicate - silicon was also estimated by reaction with acid - molybdate and ascorbic acid in the presence of oxalic acid. The interference of phosphate is prevented by addition of oxalic acid. The absorbance of the resultant silico - molybdenum blue complex was measured at 810 nm in Spectrophotometer against a standard. Concentrations of  $\text{SiO}_4^{2-}$  - Si in effluent sample was expressed in  $\mu\text{mol/l}$ . The precision of analysis, expressed as standard deviation, is  $\pm 0.02 \mu\text{mol/l}$

**i) Total suspended matter (TSM)**

One litre of effluent sample was filtered through pre-weighed Polycarbonate filter ( $0.47 \mu\text{m}$ ; Millipore) and after filtration the filter was dried for about 2 days at  $60^\circ\text{C}$ . The dried filter was weighed and noted down the reading. The filter was dried again and took the weight measurement. This procedure was continued until the weight loss of the filter due to drying is zero. The weight of the material retained on the filter was considered as TSM concentration and was expressed mg/L.

**j) Bio-assay test (Eco-toxicology test)**

The bio-assay test was performed following the CPCB standard method (IS:6582-2001) using zebra fish (*D. Rerio*) as test species. Bio-assay test was conducted on different effluent concentrations, such as 0% (control), 10%, 20%, 30%, 50%, 60%, 90% and 100% and the test was conducted for 4 days (96 hours.). Mortality of zebra fishes in different concentrations were noted down at regular time intervals of 1h, 6h, 12h, 24h, 36h, 48h, 60h, 72h, 84h and 96 hours. LDP line software was used to calculate the median lethal concentration (LC50) of treated effluent for 24h, 48h, 72h and 96 hours.

**k) Trace metals**

Trace metal concentrations in the treated effluent sample collected from the guard pond of the industry was filter through 0.22  $\mu\text{m}$  polycarbonate filter to remove the particles. The filter water was analysed for trace metals by Inductively Coupled Plasma – Mass Spectrometer (ICP-MS). Internal standards, such as Li, Sc, Ge, Y, In, Tb and Bi were added in the effluent sample and determined the concentrations of these elements along with other trace metals to monitor the performance of the ICP-MS instrument. International standard (NIST 1640a) was run to check the accuracy of the trace metal concentration. Calibration curve was established by running the standards of different concentrations (0.5, 1.0, 5.0, 25, 50 and 100 PPB) before the analysis of effluent samples. In most of the cases, the linear fit with a  $r^2$  value of 0.9999 was obtained.

About 100 ml of sample was sub-sampled into a pre-sterilized bottle for bacterial analysis. All samples were collected with precautions required for microbiological analysis, analyzed in the laboratory. Sample serially diluted to 3 times of  $10^{-1}$  to  $10^{-3}$  with sterile salt water. Heterotrophic bacterial counts were determined using R2A agar. Around 100  $\mu\text{l}$  of each serially diluted water samples are plated on R2A agar plates and spread with sterile glass rod and incubated at 37  $^{\circ}\text{C}$  for 48-72 hours. The colonies formed on the plates are counted using colony counter and represented as number of colony forming units per ml of water sample after considering dilution factor. Total coliform counts were obtained by plating water samples on MacConkey agar. The colonies formed on the plates are counted using colony counter and represented as number of colony forming units per ml of water sample after considering dilution factor. The colonies of pink-red colour and with bile precipitate are counted as ECLO on MacConkey agar plates. The colonies of colourless to pale pink are counted as EFLO on MacConkey agar plates. PALO counts were obtained by plating water samples on Cetrimide agar. The colonies exhibiting fluorescence at 250nm and a blue green pigmentation are considered as PALO. VLO counts were obtained by plating water samples on TCBS agar. The

colonies formed on the TCBS agar plates are counted as VLO. The colonies of yellow colour are counted as VCLO on TCBS agar plates. The colonies of bluish green colour are counted as VPLO on TCBS agarplates.

## 2. Results

### 2.1 Treated effluent characteristics

Treated effluent was tested for DO, BOD<sub>5</sub>, pH, TSM and dissolved inorganic nutrients and the results were provided in Table 2.1.

S. No.	Parameter	Concentrations	CPCB standard*
1	DO (mg/l)	5.49	-
2	BOD <sub>3</sub> (mg/l)	3.88	30
3	pH	7.455	6.0 – 8.5
4	Nitrate-N	0.8	-
5	Phosphate -P	1.2	5.0
6	Silicate -Si	8.4	-
7	TSM (mg/l)	77.3	100
8	Chl-a (mg/m <sup>3</sup> )		-

\*: as per Environment (Protection) Second Amendment Rules, 2021

Dissolved oxygen (DO) concentration of the treated effluent is 5.49 mg/l. BOD<sub>3</sub> of the effluent is 3.88 mg/l which is far below the standard limit of 30 mg/l set by CPCB. pH of the treated effluent is 7.455 and it is well within the CPCB limit of 6.0 - 8.5 (Table 2.1). Concentration of total suspended matter (TSM) is 77.3 mg/l and it is also within the limit of 100 mg/l set by CPCB. Dissolved inorganic nutrients such as nitrate and phosphate concentrations in the effluent are within the standard limits of CPCB.

Abundance (CFU/ml) of various bacterial populations in the effluent of M/s Divis Laboratories Limited is given in Table 2.2. Both ECLO (*Escherichia coli* like organism) and VCLO (*Vibrio cholerae* like organism) were not grown. Total viable count (TVC) was  $1.65 \times 10^5$  CFU/ml and it is within the range of the TVC found in the coastal waters off north Andhra coast ( $0.003 - 1.94 \times 10^5$  CFU/ml). Counts of VLO was found to be 130 CFU/ml in the treated effluent and it is also within the range EFLO values reported for north Andhra coastal waters in 2018 (1.0 – 295 CFU/ml). VPLO count found in the effluent (130 CFU/ml) is also considerably lower than the mean VPLO count found in the coastal waters of North Andhra Pradesh in 2018 (mean: 460 CFU/ml; range: 0-1168 CFU/ml).

**Table 2.2: Abundance of various bacterial populations in the effluent of M/s Divis Laboratories Limited**

Bacteria	Abundance (CFU/ml)
TVC	$1.65 \times 10^5$
ECLO	NG
EFLO	$19.3 \times 10^3$
VLO	$1.3 \times 10^2$
VCLO	NG
VPLO	$1.3 \times 10^2$

<b>TVC</b>	Total Viable Count
<b>ECLO</b>	<i>Escherichia coli</i> like organism Count
<b>EFLO</b>	<i>Enterococcus faecalis</i> like organism Count
<b>VLO</b>	<i>Vibro</i> like organism Count
<b>VCLO</b>	<i>Vibrio cholerae</i> like organism Count
<b>VPLO</b>	<i>Vibrio parahaemolyticus</i> like organism Count
<b>NG</b>	No Growth

## 2.2 Bio-assay test

Survival rate of zebra fish at various time intervals during the experiment period of 96 hours in different concentrations of treated effluent was given in Table 2.2

Effluent concentration of 0% represent the control and no mortality of zebra fish was observed in the control. The first mortality of zebra fish was observed in the effluent concentration of 50% in the last 12 hours of the experiment. In the 100% effluent concentration, the first mortality was observed in the first 6 hours of the experiment and 90% of the zebrafish were survived after the completion of the experiment (i.e., 96 hours) (Table 2.2).

**Table 2.2: Survival rate (%) of zebra fish at different time periods exposed to different concentrations of effluent**

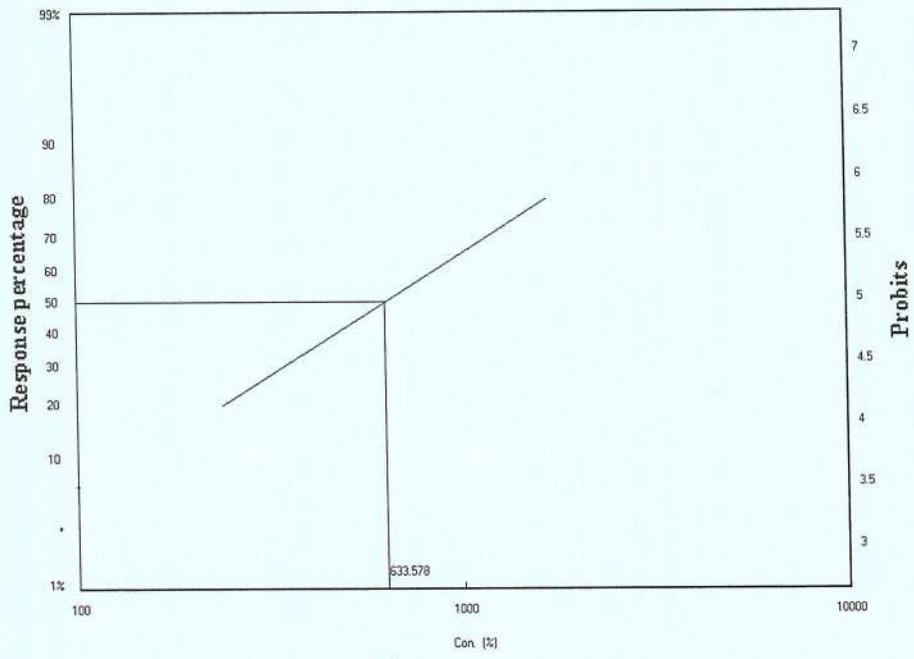
Exposure time	Effluent Concentration							
	Control	10%	20%	30%	50%	60%	90%	100%
1 hr	100	100	100	100	100	100	100	100
6 hr	100	100	100	100	100	100	96.66	96.66
12 hr	100	100	100	100	100	96.66	96.66	96.66
24 hr	100	100	100	100	100	96.66	96.66	93.33
36 hr	100	100	100	100	100	96.66	96.66	93.33
48 hr	100	100	100	100	100	96.66	93.33	93.33
60 hr	100	100	100	100	100	96.66	93.33	93.33
72 hr	100	100	100	100	100	96.66	93.33	90
84 hr	100	100	100	100	100	93.33	90	90
96 hr	100	100	100	100	96.66	93.33	90	90

Mortality rate of zebra fish (%) observed in the test concentrations of 0%, 10%, 20%, 30%, 50%, 60%, 90% and 100% during the exposure time of 24 h, 48 h, 72 h and 96 hours was given in the Table 2.3.

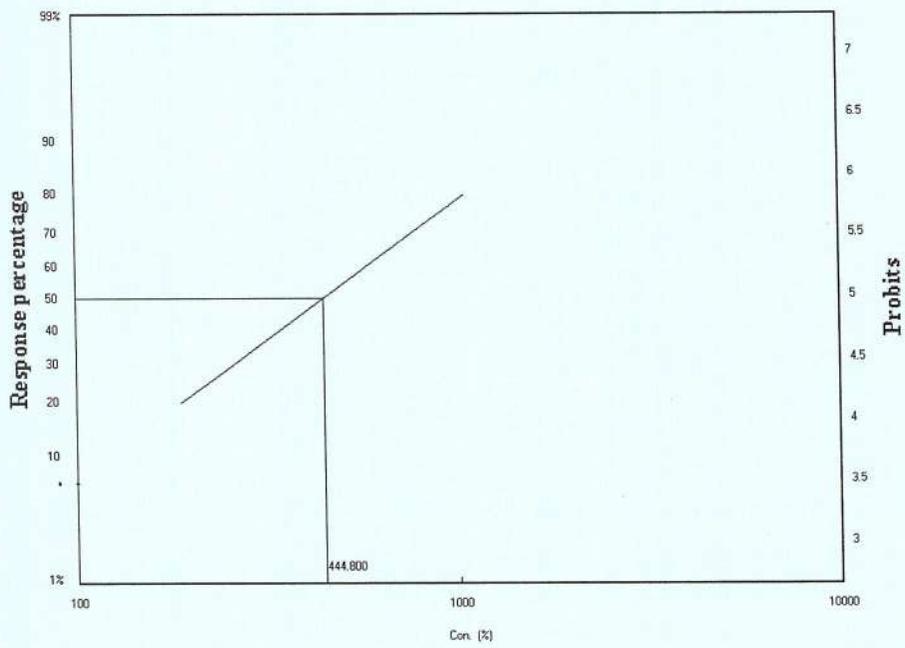
**Table 2.3: Cumulative mortality of zebra fishes in different concentrations of effluent at exposure periods of 24h, 48h, 72h and 96 hours.**

Test concentrations (% v/v)	Cumulative Mortality (%) of zebra fish			
	Exposure periods			
	24 hrs	48 hrs	72 hrs	96 hrs
Control (0%)	0	0	0	0
10%	0	0	0	0
20%	0	0	0	0
30%	0	0	0	0
50%	0	0	0	3.33
60%	3.33	3.33	3.33	6.66
90%	3.33	6.66	6.66	9.99
100%	6.66	6.66	9.99	9.99

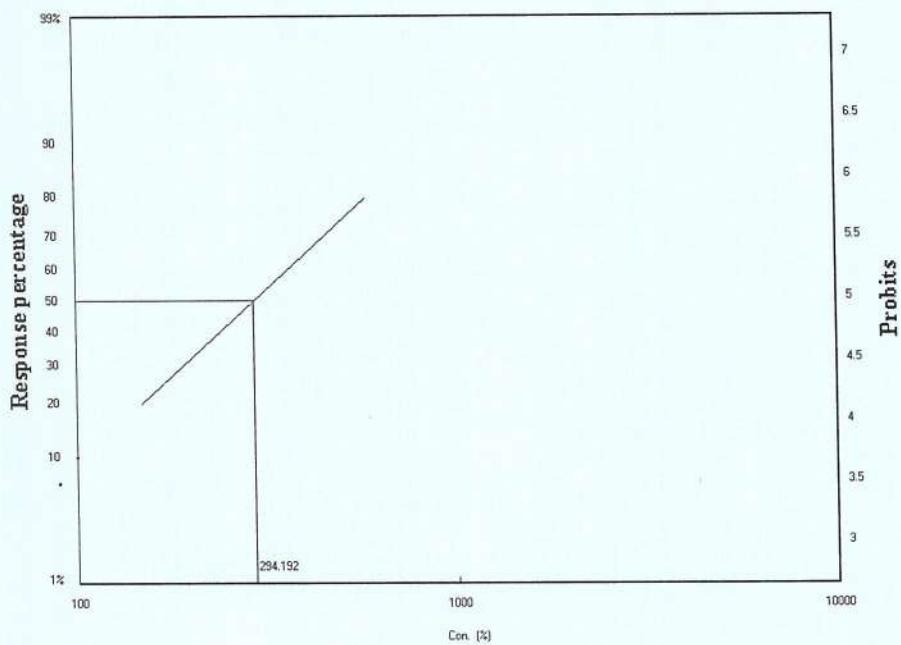
Based on the above observations, median lethal concentrations of treated effluent of 24h, 48h, 72h and 96h were calculated using LDP Line software and were given in Table 2.4.



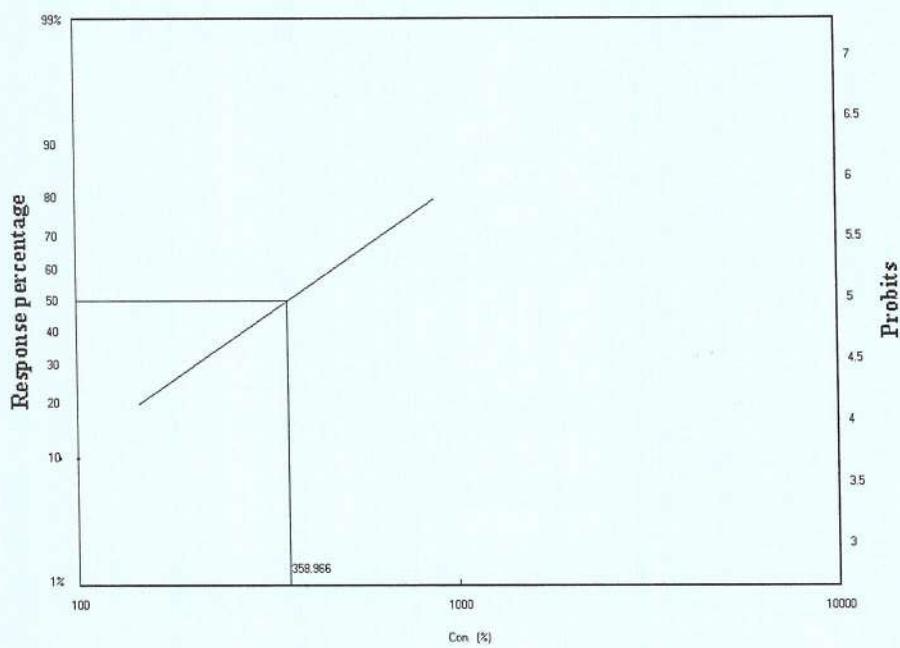
24 h



48 h



72 h



96 h

**Table 2.4: Median Lethal concentrations (LC<sub>50</sub>) of effluent at exposure periods of 24h, 48h, 72h and 96 hours.**

Exposure time (h)	LC <sub>50</sub> (%)	Upper limit	Lower limit
24	633.6	-	-
48	292.8	1360.5	181.6
72	294.1	1360	181.6
96	358.9	1411	211.3

### 2.3 Trace metals

Trace metals in the seawater are essential for biota, however, elevated concentrations of trace metals cause negative impact on the biological organisms. Further, accumulation of heavy metals in the tissues of edible fishes through biomagnification enters into humans. Hence, determination of trace (heavy) metals concentrations in the coastal waters are very important. Treated effluent release in to the sea from industries is one of the possible sources of trace metals in the coastal waters. Hence, trace metals such as vanadium (V), chromium (Cr), manganese (Mn), Iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), Arsenic (As), Selenium (Se), cadmium (Cd) and lead (Pb) were analysed by ICP-MS in the treated effluent collected from M/s Divis Laboratories Limited. Concentrations of these metals in the effluent are given in Table 2.5 and compared with the standard (maximum) limits of CPCB for these trace metals in the treated effluent for sea discharge.

**Table 2.5: Trace element concentrations in the treated effluent**

Element	Effluent Conc. ( $\mu\text{g/l}$ )	CPCB limit
V	9.0	200
Cr	5.5	2000
Mn	570.0	2000
Fe	80.7	3000
Co	4.1	-
Ni	22.9	2000
Cu	28.0	3000
Zn	200.7	5000
As	1.6	200
Se	14.0	50
Cd	1.0	50
Pb	6.2	100

All the elements listed above are very well within the standard limits of CPCB for effluent for sea discharge, suggesting that treated effluent release into the sea from M/s Divis Laboratories Limited may not result in any accumulation of trace elements in the coastal waters of north Andhra coast.

### 3. Conclusion

Treated effluent collected from the guard pond No. 9 of M/s Divis Laboratories Limited has qualified for the bio-assay test and trace metal concentrations in the effluent are very well within the limits of CPCB.

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## Assessment of heavy metals in farmed shrimp, *Penaeus monodon* sampled from Khulna, Bangladesh: An inimical to food safety aspects

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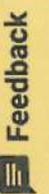
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### Abstract

The analytical experiment was executed to present detailed reports on the concentration of heavy metals (nickel, iron, zinc, manganese, chromium, lead, and cadmium) in farmed shrimp, *Penaeus monodon* and its concomitant human health risks upon consumption. A total of 147 farms from six sub-districts of Khulna were selected for sample collection and concentration of heavy metals were determined by Atomic Absorption Spectrometry (AAS) method, following electro-thermal heater digestion. Ni and Cr were found considerably below the detectable limit (BDL) in four sub-districts, while Cr found in shrimps from Rupsa and Paikgacha were far higher than the maximum recommended limit defined by FAO and WHO. The average concentrations of Fe and Mn in all sub-districts crossed the recommendations, whereas average concentrations of Zn, Ni, Cd, and Pb were within the recommendations. Regardless of sampling site, target hazard quotients (THQ) of more than 1 contributed by Fe confirmed higher level of hazard index (HI), indicating potential human health risk. Fortunately, no heavy metal or their additive effect found to offer lifetime potency of carcinogenesis upon consumption of these shrimps. Therefore, probabilistic non-carcinogenic human health risk from Fe contamination necessitates stringent monitoring and controlling of this metal from different sources to farms.

