

# **The Limnology of Wetlands**

**Understanding their Dynamic Physico-Chemical and Biotic Responses to  
Anthropogenic Exploitations within the Aquatic Ecosystems**

**Ph.D. THESIS**

By

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May 2022**

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**The Limnology of Wetlands: Understanding their Dynamic  
Physico-Chemical and Biotic Responses to Anthropogenic  
Exploitations within the Aquatic Ecosystems**

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*A thesis submitted in partial fulfilment of the requirements  
for the award of the degree of*

**Doctor of Philosophy**

in

**Environmental Engineering**

by

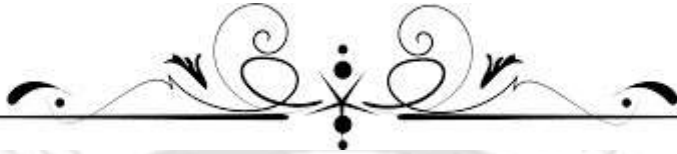
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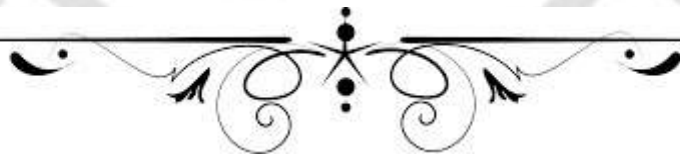




IN EXPRESSION OF MY THANKFULNESS TO MY

**Maa and Baba**

*For their unconditional love and support even during my hardest times...*







भारतीय प्रौद्योगिकी संस्थान गुवाहाटी  
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## **Declaration of Originality**

I, Siddhant Dash, declare that this thesis titled, “**The Limnology of Wetlands: Understanding their Dynamic Physico-Chemical and Biotic Responses to Anthropogenic Exploitations within the Aquatic Ecosystems**” and the work presented in it are my own. I confirm that:

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Date: 01-May-2022

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## Certificate

This is to certify that the thesis entitled “**The Limnology of Wetlands: Understanding their Dynamic Physico-Chemical and Biotic Responses to Anthropogenic Exploitations within the Aquatic Ecosystems**”, submitted by Siddhant Dash (176104004), a Research Scholar in the Department of Civil Engineering, Indian Institute of Technology Guwahati, for the award of the degree of Doctor of Philosophy, is a record of an original research work carried out by him under my supervision and guidance. The thesis has fulfilled all requirements as per the regulations of the institute and in my opinion, has reached the standard needed for submission. The results embodied in this thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

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Place: IIT Guwahati

**Dr. Ajay Kalamdhad**



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**Siddhant Dash**

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# List of Abbreviations

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AAS	Atomic Absorption Spectrometer
AHP	Analytical Hierarchy Process
ANN	Artificial Neural Networks
APHA	American Public Health Association
BAF	Bioaccumulation Factor
BDL	Below Detectable Limits
BOD <sub>5</sub>	5-day Biochemical Oxygen Demand
CCME	Canadian Council of Ministers of the Environment
CF	Contamination Factor
COD	Chemical Oxygen Demand
CDI	Chronic Daily Intake
CPHEEO	Central Public Health and Environmental Engineering Organisation
DA	Discriminant Analysis
DO	Dissolved Oxygen
EC	Electrical Conductivity
EF	Enrichment Factor
FA	Factor Analysis
FAO	Food and Agriculture Organization
GIS	Geographic Information System
GPS	Global Positioning System
HCA	Hierarchical Cluster Analysis
HDPE	High Density Poly Ethylene
HM	Heavy Metals
HRA	Health Risk Assessment
IC	Ion Chromatograph
IS	Indian Standards
KMO	Keiser-Meyer-Olkin
LCR	Lifetime Cancer Risk
LULC	Land-Use-Land-Cover
MoEF	Ministry of Environment and Forests
MST	Multivariate Statistical Techniques

N	Nitrogen
NSF	National Sanitation Foundation
OAT	One-At-a-Time
PCA	Principal Component Analysis
PLI	Pollution Load Index
PMF	Positive Matrix Factorization
POME	Principle of Maximum Entropy
PRISMA	Preferred Reporting Items for Systematic Reviews and Meta-Analysis
SEM-EDS	Scanning Electron Microscopy - Energy Dispersive X-Ray Spectroscopy
SEP	Sequential Extraction Procedures
SVD	Singular Value Decomposition
SWAT	Soil and Water Assessment Tool
SWM	Solid Waste Management
TA	Total Alkalinity
TDS	Total Dissolved Solids
TH	Total Hardness
TKN	Total Kjeldahl Nitrogen
TSS	Total Suspended Solids
WHO	World Health Organization
WQ	Water Quality
WQI	Water Quality Index
XRD	X-ray Powder Diffraction

# List of Notations

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$^{\circ}\text{C}$	Degree Celsius
$\mu_{\text{max},20}$	Maximum bacterial growth rate at 20°C (day <sup>-1</sup> )
$\mu_{\text{mpu}}$	Maximum phosphorus uptake rate by plants (day <sup>-1</sup> )
$\mu_{\text{mpu1}}$	Maximum ammonia uptake rate by plants (day <sup>-1</sup> )
$\mu_{\text{mpu2}}$	Maximum nitrate uptake rate by plants (day <sup>-1</sup> )
$\mu_n$	Maximum growth rate for nitrifying bacteria (day <sup>-1</sup> )
A	Area of Deepor Beel (m <sup>2</sup> )
Ca <sup>2+</sup>	Calcium
Cd	Cadmium
Cl <sup>-</sup>	Chloride
Cr	Chromium
Cu	Copper
F <sup>-</sup>	Fluoride
Fe	Iron
K <sup>+</sup>	Potassium
K <sub>1</sub>	Ammonia uptake half saturation constant (g/m <sup>2</sup> /day)
K <sub>2</sub>	Nitrate uptake half saturation constant (g/m <sup>2</sup> /day)
K <sub>nh</sub>	Ammonia nitrifying half saturation constant (g/m <sup>2</sup> /day)
K <sub>no</sub>	Oxygen half saturation constant (g/m <sup>2</sup> /day)
K <sub>p1</sub>	Ammonia plant uptake half saturation constant (g/m <sup>2</sup> /day)
K <sub>p2</sub>	Nitrate plant uptake half saturation constant (g/m <sup>2</sup> /day)
K <sub>p3</sub>	Phosphorus plant uptake half saturation constant (g/m <sup>2</sup> /day)
Mg	Magnesium
Mn	Manganese
Na <sup>+</sup>	Sodium
NH <sub>3</sub> <sup>+</sup>	Ammonium in water column
NH <sub>3</sub> N	Ammonia Nitrogen
NH <sub>3</sub> N <sub>e</sub>	Concentration of NH <sub>3</sub> N in outflowing water from the lake (g/m <sup>3</sup> /day)
NH <sub>3</sub> N <sub>i</sub>	Concentration of NH <sub>3</sub> N in inflowing water to the lake (g/m <sup>3</sup> /day)
NO <sub>3</sub> <sup>-</sup>	Nitrate
NO <sub>3</sub> N	Nitrate Nitrogen

$\text{NO}_3\text{N}_e$	Concentration of $\text{NO}_3\text{N}$ in outflowing water from the lake ( $\text{g}/\text{m}^3/\text{day}$ )
$\text{NO}_3\text{N}_i$	Concentration of $\text{NO}_3\text{N}$ in inflowing water to the lake ( $\text{g}/\text{m}^3/\text{day}$ )
OrgN	Organic Nitrogen
$\text{OrgN}_e$	Concentration of OrgN in outflowing water from the lake ( $\text{g}/\text{m}^3/\text{day}$ )
$\text{OrgN}_i$	Concentration of OrgN in inflowing water to the lake ( $\text{g}/\text{m}^3/\text{day}$ )
P	Total Phosphorus in water column
$P_1$	Preference factor for ammonia
$P_2$	Preference factor for nitrate
Pb	Lead
$P_e$	Concentration of P in outflowing water from the lake ( $\text{g}/\text{m}^3/\text{day}$ )
$P_i$	Concentration of P in inflowing water to the lake ( $\text{g}/\text{m}^3/\text{day}$ )
PN	Plant Nitrogen
$\text{PN}_{\max}$	Maximum plant nitrogen in plant biomass ( $\text{g}/\text{m}^2/\text{day}$ )
$\text{PO}_4^{3-}$	Phosphate
PP	Plant Phosphorus
$\text{PP}_{\max}$	Maximum plant phosphorus in plant biomass ( $\text{g}/\text{m}^2/\text{day}$ )
ram	Rate of ammonification for organic nitrogen ( $\text{g}/\text{m}^2/\text{day}^2$ )
$R_{\text{am}}$	Ammonification rate coefficient ( $\text{day}^{-1}$ )
$r_b$	Reaction rate of the plant-biofilm biomass ( $\text{day}^{-1}$ )
rdn	Denitrification Rate for nitrate ( $\text{g}/\text{m}^2/\text{day}^2$ )
$R_{\text{dn},20}$	Rate constant of denitrification at $20^\circ\text{C}$ ( $\text{day}^{-1}$ )
rmu1	Ammonia uptake growth rate by the microorganisms ( $\text{g}/\text{m}^2/\text{day}^2$ )
rmu2	Nitrate uptake growth rate by the microorganisms ( $\text{g}/\text{m}^2/\text{day}^2$ )
rn	Ammonia nitrification rate ( $\text{g}/\text{m}^2/\text{day}^2$ )
rndc	Decay rate of plant nitrogen ( $\text{g}/\text{m}^2/\text{day}^2$ )
$R_{\text{ndc}}$	Decay coefficient of plant nitrogen ( $\text{day}^{-1}$ )
rnhne	Rate of outflow of $\text{NH}_3\text{N}$ ( $\text{g}/\text{m}^2/\text{day}^2$ )
rnhni	Rate of inflow of $\text{NH}_3\text{N}$ ( $\text{g}/\text{m}^2/\text{day}^2$ )
rnone	Rate of outflow of $\text{NO}_3\text{N}$ ( $\text{g}/\text{m}^2/\text{day}^2$ )
rnoni	Rate of inflow of $\text{NO}_3\text{N}$ ( $\text{g}/\text{m}^2/\text{day}^2$ )
rnrs	Ammonia regeneration rate ( $\text{g}/\text{m}^2/\text{day}^2$ )
$R_{\text{nrs}}$	Sediment nitrogen resuspension coefficient ( $\text{day}^{-1}$ )
rns	Organic nitrogen settling rate in water ( $\text{g}/\text{m}^2/\text{day}^2$ )
$R_{\text{ns}}$	Settling rate coefficient of organic nitrogen ( $\text{day}^{-1}$ )
orgne	Rate of outflow of OrgN ( $\text{g}/\text{m}^2/\text{day}^2$ )
orgni	Rate of inflow of OrgN ( $\text{g}/\text{m}^2/\text{day}^2$ )

$r_{pdc}$	Decay rate of plant phosphorus ( $\text{g/m}^2/\text{day}^2$ )
$R_{pdc}$	Decay coefficient of plant phosphorus ( $\text{day}^{-1}$ )
$r_{pe}$	Rate of outflow of P ( $\text{g/m}^2/\text{day}^2$ )
$r_{pi}$	Rate of inflow of P ( $\text{g/m}^2/\text{day}^2$ )
$r_{ppu}$	Phosphorus utilization growth rate by plants ( $\text{g/m}^2/\text{day}^2$ )
$r_{prs}$	Phosphorus regeneration rate ( $\text{g/m}^2/\text{day}^2$ )
$R_{prs}$	Sediment phosphorus resuspension coefficient ( $\text{day}^{-1}$ )
$r_{ps}$	Settling rate of total phosphorus ( $\text{g/m}^2/\text{day}^2$ )
$R_{ps}$	Settling rate coefficient of total phosphorus ( $\text{day}^{-1}$ )
$r_{pu1}$	Ammonia utilization growth rate by plants ( $\text{g/m}^2/\text{day}^2$ )
$r_{pu2}$	Nitrate utilization growth rate by plants ( $\text{g/m}^2/\text{day}^2$ )
SN	Sediment Nitrogen
$\text{SO}_4^{2-}$	Sulphate
SP	Sediment Phosphorus
T	Temperature ( $^{\circ}\text{C}$ )
$Y_n$	Coefficient of yield for nitrifying bacteria ( $\text{mg VSS/mg N}$ )
$\theta_1$	Microbial growth temperature coefficient for ammonia
$\theta_2$	Microbial growth temperature coefficient for nitrate
$\theta_3$	Microbial growth temperature coefficient for denitrification



# Abstract

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Vanishing wetlands have been a matter of grave concern to researchers worldwide in recent decades. The chief reason for such a situation has been human interventions through rapid changes in land-use patterns. With the continuation of this scale of wetlands' deterioration, the shift in the natural world balance is inevitable, given the various significant roles the wetlands play in keeping the natural ecosystem in balance. The only option by which this may be avoided is through sustainable measures of conserving the wetlands. This comes through comprehensive yet effective monitoring programs that help understand the symbiotic functioning of the wetland components.

This doctoral research thesis presents and discusses the limnology of wetlands, thereby attempting to understand the dynamic physico-chemical and biotic responses to the anthropogenic contaminations within their ecosystems. Deepor Beel (a site under the list of Ramsar sites) has been considered, owing to its rapid anthropogenic deterioration in recent times. Although a Ramsar site, no proper conservation measures have been carried out, making it highly vulnerable to contamination. In the first stage, a reconnaissance survey was carried out. Sampling locations for water, sediment, water hyacinth (representative of the floral element), and three indigenous fish species were fixed. Twenty-three sampling locations were identified for collecting water and sediment (abiotic) samples. For collecting the fish and water hyacinth (biotic) samples, the wetland was divided into three zones, based on the proximity to the pollution sources. Comprehensive monitoring of all the components was carried out every month, ranging from October 2017 to February 2019. Additional data such as rainfall, evaporation, transpiration, discharge, etc., were also obtained.

To understand the dynamics of responses of various components to different anthropogenic contaminations, the present research was conducted involving five distinct objectives. The first step involved identifying various latent pollution sources and quantifying their contribution to the wetland contamination. For this purpose, four Environmetrics tools, i.e., hierarchical cluster analysis (HCA), discriminant analysis (DA), principal component analysis (PCA), and positive matrix factorization (PMF), were employed. HCA categorized the sampling locations into statistically significant clusters; DA helped identify the parameters responsible for discrimination of the sampling locations; PCA helped identify probable pollution sources through its component loadings; finally, PMF quantified the significant factors of Deepor Beel's contamination.

Following this, the second step was to assess the impacts of these sources on the water body's health—this required evaluation of both water and sediment quality. For the assessment of water quality, objective-based indexing techniques were adopted. Two novel indexing approaches, one each for short-term and long-term monitoring programs, and different end-uses of water were proposed. For short-term programs, the use of multivariate statistics, i.e., the use of HCA and PCA deemed more suitable. On the contrary, the modified entropy-weighted approach proved highly reliable and efficient for long-term programs. Both methods were checked for their reliability and correctness through sensitivity analysis and were found to be better than the existing approaches.

For assessing the sediment quality, various indices such as contamination factor (CF), pollution load index (PLI), enrichment factor (EF), and the geo-accumulation index ( $I_{geo}$ ) were employed. Results showed that Deepor Beel is most affected in the post-monsoon season, compared to other seasons. At the same time, the monsoon remains the best. The potential ecological risk of contaminants further displayed that the post-monsoon period has the most significant number of sites under the moderate risk category. The chemical speciation studies of seven heavy metals (Cr, Cd, Fe, Mn, Cu, Pb and Mg) were conducted to determine their available forms in the sediment column. Cd, Mn, and Mg were observed to profoundly negatively impact aquatic ecology (available in F1 fraction in higher percentages). While Fe was predominant in reducible (F3) form, Cr, Cu, and Pb had equal contributions from reducible and oxidizable (F3 and F4, respectively) forms. The sediment samples were further subjected to elemental analysis; X-ray powder diffraction (XRD) followed by Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDS), to determine the elemental composition and forms of heavy metals present in the sediment columns from various parts of the wetland. Sediment sample collected from the proximity of the landfill site was observed to be affected the most, primarily due to leaching of heavy metals from the landfill. However, the central zone was found to be devoid of any anthropogenic contaminations, while the sediment column near the industrial complex was found to be contaminated to a moderate extent.

Furthermore, an investigation was carried out correlating the heavy metal contamination, its distribution, and the human health risk associated with different aquatic ecosystem components. For this purpose, water, sediment, and fish samples (three species, notably *Notopterus notopterus*, *Clarias batrachus*, and *Channa striata*) from Deepor Beel were considered, and their heavy metal contamination and distribution were determined. The corresponding health risks (carcinogenic and non-carcinogenic) due to prolonged exposure levels were evaluated for six different heavy metals; Cr, Cd, Fe, Mn, Cu, and Pb. Results indicated that Pb and Mn significantly impacted the non-carcinogenic human health risks concerning the

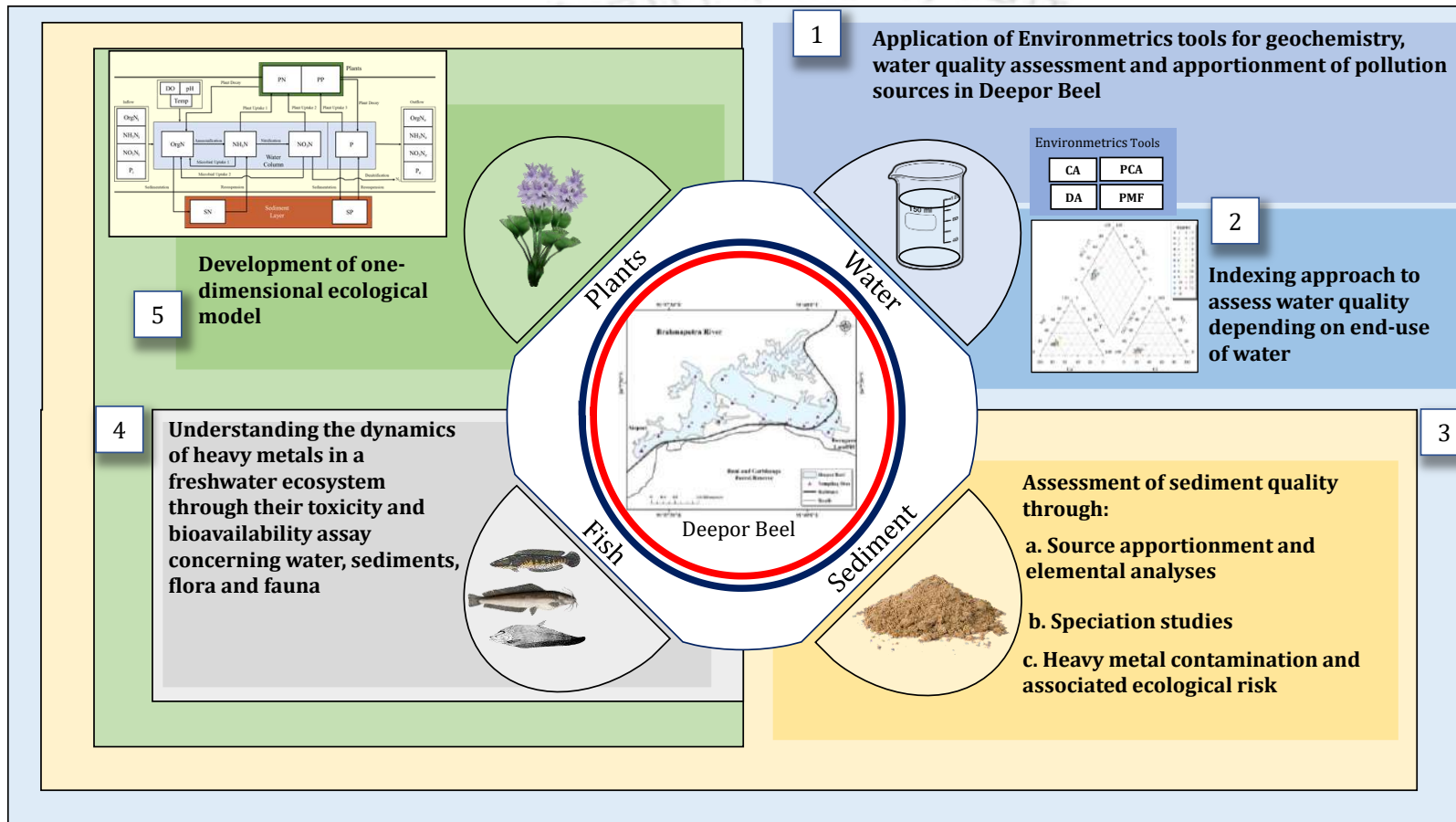
water column. For all three components, children were found to have considerably higher effects (both carcinogenic and non-carcinogenic) of prolonged exposure to contamination than adults. Finally, it was observed that the sediment column substantially contributed to the bioaccumulation factor in the fish biota compared to the water column.

The final study encompassed formulating a eutrophication-based ecological model, assisting in determining the nutrient dynamics of the Deepor Beel ecosystem, thereby providing an idea of the significant causative parameters aiding eutrophication. A conceptual diagram was first constructed, and the corresponding differential equations about different functions were formulated. Subsequently, a code was developed in MATLAB based on the logic formulated through the conceptual diagram. Sensitivity analysis was first performed on various state variables, identifying the most sensitive parameters and exhibiting maximum variability in the model. The model was then subjected to calibration for defining the rate constants, which were further validated. Finally, the model was simulated for two plausible management options to curb the eutrophication levels in Deepor Beel; (i) Harvesting of water hyacinths and (ii) Setting up a treatment unit for nitrogen and phosphorus removal. The results obtained for both cases indicated that harvesting of water hyacinths would not provide a suitable long-term and effective solution. However, setting up a treatment unit for phosphorus and nitrogen removal can significantly reduce the nutrient levels in the wetland, thereby assisting in curbing the eutrophication levels.

Based on this investigation, it is anticipated that incorporating these researches will pave the way for a more sustainable future by protecting Deepor Beel and our other natural wetlands from plausible future degradation.

**Keywords:** wetlands; environmetrics tools; water quality indices; sediment quality; heavy metals; toxicity and bioavailability assay; nutrient dynamics; ecological model





# Graphical Abstract



One of the first conditions of happiness is that the link between man and nature shall not be broken.

---

- Leo Tolstoy

# 1

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## Introduction

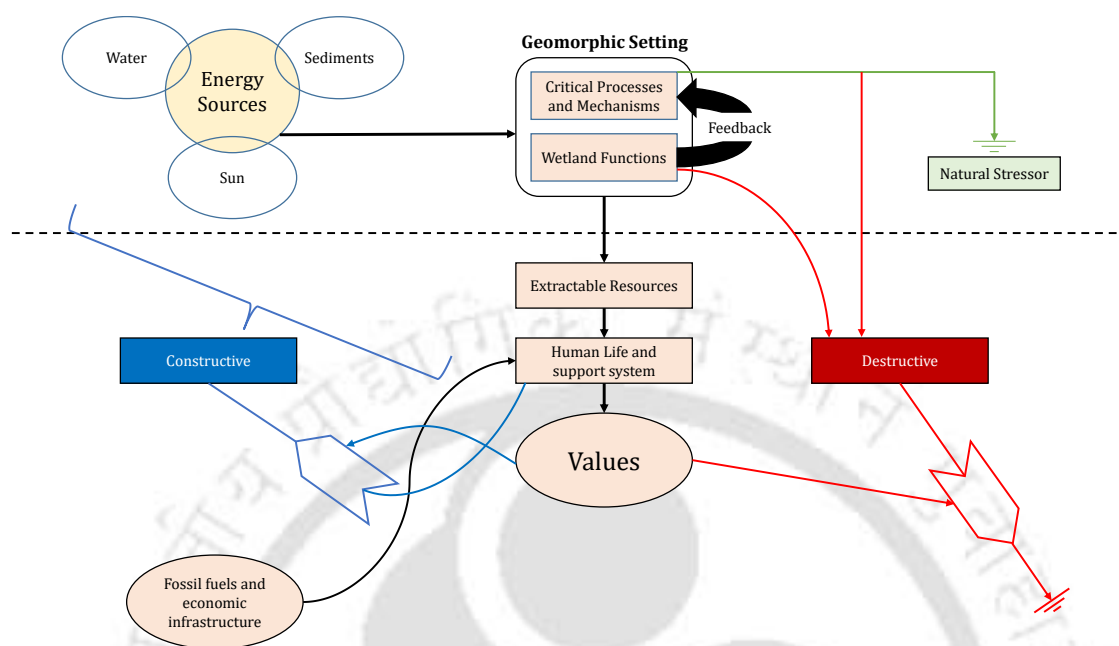
This chapter provides a brief overview of wetlands and their importance in society. This is followed by the background of the research conducted, the need for the study, and the thesis's scope. This chapter also introduces the readers to the outline of the entire dissertation.

### 1.1. Overview

Wetlands play a significant role in serving a wide range of functions. They act as “*ecological hotspots*” as they provide habitats to various species of birds, fishes and other wildlife (Bhattacharyya & Kapil 2010). The ecological processes responsible for its occurrence and sustenance also generate a large number of wetland resources that sometimes find ways to benefit human societies. Along with these resources, some wetlands act as storage zones by accommodating large amounts of water and slowly releasing it downstream into a larger water body (like river, sea or ocean). This is very helpful in controlling damages due to flooding. Moreover, water storage reduces its energy levels, thereby decreasing its erosive capacity as it flows downstream. Groundwater recharge is also achieved as a result of this (Maltby & Barker 2009). Water from the wetlands can also be used for a variety of other purposes, such as drinking, agriculture, industrial, etc. Undoubtedly, there exists a definite relationship between the wetlands' ecological functions and their societal requirements and activities (Fig. 1. 1). While ecological processes are independent of society's actions, societal activities will cease to exist without them.

However, recent times have witnessed severe threats to rivers' and wetlands' conditions due to numerous natural and anthropogenic events (Hu *et al.* 2020). Natural phenomena include changes in precipitation inputs, erosion and weathering of crustal material, whereas anthropogenic activities such as urbanization, industrial and agricultural boom, increased

consumption of water resources due to population growth, lifestyle, economic status, etc., are wreaking havoc on the wetlands.



**Fig. 1. 1.** Relationship between ecological functions of wetlands and their societal values (Brinson 1993).

In fact, due to the intangibility of some of the services that the wetlands provide, there remains an ignorance in the policymaking processes and, as a result, continuous degradation of the wetlands occur (Turner *et al.* 2000). This includes all the major components, i.e., the water, sediment, flora, and fauna.

Generally speaking, the water column, of all the components of the wetland ecosystem, receives the most direct impact of any changes to the natural processes. As a result of this, it is also regarded as the most dynamic constituent. The sediment column, flora and fauna have a more indirect influence from the external contamination factors. While sediment contamination is primarily associated with the precipitation of contaminants from the water column, the emergence of contamination levels in flora and fauna in the ecosystem comes via their food chain (uptake and intake, respectively). This food chain may directly associate with the water column or indirectly through the sediment column due to the various physico-chemical process occurring within the ecosystem. Therefore, it is necessary to carry out reliable ecological monitoring programmes that include monitoring all different ecosystem components, both spatial and temporal, for quality check purposes to assess the possible factors responsible for the degradation of the wetlands (Alberto *et al.* 2001). Monitoring over a long period also helps in identifying significant changes in the natural ecosystem.

## 1.2. Background of the research

Continuous monitoring provides a reliable yet sophisticated dataset, which becomes relatively ineffective when it comes to interpretation, owing to its complexity (Vega *et al.* 1998; Simeonov *et al.* 2003; Iscen *et al.* 2008; Chow *et al.* 2016; Hajigholizadeh & Melesse 2017; Singh *et al.* 2019b). However, in recent years, the Environmetrics approach, i.e., application of various statistical techniques, has eased how the datasets are understood, including the classification of spatially distributed monitoring sites and the primary factors or contaminants responsible for the deterioration of the water body (Jha *et al.* 2014; Machiwal & Jha 2015; Bodrud-Doza *et al.* 2016; Chow *et al.* 2016; Kumar *et al.* 2017).

Hierarchical clustering of sampling sites through cluster analysis (CA) and the identification of probable pollution sources through principal component analysis (PCA) have been widely used and accepted. The use of discriminant analysis (DA) as a supervised pattern recognition tool to recognize the most significant water quality variables accountable for spatial and temporal variability has also been used more recently than the other two methods (Hajigholizadeh & Melesse 2017). However, these statistical tools cannot solely quantify the contribution of potential pollution sources. For this purpose, various receptor models, such as the positive matrix factorization (PMF) model, are used. The PMF models were initially applied to the dataset pertaining to atmospheric pollution to determine how much is the contribution of various pollution sources. Only in recent times, they have been applied to the water quality (WQ) datasets along with PCA and CA for quantifying the contributions of pollution sources (Zhao *et al.* 2013; Mustafa *et al.* 2014; Chen *et al.* 2015; Gholizadeh *et al.* 2016).

However, identifying and apportioning the pollution sources merely reflects the quantification of pollution entering a water body. To evaluate the status of a water body's true health with respect to its water quality, it is essential to assess the raw water quality dataset obtained from the monitoring programme with regards to a standard recommended for the general public. Given the vastness and complexity of the raw dataset, it becomes impossible to assess each parameter independently for all the monitoring locations (i.e., spatially) and each frequency (i.e., temporally). Indexing approaches have been used extensively for quite a long time, first coined by Horton (1965). Water quality indices (WQIs) are mathematical tools representing the water quality status of a particular water body. They consider the desired parameters for estimating a numeric value, thus delivering a much easy interpretation of the water health, which otherwise becomes extremely tough due to the complexity of large datasets. These indices are based on the end-use of water and vary from an individual's perception. Three major categories of indices are usually studied, depending on the water use; they are overall WQI, which takes into account the drinking or domestic use of the water, indices

that assess the heavy metal contamination in a water body; and finally, indices that account for the water body's irrigation suitability.

Intense industrialization and other natural and anthropogenic activities in the ecosystem have been a major concern regarding safe and potable water (Li *et al.* 2011; Islam *et al.* 2015a). Various geological processes, involving weathering of bedrocks and volcanic eruption, anthropogenic activities including large-scale use of metal-containing fertilizers and pesticides for agricultural practice, metal smelting, mining, and other various metallurgical processes have resulted in deep scale contribution of heavy metals in the natural aquatic ecosystem (Meng *et al.* 2016; Kumar *et al.* 2017; Wang *et al.* 2017). This has not only rendered the water systems unsuitable for drinking but has also degraded the quality of water to an extent unfit for agricultural or industrial purposes. Furthermore, the enrichment of trace heavy metal concentrations in the water bodies causes severe health risks by getting absorbed by various organisms, thereby entering into the food chain (Banerjee *et al.* 2011; Forti *et al.* 2011; Yi *et al.* 2011; Rahman *et al.* 2013; Ahmed *et al.* 2015; Bhuyan *et al.* 2017). Reports have also suggested that these dissolved trace heavy metals prove carcinogenic if consumed in considerable amounts persistently. These potential hazards to human health and aquatic ecosystems render the heavy metal pollution in water systems a severe environmental issue (Giri & Singh 2014; Farahat & Linderholm 2015; Wang *et al.* 2017). Therefore, a systematic study of the heavy metal concentrations, their sources and distribution, and their impact on the quality of water for the abatement of possible future contamination and protection of natural water resources is inevitable. Likewise, with the increasing food security problems around the globe, it becomes highly essential that the hydro-geochemical analyses of natural waters for both irrigation and drinking purposes be taken care of.

Similar to water contamination, surficial sediment contamination as a consequence of various anthropogenic activities has also been a cause of serious concern in recent times. Primary contaminants possessing critical issues to the global sediment flux constitute various heavy metals, accumulated due to heavy discharge of effluents (majorly industrial, agricultural and domestic wastewater) into the aquatic ecosystem (Syvitski *et al.* 2005; Ouyang *et al.* 2006; Zhang *et al.* 2007b; Azhar *et al.* 2015; Dhamodharan *et al.* 2019). These heavy metals have typical characteristics of being persistent and thus do not deteriorate or decompose with time, thereby making them toxic when concentrations exceed permissible limits. Furthermore, these compounds have less mobility in water columns. Therefore, their continuous accumulation in the natural water systems forces them to precipitate on the sediment column of the waterbody. This makes the sediment columns of the water bodies potential sources of heavy metals, where they can be released back into the water columns or the aquatic flora

and fauna via natural or anthropogenic ways, thus joining the food-chain system (Yin *et al.* 2011; Dhamodharan *et al.* 2019). Lakes and wetlands play pivotal roles in providing nutrients to living organisms. Therefore, their bottom sediments are sensitive indicators to determine the pollution loadings as they act as both sources and sinks for the contaminants in an aquatic environment (Varol 2011; Yin *et al.* 2011). This necessitates their continuous monitoring and assessment as well.

Heavy metals are naturally occurring elements present in all three spheres of the environment, i.e., the atmosphere, hydrosphere and lithosphere. Few of these metals (such as Cr, Co, Cu, Mn, Fe, Mo, Se, Ni, and Zn) are usually present in trace quantities, which are beneficial for the existence and sustenance of living organisms as they play pivotal roles in catalytic and enzymatic actions as well as various oxidation-reduction reactions in the body (WHO/FAO/IAEA 1996). However, certain metals (such as Hg, Pb, Cd, and As) also exist in the ecosystem, which is primarily the direct result of various human-made or anthropogenic contributions such as industrial, pharmaceutical, agricultural and technological applications (Tchounwou *et al.* 2012; Grigoratos *et al.* 2014; Martín *et al.* 2015; Sobihah *et al.* 2018). These metals do not possess any biological functions and are rendered non-essential and potentially toxic compounds, even at insignificant concentrations (Tchounwou *et al.* 2012). When present in significant concentrations, i.e., more than the desired limits, these compounds fabricate cellular and tissue damage in the living bodies, thus resulting in various health risks (Bonsignore *et al.* 2018). The persistence, long biological half-life and toxicity impact these heavy metals possess render them highly risky for humans to consume (Bortey-Sam *et al.* 2015). This is primarily because of the negative influences on the human digestive, cardiovascular and central nervous systems upon accumulating these heavy metals (Crespo-López *et al.* 2007). In addition to these cancerous impacts, some compounds (such as As, Pb, Cd and Hg) can also contribute to the teratogenic, mutagenic and carcinogenic consequences on the living organisms (Wong 1988). The heavy metals, released from multiple natural and anthropogenic events, enter the aquatic ecosystem and get transported through numerous geochemical and biological cycles. These phenomena make them bioaccumulated in the natural ecosystem, thus entering the water, sediment and aquatic food chains and eventually getting biomagnified (Atwell *et al.* 1998; Graci *et al.* 2017; Rajeshkumar *et al.* 2018). These processes can be well established and correlated in an aquatic environment by analyzing the heavy metal concentrations in all three components, i.e., sediment, water and the living entities. The heavy metal components discharged into the aquatic ecosystem first come in contact with the water column. These metals get precipitated into the sediment column with time, owing to various physico-chemical and biological metabolisms and their immobile nature in the water column. However, heavy metals' accumulation is not limited to the sediment columns only, as

they get reverted to the water column via several natural and anthropogenic compartments (Dhamodharan *et al.* 2019). The aquatic flora and fauna, especially fish, additionally play crucial roles in the bioaccumulation and biomagnification processes. Recent years have witnessed a significant surge in fish consumption volume, owing to its high nutritional value and lower saturated fat and omega-3 fatty acid content (FAO 2013; Bosch *et al.* 2016). Fishes are considered major bio-accumulators and bio-magnifiers in the natural aquatic ecosystems, capable of harming individuals exposed to them (Taweel *et al.* 2013; Ahmed *et al.* 2015; Saha *et al.* 2016; Rajeshkumar *et al.* 2018). There are two principal entrance mechanisms for the heavy metals into the aquatic food chain; first through the direct ingestion, i.e., the digestive tract and second through permeation, i.e., non-dietary routes such as muscles and gills (Ribeiro *et al.* 2005). Fishes have become a part of vital nutritional elements, and hence, the assessment of their quality and safety has become paramount. Typically, the levels of heavy metal contaminants found in the fish reflect the sediment and water contamination from where it has been sourced and the exposure time (Annabi *et al.* 2013).

Apart from the heavy metals, nutrient discharges from different anthropogenic sources, such as the release of untreated or partially treated domestic, industrial and nutrient-rich agro-wastewaters, have rendered many wetlands to die due to excessive eutrophication. The entire ecology of a eutrophic wetland gets severely affected due to the substantial degradation of its water quality. The rise in eutrophication levels has been a challenge for environmentalists, as this leads to lowering the dissolved oxygen (DO) levels, excessive growth of phytoplankton, and an increased frequency of algal blooms. Effects on the drinking water supply, food security, and public health have also been substantial (Wu *et al.* 2017). Of all the surface water bodies, wetlands have been a primary victim of the increasing eutrophication levels. Therefore, various ecological monitoring programs, including monitoring water quality on a continuous scale, have become quintessential for assessing the possible factors responsible for the deterioration of the wetlands (Alberto *et al.* 2001). Although monitoring various parameters in the wetlands provides information about the wetland's current state, it vaguely provides the factors that influence the current state. Hence, in order to have a better insight into the influencing factors, ecological models are formulated. Ecological models are mathematical or physical representations of a particular ecosystem. These models can comprehend the nutrient/contaminant cycles, identify various characteristics of a concerned parameter or highlight the underlying process mechanism (Hu 2016). In fact, ecological models can also predict the fate of nutrients in the natural ecosystem by revealing the extent and means by which several nutrients such as nitrogen and phosphorus are transformed or removed. In some cases, models can also be developed to answer various "what-if" questions that help decision-makers make a correct choice. Thus, ecological models can serve as perfect

management tools in deciding the right course of action for a particular ecosystem when appropriately developed. Ecological models are also helpful to the researchers because well-designed and calibrated models can reveal the missing piece of the puzzle that allows them to understand a particular mechanism or behaviour of the ecosystem (Das *et al.* 2018). A study of different ecological models developed across the world has provided significant insights into the process of ecological modelling along with the extent to which ecological models can be utilized effectively. The need to develop an ecological model for a water body becomes far more urgent if it is currently endangered.

Keeping in view the above-mentioned problems associated with wetlands, the present research's overarching primary objective is to study their limnology, thereby assessing their responses to different anthropogenic interventions. Accordingly, to achieve the overall aim, different objectives were formulated in the course of this research, described in detail in Chapter 3.

### 1.3. Need for the study

With the ever-growing problem of vanishing wetlands due to human interventions, there is an urgent need to search for options that will aid in restricting any future deterioration. This is possible only if we can deeply understand the wetland ecosystem dynamics through intensive monitoring programs, paving the way for newer alternatives of addressing vital issues like complex data handling operations. In addition to this, novel techniques of assessing water quality through different Environmetrics tools such as multivariate statistics and information entropy will help the scientific community in a more comprehensive and time-conserving manner. This study will also provide substantial aid in understanding the current pollution levels of the sediment column, thus assisting the concerning authorities related to wetland conservation and administration to carry out necessary steps for planning proper management of resources.

Furthermore, given the extensive monitoring and assessment carried out in the present research, the results of this study will provide a comprehensive understanding of the heavy metals and nutrient dynamics in an aquatic ecosystem. Finally, integrating the dataset to frame a eutrophic ecological model will provide significant assistance to the various government as well as private agencies and policymakers for carrying out effective solutions to the increasing eutrophication levels in different wetlands worldwide, which would thereby help in reviving them.

## 1.4. Scope of the thesis

This thesis is a compilation of the research carried out to achieve the overarching objectives of understanding the limnology of wetlands. The first and foremost accomplishment was collecting, transporting, and storing water, sediment, flora and fauna samples on a continuous basis. Following this, laboratory analyses were carried out for different parameters and different ecosystem components, i.e., water, sediment, fish and water hyacinth. From sample collection to analyses, the entire process required a deep understanding of the standard protocols, which remains one of the most important scopes of the research. Since the entire thesis is principally focused on extensive dataset handling and analyses, different computational works were undertaken, including various programmable software such as Microsoft Excel, SPSS (v. 25), and EPA-PMF (v. 5.0). ArcGIS-ArcMap (v. 10.2) was used for creating Spatio-temporal maps of the study area. In addition to the computational software, to formulate the eutrophication-based model, codes in MATLAB (v. R2018b) were written and simulated for different plausible conditions in the wetland.

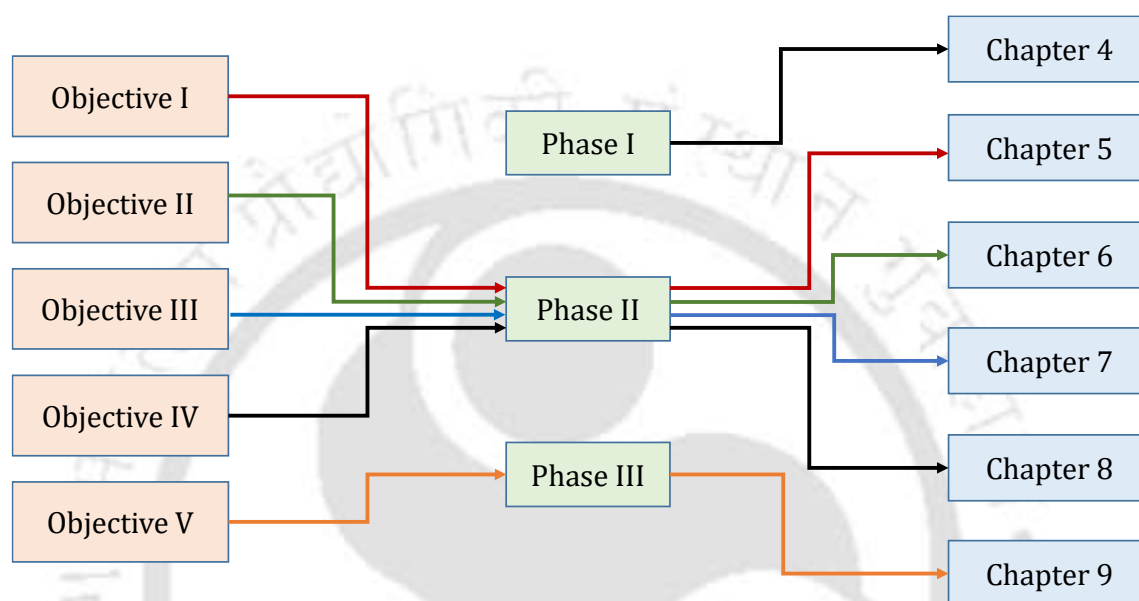
This thesis is intended for researchers and practitioners who intend to carry out extensive research in the domain. All the chapters provide detailed insights into the fundamental aspects of wetland monitoring. Where possible, analytical methods and models incorporated have been discussed that will pave way for successful implementation of restoration of wetlands.

## 1.5. Outline of the Thesis

The outline of this thesis and the objectives achieved in the study are shown in Fig. 1. 2. The entire thesis has been divided into the following chapters:

- Chapter 1 introduces the readers to the world of wetlands and their significances. A brief overview of the various attributes governing the pollution of wetlands is also discussed. In addition to this, some background detailing the assessment of various components of an aquatic ecosystem is also presented. The chapter closes with the need of carrying out the study, the scope of the research and the thesis layout.
- Chapter 2 deals with a detailed backdrop of water quality, sediment contamination and eutrophication-based ecological models. Systematic bibliometric analyses were carried out on the published articles in the respective research domains.
- Chapter 3 identifies the possible gaps in the published literature obtained through bibliometric analyses on water quality, sediment quality, and eutrophication-based ecological models. Based on the associated gaps in the published literature, the objectives of the study were formulated.

- Chapter 4 introduces the materials and methods used in the research, including the design of research, detailed description of the study area, sample collection and analyses for different physico-chemical parameters. Also, different novel methodologies developed during the research are discussed in this chapter.
- Chapter 5 presents the results of the I<sub>st</sub> objective that includes employing different Environmetrics tools to identify and apportion the probable pollution sources.



**Fig. 1. 2.** Thesis outline with objectives.

- Chapter 6 assesses the water quality of a water body using proposed novel objective-based methodologies. The water quality of Deepor Beel is assessed and presented, taking into consideration different usages of water.
- Chapter 7 details sediment quality and assessing the sediment contamination through different approaches concerning heavy metals. This also includes different elemental analyses for validation of the obtained results.
- Chapter 8 deals with understanding the heavy metal dynamics of the wetland ecosystem through their toxicity and bioavailability assay. Human health risks concerning prolonged exposure to these heavy metals for both children and adults are also discussed.
- Chapter 9 presents a detailed understanding of the nutrient (N & P) dynamics in the wetland ecosystem through the developed eutrophication-based ecological model. The model was checked for its reliability and correctness through the sensitivity analysis and then subjected to calibration and validation. Plausible solutions to curb the eutrophication levels in Deepor Beel were addressed.

- Chapter 10 provides overall concluding remarks from the present study and recommendations for future research, which may be carried out as an extension to this research.



A nation that destroys its soils destroys itself.  
Forests are the lungs of our land, purifying the  
air and giving fresh strength to our people.

- Franklin D. Roosevelt

# 2

## Bibliographical Research

This chapter provides a detailed systematic literature review (SLR) on different aspects of wetland limnology. It also describes the need for carrying out an SLR and its advantages over the conventional approach.

### 2.1. A brief overview of wetlands

One of the tricky questions to answer about wetlands is their actual definition. There are 50 different definitions of wetlands available in the literature (Dugan & Dugan 1990). Some of the key definitions are provided in the following paragraph.

According to Goodwin (2017), commonly known as the Ramsar Convention, wetlands are described as "*areas of marsh, fen, peatland or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish, salt including areas of marine water, the depth of which at low tide does not exceed 6m*". Later, this definition was further broadened by including "*riparian and coastal zones adjacent to the wetlands and islands or bodies of marine water deeper than 6m at low tides within the wetlands*". While this definition provides a detailed description of wetlands, it fails to provide scientific precision. NRC (1995) provided another definition which is as follows: "*A wetland is an ecosystem that depends on constant or recurrent, shallow inundation at or near the surface of the substrate. The minimum essential characteristics of a wetland are recurrent, sustained inundation or saturation at or near the surface and the presence of physical, chemical and biological features reflective of recurrent, sustained inundation or saturation. Common diagnostic features of wetlands are hybrid soils and hydrophytic vegetation. These features will be present except where specific physio-chemical, biotic, or anthropogenic factors have removed them or prevented their development*". A shorter yet inclusive definition was provided by Keddy (2010), which states that "*a wetland*

is an ecosystem that arises when inundation by water produces soil dominated by anaerobic processes and biota forces, particularly rooted plants, to exhibit adaptations to tolerate flooding". Cook (1996) described wetlands as *areas where inundation lasted for a minimum of two weeks, and saturated condition in soil remained for at least 60 consecutive days*.

Hence, it can be concluded that there is no universally accepted definition of wetlands. However, all these definitions together give the basic idea that a wetland is an ecosystem that bridges between land and water, providing a unique environment for a variety of flora and fauna to flourish and also act as an interceptor and filter for the influent waters before it enters into rivers, lakes and coastal areas (Turner *et al.* 2000).

Wetlands can be classified in many ways. A broad classification of wetlands can be done as permanent wetlands, temporal wetlands and ephemeral wetlands. Permanent wetlands contain water throughout the year, whereas the temporal wetlands have water only during a particular season. Ephemeral wetlands are filled with water only on heavy rains and flood events that may occur once in a few years.

## 2.2. Wetland biodiversity and significance

Wetlands are house to a wide variety of habitats owing to the dynamic interaction of different factors such as hydrology, geomorphology, water chemistry, edaphic characteristics, dominant vegetation and climatic features (Finlayson & van der Valk 2012). For example, consider the mires (bogs and fens). Among the mires alone, there is a wide diversity of habitats such as raised bogs, Aapa mires and Palsa mires (Gore 1983). Even within a wetland itself, there can be different types of habitats in existence. For example, in Canada, Zoltai and Pollett (1983) had observed that, depending on conditions such as surface morphology, the physiognomy of plant cover and phytosociological units, different types and forms of wetlands existed within the same bogs, fens and marshes. Consequently, different species of living organisms belonging to different habitats can sustain together to introduce diversity within the species and between the species.

Considering species diversity, there can be great variety in it as well. Numerous species of birds, animals, fish, amphibians, reptiles and insects, migratory or residential, are found in the wetlands depending on the habitat's characteristics. These species are dependent on the habitat for food, shelter and reproduction. Due to flight ability, birds form a significant fraction of the migratory population (Keddy 2010). Wetlands are also very rich in floral diversity. In the US, wetlands' floral diversity accounts for 31% of the total flora (Reed 1988). Around 1000 species of wetland plants from India, excluding the Himalayan belt above 1000m altitude, were reported (Cook 1996). The floodplain of Amazon is reported to support more than

3000 species of fish. Different wetlands are found to be rich in waterfowl (Maltby & Barker 2009). Mekong delta's Vietnamese part alone supports 247 species of birds, partly or wholly dependent upon wetland habitats (Buckton & Safford 2004).

Thus, it is beyond doubt that the wetlands are ecological hotspots and crucial in maintaining ecological balance. Apart from being an ecological regulator, wetlands perform several other functions, some of which are mentioned in this section.

- *Water storage and flood control*

Wetlands act as natural storage tanks, storing the influent water from the watershed and slowly releasing it downstream as and when possible. As the flow of the influent water is retarded, the erosion potential of water is reduced. Moreover, by acting as a sink, a large water volume can be stored in the wetland, reducing the chances of high flood levels in the downstream area. In other words, the wetlands act as natural sponges, soaking in the runoff and mitigating flood hazards.

- *Filtration*

Wetlands have a remarkable capacity to act as buffer zones, intercept and filter different pollutants that the watershed's influent waters may carry. Some wetlands also have a dilution effect on the influent pollutant concentration.

- *Denitrification*

Among the many benefits of wetlands is their ability to reduce the levels of nitrate-nitrogen ( $NO_3^- - N$ ) via denitrification. Definite prerequisites for denitrification are anoxic conditions and the presence of  $NO_3^-$  as electron acceptor. In wetland soils, anoxic conditions predominate because the chemical and microbial demands for  $O_2$  greatly exceeds its supply, and the diffusion of  $O_2$  in water is about 104 times slower than in air.

- *Carbon Sequestration*

Carbon Sequestration (CS) refers to the practice of capturing and storing  $CO_2$  for a long-term measure in natural or human-engineered systems with minimum possibility of getting released back to the atmosphere. The carbon sequestration potential of a natural wetland refers to the maximum amount of C a wetland can store within itself on a given spatio-temporal scale. This includes the maximum amount as well as rate of storage. Natural wetlands have proved to be excellent and cost-effective measures for sequestering  $CO_2$ . The wetland plants utilize the photosynthesis process as a tool to accumulate and sequester C in forms of plant biomass and organic matter in the sediment column. The high rates of primary production of wetland plants, compared to the terrestrial plants, further enhance their assimilative capacity for  $CO_2$ . Additionally, there exists anoxic condition in the wetlands due to waterlogging, as a

result of which, the rate of biomass decomposition is low. This results in vast amounts of C to accumulate in the wetlands, making them a C sink. Furthermore, apart from CO<sub>2</sub> and CH<sub>4</sub>, four other forms, viz, particulate organic (POC), particulate inorganic (PIC), dissolved organic (DOC) and dissolved inorganic carbons (DIC) have been found to enter and exit the wetland system.

- *Sediment control*

Wetlands also improve the water quality by behaving as sediment sink. The roots of the vegetation flourishing over the wetland retard the flow of influent water and allows the sediment in the influent water to settle down. Sediment control is more effective for slow-moving water.

- *Groundwater recharge*

Due to wetlands' extensive water holding capacity, water from wetlands percolate downwards and enrich the groundwater beneath. The groundwater, consequently, contributes towards the base flow and surface water bodies.