**Keywords:** Heavy metals, Food safety, Human health risk assessment, Shrimp (*Penaeus monodon*)



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Heavy metals; Food safety; Human health risk assessment; Shrimp (*Penaeus monodon*)

## 1. Introduction

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Shrimp (*Penaeus monodon*), rich in protein, minerals, vitamins, antioxidants, essential amino acids, and unsaturated fatty acids [1, 2], is considered as one of the most beneficial shellfish aliments for human consumption. Bangladesh, the 5<sup>th</sup> ranked aquaculture producing country [3], produces vast amount (0.239 million metric tons in Fiscal Year 2017–18) of shrimp each year. This huge production earns significant amount of foreign currency (503.93 million USD in 2018) [4] by exporting to the global markets, particularly, in the USA, Europe and Japan [5]. Recently, ceiling concern on nutritional and medicinal values of shrimps have made the national consumption ever increased in Bangladesh [6].

Various types of toxicities arisen from the pollutants including heavy metals [6, 7], microplastics [8, 9], pesticides [10, 11] etc. have made the aquatic faunal communities one of the most unvoiced victims. Among the pollutants, heavy metals in aquatic systems are mainly sourced from anthropogenic practices, including agricultural deeds, landfill erosions, embarkation and docking activities, industrial and domestic wastewater as well as natural processes [6, 12, 13]. In general, non-degradable heavy metals even in trace amount can cause toxicities in aquatic ecosystems through assimilation, deposition, or incorporation at a specific concentration into abiotic components and finally, adopting the path of bio-accumulation into aquatic animals [14]. In aquatic ecosystems, food chain is considered as the main pathway of heavy metals accumulation and metals can create human health hazards upon consumption of these contaminated aquatic foods [15].

Although a number of metals are essential for living organisms, some are highly toxic or become toxic at high concentration. Metals such as lead (Pb), tin (Sn), nickel (Ni), cadmium (Cd), and chromium (Cr) are not generally required for metabolic activities. Moreover, trace amount of these heavy metals can cause toxicities to animals [16]. Besides their carcinogenic effects, heavy metals can cause serious problems, such as liver disorders, cardiovascular anomalies, kidney failure and death in case of extreme situation [17, 18]. Crossing the maximum tolerable limits, heavy metal contamination not only constitutes significant human health risks [6, 15] but also possesses several negative effects on natural balances of the ecosystem [19, 20]. Considering these negative impacts and associated health risks, heavy metal contamination is considered as the most dangerous problem in aquatic ecosystems.

Being a top trencherman in aquatic food chain, shrimp is normally more susceptible to the accumulation of heavy metals from different sources including water, sediments, and foods [13]. Human are exposed to heavy metals mainly through foods, including seafoods, though other media like water, air, and soil can contribute largely [21]. Thus, toxicities arising from the heavy metal accumulation avert the health beneficiary aspects of shrimps, while consumers are paying more attention to the food safety issues nowadays. Therefore, determination of heavy metal in widely consumed farmed shrimps with its possible health risk is of prior importance [22]. To mediate human health risk posed by the heavy metal contaminations, FAO and WHO defined the maximum recommended limits for each heavy metal (Table 1). However, these recommended values solely

can't measure the probabilistic carcinogenic and non-carcinogenic human health risks. Hence, US Environmental Protection Agency established quantitative frameworks in favor of quantifying potential hazard index (HI) and target cancer risk (TR) posed by heavy metals [23]. In current study, levels of heavy metals (mg/kg) in shrimps from Khulna, a major shrimp producing hotspot of Bangladesh, were determined by Atomic Absorption Spectrometry (AAS) method. Besides comparing with the maximum limits recommended by FAO and WHO [24], probabilistic HI and TR were also enumerated to interpret whether shrimps from the study areas are safe for human consumption or not.

Table 1

Maximum recommended limits of heavy metals for human consumption defined by WHO and FAO [1].

Heavy metals	Maximum recommended limits for human consumption
Nickel	1 mg/kg
Iron	100 mg/kg
Zinc	100 mg/kg
Manganese	1 mg/kg
Chromium	0.05 mg/kg
Lead	2 mg/kg
Cadmium	1 mg/kg

## 2. Materials and methods

### 2.1. Study location and ethical approval

Based on outstanding signature in shrimp production, six sub-districts of Khulna, namely Phultola (22.9750°N 89.4583°E), Rupsa (22.8333°N 89.5833°E), Dumuria (22.8083°N 89.4250°E), Paikgacha (22.5889°N 89.3361°E), Batiaghata (22.7417°N 89.5167°E) and Dacope (22.5722°N 89.511°E) were selected for sample collection (Figure 1). Further digestion and analysis were performed in Fish Nutrition Laboratory and Interdisciplinary Institute for Food Security (IIFS) Laboratory of Bangladesh Agricultural University (BAU). The Ethical committee of Bangladesh Agricultural University Research System (BAURES) approved the design and execution of the study.

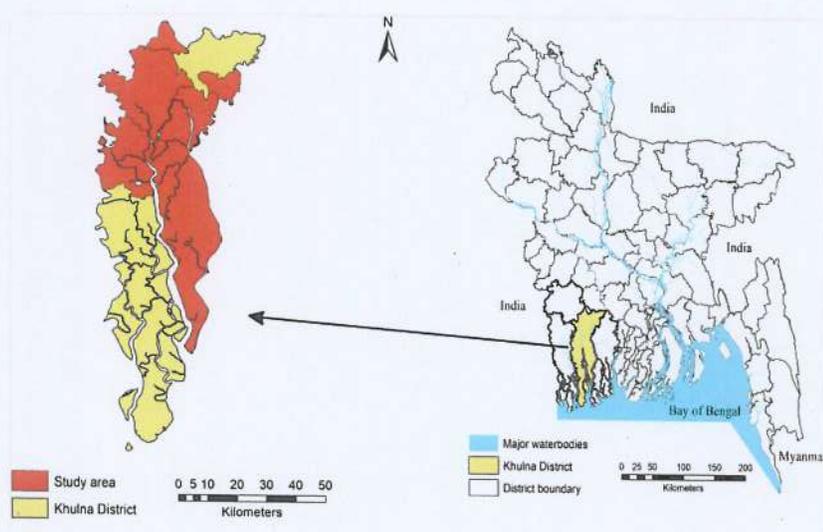


Figure 1

Study area.

## 2.2. Sample collection

Samples were collected from 147 extensive farms (24 from Rupsa, 24 from Phultola, 24 from Dacope, 25 from Batiaghata, 30 from Paikgacha and 20 from Dumuria). After washing with distilled water, shrimps were carried to the Fish Nutrition Laboratory for further processing in sealed, labeled and iced condition.

## 2.3. Analysis of heavy metals

**2.3.1. Sample preparation** From each sample, approximately 100 g of edible muscle was taken in a clean brown envelope and placed in a hot-air oven to dry at 105 °C for a period of 24 h. After drying, the samples were pulverized with the help of a grinder. Prior to use, all the glass equipment were kept in diluted  $\text{HNO}_3$  for 24 h and then washed with distilled water.

**2.3.2. Electro-thermal heater digestion** After treatment with 10 ml  $\text{HNO}_3$  and 5 ml  $\text{HClO}_4$  solution, exactly 1 g from each sample was digested at 80 °C for 30 min in an electro-thermal heater (Model-VELP). The digested samples were cooled and transferred into clean volumetric flasks. Double distilled water was added to make each solution exactly 100 mL. Finally, Whatman Filter paper No. 42 was used to filtrate the solutions before keeping in sealed and labeled plastic bottles.

**2.3.3. Blank preparation** Using standard procedure, a blank containing same digestion inputs except sample was prepared to make sure that impurities or contaminations (if any) from the chemicals didn't bias the values [25]. The blank value found through the analysis by AAS was subtracted from each of the sample value to get the true value.

2.3.4. Sample analysis A flame atomic absorption spectrophotometer (Model Shimadzu AA-7000) was used to determine heavy metals concentration, where acetylene gas and air were used as fuel and oxidizer, respectively. Aspiration of the digested samples was performed using the air acetylene flame. The concentrations of heavy metals were determined with the support of calibration curves relying on Beer Lambert's law [26]. Calibrations by consecutive dilution were achieved using standard solutions as manufacturer's protocol. Determination was based on average values of triplicates for each sample. Absorption wavelengths of 228.0 nm, 217.0 nm, 213.9 nm, 279.5 nm, 232.0, 248.3, and 357.9 were maintained for determination of Cd, Pb, Zn, Mn, Ni, Fe, and Cr, respectively. Detection limit of the spectrophotometer is 0.01 mg/kg and the concentrations below the limit were termed as BDL (Below detectable limit).

#### 2.4. Data processing

After determination of heavy metals concentration, all recorded data were collected and processed using Microsoft Excel (MS 2010) to produce graphical and tabular presentation comparing with maximum recommended limits.

#### 2.5. Human health risk assessment

To assess the potential health risk, target hazard quotient (THQ) for each heavy metal was calculated adopting the scientific formula (Eq. (1)) established by USEPA [27].

$$\text{THQ} = \frac{E_D \times F_{IR} \times E_F \times C_i}{R_{FD} \times W_{AB} \times T_A} \times 10^{-3} \quad (1)$$

where,

$E_D$  = Exposure duration (Average life span, 72.32 years)

$F_{IR}$  = Daily ingestion rate (2.43 gm/person/day, determined from an online based survey with 5 thousand respondents throughout the country)

$E_F$  = Exposure frequency (365 days/year)

$C_i$  = Concentration of respective heavy metal (mg/kg)

$R_{FD}$  = The reference oral dose in mg/kg/day (0.001 for Cd, 0.004 for Pb, 1.5 for Cr, 0.3 for Zn, 0.02 for Ni, 0.007 for Fe, 0.14 for Mn according to USEPA [27])

$W_{AB}$  = Average body weight for an adult consumer (54.6 kg for Bangladesh, according to the online based survey)

$T_A$  = Average exposure time, calculated as  $E_D \times E_F$

The overall hazard index (HI) was calculated using following formula (Eq. (2)) according to USEPA [27].

$$HI = THQ_{Fe} + THQ_{Zn} + THQ_{Ni} + THQ_{Mn} + THQ_{Cd} + THQ_{Pb} + THQ_{Cr} \quad (2)$$

Among the analyzed heavy metals, Cd, Cr, Ni, Pb were considered as potent carcinogens. Target cancer risk (TR) posed by the determined heavy metals was calculated according following formula (Eq. (3)) [28]:

$$TR = \frac{E_D \times F_{IR} \times E_F \times C_i \times C_{SF}}{W_{AB} \times T_A} \times 10^{-3} \quad (3)$$

The values of cancer slope factors ( $C_{SF}$ ) were adopted from USEPA [27] (for Cd (6.3 mg/kg/day) and Pb (0.0085 mg/kg/day)) and Zeng et al. [29] (for Ni (0.91 mg/kg/day) and Cr (0.5 mg/kg/day)).

### 3. Results

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#### 3.1. Heavy metals concentration

The overall finding of metal concentrations found from analyzed shrimp samples is presented in [Table 2](#).

Table 2

Average concentration of heavy metals (Ni, Fe, Zn, Mn, Cr, Pb, Cd) in shrimps collected from six sub-districts of Khulna.

Sub-districts	Concentrations of heavy metals (mg/Kg)						
	Ni	Fe	Zn	Mn	Cr	Pb	Cd
Rupsa	BDL <sup>1</sup>	358.990 ± 52.139	82.280 ± 3.851	17.250 ± 3.397	0.084 ± 0.022	0.691 ± 0.074	0.049 ± 0.001
Phultola	BDL	331.130 ± 57.795	84.103 ± 6.589	26.450 ± 9.295	BDL	0.502 ± 0.036	0.044 ± 0.002
Dacope	BDL	310.910 ± 22.459	73.368 ± 9.976	6.550 ± 2.576	BDL	0.418 ± 0.027	0.041 ± 0.006
Batiaghata	BDL	184.084 ± 32.636	74.864 ± 14.088	37.870 ± 11.247	BDL	0.362 ± 0.022	0.040 ± 0.004
Paikgacha	0.080 ± 0.0515	219.888 ± 20.795	80.678 ± 6.443	35.220 ± 11.369	0.235 ± 0.071	0.361 ± 0.019	0.041 ± 0.001
Dumuria	0.042 ± 0.013	211.012 ± 37.813	74.464 ± 4.169	34.780 ± 8.877	BDL	0.354 ± 0.040	0.041 ± 0.003

<sup>1</sup>Below detectable level.

3.1.1. Ni concentrations Average Ni concentrations in the shrimps of Paikgacha and Dumuria were found 0.080 (±0.052) mg/kg and 0.042 (±0.013) mg/kg, respectively (Figure 2). Other sub-districts were reported to have Ni below detectable level (BDL). However, recorded Ni concentration didn't cross the recommended limits [24].

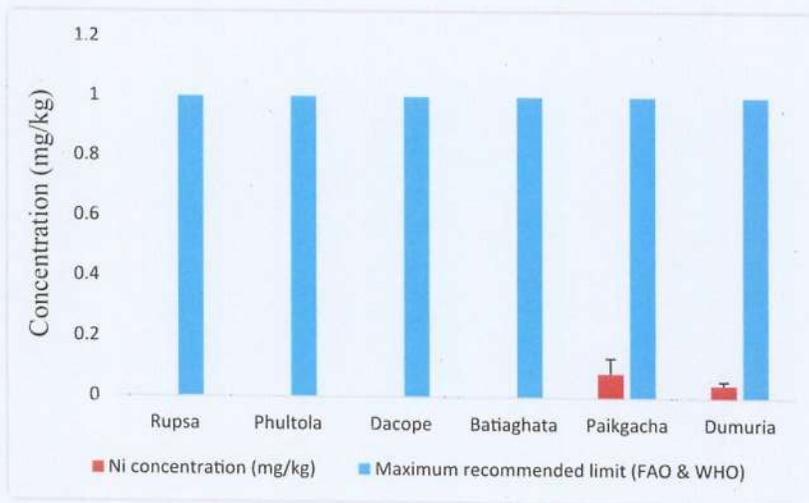


Figure 2

Average nickel (Ni) concentrations (mg/kg) in shrimp of Khulna district compared with maximum recommended limit.

3.1.2. Fe concentrations The highest average concentration of Fe ( $358.995 \pm 52.139$  mg/kg) was observed in the shrimps collected from Rupsa whereas the lowest average ( $184.084 \pm 32.636$  mg/kg) from Batiaghata (Figure 3). However, the average Fe concentrations determined from all sampling sites exceeded the maximum recommended limit [24].

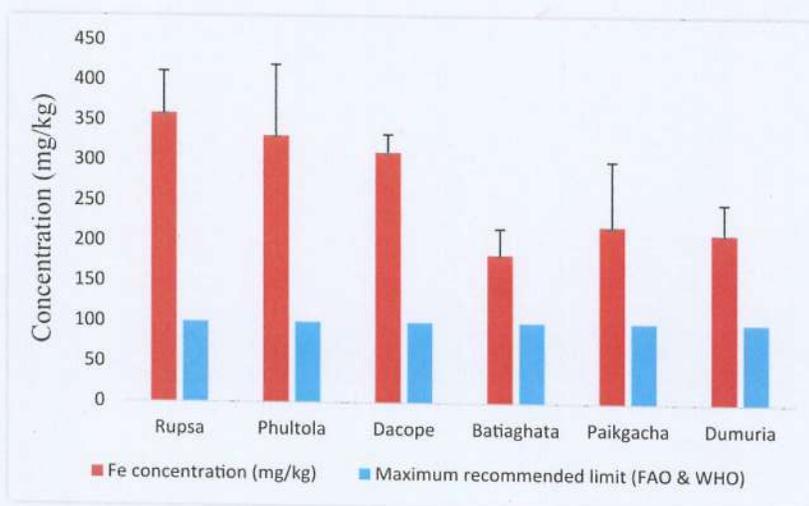


Figure 3

Average iron (Fe) concentrations (mg/kg) in shrimp of Khulna district compared with maximum recommended limit.

3.1.3. Zn concentrations The highest average level of Zn ( $84.103 \pm 6.589$  mg/kg) was observed in the shrimps of Phultola, while the shrimps from Dacope offered the lowest average concentration ( $73.368 \pm 9.976$  mg/kg) (Figure 4). However, average Zn concentrations found in shrimps from different sub-districts were lower than the recommendation [24].

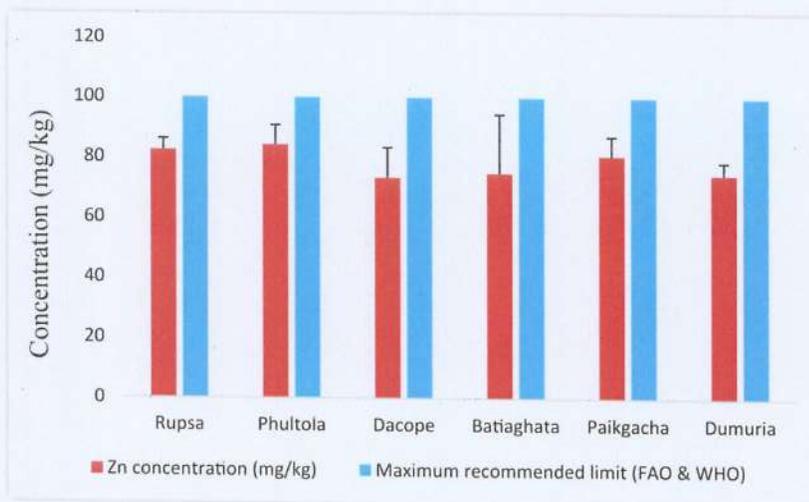
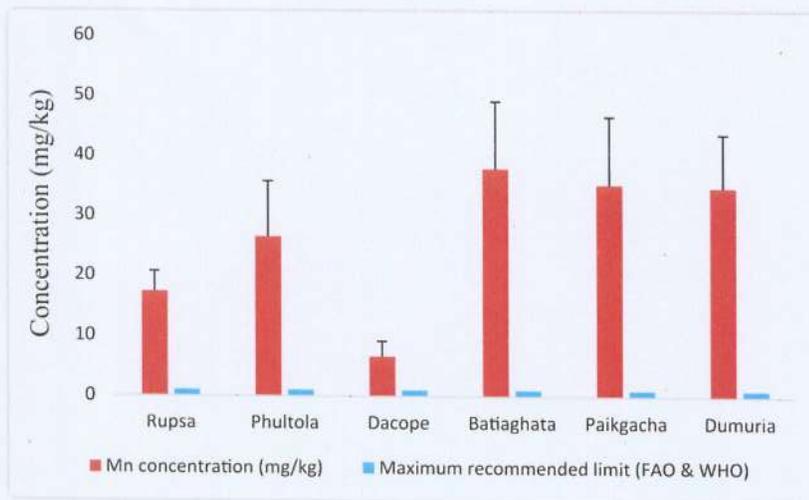


Figure 4

Average zinc (Zn) concentrations (mg/kg) in shrimp of Khulna district compared with maximum recommended limit.

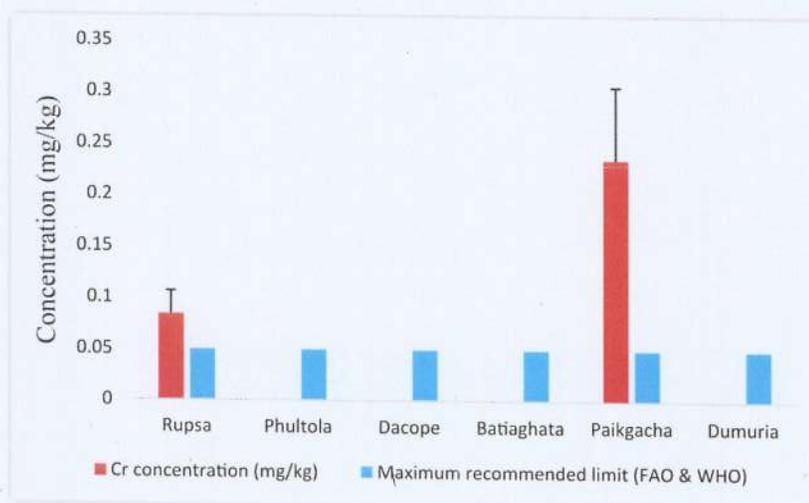
3.1.4. Mn concentrations Average Mn concentration was found to be the highest ( $37.87 \pm 11.247$  mg/kg) in Batiaghata and the lowest ( $6.550 \pm 2.576$ ) in Dacope (Figure 5). The average concentrations found in all sub-districts were far higher than the maximum recommended level of FAO and WHO [24].



[Figure 5](#)

Average manganese (Mn) concentrations (mg/kg) in shrimp of Khulna region compared with maximum recommended limit.

3.1.5. Cr concentrations Shrimps of Rupsa and Paikgacha were suffered from Cr contamination with an average concentration of  $0.084 (\pm 0.022)$  and  $0.235 (\pm 0.071)$  mg/kg, respectively where both values crossed the recommendation. Average chromium concentrations in the rest sub-districts were below detectable limit ([Figure 6](#)).



[Figure 6](#)

Average chromium (Cr) concentrations (mg/kg) in shrimp of Khulna district compared with maximum recommended limit.

3.1.6. Pb concentrations The maximum average concentration of Pb ( $0.691 \pm 0.074$  mg/kg) was reported from Rupsa, while the minimum ( $0.354 \pm 0.040$  mg/kg) from Dumuria (Figure 7). However, values recorded from all sampling sites were far below than the maximum recommended value [24].

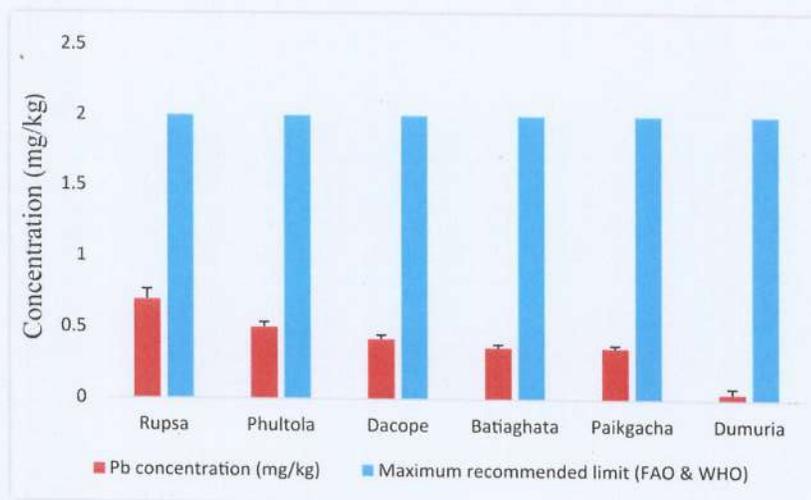


Figure 7

Lead (Pb) concentrations (mg/kg) in shrimp of Khulna district compared with maximum recommended limit.

3.1.7. Cd concentrations The highest average Cd concentration ( $0.0491 \pm 0.001$  mg/kg) was found in shrimps from Rupsa and somewhat similar results were reported from other sub-districts (Figure 8). However, no determined concentration crossed the maximum recommended limits defined by FAO and WHO [24].

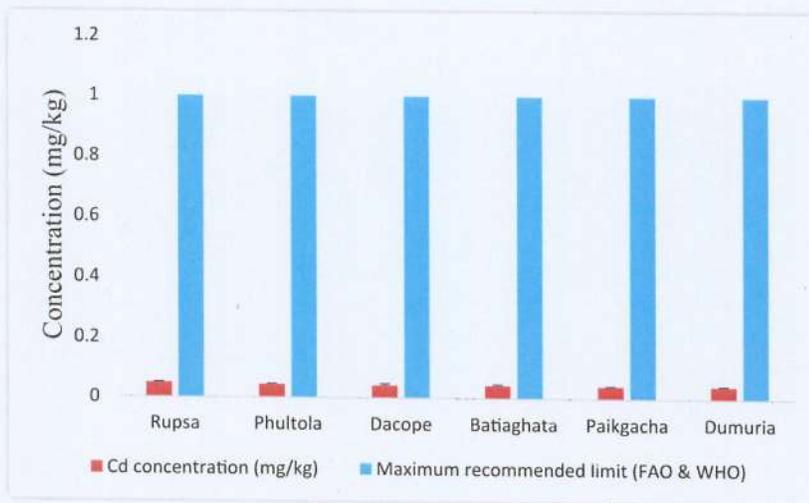


Figure 8

Average cadmium (Cd) concentrations (mg/kg) in shrimp of Khulna district compared with maximum recommended limit.

### 3.2. Human health risk assessment

Though the determined concentrations of Mn and Cr (in Rupsa and Paikgacha) crossed the recommended values, THQ values solely for Fe were higher than 1 in all sub-districts ([Table 3](#)). This made the HI elevated over 1 in all sites. From spatial consideration, shrimps of Rupsa possessed highest level of non-carcinogenic health risk, whereas Batiaghata did the lowest. No determined TR value, nor their additive effect (TRt) exceeded the recommended value ( $<10^{-4}$ ). However, Phultola presented the highest TR values contributed largely by Cd, whereas Dumuria did the lowest.

Table 3

Calculated target hazard quotients (THQ), hazard index (HI) and target cancer risk (TR) for each heavy metal traced from the shrimp samples.

Risk indexes	Rupsa	Phultola	Dacope	Batiaghata	Paikgacha	Dumuria
Target hazard quotients (THQ)						
THQ <sub>Ni</sub>	NA	NA	NA	NA	3.24E-06	9.35E-05
THQ <sub>Fe</sub>	<b>2.282</b>	<b>2.105</b>	<b>1.977</b>	<b>1.170</b>	<b>1.398</b>	<b>1.341</b>
THQ <sub>Zn</sub>	0.012	0.013	0.011	0.011	0.012	0.011
THQ <sub>Mn</sub>	0.006	0.008	0.002	0.012	0.011	0.011
THQ <sub>Cr</sub>	2.49E-06	NA	NA	NA	6.96E-06	NA
THQ <sub>Pb</sub>	0.008	0.006	0.005	0.004	0.004	0.004
THQ <sub>Cd</sub>	0.002	0.006	0.002	0.002	0.002	0.002
HI	<b>2.310</b>	<b>2.137</b>	<b>1.996</b>	<b>1.199</b>	<b>1.427</b>	<b>1.370</b>
Target cancer risk (TR)						
TR <sub>Ni</sub>	NA	NA	NA	NA	3.24E-06	1.701E-06
TR <sub>Cd</sub>	1.38E-05	3.52E-05	1.16E-05	1.18E-05	1.15E-05	1.15E-05
TR <sub>Cr</sub>	1.87E-06	NA	NA	NA	5.22E-06	NA
TR <sub>Pb</sub>	2.62E-07	1.90E-07	1.59E-07	1.37E-07	1.37E-07	1.34E-07
TR <sub>t</sub>	1.59E-05	3.54E-05	1.18E-05	1.19E-05	2.01E-05	1.34E-05

Values Exceeded recommendation are indicated as bold.

#### 4. Discussion

This study was undertaken to determine heavy metal concentrations in shrimps collected from six sub-districts of Khulna and to assess the probabilistic human health impacts upon consumption. According to afore mentioned findings, [Figure 2](#) points that Ni was considerably low (below detectable limit) in shrimps of Rupsa, Phultola, Dacope, and Batiaghata. Though traced in shrimps of Paikgacha and Dumuria, did not cross the maximum recommended level (1 mg/kg) of Ni [24] and also the value (2.5 mg/kg) determined by Vinodhini and Narayana [30] in *Cyprinus carpio*. Another study by Rejomon et al. [31] which found Ni concentrations to vary between 12.12 and 13.92 mg/kg in the marine fishes from southwest coast of India disagrees with our findings. This may be because, Ni concentrations and their sensitivity in water fluctuates with species, abiotic components including salinity of water, location and industrial process around the water [32]. However, an average THQ lower than 1 for Ni in our study areas suggests no human health concern from Ni consideration.

Figure 3 shows that the Fe concentrations in all shrimps were far higher than the recommended limit [24]. The results also crossed all other findings of 36.211 mg/kg [33] and 6.570 mg/kg [34], of 27.22 mg/kg [35], and of 8.819 mg/kg [36] in fishes from Turkey, Cambodia, and Italy, respectively. Among heavy metals, Fe concentrations were highest in all shrimp samples (Table 2).  $THQ_{Fe}$  values more than 1 confirm that shrimps from the study areas were not safe for human consumption. Generally, this 2<sup>nd</sup> most abundant metal [37] is accumulated in shrimps from the feed fed, ground water contamination from mining, and industrial effluents etc. Fe is necessary for binding proteins, activation of coenzymes, and other metabolic activities in human [38]. But a number of detrimental effects are experienced due to high level of Fe when it fails to bind proteins and thus unbound Fe become erosive to the gastrointestinal tracts [39].

The observations on Zn are similar to various studies [39, 40, 41, 42, 43], but higher than the concentrations found in fishes from eastern Taiwan [44], Malaysia [45], Turkey [46], and lower from south west coast of India [31], Indonesia [47] and Iran [48, 49]. However, average  $THQ_{Zn}$  values in all sampling sites were within the recommendation. Thus, the study can propose that shrimps from these areas were not harmful from the consideration of Zn contamination. On contrary, this low level of Zn, possibly sourced from feedstuff, water and sediments may accelerate the metabolic process of cultured shrimp to favor the growth [50].

Mn concentrations found in current study are in proximity with the previous studies undertaken by Yilmaz [12] and Abu Hilal and Ismail [51]. This metal, running into water from pharmaceutical, industrial, and agricultural sources, can cause gastro-intestinal and neurological abnormalities to human. Besides, long term exposure of this metal may also cause Parkinson, lung embolism, cancer, thyroid and other abnormalities [52]. Though the concentrations, far higher than the certified level of WHO and FAO, recommend great concern regarding the consumption of shrimps from these areas, tolerable  $THQMn$  values allow the Mn concentrations and infer no possible.

Our findings regarding Cr concentrations agree with the results obtained from a study carried out in the Bangsi river of Bangladesh [53], but differ from the results reported from the Kabdak river of Satkhira, Bangladesh [54]. Articulation revealed that concentrations of Cr in shell (1.03 mg/kg) was much higher than in tissue (0.68 mg/kg) of black tiger shrimps of Batiaghata, while similar concentration (0.14 mg/kg) was observed in both tissue and shell for freshwater prawn of the Bhairab river of Bangladesh [6]. However, both findings exceed our determined values. As feed inputs, poultry droppings and tannery wastes are frequently used in shrimp farms in Bangladesh. These Cr-rich wastes cause Cr uptake into shrimp body and this made the understanding behind the Cr concentrations in shrimps of Rupsa and Paikgacha that crossed the maximum recommended limit of WHO and FAO. Cr uptake in human body for a long time can cause disruption of cellular integrity and functions by damaging protein and lipid membrane [55, 56]. Fortunately,  $THQ_{Cr}$  values are very negligible and confirm no potent human health risk from Cr consideration.

Ahmed et al. [57] and Sarkar et al. [6] documented Pb concentrations of 0.51 mg/kg in freshwater prawn from the Buriganga river and 0.52–1.16 mg/kg in shrimps from Khulna-Satkhira region of Bangladesh, respectively, which are somewhat close to our findings. Pb can cause renal failure and liver damage [58] upon consumption of Pb contaminated foods and prolonged exposure may lead

to mental retardation, comma, and even death in severe cases [18]. However, far lower concentration than the recommendation and lower average  $THQ_{Pb}$  values in all sub-districts avoid these human health risks.

WHO and FAO defined 1 mg/kg as the maximum recommended limit for Cd while 0.05 mg/kg and 0.5 mg/kg were defined by the European Community legislation [59] and Codex Committee on Food Additives and Contaminants [60], respectively. However, the average Cd concentrations determined in the current study were far below from the recommended level by FAO and WHO; and very close to the European Union recommendation. Our result on Cd concentrations agrees with the finding where authors determined Cd level of 0.05–0.13 mg/kg in shrimps of Khulna- Satkhira region [6]. however, the result for shellfish (1.51 mg/kg) from the Buriganga river [57] counters our findings. Renal and hepatic dysfunctions may be accelerated by high dose Cd exposure while long term exposure may obstruct bone formation, hypertension, tumors and even cancer in urinary bladder [6, 61]. Nevertheless, lower  $THQ_{Cd}$  values in all shrimps sampled from Khulna region deny these health risks posed by cadmium.

An HI index of more than 1 recommends possible human health risk. Though no other metals did, iron contributed to a THQ more than 1 and made the hazard index far higher than the recommendation. From individual metal perspective, though THQ calculated from Ni, Zn, Mn, Pb, Cr, Cd concentrations complied the human health safety issues, Fe threatens the consumption of shrimps from these areas. Providentially, adverse effects of iron for human health are not so serious like other heavy metals and comprehensive actions regarding minimization of its availability in farms can improve the shrimp's quality.

Target cancer risk values augur the lifetime potency of carcinogen(s) [22] and values greater than  $10^{-4}$  are considered to exert potential carcinogenic risks [23]. Recorded TR values for Ni, Cr, Cd and Pb, ranging from  $10^{-7}$  to  $10^{-5}$ , are considered acceptable. Cumulative target cancer risk values (TRt) in all sub-districts suggest no potential risk of carcinogenesis from these shrimps.

## 5. Conclusion

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The study revealed that the average concentrations of Fe, Mn, and Cr (in Rupsa and Paikgacha) in shrimps from Khulna were considerably higher than the maximum recommended limits. Target hazard quotients of Fe made the hazard indices more than 1 in all sub-districts. However, risk of carcinogenesis posed by Ni, Cr, Pb, and Cd were within the acceptable range. This can wrap a conclusion that the shrimps from these areas can cause non-carcinogenic harm to human upon consumption. Therefore, to ensure the food safety aspects from detrimental consequences of heavy metal contaminations, execution of standards in all steps of shrimp production is obligatory.

## Declarations

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### Author contribution statement

Chinmoy Biswas: Conceived and designed the experiments; Performed the experiments.

Sadia Sarmin Soma, Hamidur Rahman: Performed the experiments.

Fazle Rohani, Abul Bashar: Analyzed and interpreted the data; Wrote the paper.

Sazzad Hossain: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

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#### Data availability statement

Data will be made available on request.

#### Declaration of interests statement

The authors declare no conflict of interest.

#### Additional information

No additional information is available for this paper.

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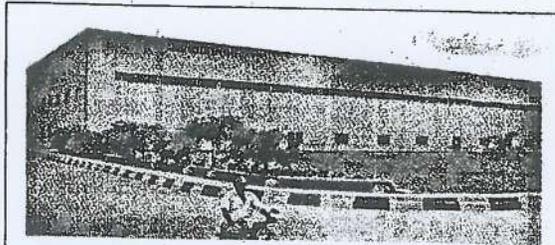
## AP pollution board orders Aurobindo Pharma, other companies to shut units

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Hyderabad, July 13: The Andhra Pradesh Pollution Control Board (APPCB) has ordered closure of 12 manufacturing units of various pharma companies, including Aurobindo Pharma and Hetero Drugs, in and around Hyderabad for allegedly violating pollution norms.

According to a board's release, the notices have been issued to the facilities to stop all industrial activities with effect from July 23 to complete the on-going batches.

"The AP Pollution Control Board has reviewed certain bulk drug industries before the Board's Task Force committee meeting on July 9. After detailed discussions, the board is of the firm opinion that certain industries are violating the orders of Supreme Court of India, ban notification issued by the Andhra Pradesh government, Appellate Authority order and directions issued by the board,"



**THE UNITS INVOLVED ARE ALSO DIRECTED TO STOP ALL INDUSTRIAL ACTIVITIES WITH EFFECT FROM JULY 23 TO FACILITATE COMPLETION OF ALL ONGOING BATCHES**

the release said.

"Also, these units were found using un-consented products and changing the product mix. This only further increased the pollution load." PCB officials revealed, adding that "the appellate authority actually wanted to allow such malpractices to continue and had even suggested that the units could change their mix after consultation with PCB. However, no such arrangement was acknowledged by

the department," it said.

The facilities named in the order include two facilities of Aurobindo Pharma, four facilities of Hetero Labs, one each of Cirox Pharmaceuticals, Covalent Laboratories, Divis Pharmaceuticals, Sri Krishna Pharmaceuticals and Innogent Laboratories and SMS Pharma. "These industries are also directed to stop all industrial activities with effect from July 23 to facilitate completion of all on-going batches," it added.

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Figure 1. Drivers and benefits of zero liquid discharge (ZLD).

applied only to feedwaters with a limited salinity range. Accordingly, other salt-concentrating technologies that can treat higher salinity feedwaters, such as electro dialysis (ED), forward osmosis (FO), and membrane distillation (MD), have emerged recently as alternative ZLD technologies to further concentrate wastewater beyond RO.

Although ZLD holds great promise to reduce water pollution and augment water supply, its viability is determined by a balance among the benefits associated with ZLD, energy consumption, and capital/operation costs. Therefore, it is imperative to understand the drivers and benefits that make ZLD a realistic option. Incorporating new technologies, such as emerging membrane-based processes, provides opportunities to reduce the associated energy consumption and costs and to expand the applicability of ZLD.

In this critical review, we discuss the drivers, incentives, technologies, and environmental impacts of ZLD as an important strategy for wastewater management. We highlight the evolution of ZLD from thermal to membrane-based processes, with a detailed analysis of the advantages and limitations of both existing and emerging ZLD technologies. Lastly, we discuss the environmental impacts of ZLD, the prospects of ZLD technologies, and research needs for improving its feasibility and sustainability.

## ACHIEVING ZERO: DRIVERS AND BENEFITS

**Why ZLD?** Figure 1 describes the major drivers and benefits of ZLD implementation. Stricter regulations for wastewater disposal are the primary driver for ZLD. More costly non-compliance penalties along with increasing costs for wastewater disposal can outweigh the high expenses of ZLD installation. As water scarcity intensifies globally, the capability of ZLD to recover wastewater to the largest extent further enhances its prospects. Increased public environmental awareness constitutes an additional driver, as ZLD avoids negative environmental impacts of wastewater discharge and reduces the corresponding public concerns.

In practice, the incentives behind ZLD implementation vary depending on its application and geographical location. Therefore, the drivers and benefits of ZLD are discussed in this section in the context of its global applications. Although ZLD has been applied in places such as the European Union, Australia, Canada, the Middle East, and Mexico,<sup>6,7,9,10</sup> examples from the United States, China, and India are highlighted, as they represent the major ZLD markets with the largest served populations and economic power.