- *Recreational scope*

Wetlands provide a broad scope of recreational activities such as fishing, boating, picnic spots, bird watching, ecotourism etc. Proper management of the wetland and wise utilisation of the wetland resources can significantly boost the tourism economy.

### **2.3. Attributes to wetland pollution**

Wetlands are polluted by several means. Some of the sources of wetland pollution are mentioned in this section. It must be noted that though pollution has been a significant factor in degrading the quality of wetlands, the role of management and lack of global awareness regarding the usefulness of wetlands has also played a key in its destruction.

- *Domestic wastewater runoff*

Domestic wastewater comprises black water (excreta, urine and faecal sludge) and greywater (kitchen and bathroom wastewater). Domestic wastewater quality relies on several factors: quality of water supplied, waste supply and sanitation facilities, water use practices, and social norms. When the domestic water interacts with the wet-land components, it leads to degradation of the wetland through water pollution, loss of biodiversity or change in climatic conditions. The wetland degradation may also have a social impact, leading to loss of livelihood and abandonment of traditions and culture.

- *Urban drainage and stormwater flow*

If not properly managed, the surface water runoff and stormwater flowing through the towns and cities' open drainage systems can bring about the same detrimental effect to the wetlands as the domestic wastewater.

- *Industrial wastewater*

Industrial wastewater can be classified as diffused industrial discharges, such as mining and agro-based industries and end-of-pipe point discharges. The former is highly polluting and difficult to contain and treat, while the latter can be contained, controlled and treated in circumstances where there is sufficient political will, regulatory power and resources (economic and human capacity) to ensure compliance. However, when these discharges reach wetland untreated, not only do they inflict considerable environmental damage, especially to sensitive ecosystems, but also often come into direct (as well as indirect) contact with humans and animals with consequent damage to health.

- *Agricultural wastewater*

Agriculture has long been recognized as an essential non-point or diffused source of water pollution. Agricultural wastewater can aid in siltation problems and thereby increase flood risk. This wastewater is also rich in nutrients such as nitrogen and phosphorus applied to the farmland to increase crop production. When they reach the wetland, these nutrients help in the plants' rapid growth and cause eutrophication. Along with nutrients, agricultural wastewater contains microbes, which originate from livestock or excreta as fertilizers. The wetlands can also be contaminated from agricultural wastewater because of pesticides, herbicides, and other chemicals used during agriculture. These pollutants may enter into the food chain and affect it at different trophic levels.

- *Eutrophication*

When water bodies of the wetlands receive excess nutrients, especially nitrates and phosphates, these nutrients can stimulate excessive plant growth (eutrophication), including algal blooms, leading to oxygen depletion, decreased biodiversity, changes in species composition and dominance, and degradation of water quality. Although there are natural causes, much of the eutrophication today results from inadequately treated wastewater and agricultural runoff. The deterioration in water quality due to eutrophication is estimated to have already caused around one-third reduction in biodiversity in rivers, lakes and wetlands globally (Maltby & Barker 2009). Population pressure, urbanization, and industrialization contribute considerable waste, altering the physio-chemical quality of water that eventually upset the aquatic system's biotic components.

## 2.4. The Ramsar Convention

With the increasing concerns for depleting wetland habitats for migratory birds worldwide, a treaty was negotiated by the countries and non-governmental organizations in the 1960s. It was later adopted in 1971 and came into force in 1975 in the Iranian city of Ramsar, hence the name Ramsar Convention (Gardner & Davidson 2011). The Convention's sole mission is *"the conservation and wise use of all wetlands through local and national actions and international cooperation, as a contribution towards achieving sustainable development throughout the world"*. Under the "three pillars" of the Convention, the Contracting Parties commit to:

- work towards the wise use of all their wetlands;
- designate suitable wetlands for the list of Wetlands of International Importance (the "Ramsar List") and ensure their effective management;
- cooperate internationally on transboundary wetlands, shared wetland systems and shared species.

The first country to put an accession to the Convention was Australia on the 1<sup>st</sup> of January 1974, and on the 8<sup>th</sup> of May 1974, Australia coined the Cobourg Peninsula as the first Ramsar Site. Today 170 nations are signatories to the Ramsar Convention, India being one of them. As of this date, India has designated 42 ecological hotspots as Ramsar sites, the details of which can be visualized through Fig. 2. 1. These sites are highly delicate when it comes to the natural ecosystem and demand significant attention towards their proper nourishment. Hence, there is a need to continually monitor these water bodies' health status, including the components contributing to the aquatic ecosystem. This necessitates extensive monitoring programs that can provide details regarding the spatial and temporal variability of water bodies' health.

However, these programs also generate vast and complex datasets that are difficult to interpret by ordinary people. Therefore, mathematical tools are utilized to incorporate on the datasets such that they become easily understandable. These include statistical techniques, probabilistic and stochastic models, computations for predicting different parameters, etc. Additionally, models replicating real-life situations are also developed to understand the dynamics of the natural ecosystem better.

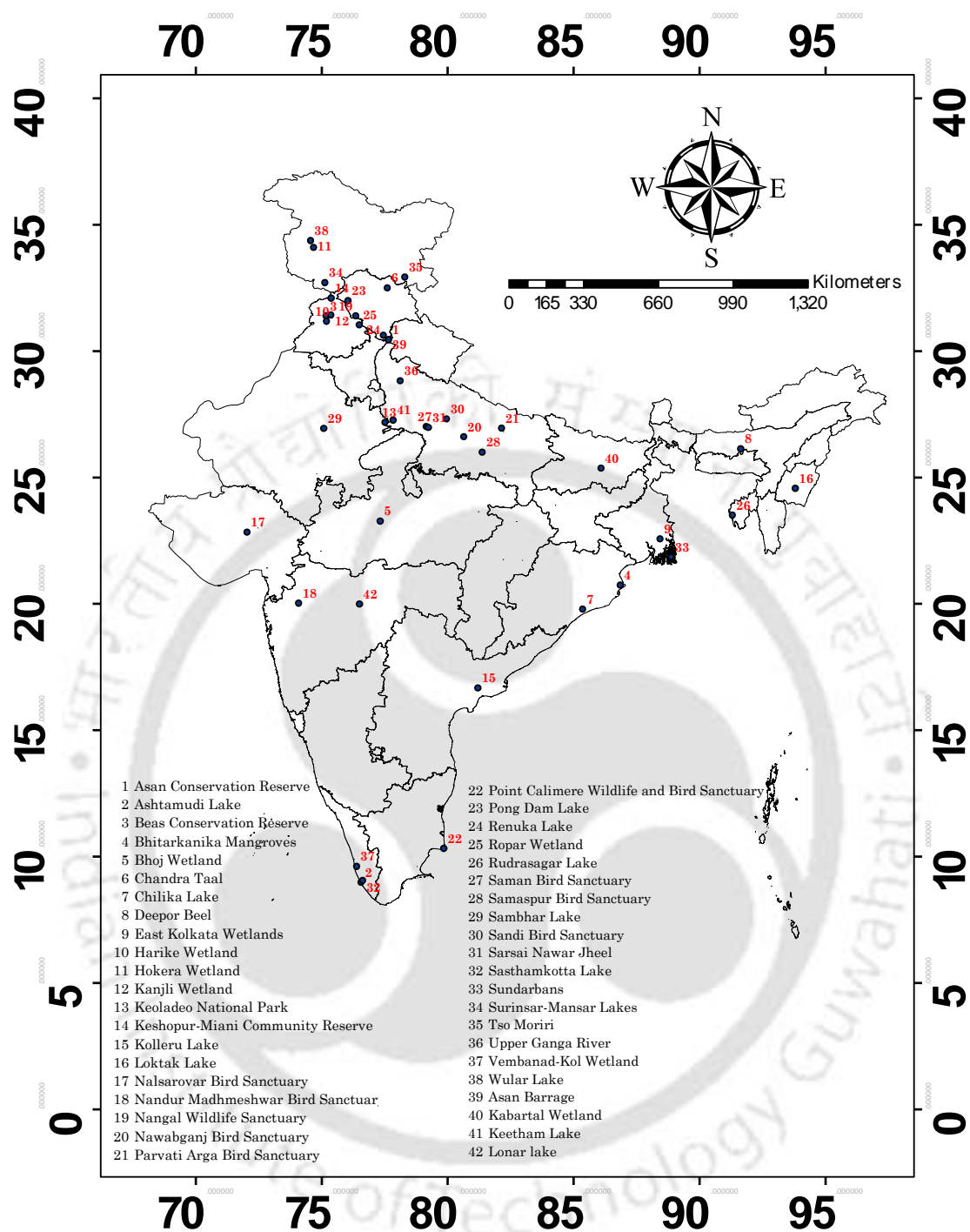


Fig. 2. 1. Ramsar sites in India.

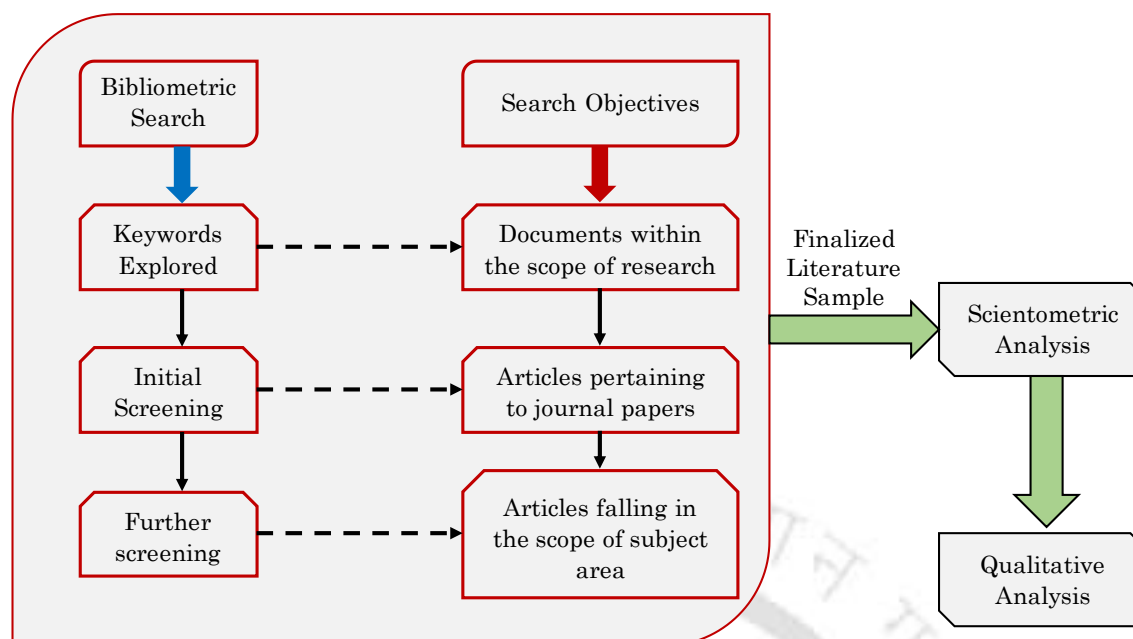
## 2.5. Introduction to Bibliometric analyses

Literature review studies provide an in-depth understanding of the existing methodologies in a research domain (He *et al.* 2017; Jin *et al.* 2019). It also provides a deeper understanding of existing approaches' limitations, thereby providing a guiding path towards systematic innovations. However, some of the existing reviews conducted on WQIs are highly subjective

and purely based on individual perceptions, which may be prejudiced and misleading (Lumb *et al.* 2011; Sutadian *et al.* 2016). Hence, the scientific conduct of the literature review needs attention, which can be attained through the science-mapping approach. The science-mapping technique of understanding a research domain or areas concerning specific queries regarding the conduct of research is achieved through a broad process of domain analysis and visualizing the results attained (Chen 2017). A science-mapping analysis consists of specific tools or indicators, principally, a set of scientific literature and a group of scientometric and graphical analytical tools, metrics, and indicators that emphasize essential patterns, trends, and notions of scientific change (Chen 2017). Thus, it provides a holistic approach to reviewing the existing literature, emphasizing a qualitative discussion addressing the fundamental limitations that could lead the way forward for future scholarly innovations.

The novelty of the current bibliographic research lies in the (a) application of science-mapping in different research domains, which could minimize the subjectivity and prejudice in reviewing published literature, (b) analyzing the existing mainstream topics, (c) a qualitative discussion, explicitly pointing out the limitations and gaps in the existing literature, thus giving it a more comprehensive approach, and finally (d) proposing a research framework which will pave the way for future research works. The review-based investigation adopted a three-step all-inclusive approach. The detailed workflow of the approach has been represented through Fig. 2. 2, which comprises all three steps; Bibliometric search, Scientometric analysis, and Qualitative assessment. The bibliometric analysis followed the Preferred Reporting Items for Systematic Reviews and Meta-Analysis (PRISMA) technique, working on four independent levels.

The first step towards the PRISMA process involved “identification”, wherein keywords were entered based on the search criteria in various databases, and the records were extracted. The database chosen for the bibliometric search was *Scopus*, which is considered one of the prime search engines for academicians and researchers. The main reason for selecting *Scopus* as the search engine is that *Scopus* is believed to cover a broader range of journals and possess more recent publications than other search engines such as *Web of Science*, *Google Scholar*, *PubMed*, etc. (Aghaei Chadegani *et al.* 2013). The subsequent sections provide an in-depth analysis of the review of published literature in assessing the quality of all the components of the wetland ecosystems, i.e., water and sediment. A detailed review of the developed ecological models worldwide is also presented through scientific analyses of the available literature.



**Fig. 2. 2.** Flowchart depicting the three-step scientific approach to reviewing published literature.

## 2.6. Water Quality

Sustainable development of the human race has always revolved around water and its extensive daily use. The freshwater availability is definite, whilst its exploitation has been rising ever since. The anthropogenic interferences such as large-scale urbanization resulting in unplanned watershed management practices, discharge of harmful toxic chemicals from industries, nutrients from the agricultural sector, and even the airborne metallic contaminants have reached scales that have rendered some of the water bodies around the world polluted beyond repair (Bartram & Ballance 1996; Carpenter *et al.* 1998; Singh *et al.* 2005a; Todd *et al.* 2012; Wu *et al.* 2018). Hence, several viable steps need to be undertaken for the restoration and conservation of water resources. This makes water quality monitoring programs an indispensable part of assessing the health of a water body and its effective management (Ward *et al.* 1986; Astel *et al.* 2006; Behmel *et al.* 2016; Romero *et al.* 2016). These water quality monitoring programs can be categorized into three classes; (a) monitoring, (b) surveys, and (c) surveillance, depending on whether the monitoring program is long-term, short-term or a continuous process, respectively (Chapman 1996). These monitoring programs lead to the generation of vast sets of data, comprising various water quality parameters, distributed spatially as well as temporally, making them data-rich but information-poor, thereby rendering their interpretation extremely difficult and complicated. Hence, various researchers have tried to use methods by which information regarding water quality can be easily transmitted without damage of any significant information (Shastry *et al.* 1972; Aston *et al.* 1974; Lizcano

*et al.* 1974; Afşin 1997; Nunes *et al.* 2003; Subramani *et al.* 2005; Tsegaye *et al.* 2006; Moeller *et al.* 2007).

The water quality indexing (WQI) technique, of all the techniques, has proved to be the most efficient and has played a pivotal role in effective water resources management (Debels *et al.* 2005; Lumb *et al.* 2011; Mohebbi *et al.* 2013; Sutadian *et al.* 2016). Its integration with more advanced and sophisticated tools such as the geographic information system (GIS) has made it extremely handy in determining the spatial and temporal variability, as well as the distribution of various water quality parameters (Şener *et al.* 2017a; Şener *et al.* 2017b). WQI is a mathematical approach, wherein several water quality parameters (variables) are associated together to frame a single integer value, depicting the overall health status of a water body (Bordalo *et al.* 2006; Sánchez *et al.* 2007; Abbasi & Abbasi 2012; Tian *et al.* 2019). This approach not only makes data interpretability easy, but also makes the understanding of the spatio-temporal variability of the water quality parameters simplified (Noori *et al.* 2019). The WQI approach is considered to be primarily of two types; *pollutant index* and *quality index*. In the pollutant-index, the WQI values increase with the rise in pollution level, while in the quality index, it is vice-versa (Misaghi *et al.* 2017). Additionally, the WQIs are classified into four categories, depending on the end-use of water (Jena *et al.* 2013):

- No consideration of the end-use of water: Provides a holistic view of the WQI.
- Highly target-specific: Depends heavily on the water-use such as drinking, irrigation, industrial discharge and assessment of heavy metal contamination, etc.
- Planning and management: Usually employed in cases wherein effective management and planning of water resources are of primary focus.
- Use of Mathematical tools: Statistical and other mathematical models are employed to determine the overall health of a water body.

While the first three approaches consider consultation from specific experts in relevant areas of expertise, the fourth approach is based entirely on the dataset and thus, devoid of any personal judgement or opinion, which otherwise, in many cases, has led to ambiguities among researchers.

The major limiting factors in water quality indexing are the subjective approach towards inducing sub-weights, which can be prejudiced and misleading in some cases. This is primarily because the use of expert opinions is often deemed as unscientific as they may vary from one person to another, based on each individual's perception. To minimise the effects of subjective judgements, mathematical tools, also known as Environmetrics or Chemometrics tools, have come into effect in recent years. The development of WQIs involves the following four steps (Abbasi & Abbasi 2012):

- a. Selecting water quality parameters.
- b. Computation of sub-index values through a transformation of the parameters to a standard scaling factor.
- c. Estimation of weights for all parameters.
- d. Aggregating the sub-index values to obtain the final WQI.

The research on the development of newer techniques pertaining to attaining a comprehensive WQI revolves primarily around the second and third step, i.e., determining the sub-indices and eventually the weights, leading to the final WQI value. The first reported use of the indexing technique dates back to the 1960s when Horton (1965) associated the term index with water quality. Since then, there have been numerous attempts made by several researchers around the globe to introduce novel techniques in arriving at a comprehensive water quality index. Hence, there is a need to have a more in-depth look into the various methodologies adopted in attaining various WQIs and thereby understand the pros and cons of their adaptations. This will eventually pave the way to discovering newer strategies and techniques while adopting the pros of the existing methods and, at the same time, addressing their limitations.

For this purpose, the following keywords were entered in *Scopus*:

**TITLE-ABS-KEY** ("water quality index" OR "wqi")

A total of 3261 published documents was initially extracted.

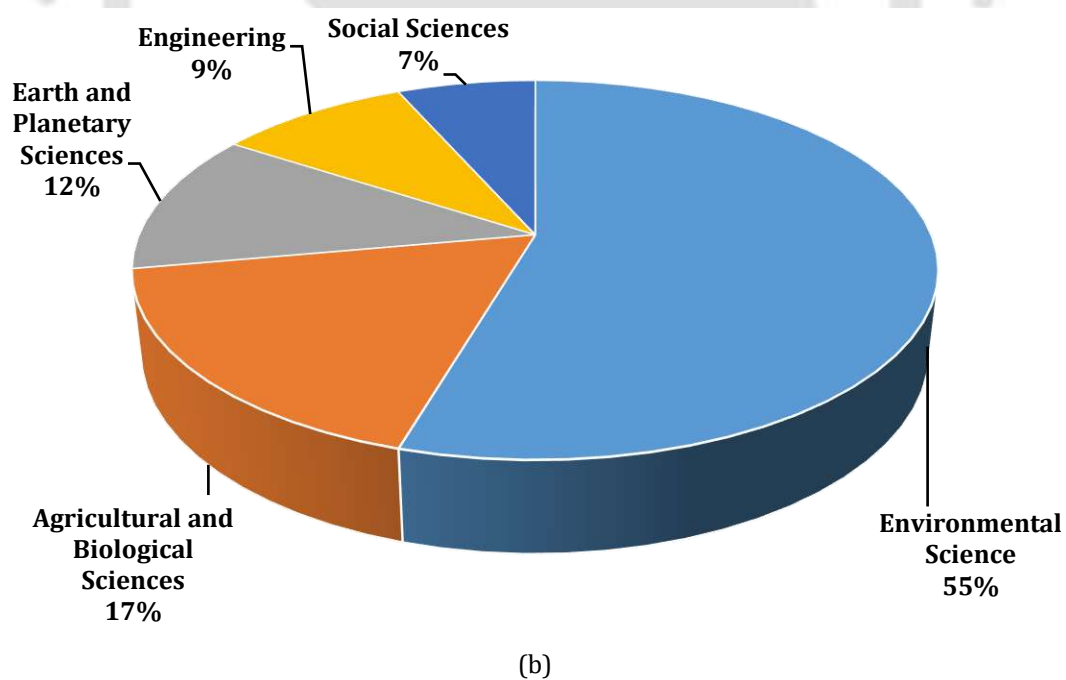
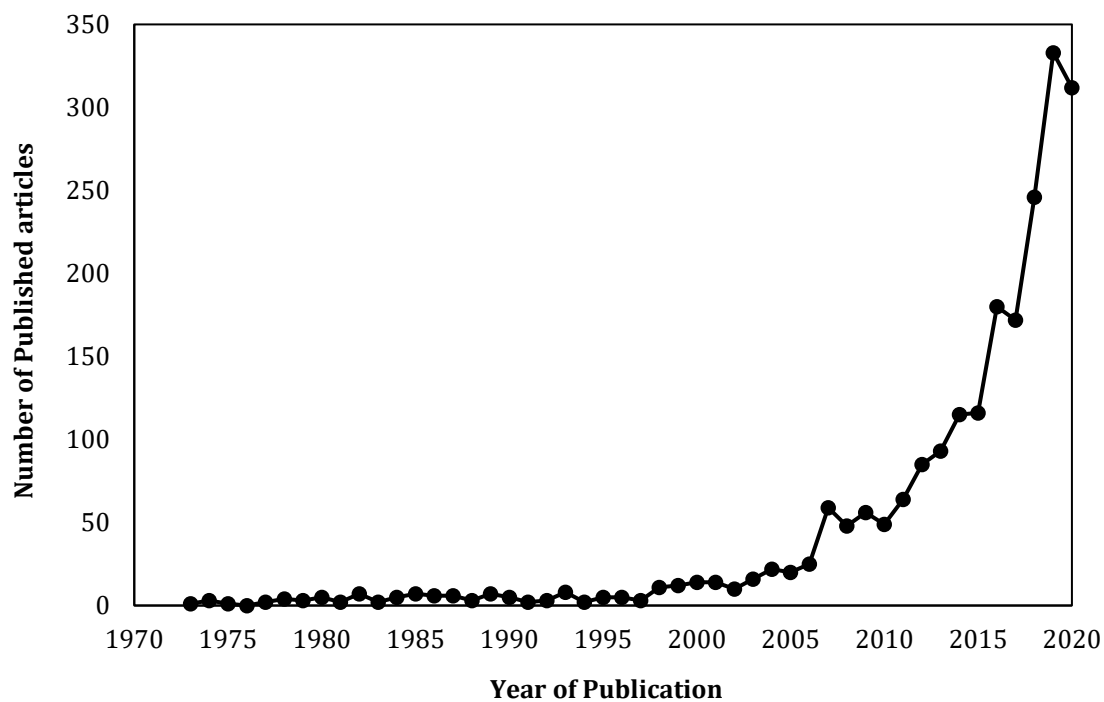
These published works of literature were then subjected to the second step, which is the "screening" process, based on the inclusion-exclusion criteria. A three-step screening process was adopted based on the scope of the current research. Firstly, the articles available online and are under process for publication till the year 2020 were considered. Secondly, the articles falling under the scope of "*Environmental Science*", "*Agricultural and Biological Sciences*", "*Earth and Planetary Sciences*", "*Engineering*", and "*Social Sciences*" were considered, as our scope limits to these areas only. Finally, only research articles published in English were considered, whilst the conference papers and book chapters were excluded as the article publications provide more detailed and significant information as compared to the other two modes of publications.

After the screening process, the third step involved the "eligibility" criteria, where the extracted articles after screening were subjected to quality assessment to avoid any duplicity of data. Furthermore, all articles were studied for their titles, abstracts and keywords to identify whether the articles fall within the scope of the research. All irrelevant articles which were beyond the scope of the investigation were excluded.

The fourth and final step describes the significance of the use of a single word or a combination of words through the “included” function. While using a combination of words, the keywords are entered using the Boolean operators such as AND or OR, based on the requirements. After the final round of screening, a total of 2049 articles were selected for the scientometric analysis. The results of the scientometric analyses are discussed in the following subsections.

### 2.6.1. An overview of the literature sample

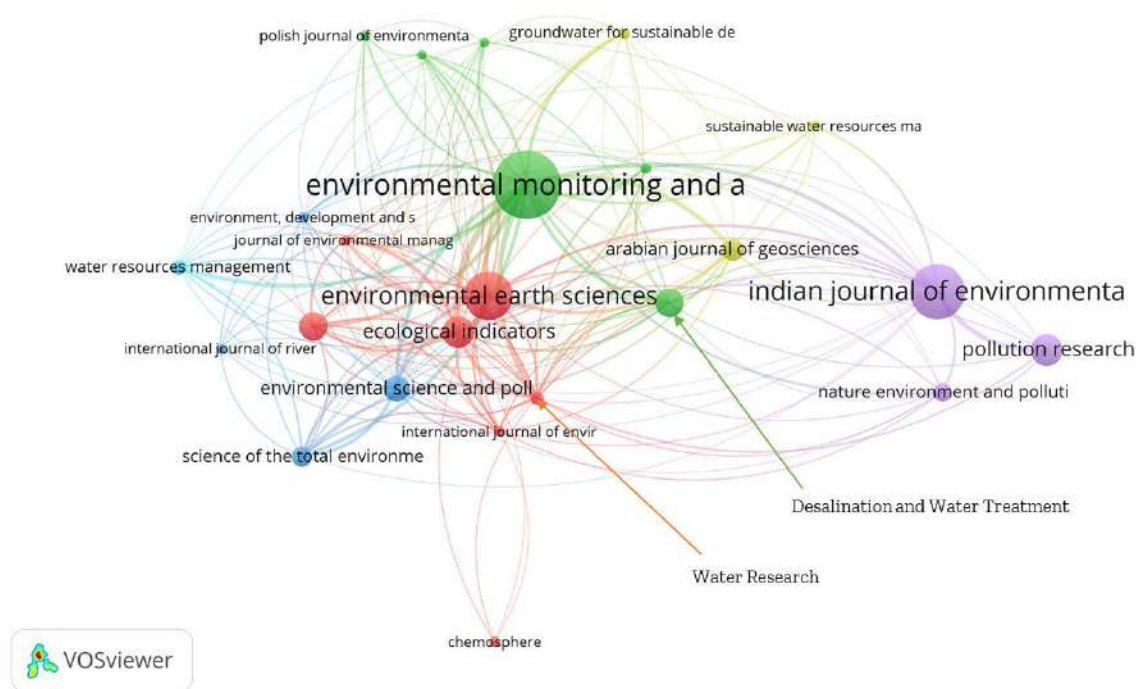
Fig. 2. 3 presents a scientometric analysis of the published literature based on the number of articles published until the year 2020. The data showed an overall trend of the research outputs in the domain of water quality indexing. It was observed that not many articles were published until the dawn of the 21<sup>st</sup> century. Post the year 2000; there has been a steep rise in the publication of articles about the indexing of water quality. In the past decade, i.e., from the year 2010, a vast number of articles have been published, with the annual figures going well above 300 in the last two years, from being ranged between 100-250 in the past decade (Fig. 2. 3a). This is indicative of the growing research in this domain, and it is expected that these numbers will go even higher in the upcoming years, owing to the development of newer methodologies and an everlasting wide range of scope in this domain of research. Also, it was observed that more than half of the research (about 55%) fell in the area of Environmental Science, which was further followed by Agricultural and Biological Sciences (17%), Earth and Planetary Sciences (12%), Engineering (9%), and Social Sciences (7%). This shows that the domain of water quality indexing is primarily focused on Environmental and Agricultural, and Biological Sciences (Fig. 2. 3b). Thus, there exists a vast scope for engineers and scientists worldwide, specializing in Environmental Science and Agricultural and Biological Sciences, in working in the domain of water quality indexing. Additionally, with the development of novel mathematical models and techniques, significant demand for collaborative efforts with mathematicians and computer engineers might arise.



**Fig. 2. 3.** Results of the scientometric analysis showing (a) Year-wise distribution of published articles, and (b) Classification of documents based on relevant subject areas. (Data extracted from Scopus Database)

### 2.6.2. Journal Sources

Journal sources involved in the publication of articles related to water quality indexing were assessed and visualized. The results of the scientometric analysis involving the journal sources are reported in Fig. 2. 4 and Table 2. 1. A minimum of 15 articles and 30 citations were set for analysis in *VOSViewer*, which provided a cumulative of 24 out of a total of 493 journals meeting the tolerance level. Fig. 2. 4 exhibits the clusters of journal sources and their inter-relationships through the connected lines. It is important to note that all the relevant journals may not be visible through Fig. 2. 4. Hence, a more detailed quantitative analysis of the journal sources and their influence is provided in Table 2. 1.



**Fig. 2. 4.** Mapping of mainstream journals in the domain of water quality indexing.

In the network representation of the journal sources, as shown in Fig. 2. 4, the sizes of the fonts and nodes are proportional to the number of publications from that particular journal, i.e., the larger the font and node size, the more is the number of published articles contributed from that journal. Furthermore, the cluster colours, as well as the colours of the connecting lines, indicate the relative closeness among the various journals with respect to mutual citations. Citations are considered to be of high regard in the field of re-search as it is considered as a standard measure to identify the influence of the studies in that particular domain of research (Van Eck & Waltman 2014). From Fig. 2. 4, it was observed that journals like *Environmental Monitoring and Assessment*, *Indian Journal of Environmental Protection*, *Environ-*

*mental Earth Sciences, Ecological Indicators, and Pollution Research* provided a significant contribution to the research pertaining to the domain of water quality indexing. Additionally, these journals also have dense networking of the connecting lines, thus indicating their closeness with respect to the published articles. A more quantitative assessment has been reported in Table 2. 1.

**Table 2. 1.** Quantitative measurements of journals publishing water quality index research.

Source	Number of documents	Total citations	Average citations <sup>A</sup>	Normalized citations	Average Normalized citations <sup>B</sup>
Environmental Monitoring and Assessment	103	2567	25	151.14	1.47
Indian Journal of Environmental Protection	83	481	6	13.11	0.16
Environmental Earth Sciences	73	1188	16	108.44	1.49
Ecological Indicators	48	1854	39	134.11	2.79
Pollution Research	48	215	4	7.75	0.16
Desalination and Water Treatment	43	250	6	23.94	0.56
Water (Switzerland)	43	269	6	49.83	1.16
Environmental Science and Pollution Research	40	342	9	42.03	1.05
Arabian Journal of Geosciences	33	506	15	42.21	1.28
Science of the Total Environment	31	966	31	121.25	3.91
Nature Environment and Pollution Technology	29	185	6	16.18	0.56
Water Resources Management	23	372	16	35.64	1.55
Water Research	20	1355	68	45.42	2.27

<sup>A</sup> Average citations are estimated by dividing the total number of citations received by the total number of articles published.

<sup>B</sup> The Ave. Norm. Citation represents the normalized number of citations of a journal, document, author, or an organization. It corresponds to the total number of citations divided by the average number of citations published in the same year. The normalization concept rectifies the misinterpretation that older documents have more time to receive citations than more recent one (Van Eck & Waltman 2014). The Norm. Citation in Table 2. 1 measures the citation of all the articles within the same journal, while the Ave. Norm. Citation represents the normalized citation per article, it is calculated by dividing the Nor. Citation by the number of articles. All the normalized citation scores presented throughout the thesis are based on this concept.

Groundwater for Sustainable Development	18	202	11	33.71	1.87
Environment, Development and Sustainability	17	72	4	14.87	0.87
Water Science and Technology	17	208	12	13.61	0.80
Chemosphere	16	284	18	21.29	1.33
International Journal of Environmental Research and Public Health	16	241	15	22.72	1.42
Polish Journal of Environmental Studies	16	108	7	9.49	0.59
Sustainable Water Resources Management	16	124	8	13.98	0.87
Human and Ecological Risk Assessment	15	287	19	65.22	4.35
International Journal of Environmental Science and Technology	15	166	11	13.11	0.87
International Journal of River Basin Management	15	89	6	11.53	0.77
Journal of Environmental Management	15	753	50	34.84	2.32

Five different measuring parameters corresponding to the productivity and influence of journals in the domain of water quality indexing are listed in Table 2. 1; the number of listed documents, total citations, the average citations, normalized citations, and the average normalized citations. While the former two parameters are found to be highly correlated to each other in general, the other three parameters are relatively non-aligned with the other two, i.e., the journals governed by a high number of publications or citations may not necessarily display a higher average citation score. It was observed that Fig. 2. 4 and Table 2. 1 showed consistent results, with respect to the most productive journals, i.e., *Environmental Monitoring and Assessment*, *Indian Journal of Environmental Protection*, *Environmental Earth Sciences*, *Ecological Indicators*, *Pollution Research*, *Desalination and Water Treatment*, *Water (Switzerland)*, and *Environmental Science and Pollution Research*. Out of these, *Environmental Monitoring and Assessment*, *Environmental Earth Sciences*, and *Ecological Indicators* are the journals receiving a higher range of average citations, thereby indicating stronger influence in terms of both productivity and research significance. However, when it comes to the journals

having the most influential publications, i.e., in terms of average normalized citations received, the journal of *Human and Ecological Risk Assessment* had the highest research significance, with an average normalized citation score of 4.35. Other journals such as *Science of the Total Environment* (3.91), *Ecological Indicators* (2.79), *Journal of Environmental Management* (2.32) and *Water Research* (2.27) are among journals with a considerable research significance in the domain of water quality indexing, with average normalized citation scores of more than 2.00. These journals do not possess a higher quantum of articles in this research domain but significantly contribute to the research.

### 2.6.3. Co-occurrence of Keywords

Keywords in research provide a comprehensive idea about the topics that have been primarily focused on the domain (Su & Lee 2010). Therefore, a network of keywords provides a clear demonstration of the inter-relationships and closeness between them (Van Eck & Waltman 2014). Based on the references by Oraee *et al.* (2017) and Hosseini *et al.* (2018), the current study considered the “Author Keywords” and “Fractional Counting” method of analysis in *VOSViewer*. The minimum number of occurrences was set as 10, which yielded 78 keywords out of a cumulative total of 4308 keywords. The 78 keywords were then filtered by removing some more generalist and repetitive items such as “Monitoring”, “pH”, “Turbidity” etc., while some other keywords with closer resemblances such as “Physicochemical parameters”, “Nutrients”, etc. were considered in the second round of analysis. Eventually, a total of 48 keywords were selected, as given in Table 2. 2 and shown in Fig. 2. 5.

As shown in Fig. 2. 5, the nodal sizes indicate the frequency of occurrences of the keywords, like “Water quality index”, “Water quality”, and “Groundwater” displaying higher size nodes, thereby indicating a higher frequency of occurrence. This also indicates the assessment of groundwater quality has been primarily carried out compared to the surface waters. Additionally, the colours of the nodes indicate the clusters, i.e., each keyword is divided into different clusters depending upon the relative closeness between them. For example, “Cluster analysis”, “Principal Component analysis”, “Factor analysis” can be seen to have a single colour representation, thus, suggesting their close relations to each other. Furthermore, keywords from different clusters may also have a strong linkage, such as “Drinking water”, “Groundwater”, and “Principal component analysis” (Fig. 2. 6). From the clustering of keywords obtained, the fundamental research on water quality indexing can be categorized in terms of Statistical analyses, WQI based on LULC and risk assessment, Groundwater quality indexing, Surface water quality indexing, Mathematical Approaches, and the Areas of research active in various countries. Each of the above-mentioned categories have been discussed in details below.

- *WQI based on LULC and risk assessment*

Some of the recent studies have shown the variation of water quality with respect to the changes in the land-use and land-cover patterns of different areas (Zhang *et al.* 2009; Singh & Khan 2011; Srivastava *et al.* 2013; Wilson 2015; de Oliveira *et al.* 2017; Wang *et al.* 2018). Modelling LULC patterns remains one of the major methods of adaptation. Also, some of the most recent literature has associated WQI with health risks, such as (Adimalla 2019; Adimalla & Qian 2019; He & Wu 2019; Karunanidhi *et al.* 2020; Ustaoglu *et al.* 2020; Wu *et al.* 2020). These WQIs have primarily focused on drinking water guidelines and the health risks associated with the consumption of water polluted with majorly heavy metals.

- *Groundwater quality indexing*

Studies involving groundwater quality indexing specifically focused on assessing the hydrogeology of the study area, so that the groundwater can be rendered fit for drinking as well as irrigation purposes (Reza & Singh 2010; Saeedi *et al.* 2010; Vasanthavigar *et al.* 2010; Mohebbi *et al.* 2013; Adimalla *et al.* 2018). Areas facing scarcity of surface water were the primary regions of focus, as they are entirely dependent on the local aquifers for meeting their water demands.

- *Surface water quality indexing*

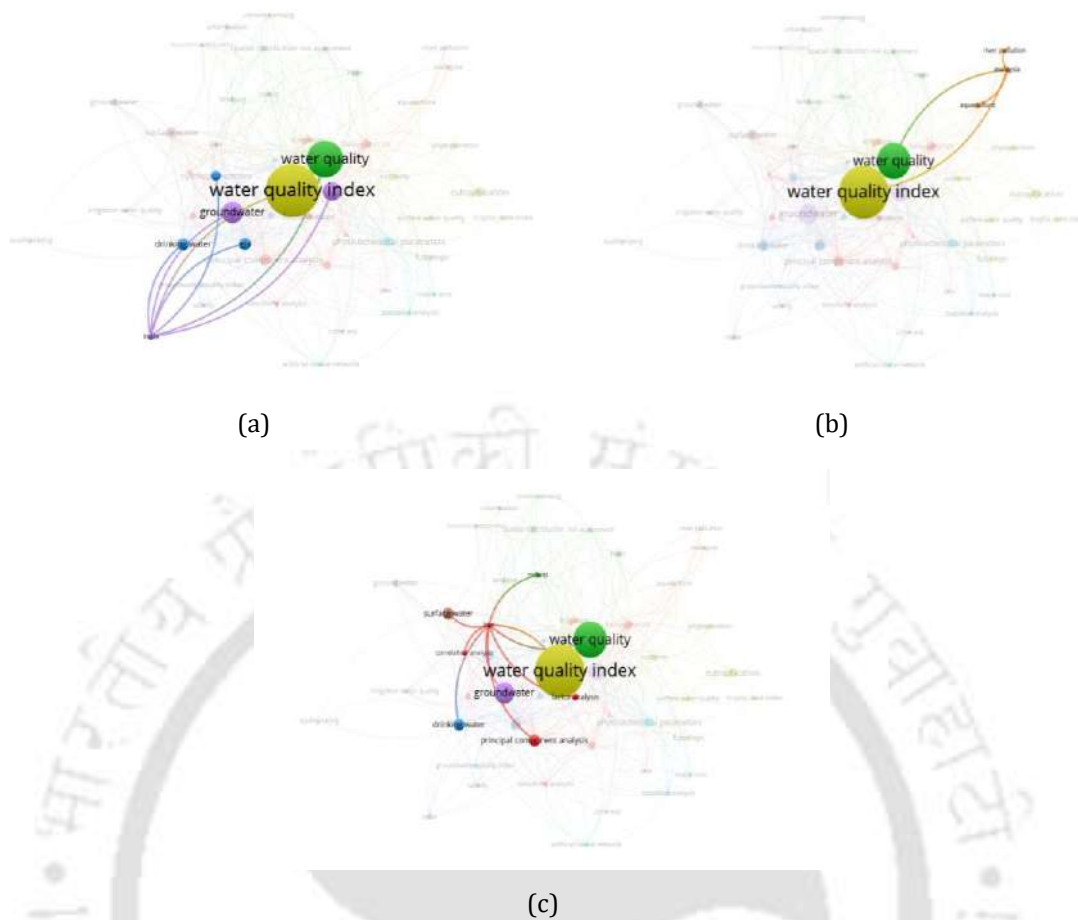
Indexing approaches involving surface waters involved a wider range of areas, compared to the groundwater studies (Varol & Şen 2012; Dede *et al.* 2013; Chang *et al.* 2015; Whittaker *et al.* 2015; Avigliano & Schenone 2016; Gao *et al.* 2016; Gopal *et al.* 2018; Wu *et al.* 2018). The studies involved research areas other than drinking, like assessing the water quality for nutrients, thereby determining their eutrophication potential. Also, the surface waters included both freshwaters such as rivers, lakes, wetlands, etc. and marine waters such as seas and oceans (Jha *et al.* 2015).

- *Mathematical approaches*

The development of WQIs based on mathematical approaches is the newest addition to the domain, as these methods did not involve subjective assessments. Instead, they were purely based on mathematical models. Some of the models involved in the research of water quality indexing include relational method or statistics (Srivastava *et al.* 2011; Yan *et al.* 2016; Tian *et al.* 2019), geographically variable (Dunnette 1979; Melloul & Collin 1998; Cude 2001; De Rosemond *et al.* 2009), multivariate statistics (Melloul & Collin 1998; Howladar *et al.* 2018; Rana *et al.* 2018; Khalid 2019; Kükrcer & Mutlu 2019; Patil *et al.* 2020), probability and fuzzy approach (Nasiri *et al.* 2007; Lermontov *et al.* 2009; Song & Kim 2009; Gazzaz *et al.* 2012; Yaseen *et al.* 2018), and finally information entropy (Amiri *et al.* 2014; Fagbote *et al.* 2014; Adimalla *et al.* 2019; Islam *et al.* 2020b; Rao *et al.* 2020; Ukah *et al.* 2020).







**Fig. 2. 7.** Research areas and countries active in water quality indexing.

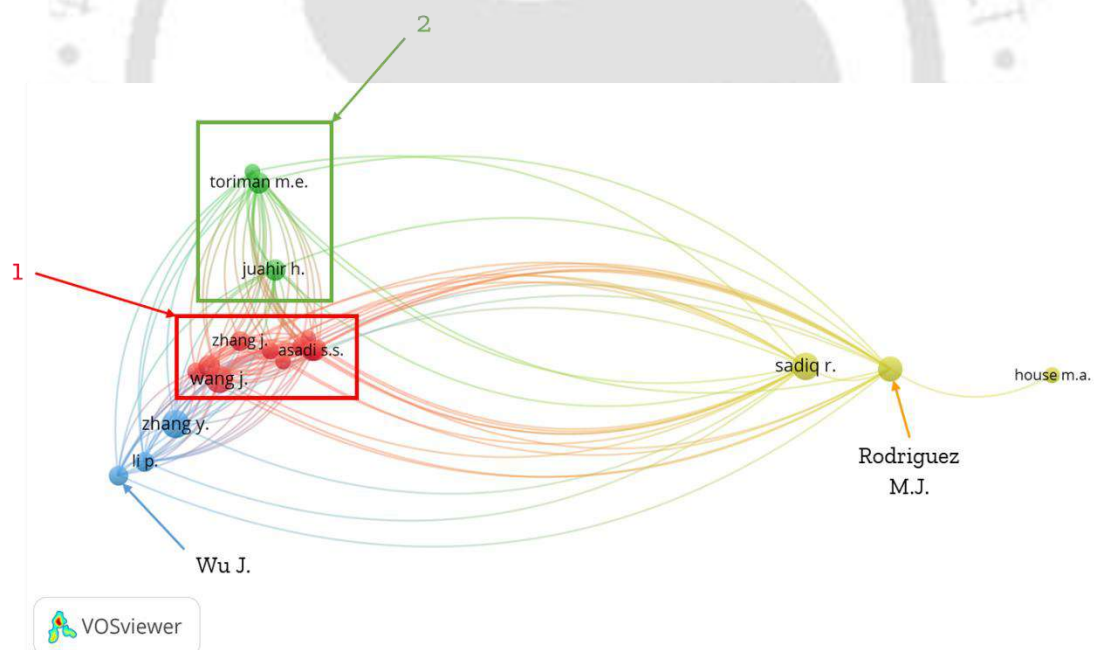
**Table 2. 2.** Summary of main keywords in water quality index research.

<b>Keyword</b>	<b>Occurrences</b>
Water quality index	650
Water quality	340
Groundwater	137
WQI	108
Drinking water	53
GIS	53
Principal component analysis	51
Surface water	47
Eutrophication	44
Physicochemical parameters	42
Heavy metals	37
Hydrogeochemistry	34
Cluster analysis	33
Irrigation	33
Health risk assessment	23

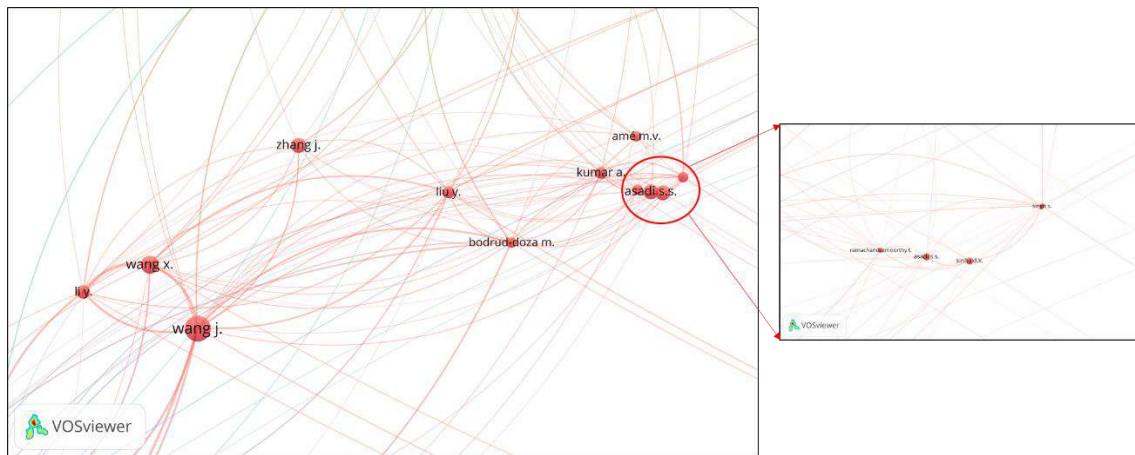
Multivariate analysis	21
River	21
Factor analysis	20
Spatial distribution	20
Nutrients	19
Phytoplankton	19
India	17
Land use	17
Fuzzy logic	16
Quality rating	16
Artificial neural network	15
Statistical analysis	15
Risk assessment	14
Iran	13
Malaysia	13
Surface water quality	13
Aquaculture	12
Groundwater quality index	12
Irrigation water quality	12
Multivariate statistical analysis	12
Trophic state index	12
Correlation analysis	11
Discriminant analysis	11
Macroinvertebrates	11
Major ions	11
River pollution	11
Salinity	11
Sensitivity analysis	11
Urbanization	11
CCME WQI	10
NSFWQI	10
Remote sensing	10

### 2.6.4. Co-authorship analysis

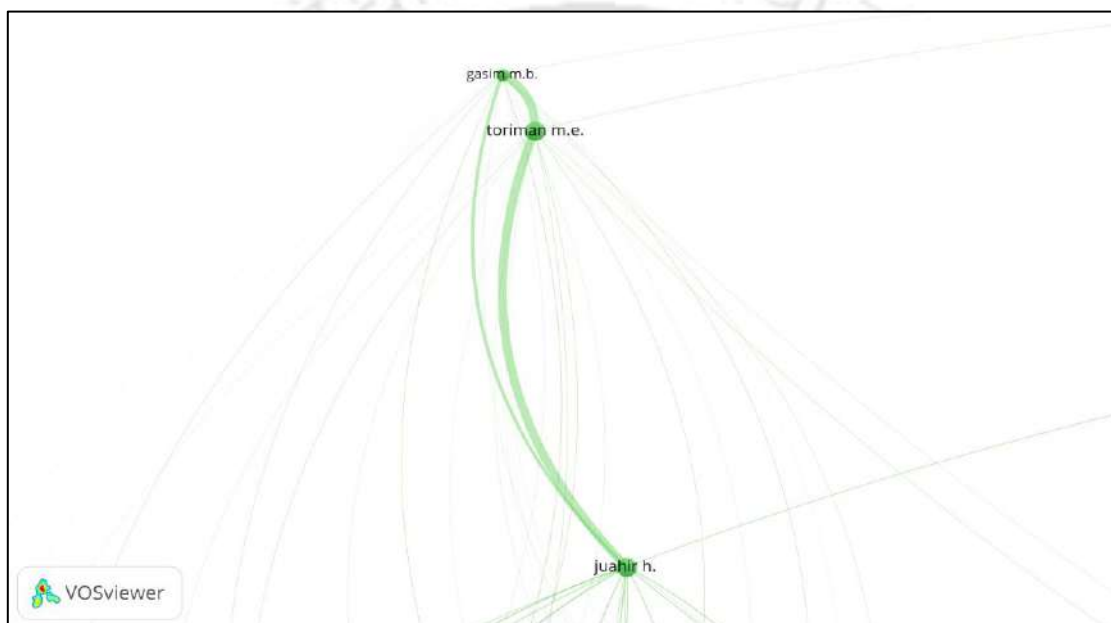
Mutual collaborations amongst various researchers around the world are a usual affair. The awareness among the researchers regarding the existing collaborations helps improve their productivity and prevent them from being isolated (Hosseini *et al.* 2018). Hence, a scientometric analysis regarding the co-authorship details was carried out using *VOSviewer*. Authors having published more than 7 articles and having a minimum of 30 citations were considered for the analysis. 21 scholars around the world, out of a total of 5686 researchers, met the selection criteria. The most influential researchers were shown in Fig. 2. 8 and Table 2. 3. As shown in Fig. 2. 8, the scholars were classified into four different categories based on their research in the domain of water quality indexing, for example, the research group of Zhang Y., Li P., and Wu J. Table 2. 3 lists out five key quantitative estimations, namely, the total number of documents, total number of citations, average citations, normalized citations, and average normalized citations in *Scopus*. The former two quantitative measurements provide productivity, while the remaining three measurements provide the research influence.



(a)



(b)



(c)

**Fig. 2. 8.** Map showing the (a) Overall co-authorship analysis, (b) Expansive view of cluster 1, and (c) Expansive view of cluster 2.

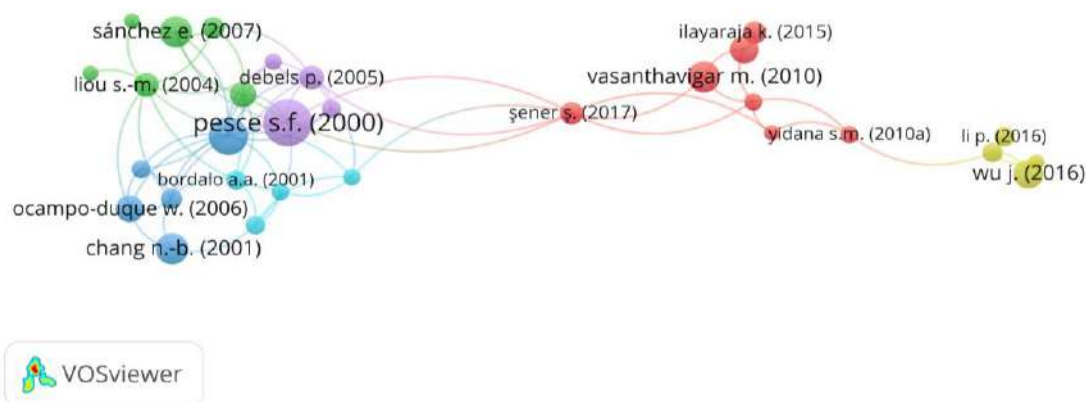
From Table 2. 3, it is evident that Zhang Y. was deemed as the most productive in terms of research outcomes, whereas Wu J. was the most influential researcher, with the average normalized citation significantly higher than all other researchers, at 10.43. The scholars were also found to be highly collaborative, as can be visualized from the density of nodal connectors, as shown in Fig. 2. 8.

**Table 2. 3.** Quantitative summary of the impacts of scholars in the domain of water quality indexing.

Scholar	Number of documents	Total citations	Average citations	Normalized citation	Average Normalized citation
Zhang Y.	18	388	22	60.03	3.34
Sadiq R.	17	256	15	17.60	1.04
Wang J.	17	300	18	39.08	2.30
Rodriguez M.J.	15	159	11	11.61	0.77
Wang X.	12	275	23	32.68	2.72
Juahir H.	11	204	19	16.70	1.52
Toriman M.E.	11	57	5	6.00	0.55
Asadi S.S.	10	115	12	5.34	0.53
Li P.	10	422	42	61.86	6.19
Sinha D.K.	10	51	5	1.57	0.16
Wu J.	10	769	77	104.32	10.43
Zhang J.	10	112	11	10.85	1.09
Li Y.	9	198	22	13.89	1.54
Kumar A.	8	112	14	8.81	1.10
Liu Y.	8	68	9	11.38	1.42
Amé M.V.	7	135	19	9.53	1.36
Bodrud-Doza M.	7	141	20	15.71	2.24
Gasim M.B.	7	38	5	2.89	0.41
House M.A.	7	146	21	7.36	1.05
Ramachandra-moorthy T.	7	38	5	1.97	0.28
Singh S.	7	66	9	6.72	0.96

### 2.6.5. Articles' citations

Citations of articles provide their influence in any domain of research. The most influential articles published in the domain of water quality indexing was analysed in *VOSViewer*. A minimum of 100 citations was set for the investigation, which resulted in 30 articles, listed in Table 2. 4 and the network, shown in Fig. 2. 9. The most cited article was found to be Pesce and Wunderlin (2000), which was one of the first researches conducted on indexing studies, integrating both subjective and objective criteria. The introduction of the objective criteria into the indexing technique was considered very important as it removed major ambiguities related to the subjective criteria, which was primarily based on personal judgements from various researchers.



**Fig. 2. 9.** Science mapping of the most influential publications in the water quality indexing research.

Other research works such as (Tiwari & Mishra 1985; Chang *et al.* 2001; Cude 2001; Sánchez *et al.* 2007; Vasanthavigar *et al.* 2010; Wu & Sun 2016) were found to have more than 200 citations each, signifying their relative importance in the field of research. It is also important to note that all articles except Bordalo *et al.* (2001) displayed normalized citations more than 2.00, which further indicated a high impact of research in the domain of water quality indexing. Also, all recently published articles like (Vasanthavigar *et al.* 2010; Ilayaraja & Ambica 2015; Li *et al.* 2016b; Wu & Sun 2016; Şener *et al.* 2017b; Zhang *et al.* 2018b) displayed a higher normalized citation score, thus indicating that the influence of the relatively newer articles is considerably higher than other articles which are comparatively old. Thus, newer techniques or methods are gaining more importance in a significantly lesser duration of time.

**Table 2. 4.** List of highly cited publications in the water quality indexing domain.

Document	Total citations	Normalized citations
Pesce and Wunderlin (2000)	359	7.95
Cude (2001)	280	3.86
Vasanthavigar <i>et al.</i> (2010)	230	10.25
Sánchez <i>et al.</i> (2007)	229	8.93
Chang <i>et al.</i> (2001)	229	3.16
Wu and Sun (2016)	211	16.45
Tiwari and Mishra (1985)	201	4.19
Ocampo-Duque <i>et al.</i> (2006)	195	5.05
Kannel <i>et al.</i> (2007)	180	7.02
Liou <i>et al.</i> (2004)	171	5.92
Debels <i>et al.</i> (2005)	168	9.85
Şener <i>et al.</i> (2017b)	158	15.74
Ilayaraja and Ambica (2015)	157	14.59

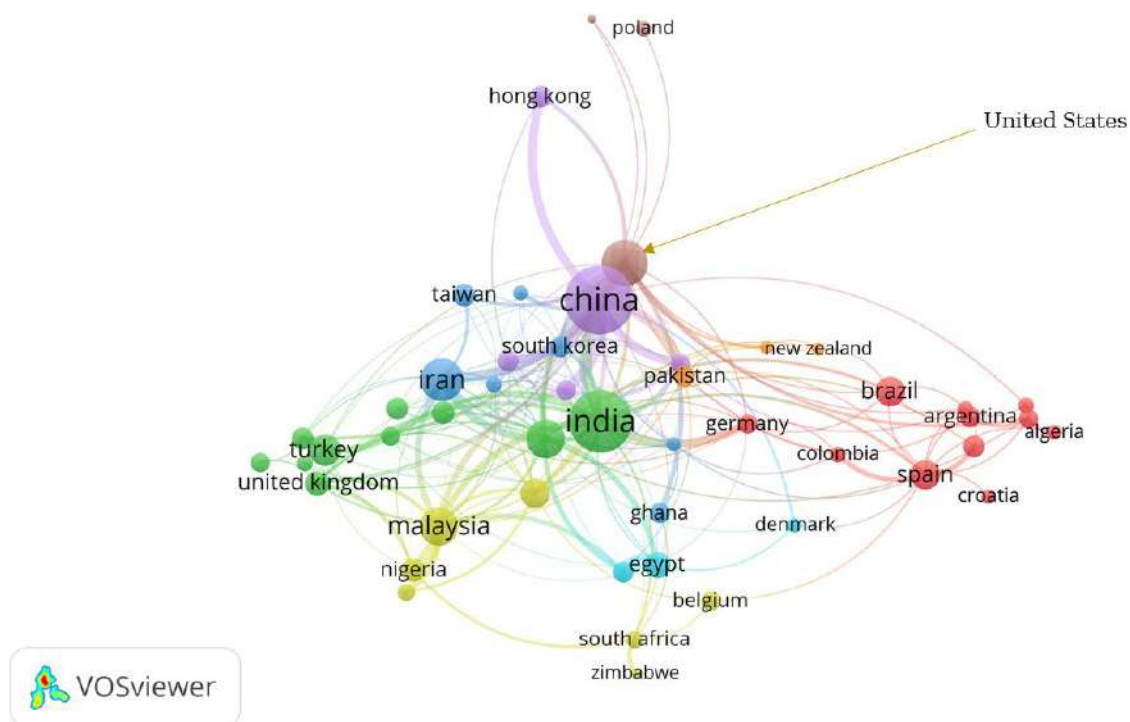
Jonnalagadda and Mhere (2001)	153	2.11
Lermontov <i>et al.</i> (2009)	143	5.50
Bordalo <i>et al.</i> (2001)	138	1.90
Li <i>et al.</i> (2016a)	136	10.6
Li <i>et al.</i> (2014)	135	7.79
Simões <i>et al.</i> (2008)	129	7.00
Said <i>et al.</i> (2004)	128	4.43
Gazzaz <i>et al.</i> (2012)	127	7.64
Sahu and Sikdar (2008)	121	6.57
Yidana <i>et al.</i> (2010)	120	5.35
Smith (1990)	118	3.83
Boyacioglu (2007)	115	4.48
Bordalo <i>et al.</i> (2006)	114	2.95
Yidana and Yidana (2010)	106	4.72
Zhang <i>et al.</i> (2018a)	104	16.53
Wu and Chen (2013)	103	8.40
Swamee and Tyagi (2000)	103	2.28

#### 2.6.6. Countries active in the research domain of water quality indexing

The co-occurrence of author keywords showed some insight into the countries active in the research involving water quality indexing. However, a detailed analysis was carried out by *VOSViewer* to comprehend the countries' contributions to global research. The minimum number of articles produced and the minimum citations were established at 5 and 50, respectively. 49 out of a total of 121 countries fitted the limit. Fig. 2. 10 and Table 2. 5 depict a clearer picture of the various countries actively participating in the research domain of water quality indexing.

As depicted in Fig. 2. 10, the connection lines are indicative of the mutual citations between different countries. Furthermore, the nodal sizes and connection lines proportion-ate to the total number of publications by individual countries. All countries active in the research were categorized into 8 clusters. It was observed that developing countries like India, China, Malaysia, and Iran have contributed significantly in the domain of water quality indexing, which shows their active participation in this research domain. A detailed quantitative assessment of the country-wise published works of literature is listed in Table 2. 5, including the total number of publications, total citations, average citations, normalized citations, and the average normalized citations.

The major bulk of publications in the domain of water quality indexing was seen to have come from two countries; India, followed by China. Both countries also have a considerably higher number of citations. South-Asian countries like India and China are rapidly undergoing changes in land-use-and-land-cover. The economic prosperity has led to uncontrolled urbanization in these countries, which has taken its toll on their water resources, both quantitatively and qualitatively (Karn & Harada 2001). India thrives on agriculture, and with the advent of newer technologies leading to increased productivity, the usage of chemical fertilizers and pesticides have rendered the pollution of surface waters even worse, owing to agricultural runoffs. Also, the discharge of untreated sewage and the dumping of solid wastes near the proximity of water bodies are other reasons for the severe degradation of water quality in India (Sinha & Nazimuddin 2008). Hence, there has been a major shift in focus towards research on water quality and its qualitative estimation through the indexing approach so that necessary steps could be undertaken to reduce the contamination levels significantly, thereby restoring the natural aquatic ecosystems. The average normalized citations indicate that countries like China (2.04), Australia (2.12), Taiwan (2.06), Hong Kong (3.07), Belgium (3.07), and Denmark (2.09) have created a considerable yearly impact on the research community, with their average normalized scores exceeding 2.00.



**Fig. 2. 10.** Mapping of active countries in the domain of water quality indexing.

**Table 2. 5.** Countries active in the domain of water quality indexing.

Country	No. of documents	Total citations	Average citation	Normalized citation	Average Normalized citation
India	576	4819	8	383.10	0.67
China	242	4194	17	492.51	2.04
Malaysia	145	1450	10	114.68	0.79
Iran	122	1540	13	146.96	1.20
United States	119	3055	26	176.69	1.48
Brazil	89	914	10	62.46	0.70
Canada	85	1905	22	115.52	1.36
Egypt	46	464	10	43.09	0.94
Nigeria	44	253	6	34.96	0.79
Japan	43	332	8	24.01	0.56
Iraq	41	234	6	29.11	0.71
Turkey	41	782	19	70.77	1.73
Spain	37	1174	32	59.33	1.60
Mexico	34	425	13	27.92	0.82
United Kingdom	33	543	16	38.27	1.16
Australia	29	726	25	61.44	2.12
Poland	29	174	6	12.24	0.42
Pakistan	27	224	8	27.97	1.04
Romania	26	181	7	19.77	0.76
Saudi Arabia	26	206	8	25.43	0.98
South Korea	26	467	18	26.90	1.03
Argentina	25	682	27	27.16	1.09
Thailand	24	278	12	21.17	0.88
Italy	23	652	28	32.07	1.39
South Africa	20	295	15	16.31	0.82
Bangladesh	18	219	12	24.95	1.39
Algeria	17	114	7	11.56	0.68
Serbia	17	145	9	12.58	0.74
Germany	16	303	19	20.33	1.27
Ghana	16	362	23	22.43	1.40
Sweden	16	137	9	20.79	1.30
Vietnam	16	75	5	12.94	0.81
Greece	15	346	23	28.61	1.91
Taiwan	15	808	54	30.83	2.06

France	14	357	26	20.89	1.49
Indonesia	14	180	13	15.74	1.12
Tunisia	13	128	10	13.34	1.03
Portugal	12	416	35	13.18	1.10
Colombia	11	293	27	12.54	1.14
Netherlands	11	153	14	9.58	0.87
Russian Fed- eration	11	50	5	2.08	0.19
Israel	10	204	20	8.60	0.86
Hong Kong	9	447	50	27.66	3.07
Croatia	8	249	31	9.57	1.20
New Zealand	8	183	23	8.70	1.09
Belgium	7	307	44	21.49	3.07
Zimbabwe	7	187	27	4.97	0.71
Nepal	6	241	40	11.59	1.93
Denmark	5	93	19	10.47	2.09

### 2.6.7. Qualitative Discussion related to water quality - Current research topics within “water quality indexing”

The water quality indexing approach has been classified into several categories of domains, owing to its widespread applicability; some of the domains being *Engineering*, *Environmental Sciences*, and others such as *Social Sciences*. Based on the respective domains, various approaches or tools have been adopted for developing WQIs. These include interview with resident public dependent on a particular study area (water body) and recording feedbacks on the problems associated with the water-use (Chesoh & Lim 2014; Bansah *et al.* 2018; Ngasala *et al.* 2019; Loc *et al.* 2020), author questionnaires (Kumar & Alappat 2009; Proulx *et al.* 2010; Wanda *et al.* 2014; Sutadian *et al.* 2017; Bansah *et al.* 2018), case studies (Ramesh *et al.* 2010; Akkoyunlu & Akiner 2012; Sutadian *et al.* 2017; Sabia *et al.* 2018; Tripathi & Singal 2019; Varol 2020b), computer simulations (Azevedo *et al.* 2000; Yamashiki *et al.* 2003; Asadi *et al.* 2007), modelling (Song & Kim 2009; Wu & Chen 2013; Feng *et al.* 2018; Ho *et al.* 2019; Kadam *et al.* 2019; Rissmann *et al.* 2019), and method development (Cude 2001; Said *et al.* 2004; Boyacioglu 2007; Thi Minh Hanh *et al.* 2011; Lobato *et al.* 2015; Yaseen *et al.* 2018). The current study divides the conventional studies into the following vital classifications.

- *Subjective approach*

A subjective approach employed for the development of a WQI implies inducting personal opinions of various individuals, based on which, the sub-indices are calculated. This approach

is based on the analytical hierarchical process (AHP) and is often termed as the G1 method (Kamrani *et al.* 2016; Gao *et al.* 2020). These methods usually determine the relative importance of a particular parameter, through investigations in the form of house-to-house surveys or author questionnaires to specific experts in the corresponding area of expertise. The relative importance to different parameters is then estimated based on the recorded responses, which finally leads to a WQI score.

▪ *Objective approach*

In more recent water quality studies, the focus has shifted to a more objective-oriented approach. These approaches make use of various mathematical tools for estimation of sub-indices, often including software applications and computer simulations. The first universally accepted objective approach was developed by CCME (2001), which was adopted by various researchers subsequently (Khan *et al.* 2005; Lumb *et al.* 2006; Hurley *et al.* 2012; Abtahi *et al.* 2015; Wagh *et al.* 2017). The method takes into account three factors; F1: the number of variables whose objectives are not met (scope), F2: the frequency by which the objectives are not met (frequency), F3: the amount by which the objectives are not met (amplitude), and combines them to estimating index scores. Another method involved employing fuzzy and artificial neural networks for estimating and predicting water quality (Nasiri *et al.* 2007; Lermontov *et al.* 2009; Gazzaz *et al.* 2012; Yaseen *et al.* 2018). In this approach, a fuzzy-based multiple attribute decision support system is utilized for modelling various parameters to compute the water quality index. Another tool used in the objective approach is multivariate statistics. Till date, this method has been regarded as one of the most effective tools in determining the water quality of a particular body. It employs several (primarily two) statistical techniques, known as the principal component analysis/factor analysis (PCA/FA) and cluster analysis (CA). CA categorizes monitoring locations into different statistically significant clusters, based on high intra-cluster similarity and low inter-cluster similarity. This makes computations of large and complex water quality datasets extremely convenient. Furthermore, PCA reduces the dimensionality of the water quality datasets, retaining significant information, thereby maintaining its consistency. The component scores (computed from the covariance of the dataset matrix) obtained from the PCA are used for estimating the sub-index values. Various researchers have been carrying out investigations on this technique due to its reliability and effectiveness (Yidana & Yidana 2010; Mostafaei 2014; Varol & Davraz 2015; Singh *et al.* 2016; Howladar *et al.* 2018; Kükreer & Mutlu 2019; Patil *et al.* 2020). Finally, the latest methodology, which is gaining significance in the research community in the domain of water quality indexing, is employing probability and thereby extending it to entropy, also known as entropy weights. It is a well-known fact that extensive monitoring studies constitute immense randomness, owing to the location of monitoring sites, climatic changes and

many other natural and anthropogenic contributions. Hence, information entropy concept has been introduced lately to the indexing of water quality by Wang *et al.* (2009). He investigated the stochastic observation error and uncertainty in water quality monitoring programs and determined index values integrating Monte-Carlo simulation, Shannon entropy, the Principle of Maximum Entropy (POME) and Tsallis entropy. The research was finally carried forward by Li *et al.* (2014), where the authors proposed a new methodology of employing entropy weights through the use of a dataset matrix. Further research was also carried out by subsequent scholars from around the world employing this concept (Li *et al.* 2016a; Islam *et al.* 2017; Singaraju *et al.* 2018; Adimalla *et al.* 2019; Gao *et al.* 2020; Hasan & Rai 2020; Islam *et al.* 2020a; Ji *et al.* 2020; Maskooni *et al.* 2020; Xiao *et al.* 2020).

- *WQI for specific end-use of water*

When it comes to water quality, the health of a particular water body is characterized as good or poor, depending on the end-use of the water from that body. The suitability of water varies differently depending on the varying end usages; for example, some water body rich in nutrients is rendered extremely suitable for agricultural use but is rendered unsuitable for drinking or industrial applications. Hence, the water quality indices are usually highly specific of the varying objectives they fulfil. Majority of the indices developed are based on the drinkability prospect, as growing demand of water supply is the prime focus for all countries. These indices make use of the standards for drinking water, prescribed by various organizations around the world, like the World Health Organization (WHO) (WHO/FAO/IAEA 1996; WHO 2006), Indian Standards (IS:10500 2012), European Standards (WHO 1970), and so on (Farzadkia *et al.* 2015; Sun *et al.* 2016; Misaghi *et al.* 2017; Beshiru *et al.* 2018; Mukate *et al.* 2019; Islam *et al.* 2020a; Scheili *et al.* 2020). Some recent studies on risk assessment involving heavy metals (Bereskie *et al.* 2017; Gao *et al.* 2019; Sharma *et al.* 2019; Xiao *et al.* 2019; Maity *et al.* 2020; Zhang *et al.* 2020), heavy metal indexing (Singh *et al.* 2017; Haque *et al.* 2020; Mokarram *et al.* 2020), irrigation WQI (Misaghi *et al.* 2017; Abbasnia *et al.* 2019; Singh *et al.* 2019; Muniz *et al.* 2020) are suggestive of the various wide range of applications of water quality indexing.

## 2.7. Sediment quality assessment

Surficial sediment contamination due to various anthropogenic activities has been a cause of serious concern in recent times. Primary contaminants possessing critical issues to the global sediment flux constitute various nutrients and heavy metals, accumulated due to heavy discharge of effluents (majorly industrial, agricultural and domestic wastewater) into the aquatic ecosystem (Syvitski *et al.* 2005; Ouyang *et al.* 2006; Zhang *et al.* 2007b; Azhar *et al.*

2015; Dhamodharan *et al.* 2019). These nutrients and heavy metals have typical characteristics of being persistent and thus, do not deteriorate or decompose with time, thereby making them toxic when concentrations exceed permissible limits. Furthermore, these compounds have less mobility in water columns. Therefore, their continuous accumulation in the natural water systems forces them to precipitate on the waterbody's sediment column. This makes the sediment columns of the water bodies potential sources of heavy metals, where they can be released back into the water columns or the aquatic flora and fauna via natural or anthropogenic ways, thus joining the food-chain system (Yin *et al.* 2011; Dhamodharan *et al.* 2019).

Additionally, lakes and wetlands play pivotal roles in providing nutrients to living organisms. Therefore, their bottom sediments are sensitive indicators to determine the pollution loadings as they act as both sources and sinks for the contaminants in an aquatic environment (Varol 2011; Yin *et al.* 2011). This necessitates their continuous monitoring and assessment.

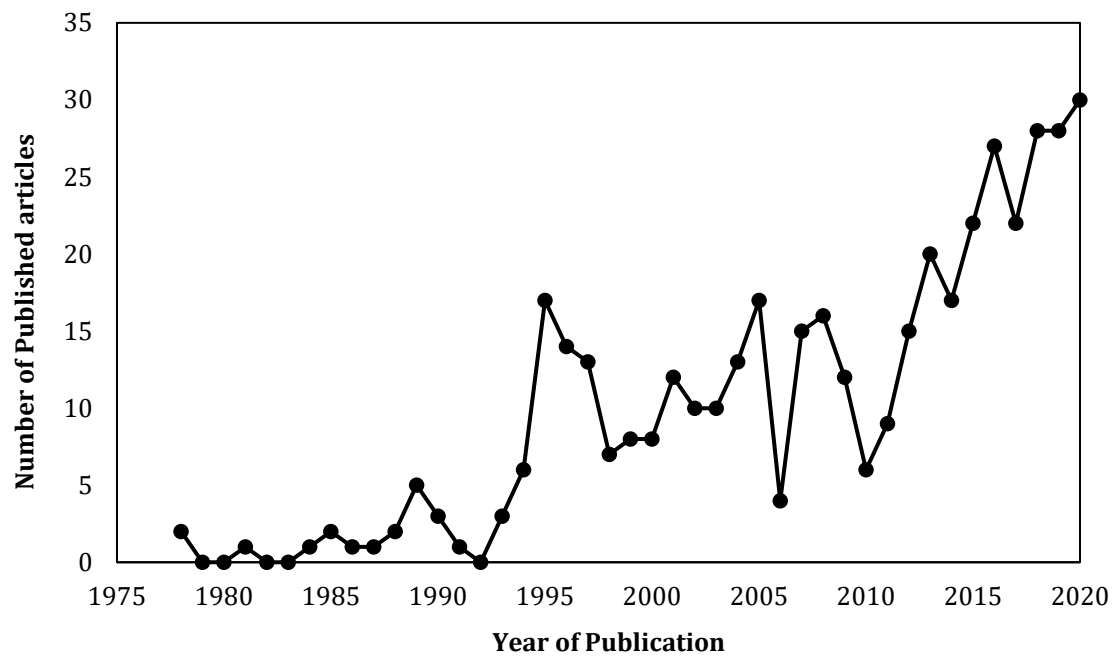
Various aspects covering the pollution of sediments have been studied in the recent past. A detailed literature review is inevitable to understand better the studies carried out on sediment contamination. Hence, following the procedure of scientific bibliometric analyses, as described in Section 2.6, the following keywords were entered in *Scopus*:

**TITLE-ABS-KEY** ("sediment contamination") **AND** **TITLE-ABS-KEY** ("heavy metals" **OR** "nutrients")

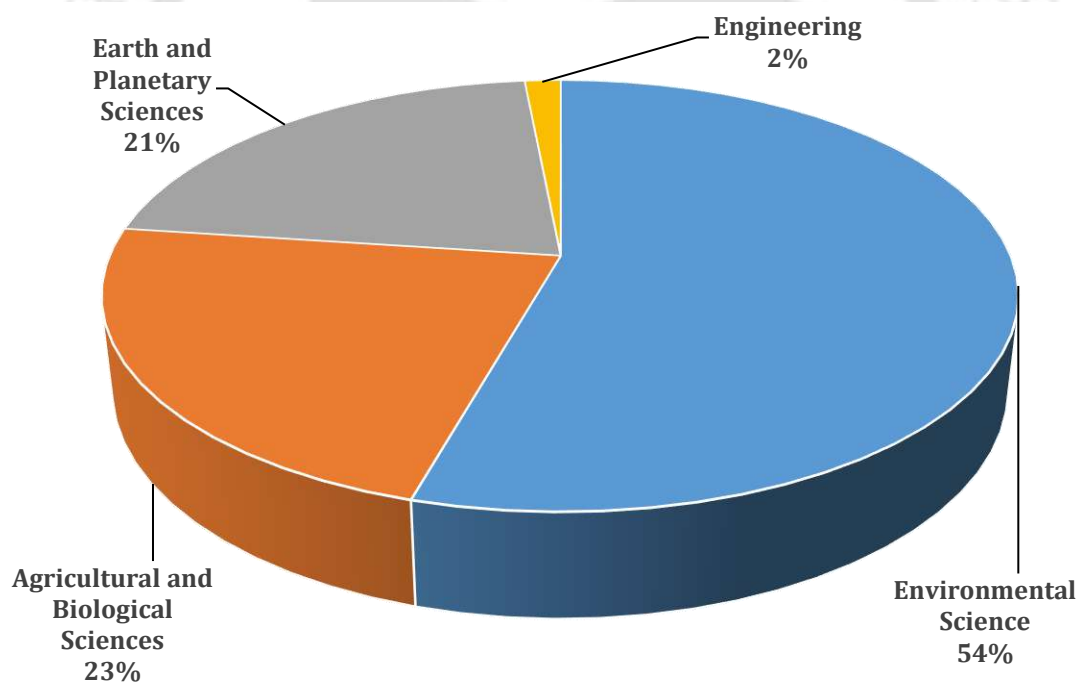
Since the primary contaminants contributing to the sediment contamination in a natural aquatic ecosystem are nutrients and heavy metals, we restricted our search to these two parameters. Similar procedures were adopted for extracting the final set of published literature (a total of 428 articles were finally extracted and subjected to analyses). Only in this case, the subject areas were limited to *Environmental Science, Agricultural and Biological Sciences, Earth and Planetary Sciences, and Engineering*. The results obtained are discussed in the following sub-sections.

### 2.7.1. An overview of the literature sample

The 428 articles considered for the final analyses were arranged to their year of publication, as shown in Fig. 2. 11a. It was observed that the majority of the works have been carried out in the 2010s, i.e., from 2010 onwards. This indicates the growing popularity among researchers worldwide in the domain of sediment contamination. This domain is also relatively fresher, as much emphasis had not been given to this particular domain in the past. Hence, a broad scope of research in this domain is believed to impact sediment contamination dynamics significantly.



(a)



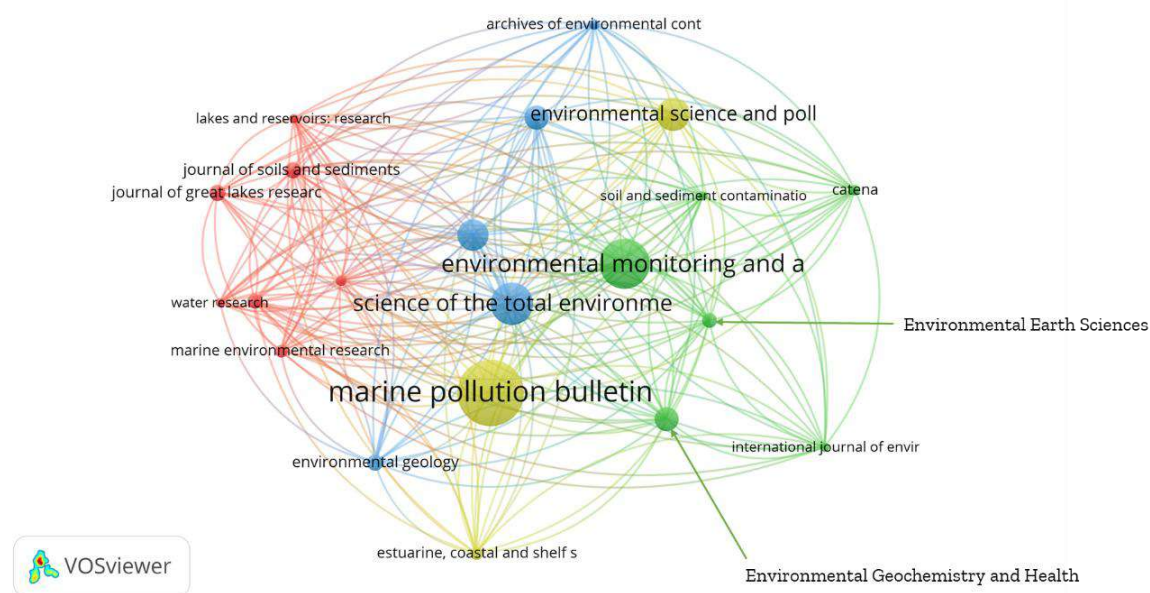
(b)

**Fig. 2. 11.** An overview of literature sample related to sediment contamination; (a) Yearly publications, and (b) Classification of documents based on the respective subject areas (Data extracted from the Scopus database).

Furthermore, the articles have been divided as per the subject areas under the scope of this thesis. It was observed that more than half of the articles fell under the *Environmental Science* sphere, followed by *Agricultural and Biological Sciences*, *Earth and Planetary Sciences* (Fig. 2. 11b). This is suggestive of the dominance of *Environmental Science* in the domain of sediment contamination domain.

### 2.7.2. Journal Sources

Details of the journal sources actively involved in publishing articles related to sediment contamination are shown in Fig. 2. 12 and Table 2. 6. Journals having published at least five articles and having a minimum of 20 citations have been considered for the analyses. This resulted in 21 out of a cumulative of 148 journals. It was observed that *Marine Pollution Bulletin*, *Environmental Monitoring and Assessment*, *Science of the Total Environment*, *Environmental Science and Pollution Research*, and *Chemosphere* are the most productive, with at least 15 publications in this domain of research. However, when it comes to the journals having the maximum impact, *Environmental Monitoring and Assessment* (13.68), *Environmental Earth Sciences* (13.61), *Environmental Geochemistry and Health* (10.46), *Ecotoxicology and Environmental Safety* (6.57), and *Environmental Geology* (5.67) displayed the highest average normalized citation scores. Thus, it may be stated that the journal of *Environmental Monitoring and Assessment* is both highly productive and possesses the highest impact, thus having a significant contribution to the research in the domain of sediment contamination.



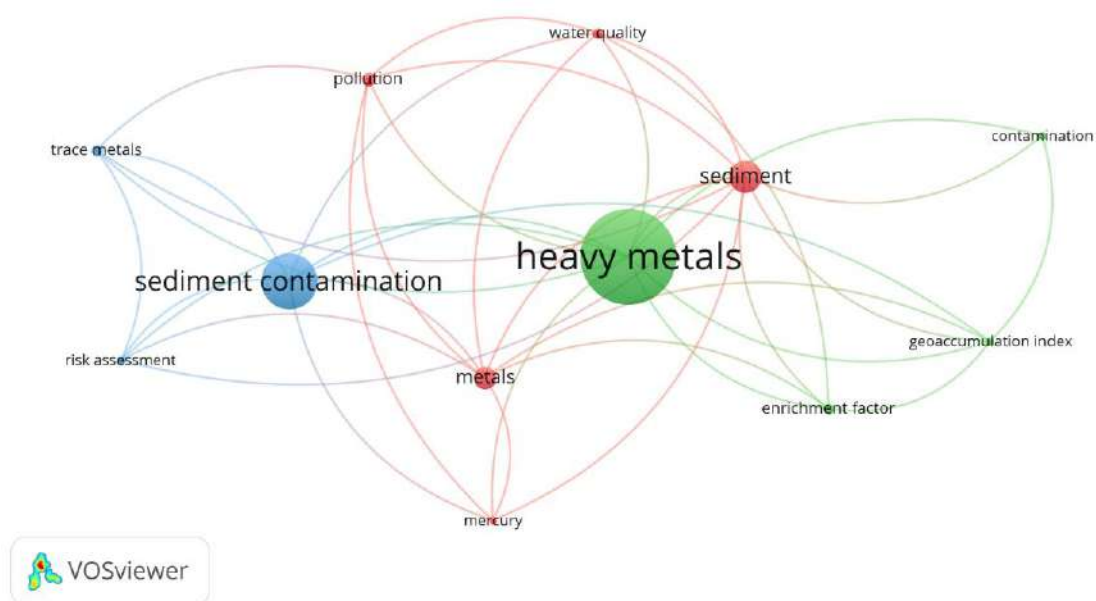
**Fig. 2. 12.** Journal sources in the domain of sediment contamination.

**Table 2. 6.** Journals actively publishing articles related to sediment contamination.

Source	Docu- ments	Cita- tions	Avg. Ci- tations	Norm. Cita- tions	Avg. Norm. Cita- tions
Marine Pollution Bulletin	36	1804	50	44.15	1.23
Environmental Monitoring and Assess- ment	27	802	30	369.42	13.68
Science of the Total Environment	23	916	40	34.36	1.49
Environmental Science and Pollution Research	18	302	17	22.74	1.26
Chemosphere	17	1066	63	32.03	1.88
Ecotoxicology and Environmental Safety	13	402	31	85.43	6.57
Environmental Geochemistry and Health	13	199	15	135.95	10.46
Environmental Geology	9	267	30	51.01	5.67
Journal of Great Lakes Research	9	287	32	6.52	0.72
Journal of Soils and Sediments	9	126	14	5.42	0.60
Environmental Earth Sciences	8	132	17	108.90	13.61
Water, Air, and Soil Pollution	8	235	29	7.37	0.92
Estuarine, Coastal and Shelf Science	7	362	52	9.12	1.30
Marine Environmental Research	7	309	44	10.41	1.49
Archives of Environmental Contamina- tion and Toxicology	6	87	15	4.37	0.73
Catena	6	113	19	6.45	1.08
Environmental Pollution	6	298	50	6.48	1.08
International Journal of Environmental Science and Technology	5	54	11	2.67	0.53
Lakes and Reservoirs: Research and Management	5	183	37	4.20	0.84
Soil and Sediment Contamination	5	84	17	3.13	0.63
Water Research	5	205	41	6.05	1.21

### 2.7.3. Co-occurrence of keywords

For the keyword analyses, a criterion minimum of 10 occurrences was set. This resulted in 14 out of a total of 1099 registered keywords. However, specific keywords were repetitive, which were omitted from the list. The final list contained 12 keywords, the details of which may be seen through Fig. 2. 13 and Table 2. 7.



**Fig. 2. 13.** Analysis of author keywords.

**Table 2. 7.** Details of occurrences of author keywords.

Keyword	Occurrences
heavy metals	129
sediment contamination	75
sediment	44
metals	31
pollution	19
enrichment factor	15
trace metals	15
water quality	15
contamination	12
geoaccumulation index	12
risk assessment	11
mercury	10

It was observed that both Table 2. 7 and Fig. 2. 13 displayed consistent results, with terms like “heavy metals”, “sediment contamination”, and “sediment” being the most frequently used, as is evident from the nodal size of the map. Based on the different clusters of author keywords, certain vital conclusions can be made, as follows:

- *Sediment contamination is associated with water quality:* This is evident from the fact that the term “water quality” lies in the same cluster as “mercury”, “metals”, “pollution”, and

“sediment”, Also, it shares a reasonable intra-cluster association with “heavy metals” and “sediment contamination”.

- *Works on sediment indices*: Indices are the easiest and the most convenient method of analysing any dataset. Like water quality indices, certain sediment factors and indices help assess an aquatic ecosystem's sediment quality in continuous monitoring programs. These include the Enrichment factor and the Geo-accumulation index. The use of these keywords suggests comprehensive monitoring programs being carried out to understanding sediment contamination lately.
- *Assessing the risks associated with the sediment column*: The third kind of study involves assessing different risks related to sediment contamination. These risks are primarily of two types; (a) human health risks and (b) ecological risks. The human health risks associated with the sediment column are primarily due to their exposure to different conditions and levels. In contrast, ecological risks are related to the impact of one or more elements on the ecology of a particular study area.
- *More studies on heavy metals compared to nutrients*: It was observed that the quantum of studies on sediment contamination relating to heavy metals is much higher as compared to nutrient contamination. This may be attributed to more significant impacts of heavy metals on the aquatic ecology in contrast to nutrient contamination.

#### 2.7.4. Co-authorship analysis

A minimum criterion was set for conducting the co-authorship analyses; authors should have at least three documents and 30 citations under their name. 22 authors out of a total of 1700 met the threshold limit, the details of whom are listed in Table 2. 8. A detailed classification of the researchers working on sediment contamination worldwide is shown in Fig. 2. 14. The 22 authors have been categorized into six independent clusters, based on their relative closeness in research, for example, cluster 2 containing *Capello M.*, *Cutroneo L.*, and *Vagge G.* Table 2. 8 shows that *Karbassi A.R.* is the most productive researcher, followed by *Zhang L.*, *Delvalls T.A.*, and *Wildi W.* All these researchers are among the most productive with more than 3 articles to their name.

However, when it comes to the most influential authors, *Liu L.*, *Zhang L.*, and *Liu J.* are among the top influential researchers with average normalized citation scores of more than 2.00. Thus, it may be concluded that *Zhang L.* is among the most productive and influential researchers in the domain of sediment contamination. All the authors were also found to be highly collaborative, as is visualized from the density of the nodal connectors (Fig. 2. 14).

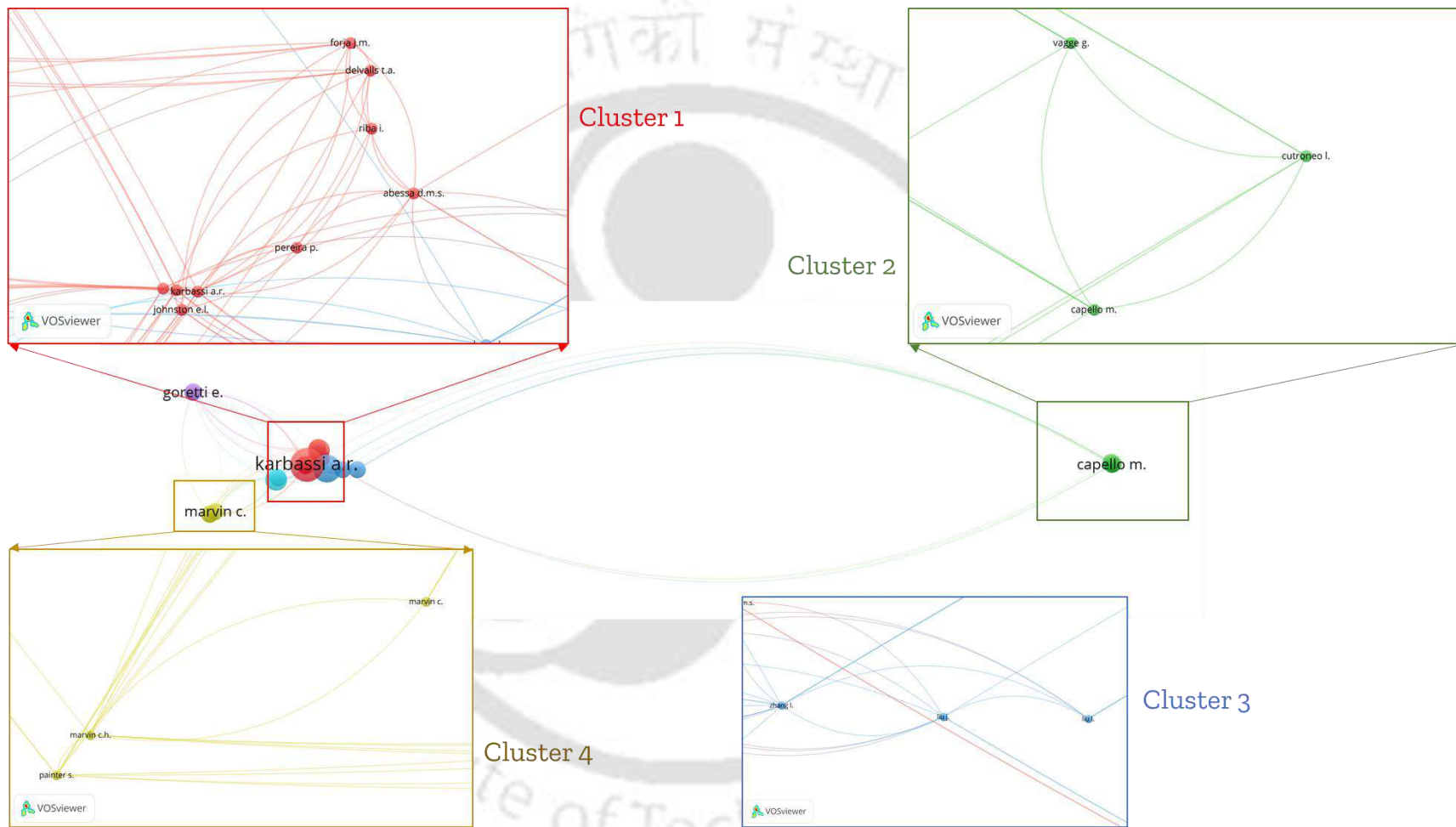


Fig. 2. 14. Co-authorship mapping in the domain of sediment contamination.

**Table 2. 8.** Co-authorship details in the sediment contamination research.

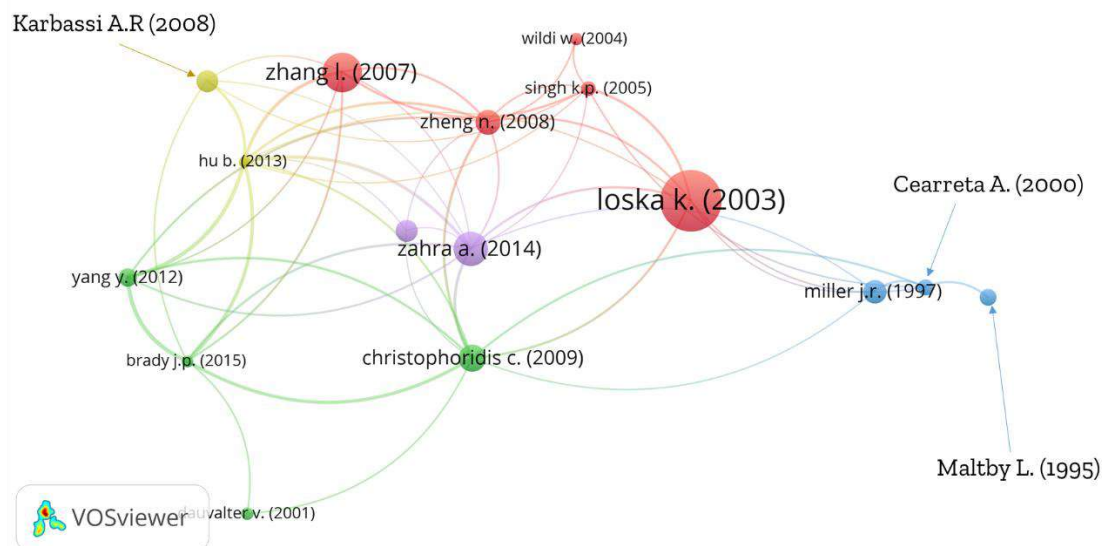
Author	Documents	Citations	Avg. Citations	Norm. Citations	Avg. Norm. Citations
Karbassi A.R.	6	308	51	9.77	1.63
Zhang L.	5	540	108	16.04	3.21
Delvalls T.A.	4	226	57	5.39	1.35
Wildi W.	4	273	68	6.40	1.60
Abessa D.M.S.	3	140	47	3.85	1.28
Capello M.	3	30	10	2.67	0.89
Cutroneo L.	3	30	10	2.67	0.89
Forja J.M.	3	154	51	3.95	1.32
Goretti E.	3	70	23	4.27	1.42
Ismail A.	3	71	24	2.85	0.95
Johnston E.L.	3	55	18	2.17	0.72
Liu J.	3	175	58	6.76	2.25
Liu L.	3	171	57	10.80	3.60
Loizeau J.-L.	3	215	72	4.91	1.64
Martin C.W.	3	146	49	4.01	1.34
Marvin C.	3	84	28	1.98	0.66
Marvin C.H.	3	124	41	1.98	0.66
Painter S.	3	160	53	2.99	1.00
Pereira P.	3	32	11	2.12	0.71
Riba I.	3	145	48	3.06	1.02
Selvaggi R.	3	70	23	4.27	1.42
Vagge G.	3	30	10	2.67	0.89

### 2.7.5. Articles' citations

The most influential articles in the sediment contamination domain were analysed in *VOSViewer*; the mapping result is shown in Fig. 2. 15. Only the articles with a minimum of 100 citations were considered for the analyses, resulting in 23 out of 428 filtered articles.

The most cited article was Schnoor *et al.* (1995), who demonstrated the use of vegetation in improving the quality of soils and sediments from hazardous wastes. The authors presented the various aspects of phytoremediation, including its pros and cons. It is also the most influential article, with an average normalized citation score of 9.68. Loska & Wiechuła (2003) and Singh *et al.* (2005c) provided insights into pollution source identification using multivariate statistical techniques. Other research articles primarily focused on the factors and indices for heavy metal contamination in the sediment columns of different water bodies (Zhang *et*

*al.* 2007a; Christophoridis *et al.* 2009; Zahra *et al.* 2014a). Also, it was observed that relatively newer articles have a higher average normalized impact score, thus indicating the significance of their research in a lesser duration (Table 2. 9).



**Fig. 2. 15.** Science mapping of the most influential publications in the domain of sediment contamination.

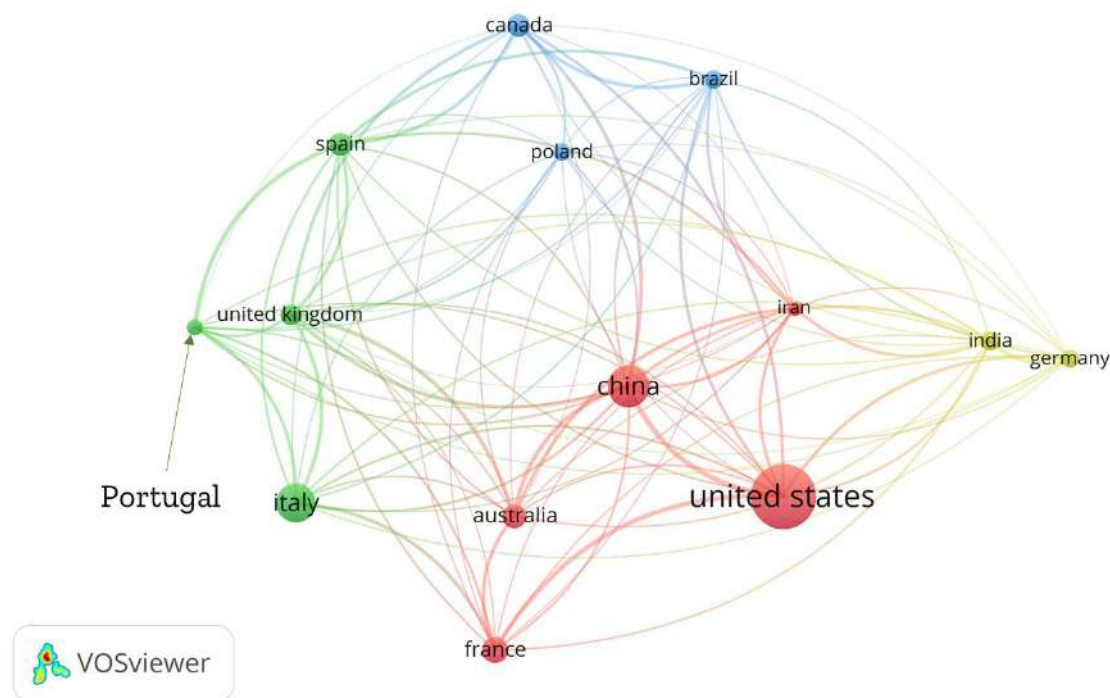
**Table 2. 9.** List of highly cited publications in the domain of sediment contamination.

Document	Citations	Norm. Citations
Schnoor <i>et al.</i> (1995)	746	9.68
Loska and Wiechuła (2003)	523	6.60
Zhang <i>et al.</i> (2007a)	337	6.71
Zahra <i>et al.</i> (2014b)	292	7.33
Long and Chapman (1985)	283	1.74
Christophoridis <i>et al.</i> (2009)	231	5.68
Zheng <i>et al.</i> (2008)	213	3.89
Miller (1997)	198	5.22
Dauer <i>et al.</i> (2000a)	189	3.02
Karbassi <i>et al.</i> (2008)	189	3.45
Fernandes <i>et al.</i> (2007)	161	3.21
Yang <i>et al.</i> (2012)	158	5.60
Huang <i>et al.</i> (2017)	146	8.80
Maltby <i>et al.</i> (1995)	145	1.88
Cearreta <i>et al.</i> (2000a)	139	2.22
Singh <i>et al.</i> (2005b)	126	4.21
Borg and Jonsson (1996)	106	2.73
Wildi <i>et al.</i> (2004)	106	2.29

Dauvalter and Rognerud (2001)	105	2.69
Warren (1981)	104	1.00
Brady <i>et al.</i> (2015)	103	5.37
Hu <i>et al.</i> (2013)	101	3.85
Romano <i>et al.</i> (2004)	101	2.18

### 2.7.6. Countries active in sediment contamination research domain

A detailed analysis of the countries actively participating in the research on sediment contamination has been carried out in *VOSviewer*. Countries that have produced at least 10 articles and possessing 30 citations have been considered for the analysis. 14 countries out of a total of 81 countries met the threshold limit. Fig. 2. 16 provides the scientific mapping of the countries involved, while Table 2. 10 provides the details, including all the statistical and research computations. Interestingly, all 14 countries have been classified into four independent clusters based on the relative closeness of their respective research domain (Fig. 2. 16).



**Fig. 2. 16.** Countries active in the domain of sediment contamination.

The major contributing country in this particular domain has been the *United States*, followed by *China*, *Italy*, *France*, *Australia*, *Spain*, and *Canada*. All these countries have at least 20 published works under their name, thereby making them the most productive. However, when it comes to the most impactful countries, *China*, *India*, *United States*, *Spain*, and *Iran* have the highest average normalized scores (more than 1.00).

**Table 2. 10.** List of countries proactive in research on sediment contamination.

Country	Documents	Citations	Avg. Citations	Norm. Citations	Avg. Norm. Citations
United States	59	2935	50	68.83	1.17
China	38	1773	47	65.08	1.71
Italy	36	614	17	35.09	0.97
France	24	563	23	18.87	0.79
Australia	22	556	25	16.27	0.74
Spain	21	830	40	23.03	1.10
Canada	21	720	34	12.94	0.62
United Kingdom	19	613	32	14.20	0.75
India	18	444	25	23.54	1.31
Germany	17	420	25	14.11	0.83
Brazil	17	250	15	13.40	0.79
Poland	16	727	45	15.59	0.97
Portugal	15	436	29	13.82	0.92
Iran	14	414	30	14.76	1.05

### 2.7.7. Qualitative Discussion related to sediment contamination – Current research topics

The sediment contamination studies have come a long way from the studies that used to be carried out during the initial days. A pattern-wise distribution of the related studies has been presented here through the following points.