**The United States.** The birth of ZLD dates back to the 1970s when the increased salinity of the Colorado River led to a regulatory mandate of ZLD for nearby power plants.<sup>6,11</sup> In those days, obtaining approval for discharge agreements for new industrial projects required several years, whereas adoption of

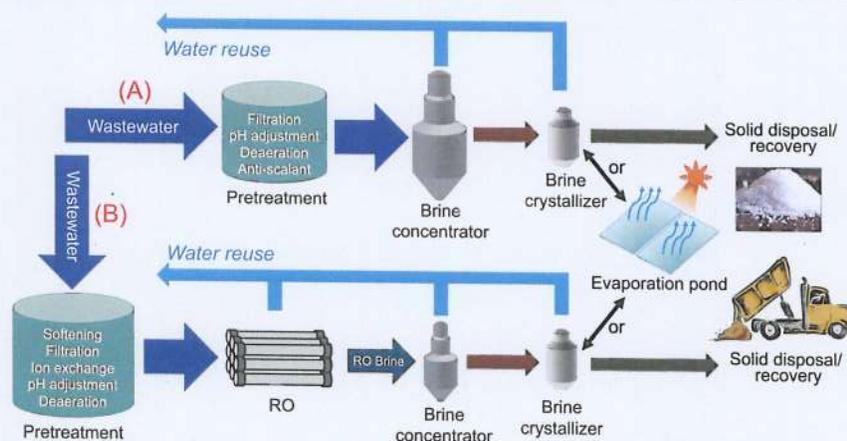
ZLD reduced this period to only a few months.<sup>6,12</sup> Today, power plants remain the major domain of ZLD implementation in the U.S., where feedwaters, such as flue gas desulfurization (FGD) wastewater and cooling tower blowdown, are treated and recycled. For example, ZLD has been adopted at the Dallman Power Plant in Illinois to avoid the environmental impacts of boron from the FGD wastewater.<sup>13</sup> Among the 82 ZLD plants listed in a survey by Mickley in 2008,<sup>11</sup> more than 60 plants were associated with the power industry; the rest were distributed across areas such as electronics, fertilizer, mining, and chemical industries.

The U.S. EPA recently completed its guidelines revising the existing regulations on wastewater discharge from thermal power plants.<sup>14</sup> This new rule, which sets the first federal limits on the level of toxic metals and other harmful pollutants in wastewater discharged from power plants, considers zero discharge as the preferred option for pollutants in fly ash transport water, bottom ash transport water, and wastewater from flue gas mercury control systems.<sup>15</sup> Compliance with these tighter wastewater discharge standards provides new regulatory incentives for ZLD installation in U.S. power plants.

ZLD can also be used for brine management in inland desalination plants. Compared to seawater desalination, brackish water desalination requires much less energy<sup>16</sup> and is particularly suitable for semiarid inland regions where seawater is inaccessible.<sup>17</sup> However, the management of concentrated brines represents one of the biggest challenges for inland desalination. Traditional brine management practices, including direct discharge into surface water or publicly owned treatment works (POTW) as well as deep-well injection,<sup>11,18</sup> can be excluded, due to potentially adverse impacts on surface water and groundwater, insufficient POTW capacity, geological and legal restrictions, and increasing disposal costs. As a result, inland desalination is still not installed at many locations where water is critically needed, such as Las Vegas, Phoenix, and Denver.<sup>11</sup>

ZLD overcomes the challenge of brine discharge, thereby enabling inland desalination in water-scarce areas. So far, multiple governmental agencies and organizations, including the U.S. Bureau of Reclamation and California Energy Commission, have investigated ZLD application to inland desalination under hypothetical scenarios in Arizona, California, Colorado, Nevada, and Texas.<sup>11,19–22</sup> These pioneering studies, however, have not resulted in full-scale ZLD inland desalination plants in the U.S., with cost and energy consumption providing the main barriers to implementation.

**China.** Rapid economic development and urbanization have led to rising water consumption and rampant pollution in China. In response to this great challenge, China recently announced a new Action Plan to tackle water pollution, aiming to largely improve the quality of local water resources and ecosystems by 2020.<sup>23</sup> This plan, enforced by the central government,



**Figure 2.** Schematic illustration of (A) thermal and (B) RO-incorporated ZLD systems. Incorporation of RO, an energy-efficient technology, into ZLD reduces the volume of wastewater entering the brine concentrator, which consumes much higher energy per volume of treated water than RO.

emphasizes rigorous control of pollutant discharge and promotes water recycling and reuse, thereby providing regulatory support for ZLD installation.

As in the U.S., the power industry is an important contributor to the Chinese ZLD market. Although coal-fired power plants provide more than 70% of the total electricity generated in China,<sup>24</sup> 65–84% of water-intensive thermal power plants operated by the five largest state-owned companies are located in regions that suffer water scarcity or deficit.<sup>25</sup> This sharp conflict between energy demand and water deficiency makes ZLD one of the few sustainable solutions at the energy-water nexus in China. Although no data have been revealed on the overall ZLD installation in Chinese power industry, a rising trend of ZLD adoption is indicated by the recent construction of the world's first FO-based ZLD system at the Changxing coal-fired power plant in Zhejiang Province.<sup>26</sup>

The recent boom of the coal-to-chemicals industry in China generates another promising niche for ZLD application. The coal-to-chemicals industry, utilizing coal rather than oil or natural gas to produce raw materials for chemical production, is currently under pressure to reduce dependence on imported energy.<sup>27</sup> Coal-to-chemicals plants consume a considerable amount of freshwater but are often located in water-stressed areas, such as Inner Mongolia where ample coal reserves and environmentally sensitive grassland coexist. As a consequence, ZLD is mandatory at coal-to-chemicals plants in those areas to preserve both local water resources and ecosystems.<sup>28</sup> Several ZLD facilities are already installed or in the stage of design/construction at Chinese coal-to-chemicals plants, with a wide range of feedwater salinities (2,000–16,000 mg/L of total dissolved salts, TDS) and treatment capacity (110–2300 m<sup>3</sup>/hour).<sup>29–32</sup>

In addition, greater public awareness of water pollution may facilitate ZLD implementation in China. Multiple projects, including several *para*-xylene (PX) chemical plants<sup>33</sup> and a wastewater discharge pipeline for a paper mill,<sup>34</sup> have been recently suspended or canceled as a result of public protests. The growing influence of public concern may force industries to adopt ZLD as a necessary solution to gaining public acceptance.

**India.** Facing a situation similar to that in China, India is taking aggressive actions to curb severe water pollution, even in the holy river Ganga. The recent three-year target set by the Indian government, known as the “Clean Ganga” project, imposes stricter regulations on wastewater discharge and moves high-polluting industries toward ZLD.<sup>35</sup> In 2015, the govern-

ment issued a draft policy that requires all textile plants generating more than 25 m<sup>3</sup> of wastewater effluent per day to install ZLD facilities.<sup>36,37</sup> As reported by Vishnu et al.,<sup>38</sup> 29 dyeing plants in the city of Tirupur had already implemented ZLD by 2008, which recovered not only water but also valuable salts from textile wastewater for direct reuse in the dyeing process. According to a recent technical report,<sup>39</sup> the ZLD market in India was valued at \$39 million in 2012 and is expected to grow continuously at a rate of 7% from 2012 to 2017. In this market, the textile, brewing and distilling, power, and petrochemical industries are the major application areas.<sup>39</sup>

## CONVENTIONAL ZLD SYSTEMS

**Thermal ZLD Systems.** Early ZLD systems were typically based on a series of thermal processes (Figure 2A). In such systems, the feed wastewater undergoes a pretreatment step that reduces scaling potential, and is then concentrated sequentially by two core elements — a brine concentrator and a brine crystallizer (or an evaporation pond). The distillates generated by the brine concentrator and crystallizer units are reused as clean product water, whereas the solids produced are either stored (in evaporation ponds), further processed for landfill disposal, or reused as valuable byproducts.

Brine concentrators commonly use mechanical vapor compression (MVC) for water evaporation. Although other thermal desalination technologies, such as multieffect distillation (MED) and multistage flash (MSF), have been extensively used in seawater desalination,<sup>40</sup> their applications in ZLD systems have not been reported in literature. In MVC, the feedwater is preheated by heat exchangers utilizing the sensible heat from the distillate product water, and then mixed with the recirculating brine slurry at the sump of the brine concentrator. The brine slurry is conveyed to the top of the concentrator and flows down inside a bundle of heat transfer tubes. The flowing brine forms a thin film on the internal tube surface where water evaporation occurs. Calcium sulfate seeds are often added into the recirculating brine to provide preferential precipitation sites, which keep precipitating salts in suspension and prevent scale formation on the heat transfer tubes.<sup>11,41</sup> The produced water vapor flows to the vapor compressor, which delivers the compressed vapor to the external surface of the heat transfer tubes. The superheated vapor condenses, transferring its latent heat to vaporize the falling brine slurry. The condensate travels

down the heat transfer tubes and is collected as distillate that preheats the incoming feedwater before being reused.

The formation of a falling thin film enhances the heat transfer rate, thereby reducing the compression ratio and required energy of the compressor.<sup>42</sup> The use of energy recovery devices (e.g., heat exchangers) further decreases the energy consumption. Even so, MVC brine concentrators are still very energy-intensive and require high-grade electric energy. They typically consume 20–25 kWh<sub>e</sub>/m<sup>3</sup> of treated feedwater,<sup>41,22</sup> with higher values (up to 39 kWh<sub>e</sub>/m<sup>3</sup> of feedwater) reported in the literature.<sup>43</sup> As an established technology that has been applied successfully in ZLD processes for decades,<sup>41</sup> MVC brine concentrators set a benchmark for energy comparison with other technologies, which guides efforts to reduce energy consumption in ZLD. Further, brine concentrators are able to reach salinity concentrations of 250 000 mg/L, with a water recovery of 90–98%, and produce high-quality product water (TDS < 10 mg/L).<sup>20,22</sup> However, capital costs of MVC are high due to the use of expensive materials such as titanium and stainless steel, which are required to prevent corrosion by the boiling brine.<sup>20,41</sup>

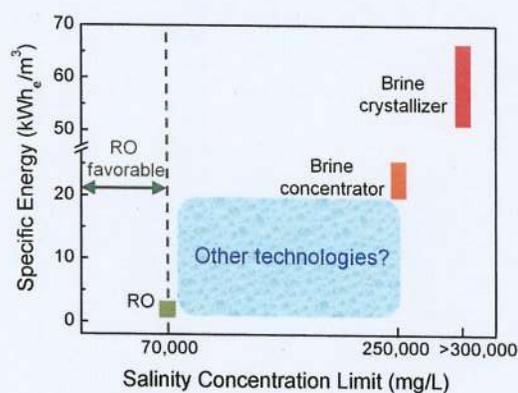
The concentrated brines produced by brine concentrators are usually sent to a brine crystallizer where the remaining water is further recovered. Similar to brine concentrators, vapor compressors are employed in crystallizers to supply the heat needed for water evaporation. However, for small systems (less than 23 L/min), steam-driven crystallizers are economically favorable.<sup>11,20</sup> Vapor compressor crystallizers are commonly operated in a forced-circulation mode. The viscous brine is pumped through submerged heat exchanger tubes under pressure, thereby preventing boiling and subsequent scaling inside the tubes.<sup>41</sup> The energy consumption of crystallizers is as high as 52–66 kWh<sub>e</sub>/m<sup>3</sup> of treated feedwater,<sup>11,22</sup> which is nearly three times that consumed by MVC brine concentrators. This dramatic energy increase is inevitable as crystallizers are treating feed brines with much higher salinity and viscosity.

Evaporation ponds can be used as competitive alternatives to brine crystallizers. Evaporation ponds utilize natural solar energy and have a lower operation cost.<sup>20,22</sup> Nevertheless, they are only suitable when treating small volumes at locations with a high evaporation rate and inexpensive land. Their high capital cost and environmental concerns for potential leakage of hazardous waste further hinder widespread application.<sup>22</sup> In a hypothetical scenario of ZLD inland desalination in Las Vegas, Nevada,<sup>44</sup> the cost of land acquisition for evaporation ponds, not including the infrastructure, was estimated to be nearly three times that of the total treatment cost by brine concentrators followed by crystallizers. In addition, water evaporated from evaporation ponds cannot be collected and reused, thereby making no contribution to improving water usage efficiency.

**Thermal ZLD with RO Preconcentration.** Despite their limitations, brine crystallizers or evaporation ponds are still indispensable for ZLD processes. Therefore, the focus of ZLD technology has been on reducing the volume of concentrated brine entering the brine crystallizers or evaporation ponds. RO, a well-established, pressure-driven desalination technology with excellent energy efficiency compared to thermal desalination, has been incorporated into ZLD operation to lower energy consumption (Figure 2B).

Unlike thermal processes, RO does not require product water to undergo phase transition to achieve separation, thereby eliminating irreversible losses associated with evaporation and condensation in thermal processes. The energy consumed by the RO stage in seawater desalination at 50% recovery is as low as ~2

kWh<sub>e</sub>/m<sup>3</sup> of product water,<sup>8</sup> which is significantly lower than that by brine concentrators and crystallizers (Figure 3). A smaller

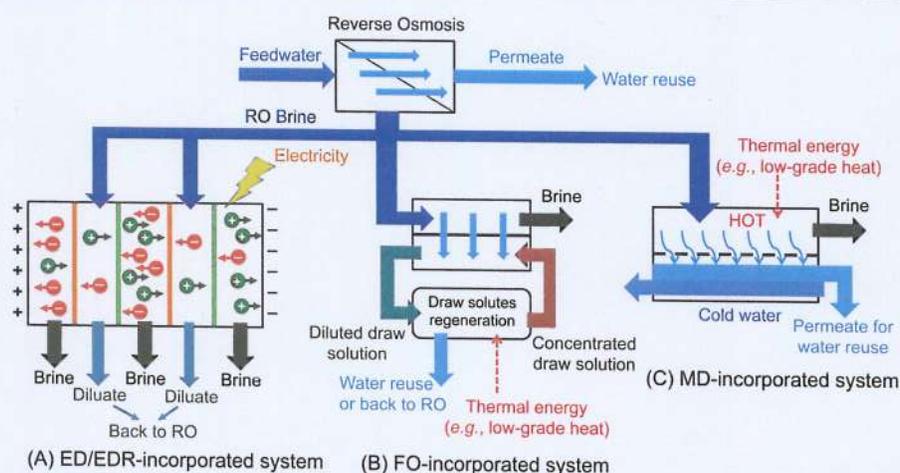


**Figure 3.** Specific energy consumption by RO, brine concentrator, and brine crystallizer. Although RO is energy efficient, its limited salinity range (typically with an upper concentration of ~70 000 mg/L) provides opportunities for other technologies to be applied in ZLD systems. The specific energies shown in the figure are in kWh<sub>e</sub> per cubic meter of feedwater.

amount of energy is required when treating feedwater with lower salinity than seawater (e.g., brackish water RO, BWRO).<sup>16</sup> In addition, the modular nature of membrane-based technologies provides further versatility in adapting RO into wastewater treatment facilities. As a result, RO can be used to preconcentrate the feedwater prior to the more energy-intensive thermal processes, increasing both energy and cost efficiencies of ZLD systems. For example, Bond et al. reported that incorporating a secondary RO to treat RO brines from inland desalination saved 58–75% of energy and 48–67% of treatment cost as compared to using only a brine concentrator followed by an evaporation pond.<sup>19,21</sup> Notably, although the secondary RO largely reduced the volume of brine entering the brine concentrator, the capital/operation cost of the brine concentrator remained a major contributor to the total treatment cost.<sup>21</sup>

However, application of RO in ZLD is constrained by two inherent limitations: membrane fouling/scaling and a limited upper level of salinity that can be treated. Membrane fouling/scaling reduces water permeability and the lifespan of RO membranes. This problem is particularly significant for ZLD, as the feedwater is concentrated more substantially than conventional SWRO or BWRO. Therefore, extensive pretreatment, such as chemical softening, pH adjustment, and ion exchange, is required in RO-incorporated ZLD systems (Figure 2B). These pretreatment methods mostly involve intensive use of chemicals, producing additional solid waste and increasing operation costs. Low-pressure membrane filtration, like ultrafiltration (UF), also performs as effective RO pretreatment.<sup>45</sup> Loganathan et al. recently reported a pilot ZLD system which incorporated RO with UF pretreatment to treat basal aquifer water with high fouling/scaling potential and an average TDS of 21 300 mg/L.<sup>46</sup> UF pretreatment removed most of the total suspended solids and total iron, as well as nearly 50% of oil and grease present in the feedwater, thereby enabling the subsequent RO stage to operate at high recovery rates prior to evaporation/crystallization.<sup>46</sup>

Altering the operating conditions of RO can further reduce membrane fouling/scaling. For example, a proprietary technology—high-efficiency RO (HERO)—achieves low fouling/



**Figure 4.** Schematic illustration of emerging membrane-based ZLD technologies in which (A) ED/EDR, (B) FO, or (C) MD is incorporated. ED/EDR uses an array of cation-exchange (green) and anion-exchange (orange) membranes that selectively reject anions and cations, respectively; FO employs a semipermeable membrane that allows water to pass through but ideally rejects all salts; MD employs a porous hydrophobic membrane that allows passage of water vapor through the membrane (as indicated by the blue curved arrows) but not liquid or salt. The produced brine is further concentrated by brine crystallizers or evaporation ponds to achieve ZLD.

**Table 1. Advantages, Limitations, And Energy Consumption of Different Salt Concentrating Technologies used in ZLD Operations**

technology	advantages	limitations	energy consumption
RO	energy efficient modular technical maturity	limited salinity range (upper concentration $\sim 75\,000$ mg/L) high fouling propensity	seawater: $2\text{--}6$ kWh <sub>e</sub> /m <sup>3</sup> of product water; <sup>8,16</sup> brackish water: $1.5\text{--}2.5$ kWh <sub>e</sub> /m <sup>3</sup> of product water <sup>16</sup>
ED/EDR	high salinity limit (upper concentration $>100\,000$ mg/L) low fouling propensity (especially for silica-enriched feedwater) modular	high energy consumption and cost when treating high salinity feedwater with high-quality water product incapability of removing noncharged contaminants using only prime energy	$7\text{--}15$ kWh <sub>e</sub> /m <sup>3</sup> of feedwater (with feed salinity $>15\,000$ mg/L) <sup>52-55</sup>
FO (with NH <sub>3</sub> /CO <sub>2</sub> thermolytic draw solution)	high salinity limit (upper concentration $>200\,000$ ppm) utilization of low-grade heat low fouling propensity modular	low water flux at very high feed salinities reverse solute flux (NH <sub>3</sub> may contaminate product water) emerging technology with limited field performance data	$21$ kWh <sub>e</sub> /m <sup>3</sup> of feedwater (with feed salinity of $73\,000$ mg/L and recovery of 64% in average) <sup>43</sup>
MD	high salinity limit (upper concentration $>200\,000$ ppm) utilization of low-grade heat low fouling propensity modular	low water flux and water recovery potential of membrane wetting post-treatment is needed if volatile pollutants are present emerging technology with limited field performance data	$40\text{--}45$ kWh <sub>e</sub> /m <sup>3</sup> of product water <sup>76</sup> $22\text{--}67$ kWh <sub>e</sub> /m <sup>3</sup> of product water <sup>72</sup>
MVC brine concentrator	technical maturity high salinity limit (upper concentration $>200\,000$ ppm)	high energy consumption high capital and O&M costs operating at high temperature using only prime energy not modular	$20\text{--}25$ kWh <sub>e</sub> /m <sup>3</sup> of feedwater <sup>11,22</sup> $28\text{--}39$ kWh <sub>e</sub> /m <sup>3</sup> of feedwater <sup>43</sup>

scaling propensity and high water recovery by a combination of extensive pretreatment and high pH condition.<sup>22,47,48</sup> The feedwater is treated by a weakly acidic cation exchange system to remove divalent ions, after which CO<sub>2</sub> is removed by degasification and pH is raised to above 10. This high solution

pH increases silica solubility and suppresses silica scaling as well as organic and biological fouling, thereby allowing RO to operate at high recoveries (e.g.,  $>90\%$  for brackish water<sup>48</sup>). The HERO process has been applied in multiple full-scale ZLD systems

worldwide,<sup>29,31,49</sup> including a recent project for a Chinese coal-to-liquids plant with a high treatment capacity of 2300 m<sup>3</sup>/h.<sup>31</sup>

Current RO membrane modules cannot operate at very high hydraulic pressure, which typically corresponds to a salinity of ~70 000 mg/L of the RO exit brine.<sup>42</sup> This restriction of RO systems imposes a ceiling on the salinity of water that can be treated by RO in ZLD systems. This salinity limit is much lower than that achieved by brine concentrators (i.e., up to 250 000 mg/L). Thus, a stand-alone RO system is not able to reduce the volume of concentrated brine to the same extent as brine concentrators. Accordingly, RO is usually followed by a brine concentrator in ZLD processes.<sup>11,19,20</sup> Developing new technologies, which tolerate higher salinities than RO and consume less energy than brine concentrators (as highlighted in Figure 3), is of paramount importance for advancing ZLD technology.