#### a. Assessing the spatial distribution of contamination levels in bottom sediments

From the late-1970s till the mid-1990s, studies suggested a more comprehensive approach in determining the spatial distribution of various contaminants, especially heavy metals in the bottom sediments of both freshwater and marine environment (Griggs & Johnson 1978; Hiraizumi *et al.* 1978; Fallon & Horvath 1985; Schults *et al.* 1987; Fuge *et al.* 1989; Chan-Won *et al.* 1990; Fuller *et al.* 1990; Lewandowski & Szczepanska 1993; Borovec 1994; Dauvalter 1994; Joksas 1994). Various factors such as grain size distribution of the sediment column hydrological aspects were associated with the pattern of heavy metal distribution (Hiraizumi *et al.* 1978; Hoover 1988; Roper *et al.* 1988; Marron 1989). The pattern then shifted from simply finding out the spatial distribution to source identification through the use of various statistical and data-reduction techniques (DelValls *et al.* 1998; Galvez-Cloutier & Dubé 1998b), understanding the toxicity assay (Gupta & Karupiah 1996; Hartwell *et al.* 1998), and determining their elemental composition (Galvez-Cloutier & Dubé 1998a).

b. *Associations between macrobenthic communities*

As the years progressed and with the arrival of the 21<sup>st</sup> century, the focus shifted to correlating the various aspects of sediment contamination, such as water pollution, watershed management, anthropogenic activities monitoring, etc. (Camusso *et al.* 2000; Cearreta *et al.* 2000b; Dauer *et al.* 2000b; Lau 2000; Lau & Chu 2000; Martin 2000). Furthermore, attempts were made to establish a significant correlation between different ecological components, such as plant-sediment (Dauer *et al.* 2000b; St-Cyr & Campbell 2000; Marín-Guirao *et al.* 2005; Carter *et al.* 2006; Apitz *et al.* 2007; Ozdilek *et al.* 2007), fish-sediment (Isidori *et al.* 2004; Diz 2005; Hallare *et al.* 2005; Mayer *et al.* 2008; Cooper *et al.* 2009) and water-sediment (Dauer *et al.* 2000b; Dauvin 2008; Poté *et al.* 2008; Zheng *et al.* 2008; Teodorović 2009).

c. *Indexing approach to assessing sediment quality*

With increasing contamination levels of the sediment columns of the aquatic ecosystems, continuous monitoring programs became inevitable to understand the spatio-temporal variability. This resulted in massive datasets, which eventually became difficult to infer. Hence, researchers worldwide postulated different indices, which made the readability easy and saved considerable time. Some of the significant indices include the Geoaccumulation index ( $I_{geo}$ ), contamination factor ( $CF$ ), pollution load index ( $PLI$ ), etc. Various studies have been carried out in the recent past incorporating these indices in determining the pollution levels of the sediment columns of different aquatic ecosystems (Calace *et al.* 2008; Christophoridis *et al.* 2009; Sheela *et al.* 2012; Ferati *et al.* 2015; El Azhari *et al.* 2016; Alves *et al.* 2018; Dietrich *et al.* 2018; Reis *et al.* 2019; Siddiqui & Pandey 2019; Ustaoglu & Tepe 2019; Arienzo *et al.* 2020; Dharmendra *et al.* 2020; Samanta *et al.* 2020; Yeh *et al.* 2020).

d. *Speciation and risk assessment studies*

Various aspects covering the pollution of sediments have been studied in the past. These include spatial distribution of the contaminants, health risk assessment and pollution source identification through various statistical tools such as factor analysis, cluster analysis, correlation analysis and geostatistical analysis employing GIS (Maas *et al.* 2010; Sun *et al.* 2010; Mohamed *et al.* 2014; Luo *et al.* 2015; Qing *et al.* 2015; Liu *et al.* 2016; Chen & Lu 2018). It has been observed that an unpolluted environment makes the heavy metals get attached to the sediment columns in the form of silicates and minerals. However, anthropogenic conditions force these heavy metals to occur in the form of liable fractions such as oxides, carbonates, sulphides, hydroxides, etc. (Pandey *et al.* 2015). Thus, various sequential extraction procedures (SEP) for surficial sediment have been developed and accepted widely for determining the speciation of heavy metals and the form in which they are present. Various forms in which

the heavy metals may be present in the environmental conditions include exchangeable fraction (F1), bound to carbonate fraction (F2), bound to Fe/Mn Oxides (F3), bound to organic matter/ sulphate (F4) and residual fraction (F5) (Tessier *et al.* 1979; Sutherland 2010). However, various complications and human errors persist while performing these experiments, as a result of which total metal concentrations usually assess the pollution status of a particular water body (Duodu *et al.* 2016; Villanueva & Ibarra 2016; Vu *et al.* 2017). Studies pertaining to various risks associated with sediment contamination have also been conducted. This includes both human health risks due to increasing exposure levels and potential ecological risks, which provides an idea regarding the cumulative effects of various heavy metals on the overall ecology of the surrounding ecosystem (Li *et al.* 2017; Soliman *et al.* 2018; Hamza *et al.* 2019; Huang *et al.* 2019; Rasool & Xiao 2019; Tokatli 2019; Bāk *et al.* 2020; Islam *et al.* 2020c; Khaled *et al.* 2020; Varol 2020a; Yeh *et al.* 2020; Zhu *et al.* 2020).

## 2.8. Anthropogenic influences on aquatic ecology and their modelling

All the major pollutants discussed above relate to the alteration in the aquatic ecology due to primarily two reasons; (a) excessive heavy metal concentrations and (b) excessive nutrients. Heavy metals result in bioaccumulation and biomagnification processes as they involve in the food chain. On the contrary, the eutrophication of wetlands is a direct result of the discharge of excessive nutrients. It is important to note that though pollution has been a significant factor in degrading the quality of aquatic ecosystems, the role of lack of management and global awareness regarding the protection and conservation of water bodies worldwide cannot be abandoned. Hence, there lies an inherent sense of responsibility to restore the aquatic ecosystems to their natural state. Numerous techniques/treatment options are available for varying conditions, such as climatic, socio-economic factors, and so on. However, understanding any independent aquatic ecosystem dynamics is of prime importance before ascertaining a treatment alternative. This necessitates using a reliable model, which can provide information regarding the physical processes and dynamic occurrences in the water bodies.

Models can be termed a representation of a particular individual, idea or condition (Frigg & Hartmann 2006). The level of complexity can widely vary during the modelling process. It can be a simple physical representation such as a map or a highly complicated series of mathematical expressions such as a detailed description of the ecosystem's nitrogen cycle. Broadly, the modelling process involves a series of steps taken to transform the theoretical concepts of conceptual diagrams into a quantitative paradigm.

Ecological modelling refers to the formation of dynamic and complex relationships of the organisms found in the ecosystem and the surrounding. It attempts to unravel the effects of certain relationships in the ecosystem that are not so apparent at first glance. In other words, it helps the modeller to identify the concealed implications (Breckling *et al.* 2011). This provides the modeller new insights into the unobtainable ecosystem with direct observation, evaluation and interpretation. An ecological model usually contains five components (Jørgensen & Bendoricchio 2001):

- *Forcing functions*

Forcing functions can be described as the inputs to the model that may change its behaviour upon feeding to the model. These are also called “*controlled functions*” due to their susceptibility to human interference and hence, plausible human control. For example, the forcing function for a eutrophication model is the discharge of nutrients into the ecosystem.

- *State variables*

State variables refer to those components of the model whose behaviour are being modelled. It is best understood with an example of a eutrophication model. Here, the state variables are the concentrations of various nutrients and phytoplankton. As the forcing functions of the model change, the concentration of nutrients and the phytoplankton population also change.

- *Mathematical equations*

Mathematical equations describe various biological, chemical and physical processes that link the forcing functions to the state variables. There are many equations suitable for particular functions available in the literature (Jackson *et al.* 2000). Some mathematical can also be derived from the first principles (i.e., physical laws).

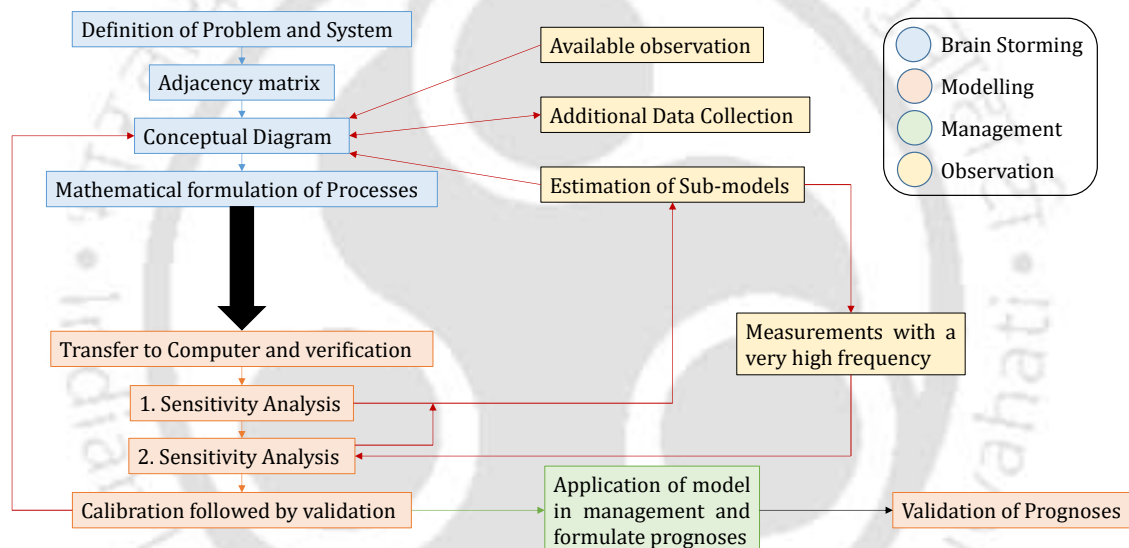
- *Parameters*

Parameters are the coefficients of the mathematical equations used in the model. These may be considered constant or a function of time and space. The application of parameters is the weakest link in the model (Jørgensen & Bendoricchio 2001). They are estimated using the data from the literature or by an iterative method so that the calculated value is close enough to the observed value. Even when the parameter value is provided in the literature, they are usually provided within a range. Hence, there is a need to adjust the value of the same parameter for different models. This process of adjusting the parameter value is called calibration. Calibration can be done systematically or by trial-and-error method. Usually, the least square method and the maximum likelihood estimation are used to determine the estimated parameter value's degree of fitness. Maximum likelihood estimations are suitable for nonlinear parameters (Jackson *et al.* 2000).

- *Universal constants*

Universal constants such as ideal gas constant and atomic weights are also sometimes used in the model.

A generalised flowchart portraying the ecological modelling process was given by Jørgensen and Bendoricchio (2001) (Fig. 2. 17). The first step involved in the modelling process is determining the purpose of the model. This involves the description of the problem and the system for which the model is being developed. This step is followed by developing the adjacency matrix, which describes the interdependence of the various state variables to be used in the model. Subsequently, the conceptual diagram is designed. A Conceptual diagram is a compact, visual statement of the research problem (Jackson *et al.* 2000). It describes the relationship between the various state variables of the model using boxes and arrows.



**Fig. 2. 17.** Ecological modelling process (Jørgensen & Bendoricchio 2001).

Ideally, the dataset needed for the development of the model is determined after the development of the conceptual diagram. However, in practice, most models are developed after collecting data as a compromise between the model scope and the available data. Sometimes additional data is collected at later stages of the modelling process to strengthen the model. Once the data collection and conceptual diagram development are concluded, the modeller proceeds towards the mathematical formulation of the processes involved in the model.

Subsequently, the model is programmed into a computer, and the internal logic of the model is verified. Following this, the sensitivity analysis, calibration and validation of the models are carried out. Sensitivity analysis of the model refers to determining which parameters, forcing functions, or sub-models are sensitive and to what degree to the state variables

(Jørgensen & Bendoricchio 2001). Validation refers to the test of the model's behaviour when exposed to an independent set of data.

The history of ecological modelling dates back to the 1920s when the Streeter-Phelps model was developed, and since then, ecological modelling has come a long way in its journey (Streeter & Phelps 1925). During the 1960s and 1970s, the confluence of improved computing technologies, scientific approaches, application needs and available funding boosted its growth tremendously (Fath *et al.* 2011). The eutrophication models were mainly developed during the 1970s, as water quality became a critical environmental issue. Different models with different levels of complexity were developed, which were further improved upon application in different case studies (Fath *et al.* 2011). Since the 1980s, enough eutrophication models have been developed to model any lake with an available data set (Jørgensen 2010). However, the quest for an improved ecological model is far from over, and many new eutrophication models have been developed over time.

To better understand the works carried out on eutrophication-based ecological modelling, the following keywords were entered in *Scopus*:

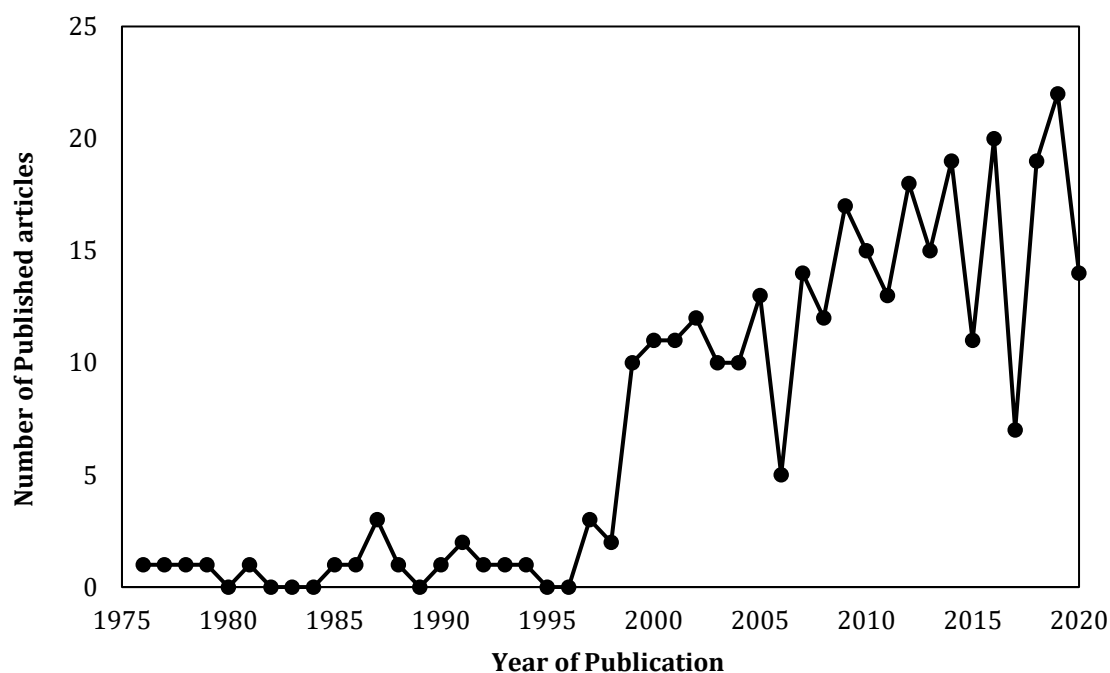
**TITLE-ABS-KEY (“ecological model”) OR TITLE-ABS-KEY (“ecological modelling”) AND TITLE-ABS-KEY (eutrophication).**

An aggregate of 399 published documents was initially extracted from the search, which was then considered for further analyses, as already discussed in the previous sections. A final set of 320 articles lying within our research scope was considered for the subsequent review process. The following critical observations were noted, discussed in the subsequent sub-sections.

### **2.8.1. An overview of the literature sample**

The 320 published articles have spread across a broad time scale, ranging from 1976 to 2020 (Fig. 2. 18). However, it was observed that 90% of the articles have been published at the onset of the 21st century (i.e., from the year 2000, 288/320 articles have been published).

Furthermore, the trend of research in the current domain has seen a steady increase as the years progressed, the year 2019 having the highest number of published articles. This indicates the relevance of the research in the domain of eutrophic-based models, and with this trend, it is expected that more articles will come into circulation due to the development of more sophisticated computational methodologies. Also, the growing problem of eutrophication in surface water bodies and a wide range of research scope has triggered researchers across the globe to research this domain.

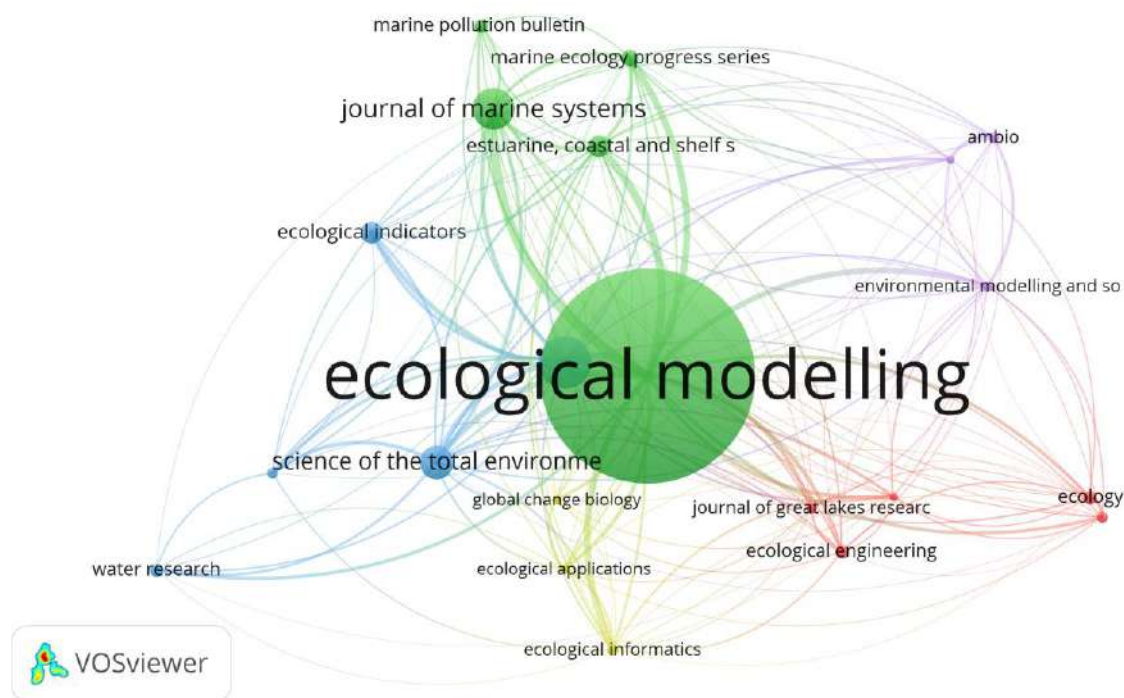


**Fig. 2.18.** An overview of the year-wise distribution of published articles in the domain of eutrophication-based ecological modelling (Data extracted from the Scopus database).

### 2.8.2. Science Mapping of Journal sources

All 320 articles published were sourced from 116 journals. However, only 21 journals were having at least 3 articles and 30 citations. The networking of the journal sources meeting the threshold criteria was acquired through mapping in *VOSViewer*, wherein the nodal and font sizes represented the number of published works from a specific journal (Fig. 2.19). Each node is divided into different clusters and is inter-connected through connecting lines, indicating the relative closeness among the journals with respect to mutual citations. The results showed that *Ecological Modelling* displayed the highest productivity, providing the maximum number of published works in the eutrophic-based ecological modelling research domain. A more detailed analysis of the journal sources has been reported in Table 2.11.

Only 4 journals have more than 10 published works; namely *Ecological Modelling*, *Hydrobiologia*, *Journal of Marine Systems*, and *Science of the Total Environment*. These journals were also found to have a large number of citations, thus indicating their high productivity and significance in the research domain. The total number of articles, citations and normalized citations were sourced from the records. It was observed that *Ecology Letters*, *Global Change Biology*, and *Marine Pollution Bulletin* held a significant impact in the research domain, having average normalized citation scores of more than 1.50. However, these journals do not have a considerable number of published articles under them.



**Fig. 2. 19.** Mapping of the mainstream journals in the domain of ecological modelling.

**Table 2. 11.** List of mainstream journal publishing articles on ecological modelling.

Source	No. of documents	Total Citations	Avg. Citations	Norm. Citations	Avg. Norm. Citations
Ecological Modelling	77	3476	45	70.86	0.92
Hydrobiologia	19	497	26	15.99	0.84
Journal of Marine Systems	15	488	33	10.4	0.69
Science of the Total Environ-					
ment	12	232	19	17.54	1.46
Ecological Indicators	8	165	21	11.84	1.48
Estuarine, Coastal and Shelf					
Science	8	286	36	5.21	0.65
Marine Ecology Progress Series	6	441	74	5.41	0.90
Ecological Engineering	5	176	35	4.85	0.97
Ecology	5	339	68	7.06	1.41
Marine Pollution Bulletin	5	165	33	8.52	1.70
Water Research	5	249	50	6.56	1.31
Ambio	4	42	11	1.45	0.36
Ecological Informatics	4	49	12	2.95	0.74
Ecology Letters	4	466	117	9.3	2.33

Environmental Modelling and Software	4	112	28	5.23	1.31
Journal of Great Lakes Research	4	54	14	4.55	1.14
Journal of Hydrology	4	218	55	5.31	1.33
Ecological Applications	3	107	36	2.97	0.99
Global Change Biology	3	619	206	6.76	2.25
Journal of Applied Ecology	3	71	24	2.78	0.93
Journal of Environmental Management	3	30	10	4.12	1.37

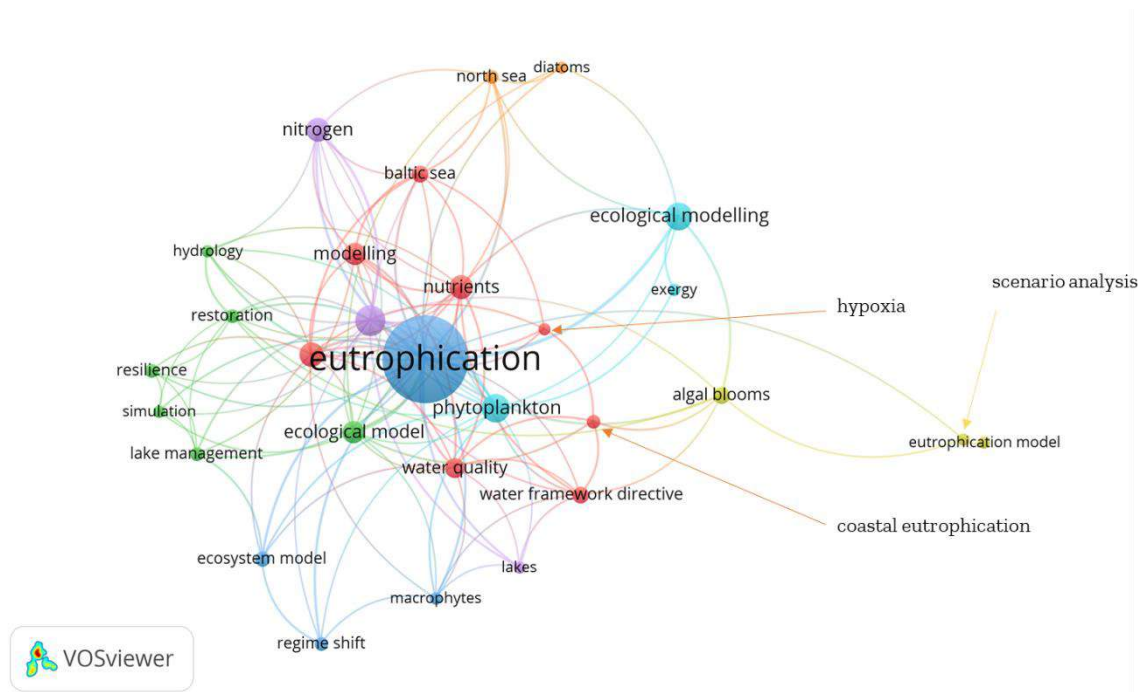
### 2.8.3. Analysis of co-occurrence of keywords

A minimum number of 5 occurrences was set as the critical limit, which provided a total of 31 out of 1061 registered keywords. These 31 keywords were further subjected to screening, wherein the repetitive keywords were filtered out. Finally, 27 keywords were subjected to analysis, the results of which are shown through Table 2. 12 and Fig. 2. 20. Fig. 2. 20a shows the network of all 27 keywords used for the analysis. It was seen that these keywords were classified into seven different clusters, depending upon their inter-relative closeness.

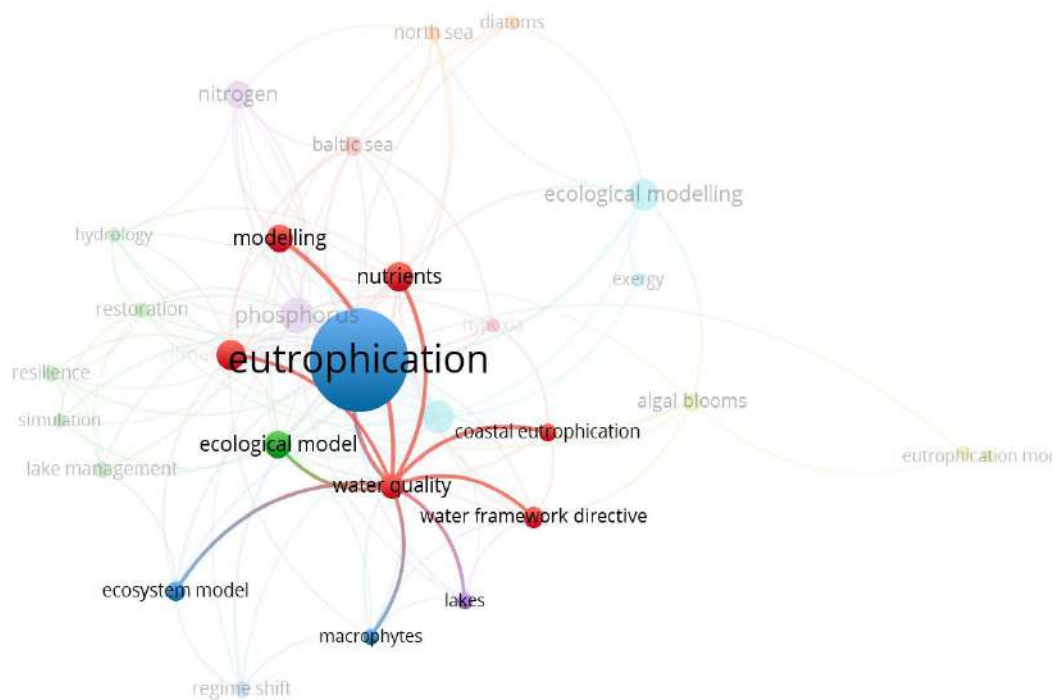
Keywords in Cluster 1, represented by the red colour, suggest that studies primarily focused on coastal eutrophic models, taking climate change into account. Water quality parameters, especially nutrients, were considered for modelling the water frame directives. Since most of the studies carried out fell under the seawater or oceanic eutrophication levels, it also considers the hypoxic condition, which is a state where the human body suffers from inadequate oxygen levels in the body. Keywords falling under cluster 2, denoted by green, suggest that the studies focused on lakes and wetlands considering their hydrological simulations. The prime focus was to restore the water bodies to their natural states through watershed management techniques.

Keywords forming cluster 3, denoted by blue colour, suggest the studies limiting to eutrophication of macrophytes, thereby indicating a regime shift. Similarly, keywords in cluster 4, denoted by yellow colour, suggest eutrophication studies limiting algal blooms in various water bodies due to the nutrient discharges. Likewise, the keywords in cluster 5, denoted by purple colour, indicate studies about lakes polluted explicitly by nitrogen and phosphorus. Keywords in cluster 6, denoted by sky blue colour, indicate studies on ecological modelling as a function of exergy, i.e., chemical and mechanical processes occurring within an aquatic eco-

system, with respect to phytoplankton. Finally, keywords categorized under cluster 7, indicative of the orange colour, show studies on North Sea ecological models with respect to diatoms.



(a)



(b)

**Fig. 2. 20.** Relevant keywords occurred in published literature.

Furthermore, the network also suggests that not only intra-cluster but inter-cluster keywords also possess strong linkage, for example, as shown in Fig. 2. 20b, “water quality” had a strong linkage with keywords such as “eutrophication”, “ecological model”, “nutrients”, “lake”, “ecosystem model”, “macrophytes”, etc. A detailed analysis of the keywords predominately used in the research domain has been listed in Table 2. 12. It was observed that words like “climate change”, “Water framework directive”, “simulation”, and “exergy” are being used lately, which shows a gradual shift in the process of framing models, i.e., shift from the development of traditional models to more complex and sophisticated models approximating real-life conditions through computer simulations.

**Table 2. 12.** List of author keywords in the published literature in ecological modelling domain.

Keyword	Number of occurrences
Eutrophication	123
Phosphorus	22
Phytoplankton	19
Ecological modelling	18
Climate change	15
Nitrogen	14
Nutrients	14
Modelling	13
Water quality	11
Algal blooms	8
Baltic sea	8
Water framework directive	8
Coastal eutrophication	6
Lake management	6
North Sea	6
Regime shift	6
Resilience	6
Restoration	6
Diatoms	5
Eutrophication model	5
Exergy	5
Hydrology	5
Hypoxia	5
Lakes	5
Macrophytes	5
Scenario analysis	5
Simulation	5

### 2.8.4. Co-authorship analysis

Authors having published at least 3 documents and having a minimum of 30 citations were considered for the analysis. This resulted in 42 out of 1211 authors, the details of which are provided in Fig. 2. 21 and Table 2. 13. From Fig. 2. 21, it is evident that all the researchers are highly collaborative, which is indicated by the intense density of the connectors. Also, the authors are classified into five distinct clusters based on their relative closeness in research areas. Cluster 1 had the maximum number of authors listed under it, followed by cluster 2 and so on.

Furthermore, from Table 2. 13, it was found that Arhonditsis G.B. (University of Toronto), Jørgensen S.E. (DFH, Institute A, Denmark), Lancelot C. (Université Libre de Bruxelles, Brussels, Belgium), Billen G. (University Pierre et Marie Curie), Garnier J. (UMR CNRS 7619 Sisyphe), Gypens N. (Université Libre de Bruxelles, Brussels, Belgium), Lacroix G. (Royal Belgian Institute for Natural Sciences (RBINS)), and Scavia D. (University of Michigan) were among the most productive researchers, having more than five research articles published under their name. All these authors also had a considerable number of citations, which depicts the magnitude of their research. However, when it comes to the average normalized citations, *Billen G.* (University Pierre et Marie Curie), *Garnier J.* (UMR CNRS 7619 Sisyphe), and *Reckhow K.H.* (Duke University) hold the maximum impact, with the normalized citation scores of more than 2.00.

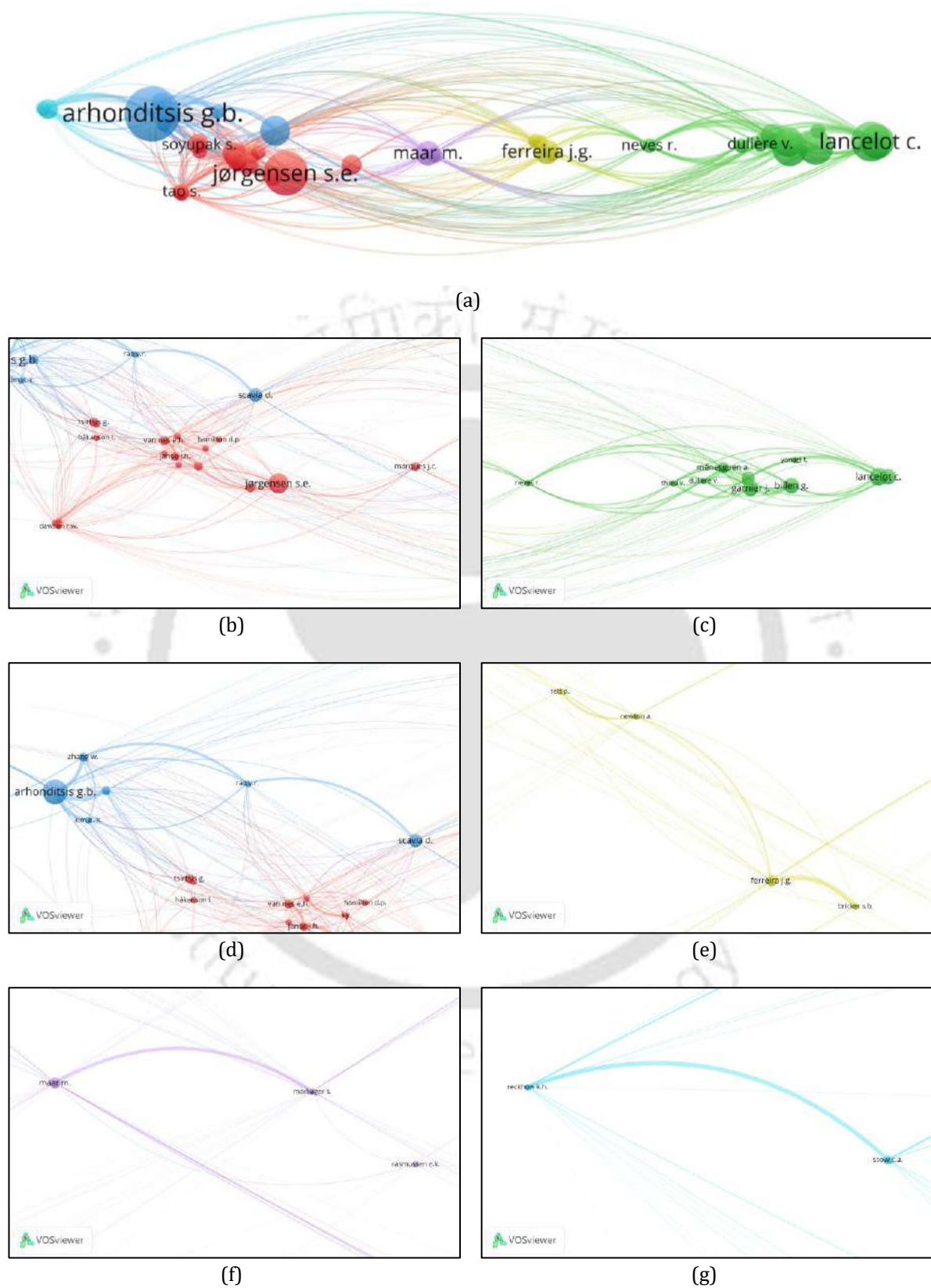
**Table 2. 13.** Quantitative summary of the impacts of scholars.

Scholar	No. of Documents	Total citations	Avg. Citations	Norm. Citations	Avg. Norm. Citations
Arhonditsis G.B.	11	753	68	12.56	1.14
Jørgensen S.E.	9	370	41	7.09	0.79
Lancelot C.	8	310	39	8.24	1.03
Billen G.	7	870	124	16.33	2.33
Garnier J.	7	759	108	15.36	2.19
Gypens N.	7	241	34	7.42	1.06
Lacroix G.	6	249	42	9.56	1.59
Scavia D.	6	97	16	5	0.83
Ferreira J.G.	5	218	44	7.55	1.51
Maar M.	5	47	9	9.09	1.82
Ménesguen A.	5	223	45	7.47	1.49
Brett M.T.	4	508	127	6.18	1.55
Janse J.H.	4	148	37	4.88	1.22
Marques J.C.	4	296	74	5.6	1.40

Mooij W.M.	4	150	38	5.07	1.27
Stow C.A.	4	531	133	7.26	1.82
Tsirtsis G.	4	80	20	2.18	0.55
Van Nes E.H.	4	142	36	3.61	0.90
Zhang J.	4	155	39	2.71	0.68
Zhang W.	4	164	41	3.4	0.85
Bricker S.B.	3	113	38	4.52	1.51
Carpenter S.R.	3	135	45	3.72	1.24
Dawson R.W.	3	206	69	3.93	1.31
Dulière V.	3	56	19	5.86	1.95
Håkanson L.	3	54	18	0.99	0.33
Hamilton D.P.	3	35	12	4.17	1.39
Kim D.-K.	3	98	33	2.61	0.87
Li Y.	3	44	15	2.61	0.87
Liu Y.	3	70	23	2.83	0.94
Markager S.	3	67	22	2.84	0.95
Neves R.	3	110	37	3.79	1.26
Newton A.	3	88	29	1.59	0.53
Rao Y.R.	3	71	24	3	1.00
Rasmussen E.K.	3	88	29	2.8	0.93
Reckhow K.H.	3	506	169	6.47	2.16
Soyupak S.	3	174	58	5.84	1.95
Tao S.	3	206	69	3.93	1.31
Tett P.	3	106	35	3.19	1.06
Thieu V.	3	55	18	4.54	1.51
Xu F.-L.	3	206	69	3.93	1.31
Yanagi T.	3	33	11	0.41	0.14
Zhang Y.	3	45	15	4.04	1.35

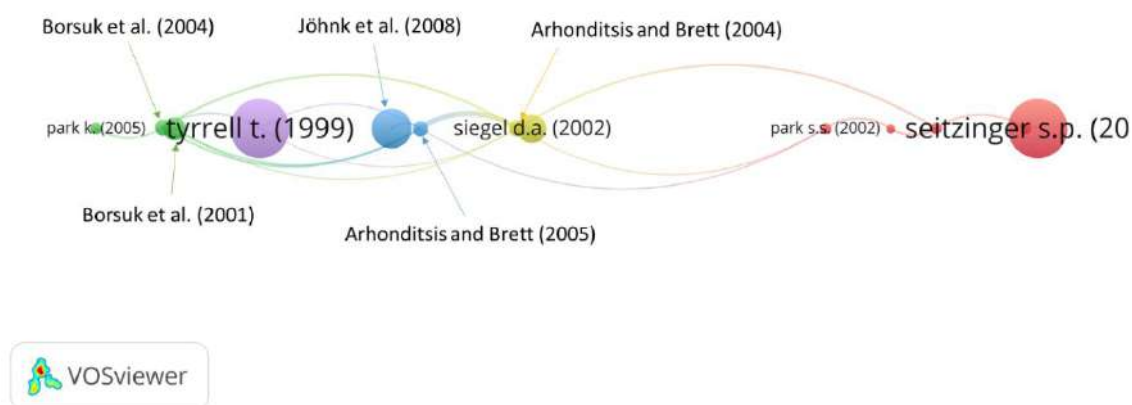
### 2.8.5. Articles' citations

A minimum of 100 citations for each research article was set in *VOSViewer*, which resulted in 22 articles out of a total of 320 meeting this criterion. Mapping of these 22 articles was carried out, as shown in Fig. 2. 22. It is clearly evident that articles Tyrrell (1999); Siegel *et al.* (2002); Borsuk *et al.* (2004); Guttal and Jayaprakash (2008); Jöhnk *et al.* (2008); Seitzinger *et al.* (2010) were the most influential, having the maximum number of citations. Also, all the articles were observed to have considerable mutual citations, which is evident from the connecting lines. Further detailed analysis concerning the normalized citation scores is presented in Table 2. 14, which clearly shows consistent mapping outputs.



**Fig. 2.21.** Mapping of co-authorship analysis showing (a) Overall map and expansive view of (b) Cluster 1, (c) Cluster 2, (d) Cluster 3, (e) Cluster 4, (f) Cluster 5, and (g) Cluster 6.

Based on the results extracted from *Scopus* with relation to the normalized citation scores, it was observed that Seitzinger *et al.* (2010), Tyrrell (1999), and Jöhnk *et al.* (2008) possess the most decisive influence, owing to their very high normalized citations (more than 5.00). It was also seen that newer articles displayed significantly higher normalized citations than the older counterparts, thus suggesting the effectiveness and the impact of the newer articles in the research domain.



**Fig. 2. 22.** Mapping of most influential scholars in the domain of ecological modelling.

**Table 2. 14.** List of most influential publications in the domain of ecological modelling.

Document	Total Citations	Normalized Citations
Tyrrell (1999)	958	7.95
Jöhnk <i>et al.</i> (2008)	577	5.35
Seitzinger <i>et al.</i> (2010)	404	8.01
Borsuk <i>et al.</i> (2004)	352	3.11
Siegel <i>et al.</i> (2002)	323	3.82
Thomas <i>et al.</i> (2002)	295	3.49
Guttal and Jayaprakash (2008)	257	2.38
Arhonditsis and Brett (2004)	240	2.12
Lee <i>et al.</i> (2003)	201	3.29
Soons <i>et al.</i> (2004)	188	1.66
Arhonditsis and Brett (2005)	154	2.02
Marques <i>et al.</i> (1997)	154	2.2
Xu <i>et al.</i> (2001)	145	2.78
Karul <i>et al.</i> (2000)	133	3.27
Hu <i>et al.</i> (2008)	132	1.22
Cugier <i>et al.</i> (2005)	119	1.56
Park <i>et al.</i> (2005)	119	1.56
Park and Lee (2002)	119	1.41

Lancelot <i>et al.</i> (2005)	118	1.55
Borsuk <i>et al.</i> (2001)	112	2.15
Johnson <i>et al.</i> (2013)	106	3.29
Justić <i>et al.</i> (2002)	104	1.23

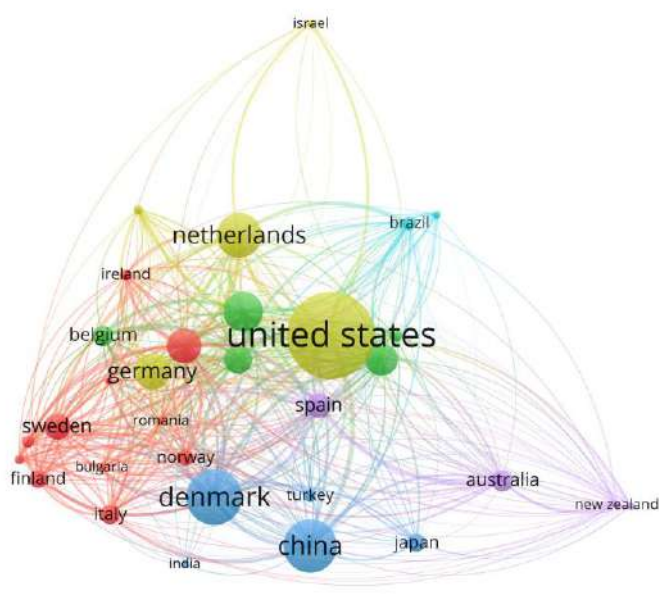
### 2.8.6. Countries active in the research domain of ecological modelling

A minimum of 3 articles and 30 citations from each country were considered for analysing the countries actively participating in the domain of ecological modelling. The results were subjected to mapping in *VOSViewer*, shown in Fig. 2. 23. It was observed that the most actively participating countries are primarily those countries that are highly developed, for example, *The United States, Denmark, China, Netherlands, France, Germany, and The United Kingdom*, whereas the developing or less developed countries have insignificant contributions. It was also observed that all countries involved have excellent mutual collaborations, which is evident from the density of the connecting lines. Furthermore, these countries have been categorized into six clusters, depending on their research (Fig. 2. 23). A more detailed representation of the extracted data on the active countries in the research domain is represented in Table 2. 15. It was found that although the *United States'* contribution in the research on eutrophication-based ecological modelling is the most significant, the average normalized citation score of the *United Kingdom* is the highest, depicting a considerable impact of the researches carried out in the country. The *UK* is followed by *Switzerland, Bulgaria, Netherlands, United States, South Korea, and Germany*, having scores of more than 1.20. It is also important to note that only four Asian countries (*China, Japan, India, and South Korea*) make up the list out of the 32 countries analysed, while a majority of the contributions have been from the European and American countries. This is indicative of the massive gap in the research on ecological modelling in Asian countries compared to others.

**Table 2. 15.** Countries actively participating in the research domain of ecological modelling.

Country	No. of Documents	Total Citations	Avg. Citations	Norm. Citations	Avg. Norm. Citations
United States	69	4057	59	90.36	1.31
Denmark	42	1179	28	43.97	1.05
China	40	794	20	45.3	1.13
Netherlands	33	2369	72	46.68	1.41
France	29	1319	45	34.59	1.19
Germany	26	1492	57	32.15	1.24
United Kingdom	25	2709	108	44.09	1.76
Canada	23	560	24	17.4	0.76

Portugal	20	703	35	21.3	1.07
Sweden	18	720	40	20.73	1.15
Spain	17	337	20	17.29	1.02
Australia	15	290	19	11.81	0.79
Belgium	14	490	35	16.18	1.16
Italy	13	365	28	11.17	0.86
Finland	12	228	19	8.5	0.71
Japan	12	177	15	5.42	0.45
Norway	11	262	24	11.57	1.05
Brazil	9	252	28	8.47	0.94
Estonia	8	116	15	4.94	0.62
Greece	8	184	23	5	0.63
Turkey	8	364	46	8.85	1.11
Ireland	7	200	29	6.78	0.97
Poland	6	121	20	3.11	0.52
Switzerland	6	489	82	9.09	1.52
Mexico	5	70	14	4.29	0.86
New Zealand	5	89	18	5.05	1.01
Austria	4	65	16	2.76	0.69
Israel	4	238	60	3.22	0.81
Romania	4	55	14	2.39	0.60
Bulgaria	3	172	57	4.39	1.46
India	3	51	17	0.82	0.27
South Korea	3	292	97	3.85	1.28



**Fig. 2. 23.** Mapping of most active countries in the domain of ecological modelling.

### 2.8.7. Qualitative assessment - Current research topics within “eutrophication-based ecological modelling”

A modelling software usually aids the development of an ecological model, but the level of dependence on the modelling software depends on the modeller's comfort (Jackson *et al.* 2000). There is a broad spectrum of modelling software available to the modeller. On one end of the spectrum, there are general programming languages such as *C*, *Basic*, *FORTRAN*, *Pascal*, etc., which give the user complete freedom over the model construction but at the same time total responsibility of handling all the tedious details. At the other end of the spectrum, user-friendly modelling software with attractive graphical interfaces such as *STELLA*, *Simulink*, *ModelMaker*, etc., give the user freedom from handling the underlying implementation details that have limitations over model construction. Between these two extremities lies several programming packages such as *MATLAB* and *spreadsheets*, which provide different functions to ease the user from handling programming details while at the same time allowing some control to the modeller.

Different ecological models can be broadly categorised into the white box and black box models (Jørgensen & Bendoricchio 2001). The white box model is one in which the causality of the input-output relation is known. On the other hand, a black-box model does not explain why a particular behaves in a specific manner for a given input. In practice, most models can be described as grey models as they combine white and black box models. Jørgensen and Bendoricchio (2001) further made another classification of the ecological models based on their application given in the following list.

- *Biogeochemical and bioenergetics dynamic models*

The biogeochemical and bioenergetics dynamic models are mostly white-box models, which apply the principles of mass and energy conservation to develop the differential equation. These models are easy to understand, interpret and develop, but a relatively good database is required and becomes challenging to calibrate when many parameters are involved in the model. Eutrophication models are a type of biogeochemical models.

- *Steady-state biogeochemical models*

The steady-state biogeochemical models are used when the database for model construction is small, but these models fail to give any information about the ecosystem's behaviour with the change in time.

- *Population dynamic models*

The population dynamic models are one of the most popular ecological models that can predict the development of a population with time, incorporating the age structure and impact factors. However, there is a requirement for a relatively good and homogenous database.

- *Structurally dynamic models*

The structurally dynamic models allow modellers to incorporate dynamic parameters, considering the adaptation factor of different species and shift in the species composition. However, there is a need for goal function or artificial intelligence for this model to work correctly, making this model time-consuming.

- *Fuzzy models*

As the name suggests, the fuzzy models apply to a fuzzy dataset and semi-quantitative information (linguistic formulation). These models are not suitable for complex model formulation.

- *Artificial Neural Networks*

Artificial neural networks can be described as black-box models, which requires a sizeable heterogeneous dataset from different ecosystems or a homogenous dataset from a specific ecosystem to represent the relationship between the state variables and forcing functions of the model.

- *Spatial models*

The spatial models are those models that show the spatial distribution of different processes, forcing functions and state variables. GIS can be used to describe those models.

- *Individual-based models*

The individual-based models consider the uniqueness of the different individuals within a species, which, though disregarded in biogeochemical models, may be vital for the survival of that species. These models can be very complex.

- *Ecotoxicological models*

Ecotoxicological models are, basically, biogeochemical or population dynamic models that are being applied to ecotoxicology. These models earn a particular place in classification due to limited knowledge of ecotoxicological parameters and the use of safety factors.

- *Stochastic models*

Stochastic models incorporate randomness either in forcing functions or model parameters. A stochastic model can be any of the previously described models with randomness factored in it.

- *Hybrid models*

Hybrid models are a combination of any two previously described models. Such models bring the dual advantage of coupling the advantages and minimising the disadvantages of the parent models. One example of the hybrid model is the outcome of combining a biogeochemical dynamic model and an ANN model.

In the following part of this section, some of the developments in ecological modelling, especially in eutrophication modelling since the 1980s, are discussed.

Scavia (1980) developed an ecological model consisting of *epilimnion*, *hypolimnion* and sediments of Lake Ontario that simulates various state variables such as phytoplankton, zooplankton, different forms of nitrogen, phosphorus, silicon, carbon, dissolved oxygen, particulate sediment and pore water dynamics. This ecological model illustrated the significance of detritus and herbivorous zooplankton in the lake, thereby serving as an analytical tool for the large ecosystem.

Matsuoka *et al.* (1986) developed a mathematical model to predict the fate of nutrients among four levels, with fourteen state variables in each segment, for Japan's largest shallow lake, Kasumigaura that was suffering from the problem of artificial eutrophication caused by urbanization, agricultural growth and fishing culture. These state variables included phytoplankton, zooplankton, fish, crustacean, external nutrients and fresh sediments. One of the highlights of this eutrophication model is that most of the parameter values were based on the in-situ measurements and batch-culture experiments using strains from the lake while calibrating the model. This model was applied as a predictive device to get the nature of water quality in the future.

Dejak *et al.* (1987) integrated a two-dimensional diffusion model with a two-dimensional advection model for the lagoon of Venice to develop a three-dimensional model which is capable of simulating the dispersion of eight state variables: phytoplankton, zooplankton, ammonia, nitrites and nitrates, degradable organic compounds and temperature. The three-dimensional eutrophication model can estimate the eddy diffusion constant that incorporates the tide's dispersion action.

Lake Taihu is among the five largest freshwater lakes in China that have been severely affected by eutrophication since the 1980s. Different models have been developed to study this lake, such as Hydrodynamic models, Mass transportation and cycling models and ecological models. The first ecological model was developed by Dou *et al.* (1995) to link the hydrodynamic aspects of the lake to chemical and biological processes occurring in the lake. The entire lake was divided into thirty sub-zones, and various sub-models were developed for

each sub-zone. In 1999, Hu created another model for eutrophication in Lake Taihu. It was one of the earliest versions of the *EcoTaihu model* (Hu 2016). This three-dimensional model was developed by combining another three-dimensional hydrodynamic model (Hu *et al.* 1998a; Hu *et al.* 1998b), a model describing the impacts of water hyacinth on the water quality of Lake Taihu (Hu *et al.* 1998c) and a model based on a physio-biological engineering experiment for water purification using *Trapa natans var. bispinosa* (Hu *et al.* 1998b). This model was further developed by incorporating the carbon cycle, which allowed the depiction of pH in the lake and revealed that the lake acted either as a sink or as a source at different times (Zhang *et al.* 2008; Weiping *et al.* 2011). In 2010, another improvement was incorporated into the *EcoTaihu model* by redefining the sub-model for fish. This improved model revealed that by introducing the fish into the lake, the production of the released fish could increase and change the population structure in the lake. This model also revealed that by releasing certain species of fish, the nature of the lake could also be changed. For example, if the *Ctenopharygodon idellus* was released, it could temporarily curb the fast-growing macrophytes population. On the other hand, if the grass carp was released into the lake, it bolstered the phytoplankton and algae population. Zhang *et al.* (2013) further improved the *EcoTaihu model* by incorporating an additional layer of algae to explain the movement and disappearance of the mat-like algal bloom on the surface of water under weak and strong wind respectively.

Karul *et al.* (2000) developed a three-layered *Levenberg-Marquardt* feed-forward learning algorithm to develop eutrophication models for three water bodies of Turkey — Keban Dam, Mogan and Eymir Lakes. To develop neural networks, the eutrophication phenomenon was converted into an input-output problem and data for the input layer was collected through an extensive six-year-long field-monitoring program. The input parameters for the Keban Dam were phosphate, nitrate, alkalinity, suspended solids, pH and water temperature, electrical conductivity, dissolved oxygen and Secchi depth. For the Mogan and Eymir Lakes, the authors' input parameters were total phosphorus, nitrate and ammonia, the temperature in water, electrical conductivity, pH, turbidity, Secchi depth, and suspended solids. Suspended solids, turbidity and Secchi depths were considered in the neural network to simulate the role of light in the euphotic zones. *Chlorophyll-a* was selected as the primary target output for the network. Additionally, three typical eutrophication indicators, *Cyanophyceae* species, *Aphanizomenon sp.*, *Microcystis sp.* and *Oscillatoria sp.*, were used as target outputs. The so developed eutrophication models' results revealed a relatively good correlation between calculated and measured values for Keban Dam and a high correlation between the same for the much smaller and more homogenous Mogan and Eymir Lakes.

Drago *et al.* (2001) used a three-dimensional model, *TROPHY3D*, to analyse the advection and diffusion of suspended solids and conservative pollutants in the ambient water and their effect on trophic behaviour. The *TROPHY3D* model used a finite difference method for spatial integration and a Runge-Kutta-IV or Euler method for temporal integration of the differential equations used in the model. The model was also able to predict the biochemical interactions between detritus, phytoplankton, nutrients, zooplankton and dissolved oxygen.