#### ■ BEYOND THERMAL EVAPORATORS: EMERGING MEMBRANE-BASED ZLD TECHNOLOGIES

Three membrane-based processes—ED, FO, and MD—emerge as alternative ZLD technologies to brine concentrators to further concentrate the wastewater after the RO stage. The produced brine from these processes serves as a feed to the crystallizer or evaporation pond. A schematic illustration of ZLD systems incorporating these technologies is shown in Figure 4. Their advantages, limitations, and energy consumption, along with those of RO and MVC brine concentrators, are summarized in Table 1. Some of these technologies (i.e., thermolytic FO and MD) are hybrids of both thermal- and membrane-based processes. While the energy input to these processes is thermal, membranes are the core separation components of these technologies.

**Electrodialysis.** ED applies an electric potential as the driving force to remove dissolved ions through ion exchange membranes. In contrast to RO membranes that reject all ions, ion exchange membranes selectively permit the transport of counterions but prevent the passage of co-ions.<sup>50</sup> As shown in Figure 4A, cations move toward the negatively charged cathode by passing through cation-exchange membranes, whereas anions migrate in the opposite direction through anion-exchange membranes. These concurrent processes generate two streams—salt-depleted diluate and concentrated brine. In a modified form of ED, electrodialysis reversal (EDR), the polarity of the electrodes is reversed frequently for minimizing fouling and scaling,<sup>20</sup> thereby requiring much less pretreatment than RO.<sup>51</sup> ED and EDR also have a low scaling propensity for silica-enriched feedwaters (e.g., BWRO brines), as neutral silica is not accumulated in the brine stream.<sup>20</sup>

Compared to RO, ED and EDR are able to concentrate feed waters to higher salinity (>100 000 mg/L).<sup>5,52–54</sup> When concentrating brines to such high salinities, ED and EDR consume 7–15 kWh<sub>e</sub>/m<sup>3</sup> of feedwater,<sup>52–55</sup> which is less than that required by MVC brine concentrators. Also, the total cost for equipment and energy by ED was estimated to be lower than that of MVC.<sup>56</sup> However, in contrast to the very low TDS of water produced by brine concentrators and RO, the salinity of ED/EDR effluent can be much higher (e.g., TDS > 10 000 mg/L<sup>53</sup>), indicating a trade-off between the quality of the desired product water and overall energy consumption and capital cost.

For ED/EDR treating concentrated feedwater in ZLD systems, low-salinity product water results in a large voltage drop, high electric resistance, low current efficiency, and diluate loss, further increasing the energy consumption.<sup>57,58</sup> Furthermore, a decrease of diluate salinity reduces the limiting current

density, which increases the required membrane area and capital/operation cost.<sup>51</sup> As estimated by McGovern et al.,<sup>56</sup> the cost of salt removal by ED is higher at lower diluate salinities. As such, a stand-alone, single-stage ED/EDR system is not suitable for reaching ZLD in most cases, since one of the benefits of ZLD is the production of usable water. A multistage configuration is a feasible solution,<sup>56–58</sup> but it increases the capital cost.

As a partial desalination process, ED/EDR has been applied in combination with RO in several ZLD systems. Such systems achieved the dual function of extending the salinity limit of RO and reducing the energy consumption relative to brine concentrators. For example, Oren et al. demonstrated a pilot RO-EDR system for brackish water desalination with a water recovery of 97–98%.<sup>5</sup> In that system, EDR concentrated the RO brine to a salinity of 100 000–200 000 mg/L prior to a side-loop crystallizer and wind-aided intensified evaporation. In another pilot study,<sup>53</sup> EDR effectively removed hardness to reduce the scaling potential of saline basal aquifer water, thereby improving the subsequent RO recovery without chemical addition. The EDR brine could reach a salinity of 125 000 mg/L and was further concentrated by a brine crystallizer to approach ZLD. In both cases, the EDR effluent was further desalinated by RO or partially blended with RO permeate to attain a desired product water quality.<sup>5,53</sup>

**Forward Osmosis.** Unlike hydraulic pressure-driven RO, FO utilizes an osmotic pressure difference to drive water permeation across a semipermeable membrane.<sup>59</sup> In FO, water flows from the feedwater to a concentrated draw solution with a higher osmotic pressure (Figure 4B). The produced brine is sent to a brine crystallizer or an evaporation pond, whereas the draw solutes are separated from the desalinated water to regenerate the concentrated draw solution. Since the driving force in FO is osmotic pressure, FO can treat waters with much higher salinity than RO. When using FO to concentrate feedwater beyond the salinity limit of RO, the osmotic pressure of diluted draw solution will surpass the bearable pressure limit of RO. Hence, in this case, draw solutes that depend on RO for regeneration (e.g., NaCl and MgSO<sub>4</sub>)<sup>60</sup> will not be suitable.

The development of thermolytic draw solutes, such as the ammonia–carbon dioxide (NH<sub>3</sub>/CO<sub>2</sub>), paved the way for FO-incorporated ZLD systems. The NH<sub>3</sub>/CO<sub>2</sub> draw solution generates very high osmotic pressure-driving forces and can be regenerated by low-temperature distillation.<sup>61,62</sup> A recent pilot study demonstrated the application of FO with NH<sub>3</sub>/CO<sub>2</sub> draw solution to concentrate produced water from the Marcellus shale region to an average salinity of 180 000 mg/L.<sup>43</sup>

Because the thermolytic NH<sub>3</sub>/CO<sub>2</sub> draw solution decomposes at moderate temperature (approximately 60 °C at atmospheric pressure),<sup>61</sup> low-grade thermal energy, including industrial waste heat and geothermal energy, can be utilized to regenerate the concentrated draw solution. A recent study estimated that U.S. power plants produced 803 million GJ of waste heat at temperatures greater than 90 °C in 2012.<sup>63</sup> This amount of heat, if utilized to power the NH<sub>3</sub>/CO<sub>2</sub> FO, could potentially produce a maximum of 1.9 billion m<sup>3</sup> of water annually, which would meet the treatment demands for boiler water makeup and FGD wastewater systems of all U.S. power plants.<sup>64</sup> Also, geothermal energy is abundantly available in major ZLD markets such as the U.S. and China.<sup>42,65,66</sup>

FO operates at low pressure, resulting in foulant layers that are less compact and more reversible than in hydraulic pressure-driven RO systems. Accordingly, FO has a much lower fouling propensity than RO,<sup>59</sup> which not only reduces the operation cost

for fouling control but also extends the applicability of ZLD to wastewaters with high fouling potential.

The thermolytic FO process can be used as a brine concentrator after the RO stage. Compared to MVC brine concentrators, the  $\text{NH}_3/\text{CO}_2$  FO can be competitive because a small volume of the more volatile draw solutes (i.e.,  $\text{NH}_3$  and  $\text{CO}_2$ ), instead of water, is vaporized to regenerate the concentrated draw solution.<sup>43</sup> Furthermore, the modularity of FO results in smaller area footprint and also renders ZLD systems more adaptable to fluctuations in the flow rate and quality of feedwater.<sup>67</sup>

Recently, the world's first FO-based ZLD system was constructed at the Changxing power plant in Zhejiang Province, China.<sup>26,67</sup> The system treats a mixture of FGD wastewater and cooling tower blowdown at 650 m<sup>3</sup>/day. The feedwater is first concentrated by RO to a concentration of ~60 000 mg/L. The  $\text{NH}_3/\text{CO}_2$  FO process is then used as a brine concentrator to further concentrate the RO brine to above 220 000 mg/L TDS. As the last step, the FO brine is fed to a crystallizer for further concentration, while a high-quality product water (TDS < 100 mg/L after polishing by a secondary RO) is produced for reuse as boiler makeup water.<sup>67</sup>

**Membrane Distillation.** MD is a thermal, membrane-based desalination process, in which a partial vapor pressure difference drives water vapor across a hydrophobic, microporous membrane.<sup>68</sup> In MD, the feedwater is heated and the resultant temperature difference between the hot feedwater (typically 60–90 °C<sup>69,70</sup>) and colder permeate side creates a vapor pressure difference to drive the water vapor flux (Figure 4C). The aqueous permeate can be in direct contact with the membrane (direct contact membrane distillation, DCMD). Alternatively, the water vapor can be collected on a condensation surface separated from the membrane, such as in air gap membrane distillation (AGMD), vacuum membrane distillation (VMD), or sweeping gas membrane distillation (SGMD).<sup>68,71–74</sup>

MD is more energy intensive than RO and ED/EDR, because water separation by MD requires liquid–vapor phase transition. The theoretical minimum energy of seawater desalination by single-pass DCMD with heat recovery and a feed temperature at 60 °C is 27.6 MJ/m<sup>3</sup> of product water,<sup>75</sup> which is much higher than that by RO with a typical recovery of 50% (3.8 MJ/m<sup>3</sup> of product water).<sup>8</sup> In practical use, DCMD was estimated to consume 143–162 MJ (40–45 kWh<sub>e</sub>) per m<sup>3</sup> of product water for seawater desalination,<sup>76</sup> and a comparable value of 80–240 MJ (22–67 kWh<sub>e</sub>)/m<sup>3</sup> of product water was reported for AGMD.<sup>72</sup> However, this thermal-based energy consumption cannot be directly compared with the energy consumption of electricity-driven technologies (RO, ED/EDR, and MVC brine concentrators), because the efficiency of electricity generation from thermal energy varies with the quality (temperature) of the thermal energy. Compared to MVC brine concentrators with well-designed energy recovery devices, efficient heat recovery (e.g., use of heat exchangers<sup>75</sup> or brine recycling<sup>77</sup>) is critical to improve the energy competitiveness of MD.

Similar to thermolytic FO, MD is beneficial due to its ability to treat high salinity feed waters that cannot be desalinated by RO, and MD's potential to leverage low-grade thermal energy. When low-grade energy is available, MD achieves both cost saving and a reduced carbon footprint relative to electricity-driven desalination technologies. Furthermore, MD is modular, can operate at low pressure and temperature, and has low fouling propensity.<sup>70,72,76,78</sup> However, when volatile pollutants or surfactants are present in the feedwater (e.g., in coal-to-chemical,<sup>79</sup> brewery,<sup>80</sup>

and shale gas industries<sup>42</sup>), MD suffers from membrane wetting and the passage of volatile compounds into the permeate, which deteriorate product water quality and cause process downtime.<sup>42,70,81</sup>

The potential application of MD in ZLD inland desalination has been demonstrated at the bench scale.<sup>82</sup> When applying MD to further concentrate a secondary RO brine (with TDS of ~17 500 mg/L), a total water recovery of >98% was obtained for a brackish groundwater in California.<sup>82</sup> Recently, a conceptual near-ZLD system incorporating MD with reverse electrodialysis (RED) was shown to achieve both water and energy production in seawater desalination.<sup>83</sup> In that system, MD reduced the volume of simulated SWRO brine (1 M NaCl) by more than 80%. The produced MD brine was then mixed with seawater in a RED stack to generate electrochemical energy. To date, however, large-scale applications of MD are still hindered by its technical immaturity and low single-pass, single-module water recovery.<sup>20,75</sup> No pilot-scale applications of MD in ZLD have been reported in the literature.

## ENVIRONMENTAL IMPACTS

Despite the main goal of ZLD to reduce water pollution and improve water sustainability, application of ZLD also results in unintended environmental impacts. One risk stems from the produced solid wastes. For example, solid wastes stored in evaporation ponds have raised concerns about their odors, potentially negative impact on wildlife, and risk of leakage.<sup>22</sup> Similarly, solid wastes disposed in landfills may result in leaching of chemicals into groundwater.<sup>84</sup> Accordingly, impervious liners and reliable monitoring systems are typically required to prevent potential contamination from solid wastes.

As discussed earlier, ZLD consumes large amounts of energy, leading to significant emission of greenhouse gases (GHG). Some pretreatment methods, such as acidification followed by degasification, release  $\text{CO}_2$  from the feedwater into the atmosphere. For example, the application of ED in concentrating RO brine increases  $\text{CO}_2$  emission via both energy consumption and decarbonation for scaling control.<sup>85</sup> A life-cycle study showed that GHG emission would increase by 50% if California water supply was switched from imported water to BWRO inland desalination.<sup>86</sup> According to the U.S. Energy Information Administration,<sup>87</sup> the amount of  $\text{CO}_2$  produced by electricity generation varies depending on the fuel type. Assuming 939 g of  $\text{CO}_2$  per kWh<sub>e</sub> generated by bituminous coal,<sup>87</sup> MVC brine concentrators will typically produce 19–23 kg of  $\text{CO}_2$  per m<sup>3</sup> of treated feedwater solely from electricity usage (corresponding to energy consumption of 20–25 kWh<sub>e</sub>/m<sup>3</sup><sup>311,22</sup>). Incorporating technologies with higher energy efficiency, such as RO, will significantly reduce the GHG emission. In addition, emerging ZLD technologies that can utilize low-grade or renewable energy (e.g., waste heat, solar energy, geothermal energy<sup>18,42,63,64</sup>) enable further reduction of GHG footprint of ZLD systems.

## OUTLOOK

ZLD implementation is growing globally as an important wastewater management strategy to reduce water pollution and augment water supply. However, high cost and intensive energy consumption will remain the main barriers to ZLD adoption. As the feedwater becomes more concentrated along the ZLD treatment train, its salinity increases and so does the minimum energy required for desalination.<sup>8</sup> Therefore, the energy demand

of ZLD, along with its associated costs, will still be higher than that of conventional wastewater treatment or disposal options.

Future growth of the ZLD market will heavily rely on regulatory incentives that outweigh its economic disadvantages. As the severe consequences of water pollution are increasingly recognized and attract more public attention, stricter environmental regulations on wastewater discharge are expected, which will push more high-polluting industries toward ZLD. Intensified freshwater scarcity, caused by both climate change and freshwater overexploitation, will likely facilitate ZLD implementation. The prolonged drought in the Southwest U.S.<sup>88</sup> and accelerating growth of water-intensive industries (e.g., coal-fired power plants) in China<sup>89</sup> exemplify a worldwide freshwater deficiency. In such cases, a water quota may be imposed to limit the total freshwater withdrawal by high water-consuming industries.<sup>90</sup> In this case, ZLD may be a needed strategy to guarantee sustainable water supply.

Due to the unrivaled energy efficiency of RO, expanding the salinity range of RO is of paramount importance in ZLD systems. A robust RO system with higher resistance to hydraulic pressure and fouling/scaling will effectively improve the energy efficiency and economic feasibility of ZLD. At the core of such systems are fouling mitigation technologies, such as fouling- and scaling-resistant membranes, which will reduce the operation cost through less extensive pretreatment and cleaning needs<sup>91,92</sup> and enhance the quality of the product water for reuse.<sup>93</sup> Major progress has been made to develop RO membranes with resistance to organic and biological fouling,<sup>94–96</sup> but more remains to be done to test their performance in ZLD systems with various feedwater composition and very high concentration factors. Membranes with low propensity to inorganic scaling (e.g., gypsum and silica scaling) are particularly desirable.

We have reviewed three membrane-based technologies — ED/EDR, thermolytic FO, and MD — as three emerging ZLD technologies to further concentrate the feedwater after the RO stage. However, compared to the technical maturity of RO and MVC brine concentrators, these technologies are less established. More pilot or field studies are desirable to validate their large-scale performance and viability in pursuing ZLD. Especially, their energy consumption and cost need to be further evaluated to make a direct comparison with MVC brine concentrators. For MD and thermolytic FO, their capability of harnessing low-grade energy will significantly reduce the prime energy demand, operation cost, and GHG footprint of ZLD.

Resource recovery may provide an additional economic incentive for ZLD. Beneficial components in the feedwater (e.g., valuable salts, nutrients, critical metals and elements) can precipitate or be largely enriched when the feedwater is concentrated. For example, a proprietary technology has been used for sequential salt recovery while achieving ZLD.<sup>11,97</sup> This technology involves multiple mineral precipitation and crystallization steps, producing useful salts such as gypsum-magnesium hydroxide, magnesium hydroxide, and precipitated calcium carbonate.<sup>11,97</sup> The economic values of these byproducts (e.g., \$350/ton of precipitated calcium carbonate<sup>11</sup>) can partially compensate for the operation cost of ZLD. Further, the emerging ZLD technologies reviewed in this article can recover various nutrients from wastewater,<sup>98</sup> and harvesting critical metals and elements from ZLD desalination systems has been recently proposed.<sup>99</sup>

In addition, the environmental impacts of ZLD need to be better understood. A life-cycle assessment analysis of the energy demand and GHG emission will provide additional insights into

the cost-benefit balancing of ZLD. Along with advances in improving the energy and cost efficiencies of ZLD technologies, particularly by incorporating membrane-based processes, ZLD may become more feasible and sustainable in the future.

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### Notes

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# Can solar energy help ZLD technologies to reduce their environmental footprint? - A Review

Abhishek Gautam  , Tapan Dave, Shankar Krishnan

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## Abstract

Water is the primary factor for life on earth, and its demand is continuously increasing significantly. Therefore, freshwater scarcity is one of the world's critical challenges due to the depletion and contamination of its reservoirs. Climate change, irrational exploitation, and waste disposal from various sources to the natural water reserves are the major causes of the contamination. Moreover, the increased utility of desalination systems has also magnified the production of rejected brine, whose disposal in water bodies and land will also result in a hazardous situation for future generations. Therefore, it is necessary to adopt sustainable approaches in the present for the welfare of future generations. Given the same, the concept of zero liquid discharge (ZLD) has emerged as a strong alternative for freshwater production in the most sustainable manner. It is a dual-purpose technology of fresh water production with dry salts from the brine by preventing the brine discharge into the environment. The sustainability of ZLD desalination systems can be further increased by using solar energy to fulfill their energy requirement. Hence, various technical and economic aspects of ZLD desalination technologies are presented in this review, along with the discussion on the feasibility of solar energy to achieve ZLD. An analysis is carried out on the impact of solar energy on the energy, economic and environmental potential of ZLD desalination technologies, whose outcome shows wind-aided intensified evaporation, reverse osmosis, and electrodialysis metathesis have higher potential compared to rest technologies.

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## Introduction

Water is one of the basic needs for life on earth. The quantity of fresh water is depleted with time due to advancements in industrialization, rising living standards, climate change, and contamination of freshwater reserves. The earth is considered a blue planet because water occupies 71% of its surface. However, humanity and other water-dependent species are dealing with water scarcity, as 96.5% of available water on earth is not potable due to its salinity and brackish form [1]. This quantity of water can only be utilized in industries for various processes such as mining and power generation. As per the United Nations world water development report 2021, nearly 2/3rd of the global population faces water scarcity for at least one month each year, whereas 1/4th of the global population may deal with the same trouble for the whole year by 2040 [2]. The curves between clean water availability and its demand presented by Boretti and Rosa [3] about the alarming situation of water crises till 2040 are shown in Fig. 1.

The stakeholders have been trying to overcome this issue of water scarcity for the last few decades [4]. The distillation and membrane processes have been common practice for many years because of the same. Desalination of saline water is one of the standard methods to get fresh water for utility [5]. In the last decade, a positive phase transformation has been observed worldwide in utilizing desalination systems to overcome water scarcity. Countries like China, India, Israel, Australia, and nations of Arab and Africa are developing desalination systems/plants due to the limited freshwater availability in their region [6]. As per the International Desalination Association (IDA), nearly 22700 desalination plants with a capacity of almost 107 million m<sup>3</sup>/day are operational worldwide until 2022 [7].

Irrespective of the technology used for water desalination, brine disposal and its environmental impact are major issues [8]. The generalized processes involved in managing brine obtained from the desalination plant are shown in Fig. 2. The rejected water with many concentrated salts (called brine) is usually discharged into inland water bodies or seawater, which harms marine ecosystems and aquatic species and also affects the human health [[9], [10], [11]]. Therefore, several international agreements have been signed to encourage and support building solutions for protecting ecosystems, conserving water bodies, and improving water quality [12,13].

Due to the exponential increment in desalination plants acting as a source for wastewater production, the amount of brine is also increasing rapidly. Thus, the harmful environmental impacts of rejected brine from such sources emphasize the world to improve their disposal methods and explore alternative sustainable technologies. Zero liquid discharge (ZLD) is one such concept for freshwater production using desalination technology to provide an alternative to all the existing disposal methods. Stringent regulations, increasing cost of wastewater disposal, and steepened significance of freshwater emphasize a ZLD approach for freshwater production.

Apart from the associated benefits, the decision to implement the ZLD approach is not easy. The involvement of intensive energy requirements and high capital/operation costs are the major barriers to its success; hence, the ZLD approach is adopted by limited plants worldwide. A feasible ZLD-based plant should have an optimum balance among the benefits, energy requirements, and associated costs [15]. On the other side, fossil fuels are the primary energy sources to fulfill the energy needs of such systems, which are indirectly associated with similar drawbacks to nature as in the case of conventional desalination plants. Solar energy is emerging as a strong alternative to fossil fuels, which has the potential to play a significant role in accomplishing the energy requirement of ZLD systems without leaving any harmful impact on the environment [16].

Solar energy has been established as an effective alternative to fossil fuels due to its abundant quantity and superior quality. It is a freely available and environmentally friendly energy resource [17]. Solar energy-based desalination systems have received significant research attention recently and have achieved cost-effectiveness, environmental benefits, and comparatively simpler operations [18]. Several researchers have also reported their studies on solar energy-based hybrid desalination systems in the last few years [16,[19], [20], [21], [22], [23], [24]]. Moreover, the economic feasibility of such systems is also reported in recent studies [25,26]. Thereby, the potential, feasibility, and challenges allied with using solar energy to achieve ZLD have been explored and discussed in this review paper.

A number of reviews were reported to address the various aspects of the ZLD strategy, such as technologies, energy analysis, salt recovery, economic feasibility, and environmental footprints [27,28]. It was found that the high energy requirement, lesser monetary benefits, and negative impact of conventional energy sources are the common issues raised in such studies. The feasibility of solar energy in desalination and integrated desalination systems with solar power plants have also been reported by researchers. However, solar energy's potential to achieve ZLD has not been reviewed so far. Therefore, the current review presents the potential and feasibility of solar energy to achieve ZLD. Initially, the existing conventional methods of brine disposal are discussed in detail. Thereafter, the need and features of ZLD are discussed along with various technologies, followed by a discussion on the feasibility of solar energy to achieve ZLD. Moreover, the present review also presents a discussion on the economic aspect of the same and an analysis of solar energy's technical, economic, and environmental potential to achieve ZLD with various desalination methods. The conclusions drawn from the extensive literature review are presented with future scope and recommendations.

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## Section snippets

### General brine management methods and related aspects

With desalination technologies, the feed water is parted into fresh water as a major product and brine as a by-product. The term brine is broadly used for the by-product regardless of its salinity level. However, it is generally used for salinity levels higher than 55000mg/L of total dissolved solids (TDS). Brine is highly concentrated water containing heavy metals, microbial contaminants, nutrients, and pathogenic microorganisms [29]. It also contains the chemicals added during the...

### Zero liquid discharge desalination

The ZLD desalination involves a closed loop of water to retreat the rejected portion obtained after the conventional desalination process so that the quantity of rejected water leaving the plant is reduced to zero [13]. The purity level of freshwater produced from the ZLD-based systems/plants is sufficient to utilize it for domestic and industrial purposes. At the same time, the recovered salt in a solid state can be used in any industrial application or disposed of in the most...

### Solar energy to achieve ZLD

The intensive energy requirement and higher associated costs are the major barriers to implementing ZLD systems. At present, maximum desalination systems are based on conventional sources of energy, which are harmful to the environment and will run out after a few decades. These drawbacks of using fossil fuels in ZLD systems can be conquered by developing highly efficient technologies and incorporating solar energy [[152], [153], [154], [155]]. The feasibility and other important aspects of...

## Economics

Apart from the technical aspect, the economic feasibility of the ZLD system plays a significant role in obtaining favorable outcomes. Therefore, it is also necessary to explore the economic feasibility at the preliminary stage of the system and maintain the optimum balance between technical and economic aspects [192]. More than 150 countries are practicing desalination, and the majority of these plants are established in the United States of America, Saudi Arabia, Kuwait, United Arab Emirates,...

## Potential of solar energy

As stated in section 4, solar energy has great potential to play a significant role in achieving ZLD. In order to estimate its economic and environmental potential, a critical analysis is carried out in terms of SEC (in kWh/m<sup>3</sup>), cost (in US\$/m<sup>3</sup>), and CO<sub>2</sub> mitigation (in kg/m<sup>3</sup>) for the production of 1 m<sup>3</sup> freshwater using various desalination techniques discussed in section 3. The assessment is carried out for SPV and CSP systems, whereas the obtained results are compared with the corresponding...

## Conclusions

The ZLD is an emerging approach for freshwater production in the most sustainable manner. It is a dual-purpose technology for freshwater production with dry salts from the brine by preventing the brine discharge into the environment. The presented review discussed the state-of-the-art technologies used for brine management using the ZLD strategy, the feasibility of solar energy to achieve ZLD, and its economic aspect. The major conclusions drawn based on the extensive literature review of ZLD...

## CRedit authorship contribution statement

**Abhishek Gautam:** Writing – original draft, Validation, Methodology, Formal analysis, Conceptualization.

**Tapan Dave:** Writing – review & editing, Writing – original draft, Formal analysis, Conceptualization.

**Shankar Krishnan:** Writing – review & editing, Supervision....

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper....

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## Studies on Zero Liquid Discharge (ZLD) plant in API Manufacturing Unit

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### ABSTRACT

The concerns over the environmental impact of water pollution has increased, and also ground water resources are gradually being depleted. In the current situation, it is required to recycle the wastewater generated from industrial outlets. On other hand, environmental authorities are being directed to establish "Zero Liquid Discharge (ZLD) plants" in all industrial sectors. A study was conducted in a medium scale API (Active Pharmaceutical Ingredients) manufacturing industry where wastewater recycling through ZLD plant. The investigation shown that the plant was generated high quality water which was suitable to recycle in plant premises and which resulted in reduction of water consumption to 40KLD (Kilo Liter per Day). Total source of effluents generated in operations were categorized to HCS (High Concentration Streams) and LCS (Low Concentration Streams). HCS are treated in HCS effluent treatment unit and LCS in LCS effluent treatment unit. The HCS effluent treatment unit made of a Solvent stripper, MEE (Multiple Effective Evaporator) and ATFD (Agitated Thin Film Drier), and LCS effluent treatment unit made of a SBR (Sequential Batch Reactor) and MBR (Membrane Bio-Reactor). The other unit which is called as water recycling unit consisting RO (Reverse Osmosis) plant and P. RO (Polishing RO) plant. The pilot plant of ZLD shown a huge reduction in TDS (Total Dissolved Solids), TSS (Total Suspended Solids), BOD (Biological Oxygen Demand) and TSS (Total Suspended Solid) to 99.2, 100, 100 and 99.9 percent respectively.

### Key words

ZLD, Re-cycle, API wastewater, MEE, Stripper, SBR, MBR, RO

### 1. INTRODUCTION

Industrialization needs to improve the country economy. Increase of industrial treated has raised water consumption, and which leads to depletion of water resource. In other hand, water pollution is a keeping mankind in worry [1]. People have long been trying to find cost effective and reliable ways to treat wastewater and recycle of wastewater has become an absolute necessity [2]

There is as increased awareness among the general public on environmental pollution aspects and consequently environmental regulations have become very stringent. Rapid advances made in the wastewater treatment technologies during the past one decade, particularly in the bulk drug sector. Now it is possible to reduce water consumption and wastewater generation considerably and even achieve the Zero discharge levels [3, 4, 5].

India in the forefront of manufacturing APIs in the world. The primary character of API /Bulk drug manufacturing industry is to produce substances that have therapeutic value of Human and

animals. Pharmaceuticals are an important part in maintaining human health. But compounds in pharmaceuticals with therapeutic benefits for human at right does can be pollutants in the environment [6, 7].

Active Pharmaceutical Ingredients (API) manufacturing is a complex blend of operations. In general, wastewater management is one of the critical areas and of major concern in this sector industry. There are number of streams with different characteristics which originate from various sections of the industry, requiring segregation and corresponding treatment [8, 9].

Major industrial establishments in the region have established in-house wastewater treatment facilities. Small and medium scale industries might need to send the wastewater to common treatment facilities or to be recycle within the premises through ZLD (Zero Liquid Discharge) plant. As per local and national regulations, it is mandatory to establish ZLD plant, and treated water should be recycled within the premises [10].

An assessment was made to evaluate the ZLD plant performance in a medium scale API manufacturing industry, where variety of effluents generated, treated through ZLD plant and recycled within the plant premises.

## 2. MATERIALS AND METHODS

### 2.1 Source of wastewater

The source of wastewater used in the pilot plant studies generated from various source of API manufacturing unit, which includes process outlets, process equipment washings, process area floor washings, utilities wastewater (i.e., cooling tower blow downs, boiler blow downs and utilities washings), effluent treatment plant washings, etc.

### 2.2 Segregation of wastewater

Total effluents were broadly segregated to High Concentration Streams (HCS) and Low Concentration Streams (LCS), which was based on COD (Chemical Oxygen Demand) and TDS (Total Dissolved Solids). If a wastewater stream characteristics, i.e., COD >15000 mg/l and TDS >8000 mg/l, segregated to HCS. If both the above said parameters were within the below levels (i.e., COD <15000 mg/l and TDS <8000 mg/l), the wastewater streams falls under LCS. If anyone characteristics of wastewater crosses their limits to HCS (i.e., >15000 COD or >8000 TDS), those are also segregated as HCS.

### 2.3 Characterization of wastewater

Wastewater characterized by approved methods (i.e., pH by pH Electrode, COD by HACH COD track, BOD by HACH BOD track, TSS by Gravimatory, Millipore, and TDS by Gravimatory, watt man). Characteristics of wastewater in various stages has been characterized and tabulated in table 1.

Studies on Zero Liquid Discharge (ZLD) plant in API Manufacturing Unit

Table 1: Characteristics of wastewater.

S.No.	Parameter	Unit	HTDS Effluents from process/Stripper Feed	LTDS Effluents from Process & Utilities	Stripper Outlet/MEE feed	MEE Condensate	ATFD Feed/MEE Concentrate	ATFD Condensate	SBR Outlet/ MBR Feed	MBR Outlet/RO Feed	RO permeate	Polishing RO permeate
1	pH	---	7.75	7.91	6.58	8.52	5.92	8.13	7.96	6.68	6.91	6.84
2	COD	mg/l	54105	7712	33148	8951	83216	11520.7	2318	658	71	35
3	BOD		15846	3103	10206	3128	---	2751	652	128	2	0
4	TSS		114	1862	263	24	---	127	364	0	0	0
5	TDS		42202	7703	43814	1981	140683	1510	3372	3235	324	32

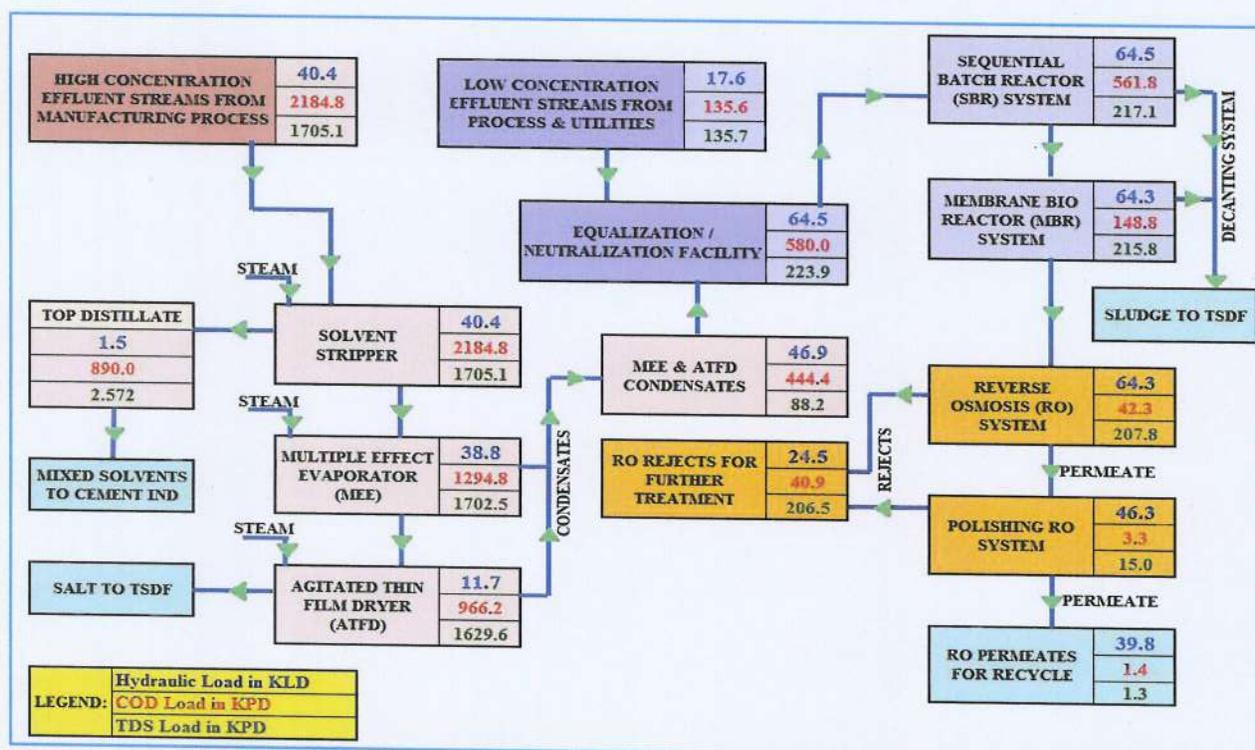


Figure 1: Schematic of pilot ZLD plant showing system wise loads (i.e., Feed, COD and TDS) movement during wastewater treatment of API manufacturing industry.

2.4 Structure of ZLD plant

As shown in figure 1, in API manufacturing site, ZLD plant consists three units, such as; (i) HCS treatment unit (ii) LCS treatment unit and (iii) Effluents recycling unit. The HCS treatment unit consists a solvent stripper, followed by a MEE (Multiple Effective Evaporator) and an ATFD (Agitated Thin Film Drier). The LCS unit comprises a wastewater equalization system, followed by a biological system Sequential Batch Reactor (SBR) and a Membrane Bioreactor (MBR). The third unit was a wastewater recycling unit where semipermeable (Reverse Osmosis) membranes used to filter the wastewater to recycle.

2.5 Wastewater flow and treatment in experimental ZLD

Effluents generated from various sources has been collected in HCS and LCS collection tanks. Wastewater collected in HCS collection tanks were fed to Solvent stripper, where mixed solvents were stripped and collected in top distillate collection tank. Stripper processed effluent collected from stripper column bottom fed to MEE, where maximum liquid extracted and condensate collected to condensate collection tank. The concentrate collected from MEE fed to ATFD, and condensate generated during ATFD operations were collected to condensate collection tank and salts generated was disposed to TSDF (Transport Storage Disposal Facility). The condensates from condensate collection tanks were transferred to Low concentration wastewater collection tanks for further treatment.

Effluents collected in Low concentration streams collection tanks were fed to Equalization cum neutralization system where all effluents were equalized to uniformed and neutralized to required pH (6.5 to 8.5). After neutralization and equalization process, effluents fed to SBR which is a fill and draw activated sludge process and where microbial cells reduces the Organic load. SBR processed wastewater was passed through Decant tank followed by Lamella clarifier to remove settleable solids. The overflow of Lamella clarifier was fed to MBR system which removes suspended solids to zero in permeate. The tanks and settlers bottom drains were collected in sludge collection tank and which was fed to sludge decanting system. The sludge generated during this process was disposed to TSDF.

The permeate collected from MBR system fed to RO system which filters the wastewater through semipermeable membrane. The permeate generated from RO system fed to Polishing RO, where wastewater polished to portable water quality. Polished water was recycled to Utilities for use and rejects generated in the process was sent to MEE for treatment.

Effluent flow quantity was followed as per system design. The entire system and individual units performance was investigated with the help of physical, chemical and biological parameters in various intervals (i.e., end of the day 1, 2, 3, 4, 5... and 30). Values were considered after stabilizing the system.

**3. RESULTS AND DISCUSSION**

**3.1 Effluent Characteristics and Hydraulic Loads**

Characteristics of effluents in various stages of pilot plant operations are presented in table 1. Loads of raw effluents fed to the system was within the designed specifications. Hydraulic loads fed to the various system were presented in figure 1. For ease of discussion, henceforth, loads of all parameters, viz., COD, BOD, TDS and TSS are presented in terms of kilograms per day (KPD) based on average volumes of fed to individual systems.

**3.2 Performance of HCS treatment unit**

As shown in fig.1 and 2, a huge reduction in loads were achieved in HCS treatment system. 890 KPD of COD reduced in stripper alone out of 2184.8 KPD, also in MEE system, it was 966.2 KPD out of 1294.8. As shown in fig. 2, a significant quantity of TDS was reduced in MEE (i.e., 1629.6 KPD, out of 1705.1 KPD). The BOD also reduced in the quantity of 244 and 281.2 KPD (out of 640.4 KPD) in Stripper and MEE respectively. However there is an increase of TSS in stripper outlet. It was due to formation of precipitates during initial heating process of effluents [11].

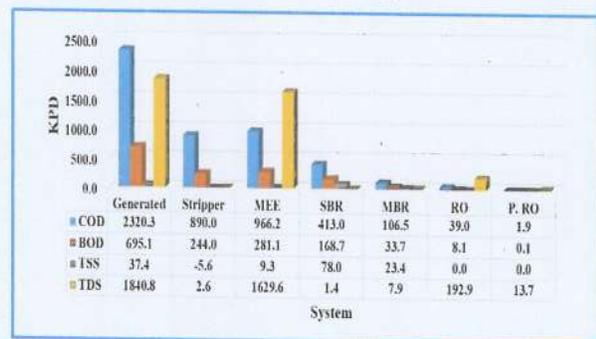


Figure 2: System wise pilot plant efficiency in load reduction.