Rukhovets *et al.* (2003) developed a new three-dimensional mathematical model for Lake Ladoga, the largest freshwater European lake located in north-western Russia, to simulate phytoplankton growth. In this model, the authors selected fourteen state variables that included different phytoplankton complexes, zooplankton, dissolved organic matter, detritus, dissolved mineral phosphorus and dissolved oxygen. It is based on the ideas of phytoplankton succession in the lake given by Petrova in the 1980s (Rukhovets *et al.* 2003). Prior to this model, Menshutkin and Vorob'eva (1989) successfully created a one-box model for eight different groups of phytoplankton communities in the Volkhov Bay. This model incorporated the temperature conditions of the lake as well as the nutrient supply, but it failed to consider the fact that the zooplankton and fish eat phytoplankton. Moreover, the modellers assumed instantaneous mixing of the nutrients in the lake. The new three-dimensional model was an improvement of the works done by Menshutkin *et al.* (1998) with a more detailed description of the phytoplankton community. Zhang *et al.* (2003) also developed a structurally dynamic eutrophication model for Lake Mogan, Ankara, Turkey, which was able to describe the competition between phytoplankton and submerged plants in the lake. In this model, the energy was used as a goal function to develop the dynamic adaptation and seasonality of plankton species.

Malmaeus and Håkanson (2004) developed an extensive dynamic model to predict the phosphorus concentration and the consequences of eutrophication on the lake ecosystem. The model is called Lake Eutrophication, Effect, Dose, Sensitivity model (LEEDS). It was developed with easily accessible lake variables. The LEEDS model was novel in many ways. It incorporated two levels for colloidal phosphorus, a seasonal factor for lake outflow, higher settling velocity for re-suspended material, a new algorithm to model the mixing between deep water and surface water, and phosphorus diffusion from sediment areas accumulation.

Trolle *et al.* (2008) used the one-dimensional lake ecosystem model, *DYRESM-CAED*, to know the effect of total phosphorus loading reduction on moderately deep lake Ravn's ecosystem dynamics in Denmark. The model was calibrated with the observed data for oxygen and temperature for seven years and then validated for another period of five years. When

put to use, the *DYRESM-CAED* was able to predict that a significant reduction in total phosphorus is needed to meet the phytoplankton biomass concentration as per the European Union Water Framework Directive (WFD).

Mukherjee *et al.* (2008) developed a model representing the carbon dynamics in a simulated pond in Ranchi, India, for cultural eutrophication assessment. The model mainly included processes such as respiration, decomposition and photosynthesis that play an essential role in the nutrient dynamics of the system. In eutrophication models, it is usually challenging to model the carbon cycle in detail, but this model successfully shows that the dependence of nutrients processes on an accurate and detailed description of the carbon cycle.

Taguchi and Nakata (2009) developed a numerical model that highlighted the role of macrophytes colonies in the shore zone in water purification. The model was applied to Lake Suwa, Lake Kasumi, Lake Biwa and some small lakes attached to Lake Biwa. The model included interactions between the compartments of pelagic and benthic regions. Meteorological and hydrodynamic conditions were considered among the forcing functions. The outcomes of the model were reported to have good agreement with the observed values obtained from the water quality monitoring campaign.

He *et al.* (2011) developed a numerical model based on the environmental fluid dynamics code (EFDC) for Beijing Gaunting Reservoir. Three state variables for phytoplankton species, cyanobacteria, green algae and diatom, were considered for the model and vertical temperature profiles, *chlorophyll-a* and nutrient concentrations in the water column were used during model calibration. The model so developed was put to use as an investigative tool, which revealed that the peak *chlorophyll-a* could be reduced by reducing external loadings of nutrients with constructed wetlands, bio-manipulation or diverting water from the Cetian Reservoir. However, one of the significant shortcomings of this model is that it was calibrated with only one year of data, and therefore, it was capable of reflecting only the short-term effects of applying management scenarios.

Xu *et al.* (2013) developed a structurally dynamic model based on the software *Pamolare-II* for the Baiyangdian Lake in North China. *Pamolare* (Planning and Management of Lakes and Reservoirs) is a modelling software developed by the International Environmental Technology Centre of UNEP (IETC-UNEP) and International Lake Environment Committee (ILEC), which offers four eutrophication models with different complexity levels. The first model is the Vollenweider plot with one state variable of phosphorus or nitrogen loading in  $\text{g/m}^2/\text{year}$ . The second model contains four state variables. The state variables are nitrogen and phosphorus in water and sediments. Several correlations were also provided to calculate other state variables. The third model is more complicated than the previous two models, providing

a two-layer model with 21 state variables. The fourth model is an improvement of the third model with the application of the structurally dynamic approach. *Pamolare-II* is the next version of the *Pamolare* software, which provides structurally dynamic models focusing on shallow lakes for eutrophication lake management. The Baiyangdian Lake model was developed by Xu *et al.* (2013) to predict the ecological health condition of the lake under different scenarios of submerged plant removal from the lake. The ecological health conditions were indicated by phytoplankton biomass, the ratio of zooplankton to phytoplankton biomass, eco-exergy and structural eco-exergy. The conceptual diagram of the Baiyangdian Lake model included 12 state variables correlated by 45 processes.

Magnea *et al.* (2013) developed a simplified mathematical model to describe the phosphorus, phytoplankton, zooplankton and fish dynamics in the alpine lake ecosystems. The model was developed to study the scenario when brook trout (*Salvelinus fontinalis*) were introduced artificially in the lake ecosystems. The model so developed was used to study twelve alpine lakes in Gran Paradiso National Park, Italy.

Zouiten *et al.* (2013) developed a mathematical eutrophication model called Environmental Hydraulics Institute Eutrophication Model (*EnvHydrEM*), especially for coastal regions, which considered 19 state variables including phytoplankton, different forms of carbon, nitrogen, phosphorus and silica, carbonaceous organic matter, zooplankton, bacterioplankton, detritus, iron and manganese. The *EnvHydrEM* described all the possible interactions between the defined state variables by considering all the biological and chemical processes involved in the ecosystem. It was further applied in the Victoria lagoon in Northern Spain to gauge its efficiency.

Prokopkin *et al.* (2014) developed an investigative mathematical model to confirm the presence of a *phytoflagellate* population in the stratified Lake Shira, Khakasia in Russia by considering the microbial dynamics and *phytoflagellate* relationship with the trophic levels of the lake. The outcome of such a model was that it confirmed the abundant presence of cryptographic algae in the water column, above the chemocline, in the summer season. This 1-dimensional model is a perfect example of how modelling can corroborate certain species in the ecosystem, which otherwise has indirect evidence of presence.

Xu *et al.* (2014) developed a simple yet effective eutrophication model, using parameters based on both literature survey and experimental investigation, that incorporated the knowledge on bioaccumulation and algal growth for eutrophication in Xikeng Reservoir, Shenzhen City, China. The authors combined the cumulative effects of meteorological factors, water quality factors and biological factors on eutrophication to develop such a cumulative

eutrophication risk evaluation model. The highlight of this model is that a large set of parameters and experiments to simulate the eutrophication process is not a prerequisite for its functioning.

Li-kun *et al.* (2017) developed a two-dimensional eutrophication model for an urban lake in the Tianjin region to describe the spatiotemporal variation of water quality and establish relationships between phytoplankton, zooplankton and nutrients. Navier-Stokes equations and finite volume method were used to define the hydraulic model, and the Bayesian method was employed for model calibration and parameter posterior distribution acquisition. The model simulated five state variables that included phosphate, nitrate, ammonia, chlorophyll-a and dissolved oxygen. The calculations from the two-dimensional model revealed higher values for the state variables in the regions closer to the lake periphery than at the centre, indicating the significant role of nutrient loading of rainfall-runoff on algal growth and water quality. Thus, the 2-dimensional model was able to provide crucial information that can result in an effective management strategy to counter severe eutrophication in urban lakes.

Das *et al.* (2018) developed a mathematical model to simulate the phytoplankton distribution and nutrient cycle along the River Jagaddal, which is an easterly branch of the Saptamukhi East Gulley of the Saptamukhi River in Sundarbans Estuarine System, India. The authors designed their model based on the compartmental ecosystem model developed by Fasham *et al.* (1990). Their model considered phytoplankton and nitrate in the water column as two state variables. The differential equations for these state variables were based on Haney and Jackson (1996). The authors further carried out a sensitivity analysis of their model based on a variance-based sensitivity analysis method. Through sensitivity analysis, they understood the crucial parameter of the model and, in turn, predicting the underlying ecological process involved for such an influence. The model equations were integrated using the fourth-order Runge-Kutta algorithm, implemented by the *C++* programming language. The sensitivity analysis was carried out in *MATLAB*.

McCullough *et al.* (2018) developed a relatively simple, dynamic, mass balanced model, incorporating five state variables of different forms of organic carbon and dissolved oxygen to investigate the dominance of allochthonous organic carbon in the organic carbon dynamics of a lake in the long run. The model so developed was validated in five different lakes in the U.S.A and Canada. McCullough *et al.* (2018) also used the model to predict the seasonal variation in organic carbon budgets.

## 2.9. Summary

This chapter presented a detailed review of the published works concerning all components of an aquatic ecosystem, starting with water quality and its assessment, sediment contamination, and finally integrating multiple components to develop ecological models replicating the real-life problems associated with the aquatic ecosystems, particularly wetlands. SLR provides critical insights into the following, thereby possessing an added advantage over the conventional approach of reviewing the published literature.

- Identifying, summarizing and evaluating the current theory and methods
- Identifying methodological problems and gaps
- Providing much-needed evidence for decision-makers when identifying and supporting priority issues, primarily through funding for policy development
- Keeping an update of the research/works carried out in the research domain by practitioners and researchers
- Justify carrying out further research in the domain to the granting agencies

Therefore, an SLR needed to be conducted on the present research to have an idea of the status and state-of-the-art wetland research. It was observed that limnological studies concerning specifically wetlands are limited and there remains a considerable scope in the research domain. Details of the significant gaps in research that need attention have been presented in Chapter 3.

The current review is limited to its sample literature. Firstly, only the articles published in journal articles were considered; other forms of publications, such as conference proceedings, book chapters, etc., were excluded. Secondly, English as a medium of publication was only considered, and all other languages were eliminated. There may be different needs to relate the uncertainty between the current research and the latest articles published. Nevertheless, this study would prove to be consequential to all researchers worldwide who wish to learn the dynamics of the published literature until the year 2020. In a large vision, this review work may be linked so the future research community will be guided.



Away, away, from men and towns,  
To the wild wood and the downs, —  
To the silent wilderness,  
Where the soul need not repress its music.

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- Percy Bysshe Shelley

# 3

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## Research Gaps and Objectives

This chapter presents provides an assessment of research gaps that help motivate the research in the following chapters. Based on the research gaps, the study's objectives have been formulated to achieve the overall aim of understanding wetland limnology.

### 3.1. Research Gaps

Chapter 2 presented extensive bibliographical research on the topics related to water quality, sediment quality and modelling techniques simulating real-life situations attributing to eutrophication in aquatic ecosystems. The review analyses resulted in qualitative discussions, wherein the current research trends for all the aspects were discussed. The research gaps were identified and discussed in the subsequent sub-sections based on those qualitative discussions.

#### 3.1.1. Research gaps relating to water quality

The current research in water quality indexing suffers from the following limitations:

##### I. *Specific indices*

Various water quality indices developed have been based on the problems associated with a regional scale, a highly specific problem, or a definite water body. For instance, Semiromi *et al.* (2011) proposed an overall water quality index to assess the Karoon River's water quality in Iran. For this purpose, six water quality variables were chosen; Dissolved Oxygen, Total Dissolved Solids, Turbidity, Nitrate, Faecal coliform and pH. Likewise, Gharibi *et al.* (2012) developed a water quality index for dairy cattle's drinking water. They considered 20 parameters, based on the literature, for assessing water quality suitable for drinking purposes of

dairy cattle, taking into consideration their health impacts. Singh *et al.* (2012) proposed a water quality index for India's rural part of the Gajraula region, based on the significant problems associated with that particular region, i.e., industrialization. Lauringson *et al.* (2012) developed an index primarily for the coastal brackish waters in the N.E. Baltic Sea, correlating the climatic and anthropogenic interferences to the region's biological diversity.

Similarly, many authors have attempted to develop several indices depending on the local problem boundary and for specific water use pertaining to a definite watershed boundary (Wu *et al.* 2017; de Almeida & de Oliveira 2018; Ng *et al.* 2018; Abbasnia *et al.* 2019; Wertz & Shank 2019; Tian *et al.* 2020). These specific indices become highly regional, and the researchers' methodologies may not be applied globally. Furthermore, the indices developed or proposed to consider those water quality parameters that are problematic in those regions, while those problems may not fit suitable for other water bodies or regions of consideration. Hence, certain tools or techniques need development that would take care of such limitations, i.e., the indices should not only deem fit for that particular study area or watershed but can be suitably applied globally. Also, each index developed for a specific end-use of water such as drinking, irrigation, industries, heavy metals, etc., which considers specific parameters, needs a comprehensive assessment when choosing the water quality parameters.

## II. *Human intervention*

The primary approach to developing a WQI from the outset has been consulting various experts from different areas of expertise. This approach is carried out through different tools such as preparing author questionnaires, conducting surveys, etc. Teikeu *et al.* (2016) presents the survey conducted in the Yaoundé area, focused on determining the quality of groundwater resources as an emergency drinking water supply program in the region. A dataset comprising various groundwater parameters from 42 bore wells were considered in the study. Malamos and Koutsoyiannis (2018) conducted a biannual survey of 104 irrigation water wells of a Mediterranean island using a multi-parameter probe. Tests were conducted to develop an irrigation-water quality index, and the results were analyzed using various spatial interpolation methods. Mazhar *et al.* (2019) prepared a questionnaire survey to examine water-borne diseases in the Gujranwala district of Pakistan. An Averaged Water Quality Index was developed to determine the region's groundwater quality status using ArcGIS model builder. Bhat *et al.* (2020) surveyed 30 villages of the Kashmir valley, about 59 in number, and recorded their responses. Based on the responses, a WQI was developed for drinking purposes of the 30 freshwater springs. There are also studies conducted based on recorded responses from experts of different fields of expertise which were considered for developing WQIs, the Delphi method being the most effective (Meyer & Booker 1990). Some of the famous

WQIs involving expert judgements include the National Sanitation Foundation (NSF) Index (Brown *et al.* 1970), the Scottish Research Development Department (SRDD) index (SRDD 1976), Ross's Index (Ross 1977), Oregon Index (Dunnette 1979), House's Index (House 1986; House & Ellis 1987; House 1989; House 1990), and Almeida's Index (Almeida *et al.* 2012). All the tools adopted for conducting surveys or recording responses from people of the regions and, in most cases, from various experts may prove inconsequential to water bodies other than those considered for the study. Additionally, these proposed WQIs may often be misleading, thereby creating ambiguities among other researchers worldwide.

### III. *Performance assessment*

The efficacy assessment of the proposed or developed WQIs is often neglected. Only a few researchers have attempted using specific tools or mathematical models for determining the general applicability of WQIs. These tools majorly include artificial neural networks for predicting the developed WQIs, thereby ascertaining its reliability (Alizadeh & Kavianpour 2015; Khan & Chai 2017; Gupta *et al.* 2019). Others primarily employ regression models (Haridas & Antony 2019) or machine learning approaches (Leong *et al.* 2019). Hence, there exists a significant scope in the area of employing various tools, mainly introducing the concept of sensitivity analysis to the domain of water quality indexing, which would help in addressing the reliability of the indices.

### IV. *Emerging techniques*

Newly emerging water quality indexing techniques such as multivariate statistics, probability, and the randomness of water quality datasets (information entropy) need further research to develop a new and more comprehensive water quality index. Furthermore, modifications in the existing mathematical approach can also prove vital in improvising the indices. At present, the applicability of mathematical tools in this domain is still in its primitive stage, which can be further enhanced through an integrated approach of adopting multiple techniques in the practice of water quality indexing.

#### **3.1.2. Research gaps relating to sediment quality**

The sediment contamination assessment has been relatively new as compared to the water quality assessment. Various aspects of the research have been covered in the past (details are provided in 2.7.7), which suffer from specific gaps, described as follows.

- i. The bulk of the studies carried out on sediment contamination assessment are attributed to heavy metals. However, there is limited literature on studying the heavy metal contamination in an aquatic ecosystem's sediment column through a large-scale monitoring program. Additionally, the use of indices and factors for determining the sediment pollution

load status is still at a dormant stage. This needs proper attention for appropriate use, like the water quality indices.

- ii. Studies pertaining to pollution source identification and their apportionment are not available. The site and source characterization studies thus demand immediate attention.
- iii. There is also limited evidence of literature on the speciation studies of the sediment column of aquatic ecosystems. Metal speciation analyses provide strong indications of the forms of heavy metals present in the sediment columns, thereby aiding in assessing the heavy metal toxicity levels. Such studies carry immense significance when it comes to determining the sediment quality of any water body.
- iv. Not much published literature provides information about the health risks associated with heavy metals due to prolonged exposure levels. Contaminated sediments carry huge toxicity concentrations with them, which carry immense health risks if exposed for a prolonged period. Therefore, it is essential that the health risks be evaluated.
- v. There is no literature available that states the spatial and temporal variability of the elemental composition and morphological changes associated with the sediment column.
- vi. Finally, since it was observed that most of the studies concentrated on addressing the heavy metal contamination in the sediment column, there exists minimal literature that addresses the nutrient contamination levels. When accumulated in the sediment column, these nutrients leach back into the water column, thereby enhancing the chances for eutrophication in an aquatic ecosystem. Hence, there is an existential need for studying the nutrient contamination in the sediment column.

### 3.1.3. Research gaps in the domain of eutrophication-based ecological modelling

While much work has been done on ecological modelling, the quest for better ecological models is far from over. Most ecological models have site-specific limitations, and hence a completely robust generalized ecological model is yet to be developed. However, developing such a model will be a herculean task, and until such a model is developed, ecological modellers have to compromise with site-specific models and continue to develop models for different wetlands separately. The need to develop an ecological model becomes far more urgent if it is currently endangered.

From the results of the qualitative analyses presented in 2.8.7, it has been observed that most ecological models developed have revolved around the more developed nations, while the lesser developed or developing nations are still in the dormant stage in this research domain. This may be attributed to technological advancements in computational facilities that these countries lack. However, the lack of studies does not mean that the problem of eutrophic

water bodies is of no concern in these countries; instead, there is significant evidence of vanishing water bodies and ecologies in these countries. Therefore, a collaborative research approach is a way forward to find proper governing measures to conserve the natural systems and restore them to their near-original state.

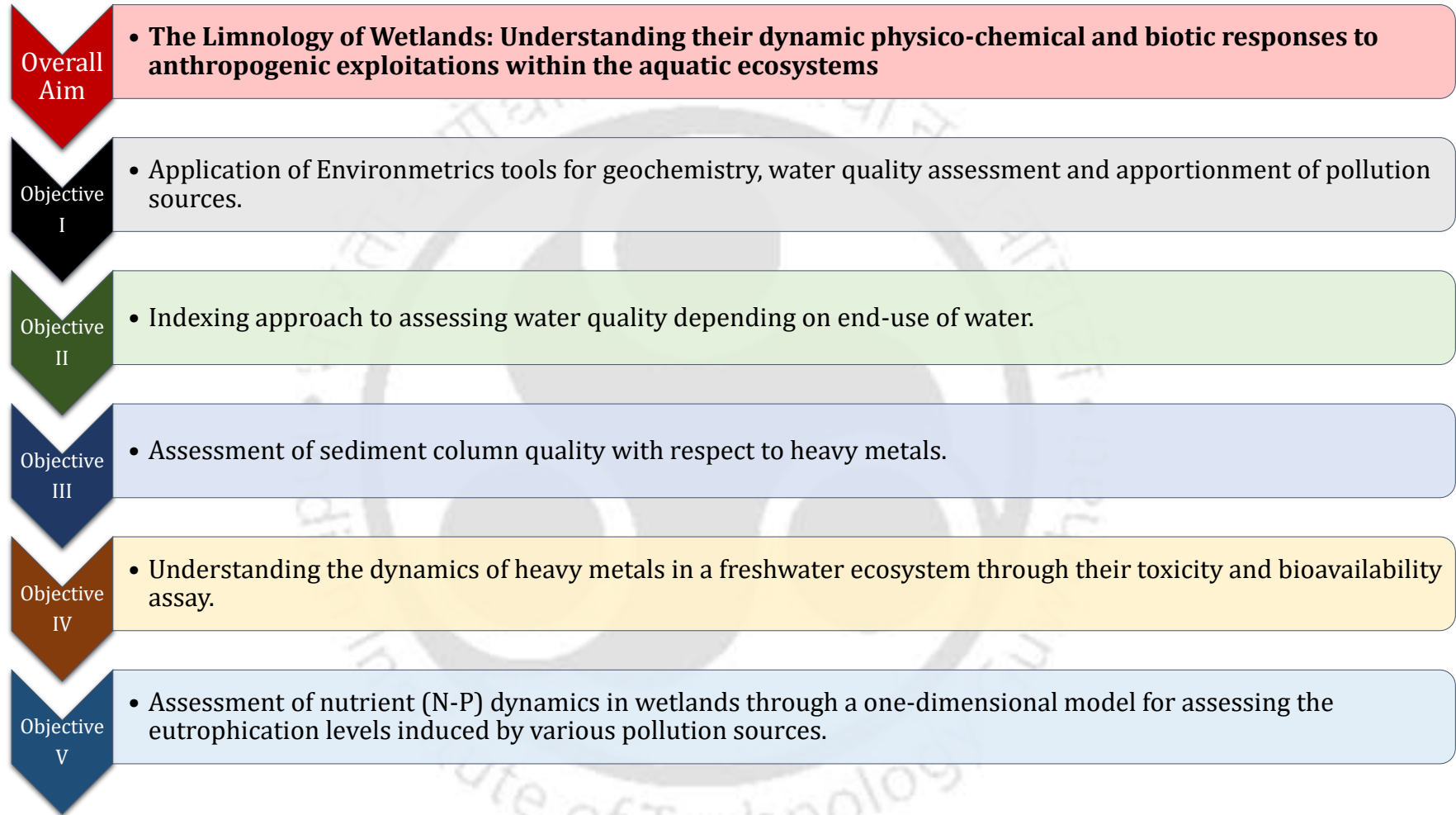
The models developed by modellers are seldom assessed for their performance and reliability. Only a handful of modellers have successfully proposed measures of evaluating the correctness of the model, which will solve real-life problems, for example, the use of artificial neural networks, regression analyses and machine learning approaches. However, the most effective tool that needs attention to all modellers is sensitivity techniques, wherein the sensitivity indices of all parameters can be computed. This, in turn, will aid in addressing the reliability and correctness of the models.

Finally, with the advancements in the programming world and the development of sophisticated languages and software, it becomes highly essential that the modellers adapt to the changes and keep updated. Also, mutual collaboration among scholars worldwide will help initiate novel ideas and scientific techniques based on their individual perceptions, which can be integrated into a single framework.

### **3.2. Research Objectives**

Based on the gaps identified from the literature survey, as pointed out in section 3.1, five objectives of the research were laid down, addressing the critical issues relating to aquatic ecology. Our primary focus was limited to the wetland ecosystem, for which Deepor Beel, a Ramsar site, was chosen. As shown in Fig. 3. 1, the entire research was carried out, keeping in mind five distinct objectives to satisfy the overarching objective of understanding the limnology of the wetlands.

The first objective involved identifying the latent pollution sources and their apportionment using various Environmetrics tools. For this purpose, the hierarchical cluster analysis (HCA), principal component analysis (PCA), discriminant analysis (DA), and the positive matrix factorization (PMF) models were employed. This was followed by the assessment of the water quality of Deepor Beel using indexing approaches. The indexing techniques used were primarily objective, i.e., not considering any expert's opinion, reducing the prejudices. The third objective dealt with assessing the sediment quality with respect to heavy metal contamination. This involved source apportionment techniques, their elemental composition and variability studies, followed by speciation studies, and finally, estimating various ecological risks involved concerning sediment contamination.



**Fig. 3. 1.** Objectives of the research program.

The fourth objective essentially focused on understanding the heavy metal dynamics in the entire wetland ecosystem. This considered assessing the contributions from water, sediment and the fauna samples collected over the entire monitoring period. Finally, the fifth objective reflected a crucial problem, usually associated with wetlands in recent times, i.e., eutrophication. The problem of eutrophication relating to Deepor Beel was addressed by developing a eutrophication-based ecological model, considering the dynamics of nutrients (essentially Nitrogen and Phosphorus) in three different components of the wetland ecosystem, i.e., water, sediment and flora.





# 4

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## Materials and methods

This chapter deals with the methodologies adopted for carrying out the research. It starts with the research design, then the description of the study area and the various methods adopted to conduct the investigation.

### 4.1. Design of research

In order to fully understand the limnological aspects of a wetland ecosystem, the research was carried out in different phases, details of which are summarized below. The work demanded a systematic investigation, and therefore, needed an experimental design, depicted in Fig. 4. 1. As the figure suggests, the entire investigation was carried out in three phases.

In the I<sub>st</sub> phase, a reconnaissance survey of the entire study area was carried out based on the land-use-land-cover (LULC) map. Sampling locations were identified using a global positioning system (GPS), and sample collection and analyses were performed.

The II<sub>nd</sub> phase considered the water, sediment, and fish samples to execute different statistical analyses on their respective datasets. This resulted in identifying and apportioning different latent pollution sources, assessing water and sediment quality, bioavailability fraction of heavy metals, and finally, the health risks associated with these three components.

Finally, the III<sub>rd</sub> phase integrated the water, sediment and water hyacinth samples' dataset for understanding the dynamics of nutrient (N and P) distribution in the entire wetland ecosystem. Furthermore, to better understand the nutrient dynamics, a systematic eutrophication-based ecological model was conceptualized and formulated.

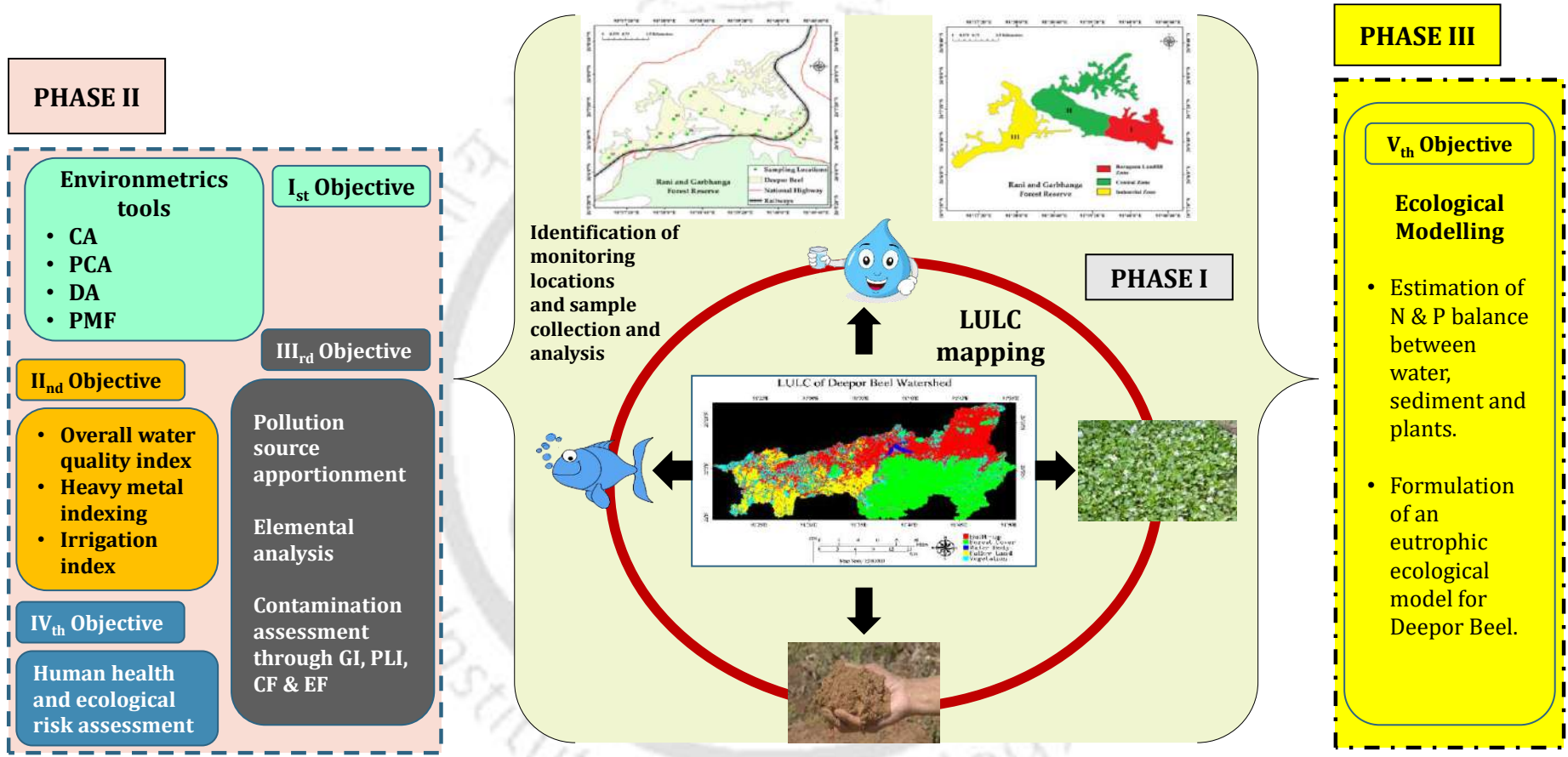


Fig. 4. 1. Design of research.

## 4.2. Study area

Deepor Beel (Fig. 4. 2) lies within the coordinates of 26°06'N to 26°09'N and 91°36'E to 91°41'E and at an elevation of 53m above the mean sea level (Bhattacharyya & Kapil 2010), existing in a former channel that connects the river Brahmaputra with the Sola Beel and the swampy areas of Pandu (MoEF 2008). Located on the mighty Brahmaputra river's southern banks, it is surrounded by National Highway No. 37 on the North, Dakhin Jalukbari, Tetelia and Paschim Boragaon on the East, Rani-Garbhanga Reserve Forest, Chakardew Hill and Chilla Hill on the South-west and Azara and Kahikuchi on the west. There are several educational institutions such as Gauhati University, Assam Engineering College, Assam Science and Technology University, Tata Institute of Social Sciences Guwahati, Government Ayurvedic College and Hospital, Assam Forest School and Girijananda Chowdhury Institute of Management and Technology on the northern side of the Beel. Although various documents describe Deepor Beel as a 40.14 km<sup>2</sup> spread area, it was estimated that the Beel was spread over around a 9.27 km<sup>2</sup> area, out of which only 4.1 km<sup>2</sup> was covered by water bodies (MoEF 2008). The depth of the Beel undergoes considerable seasonal variation, 1.5m to 6m, depending on dry or monsoon season (MoEF 2008).

The Deepor Beel receives its water mainly from the Basistha River, which lies on its South-eastern bank. Basistha River, in turn, receives its water from the Bharulu River through the Morabharulu channel. The Bharulu River runs through Guwahati and was once the source of potable water for the city. However, with time, this tributary of Brahmaputra has been turned into a drainage channel, receiving a significant amount of the city's municipal and other wastes along with stormwater runoff (Mozumder *et al.* 2014). This makes Deepor Beel susceptible to pollution during the monsoon. Moreover, the setup of a municipal solid waste dumpsite at Boragaon near the confluence point of Deepor Beel and the Basistha River (in the wetland's eastern zone) and various small-and-large-scale industries in the wetland's western zone makes it even more susceptible to the deterioration of water quality. In addition, during the lean season, when the water levels are minimum, people from the surrounding villages indulge in excessive unplanned fishing and rice cultivation within the wetland.

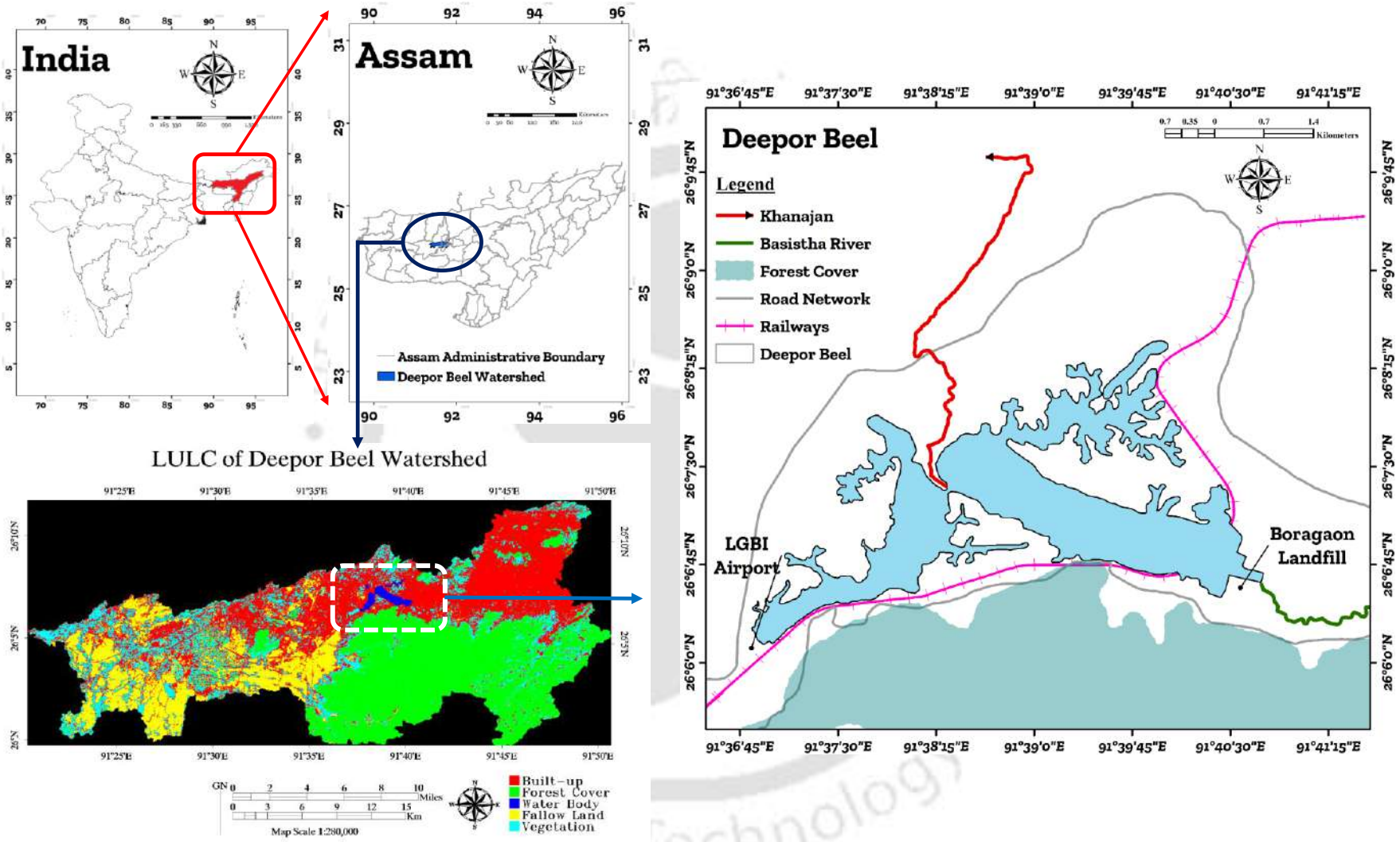


Fig. 4. 2. Study area (Deepor Beel) with LULC map.

#### 4.2.1. Ecological significance

Deepor Beel serves as a stormwater storage basin, aiding in floodwater regulation for Guwahati city during the monsoon season. Surface runoff from the neighbouring hills flows straight into the Beel. Owing to the unique endowment of a vast diversity of flora and fauna, Deepor Beel was declared a wildlife sanctuary in 1989 and included in the Directory of Asian Wetlands (Saikia 2005). Thanks to the congregation of local and migratory birds, the rich avian fauna helped it bag a seat in the list of Important Bird Area (IBA) sites by Birdlife International (MoEF 2008). In 2002, it was declared a Ramsar site (No. 1207) as a wetland of international importance for the conservation of global biological diversity and sustaining human life through the ecological and hydrological functions it performs (Bhattacharyya & Kapil 2010). Economically, the Deepor Beel supports about 30% of the 14 surrounding villages through fishing and agriculture (Mozumder *et al.* 2014). Deepor Beel also plays a vital role in balancing the ecological stability of the area. In 2005, dry fish biomass and fish yield in the lake were reported to be about 1.5 to 3.8 g/m<sup>2</sup> and 245 kg/ha, respectively (Saikia 2005). Saikia (2005) also reported nearly 600 hectares of land in the fringe area of Deepor Beel under agricultural practice. Traditionally, Deepor Beel has been used as hunting grounds for various animals, boating, sightseeing, picnic etc.

#### 4.2.2. Land-use-land-cover of Deepor Beel

Fig. 4. 2 shows the LULC mapping of the Deepor Beel's watershed, delineated through ArcGIS - ArcMap (v. 10.2) and created through ENVI (v. 4.7). It was seen that the entire wetland has been surrounded by heavy built-up on all sides, except the southern part, which is covered by the Rani and Garbhanga forest reserve. On the north-eastern part of the wetland lies the village of Tetelia, which spreads out up to NH-37 on the east. Tribal villages like Pamohi and Mikirpara lie on the southern fringe of the wetland. The villagers in these places grow boro-paddy planted during the winter season (December to January) and harvested in the pre-monsoon period of April to May. As already mentioned, numerous public institutions are located on the north and north-eastern side of the wetland. In addition to these, several industries have also come up in the southern and south-western fringes. The presence of industries within the wetland's periphery threaten the ecological structure as the effluent from these industries, partially treated or untreated, ultimately fall into the wetland (MoEF 2008).

The NH-37 surrounds the east and northeast wetland and a PWD road along the Rani-Garbhanga Reserve Forest's northern fringes on the south. The Assam Engineering College Road lies on the north, and the Dharapur-Kahikuchi section of the NH-37 is located on the west. There are also many brick kilns on the northern side of the wetland and a garbage

dumping ground on the eastern side in Boragaon, abutting the wetland margins. According to the reports submitted by the MoEF (2008), the Boragaon Dumpsite presence further exposes the wetland to environmental pollution as there is every possibility of leaching into it during the monsoon season. In fact, as per the C&AG (2012), the location of the Boragaon Dumpsite violates several prescribed parameters stipulated by the Central Public Health and Environmental Engineering Organisation (CPHEEO) as given in Table 4. 1. Despite such non-compliance, the SWM project, which came into existence in 2006, continues to exist to date.

**Table 4. 1.** Non-compliance of Boragaon dumpsite (SWM project) with CPHEEO criteria (C&AG 2012).

<b>Criteria of Project</b>		
<b>(Location of)</b>	<b>As per CPHEEO norms</b>	<b>Violation of norms</b>
River/Stream	The project site should be 100 m away from any river/stream.	A small stream passes through the site.
Flood Plain	No landfill within a 100-year flood plain.	Landfill site is within flood plain.
Wetlands	No land fill within wetland.	Landfill site is in wetland.
Ground Water table	Ground water table to be more than 2 m.	Ground water table is at the ground level.
Airport	No land fill within 20 km.	Project site is within 10 km of an airport.

Over the years, many railway tracks have come up near the wetland that has dissected it into a number of small pockets. The laying of the railway track and the reclamation of the area outside the track have contributed to the wetland's shrinkage (MoEF 2008).

#### **4.2.3. Biodiversity of Deepor Beel**

Deepor Beel is reported as one of the richest wetland ecosystems of Assam. It supports around 232 species of birds, 24 species of mammals, 61 species of fish, 32 species of reptiles and 11 amphibian species (Saikia *et al.* 2014). The lake's undulating bottom surface provides a unique balance of shallow and deep-water depths across the lake, providing excellent conditions for the sustenance of a large variety of plants and animals. Moreover, the presence of Rani-Garbhanga Reserve Hills in the adjoining area provides a suitable habitat for many endangered and threatened animals. Deepor Beel's waters support a wide variety of habitats throughout the year due to the water regime's seasonal changes. When the flood level rises in the river Brahmaputra during the monsoon season, water enters the wetland through the Basistha River, raising its water level. During this period, large parts of the wetland are covered by aquatic vegetation like the water hyacinths, aquatic grasses, water lilies and other sub-

merged, emergent and floating vegetation. The highland areas, which are completely dry during the winter, are also covered by aquatic and semiaquatic vegetation. As the monsoon recedes, the water level in the wetland goes down, exposing significant parts of the submerged land for the habitats of migratory waterfowl, residential waterfowl and terrestrial avifauna. The wetland also supports a wide variety of lizard species. Various species of flora and fauna within the same ecosystem make the energy transformation system and food web very complex (Saikia *et al.* 2014). Phytoplankton plays a significant role among the lowest levels of the producers in the Deepor Beel ecosystem. The seasonal fluctuations of the water regime also affect the diversity and abundance of the phytoplankton. According to Saikia (2005), there are 18 genera of phytoplankton from the core area of Deepor Beel alone. The available phytoplankton species were *Volvox sp.*, *Anacystis sp.*, *Oscillatoria sp.*, *Spirogyra sp.*, *Diatom sp.*, *Selenastrum sp.*, *Microcystis sp.*, *Anabaena sp.*, *Zygnema sp.*, *Closterium sp.*, *Hydrodictyon sp.*, *Tribonema sp.*, *Chlorlla sp.*, *Navicula sp.*, *Melosira sp.*, and *Synedra sp.* etc. (Sharma 2011). The phytoplankton population blooms majorly during the winter season. The summer season typically records low phytoplankton population density, while pre-monsoon and post-monsoon record relatively higher population density (Chetry 1999). Free-floating, emergent and submerged aquatic macrophytes are also abundantly found in Deepor Beel. The free-floating plants such as *Eicchornia crassipes*, *Azolla pinnate*, *Pistia stratiotes*, *Lemna minor*, *Lemna major*, *Spirodela polkyrrhiza* exist throughout the year and rapidly multiply during the summer season. The emergent vegetation includes *Trapa bispinosa*, *Utricularia flexuosa*, *Eleocharis pan-taginea*, *Nelumbo nucifera*, *N. lotus*, *Nymphaea alba*, *N. rubra*, *Sagittaria sagitifolia*, *Euryale ferox*, *Ipomea reptans*, *Oelia alismoides*, *Marsilia minuta*, *Limnophilia aquatic* and *Monochoria leaqinolis*. The submerged plants dominate the Deepor Beel habitat. The foremost are the *Potamogeton crispum*, *Valisnaria spiralis*, *Hydrilla verticillata*, *Najas foveolata*, *Paspalum serobiculatum*, *Halophila ovata*, *H. Beccari* and *Ruppia maritima*. The other cultivated and non-cultivated plants species available in the wetland are *Alium cepa*, *Pisum sativum*, *Brassica juncia*, *B. rugosa*, *Beta vulgaris*, *Momordia charantia*, *Ducus carrota* and *Triticum aestivum*. The weeds found in the wetland, are *Eupatorium odoratum*, *Achyranthus aspera*, *Cyperus esculonsis*, *Pharagmites karka*, *Imperata cylindrica*, *Vitax trifolia*, *Accum basilium*, *Saccharum spontaneum*, *Arundo donax*, *Lentena caamera*, etc. (Saikia & Bhattacharjee 1987).

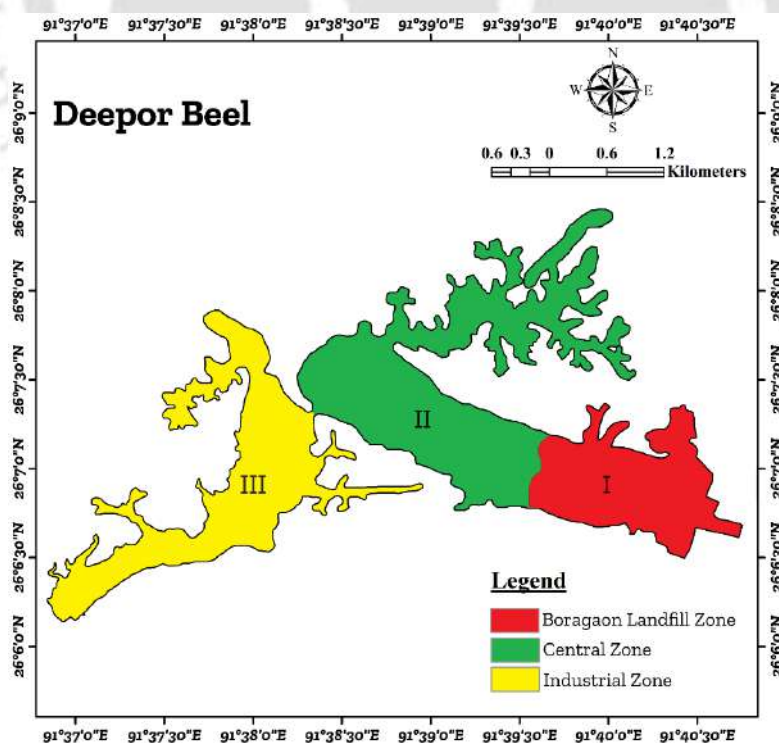
### 4.3. Phase I: Sampling strategy and data acquisition

Analytical monitoring was carried out to determine the health status of Deepor Beel. For this purpose, water, sediment, flora and fauna samples were collected. For floral samples, water hyacinth (*Eicchornia crassipes*) was considered. This is because water hyacinth (*Eicchornia crassipes*) was the dominant species among plants in the wetland. Similarly, three indigenous

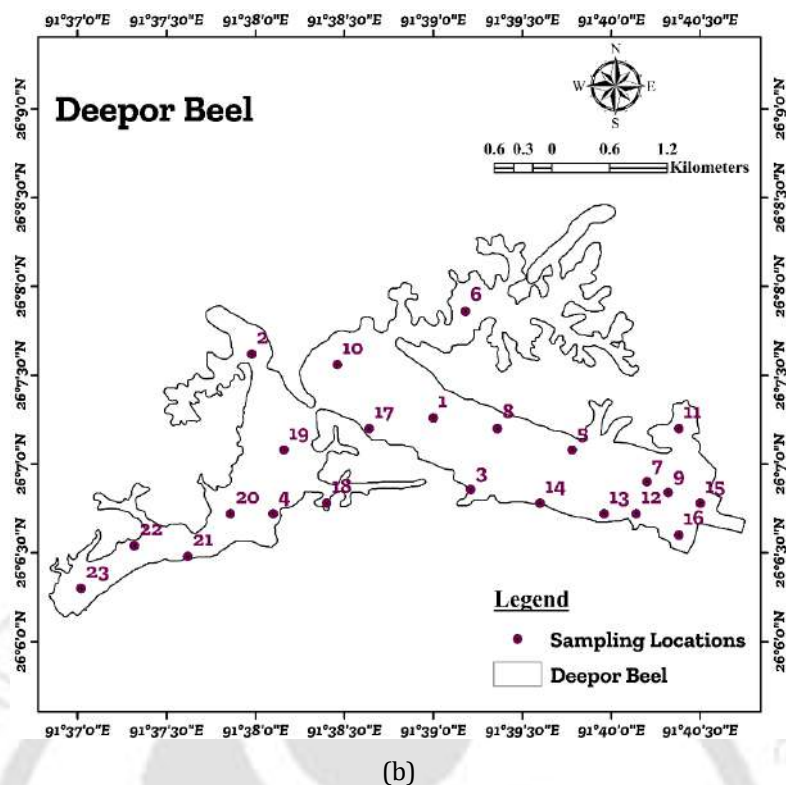
fish species, namely, *Notopterus notopterus*, *Clarias batrachus*, and *Channa striata*, were considered for the sampling and analyses. These three species were considered due to their extensive use in the diet of the local population. *N. notopterus* belongs to the *Notopteridae* family and *Osteoglossiformes* order, whereas *C. batrachus* and *C. striata* belong to *Clariidae* and *Channidae* families with *Siluriformes* and *Anabantiformes* orders, respectively.

For the collection of water and sediment samples, 23 monitoring locations were finalized from the reconnaissance survey, whereas, for the collection of water hyacinth and fish samples, the entire wetland was divided into three zones, based on the proximity of the probable pollution sources, as shown in Fig. 4. 3.

Zone I is located to the south-eastern part of the wetland and adjacent to the landfill site; Zone II lies in the middle, closer to the agricultural fields and Zone III to the South-western part where most industries are located. Three sites from each zone were selected for fish and water hyacinth samples collection; sites 11, 14, and 16 for zone I; 6, 8, and 10 for zone II and 19, 20, and 23 for zone III. Water, sediment and water hyacinth samples were collected from October 2017 to February 2019 (monthly). The water samples were collected from a depth of 30 cm below the water surface. The fish samples were collected in three months, i.e., March 2018, July 2018, and October 2018 (representing pre-monsoon, monsoon and post-monsoon periods, respectively).



(a)



**Fig. 4. 3.** Sampling strategy adopted for (a) water and sediment samples collection, and (b) water hyacinth and fish samples collection.

#### 4.3.1. Sample preservation

Containers containing samples were decontaminated following the procedure as per the guidelines laid down in APHA (2012) and Motsara and Roy (2008):

- The sampling bottles were scrubbed with a brush and laboratory-grade detergent, followed by rinsing with tap water until detergent on the bottles and caps was removed entirely. Finally, the sampling bottles were rinsed with deionized water.
- Bottle and cap were allowed to dry in clean air. In case of probable high concentration of a measured value, samples were diluted using deionized water to accurate proportions for proper evaluation of the measured value. To minimize the changes in the samples, chemically or biologically, samples were kept in an icebox during the transfer from the sampling sites to the laboratory and later in the refrigerator when the analysis was not performed immediately after the sampling process.

Details of any specific sample preservation processes taken (if any) are provided explicitly in the respective objectives explained in later sections.

### 4.3.2. Analytical procedures

Detailed analytical procedures for water, sediment, water hyacinth, and fish samples are provided in the subsequent sub-sections. Irrespective of any ecosystem component, all analyses were performed in triplicates under controlled laboratory supervision.

#### ▪ *Water samples*

Two pre-cleaned 1L HDPE plastic bottles were considered for the collection from each point; one was utilized for heavy metal analyses; thus, it was acidified with concentrated  $\text{HNO}_3$  to render the pH below 2 to avoid any precipitation, and the other was non-acidified, which was utilized for various physico-chemical parameters. Specific parameters such as pH and DO were analyzed at the earliest (within 24 hours) after sampling was completed, and the remaining samples were kept in a refrigerator at  $4^\circ\text{C}$  till further analyses of the remaining parameters were carried out. A quality control procedure was maintained throughout. Standard solutions and reagent blanks were prepared under controlled laboratory conditions to calibrate instruments prior to any analyses.

**Table 4. 2.** Different water quality parameters analyzed in the research, their units of measurement and make and model of the instruments used.