**3.3 Performance of LCS treatment unit**

The LCS system consists SBR and MBR, where biological operations are made possible to oxidize Organic matter and remaining organic matter removed through MBR respectively. As shown in fig. 1 and 2, there was a reduction of 168.7 KPD of BOD in SBR, where it was 33.7 KPD in MBR. The total BOD quantity reduced to 8.2 KPD from 210.6 KPD in LCS treatment system. SBR is an activated sludge process for treatment of wastewater where separate tanks are not required for aeration and sedimentation. This type of systems are typically suitable for small scale processes [12]. In the present investigation, TSS quantity was reduced to “ZERO” after LCS treatment unit, where 78 and 23.4 KPD of TSS reduced in SBR and MBR systems correspondingly. Pharmaceutical wastewater treatment with a pilot-scale plant was studied by a membrane bioreactor (MBR) process in southern Taiwan, the investigation reported that there is no suspended solids in outlet of MBR [13, 14]. However, there was no much significant reduction in TDS as LCS treatments unit was not designed for reduction of TDS loads. Although in the present investigation, the designed LCS treatment unit made comfort to effluent recycle unit. In similar, a laboratory study conducted with MBR system in China with wool mill wastewater shown excellent effluent quality which was useful for recycle [15]. An investigation made with MBR post treatment of secondary wastewater contains 80% textile and 20% of municipal wastewater to recycle treated wastewater in industrial premises after RO polishing of MBR outlets [16].

**3.4 Performance of Effluents recycling unit**

The quantity of TDS present in LCS treatment unit outlet was reduced to 1.3 KPD after polishing RO treatment with quality of 32 ppm (fig. 1 and table. 1). The total quantity of TDS fed to the primary RO system was 207.8 KPD and it was reduced to 15.0 KPD in permeate. As revealed in table 1, the recycle water generated after polishing RO contained COD of 35 ppm and TDS of 32 ppm, and other parameters (BOD and TSS) were “ZERO ppm” in quality. The effluent recycling unit was in key role of making effluents to portable quality. However the pressure driven RO system cannot be used to feed raw water as it was designed for tertiary treatment of effluents to generate recycle water [17, 18, 19].

**4. CONCLUSION**

The system designed for recycle of effluents has shown marvel outcome in generation of high quality permeate. The overall loads reduction was 99.2 percent in TDS, 99.9 percent in COD and 100 percent in both the TSS and BOD (figure 3). The studies relieving that the designed ZLD unit can be used effectively to treat and recycle API manufacturing unit effluents, which helps to meet statutory requirements and reduce concerns on ground water depletion.

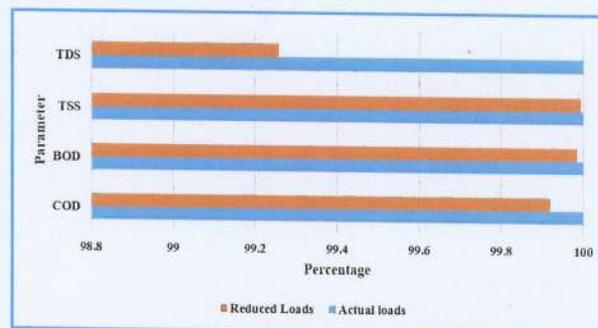


Figure 3: Overall loads reduction in Experimental ZLD system.

Studies on Zero Liquid Discharge (ZLD) plant in API Manufacturing Unit

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# Zero liquid discharge treatment systems: prerequisite to industries

## Abstract

Industrialization is necessary for country's economic growth. Increase in industrial development has elevated water consumption and is resulting in depletion of water resources. On the other hand, water pollution is a major issue. People have long been trying to find cost effective and reliable ways to treat wastewater and recycle or reusing the treated water has become a necessity. Zero Liquid Discharge (ZLD) is an ideal situation of complete closed loop cycle, where discharge of any liquid effluent is eliminated; it is a remarkable effort of every industry who implements it to meet with the environmental regulation in a challenging way. However, it is facing some challenges for its implementation including its high costs and energy efficiency. Here in this review, we have presented various ZLD technologies which are feasible for different industrial sectors and some innovative technologies by which the precious water can be saved and recycled at source.

**Keywords:** zero liquid discharge, pharmaceuticals, textiles, fertilizers, ZLD technologies

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**Abbreviations:** ZLD, zero liquid discharge; MBR, membrane bio-reactor technology; ATFD, agitated thin film dryer; TDS, total dissolved solids; BOD, biochemical oxygen demand; CPCB, central pollution control board; MD, membrane distillation; SHFCC, solid hollow fiber cooling crystallization; ZLDD, zero liquid discharge desalination; MD-C, membrane distillation-crystallization; FD, freeze desalination

## Introduction

Booming megatrends in industrialisation and urbanization are creating higher stress on the environment, including the world's freshwater resources. In many areas, globally and particularly in fast-developing and emerging economies like India, rapid growth in industries and manufacturing units are creating a threat to water quality and tremendous strain on water supplies. Concerns related to water availability risks are increased in regions prone to water scarcity.<sup>1</sup>

As these trends intensify, industries that use large amounts of water and generate high quantum of wastewater are under growing pressure to implement more sustainable water management strategies which uses less amount of water, minimise impacts to receiving waters and mitigate operational risks. This results in driving developments in technologies in the global water treatment market.<sup>1</sup>

ZLD systems are getting greater attention as useful wastewater treatment/water management solutions for complex industrial wastewaters. It is a water treatment process in which wastewater is treated, purified and further recycled. The ZLD process completely eliminates liquid discharge from industry thus reduces and eliminates possibility of pollution discharge concerns and regulatory disposal norms.<sup>2</sup>

An efficiently designed ZLD (Zero Liquid Discharge) System is used for minimising the quantum of wastewater requiring treatment and also to produce a stream of water suitable for reuse in processing

plants.<sup>3</sup> A general approach for ZLD is to increase concentration of wastewater and further crystallize to a solid.

## Background

ZLD technology was initially developed for power plants, in USA and later implemented globally. During early seventies, high salinity of the River Colorado due to discharge from power plants, developed the need for imposing Zero Liquid Discharge. Regulators were primarily concerned with discharge from scrubbers and cooling tower blow downs in power plants.

First ZLD installed was of 114-454m<sup>3</sup>/hour units, based on evaporation/crystallization. Initially low-cost ponds were used for evaporation of Reverse Osmosis (RO) reject. In Germany, ZLD systems for coal-fired power plants were a result of strict regulations and laws in the 1980s.<sup>4</sup>

Annually, worldwide investment of around 200 million USD is represented by construction of zero liquid discharge plants. Currently, there are many concentrator/evaporator systems in numerous industries round the globe. It is spreading widely to water scarce regions and to highly sensitive and polluted environments.<sup>4</sup>

Countries like China and India, where water scarcity exists and recycle/reuse of industrial water is less (i.e. water recovery ratio is less), probably require to develop solutions for ZLD systems. The ZLD market is likely to see further increase in activity based on increased water scarcity and pressure from the regulators.

## India

All textile units were required to install ZLD systems which were producing wastewater effluent greater than 25 kLD as issued in draft policy by the Government in 2015. As stated by Vishnu et al.,<sup>5</sup> ZLD systems were already implemented by 29 dyeing industries in the Tirupur city of Tamil Nadu by 2008, where not only water was recovered but also salts were recovered which were directly used in

dyeing processes. Conferring to a current technical report, the market for ZLD in India was approximated to around 39 million USD in 2012 and was projected to continuously increase from 2012 to 2017 at a rate around 7%. In this market, the power, petrochemical, textile and brewing and distillery industries are the key application areas.<sup>6</sup>

Legislation related to ZLD in India as given by Saha<sup>7</sup>:

- Supreme Court directed polluting pharmaceutical industries near Hyderabad to pay farmers Rs 4000/acre annually (between 1992-2002) due to loss of soil fertility.
- Tamil Nadu High Court Order mandated ZLD for dyeing, bleaching units, tanneries and distilleries. (2006)
- Andhra Pradesh High Court order mandated ZLD for 12 large Pharmaceutical units around Hyderabad discharging 25,000 kLD. (2008)
- Tamil Nadu Government and Central Government Scheme for a subsidy of Rs. 320 crore (interest free loan) to set up ZLDs in the state following the court order of 2006. (2010)
- Punjab Pollution Control Board mandated ZLD in 8 large electroplating industries in Ludhiana (2010).
- Punjab Pollution Control Board assisted 500+ small electroplating units in Ludhiana to set up a CETP with ZLD. (2010)
- Rajasthan Government declared a Capital Subsidy on ZLD based ETP equal to 20% of amount paid to the trader for the treatment plant excluding civil works, subjected to a maximum of Rs. 1.0 Crore (2014).

### ZLD system

It is a system consisting of unit processes or unit operations or their combination, such that there is no discharge of liquid effluent from

an industry, process plant, project etc. It indicates there is no liquid discharge since the effluent is effectively treated, recycled and reused. Zero liquid discharge is generally accomplished by concentrating the wastewater utilizing numerous technologies together with membrane-based and multi effect evaporation-based systems.<sup>8</sup> ZLD comprises of:

- Eliminating of wastewater effluent stream from the industry,
- Recycling of treated water and
- Establishing negligible liquid pollutants norm.

Generally, the incentives behind implementation of ZLD vary depending on terrestrial location and application. United States, China, and India form majority of markets for ZLD with highest economy and largest populations to be served.

### ZLD technologies

Main aim of ZLD is to recover useful products and salts from rejects, apart from recovery of maximum water for recycle. Major ZLD Technologies are as follows:

- Solvent extraction/Stripper
- Membrane Bio-Reactor Technology (MBR)
- Ultra-filtration/Reverse Osmosis
- Evaporation Technologies
- Agitated Thin Film Dryer (ATFD)
- Incinerator

As per Gujarat Pollution Control Board, India (2016), ZLD technologies, their respective uses, advantages, disadvantages and application are given in Table 1.

Table 1 ZLD technologies

ZLD Technology	Use	Advantages	Disadvantages	Application
Membrane Bio Reactor (MBR)	Used as biological secondary treatment for reduction of organic load.	Secondary clarifier not required. Treated water quality is better than conventional ASP, MBBR and SBR. Post treatment of sand filtration not required.	Capital cost is more than other aerobic biological technologies (ASP, SBR, MBBR). Membrane replacement after five years.	Textile Industry CETPs Oil Refineries Fertilizer Industry
Solvent recovery – Air Stripper	Used for recovering solvents/ammonia recovery by providing air.	Conventional proven method for removal of solvents. Economical when solvents with low solubility in water are present in wastewater.	Applicable only when large quantity of solvent with low solubility in water is present in wastewater. Difficult to capture solvent when in low concentration.	Recovery of useful solvents, ammonia in pharmaceutical industry Pesticide Industry Chemical Industry
Solvent Recovery – Steam Stripper	Used for recovering solvents by using steam. Solvents can be reused or are saleable.	Solvent recovery is more compared to air stripping. Useful even less quantity of solvent present in wastewater	Not suitable for water miscible, high boiling solvents. Scaling occurs in column which is to be cleaned periodically.	Recovery of useful solvents, ammonia in pharmaceutical industry Pesticide Industry Chemical Industry

Table continue

ZLD Technology	Use	Advantages	Disadvantages	Application
Ultra Filtration (UF)	Used for removal of colloidal matter and bacteria and viruses. Used as pre-treatment to RO.	Removes suspended, colloidal particles, bacteria, viruses. Best pre-treatment for RO. Most effective treatment for removal of salinity (TDS) with more than 99% salt rejection.	Does not filter dissolved solids, gases and organics. Frequent backwash, membrane cleaning. Replacement of membranes after 5 years required. Very high capital cost.	Pre-treatment to RO in all ZLD plants.
Reverse Osmosis (RO)	Used for removal of salinity (TDS) and residual organics by passing wastewater through semi-permeable membrane by applying high pressure.	Clean technology and no handling of chemicals like acid/alkali like ion exchange technology. Permeate water is free of ions and can be used in industrial processes.	High energy consumption due to high pressure pumps. Membrane replacement required after application of 3 years. Cleaning of membrane frequently due to membrane fouling Reject Water	Used in all industrial sectors for TDS removal and recycling the water.
Multiple Effect Evaporator (MEE)	Used to evaporate wastewater to separate water and salt by using heat of steam in sequence of vessels.	Proven method for recovery of water from saline water and separation of salt.	Very high operating cost due to steam requirement.	Pharmaceutical Industry, Textile Industry, Pesticide Industry, Dyes and Dye Intermediates, Steel Industry, Fertilizer Industry
Mechanical Vacuum Compressor (MVR)	Water vapour generated in the evaporator is compressed to higher pressure which acts as heat source for evaporation.	Eliminates thermal energy requirement. Useful when steam not available. Low operating cost.	Suitable only for liquid with narrow boiling point rise (BPR). Suitable when ready steam is not available in the industry.	Textile Industry
Crystallizer	Used to dry high TDS water or products using heat.	Used for recovery of salts like Sodium Sulphate, Sodium Chloride, Sodium Thiosulphate, Zinc Sulphate etc. Simple Evaporation method of single effect evaporation. Good heat conductivity so can be applied for highly viscous fluids.	Scaling and corrosion of unit is a problem. Requires frequent cleaning.	All industrial sectors. Application in salt recovery in Dye and Dye Intermediates
Agitated Thin Film Dryer (ATFD)	Used to dry high TDS water or products using fast revolving rotor in a heating jacket.	Gentle evaporation and high evaporation rate. Continuous cleaning of heating surface. One passes Evaporation.	Scaling and corrosion of unit is a problem. Requires very high energy.	Textile Industry Pharmaceutical Industry for final drying before disposal. Pharmaceutical Industry
Incinerator	Used for burning the concentrated effluent by thermal energy	Useful method for very high strength (High COD) effluent which is difficult to biodegrade. No further treatment is required.	Operational cost is high. Capital cost is high. Viable for only small quantities of effluent.	Dye and Dye Intermediates Pesticide Industry

### Major factors

Major factors for adopting ZLD technologies by industries are as given below<sup>6</sup>:

- Stricter regulations for wastewater disposal.
- High cost of installation of ZLD system is outweighed by high cost of wastewater disposal along with costly non-compliance penalties.
- Due to intensifying scarcity of water globally, recovery of water to larger extents through ZLD is being enhanced.
- Water from conventional sources is expensive whereas use of recycled water would be relatively cheap.
- Awareness for environmental problems resulting from growth of education and social responsibility.
- ZLD system, irrespective of high cost, may be economical solution for minimizing cost in transportation of waste in large quantities for longer distance.

### Accurate analysis of generated effluent

For efficient working of ZLD system, it is necessary to obtain accurate analysis of effluents generated from industries. Some of the major parameters to be determined as per Ahirrao<sup>8</sup> are given below:

- TDS (Total Dissolved Solids):** This parameter governs the salt handling capacity and evaporation duty.
- Organic Matter:** This parameter helps to indicate the purity of contained salt, BOD (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand) of process condensate, and the organic cut from evaporation.
- Compositional Analysis:** This parameter helps to determine the composition of pure salt and mixed salt, the process schematics, and various other operating parameters.
- Characteristics at Various Concentrations:** The characteristics of feed effluent determine process schematics and types of evaporators to be used.
- Solvents:** Solvents may be removed by solvent stripper in case low boilers are present in the feed effluent, since low boilers may interfere with evaporation and thus the efficiency of the overall system.

### Benefits

- Installation of ZLD technology encourages water usage monitoring closely, avoid wastage and recycling of water by conventional and relatively less expensive solutions, therefore being useful for a unit's water management system.
- 90-95% recovery of water and valuable salts from the wastewater justifies its high operational cost.
- Meeting most stringent regulatory norms leads the industry to a more sustainable growth.
- Using zero liquid discharge techniques, there is a possibility to recover water from sewage for municipal and industrial use.
- Water demand from industry reduces freeing up water to meet the demands for domestic use and agriculture efficiently.

- Ecology of water bodies, soil salinity and groundwater nearby discharging units are not affected.
- Recovery and reuse of treated water results in management of water resources and its conservation.

### Challenges

There are several challenges being faced for development and implementation of ZLD. Some of these<sup>9</sup> include:

- Development of high and effective recovery system to recover greater than 95% of wastewater.
- Outcomes of ZLD include challenges for disposal since high amounts of hazardous solid wastes are generated leading to think for ZWD (Zero Waste Disposal) Plants.
- Technology shortcomings.
- Increased operational cost and finances on the plant and its global, national & regional competitiveness.
- High carbon foot print.
- Selection the suitable techniques according to quantum of effluent and its characteristics.

Therefore, techno-economic contemplations are necessary for developing a zero liquid discharge approach.

### Drawbacks

The most noteworthy drawbacks of ZLD systems include

- Increase in both, capital and operation and maintenance cost.
- Difference in design of ZLD System based on different industrial units.
- Complications in dealing with complex streams of wastewater.
- Usage of high quantity of chemicals in treatment of wastewater.
- Intensive consumption of energy.
- Huge quantity of sludge (both hazardous and other solid waste) is generated.
- ZLD implementation increases the cost of processing in industries by 25–30%.

### Sector-wise concept of ZLD and treatment options

As per Central Pollution Control Board (CPCB),<sup>10</sup> New Delhi (2015), sector-wise treatment options for industries is given in Table 2. The sector wise options shows that the specific industry need to installed ZLD system as per their waste-water characteristics and their use. Here in India, the CPCB has advised to install the ZLD system to all industries and made it mandatory to reuse the water after treatment.

### Membrane distillation (MD) and solid hollow fiber cooling crystallization

A novel hybrid system of integrating membrane distillation (MD) and solid hollow fiber cooling crystallization (SHFCC) has been successfully developed for simultaneous production of fresh water and inorganic salt crystals from NaCl brine solutions. Porous PVDF hollow fibre membranes consisting of PTFE particles are spun for the MD subsystem, while non-porous PVDF hollow fibres are fabricated

as heat exchangers for the SHFCC subsystem. To optimize the operation parameters, the Taguchi's method is utilized for experiment design including three key factors; namely, feed temperature ( $T_f$ ), distillate amount ( $W_d$ ) and water amount to wash away the scallant ( $W_w$ ). As per researcher, the best combined parameters to maximize

the crystal harvested at  $W_d = 14\text{g}$  and  $T_f = 50^\circ\text{C}$ . Narrowly distributed NaCl crystals with a small mean size of  $35\text{--}45\mu\text{m}$  are successfully generated by the hybrid system, and a relatively long-term MD-SHFCC operation of 15 cycles is conducted to verify the system stability and feasibility by Luo et al.,<sup>11</sup>

**Table 2** Sector-wise treatment options for industries

S. No.	Sector	Treatment options	Remarks
1	Distillery	<p>1. Bio-methanation followed by RO/MEE followed by incineration (slop fired).</p> <p>2. Bio-methanation followed by RO/MEE followed by drying (spray/rotary).</p> <p>3. Concentration through MEE followed by coprocessing in cement/thermal power plant.</p> <p>4. Bio-methanation and RO followed by MEE followed by bio-composting.</p>	ZLD Achievable
2	Tannery	<p>Primary treatment + secondary treatment+ pre-treatment for RO + Reverse Osmosis + MEE</p> <p>(recovery of permeate, crystallised salt, reuse of the recovered condensate)</p>	ZLD Achievable
3	Pulp & Paper	<p>Primary treatment + Degasification + RO, 2 stage + NF and UF + Evaporator, Concentrator/Crystallizer</p> <p>Restricting effluent generation to 100 Litres/ton cane crushed.</p> <p>Water consumption to be restricted to 100 Litres/ton initially and further to 50 Litres/ton cane crushed.</p>	Black Liquor totally to be ZLD in any plant.
4	Sugar	<p>Condensate polishing unit mandatory Recycle of excess condensate to process or ancillary units.</p> <p>Water management/audit to reduce spray pond/cooling tower blow downs and excess condensate.</p> <p>Irrigation protocol for disposal into land applications</p>	Water conservation & irrigation protocol as alternate to ZLD
5	Pharmaceuticals	<p><b>High COD, Low TDS Effluent treatment system</b></p> <p>Primary treatment+ Secondary treatment + tertiary chemical treatment to reduce TDS (Pressure sand filter, Activated Carbon filter and filter press for dewatering of sludge). RO system (permeate is utilized as cooling tower makeup water) + Multi effect evaporator/incinerators.</p> <p><b>High COD, High TDS Effluent treatment system</b></p> <p>Primary treatment + stripper to remove VOC + 3 stages Multi Effect Evaporator (forced circulation) Agitator Thin Film Drier (ATFD)+(MEE condensate is being taken along with Low TDS effluent for further treatment)+ MEE/incineration.</p>	ZLD Achievable

Table continue

S. No.	Sector	Treatment options	Remarks
6	Textiles	<p>1. Ozonation + bio-oxidation + sand filtration + activated carbon adsorption + micro filtration + reverse osmosis(3 stage) + multiple effect evaporator</p> <p>2. Chemical precipitation + bio-oxidation + chemical precipitation + sand filtration + Activated carbon adsorption + micron filtration + reverse osmosis (3 stages) + multiple effect evaporator</p> <p>3. Chemical precipitation + bio-oxidation + sand filtration + dual media filtration + micron filtration + reverse osmosis (3 stages) + multiple effect evaporators</p>	ZLD Achievable
7	Refineries	API, primary treatment, secondary treatment and tertiary treatment. The tertiary treatment is mainly Reverse Osmosis and permeate is utilized and rejects are discharged into cooling tower	Water conservation, Reuse & partial ZLD
8	Fertilizer	Chemical treatment+ Reverse Osmosis (Rejects as filler material and permeate in the process)	Water conservation, Reuse & partial ZLD
9	Dye & Dye Intermediates	Chemical Treatment+ MEE	ZLD Achievable

### Zero liquid discharge desalination

Zero liquid discharge desalination (ZLDD) is a sustainable solution to the global water scarcity problem. It provides high water recovery, zero waste generation and valuable salt production. Lu et al.,<sup>12</sup> have developed a mathematical model of a novel ZLDD system that consists of freeze desalination (FD) and membrane distillation-crystallization (MD-C) also developed based on the theories of heat and mass transfer as well as experimental results. To improve the energy efficiency of the system, effects of important parameters, such as the feed temperature, concentration, and distillate temperature of MD and the recovery ratio of FD on system operating curves and energy consumptions have been systematically investigated with the aid of mathematical modelling. For a lab-scale hybrid ZLDD system operating at optimized conditions with a daily seawater processing capacity of 72kg, 50% of its heating energy can be supported by a 50.5m<sup>2</sup> solar panel and its cooling energy can be 100% provided by re-gasification of 207-kg liquefied natural gas.<sup>12</sup> Figure 1 has presented how the desalination works and sea water converted into pure potable water.