Parameters	Units of measurement	Analytical method [Make and model]
DO	mg L <sup>-1</sup>	Winkler's method
pH	pH units	Digital pH meter [Systronics - $\mu$ pH system 361]
EC	$\mu\text{S cm}^{-1}$	Digital Conductivity meter [VSI-04-Deluxe]
Turbidity	NTU	Nephelometric Turbidimeter [Systronics]
TA	mg L <sup>-1</sup> as $\text{CaCO}_3$	APHA titrimetric method
TH	mg L <sup>-1</sup> as $\text{CaCO}_3$	APHA titrimetric method
BOD <sub>5</sub>	mg L <sup>-1</sup>	5-day BOD test
COD	mg L <sup>-1</sup>	Closed Reflux, Titrimetric Method
TDS	mg L <sup>-1</sup>	Oven Drying at $103\text{-}105^\circ\text{C}$
TSS	mg L <sup>-1</sup>	
F <sup>-</sup>	mg L <sup>-1</sup>	Ion Chromatograph (IC) [792 Basic IC – Metrohm]
Cl <sup>-</sup>	mg L <sup>-1</sup>	
NO <sub>3</sub> <sup>-</sup>	mg L <sup>-1</sup>	
PO <sub>4</sub> <sup>3-</sup>	mg L <sup>-1</sup>	
SO <sub>4</sub> <sup>2-</sup>	mg L <sup>-1</sup>	
Na <sup>+</sup>	mg L <sup>-1</sup>	
K <sup>+</sup>	mg L <sup>-1</sup>	Flame Photometer [Systronics]
Ca <sup>2+</sup>	mg L <sup>-1</sup>	

TKN	mg L <sup>-1</sup>	APHA Distillation Method [Pelican - Kelplus Distillation Apparatus]
Mg	mg L <sup>-1</sup>	
Cr	mg L <sup>-1</sup>	
Cd	mg L <sup>-1</sup>	
Fe	mg L <sup>-1</sup>	Atomic Absorption Spectroscopy (AAS) [Varian Spectra 55B]
Mn	mg L <sup>-1</sup>	
Cu	mg L <sup>-1</sup>	
Pb	mg L <sup>-1</sup>	
NH <sub>3</sub> <sup>-</sup>	mg L <sup>-1</sup>	Semi-automated colorimetric method
OrgN	mg L <sup>-1</sup>	Kjeldahl method

The reagents were prepared following the Standard Methods for the Examination of Water and Wastewater (APHA 2012). Analytical grade chemicals were used for analysis unless otherwise stated. Deionized water was used for dilutions done during the analysis. Standard solutions were prepared by diluting the stock solutions. For analyzing heavy metals, cations and anions, the samples were first subjected to micro-filtration using Whatman (No. 42) filter papers. Sample collection, transportation, preservation, and analyses adhered to Standard Methods (APHA 2012). The water samples were subjected to analyses for 28 different water quality parameters; detailed analytical procedure and the make and model of the instruments used for the analyses are shown in Table 4. 2.

- *Sediment samples*

For the analysis of sediment samples, the samples needed to be first dried completely, subjected to the oven-drying process. They were then sieved through a 2mm Indian Standard (IS) sieve, which helped remove debris. They were then converted to powdered forms after crushing, grinding, and subsequently sieving through a 75 $\mu$  IS sieve. The powdered samples were then subjected to various analyses, i.e., heavy metals and nutrients. For heavy metal analyses, the powdered samples were digested by using a mixture of concentrated HNO<sub>3</sub> (10 mL) + HF (2 mL) + HClO<sub>4</sub> (2 mL) for a duration of 4h at a temperature of 400°C. The digested filtrates were then transferred to respective specimen tubes after diluting them to 100mL using milli-Q water and subsequently filtering them. The analyses for heavy metals were then performed through Atomic Absorption Spectroscopy (AAS). Sediment samples were also analyzed for different forms of nitrogen and phosphorus. Total Kjeldahl nitrogen, ammonia nitrogen and nitrate nitrogen in sediments were measured following the procedures described by Motsara and Roy (2008). While ammonia nitrogen was measured using the indophenol-blue method, nitrate-nitrogen was measured following the phenol-disulphonic acid method. Total phosphorus in soil was measured following the stannous chloride method after acid digestion.

- *Water hyacinth samples*

While collecting water hyacinth samples, care was taken to ensure that they had fewer possible mobility options during sampling because of their location. This ensured that the plants' measured nutrient uptake was a proper representative of the plants' actual nutrient uptake. The collected samples were then analyzed for different forms of nitrogen and phosphorus, the details of which are as follows:

- a. Total Kjeldahl nitrogen

The Kjeldahl method was used to determine the total Kjeldahl nitrogen present in the plant. The air-dried and finely ground samples were digested using potassium sulphate ( $K_2SO_4$ ), copper sulphate ( $CuSO_4$ ) and sulphuric acid ( $H_2SO_4$ ). The digested samples were then distilled using the APHA Distillation method. The distilled samples were then titrated using 0.02N  $H_2SO_4$ . Organic nitrogen was calculated by subtracting ammonia nitrogen from total Kjeldahl nitrogen.

- b. Ammonia nitrogen

Ammonia nitrogen was determined following the Phenate method described in section 4500-NH<sub>3</sub>.F in Standard Methods for the Examination of Water and Wastewater (APHA 2012) after extraction from finely ground air-dried plant samples using potassium chloride (Motsara & Roy 2008).

- c. Nitrate nitrogen

Nitrate nitrogen was determined following the procedure described in section 4500-NO<sub>3</sub>.B of Standard Methods for the Examination of Water and Wastewater (APHA 2012). Similar to the analysis of ammonia nitrogen, the air-dried and finely ground plant samples were first subjected to the potassium chloride extraction method (Motsara & Roy 2008) and subsequently analyzed in the UV spectrophotometer at 220 nm and 275 nm wavelengths.

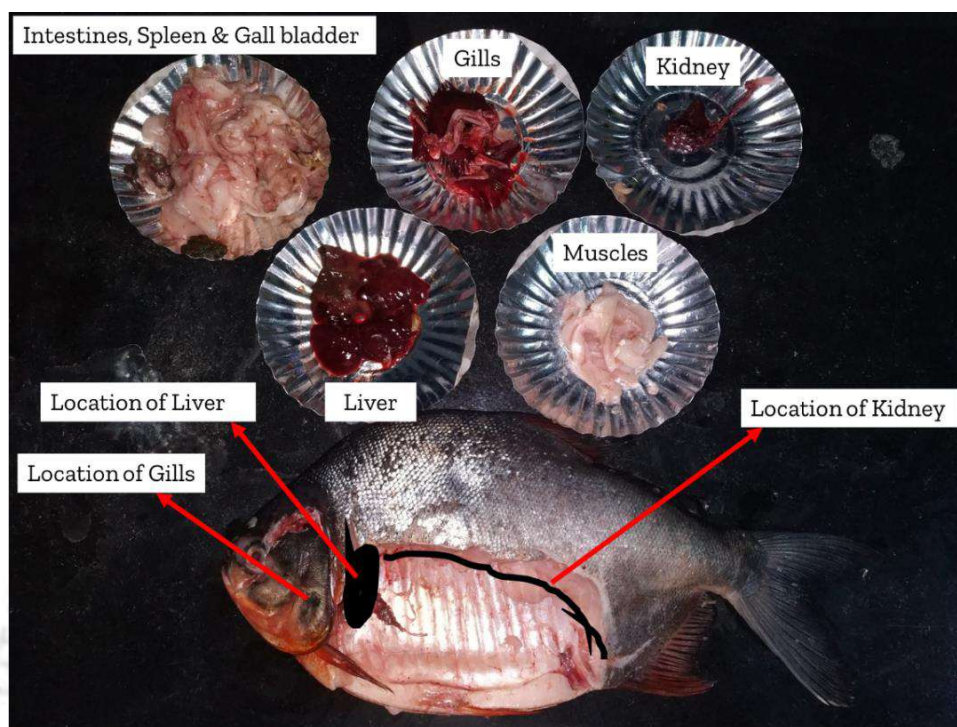
- d. Total phosphorus

Total phosphorus in the plant samples was determined by first digesting the plant samples using a mixed acid of sulphuric acid ( $H_2SO_4$ ) and perchloric acid ( $HClO_4$ ) followed by the stannous chloride method described in section 4500-P.D of the Standard Methods for Examination of Water and Wastewater (APHA 2012).

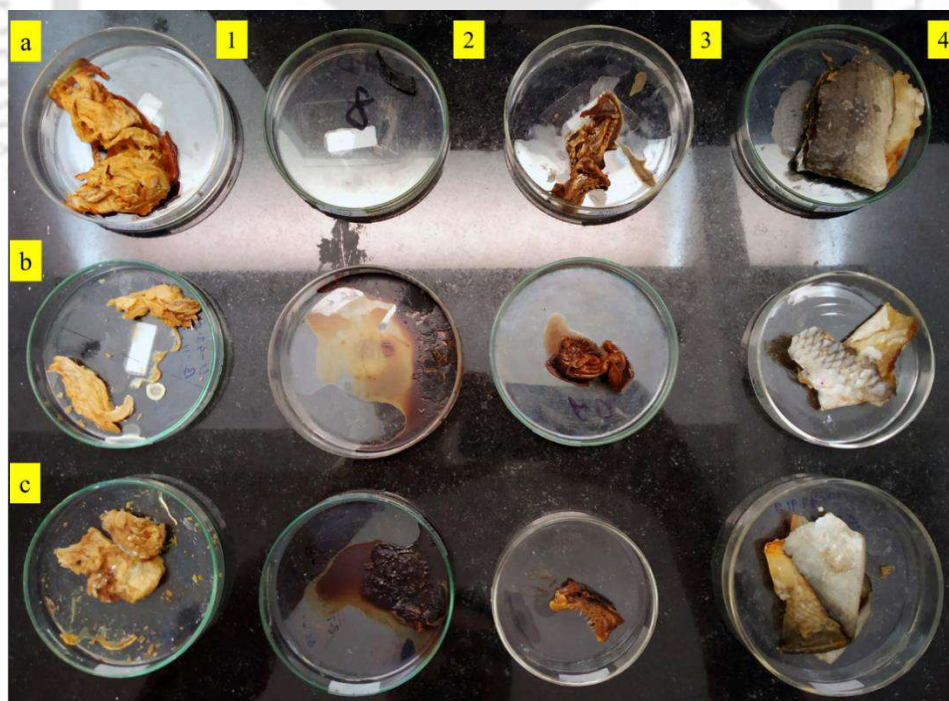
- *Fish samples*

The fish samples collected were washed five times with distilled water, after which they were subjected to dissection using scissors and stainless steel to prevent any external contamination. The muscle, liver, gill, and skin tissues were dissected separately for each sample and

stored in HDPE bags at  $-20^{\circ}\text{C}$  temperature till chemical analyses were performed (Fig. 4. 4). Before the analyses, all the individual tissues of the samples were oven-dried at  $40^{\circ}\text{C}$ .



(a) Fish anatomy (image captured during the dissection process)



(b) Samples after dissection and oven-drying

**Fig. 4. 4.** Dissected and oven-dried fish parts specimens of (a) *N. notopterus* (b) *C. batrachus* and (c) *C. striata* species. 1, 2, 3, and 4 indicate muscle, liver, gills and skin, respectively.

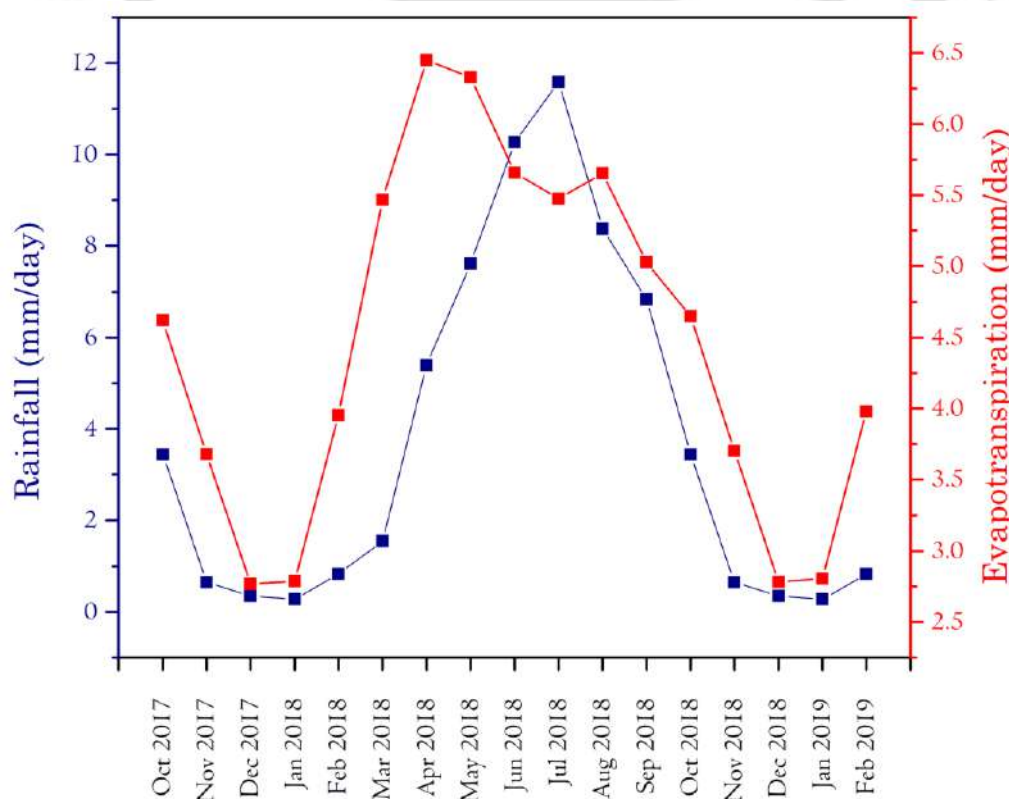
Furthermore, they were subjected to grinding and crushing, followed by passing the samples through a 150 $\mu$ m IS sieve to obtain homogeneity. 0.2g of each sample was considered for the acid digestion process (with ultra-pure nitric acid of 70% purity) for 35 minutes at 150°C. The final filtrate from each sample comprised some oil and fat content, removed through the solvent extraction process.

#### 4.3.3. Additional data acquired

For the development of the model, different data relating to Deepor Beel such as rainfall, evaporation, discharge in Basistha River, the productivity of water hyacinth, nutrients concentration in the inflowing water and depth of water in the lake has been collected either from literature or field measurement and the same has been reported here.

##### I. Rainfall data

The monthly mean rainfall in Guwahati was calculated for a period of 30 years (1971-2000) (Jaswal *et al.* 2008; Verma *et al.* 2012). An annual rainfall trend-line was established using the annual rainfall data to predict the rainfall in 2017, 2018 and 2019 (Fig. 4. 5). The monthly mean rainfall for these years was then calculated based on the relative percentage of monthly mean rainfall given by Verma *et al.* (2012).



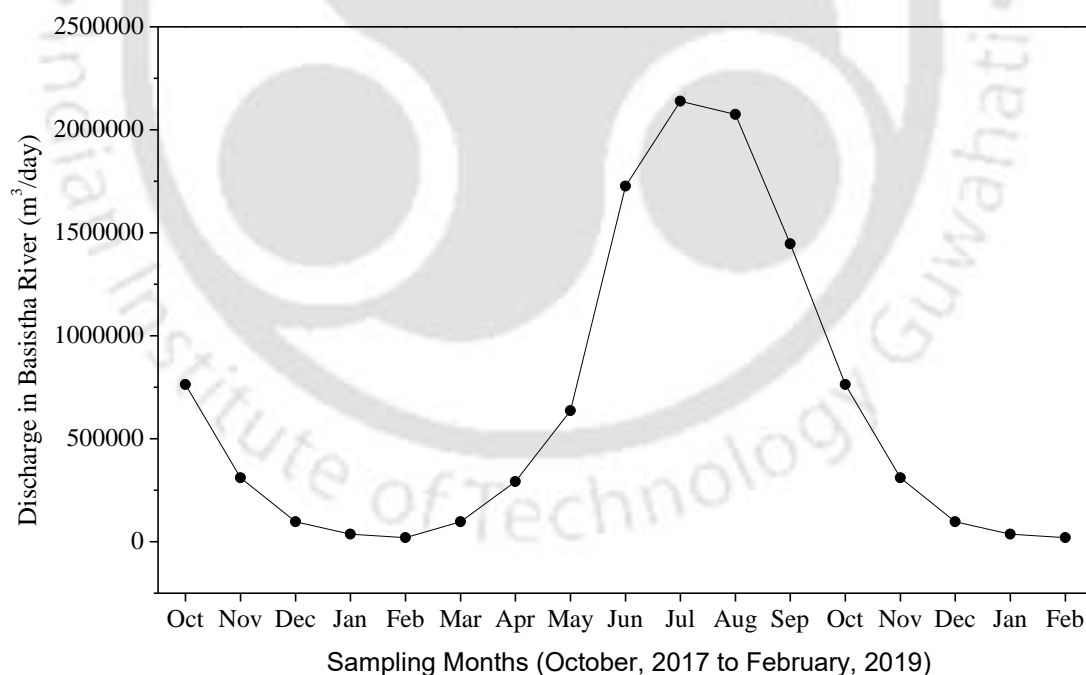
**Fig. 4. 5.** Rainfall and evapotranspiration data for Guwahati city.

## II. Evaporation data

Jaswal *et al.* (2008) and Verma *et al.* (2012) had also given the annual potential evapotranspiration data and monthly mean potential evapotranspiration data, respectively, in Guwahati for the same period of 30 years. Similar to the process adopted for rainfall data, an annual potential evapotranspiration trend-line was established to predict the potential evapotranspiration for 2017, 2018 and 2019. The monthly mean potential evapotranspiration for these years was subsequently calculated based on the relative percentage of monthly mean potential evapotranspiration given by Verma *et al.* (2012) (Fig. 4. 5). The actual evapotranspiration in Guwahati is considered equal to potential evapotranspiration as Deepor Beel can be regarded as an infinite water source.

## III. Discharge in Basistha River

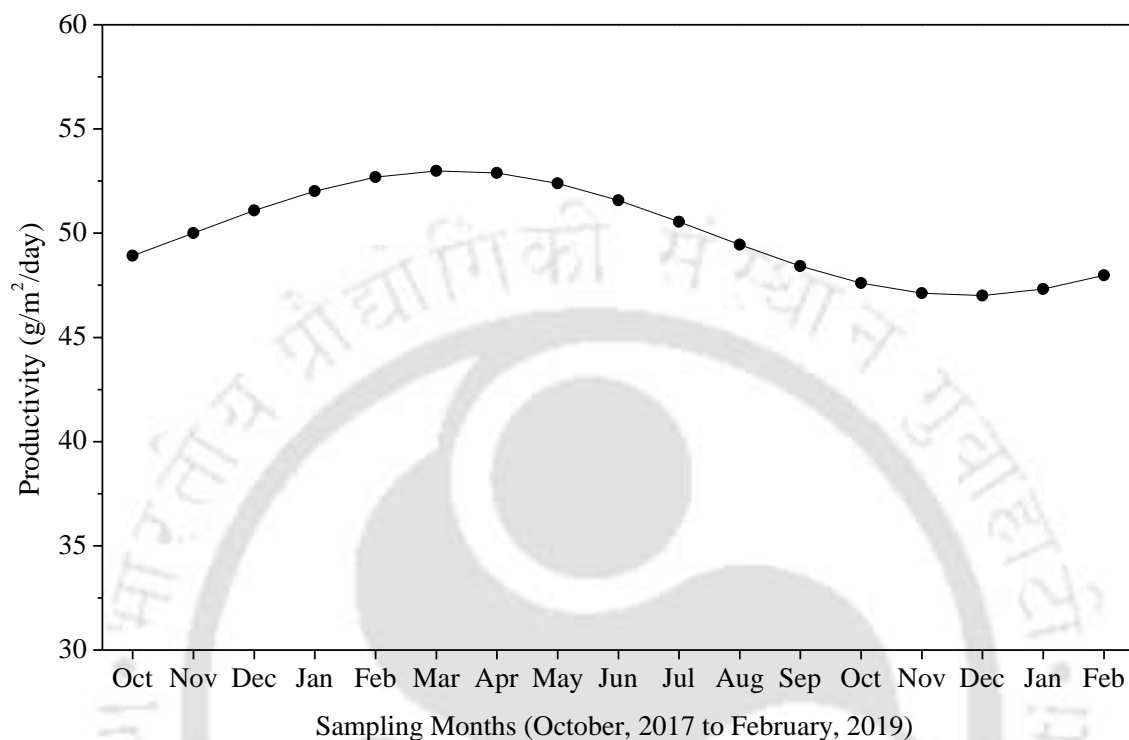
The monthly mean discharge in the Basistha River for the year 2018 has been interpolated and averaged from the SWAT (Soil and Water Assessment Tool) models used by Saharia and Sarma (2018) to predict the monthly mean discharge in the river for periods of 2046-2064 and 2081-2100. The monthly mean discharge in Basistha River in 2017 and 2019 were assumed from the interpolated data for the year 2018 (Fig. 4. 6).



**Fig. 4. 6.** Discharge in Basistha River over the sampling period (Oct 2017 to Feb 2019).

#### IV. Productivity of water hyacinth

The productivity of water hyacinth growing over Deepor Beel was measured in the month of December 2017, and the same has been reported in terms of  $\text{g m}^{-2} \text{day}^{-1}$  of dry mass (Fig. 4. 7).



**Fig. 4. 7.** Productivity of water hyacinth (Reddy and Tucker (1983)).

#### V. Nutrient concentration in the inflowing water to Deepor Beel

Water samples were collected from the mouth of the Basistha River during each sampling and analyzed for different forms of nitrogen and phosphorus used in the model. The monthly variation of different nutrients such as organic nitrogen, ammonia nitrogen, nitrate nitrogen and total phosphorus in the inflowing water of Basistha River is shown in Fig. 4. 8. Nutrients enter the river from various sources such as surface runoff, base-flow, and point sources along the river's stretch. As the Basistha River flows through the heart of the Guwahati, receiving untreated domestic wastewater all along the route, it is expected to have high nutrient concentrations.

#### VI. Water depth in Deepor Beel

The depth of water in Deepor Beel was measured approximately at all the sampling points for the entire sampling period (Fig. 4. 9). The average depth of Deepor Beel showed a wide variation throughout the sampling period. When the region sparsely receives rainfall during the winter season, the river's depth drastically decreases to as low as 34 cm.

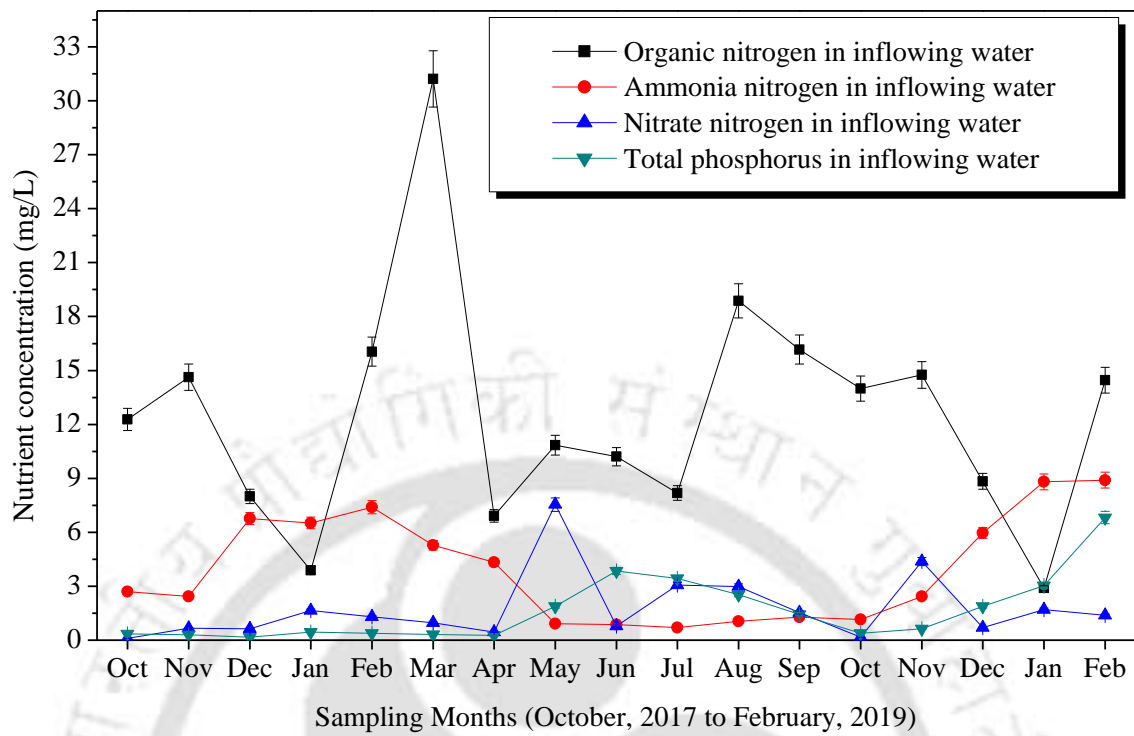


Fig. 4. 8. Monthly variation of different nutrients concentration in the inflowing water to Deepor Beel.

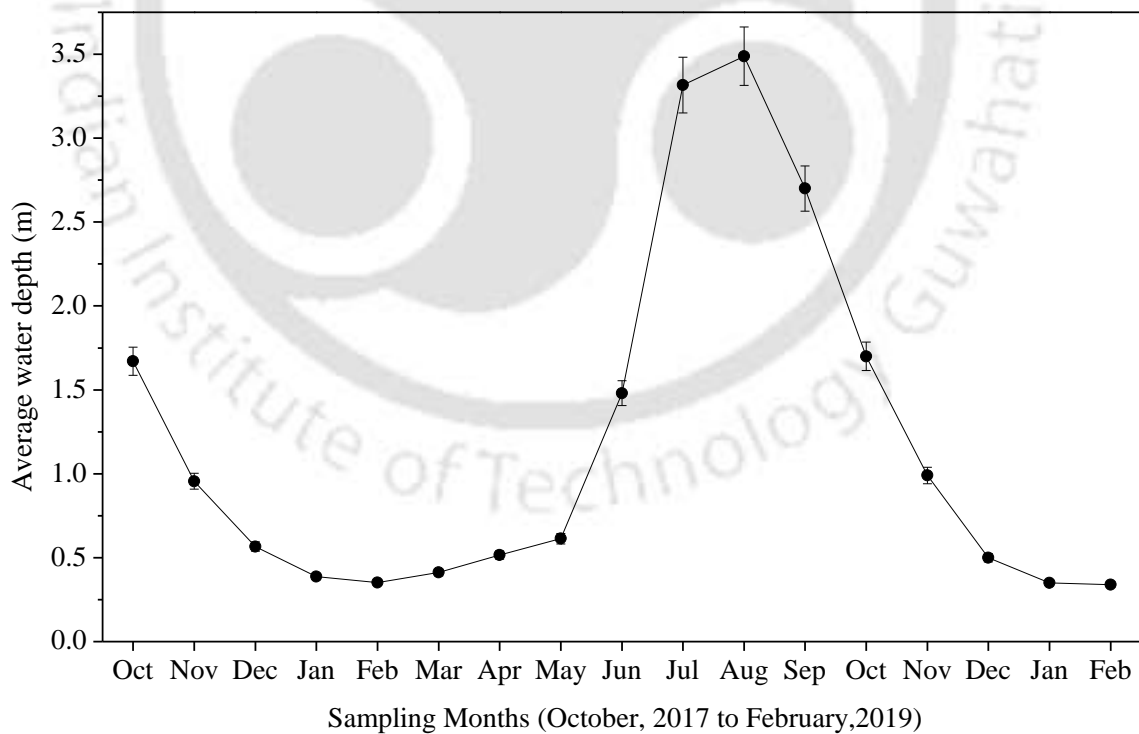


Fig. 4. 9. Average water depth in Deepor Beel.

The subsequent sections are aimed at providing detailed methodologies pertaining to each objective.

#### 4.4. Phase II; I<sup>st</sup> Objective: Application of Environmetrics tools for geochemistry, water quality assessment and apportionment of pollution sources

The present study uses four Environmetrics tools; hierarchical cluster analysis (HCA), discriminant analysis (DA), principal component analysis (PCA), and positive matrix factorization (PMF) for the assessment of water quality and geochemistry of Deepor Beel, Assam, India.

##### 4.4.1. Hierarchical Cluster analysis

The hierarchical agglomerative clustering technique is a simple algorithm for partitioning the datasets into groups (Singh *et al.* 2004; Shrestha & Kazama 2007). Each dataset is first assumed to be a unique cluster. Each cluster is then joined step-by-step depending on their proximity to each other until a stage is arrived at when all the datasets are placed under a single large cluster. The fundamental algorithm for hierarchical agglomerative clustering depends on large inter-cluster and low intra-cluster variance. The basic steps involved in the clustering process has been explained below.

##### Step 1: Computation of distances between individual data points

The matrix obtained is called the distance matrix, which provides the unit of distance between each dataset (Eq. 4. 1). It is always a lower triangular matrix ( $m \times m$ ), with zero diagonal elements, which is quite apparent.

$$\begin{array}{c|cccccc}
 & P_1 & P_2 & P_3 & P_{m-1} & P_m \\
 \hline
 P_1 & 0 & & & & \\
 P_2 & d_{21} & 0 & & & \\
 P_3 & d_{31} & d_{32} & 0 & & \\
 P_{m-1} & d_{(m-1)1} & d_{(m-1)2} & d_{(m-1)3} & 0 & \\
 P_m & d_{m1} & d_{m2} & d_{m3} & d_{m(m-1)} & 0
 \end{array} \tag{4. 1}$$

##### Step 2: Choosing the minimum value

From the distance matrix, the clusters closest (i.e., the minimum value in the matrix) to each other are categorized under a single cluster (in this case, let us suppose  $d_{(m-1)3}$ ) (Eq. 4. 2). A distance matrix is again created for  $(m - 1)$  observations  $\{(m - 1) \times (m - 1)\}$ .

	$P_1$	$P_2$	$[P_3, P_{m-1}]$	$P_m$	
$P_1$	0				
$P_2$	$d_{21}$	0			4. 2
$[P_3, P_{m-1}]$	$d_{a1}$	$d_{a2}$	0		
$P_m$	$d_{m1}$	$d_{m2}$	$d_{ma}$	0	

*Step 3: Repeat step 2*

The clusters closest to each other are further categorized into a single group, and the process is repeated for 'm' times till a single value is obtained, i.e., the entire dataset is grouped into a single cluster.

Several methods exist for the determination of distances between clusters, as well as their linkages. Minimum, maximum, and mean distances between the clusters, together with a single link, complete link, average link, centroids, and Ward's method (Wilks 2011) of clustering are some of the mostly adopted techniques. Each of the linkage methods has its significance. However, the use of Ward's method for agglomeration of clusters using the Squared Euclidean distance measure has been proved to be the most powerful, represented by the Eq. 4. 3 and 4. 4 respectively.

$$TD_{C_1 \cup C_2} = \sum_{x \in C_1 \cup C_2} D(x, \mu_{C_1 \cup C_2})^2 \quad 4. 3$$

$$Distance(P_i, P_j) = \sum_{j=1}^m (Q_{1j} - Q_{2j})^2 \quad 4. 4$$

where  $TD$  denotes the total distance from the centroids,  $x$  denotes the distance between the clusters, and  $\mu$  is the centre of the clusters  $C_1$  and  $C_2$ .  $P_i$  represents the  $i^{th}$  object, and  $Q_{ij}$  is the value of the  $j^{th}$  variable of the  $i^{th}$  object.

The result of hierarchical clustering is usually represented by a dendrogram which provides essential visual insight into the clustering process.

#### 4.4.2. Discriminant analysis

Discriminant analysis is an appropriate technique for the construction of categorically dependent values from statistically classified samples. It necessitates a prior knowledge of the statistical association of objects in any particular cluster or group for understanding which variable belongs to which group or cluster. For statistical analysis of the water quality dataset, the DA technique assists in determining the parameters which are primarily responsible for the discrimination of the clusters by creating a discriminant score (Eq. 4. 5) for each of the individuals of the raw WQ data.

$$\text{Discriminant Score, } Z = I_i + \sum_{j=1}^n w_{ij} P_{ij} \quad 4.5$$

where  $i$  and  $n$  signify the number of groups and parameters used for DA, respectively;  $I$  denote the constant value characteristic to each dataset;  $w_j$  represents the weight factor assigned by DA to each parameter  $P_j$ .

Another essential statistical tool used in DA is Wilk's Lambda (Eq. 4. 6) for determining whether there is a clear distinction between the groups. Wilk's lambda ( $\lambda$ ) represents the ratio of the variances measured within a group to the total variance. Hence, it can be established that lower values of  $\lambda$  are a clear indication that the groups are distinctive, and there is less overlapping between the clusters or groups and vice-versa.

$$\lambda = \frac{\text{Within group variance}}{\text{Total variance}} \quad 4.6$$

DA was carried out on the raw dataset for both standard, as well as stepwise modes. The standard method involves a step-by-step built-up of the discrimination model in which all the variables are assessed and evaluated to determine which one will contribute most to the discrimination between groups individually, at each step. That variable is then incorporated into the model, and the procedure starts again. On the other hand, in stepwise mode, all variables are included in the model initially, after which the variable contributing minimum to the estimation of group membership is eliminated at each step. Thus, only the "important" variables in the model that contribute the most to the discrimination between groups are kept as a successful discriminant function analysis (Astel *et al.* 2009).

#### 4.4.3. Principal component analysis

The principal component analysis (PCA) forms a powerful tool for minimizing the problem of data overfitting to a model, which has led to several confusions due to the inclusion of too many attributes and variables into it. The primary objective of the PCA is to convert a dataset having high dimensionality to a lower dimensionality dataset without actually losing vital information, thus effectively reducing the problem of overfitting (Vega *et al.* 1998; Alberto *et al.* 2001; Chen *et al.* 2007). The reduced set of variables formed are termed principal components (PCs), which depend on the number of attributes the dataset possesses and its dimension. The number of PCs formed for a particular dataset is always less than or at a maximum scale, equal to the number of attributes given for model preparation. Also, the PCs formulated should be independent and orthogonal to each other. The necessary steps involved in the formulation of PCs is described below.

*Step 1: Compute the mean values of all the attributes*

Suppose we have 'm' attributes ( $A_1, A_2, \dots, A_m$ ), the values of those for 'n' sampling locations (variables) ( $S_{11}, \dots, S_{nm}$ ) can be represented as shown in Eq. 4. 7. The first operation performed was the computation of the mean values for all the attributes ( $\bar{A}_1, \bar{A}_2, \bar{A}_3, \dots, \bar{A}_m$ ).

$$\begin{array}{cccccc}
 A_1 & A_2 & A_3 & \dots & A_m & \\
 S_{11} & S_{12} & S_{13} & \dots & S_{1m} & \\
 S_{21} & S_{22} & S_{23} & \dots & S_{2m} & \\
 \vdots & \vdots & \vdots & \ddots & \vdots & \\
 S_{n1} & S_{n2} & S_{n3} & \dots & S_{nm} & \\
 \hline
 \bar{A}_1 & \bar{A}_2 & \bar{A}_3 & \dots & \bar{A}_m & 
 \end{array} \quad 4.7$$

*Step 2: Preparation of the covariance matrix*

The next step includes preparing the covariance matrix for all the attributes (Eq. 4. 8) based on the formula given in Eq. 4. 9. The matrix formulated will be an ( $m \times m$ ) matrix (C).

$$C = \begin{pmatrix}
 cov(A_1, A_1) & cov(A_1, A_2) & cov(A_1, A_3) & \dots & cov(A_1, A_m) \\
 cov(A_2, A_1) & cov(A_2, A_2) & cov(A_2, A_3) & \dots & cov(A_2, A_m) \\
 cov(A_3, A_1) & cov(A_3, A_2) & cov(A_3, A_3) & \dots & cov(A_3, A_m) \\
 \vdots & \vdots & \vdots & \ddots & \vdots \\
 cov(A_m, A_1) & cov(A_m, A_2) & cov(A_m, A_3) & \dots & cov(A_m, A_m)
 \end{pmatrix} \quad 4.8$$

where,

$$cov(A_x, A_y) = \sum_{i=1}^m \frac{(x_i - \bar{x})(y_i - \bar{y})}{m - 1} \quad 4.9$$

*Step 3: Determination of Eigenvalues and Eigenvectors*

After the covariance matrix is generated, the eigenvalues and their corresponding eigenvectors are generated using Eq. 4. 10, 4. 11, 4. 12, and 4. 13, respectively.

$$|C - \lambda I| = 0 \quad 4.10$$

where  $I$  is the identity matrix, the size of which depends on the covariance matrix (in this case,  $m \times m$ ).

$$I = \begin{pmatrix}
 1 & 0 & \dots & 0 \\
 0 & 1 & \dots & 0 \\
 \vdots & \vdots & \ddots & \vdots \\
 0 & 0 & \dots & 1
 \end{pmatrix} \quad 4.11$$

Solving Eq. 4. 10, we obtain the values  $\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_m$ . Using these  $\lambda$  values, we compute the eigenvectors by substituting the  $\lambda$ 's as shown;

$$[C - \lambda_{a,a \in (1,m)}] \begin{Bmatrix} X_{11} \\ X_{12} \\ \vdots \\ X_{1n} \end{Bmatrix} = 0 \quad 4.12$$

Eq. 4. 12 will then provide the values for  $\{X_{ij}; (i,j) \in (1,m)\}$ . This will further lead to the formulation of the eigenvector matrix, represented by Eq. 4. 13.

$$\begin{bmatrix} X_{11} & X_{12} & X_{13} & \dots & X_{1m} \\ X_{21} & X_{22} & X_{23} & \dots & X_{2m} \\ X_{31} & X_{32} & X_{33} & \dots & X_{3m} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ X_{m1} & X_{m2} & X_{m3} & \dots & X_{mm} \end{bmatrix} \quad 4.13$$

#### Step 4: Determination of PCs

PCs depend on the eigenvalues of the corresponding attributes. The eigenvalues are first considered in the descending order of their numerical values. The eigenvectors of the corresponding largest eigenvalue become PC-1, and subsequently, other PCs are also determined (the corresponding eigenvectors) based on their descending order of eigenvalues.

Varimax rotation, Keiser-Meyer-Olkin (KMO) (Sahu *et al.* 2013) and Bartlett's sphericity (Dalal *et al.* 2010) were employed for the orthogonal rotation, evaluating the adequacy of sampling and estimating the applicability of PCA to the crude dataset, respectively. Eigenvalues greater than 1 were only considered for accountability of the factor loadings.

#### 4.4.4. Positive matrix factorization analysis

The positive matrix factorization (PMF) is one of the methods for classifying objects using linear algebra (Paatero & Tapper 1994). The preliminary step involved in this method is the representation of document class ( $d_j^T$ ) by suitable vectors  $w_{xj}; x \in (1,m)$ , as given in Eq. 4. 14.

$$d_j^T = [w_{1j}, w_{2j}, w_{3j}, \dots, w_{mj}] \quad 4.14$$

where  $w_{ij}$  indicates the weighted frequency of the  $i^{th}$  item in the  $j^{th}$  class.

Considering a matrix  $A_{m \times n}$ ;  $m$  and  $n$  denote the dependent and independent variables respectively (Eq. 4. 15),

	$d_1$	$d_2$	$d_3$	...	$d_n$
$w_1$					
$w_2$					
$w_3$					
$\vdots$					
$w_n$					

4. 15

The following inferences can be established:

- $A_{m \times n}$  spans a high dimensional space ( $A \in \mathfrak{R}_{m \times n}$ ).
- $A_{m \times n}$  may be sparse.
- This sparse nature may lead to noisy features in further data processing, eventually leading to a poor classification.

The most effective solution for addressing the above inferences is to use an appropriate dimension reduction technique such as the Singular Value Decomposition (SVD). This is the fundamental principle of the PMF technique, which makes use of only the non-negative items in the database of the matrix  $A_{m \times n}$ . Any other item with a negative value is rendered zero (Al-Dabbous & Kumar 2015; Li *et al.* 2015; Liu *et al.* 2015). This technique is based on the principle of factorization of a non-negative matrix having higher dimensionality into two matrices of smaller dimensionalities such that:

$$A_{m \times n} = P_{m \times k} \times H_{k \times n} + E_{m \times n} \quad \{K \ll \min(m, n)\} \quad 4. 16$$

where  $P$ ,  $H$  and  $E$  represent the basis matrix, weight matrix and residual error matrix, respectively.

The original dataset matrix ( $A_{m \times n}$ ) is factorized continuously, with a random initialization value, till optimum  $P$  and  $H$  matrices are obtained to fulfil the ultimate objective of minimization of function  $Q = f(P, H)$ , given by:

$$\text{Minimize } Q\{f(P, H)\} = \frac{1}{2} \|A - PH\|^2 \quad 4. 17$$

Multiple iterations are carried out until  $P$  and  $H$  converge together and stabilize using steps 1-3 as described below.

*Step 1: Initialise P & H*

$P$  and  $H$  are initialized randomly with non-negative values, as shown in Eq. 4. 18.

$$P = rand(m, k)$$

$$H = rand(k, n)$$
4. 18

*Step 2: Update*

P and H are updated using the following equation (Eq. 4. 19).

$$H_{ij} \leftarrow H_{ij} \frac{(P^T A)_{ij}}{(P^T P H)_{ij} + \epsilon}$$

$$P_{ij} \leftarrow P_{ij} \frac{(A H^T)_{ij}}{(P H H^T)_{ij} + \epsilon}$$
4. 19

where error ( $\epsilon$ ) is initialized with a small value in order to avoid division by zero.

*Step 3: Iterate*

Iterations are carried out using step 2 till  $P$  and  $H$  converge with each other and become stable.

The samples collected at the different locations were polled together in a single dataset for PMF application. This approach increases the stability of results assuming that the source profiles are spatially homogeneous (Cesari *et al.* 2016). The resulting input parameters were then classified based on the signal/noise (S/N) ratio for each of the parameters. Based on the S/N ratio, the parameters were classified as Strong ( $S/N > 2$ ), Weak ( $0.2 < S/N < 2$ ) and Bad ( $S/N < 0.2$ ) respectively (Gugamsetty *et al.* 2012).

All the statistical techniques were carried out using various software; Hierarchical clustering, DA (both standard and stepwise) and PCA using IBM-SPSS Statistics (v. 25) and the PMF model was formulated using EPA-PMF (v. 5.0).

## 4.5. Phase II; II<sub>nd</sub> Objective: Indexing approach to assessing water quality depending on end-use of water

As previously discussed in section 2.6, the water quality indexing (WQI) technique is the most effortless and comprehensive manner of determining the water quality of a particular water body. It also discussed the four categories of indices based on the various end-uses of water. The problem associated with the first three types of indices is that these indices are highly site-specific, as the weights assigned for each parameter may not deem suitable to another site or water body as the characteristics of the water bodies change drastically with locations and types. The fourth category, where various mathematical tools, also known as Environmental metrics tools, are employed, are thus becoming more recent advancements in the develop-

ment of WQIs. These indices are devoid of any personal opinions and depend only on the water quality dataset, making them exceptionally convenient (Shrestha & Kazama 2007; Terrado *et al.* 2010).

The most prominent use of mathematical tools can be understood from techniques derived and proposed by several researchers. These techniques include the use of multivariate statistics (Sarkar *et al.* 2007; Reza & Singh 2010; Singh *et al.* 2016; Rakotondrabe *et al.* 2018), artificial neural network (ANN) (Juahir *et al.* 2004; Gazzaz *et al.* 2012; Gazzaz *et al.* 2015), Fuzzy logic (Nasiri *et al.* 2007; Lermontov *et al.* 2009; Yaseen *et al.* 2018), and entropy (Fagbote *et al.* 2014; Gorgij *et al.* 2017a). Out of these, multivariate statistics and entropy weights have gained significant importance over the years, owing to their growing popularity. The multivariate statistical techniques (MSTs), through factor analysis/principal component analysis (FA/PCA), offer considerable ease of understanding of the various pollution sources affecting the water quality. Furthermore, the cluster analysis (CA) technique provides the hidden correlations existing within and between various parameters and sites (Ali *et al.* 2016; Banerjee *et al.* 2016; Khound & Bhattacharyya 2017; Wang *et al.* 2017). This makes MSTs highly influential in the development of WQI. Additionally, researchers worldwide have introduced the concept of information entropy in water quality monitoring studies. The primary use of entropy is aimed at taking into consideration the uncertainty factor in the water quality dataset that remains even after the entire dataset has been subjected to close observations. This introduced the context of probability into the problem (Beamonte *et al.* 2005).

The water of any body is primarily utilized for various purposes, the essential use being drinking. Besides this, use in agriculture and industries remains paramount. Different industries extract water from a source and subject them to treatment based upon their requirements. Hence, the examination of water quality fit for industrial use is usually restricted to the individual industries. The primary need for assessing water quality is thus limited to drinking and irrigation for most researchers worldwide.

With an increase in the global population, global food demand has risen manifold times in the past decades (Mateo-Sagasta *et al.* 2017). The land cover for human settlements has also enhanced, thereby declining forests and agricultural cover. Cumulative implications of these events have significantly impacted food security in many parts of the globe, resulting in the adaptation of newer technologies for improving productivity in limited land available (Janssen *et al.* 2017; Selemani *et al.* 2018). This includes the induction of chemical fertilizers and pesticides. The excessive utilization of these fertilizers, pesticides, herbicides, etc. has marked a substantial threat to the water quality (both surface and sub-surface) (Shah *et al.* 2019). The use of polluted water then causes major crop damage alongside having adverse

health effects on living beings. The water is not only applied to irrigating fields but also consumed for drinking as well. Thus, hydro-geochemical analyses of natural waters for both irrigation and drinking purposes is paramount. This makes monitoring of water quality for a sustainable end use inevitable. Additionally, the heavy metals present in an aquatic body's water column are also rendered harmful due to the heavy metals' capability to bioaccumulate in the natural aquatic food chain, including flora and fauna. The present research thus focuses on employing multivariate statistics and entropy theory for assessing the water quality of Deepor Beel. Water in the wetland is checked for suitability for three purposes; drinking, irrigation and heavy metal contamination to avoid bioaccumulation. Novel indexing methodologies developed and proposed are discussed. Detailed methodologies adopted for examination of the water quality follow in the subsequent sub-sections.

#### 4.5.1. Entropy as a tool for water quality assessment

The use of entropy for water quality assessment is not new. A comprehensive review of the existing literature based on the bibliographic search (published in *Scopus*) in the domain of entropy-based water quality indexing was carried out through a scientometric analysis. The first step of the literature search comprised of inserting the relevant keywords in *Scopus*; **TITLE-ABS-KEY** ("water quality index" **OR** "wqi" **AND** "entropy"). This resulted in a cumulative total of 60 documents. The search was then filtered. As per the scope of the present study, three specific filters were applied; firstly, the search was limited to research articles only, while the conference papers were excluded as they do not provide the same quantum of information as the research articles. Secondly, the documents about studies on *Environmental Science, Earth and Planetary Sciences, Agricultural and Biological Sciences, Engineering, and Social Sciences* were considered as our scope is limited to these areas only. Finally, English as a medium of publication was chosen. Eventually, a total of 47 listed articles, after the three-step filter process, were retrieved (Table 4. 3).

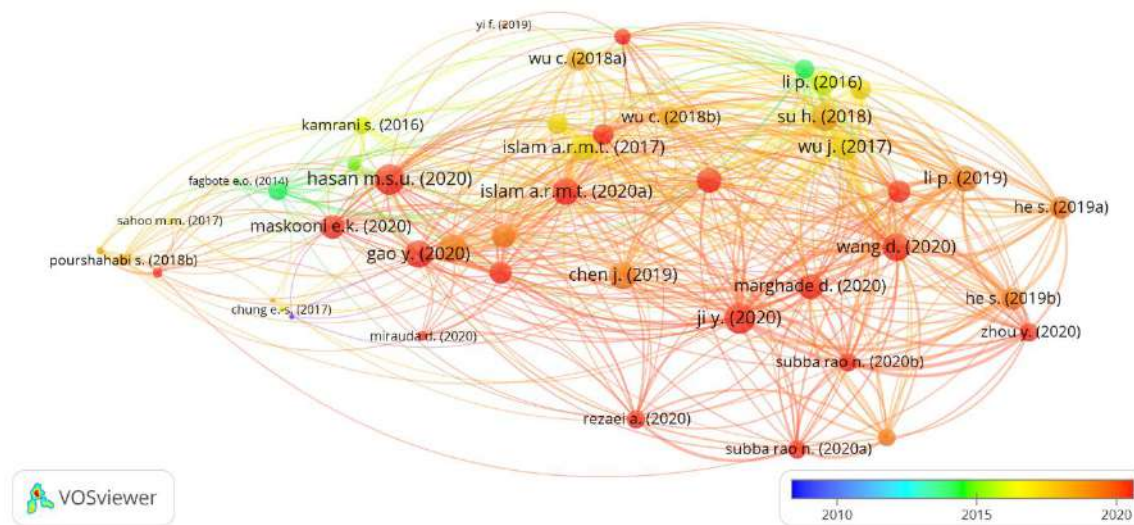
**Table 4. 3.** Quantitative measurements of published articles on entropy weighted WQI research.

Source	Citations
Li <i>et al.</i> (2016)	134
Li <i>et al.</i> (2014a)	132
Amiri <i>et al.</i> (2014)	70
Li <i>et al.</i> (2019)	64
Wu <i>et al.</i> (2017)	43
Wang <i>et al.</i> (2009)	42
Islam <i>et al.</i> (2017)	41
Fagbote <i>et al.</i> (2014)	31

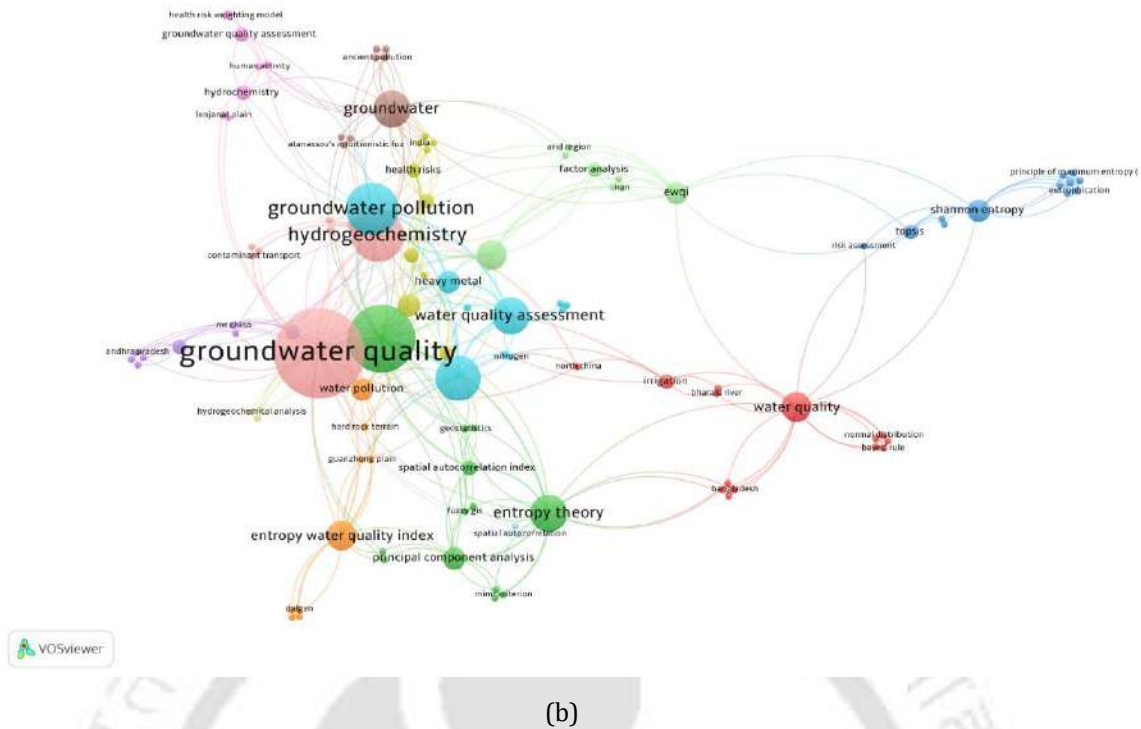
He and Wu (2019)	29
Gorgij <i>et al.</i> (2017b)	27
Wang <i>et al.</i> (2020)	26
Sahoo <i>et al.</i> (2017)	25
Amiri <i>et al.</i> (2015)	22
Su <i>et al.</i> (2017a)	20
Wu <i>et al.</i> (2018a)	17
Chen <i>et al.</i> (2019)	16
Chung <i>et al.</i> (2017)	14
He <i>et al.</i> (2019)	13
Su <i>et al.</i> (2017b)	13
Kamrani <i>et al.</i> (2016)	13
Subba Rao <i>et al.</i> (2020)	11
Pourshahabi <i>et al.</i> (2018b)	10
Ji <i>et al.</i> (2020)	7
Islam <i>et al.</i> (2020a)	7
Zhou <i>et al.</i> (2020)	5
Adimalla <i>et al.</i> (2019)	5
Gao <i>et al.</i> (2020)	4
Rezaei <i>et al.</i> (2020)	4
Pourshahabi <i>et al.</i> (2018a)	4
Islam <i>et al.</i> (2020b)	3
Singh <i>et al.</i> (2019)	3
Egbueri <i>et al.</i> (2020)	2
Maskooni <i>et al.</i> (2020)	2
Xiao <i>et al.</i> (2020)	1
Yi <i>et al.</i> (2019)	1
Lyu <i>et al.</i> (2019)	1
Wu <i>et al.</i> (2018b)	1
Singaraju <i>et al.</i> (2018)	1
Cui <i>et al.</i> (2020)	1
Subba Rao (2020)	1
Hasan and Rai (2020)	0
Singh <i>et al.</i> (2020)	0
Mirauda and Ostoich (2020)	0
Bao <i>et al.</i> (2020)	0
Marghade <i>et al.</i> (2020)	0
Kim <i>et al.</i> (2015)	0
Ghorbani Mooselu <i>et al.</i> (2020)	0

For science-based mapping, *VOSviewer* was utilized. Fig. 4. 10 provides detailed information regarding the published literature and the relevant keywords used in the previous studies. It was observed that the use of information entropy as a tool for indexing water quality is a more recent development, the first use being coined by Wang *et al.* (2009). However, since 2017, more researchers have been interested and involved in this field, and the number of literatures being published has increased significantly. Also, the major keywords identified that have been of primary focus show that most researchers have attempted to implement the concept of entropy in the water quality indexing of groundwater, thereby determining its hydrochemistry (Fig. 4. 10b).