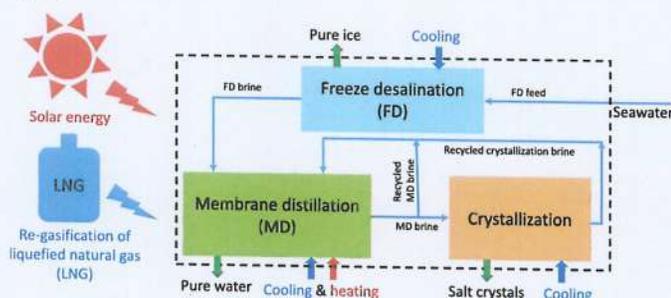


Figure 1 Zero liquid discharge desalination.<sup>12</sup>

### Case study

#### Ammonia manufacturing industry

Wastewater generation from a typical ammonia manufacturing industry is given in Table 3. Typical water balance diagram of an ammonia manufacturing plant is given in Figure 2. All the wastewater generated from industry is recycled/reused in the plant itself. Therefore, it works on the ZLD concept i.e. no effluent goes out of the industrial premises. Sewage to be generated during construction as well as operation phase from construction labour and additional technical staff will be treated in existing facility. Effluent from proposed expansion plant in form of condensate will be sent to Phosphoric Acid plant for reuse in process. No additional effluent will be sent out of company premises. All the effluent water from process shall be reused and utilized fully in the phosphoric acid plant for processing. No water from process shall be discharged outside the manufacturing unit hence it will be a ZERO effluent discharge unit (Figure 2).

#### Pharmaceutical industry

Water balance diagram and flow diagram of ETP of a typical pharmaceutical industry is depicted in Figure 3 and Figure 4 respectively. Effluent generation from industrial activities is 110.8 KLD. Total effluent generation from the industry is segregated into high COD/TDS and low COD/TDS concentration streams. High concentrated wastewater stream from manufacturing process is treated in stripper followed by Multiple Effect Evaporator. Treated water from stripper along with WTP reject is sent to MEE. Condensate water from MEE is sent to ETP along with other low COD/TDS waste streams i.e. cooling, washing and boiler. After treatment in ETP followed by RO, permeate from RO is reused for cooling and reject is sent to MEE. Hence, there is no discharge of treated effluent from the industry and unit maintains Zero Liquid Discharge.

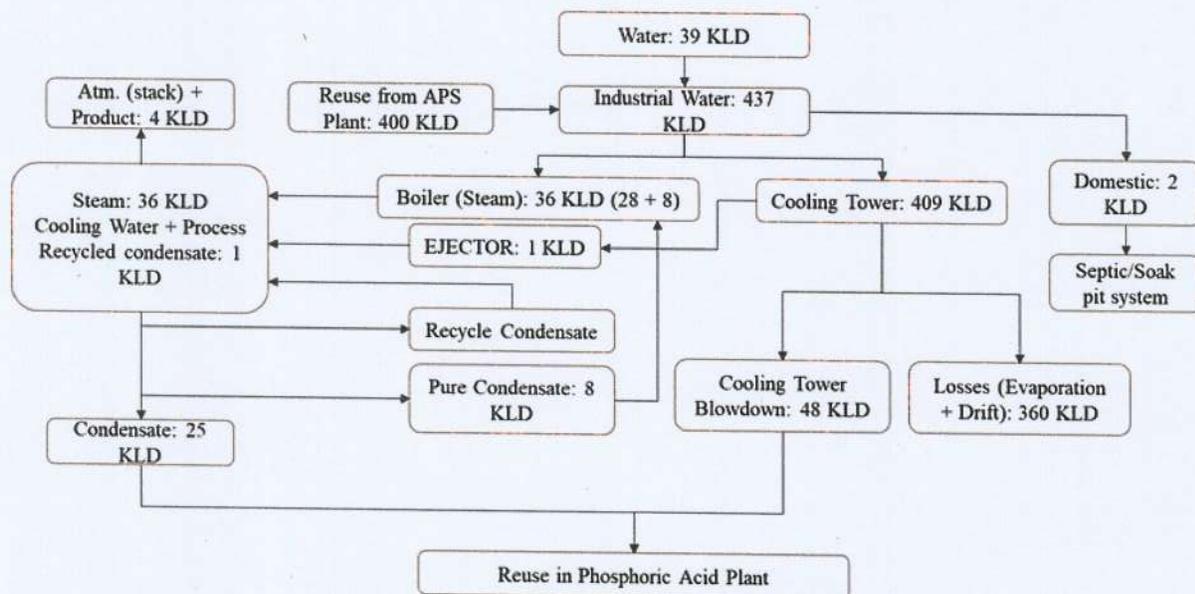


Figure 2 Water balance diagram of a typical ammonia manufacturing plant.

Table 3 Wastewater generation from ammonia manufacturing plant

S. No.	Activity	Wastewater generation (KLD)	Treatment/remarks
1	Domestic	2	Treated in existing septic tank/soak pit.
	Industrial		
2	Steam Condensate/ Process Condensate	337	312 KLD with in proposed plant (AS-I) will be recycled in process and balance 25 KLD will be sent to Phosphoric Acid plant for reuse. Hence, complete recycle in plant process.
	Cooling Tower Blowdown	48	Sent to Phosphoric Acid plant. For reuse in dust suppression/process hence, complete recycle in plant process.
	Net Total	0	No additional effluent is sent out of company premises.

Figure 3 Water balance diagram of a typical pharmaceutical industry.

### Textile processing cluster

The quantity of wastewater generation from a typical textile processing cluster depends upon the quantity of water used for various purposes. Water balance, flow diagram of CETP and flow diagram of common sewage treatment plant of a typical textile processing cluster are depicted in Figures 5–7 respectively. The effluent generated is treated in the CETP and reused for textile process. Wastewater generated from the domestic activities is treated in common sewage treatment plant and treated water is utilized for toilet flushing and greenbelt maintenance. Therefore, no wastewater is discharged outside the cluster premises and the proposed project is operated on zero

discharge condition. The blow down water from the boiler is treated in the RO system followed by deaerator. The condensate return after the evaporation and steam loss is recycled for boiler make-up, until there is any source of contamination or dissolved solids contained within the system. Hence, industry can achieve the ZERO liquid discharge system. The most important factor is to check the output parameters before using this water into any process. As per the ZLD systems installed in various industries in Gujarat, they are using the waste water after treatment into the process and other miscellaneous uses like drum and reactor washing, floor washing, dust suppression, green belt watering, etc.<sup>13</sup>

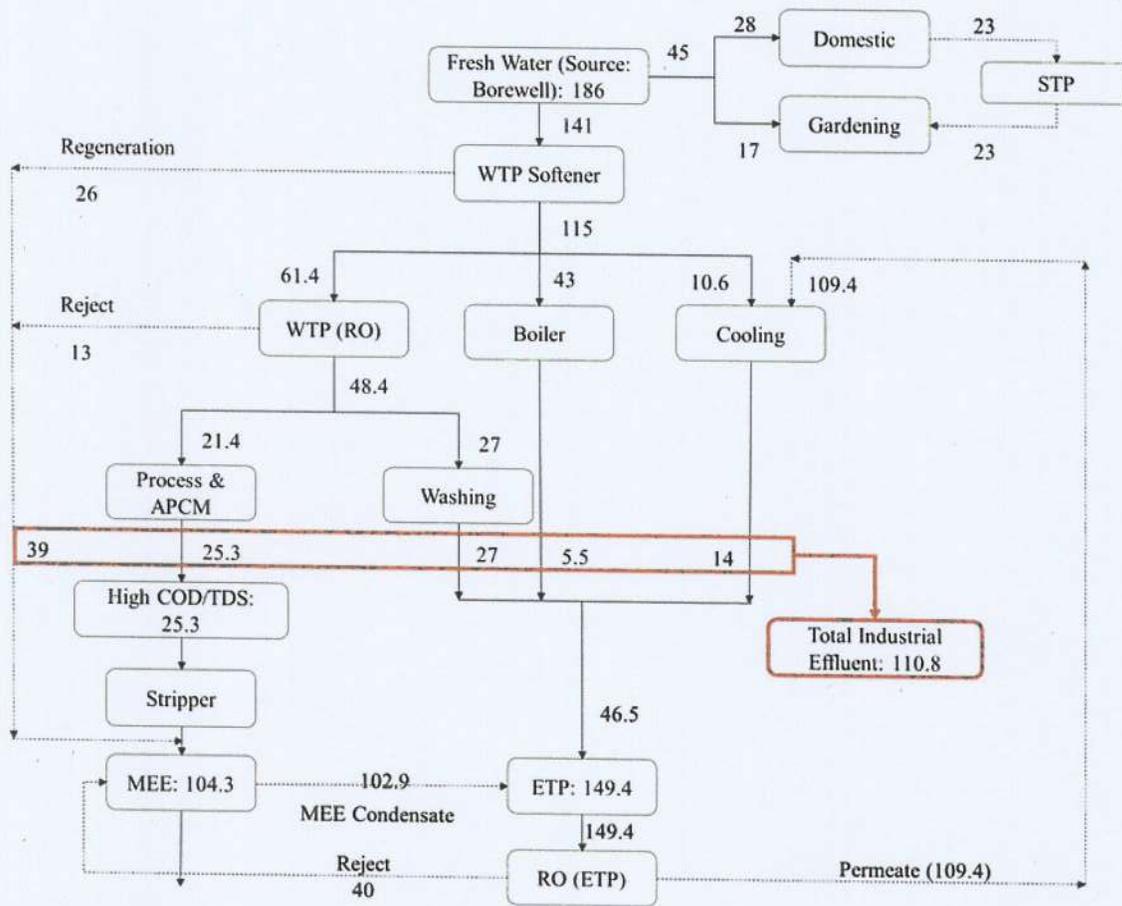


Figure 3 Water balance diagram of a typical pharmaceutical industry.

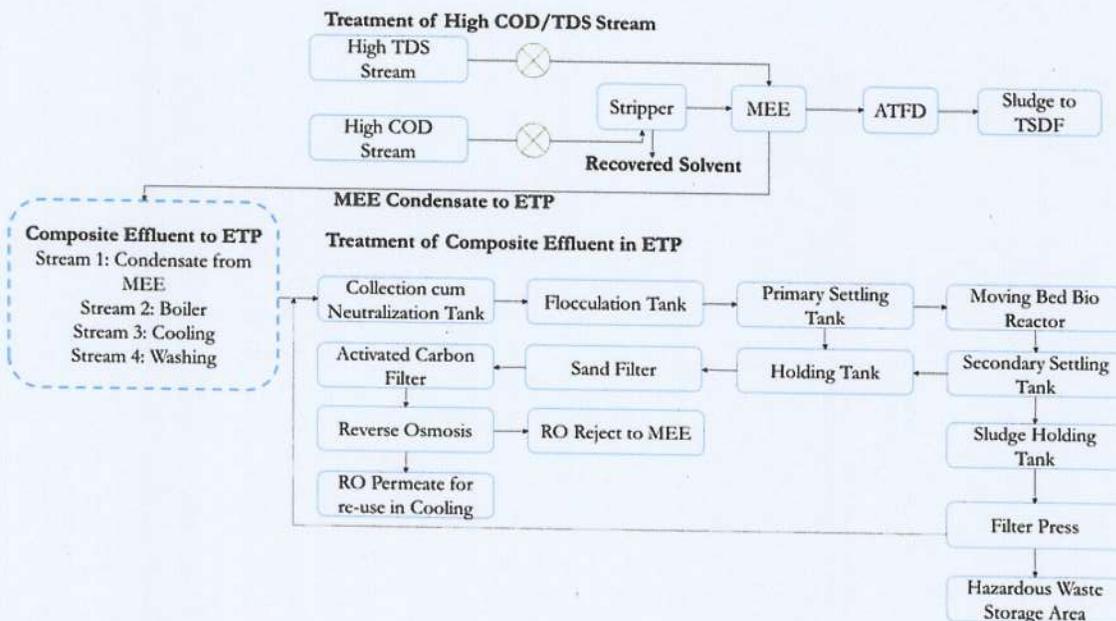


Figure 4 ETP of a typical pharmaceutical industry.

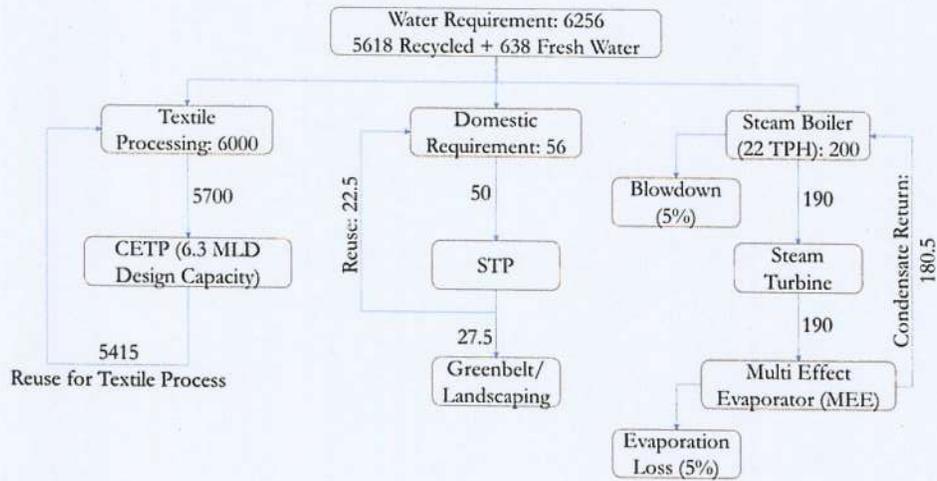


Figure 5 Water balance diagram of a typical textile processing cluster.

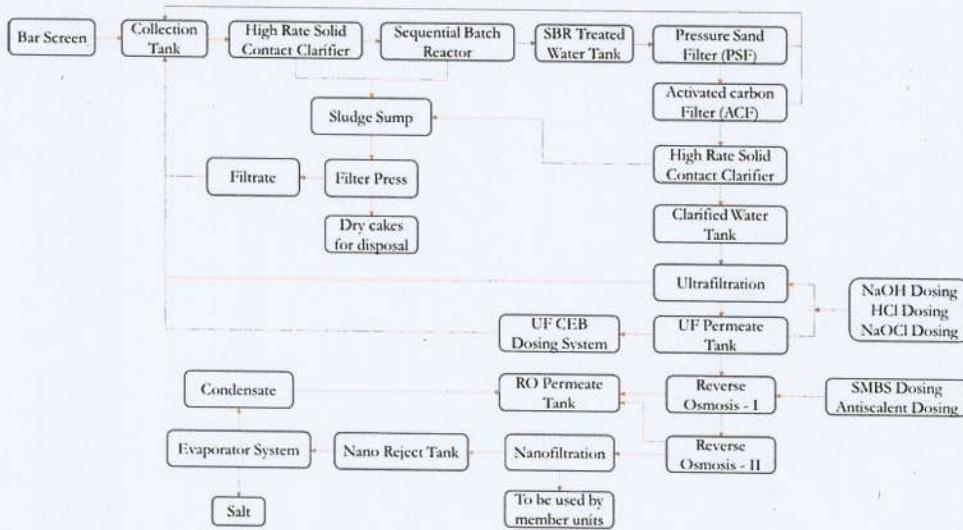


Figure 6 Flow diagram of CETP.

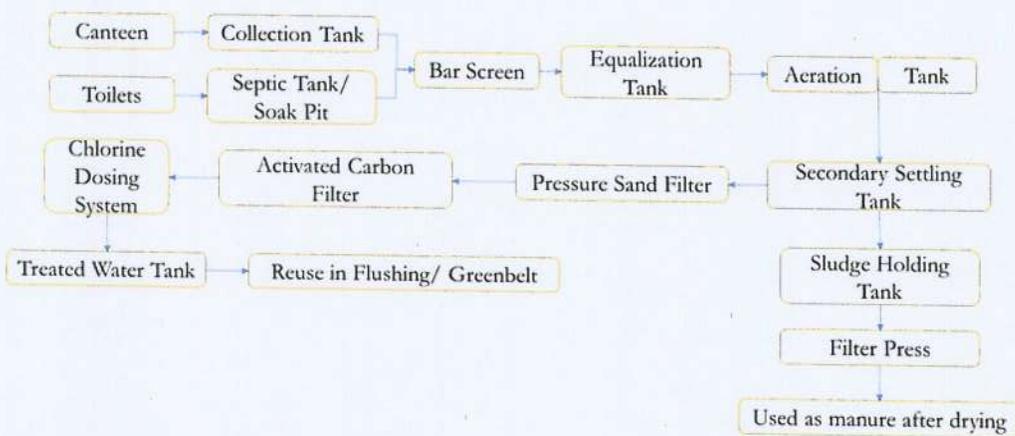


Figure 7 Flow diagram of common sewage treatment plant.

## Conclusion

The concerns over the environmental impact of water pollution have increased, and also ground water resources are gradually being depleted. In the current situation, it is required to recycle the wastewater generated from industrial outlets. On other hand, environmental authorities are being directed to establish “Zero Liquid Discharge (ZLD) plants” in all industrial sectors. Hence, for waste minimization, resource recovery, toxic industrial wastewater treatment and mitigation of potential impacts on water quality of receiving streams, ZLD (Zero-Liquid Discharge) is being thought of an evolving technology. Reduction in water pollution and augmentation of water supply are being carried out by implementation of ZLD (a significant wastewater management strategy) globally. Application of ZLD systems at industrial scale are limited due to increased energy consumption and their cost even though their capability for minimising water pollution and maximising water resources.

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## Conflicts of interest

The authors declared that there no conflicts of interest.

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