Based on the available literature, it was found that all authors have used the entropy concept as an indexing parameter in a particular manner, which, however, has certain limitations and issues in usage. Thus, the present study primarily focuses on addressing these issues, thereby proposing a novel methodology of employing information entropy as a tool for indexing water quality.



(a)



**Fig. 4. 10.** A schematic of (a) the published works on entropy weighted WQI, and (b) the network of keywords used.

#### 4.5.1.1. Existing methodology of assigning entropy weights and their ambiguities

Assigning entropy weights to each parameter is based on the water quality dataset's randomness and is thus established on the probabilistic approach (Shannon & Weaver 1949). The current use of Shannon entropy as an indexing technique by different researchers around the world is carried out employing the following steps:

*Step 1: Formulation of dataset matrix*

The initial step of the analysis includes formulating the dataset matrix ( $X$ ), given by Eq. 4. 20.

$$X = \begin{bmatrix} X_{11} & X_{12} & X_{13} & \dots & X_{1q} \\ X_{21} & X_{22} & X_{23} & \dots & X_{2q} \\ X_{31} & X_{32} & X_{33} & \dots & X_{3q} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ X_{p1} & X_{p2} & X_{p3} & \dots & X_{pq} \end{bmatrix} \quad 4. 20$$

where  $p\{a \in (1, p)\}$  and  $q\{b \in (1, q)\}$  denote the number of sampling locations and the physico-chemical parameters involved, respectively, thereby making a  $p \times q$  matrix.

*Step 2: Normalization of the dataset matrix*

The next step involves the normalization of the raw water quality dataset matrix. The normalization of the attributes can be divided into two types; Benefit type and Cost type, based on the attribution and contribution of each parameter, as given in Eq. 4. 21.

$$y_{ab} = \begin{cases} \frac{x_{ab} - (x_{ab})_{min}}{(x_{ab})_{max} - (x_{ab})_{min}}, & \text{Benefit type} \\ \frac{(x_{ab})_{max} - x_{ab}}{(x_{ab})_{max} - (x_{ab})_{min}}, & \text{Cost type} \end{cases} \quad 4.21$$

This results in the normalized decision matrix Y, as represented through Eq. 4. 22.

$$Y = \begin{bmatrix} Y_{11} & Y_{12} & Y_{13} & \dots & Y_{1q} \\ Y_{21} & Y_{22} & Y_{23} & \dots & Y_{2q} \\ Y_{31} & Y_{32} & Y_{33} & \dots & Y_{3q} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ Y_{p1} & Y_{p2} & Y_{p3} & \dots & Y_{pq} \end{bmatrix} \quad 4.22$$

### Step 3: Computation of information entropy and entropy weights

The third step comprises the estimation of information entropy  $e_b$ , and subsequently, the entropy weights for each parameter  $w_b$ , as given in Eq. 4. 23 - 4. 25.

$$P_{ab} = \frac{y_{ab}}{\sum_{a=1}^p y_{ab}} \quad 4.23$$

$$e_b = -\frac{1}{\ln p} \sum_{a=1}^p P_{ab} \ln P_{ab} \quad 4.24$$

$$w_b = \frac{1 - e_b}{\sum_{b=1}^q (1 - e_b)} \quad 4.25$$

### Step 4: Estimation of WQI

The final step involves estimating the MEWQI values through a quantitative scale, as described through Eq. 4. 26.

$$WQI = \sum_{b=1}^q w_b \times \left\{ \frac{C_b}{S_b} \times 100 \right\} = \sum_{b=1}^q \left[ \left\{ \frac{1 - e_b}{\sum_{b=1}^q (1 - e_b)} \right\} \times \left\{ \frac{C_b}{S_b} \times 100 \right\} \right] \quad 4.26$$

where the expression  $\left\{ \frac{C_b}{S_b} \times 100 \right\}$  indicates the quantitative scale of the parameters concerned,  $C_b$  and  $S_b$  being the measured and prescribed standard concentrations of a given parameter, respectively.

Based on the above formulations of estimating WQI values, the water quality of a source is classified into five categories, as given in Table 4. 4.

**Table 4. 4.** Category criteria for both existing and proposed novel methodology of entropy-weighted water quality index values.

Existing methodology		Proposed methodology	
EWQI Value	Category	MEWQI Value	Category
< 50	Excellent	< 50	Excellent
50 – 100	Good	50 – 100	Very Good
100 – 150	Moderate	100 – 150	Good
150 – 200	Poor	150 – 200	Fair
> 200	Extremely Poor	200 – 250	Poor
		> 250	Extremely Poor

#### 4.5.1.2. Details of the conflicting factors to the existing assignment of entropy weight-ages for determining WQI

The current methodology suffers from certain limitations in usage, the details of which are explained through the following paradigm.

Let us consider a small water quality dataset matrix  $X$ , given by Eq. 4. 27.

$$X = \begin{bmatrix} 1 & BDL & 8 & 5 & 0.5 \\ 1.2 & 0.005 & 12 & 7 & 12 \\ 0.8 & 10 & 0.01 & 4 & 0.7 \\ 15 & BDL & 14 & 85 & 0.6 \\ 3 & 0.001 & 28 & 3 & 0.7 \end{bmatrix} \quad 4. 27$$

where the rows and columns indicate the sampling locations and different water quality parameters, respectively.

As per the protocol of the existing method, Eq. 4. 28 represents the normalized dataset matrix, based on Eq. 4. 21.

$$y = \begin{bmatrix} 0.0141 & 0.0000 & 0.2855 & 0.0244 & 0.0000 \\ 0.0282 & 0.0005 & 0.4284 & 0.0488 & 1.0000 \\ 0.0000 & 1.0000 & 0.0000 & 0.0122 & 0.0174 \\ 1.0000 & 0.0000 & 0.4998 & 1.0000 & 0.0087 \\ 0.1549 & 0.0001 & 1.0000 & 0.0000 & 0.0174 \end{bmatrix} \quad 4. 28$$

This normalized matrix then leads to the probability matrix  $P$  (Eq. 4. 29), as per Eq. 4. 23.

$$P = \begin{bmatrix} 0.0118 & 0.0000 & 0.1290 & 0.0225 & 0.0000 \\ 0.0235 & 0.0005 & 0.1935 & 0.0449 & 0.9583 \\ 0.0000 & 0.9994 & 0.0000 & 0.0112 & 0.0167 \\ 0.8353 & 0.0000 & 0.2258 & 0.9213 & 0.0083 \\ 0.1294 & 0.0001 & 0.4517 & 0.0000 & 0.0167 \end{bmatrix} \quad 4. 29$$

From this probability matrix, the entropy weights are estimated. The following important observations are made from Eq. 4.27 - 4.29 (BDL is considered as 0).

- a. Firstly, it is observed that the value of  $P_{ab}$  is directly dependent on the observed value of the water quality parameters rather than considering the frequency factor. For example, for the first parameter, the highest probability is obtained for the fourth location, which is the same point where the particular parameter is observed to be the highest. Similar observations can be seen for the second parameter (third location), fourth parameter (fourth location), and fifth parameter (second location). Hence, the probability function, in this case, is a function of the value instead of the frequency.
- b. Secondly, it is seen that the probability values for each sampling location (for a particular parameter) are estimated as the ratio of the observed value in a particular location to the sum of all values at all locations, which is questionable. This is because the probability values do not consider any frequency factor (of parameters adhering to exceeding a standard limit).
- c. Thirdly, the probability values obtained are debatable, considering that they carry huge degrees of certainty with them. Consider, for example, the probability value of parameter 2 at the third location ( $P = 0.9994$ ); it suggests that the observed values of the specific parameter at that location will have a value close to 5 for 99.94% (almost 100%) of the times. Also, some values tend to 0, for example, the first parameter at the third location. This suggests that the values of the first parameter at the third location will have values other than 0.8 for 100% of the times, which is absurd. It is a well-known fact that natural systems are highly dynamic with respect to time and space, thus carrying a huge quantum of uncertainty.

#### 4.5.1.3. Proposed novel methodology of assigning entropy weights

Considering the several limitations, as described above, a detailed methodology of a novel technique addressing all the current issues is proposed. This technique considers a three-dimensional water quality dataset, combining both spatial and temporal water quality variations. They are the sampling locations, water quality parameters, and the number of samplings carried out (or the sampling frequency).

Let  $\alpha$  = Total number of sampling locations

$\beta$  = Total number of water quality parameters, and

$\delta$  = Frequency of sampling carried out measured in a time period (it can be daily, weekly, monthly, yearly, etc. as per the monitoring program<sup>A</sup>)

*Step 1: Preparing a preliminary water quality dataset matrix*

The first step is to prepare a dataset matrix ( $\mathfrak{R}_{m \in (1, \beta)}$ ) for each independent water quality parameter,  $m \in (1, \beta)$ , as given in Eq. 4. 30.

$$\mathfrak{R}_{m \in (1, \beta)} = \begin{bmatrix} \phi_{11} & \phi_{12} & \phi_{13} & \dots & \phi_{1\delta} \\ \phi_{21} & \phi_{22} & \phi_{23} & \dots & \phi_{2\delta} \\ \phi_{31} & \phi_{32} & \phi_{33} & \dots & \phi_{3\delta} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \phi_{\alpha 1} & \phi_{\alpha 2} & \phi_{\alpha 3} & \dots & \phi_{\alpha \delta} \end{bmatrix} \quad 4. 30$$

wherein  $\mathfrak{R}_m$  denotes the water quality dataset matrix for the  $m^{\text{th}}$  parameter and  $\phi_{ij}$  indicates the observed value at the  $i^{\text{th}}$   $\{i \in (1, \alpha)\}$  sampling location of the  $j^{\text{th}}$   $\{j \in (1, \delta)\}$  sampling frequency.

*Step 2: Probability Estimation*

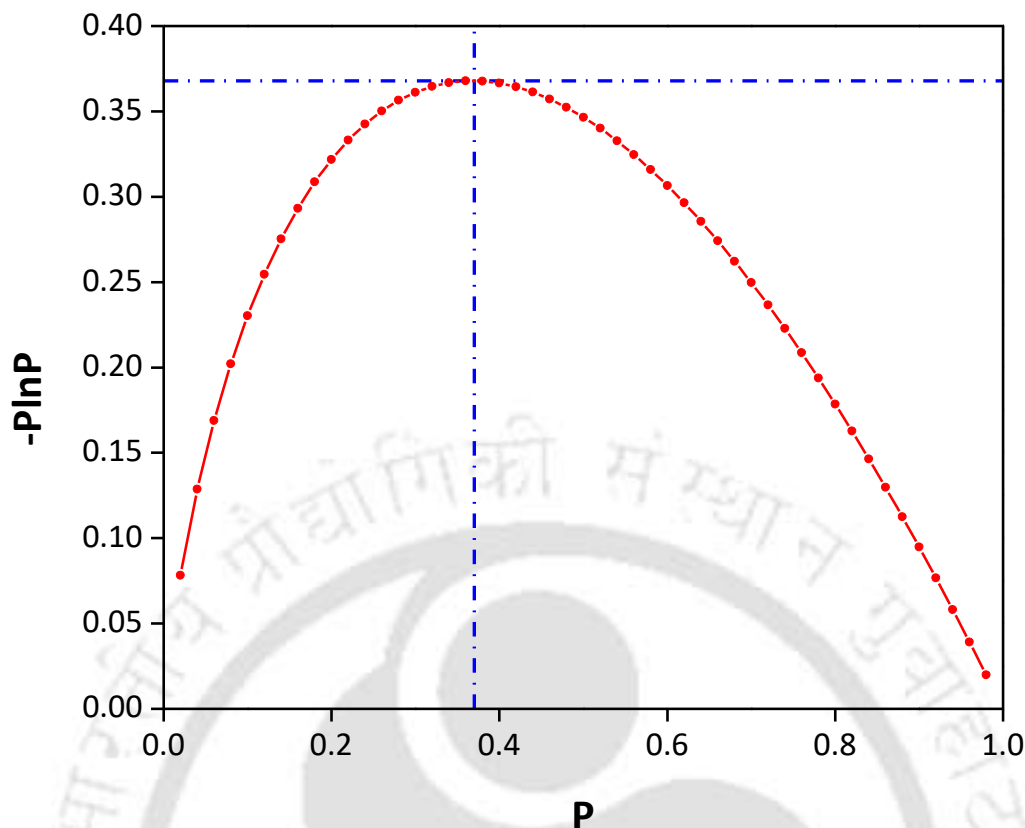
The next step involves estimating the probability, defined by the ratio of the number of occurrences (frequency) of the observed water quality values residing within the permissible limits set by various standards to the total number sampling frequency (Eq. 4. 31).

$$P_\delta = \frac{1}{4} \times \frac{\text{Number of occurrences the observed values adhere to standard limits}}{\text{Total sampling frequency}} \quad 4. 31$$

A factor of 0.25 is included in the estimation of probability because the value of  $-P_\delta \ln P_\delta$  is a natural logarithmic function, attaining the maximum value at  $\frac{1}{e} = \frac{1}{2.718} \cong 0.368$ , after which the curve again follows a decreasing trend (Fig. 4. 11).

The probability value ( $P_\delta$ ) corresponding to the  $-P_\delta \ln P_\delta$  value of 0.368 is  $\cong 0.37$ . Hence, for the sake of easy computations, we introduce a factor of 0.25 so that the  $-P_\delta \ln P_\delta$  is always an increasing function, as the probability values lie between 0 and 0.25.

<sup>A</sup> It is important to note that since the proposed methodology is based on the probabilistic approach, thus, the more the sampling frequency, the better and a more practical picture of the uncertainty, and therefore a more reliable WQI, is obtained.



**Fig. 4. 11.** Curve of  $\{-P \ln P\}$  vs.  $P$ .

*Step 3: Preparing a final water quality dataset matrix*

The matrix  $\mathfrak{R}_{m \in (1, \beta)}$  is then reorganized with respect to sampling locations, wherein each sampling location,  $n \in (1, \alpha)$ , has its independent dataset matrix,  $(\psi_{n \in (1, \alpha)})$ , given by Eq. 4. 32.

$$\psi_{n \in (1, \alpha)} = \begin{bmatrix} \xi_{11} & \xi_{12} & \xi_{13} & \dots & \xi_{1\beta} \\ \xi_{21} & \xi_{22} & \xi_{23} & \dots & \xi_{2\beta} \\ \xi_{31} & \xi_{32} & \xi_{33} & \dots & \xi_{3\beta} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \xi_{\delta 1} & \xi_{\delta 2} & \xi_{\delta 3} & \dots & \xi_{\delta \beta} \end{bmatrix} \quad 4. 32$$

where  $\psi_n$  denotes the water quality dataset matrix for the  $n^{\text{th}}$  sampling location and  $\xi_{uv}$  indicates the observed value of the  $v^{\text{th}}\{v \in (1, \beta)\}$  water quality parameter for the  $u^{\text{th}}\{u \in (1, \delta)\}$  sampling period. Thus, a total of  $\alpha$  number of matrices are formed.

*Step 4: Estimation of information entropy and entropy sub-indices*

For each  $\psi_{n \in (1, \alpha)}$  matrix, from the probability function  $P_\delta$  computed from Eq. 4. 31, corresponding entropy values ( $e_{v; \{v \in (1, \beta)\}}$ ) are estimated for each independent water quality parameter, given by Eq. 4. 33.

$$e_{v;\{v \in (1, \beta)\}} = \{-P_\delta \ln P_\delta\} \quad 4.33$$

In the case of null or zero probability value for some sampling location or water quality parameter, the corresponding  $-P_\delta \ln P_\delta$  value is taken as 0, which is consistent with the limit, described by Eq. 4.34 (Cover 1999).

$$\lim_{p \rightarrow 0^+} p \ln p = 0 \quad 4.34$$

The entropy weights are then computed using Eq. 4.35.

$$w_{v;\{v \in (1, \beta)\}} = \frac{1 - e_v}{\sum_{v=1}^{\beta} (1 - e_v)} \quad 4.35$$

Similar computations are undertaken for all  $\alpha$  sampling locations.

#### Step 5: Estimation of Modified Entropy-weighted Water Quality Index (MEWQI)

The final step of the proposed methodology is estimating MEWQI values, which are computed by Eq. 4.36.

$$MEWQI_\delta = \sum_{v=1}^{\beta} w_v \times \left\{ \frac{C_v}{S_v} \right\} \times 100 = \sum_{v=1}^{\beta} \left[ \left\{ \frac{1 - e_v}{\sum_{v=1}^{\beta} (1 - e_v)} \right\} \times \left\{ \frac{C_v}{S_v} \times 100 \right\} \right] \quad 4.36$$

where,  $MEWQI_\delta$  is the modified entropy water quality index value for the  $\delta^{th}$  period at the  $\alpha^{th}$  sampling location.

The final MEWQI values are ranked into six classes, as mentioned in Table 4.4.

#### 4.5.2. Computation of WQI values employing multivariate statistics

One of the primary problems arising from a significantly large and sophisticated dataset is its interpretability. This results in adopting various statistical tools for extracting valuable information from the dataset. Multivariate statistics, especially cluster and factor analysis, aid in acquiring information from massive datasets without any significant loss of information. Hierarchical cluster analysis (HCA) categorizes variables or cases, depending upon their similarities or variance, while principal component analysis (PCA) (a part of factor analysis) reduces the dataset dimensionality and assigns weights (called factor loadings/component scores). In the present investigation, water quality index (WQI) values are proposed based on multivariate statistics. The following stepwise measures were implemented:

##### Step 1: HCA on the overall WQ dataset

HCA was employed on the mean values of all the parameters (variables) for all 23 sampling locations (cases). This classified all the sampling locations into different clusters based on

high intra-cluster and low inter-cluster similarity. The entire dataset was first normalized through z-transformation before initiating Ward's clustering method through the squared Euclidean measure of interval (Wilks 2011). Each sampling location is initially considered an independent cluster; thereafter, the sampling locations with the closest resemblances regarding the water quality parameters are grouped as a single cluster. This process repeats until all the sampling locations are grouped under one large cluster.

#### *Step 2: PCA on independent clusters*

The clustering process was followed by applying PCA to each independent cluster, thus producing factor loadings/principal component scores (PCs). Keiser-Meyer-Olkin (KMO) criterion (Kaiser 1960) verified the sampling adequacy, whereas the PCA applicability was validated through Bartlett's sphericity test (Dalal *et al.* 2010). The PCs were subsequently rotated through Varimax rotation (Tabachnick *et al.* 2007), such that the varifactors (VFs) are orthogonal and do not correlate with each other. Only factors with eigenvalues greater than one were accounted for determining the factor loadings.

#### *Step 3: Determination of weights/sub-indices for each water quality parameter*

The weights or sub-indices for each water quality parameter were then calculated by computing the product of the relative eigenvalues and relative loading values. The relative eigenvalues and loading values were computed by dividing the corresponding eigenvalue or loading value, obtained through PCA, with the summation of all eigenvalues and loading values, making the overall sum one. This was applied to all parameters for all the clusters. If the PCA resulted in one factor, the relative eigenvalue for the single factor is taken as one, and the relative loading values are computed likewise.

#### *Step 4: Estimation of PCA-WQI*

After estimating the weights of each parameter for all sampling locations, the WQI values were determined using the formula given by Eq. 4. 37.

$$PCA - WQI = \sum_{j=1}^n \left\{ w_j \times \left( \frac{O_j}{S_j} \right) \right\} \times 100 \quad 4. 37$$

where  $w_j$ ,  $O_j$  and  $S_j$  indicate the weight assigned, observed and the standard reference value of the  $j^{th}$  parameter, respectively.

Standard reference values were considered taking into account the suitability of water for respective end-use. For estimating WQI values for domestic use and heavy metal contamination, Indian Standard IS:10500 (2012) was utilized. On the other hand, for assessing the irrigation suitability, FAO (Ayers & Westcot 1985) and WHO (WHO 2011) guidelines were

adopted. Water quality classification for irrigation suitability is shown in Table 4. 5, while water quality classification for heavy metal contamination assessment and domestic use is shown in Table 4. 6.

**Table 4. 5.** Classification of water quality for irrigation suitability.

IWQI Range	Classification
0-25	Excellent
> 25-50	Very Good
> 50-75	Average
> 75	Poor

**Table 4. 6.** Water quality classification for domestic use and assessing heavy metal contamination.

Range of WQI values	Category
WQI < 50	Excellent
50 ≤ WQI < 100	Good
100 ≤ WQI < 200	Poor
200 ≤ WQI < 300	Very Poor
WQI ≥ 300	Unsuitable for usage

#### 4.5.3. Sensitivity Assay

Sensitivity analysis is usually conducted to test a model's reliability and the impact of a particular input parameter on the assessed results. The larger the sensitivity, the more unstable are the assessed outputs (Lodwick *et al.* 1990; Gao *et al.* 2020). In the present study, sensitivity analyses were carried out for each water quality parameter to check their influence on the respective WQI values and thus, determine its reasonability. The sensitivity values were determined by employing the expression given by Eq. 4. 38.

$$S_i(\%) = \frac{\left| \frac{U_i}{N} - \frac{u_i}{n} \right|}{U_i} \times 100\% \quad 4.38$$

where  $U_i$  and  $u_i$  denote the MEWQI values in the presence of the  $i^{th}$  parameter (physico-chemical component) and after removing it, respectively.  $N$  and  $n$  are the number of water quality components while estimating  $U_i$  and  $u_i$ , respectively.

#### 4.5.4. Correctness of proposed WQIs

Developing and proposing an index is incomplete without checking for its correctness. Hence, each novel WQI developed in the present study has been subjected to correctness checking. The detailed methodologies adopted for checking the correctness are as follows.

#### 4.5.4.1. Drinking suitability

For assessing the health of the water column of Deepor Beel with regard to drinking suitability, 24 parameters were considered. To understand the proposed methods' (entropy-weighted and PCA induced) efficacy, a significantly reliable tool known as the cluster analysis was employed on the water quality dataset, averaged over the entire sampling period. IBM SPSS Statistics (v.25) was used for the computation process. Ward's method employing the Squared Euclidean distance method was employed after the entire dataset was normalized using the Z-scale transformation (Wilks 2011). The clustering process resulted in a graphical interpretation through a dendrogram, which provided information regarding the high intra-cluster and low inter-cluster similarities.

#### 4.5.4.2. Irrigation suitability

The water quality for irrigation suitability is an indicator of crop quality and its effects on the soil characteristics. Superior quality of crop production necessitates the use of water possessing all essential nutrients and devoid of any pathogenic contamination. This is attributed to the adverse effects of water quality on crop yield due to its toxicity and nutrient inadequacy. Hence, several factors have been accounted for determining the suitability of Deepor Beel water for irrigation, as described below (measurements inside the square brackets indicate the respective ionic concentration levels in meq/L of the corresponding elements).

##### a. Sodium Adsorption Ratio (SAR)

SAR (Eq. 4. 39) is measured as sodium concentration with respect to calcium and magnesium, essentially determining the measure of sodium hazard (Todd 1980).

$$SAR = \frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}} \quad 4. 39$$

##### b. Kelly's Ratio (KR)

KR (Eq. 4. 40) is another tool for measuring sodium hazard, expressed as a fraction of sodium to calcium and magnesium concentrations (Kelley 1963).

$$KR = \frac{[Na^+]}{[Ca^{2+}] + [Mg^{2+}]} \quad 4. 40$$

##### c. Soluble sodium Percentage (SSP)

When present in excess amount, sodium contributes to the retardation of plant growth by aiding in a decline in the soil's permeability. Thus, assessment of SSP (Eq. 4. 41) is critical (Ghalib 2017).

$$SSP = \frac{[Na^+] + [K^+]}{[Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}]} \times 100 \quad 4.41$$

d. *Residual Sodium Carbonate (RSC)*

RSC is another tool for evaluating the irrigation suitability of water, expressed as Eq. 4.42 (Gupta & Gupta 1997).

$$RSC = \{([HCO_3^-] + [CO_3^{2-}]) - ([Ca^{2+}] + [Mg^{2+}])\} \quad 4.42$$

e. *Permeability Index (PI)*

Soil permeability is an essential factor in considering crop productivity. It is, however, significantly affected by the long-term usage of water rich in nutrients. PI (Eq. 4.43) is thus estimated to evaluate soil suitability for crop growth (Doneen 1964).

$$PI = \left\{ \frac{[Na^+] + \sqrt{[HCO_3^-]}}{[Na^+] + [Ca^{2+}] + [Mg^{2+}]} \right\} \times 100 \quad 4.43$$

f. *Magnesium Adsorption Ratio (MAR)*

Magnesium, in excess quantities, renders the water more alkaline, thus disrupting the crop growth considerably. MAR (Eq. 4.44) helps determine the extent of magnesium hazard to the crop yield (Raghunath 1987).

$$MAR = \left\{ \frac{[Mg^{2+}]}{[Ca^{2+}] + [Mg^{2+}]} \right\} \times 100 \quad 4.44$$

Additionally, the hydro geochemistry of the water samples was tested through the use of Piper Trilinear Diagram, Durov plots, Wilcox and USSL plots, the details of which are presented in the later chapters.

#### 4.5.4.3. Heavy metal contamination

The efficacy of HMI was verified by comparing it with the existing heavy metal pollution index (HPI), contamination index (CI) and heavy metal evaluation index (HEI). The details of these indices are provided herewith.

a. *Heavy metal Pollution Index (HPI)*

The globally accepted HPI assigns weights based on the inverse proportionality of the recommended standard values for each component proposed by Mohan *et al.* (1996), given by Eq. 4.45

$$HPI = \frac{\sum_{i=1}^n W_i Q_i}{\sum_{i=1}^n W_i} \quad 4.45$$

where  $Q_i$  and  $W_i$  indicate the sub-index and unit weight assigned to the  $i^{th}$  parameter and  $n$  denotes the number of parameters considered.

The sub-index for the  $i^{th}$  parameter is estimated through Eq. 4. 46

$$Q_i = \frac{|M_i - I_i|}{S_i - I_i} \quad 4. 46$$

where  $M_i$ ,  $I_i$  and  $S_i$  represent the observed, acceptable and permissible values, respectively. The critical value for drinking water is proposed to be 100.

#### b. Contamination Index (CI)

CI evaluates the overall extent of contamination of water quality. It sums up the collective effects of a number of water quality parameters considered unsafe for domestic water (Prasanna *et al.* 2012) and was calculated using the following formula (Eq. 4. 47).

$$CI = \sum_{i=1}^n \left\{ \frac{C_{a_i}}{C_{s_i}} - 1 \right\} \quad 4. 47$$

where  $C_{a_i}$  and  $C_{s_i}$  represent the analytical value and the permissible value of the  $i^{th}$  component.

The concentrations of heavy metals exceeding the permissible limits were not considered for the estimation of CI values. The degree of contamination is usually made use of as an indication for estimating the degree of metal pollution in water. The monitoring sites were classified under three categories based on the CI values indicated in Table 4. 7.

**Table 4. 7.** Degree of contamination based on CI values.

CI values	Category
CI < 1	Low
1 ≤ CI < 3	Medium
CI > 3	High

#### c. Heavy metal Evaluation Index (HEI)

HEI provides a general quality of water with regard to heavy metals and is computed using Eq. 4. 48.

$$HEI = \sum_{i=1}^n \frac{H_i}{H_{i_{max}}} \quad 4. 48$$

where  $H_i$  and  $H_{i_{max}}$  represent the monitored and permissible values of the  $i^{th}$  parameter, respectively. Classification of the water samples for HEI is based on the multiples of the mean value obtained.

#### **4.6. Phase II; III<sub>rd</sub> Objective: Assessment of sediment column quality with respect to heavy metals**

The present study is a first of its kind on the sediment contamination in Deepor Beel, carried out in four distinct goals. The first and foremost goal was to identify the latent pollution sources contributing to the wetland's sediment contamination. For this purpose, the hierarchical clustering of the raw sediment dataset was carried out, which categorized the sampling locations into statistically significant clusters, depending on their similarities in behaviours. The principal component analysis was then carried out on the dataset for three seasons; pre-monsoon, monsoon and post-monsoon, respectively, which showed significant temporal changes in the pollution sources. This was followed by determining and quantifying the sources' contribution to the pollution. This necessitated polling the entire sediment dataset to a single matrix and carrying out multiple iterations for the simulation of the model.

After identifying and quantifying the contribution of different pollution sources, the second goal was to assess the contamination levels. Various indices such as contamination factor, pollution load index, enrichment factor, and the geo-accumulation index were employed. Additionally, the potential ecological risks associated with the sediment column was estimated—this provided information regarding the individual and cumulative effects of each heavy metal on the aquatic ecology.

Thirdly, chemical speciation analyses of all the heavy metals were conducted to determine their available forms in the sediment column. This provided information related to the leachability and bio-fractionation of the heavy metals present in the sediment column.

Finally, the studies were validated through elemental analyses; X-ray powder diffraction (XRD) followed by Scanning electron microscope - Energy Dispersive X-Ray Spectroscopy (SEM-EDS), determining the elemental composition and forms of heavy metals present in the sediment columns from various parts of the wetland.

Seven heavy metals (Cr, Cd, Fe, Mn, Cu, Pb, and Mg) were chosen for analysis based on the available literature on the probable pollution sources available near the wetland, i.e., the land-fill and discharges from various small and large-scale manufacturing units (Sun *et al.* 2001; Mohan & Gandhimathi 2009; Nibedita & Bhattacharyya 2013; El-Salam & Abu-Zuid 2015;

Vaverková *et al.* 2018). All the analyses were carried out using Atomic Absorption Spectrophotometer (AAS) (Varian-Spectra 55B), and all the measurements were taken in triplicates. All the standards were prepared under controlled conditions. The absorbance values of the standards were well within the acceptable limits, and the values obtained for the blanks were always less than the minimum detection limits (MDLs). The standard deviation of all the triplicates was observed to be less than 5%.

The details of the clustering process, principal component analysis, and positive matrix factorization model have already been explained in section 4.4. Details of other methodologies adopted are presented in the following sub-sections.

#### 4.6.1. Metal contamination and risk assessment

Various tools were employed to determine the heavy metal contamination of the sediment samples of Deepor Beel, as well as its potential ecological risk corresponding to each heavy metal. A detailed description of the indices is as follows:

##### a. Contamination Factor (CF)

The contamination factor (CF) proves to be the first step towards the risk assessment, which is estimated as the ratio of the observed metal concentration to its corresponding reference value (Eq. 4. 49) (Islam *et al.* 2015a). In the present study, the background concentrations of the metals are considered to be the reference values (Fukue *et al.* 2006). It is usually estimated to determine a metal's contamination level.

$$CF = \frac{C_m}{C_b} \quad 4. 49$$

where  $C_m$  and  $C_b$  indicate the observed metal concentration and its corresponding background value. The CF is categorized as:

$$CF = \begin{cases} < 1 & \text{low contamination} \\ 1 - 3 & \text{moderate contamination} \\ 3 - 6 & \text{considerable contamination} \\ \geq 6 & \text{very high contamination} \end{cases} \quad 4. 50$$

##### b. Pollution Load Index (PLI)

The pollution load index is determined based on Eq. 4. 51. It provides a picture of the overall pollution of a particular site or locality by providing its toxicity state (Angulo 1996; Dhamodharan *et al.* 2019). It is categorized as sites having no pollution ( $PLI \leq 1$ ), slight pollution ( $1 < PLI \leq 2$ ), moderate pollution ( $2 < PLI \leq 3$ ), or highly polluted ( $PLI > 3$ ) (Liu *et al.* 2016a; Liu *et al.* 2016b).

$$PLI = \sqrt[p]{CF_1 \times CF_2 \times CF_3 \times \dots \times CF_p} \quad 4.51$$

where CF indicates the contamination factor for each  $p$  (7 in this case) heavy metals.

c. *Enrichment Factor (EF) and Geo-accumulation index ( $I_{geo}$ )*

The enrichment factor (EF) is a well-established technique for estimating the degree of contaminants in the environment (Liaghati *et al.* 2004; Franco-Uría *et al.* 2009), given by Eq. (4.52). Here, iron (Fe) is used as a tracer distinguishing natural and anthropogenic contamination.

$$EF = \frac{\left\{ \frac{C_m}{C_{Fe}} \right\}_{sample}}{\left\{ \frac{C_m}{C_{Fe}} \right\}_{BG}} \quad 4.52$$

where BG corresponds to the background concentration of the heavy metal;  $C_m$  and  $C_{Fe}$  correspond to the concentrations of the metal and iron, respectively. EF is responsible for determining whether a particular site is affected by anthropogenic contamination. Thus, EF is categorized as:

$$EF = \begin{cases} \leq 1 & \text{BG concentration} \\ 1 - 2 & \text{Minimum enrichment} \\ 2 - 5 & \text{Moderate enrichment} \\ 5 - 20 & \text{Significant enrichment} \\ 20 - 40 & \text{Very high enrichment} \\ > 40 & \text{Extremely high enrichment} \end{cases} \quad 4.53$$

The geo-accumulation index ( $I_{geo}$ ) (Eq. 4.54) is a widely accepted tool for determining the heavy metal contamination of the sediment samples and comparing the current contamination levels to that of the pre-industrial levels (Muller 1969; Chakravarty & Patgiri 2009; El-Amier *et al.* 2017). The categorization adopted for  $I_{geo}$  is shown through Eq. 4.55

$$I_{geo} = \log_2 \left\{ \frac{C_p}{1.5B_p} \right\} \quad 4.54$$

$$I_{geo} = \begin{cases} \leq 0 & \text{Not polluted} \\ 0 - 1 & \text{No to moderate pollution} \\ 1 - 2 & \text{Moderate pollution} \\ 2 - 3 & \text{Moderate to strong pollution} \\ 3 - 4 & \text{Strong pollution} \\ 4 - 5 & \text{Strong to extreme pollution} \\ > 5 & \text{Extreme pollution} \end{cases} \quad 4.55$$

where  $C_p$  and  $B_p$  indicate the observed and background concentration of the  $p^{th}$  heavy metal. The number 1.5 is used as a background correction of the matrix.

d. *Potential ecological risk (PER)*

The potential ecological risk (PER) is introduced for assessing the impact of one or more elements on the ecology of a particular study area. The method considers the risk index (RI), which reflects the sensitivity of the biological community and their toxicity response (Islam *et al.* 2015b). The primary governing equations involved are represented by Eq. (4. 56 - 4. 58).

$$RI = \sum_{p=1}^n E_r^p \quad 4. 56$$

where,

$$E_r^p = CF^p \times T_r^p \quad 4. 57$$

$$T_r^p = \begin{cases} 10 & As \\ 30 & Cd \\ 2 & Cr \\ 5 & Cu, Pb and Ni \\ 1 & Zn \\ 40 & Hg \end{cases} \quad 4. 58$$

The basic nomenclatures involved in estimating the PER are as follows:

$E_r^p$  indicates the potential ecological risk index for each heavy metal (Yi *et al.* 2011); CF is the contamination factor;  $T_r^p$  is the toxicity response coefficient for each element given in Eq. 4. 58 (Islam *et al.* 2015a; Lu *et al.* 2015). 4 metals (Cr, Cd, Cu, and Pb) were investigated for assessing the potential ecological risk of the wetland through the sediment contamination as the values of  $T_r^p$  for other metals were unavailable. Therefore, another term called the integrated pollution degree ( $C_d$ ) has been coined as follows:

$$C_d = \sum_{p=1}^n CF^p \quad 4. 59$$

$C_d$  is categorized as given in Eq. 4. 60 (Fu *et al.* 2009).

$$C_d = \begin{cases} < 5 & Low\ pollution \\ 5 - 10 & Moderate\ Pollution \\ 10 - 20 & High\ Pollution \\ \geq 20 & Very\ high\ pollution \end{cases} \quad 4. 60$$

RI and  $E_r^p$  can be categorized as given in Eq. 4. 61 (Guo *et al.* 2010).

$$RI = \begin{cases} < 150 & \text{Low risk} \\ 150 - 300 & \text{Moderate risk} \\ 300 - 600 & \text{Considerable risk} \\ \geq 600 & \text{Significant risk} \end{cases}$$

4. 61

$$E_r^p = \begin{cases} < 40 & \text{Low risk} \\ 40 - 80 & \text{Moderate risk} \\ 80 - 160 & \text{Considerable risk} \\ 160 - 320 & \text{High risk} \\ \geq 320 & \text{Very high risk} \end{cases}$$

#### 4.6.2. Heavy metal fractionation of sediment column

Chemical proportioning of heavy metals for the sediment samples was carried out using the procedure laid down by Tessier *et al.* (1979). Five different fractional speciations were obtained, the details of which are given in Table 4. 8 (Gibbs 1973; Salomons & Förstner 1980).

**Table 4. 8.** Speciation of heavy metals in sediments and their extraction procedures.

Frac-tion	Form	Extraction protocol
F1	Exchangeable	*Sample is first extracted with 7.5mL of 0.05M ammonium acetate (Duration of 1 h).
F2	Bound to Carbonates	*Residue obtained from F1 is extracted with 10mL of 0.17M acetic acid at pH 7.0 (Duration of 5 h).
F3	Reducible (iron and manganese oxides)	**F2 residue obtained is extracted with 20mL of hydroxyl ammonium chloride in 25% (v/v) acetic acid at pH 5.0, at $96 \pm 3$ °C (Duration of 5 h).
F4	Oxidizable Bound to organic matter and sulphide	**F3 residue obtained is extracted with 5mL of 0.02M nitric acid and 5mL of 3% hydrogen peroxide at $85 \pm 2$ °C (Duration of 2 h). *This is followed by the addition of 6mL of hydrogen peroxide (Duration of 3 h). After cooling, 5mL of 3.2M ammonium acetate is added with 20% (v/v) nitric acid (Duration of 30 min).
F5	Residual (lattice)	F4 residue obtained is extracted with a mixture of hydrofluoric and nitric acid (1:1, v/v) and then is subjected to digestion under pressure and temperature in a closed container.

\* Continuous agitation is provided.  
\*\*Occasional agitation is provided.

After each extraction, the samples were centrifuged, and the supernatant was decanted before proceeding to the subsequent extraction process.

### 4.6.3. Elemental analyses

XRD analysis was carried out for three samples (powdered); (i) samples from the central zone, (ii) Boragaon landfill site and (iii) industrial zone to determine the forms in which the HMs are present in the samples. SEM-EDS quantitative analyses were furthermore carried out to determine the morphology and the elemental composition of the sediment samples. Two representative samples (powdered) were chosen; one from the eastern part of the wetland (proximate to the Boragaon landfill) and the other from the western part (industrial zone). Elemental mapping of the samples was done to determine the weight percentages of the HMs present in those samples.

## 4.7. Phase II; IV<sup>th</sup> Objective: Understanding the dynamics of heavy metals in a freshwater ecosystem through their toxicity and bioavailability assay

Heavy metal contamination has become more and more evident with the advent of anthropogenic interferences to the natural ecosystems. Environmental monitoring plays a crucial part in the sustenance of the aquatic ecosystem, allowing the researchers to understand the dynamics of the entire ecosystem on a broader scale. This helps in the sustenance of economically important biota (notably fish, hydrophytes, snails and crustaceans). With these perspectives, the present investigation is carried out intending to assess the contamination levels of six different heavy metals (Cr, Cd, Fe, Mn, Cu, and Pb) in water, sediments and three different species of fish (*Notopterus notopterus*, *Clarias batrachus*, and *Channa striata*) commonly found and consumed in the region. Furthermore, an attempt has been made to assess the human health risk associated with exposure to water, sediment and fish species. The results of this study will provide a comprehensive understanding of the dynamics of the heavy metals in an aquatic ecosystem, which would, in a broader context, prove beneficial for its conservation and restoration.

### 4.7.1. Potential human health risk assessment (HRA)

As a result of human exposure to certain specific contaminants of known concentrations, estimation of risk employs an assessment technique known as health risk assessment (HRA) (Li *et al.* 2014b; Kusin *et al.* 2018). Three principal pathways have been established through which exposure to heavy metals can occur in human beings (adults and children); 1. direct ingestion of the heavy metals (oral), 2. adsorption through skin pores (dermal), and 3. inhalation, either through mouth or nose (Wu *et al.* 2009; Luo *et al.* 2012). Hence, typically, HRA consists of three major elements, i.e., identification of hazards, assessment of exposure levels,

dose-response, and risk characterization. In the water environment, the metals usually come in contact with the human body through the first two pathways, i.e., via ingestion and dermal adsorption (EPA 2004; Wu *et al.* 2009; Singh *et al.* 2018). However, heavy metal exposure in the sediment column takes place through all three pathways. The health risk associated with the water environment can be explained through Eq. 4. 62 and 4. 63, which provides the average daily dosages for heavy metals through different pathways.

$$CDI_{ing} = \frac{C_w \times IngR \times EF \times ED}{B_w \times AT} \quad 4. 62$$

$$CDI_{derm} = \left\{ \frac{C_w \times SA \times K_p \times ET \times EF \times ED}{B_w \times AT} \right\} \times 10^{-3} \quad 4. 63$$

For the sediment column, the average daily dosage of heavy metals can be estimated by computing the following equations (Eq. 4. 64 - 4. 66).

$$CDI_{ing} = \left\{ \frac{C_{SED} \times IngR \times EF \times ED}{B_w \times AT} \right\} \times CF \quad 4. 64$$

$$CDI_{derm} = \left\{ \frac{C_{SED} \times SA \times AF_{SED} \times ABS \times EF \times ED}{B_w \times AT} \right\} \times CF \quad 4. 65$$

$$CDI_{inh} = \frac{C_{SED} \times EF \times ED}{PEF \times AT} \quad 4. 66$$

where  $CDI_{ing}$  and  $CDI_{derm}$  indicate the average daily dosage of heavy metals through ingestion and dermal adsorption, respectively. The other parameters used in the equations have been stated in Table 4. 9 (a and b).

HRA involved estimating carcinogenic (surficial sediment samples) and non-carcinogenic risk exposures (both water and sediment samples) in both adults and children through the bioavailability of the heavy metals. This quantification of risk characterization for non-carcinogenic risks was accomplished by estimating the Hazard Quotient (HQ) values expressed in Eq. 4. 67 (EPA 1989).

$$HQ = \frac{CDI}{R_f D} \quad 4. 67$$

where  $R_f D$  indicates the reference dosages for HRA calculation (USEPA 2011) (See Table 4. 10).

**Table 4. 9.** Input parameters involved for health risk assessment.**(a) Water**

Exposure parameters	Description	Unit	Value		Reference
			Adult	Child	
$C_w$	Heavy metal concentration in water samples	$\mu\text{g L}^{-1}$	Observed concentrations	-	
IngR	Ingestion rate of water	$\text{L day}^{-1}$	2.2	-	(Wu <i>et al.</i> 2009)
EF	Exposure frequency	days year <sup>-1</sup>	365	-	(EPA 2004)
ED	Exposure duration	Years	70	-	(EPA 2004)
$B_w$	Body weight	Kg	57.5 (Average Indian adult)	-	(USEPA 2011)
AT	Averaging Time (non-carcinogenic)	Days	25550	-	(DoE 2011)
SA	Surface area of skin that contacts soil	$\text{cm}^2$	5700	-	(USEPA 2011)
$K_p$	Dermal permeability coefficient	$\text{cm h}^{-1}$	Metal specific	-	(EPA 2004)
ET	Exposure time	$\text{h day}^{-1}$	0.6	-	(EPA 2004)

**(b) Sediment**

Exposure parameters	Description	Unit	Value		Reference
			Adult	Child	
$C_{SED}$	Heavy metal concentration in sediment samples	$\text{mg kg}^{-1}$	Observed concentrations		
IngR	Ingestion rate of sediment	$\text{mg day}^{-1}$	100	200	(USEPA 1997, 2011)
EF	Exposure frequency	days year <sup>-1</sup>	350*	350*	(USEPA 1991, 2011)

ED	Exposure duration	Years	24**	6	(USEPA 2011)
Bw	Body weight	Kg	57.5	15	(NFI 2010; USEPA 2011)
AT	Averaging Time (non-carcinogenic)	Days	8760 (356×24)	2190 (356×6)	(USEPA 2011)
CF	Conversion factor		$1 \times 10^{-6}$	$1 \times 10^{-6}$	(USEPA 2002)
SA	Surface area of skin that contacts soil	cm <sup>2</sup>	5700	2800	(USEPA 2011)
AF <sub>SED</sub>	Skin adherence factor for soil	mg cm <sup>-2</sup>	0.07	0.2	(USEPA 2011)
ABS	Dermal absorption factor		0.03 (As); 0.001 (for other metals)		(USEPA 2011)
PEF	Particle emission factor	m <sup>3</sup> kg <sup>-1</sup>	$1.36 \times 10^9$	$1.36 \times 10^9$	(USEPA 2002)

\*Default exposure frequency for residents assuming a person is out of station for 15 days per year (USEPA 1991).

\*\*Exposure duration is with an assumption that a person lives at one residence for 30 years (0–6 years as a child and 7–30 years as an adult) (USEPA 1991).

### (c) Fish

Exposure parameters	Description	Unit	Value		Reference
			Adult	Child	
EDI	Estimated daily fish intake	μg kg <sup>-1</sup> day <sup>-1</sup>	Observed concentrations		
C <sub>metal</sub>	Heavy metal concentration in fish samples	mg kg <sup>-1</sup>			
DFC	Daily fish consumption	g day <sup>-1</sup>	97.2	57.5	(Gupta <i>et al.</i> 2015)
WAB	Average body weight of the consumer	kg	55.9	32.7	(Gupta <i>et al.</i> 2015)
EF	Exposure frequency	Days	365	365	(Siddiqui <i>et al.</i> 2019)

ED	Exposure duration	Years	70	70	(Siddiqui <i>et al.</i> 2019)
FIR	Fish Ingestion rate	gpcd	97.2	57.5	(Siddiqui <i>et al.</i> 2019)
AT	Average exposure time for noncarcinogenic exposure	Days	25550	25550	(Siddiqui <i>et al.</i> 2019)

To estimate the total non-carcinogenic contribution of risk for multiple pathways, a new term called the Hazard Index (HI) was coined (Chang *et al.* 2014). For estimating the HI values, the law of superposition is valid, and therefore, it helps in evaluating the total non-carcinogenic risks for multiple metals based on the dose additivity assumption. HI for assessing risk concerning multiple pathways and metals is given in Eq. 4. 68 and 4. 69, respectively.

$$HI_{pathway} = HQ_{ing} + HQ_{derm} + HQ_{inh} \quad 4. 68$$

$$HI_{metal} = HQ_1 + HQ_2 + HQ_3 + \dots + HQ_m \quad 4. 69$$

where  $m$  signifies the number of heavy metals (in the current investigation,  $m = 6$ ).  $HI < 1$  represented no significant risk, while  $HI > 1$  indicated the probability of a potential non-carcinogenic risk, increasing the HI value (USEPA 2002).

The HI is generally employed as a screening tool with regards to the components having a similar target. This is primarily because the HI does not consider the components' interactions even though the additivity of the dose essentializes the action of all the components through identical mechanisms. This, in turn, aids in either overestimating or underestimating the health hazards, provided the interactions are less or more, respectively (Wilbur *et al.* 2004).

The carcinogenic investigation, involving the surficial sediment samples, associates Pb, Cr, and Cd heavy metals and As metalloid, as these compounds are labelled as carcinogenic by the International Agency for Research on Cancer (IARC 2012). Since, As is not considered in the current investigation, the carcinogenic HRA was evaluated associating the heavy metals; Pb, Cr, and Cd.

**Table 4. 10.** Reference dosage values for different heavy metals.**(a) Water ( $\mu\text{g}/\text{kg}/\text{day}$ )**

Heavy metal	RfD <sub>ing</sub>	RfD <sub>derm</sub>	Reference
Cr	3	0.015	(USEPA 2006)
Cd	0.5	0.005	(USEPA 2006)
Fe	300	45	(USEPA 2006)
Mn	20	0.8	(USEPA 2006)
Cu	40	12	(USEPA 2006)
Pb	1.4	0.42	(WHO 2006)

**(b) Sediment (mg/kg/day)**

Heavy metal	RfD <sub>ing</sub>	RfD <sub>derm</sub>	RfD <sub>inh</sub>	Reference
Cr	$4.00 \times 10^{-02}$	$8.00 \times 10^{-03}$	$1.00 \times 10^{-04}$	(Giri & Singh 2017)
Cd	$1.00 \times 10^{-03}$	$2.50 \times 10^{-05}$	$1.00 \times 10^{-05}$	(Giri & Singh 2017)
Fe	$3.00 \times 10^{-03}$	$7.50 \times 10^{-05}$		(Giri & Singh 2017)
Mn	$7.00 \times 10^{-01}$	$1.40 \times 10^{-01}$		(Giri & Singh 2017)
Cu	$2.40 \times 10^{-02}$	$9.60 \times 10^{-04}$	$5.00 \times 10^{-05}$	(Giri & Singh 2017)
Pb	$3.50 \times 10^{-03}$	$5.25 \times 10^{-04}$	$1.50 \times 10^{-04}$	(Giri & Singh 2017)

**(c) Fish (mg/kg/day)**

Heavy metal	RfD	Reference
Cr	$3.00 \times 10^{-03}$	(USEPA 2010)
Cd	$1.00 \times 10^{-03}$	(USEPA 2010)
Fe	$7.00 \times 10^{-01}$	(USEPA 2010)
Mn	$1.40 \times 10^{-01}$	(USEPA 2010)
Cu	$4.00 \times 10^{-02}$	(USEPA 2010)
Pb	$4.00 \times 10^{-03}$	(USEPA 2010)

The health risk due to carcinogenic metals is expressed as total lifetime cancer risk (LCR), which is also based on the principle of superposition, and is evaluated using Eq. 4. 70 and 4. 71.

$$\text{Cancer Risk} = \text{CDI} \times \text{CSF} \quad 4. 70$$

$$\text{LCR} = \sum \text{Cancer Risk} = \text{Cancer Risk}_{ing} + \text{Cancer Risk}_{derm} + \text{Cancer Risk}_{inh} \quad 4. 71$$

where cancer risk is estimated for each pathway described by Eq. 4. 64 - 4. 66. CSF (mg kg<sup>-1</sup> day<sup>-1</sup>) indicates the cancer slope factors for each heavy metal; 0.5 for Cr, 6.3 for Cd and 0.0085 for Pb (USEPA 2011). The United States Environmental Protection Agency (USEPA) has marked threshold limits for the cancer risk and the LCR values. The human body's cancer risks have been limited to an acceptable value of 0.0001, while the LCR's tolerable range varies from 1.0×10<sup>-6</sup> to 1.0×10<sup>-4</sup> (USEPA 2011).

Health risk associated with the consumption of fish was assessed by evaluating the estimated daily intake (EDI) of fish (Eq. 4. 72), followed by the target hazard quotient (THQ) (Eq. 4. 73) and the total target hazard quotient (TTHQ) (Eq. 4. 74). The assessment was carried out for four different organs (muscle, liver, gill, and skin) of the three fish species (*N. notopterus*, *C. batrachus*, and *C. striata*) collected from three distinct zones of Deepor Beel. The THQ values provided the non-carcinogenic influence on the human bodies due to the fish intake; THQ exceeding a unit value indicated potential non-carcinogenic health risk to human beings (USEPA 2000). The cumulative impact exposure to more than one metal was assessed by calculating the arithmetic sum of all the THQ values, which resulted in the total target hazard quotient (TTHQ).

$$\text{EDI} = \left\{ \frac{\text{DFC} \times C_{\text{metal}}}{\text{WAB}} \right\} \quad 4. 72$$

$$\text{THQ} = \left\{ \frac{\text{EF} \times \text{ED} \times \text{FIR} \times C_{\text{metal}}}{R_f D \times \text{WAB} \times \text{AT}} \right\} \times 10^{-3} \quad 4. 73$$

$$\text{TTHQ} = \text{THQ}_{\text{HM}_1} + \text{THQ}_{\text{HM}_2} + \dots + \text{THQ}_{\text{HM}_m} \quad 4. 74$$

For carcinogenic evaluation due to the consumption of the fish species, two metals labelled as "possible carcinogenic influence on humans," i.e., Cd and Pb, were considered (although Cr is also marked; however, USEPA has not published the CSF values yet) (USEPA 2010; IARC 2012). The lifetime cancer risk (TR) for both the heavy metals was evaluated using the critical slope factor (CSF) values through Eq. 4. 75.

$$TR = \left\{ \frac{EF \times ED \times FIR \times C_{metal} \times CSF}{WAB \times AT} \right\} \times 10^{-3} \quad 4.75$$

All the parameters used in Eq. 4. 72 - 4. 75 have been described with their values in Table 4. 9c. The tolerable limits for TR lie in the range  $1.0 \times 10^{-04}$  to  $1.0 \times 10^{-06}$ , i.e., the risk of developing cancer over a lifetime lies in the range 1 in 10,000 to 10,00,000.

#### 4.7.2. Bioaccumulation Factor (BAF)

Bioaccumulation means the agglomeration of contaminants to higher trophic levels from lower levels. Fishes are considered to be very good bio accumulators as far as heavy metals are concerned. The bioaccumulation of heavy metals in various fish organs is estimated through the bioaccumulation factor, governed by Eq. 4. 76 (Zhuang *et al.* 2013).

$$BAF = \left\{ \frac{(C_m)_{fish}}{C_{SED}} \right\} \quad 4.76$$

where  $(C_m)_{fish}$  and  $C_{SED}$  indicate the heavy metal concentrations in fish tissues/organs and sediment column, respectively (both expressed as  $\text{mg kg}^{-1}$ , dry weight).

### 4.8. Phase III; V<sub>th</sub> Objective: Assessment of nutrient (N-P) dynamics in wetlands through a one-dimensional model for assessing the eutrophication levels induced by various pollution sources

The present study aims to provide a suitable foundation for developing a eutrophic-ecological model for Deepor Beel, India. Water, sediment, and water hyacinth samples were collected from various parts of the wetland and subjected to analyses continuously from Oct 2017 to Feb 2019. The collected samples were analyzed for various physico-chemical parameters, quintessential for developing a eutrophication-based ecological model. Monthly water samples were analyzed for seven parameters; pH, dissolved oxygen (DO), total Kjeldahl nitrogen (TKN), ammonia, organic nitrogen, nitrate and phosphate, while monthly samples of the water hyacinths and sediments were analyzed for five parameters; organic nitrogen, total Kjeldahl nitrogen (TKN), ammonia, nitrate and total phosphorus. All the procedures pertaining to the sampling, preservation and collection of various samples adhered to the standard procedures (APHA 2012). A conceptual diagram was first constructed, and the corresponding differential equations about different functions were formulated. Subsequently, a code was developed in MATLAB based on the logic formulated through the conceptual diagram. Sensitivity analysis was first performed on various state variables, identifying the parameters most

sensitive and thus, exhibiting maximum variability in the model. The model was then subjected to calibration for defining the rate constants based on which; it was subjected to further validation. Finally, the model was simulated for two plausible alternatives to verify the reduction of the eutrophication levels in Deepor Beel; (i) Harvesting of water hyacinths and (ii) Setting up of a treatment unit for nitrogen and phosphorus removal. The detailed procedure adopted in the study follows herewith.

#### 4.8.1. Model Conceptualization

The conceptual diagram for the one-dimensional ecological model for nutrient distribution in the wetland ecosystem is given in Fig. 4. 12. The model is divided into three levels: plant layer, water column and sediment column. Eight state variables are considered for the model: organic nitrogen, ammonia nitrogen, nitrate-nitrogen and total phosphorus (OrgN,  $\text{NH}_3\text{N}$ ,  $\text{NO}_3\text{N}$ , and P, respectively) in the water column; total nitrogen and total phosphorus in the sediment layer, referred to as sediment nitrogen and sediment phosphorus (SN and SP), respectively; total nitrogen and total phosphorus in plant layer, referred to as plant nitrogen and plant phosphorus (PN and PP), respectively. OrgN in the water column transforms into  $\text{NH}_3\text{N}$  that further transforms into  $\text{NO}_3\text{N}$  by ammonification and nitrification, respectively.  $\text{NO}_3\text{N}$  further converts into nitrogen ( $\text{N}_2$ ) gas due to denitrification (Metcalf & Eddy 2017). OrgN also settles down on the sediment layer, which undergoes mineralization to transform into  $\text{NH}_3\text{N}$  that gets suspended to re-enter the water column again.  $\text{NH}_3\text{N}$  and  $\text{NO}_3\text{N}$  are consumed by microorganisms, assisting in the conversion of these compounds back into OrgN. Plants consume  $\text{NH}_3\text{N}$  and  $\text{NO}_3\text{N}$  through their roots along with the microbial biofilm developed over their root surface. Eventually, when the plants die, nutrients are returned back into the water column as OrgN. Total phosphorus in the water column also settles down on the lake bottom and is consumed by the plants' roots that later re-enter the water column by resuspension and plant decay.

The following assumptions were taken into account while developing the conceptualizing the model:

- Nitrogen in the water was assumed to exist in only three forms: organic nitrogen, ammonia nitrogen and nitrate nitrogen. As the wetland remains mainly in aerobic conditions, other forms of nitrogen such as nitrite nitrogen are considered negligible concentrations and hence not considered while formulating the conceptual diagram. Similarly, phosphorus in water is usually present in the form of phosphates (Metcalf & Eddy 2017). Hence, phosphates in water were considered representative of total phosphorus in the water.

- Uniform water depth was considered across the wetland, and the variation in concentration of different state variables and forcing functions along the depth was overlooked, keeping in view the one-dimensional nature of the model.
- Maximum plant nitrogen and plant phosphorus present in water hyacinth biomass were 10000 g/m<sup>2</sup>/day and 2500 g/m<sup>2</sup>/day, respectively.
- The average productivity of water hyacinth was assumed 50 g dry mass/m<sup>2</sup>/day over the entire surface of Deepor Beel and has been assumed to have a sinusoidal variation such that higher productivity occurs in the winter. In comparison, lower productivity occurs in the monsoon. Peak productivity was assumed to be 53 g dry mass/m<sup>2</sup>/day based on the observations made by Reddy and Tucker (1983).
- The wetland's sediment layer's depth was assumed to be 0.3 m (Van Dam *et al.* 2007).
- It was assumed that the mixing of the wetland's nutrients occurs immediately as advection and diffusion of the nutrients are not considered in the one-dimensional model.

The following generalized symbolic mass balance equation was used as the basis for developing various equations in the model:

$$V \frac{dC}{dt} = Q_i C_i + V \sum_{j=1}^m (r_c)_j - Q_e C_e \quad 4.77$$

where,

$V \left( \frac{dC}{dt} \right)$  is the volumetric rate of change of substance in the reactor (g/day).

$Q_i$  and  $Q_e$  represent the inflowing and outflowing flow rates, respectively (m<sup>3</sup>/day).

$V$  is reactor volume (m<sup>3</sup>).

$C_i$  and  $C_e$  signify the influent and effluent concentrations, respectively (g/m<sup>3</sup>).

$r_c$  is volumetric reaction rate (g/m<sup>3</sup>.day).

$m$  is the number of reactions that involve the substance.

Using the concept from Eq. 4.77, the model equations for the rate of change of different parameters were formulated.

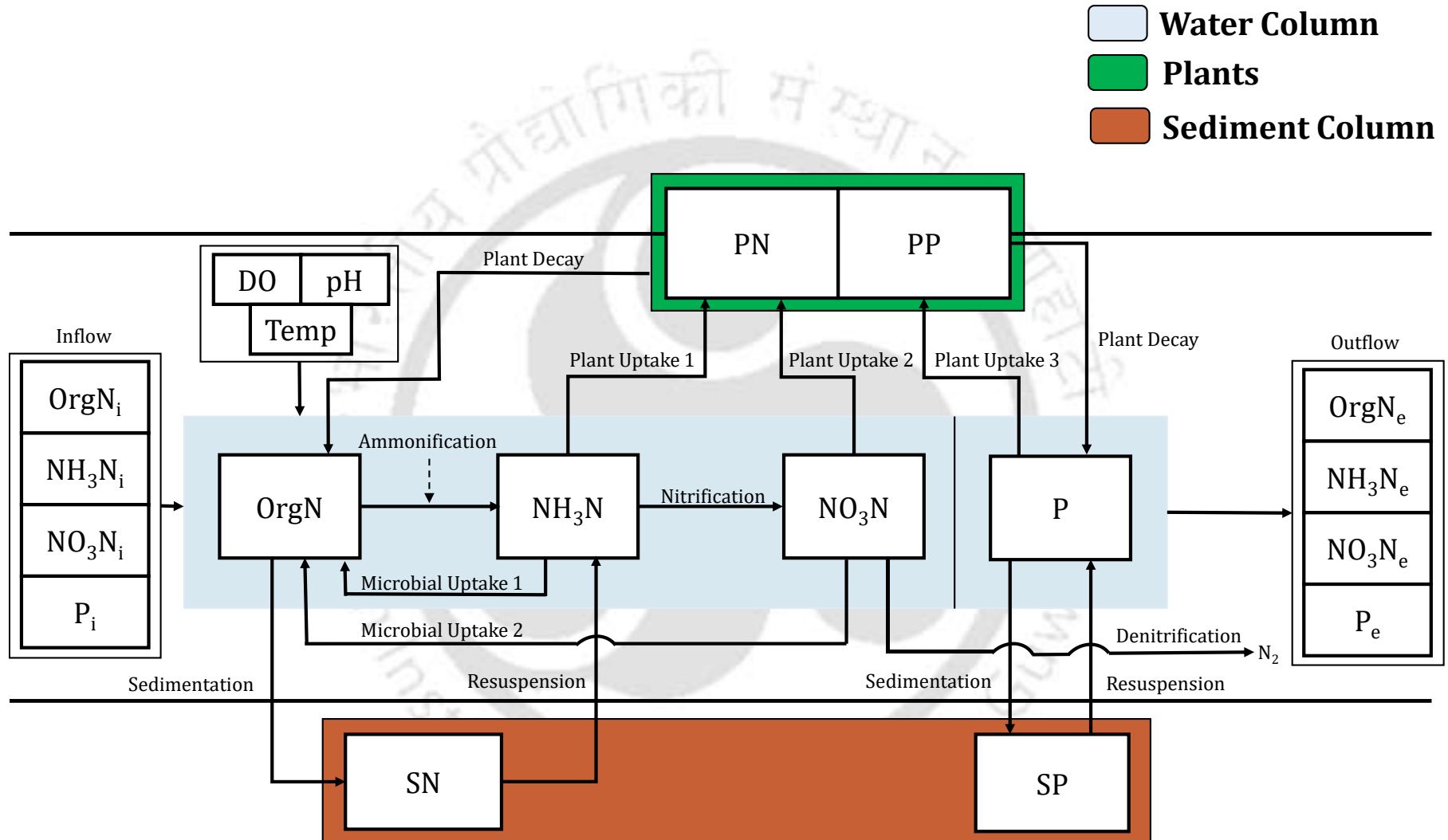


Fig. 4. 12. Conceptual diagram of the ecological model.

## I. Organic Nitrogen

$$\frac{d(OrgN)}{dt} = rorgni + rndc + rmu1 + rmu2 - ram - rns - rorgne \quad 4.78$$

The inflowing and outflowing rates of OrgN were calculated using the following equations (Eq. 4. 79 and 4. 80).

$$rorgni = \frac{Q_i}{A} \times OrgN_i \quad 4.79$$

$$rorgne = \frac{Q_e}{A} \times OrgN_e \quad 4.80$$

The rate of ammonia uptake by the microorganisms for growth was taken as a function of temperature, ammonia nitrogen and organic nitrogen present in the water column. Hence, it was represented as follows (Eq. 4. 81).

$$rmu1 = f\{T, NH_3, OrgN\} \quad 4.81$$

This function was assumed to follow the Monod kinetic equation for ammonia nitrogen with the incorporation of plant-biofilm in it (Polprasert & Agarwalla 1994). The temperature factor was incorporated by considering the Arrhenius kinetics. As it might be possible that microorganisms may prefer to feed on ammonia nitrogen over nitrate nitrogen, a preference factor,  $P_1$ , can also be incorporated (Mayo & Bigambo 2005). Thus, the rate of ammonia uptake by the microorganisms can be given by Eq. 4. 82.

$$rmu1 = \left[ (\mu_{max,20} + r_b) \times \theta_1^{T-20} \times \frac{NH_3N}{K_1 + NH_3N} \right] \times OrgN \times P_1 \quad 4.82$$

Similarly, the rate of nitrate uptake was taken as the function of temperature, nitrate nitrogen and organic nitrogen (Eq. 4. 83) and was further calculated as Eq. 4. 84.

$$rmu2 = f\{T, NO_3, OrgN\} \quad 4.83$$

$$rmu2 = \left[ (\mu_{max,20} + r_b) \times \theta_2^{T-20} \times \frac{NO_3N}{K_2 + NO_3N} \right] \times OrgN \times P_2 \quad 4.84$$

The decay rate of the PN, ammonification rate and settling rate of OrgN was calculated as first-order reactions as given by Eq. 4. 85, 4. 86 and 4. 87.

$$rndc = R_{ndc} \times OrgN \quad 4.85$$

$$ram = R_{am} \times OrgN \quad 4.86$$

$$rns = R_{ns} \times OrgN \quad 4.87$$

## II. Ammonia Nitrogen

$$\frac{d(NH_3N)}{dt} = rnhni - rn - rpu1 - rmu1 + rnrs + ram - rnhne \quad 4.88$$

The rate of nitrification of ammonia was assumed to be a function of ammonia, dissolved oxygen, pH, temperature and organic nitrogen (Eq. 4. 89).

$$rn = f\{NH_3N, DO, pH, T, OrgN\} \quad 4.89$$

To model the nitrification model, the Monod equation (Eq. 4. 90) was used, which couples both ammonia nitrogen and dissolved oxygen present in the water column (Mayo & Bigambo 2005). Correction factors were applied for pH and temperature, respectively.

$$rn = \left(\frac{\mu_n}{Y_n} + r_b\right) \times \frac{NH_3N}{K_{nh} + NH_3N} \times \frac{DO}{K_{no} + DO} \times C_T \times C_{pH} \times OrgN \quad 4.90$$

The correction for temperature ( $C_T$ ) and correction for pH ( $C_{pH}$ ) was calculated as given in Eq. 4. 91 and 4. 92 (Mayo & Bigambo 2005).

$$C_T = e^{0.098(T-15)} \quad 4.91$$

$$C_{pH} = \begin{cases} 1 - 0.833 \times (7.2 - pH) & pH < 7.2 \\ 1 & pH \geq 7.2 \end{cases} \quad 4.92$$

The rate of ammonia uptake by plants was also described by the Monod type equation (Eq. 4. 93). However, the amount of ammonia uptake by plants will also depend upon the amount of plant nitrogen already present, similar to the logistic equation (Van Dam *et al.* 2007).

$$rpu1 = \mu_{mpu1} \times PN \times \left(\frac{NH_3N}{K_{p1} + NH_3N}\right) \times \left(1 - \frac{PN}{PN_{max}}\right) \quad 4.93$$

The rate of ammonia resuspension can be modelled as first-order reaction given by Eq. 4. 94.

$$rnrs = R_{nrs} \times SN \quad 4.94$$

The inflowing and outflowing rate of  $NH_3N$  were calculated using Eq. 4. 95 and 4. 96.

$$rnhni = \frac{Q_i}{A} \times NH_3N_i \quad 4.95$$

$$rnhne = \frac{Q_e}{A} \times NH_3N_e \quad 4.96$$

### III. Nitrate Nitrogen

$$\frac{d(NO_3N)}{dt} = rnoni + rn - rpu2 - rmu2 - rdn - rnone \quad 4.97$$

The inflowing and outflowing rate of  $NO_3N$  was calculated using the following equations (Eq. 4. 98 and 4. 99).

$$rnoni = \frac{Q_e}{A} \times NO_3N_i \quad 4.98$$

$$rnone = \frac{Q_e}{A} \times NO_3N_e \quad 4.99$$

The rate of nitrate utilization will be similar to that of ammonia nitrogen (Eq. 4. 100).

$$rpu2 = \mu_{mpu2} \times PN \times \left( \frac{NO_3N}{K_{p2} + NO_3N} \right) \times \left( 1 - \frac{PN}{PN_{max}} \right) \quad 4.100$$

The denitrification rate was calculated using Eq. 4. 101.

$$rdn = (R_{dn,20} + r_b) \times \theta_3^{T-20} \times NO_3N \quad 4.101$$

### IV. Plant Nitrogen

$$\frac{d(PN)}{dt} = rpu1 + rpu2 - rndc \quad 4.102$$

### V. Sediment Nitrogen

$$\frac{d(SN)}{dt} = rns - rnrs \quad 4.103$$

### VI. Total Phosphorus

$$\frac{dP}{dt} = rpi + rprs + rpdc - rps - rppu - rpe \quad 4.104$$

The inflowing and outflowing rates of total phosphorus were calculated using the following equations (Eq. 4. 105 and 4. 106).

$$rpi = \frac{Q_i}{A} \times P_i \quad 4.105$$

$$rpe = \frac{Q_e}{A} \times P_e \quad 4.106$$

The decay rate of plant phosphorus, phosphorus regeneration rate, phosphorus settling rate and phosphorus utilization rate by plants for growth were calculated using equations similar to those used for nitrogen counterparts (Eq. 4. 107 - 4. 110).

$$rpd_c = R_{pd_c} \times P \quad 4.107$$

$$rpr_s = R_{pr_s} \times SP \quad 4.108$$

$$rps = R_{ps} \times P \quad 4.109$$

$$rppu = \mu_{mppu} \times PP \times \left( \frac{P}{K_{p3} + P} \right) \times \left( 1 - \frac{PP}{PP_{max}} \right) \quad 4.110$$

### VII. Plant Phosphorus

$$\frac{d(PP)}{dt} = rppu - rpd_c \quad 4.111$$

### VIII. Sediment Phosphorus

$$\frac{d(SP)}{dt} = rps - rpr_s \quad 4.112$$

#### 4.8.2. Sensitivity analysis

Sensitivity analysis of a model can be broadly described as an effort to gage the sensitivity of the parameters, forcing functions or sub-models involved in an ecological model (Jørgensen and Bendoricchio, 2001). It is carried out a number of times during the modelling process of an ecological system to identify the most sensitive parts of the developed model. It can be also used to refine the most sensitive components of the model.

Sensitivity analysis is performed by incrementing or decrementing the components of the model by a certain amount, depending the uncertainty involved in the component, and subsequently recording the response of the state variables to such a change. The changes in the components can be carried out one-at-a-time (OAT) or all-at-a-time (AAT) (Pianosi *et al.*, 2016). In the OAT method, the sensitivity analysis of the model is carried out by varying the value of only one of the components (generally a parameter) at a time while keeping the values of other components fixed. On the other hand, all the components of the model are varied at the same time in the AAT method to understand the sensitivity of the all the components

as well as the collective influence of the components on the model. In fact, based on the effect of collective influence of the components, the sensitivity analysis itself can be classified into two categories; local sensitivity analysis and global sensitivity analysis (Pianosi *et al.*, 2016). Local sensitivity analysis refers to that method of sensitivity analysis which neglects collective influence of the components and typically uses OAT sampling method for estimation. On the other hand, global sensitivity analysis considers the effects of the joint interactions of the components on the model while utilizing either OAT or AAT sampling approaches for the estimation, i.e., it considers simultaneous variation of all independent input parameters.

The sensitivity,  $S$ , of a parameter can be calculated using the following equation.

$$S = \frac{\left(\frac{\partial v}{v}\right)}{\left(\frac{\partial P}{P}\right)} \quad 4.113$$

where  $v$  is a state variable of the model and  $P$  denotes the parameters. The sensitivity of a sub-model can be evaluated by removing the sub-model entirely from the model or altering the mathematical equation involved in the sub-model. The consequent changes in the values of the state variables provides a qualitative measure of the sensitivity of that sub-model. Such sensitivity analysis can be helpful in structural modifications of the model.

Global sensitivity analysis of the one-dimensional ecological model was carried out by One-At-a-Time (OAT) sampling approach, following the method described by Morris (1991). In the Morris method, it is assumed that if the input variables (parameters) are changed by the same relative amount, then the input variable that causes the highest variation in the output variable (state variable) is the most sensitive in the model. The Morris method is also known as the Elementary Effects method, as it calculates the elementary effect of change in the input variable (positive or negative) on the output variable. The elementary effect is calculated by Eq. 4.114.

$$EE_i(x) = \frac{[y(x_1, x_2, x_3, \dots, x_{i-1}, x_i + \Delta, x_{i+1}, \dots, x_k) - y(x)]}{\Delta} \quad 4.114$$

where  $y$  is the output variable,  $x$  is the input vector, and  $x_i$  is an element in the input vector.  $\Delta$  is the change in  $x_i$  and  $k$  is the number of elements in the input vector. As pointed out by King and Perera (2013), the Morris method requires  $2k$  simulations of the model to determine the sensitivity of all the input variables.

In order to carry out sensitivity analysis using the Morris method, a trajectory of changes in the input variables of a  $k$  variable model was constructed. This was done by considering a normalized range of probable values for each input variable and dividing each range by equal

intervals or levels. Base values of the input variables were randomly selected from 0 to  $\Delta$  to mark the starting point of the trajectory. The trajectory was then subsequently calculated by the final trajectory matrix  $B^*$  as given by the following equations (Saltelli *et al.* 2008).

$$B^* = \left\{ J_{m,1} x^* + \left( \frac{\Delta}{2} \right) [(2B - J_{m,k})D^* + J_{m,k}] \right\} P^* \quad 4.115$$

where,

$B^*$  is a strictly lower triangular matrix of 1's

$J_{m,k}$  is a  $m - k$  matrix of 1's where  $m = k + 1$

$x^*$  is the base input vector

$J_{m-1}$  is a column vector of 1's

$D^*$  is a  $k$ -dimensional diagonal matrix in which each element is +1 or -1 with same probability

$P^*$  is a  $k$ -by- $k$  random permutation matrix of 0's and 1's in which each row contains a solitary 1 and varies from the other rows by the relative position of that 1.

The elementary effects were finally measured by two measures given by the following equations (Morris 1991; Campolongo *et al.* 2007) (Eq. 4. 115, 4. 116, and 4. 117).

$$\mu_i^* = \frac{(\sum_{n=1}^r |EE_n|)}{r} \quad 4.116$$

$$\sigma_i = \sqrt{\frac{1}{r} \sum_{n=1}^r (EE_n - \mu_i)^2} \quad 4.117$$

where,

$$\mu_i = \frac{\sum_{n=1}^r EE_n}{r} \quad 4.118$$

Moreover,  $r$  is the number of trajectories constructed during the analysis.

$\mu_i^*$  is the absolute mean of all the elementary effects due to the  $i^{th}$  input variable, free from non-monotonic behaviour of the elementary effects, which measures the degree of sensitivity of the input variables considered in the analysis. A high value of this sensitivity index indicates that the output variable is highly sensitive to the input variable considered.  $\sigma_i$  is the standard deviation of all the elementary effects due to  $i^{th}$  input variable, higher value of which indicates non-linearity or interaction of the input variable with other variables of the model.

### 4.8.3. Model calibration and validation

Calibration of the one-dimensional eutrophication model was carried out using the data obtained from October 2017 to October 2018, and the model was then validated using the data obtained during the period October 2018 to February 2019. Euler rectangular method of integration was employed to solve all the differential equations involved in the model in MATLAB R2018b version.

## 4.9. Summary

This chapter aimed at providing to understand the limnology of wetlands in response to anthropogenic interferences to the natural ecosystem. A framework for the research was designed, and this framework was further used to study different objectives. The changes occurring in the natural ecosystem were primarily attributed to heavy metal and nutrient contamination. Different novel methodologies adopted to study these changes have been presented in this chapter and finally validated through a eutrophic-based ecological model.





# 5

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## Application of Environmetrics tools for geo-chemistry, water quality assessment and apportionment of pollution sources

This chapter presents the results of the I<sub>st</sub> objective of the research. A detailed insight into the pollution source identification and apportionment has been delivered. The chapter starts with the descriptive statistics of the water quality dataset, followed by the outputs of the different Environmetrics tools employed in the research.

### 5.1. Descriptive statistics of the WQ dataset

A summary of the overall descriptive statistics of various WQ parameters is shown in Table 5. 1. It was observed that most of the elements exceeded the acceptable limit as set by IS:10500 (2012), which is an indicator for water contamination of the wetland. Only Cd exhibited negative skewness, while all other parameters exhibited positive skewness, with a majority in the highly positively skewed (skewness > 1) category. This indicates that they have a long right-hand tail curve when normally distributed. As far as the kurtosis of the observed dataset is concerned, about 57.2% of the parameters were observed to be of the Platykurtic category (Kurtosis < 3), thus indicating a flatter normally distributed curve. On the other hand, the rest were found to be Leptokurtic (kurtosis > 3), indicating a higher peak representation of the normally distributed data. Overall WQ dataset has been represented through pattern plots, given in Appendix A of the thesis.

**Table 5. 1.** Statistical summary of different physio-chemical water quality parameters of Deepor Beel, Assam.

Parameter	Unit of measurement	Max	Min	SD	Mean	Skewness	Kurtosis	IS:10500 (2012)*
DO	mg/L	17.53	0.98	3.01	7.03	0.21	0.07	-
pH	pH units	8.51	5.31	0.52	6.72	0.64	0.76	6.5 <sup>a</sup> - 8.5 <sup>b</sup>
EC	µS/cm	0.58	0.13	0.08	0.28	0.79	0.73	-
Turbidity	NTU	114.50	0.30	20.26	21.16	1.65	2.56	1 <sup>a</sup> - 5 <sup>b</sup>
TA	mg/L as CaCO <sub>3</sub>	182.00	20.06	29.83	84.15	1.31	1.71	200 <sup>a</sup> - 600 <sup>b</sup>
TH	mg/L as CaCO <sub>3</sub>	150.00	30.00	21.18	66.49	1.76	3.40	200 <sup>a</sup> - 600 <sup>b</sup>
BOD <sub>5</sub>	mg/L	98.60	4.50	14.28	20.27	2.29	7.72	-
COD	mg/L	416.87	12.12	57.43	82.05	1.87	5.75	-
TDS	mg/L	874.67	0.00	144.09	218.08	1.64	3.76	500 <sup>a</sup> - 2000 <sup>b</sup>
TSS	mg/L	624.17	4.27	111.82	153.47	1.52	2.73	-
F <sup>-</sup>	mg/L	5.71	0.00	0.44	0.41	9.48	107.62	1.0 <sup>a</sup> - 1.5 <sup>b</sup>
Cl <sup>-</sup>	mg/L	123.37	3.77	12.76	20.56	4.15	24.50	250 <sup>a</sup> - 1000 <sup>b</sup>
NO <sub>3</sub> <sup>-</sup>	mg/L	30.11	0.00	3.38	1.65	5.31	34.97	45
PO <sub>4</sub> <sup>3-</sup>	mg/L	4.99	0.00	1.13	0.92	1.61	1.57	-
SO <sub>4</sub> <sup>2-</sup>	mg/L	110.81	2.41	14.30	16.38	3.09	12.78	200 <sup>a</sup> - 400 <sup>b</sup>
Na <sup>+</sup>	mg/L	48.20	0.67	9.92	8.19	1.37	1.11	-
K <sup>+</sup>	mg/L	34.10	0.07	4.59	4.41	1.58	5.60	-
Ca <sup>2+</sup>	mg/L	184.00	4.21	28.02	56.20	1.39	3.17	75 <sup>a</sup> - 200 <sup>b</sup>
TKN	mg/L	42.30	2.38	6.87	14.89	1.10	1.46	-
Mg	mg/L	9.26	0.01	2.73	4.85	0.29	1.23	30 <sup>a</sup> - 100 <sup>b</sup>
Cr	µg/L	466.40	1.80	36.52	44.40	1.26	0.77	0.05
Cd	µg/L	16.20	1.00	3.19	5.70	-0.07	1.43	0.003
Fe	µg/L	1606	49	280.62	553.40	1.15	1.59	0.3
Mn	µg/L	870	47.40	145.37	308	0.48	0.36	0.1 <sup>a</sup> - 0.3 <sup>b</sup>
Cu	µg/L	980	45	229.43	468.8	0.33	1.26	0.05 <sup>a</sup> - 1.5 <sup>b</sup>
Pb	µg/L	87.50	3.00	14.66	21.80	1.96	5.56	0.01
NH <sub>3</sub> <sup>-</sup>	mg/L	5.57	0.20	0.70	1.19	2.12	7.24	0.5
OrgN	mg/L	39.83	2.18	6.35	13.69	1.12	1.59	-

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\* Standards prescribed by the Indian Standard Drinking Water – Specification (IS:10500 2012) (*Second Revision*).

<sup>a</sup> Requirement (Acceptable limit).

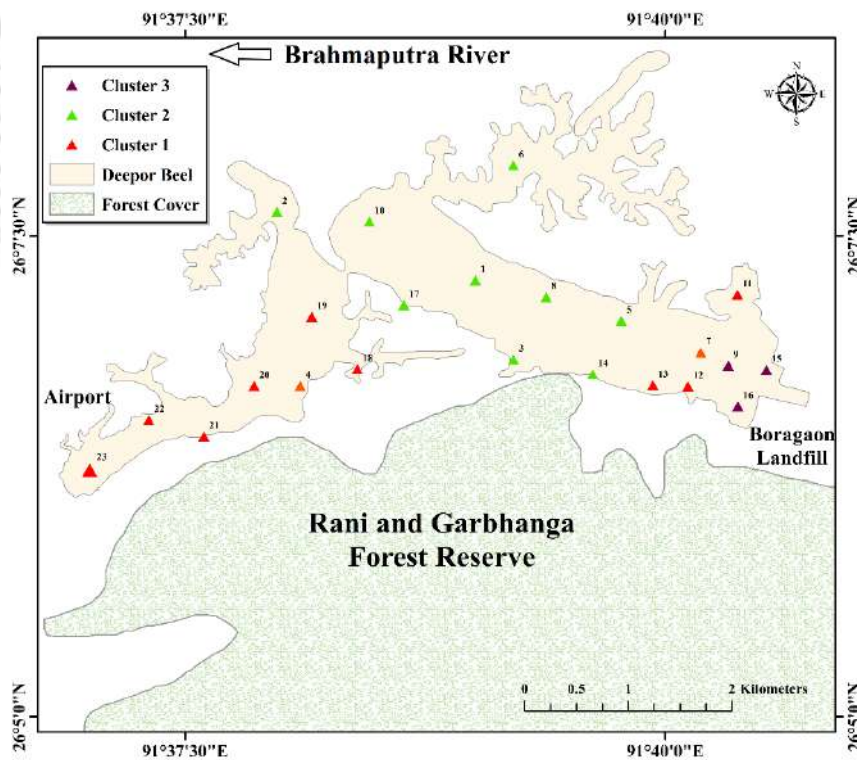
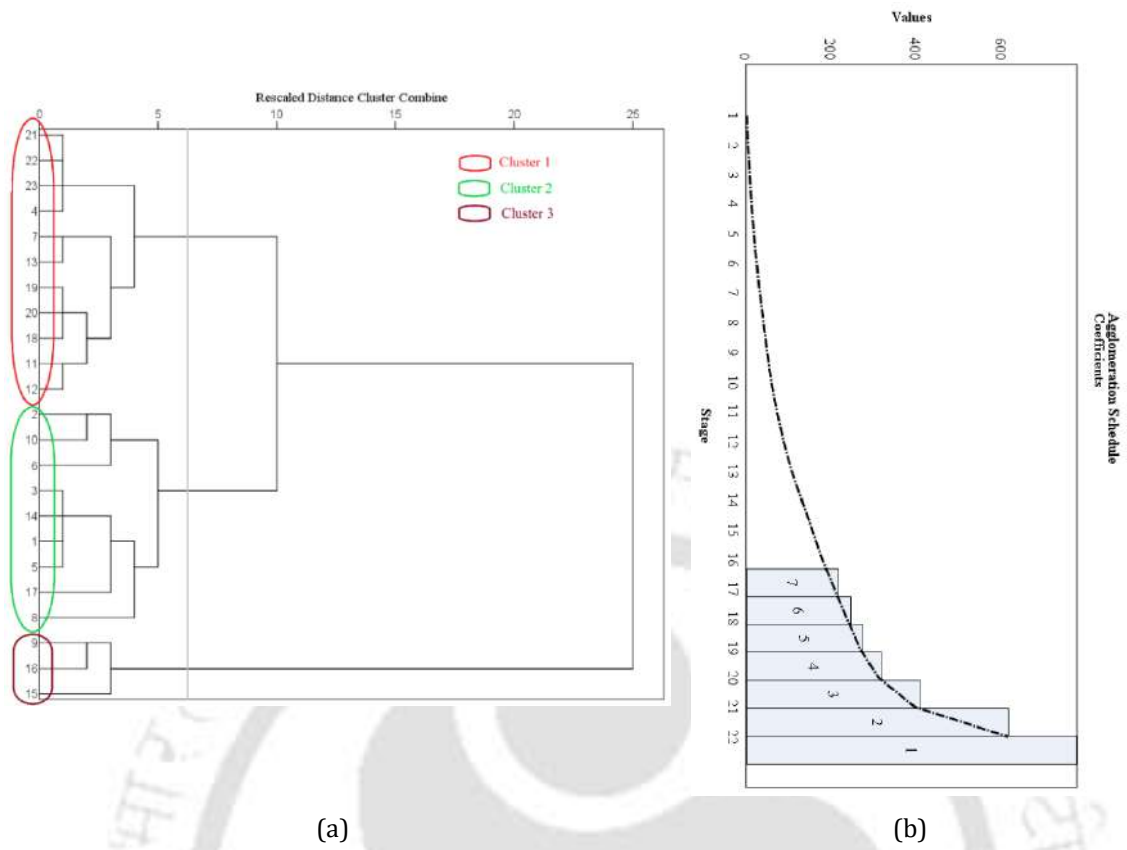
<sup>b</sup> Permissible limit in the absence of any alternate source.

It is also important to note that elements not having a permissible limit indicate no relaxation to their acceptable limit values.

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## 5.2. Hierarchical clustering of sampling locations and its validation

The hierarchical clustering of the 23 sampling locations of Deepor Beel resulted in classifying them into three major groups (clusters 1, 2, and 3), represented through a dendrogram (Fig. 5. 1a). The clustering was then validated using the agglomeration schedule coefficients, which generated a plot like a scree plot, but only backward (Fig. 5. 1b). The number of agglomerative schedule coefficients represents heterogeneity in a cluster solution (known as the *Stopping Rule* in hierarchical clustering). Hence, our main objective was to maximize the heterogeneity (distinction) for obtaining better clustering results. A single factor solution (single cluster) is the most distinct, with the following best being the split-up of the cluster into two parts, i.e., the formation of two clusters. However, often, two numbers of clusters are not considered to be ideal. Hence, the check is carried out for three clusters, then four, and so on until no significant jump (flatter slope) arises wherein the distinction is considered unsuitable. In the current study, it was observed that a steep slope was produced until the third cluster process, after which the slope of the curve became relatively flatter, thus indicating a lack of difference in the homogeneity among the clusters. This can also be visualized in Fig. 5. 1a, where distinct clusters were observed until the third clustering, after which the distance between the clustering schedule decreased significantly with the formulation of new clusters. This provided a relatively unclear picture about the further clustering process. Thus, three clusters (Fig. 5. 1a) were considered for the analysis. The sites categorized into 3 clusters were then plotted on a GIS platform to visualize the sampling locations better (Fig. 5. 1c). It was observed that the three locations belonging to cluster 3 were in the closest proximity to the Boragaon landfill site, thus providing evidence for maximum possible contamination among all the locations. Furthermore, cluster 2 categorizes all the sites located in the middle portion of the wetland, which has remained devoid of any significant anthropogenic contamination, thus indicating the sites having the least pollution. Lastly, the locations categorized under cluster 1 were observed to primarily belong to the areas proximate to the industrial complex (Western side of the wetland) or between the landfill site and the middle area. This is evidence of a moderate level of pollution, the sections between the landfill and the central portion of the wetland acting as a transition zone between high and medium contamination, respectively.



**Fig. 5. 1.** Hierarchical clustering (a) Dendrogram representation (b) validation of clustering and (c) representations of sampling locations through GIS plotting.

### 5.3. Discriminant analysis

The discriminant analysis (DA) technique was employed on the raw WQ dataset to determine the Spatio-temporal variation of the WQ parameters. Standard and stepwise modes were used for constructing the classification functions (CFs) (Table 5. 2). It was observed that only 9 (EC, TDS, TSS, PO<sub>4</sub><sup>3-</sup>, Na<sup>+</sup>, Mg, Cd, Pb and OrgN) out of the 28 parameters (based on the Fisher's Linear Discriminating Functions) were responsible for the discrimination, as well as the spatial variability among the three clusters. The generation of the CFs was validated using the classification matrix (Table 5. 3), which provided correct classifications among the discriminating functions using the stepwise mode of DA for 73.9% of the cross-validated grouped cases. The scores of the two functions were plotted (Fig. 5. 2a) along with the Wilk's lambda ( $\lambda$ ) values of the discriminating functions (Fig. 5. 2b). The values of  $\lambda$  varied from 0 - 0.14, which is numerically insignificant, thus indicating that the classes or groups formed are distinctive and that there is minimum overlapping between them.

**Table 5. 2.** Classification functions for discriminant analysis of the spatial variations along Deepor Beel.

	Classification Function Coefficients					
	Standard mode			Stepwise mode		
	Cluster			Cluster		
	1.00	2.00	3.00	1.00	2.00	3.00
DO	-279.321	-217.418	-517.047			
pH	-244.949	621.552	-1946.884			
EC	44886.626	56994.354	17176.709	15857.332	13221.401	13926.393
Turbidity	11.420	-16.576	58.262			
Alkalinity	278.840	227.627	389.087			
Hardness	40.375	-16.160	136.897			
BOD <sub>5</sub>	-516.219	-422.640	-648.016			
COD	69.615	31.753	120.657			
TDS	54.132	44.286	79.294	-5.362	-4.031	-2.896
TSS	-1.473	.097	-1.858	-.418	-.177	.180
F <sup>-</sup>	1972.947	1646.654	2419.821			
Cl <sup>-</sup>	-81.130	-56.241	-109.744			
NO <sub>3</sub> <sup>-</sup>	-66.961	-47.201	-57.353			
PO <sub>4</sub> <sup>3-</sup>	517.219	489.412	1596.487	524.481	569.092	943.303
SO <sub>4</sub> <sup>2-</sup>	3.645	13.609	-20.632			
Na <sup>+</sup>	301.637	326.161	218.933	92.884	86.114	118.290
K <sup>+</sup>	187.663	85.017	440.358			
Ca <sup>2+</sup>	-69.354	-49.078	-110.620			
TKN	98.193	20.189	203.213			

Mg	524.014	499.660	488.266	553.758	466.641	490.048
Cr	726.350	713.277	582.055			
Cd	20755.572	20470.825	28886.247	64908.078	63699.964	95741.628
Fe	-3866.103	-3853.944	-3543.238			
Mn	4096.467	4151.461	3587.756			
Cu	18679.943	18892.675	17487.073			
Pb	4560.400	4596.263	3600.740	-13594.566	-12600.372	-16764.891
NH <sub>3</sub> <sup>-</sup>	-422.741	-441.312	-448.577			
OrgN	72.609	73.789	75.372	60.170	55.527	72.409
(Constant)	-25656.941	-24058.597	-29344.87	-4213.607	-3517.647	-6156.426

Fisher's linear discriminant functions

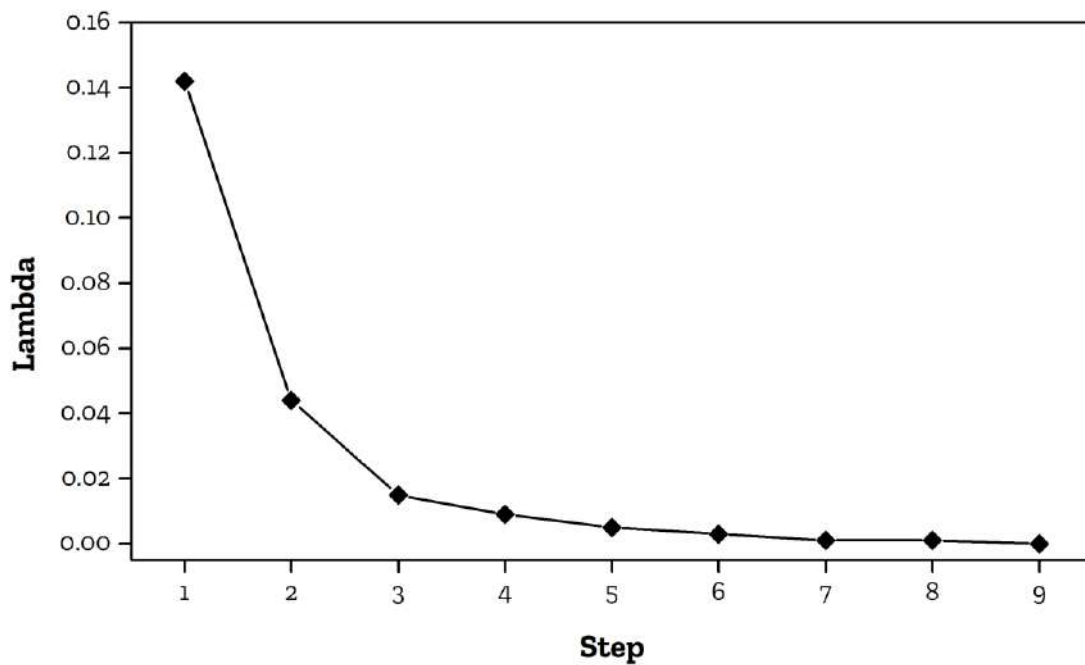
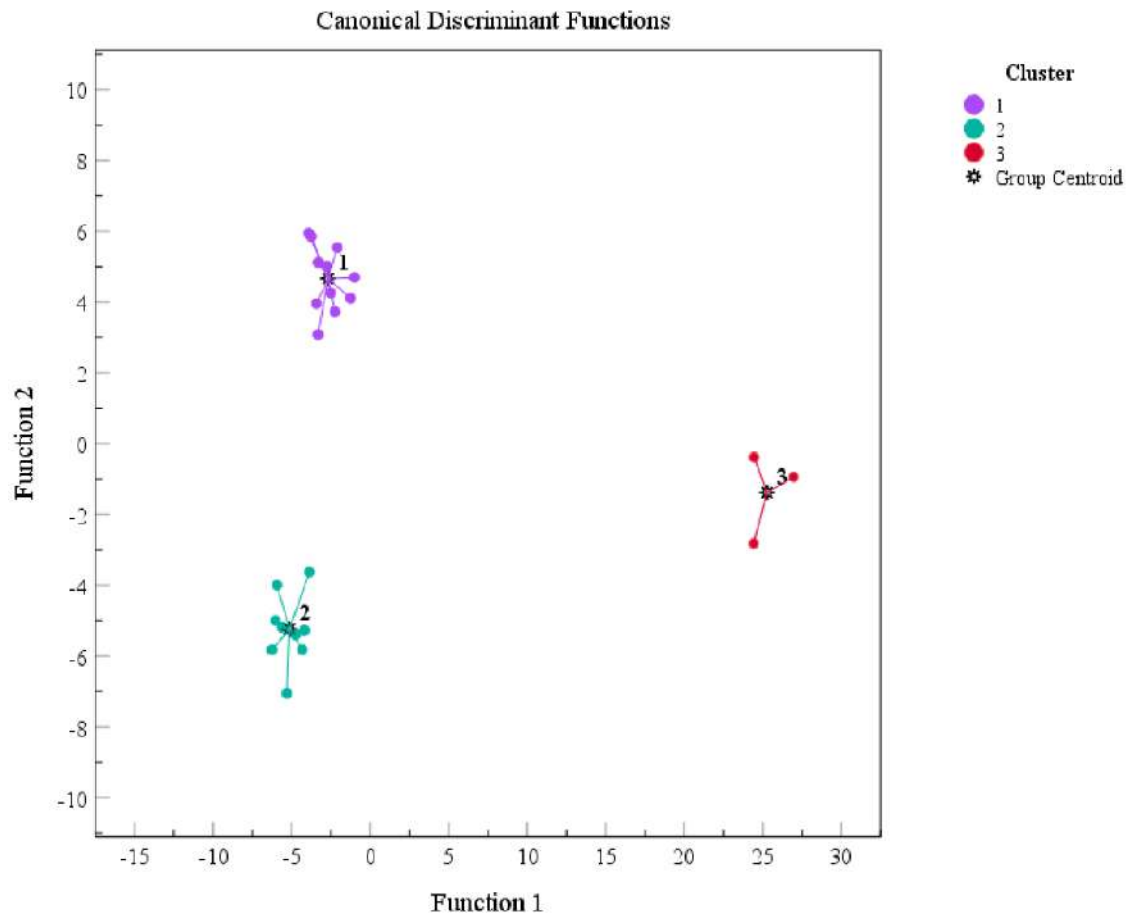
**Table 5. 3.** Classification matrix for discriminant analysis of the spatial variation along Deepor Beel.

		Classification Results <sup>a,c</sup>				
		Cluster	Predicted Group Membership			Total
	1		2	3		
Original	Count	1	11	0	0	11
		2	0	9	0	9
		3	0	0	3	3
	% Correct	1	100.0	0	0	100.0
		2	0	100.0	0	100.0
		3	0	0	100.0	100.0
Cross-validated <sup>b</sup>	Count	1	8	1	2	11
		2	0	7	2	9
		3	1	0	2	3
	% Correct	1	72.7	9.1	18.2	100.0
		2	0	77.8	22.2	100.0
		3	33.3	0	66.7	100.0

a. 100.0% of original grouped cases correctly classified.

b. Cross validation is done only for those cases in the analysis. In cross validation, each case is classified by the functions derived from all cases other than that case.

c. 73.9% of cross-validated grouped cases correctly classified.



**Fig. 5. 2.** (a) Scatter plot for the spatial discrimination analysis of water quality variations across three clusters (DA stepwise mode) (b) Wilk's Lambda values for the nine discriminating parameters.

## 5.4. Latent pollution sources

PCA employed on the normalized WQ dataset resulted in the formation of two primary principal components (PC-1 and PC-2), with eigenvalues  $> 1$ . KMO and Bartlett's sphericity test results (Table 5. 4) revealed the measure of sampling adequacy to be 0.742, with 253 degrees of freedom and a chi-square value of approximately 3743.39 and the value of  $p$  close to zero ( $p < 0.05$ ). This indicates the validity of the PCA due to their statistical significance between the variables (Kaiser 1974). Fig. 5. 3 represents the rotation factor matrix (Varimax rotation) of the two PCs. Values of PCs, numerically less than  $\pm 0.3$ , were considered weak loadings, while those with numerically higher values than  $\pm 0.7$  were regarded as PCs with a significant contribution with strong loading values. PCs with intermediate values  $\pm (0.3-0.7)$  were regarded to having a moderate impact.

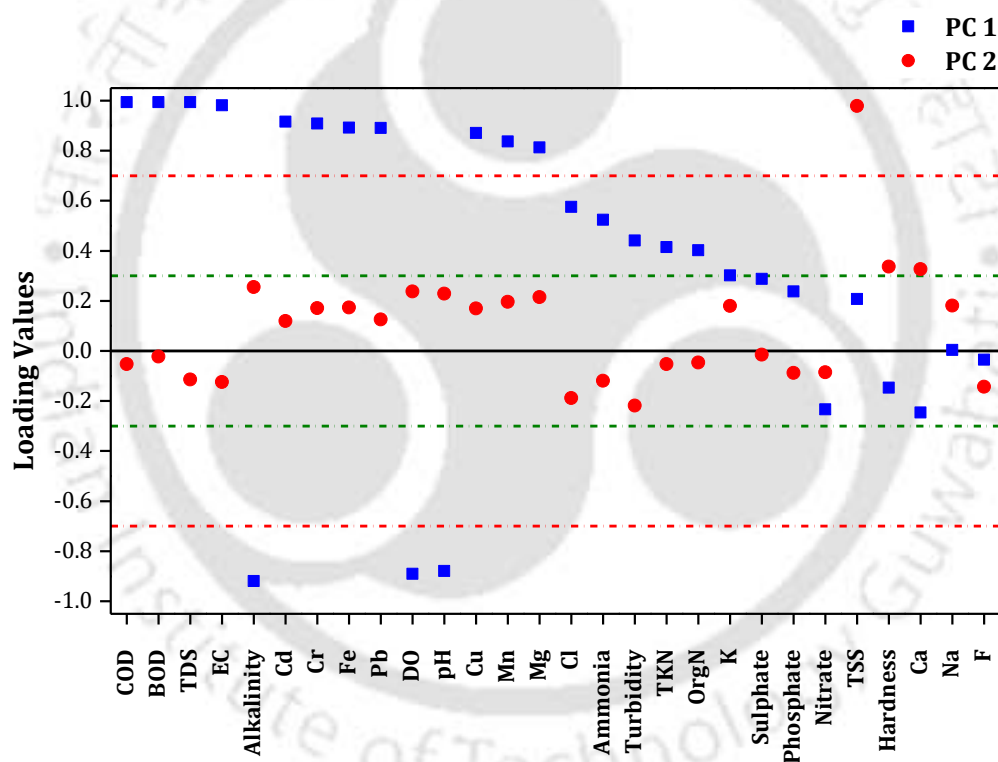


Fig. 5. 3. Rotation factor matrix (Varimax with Kaiser Normalization).

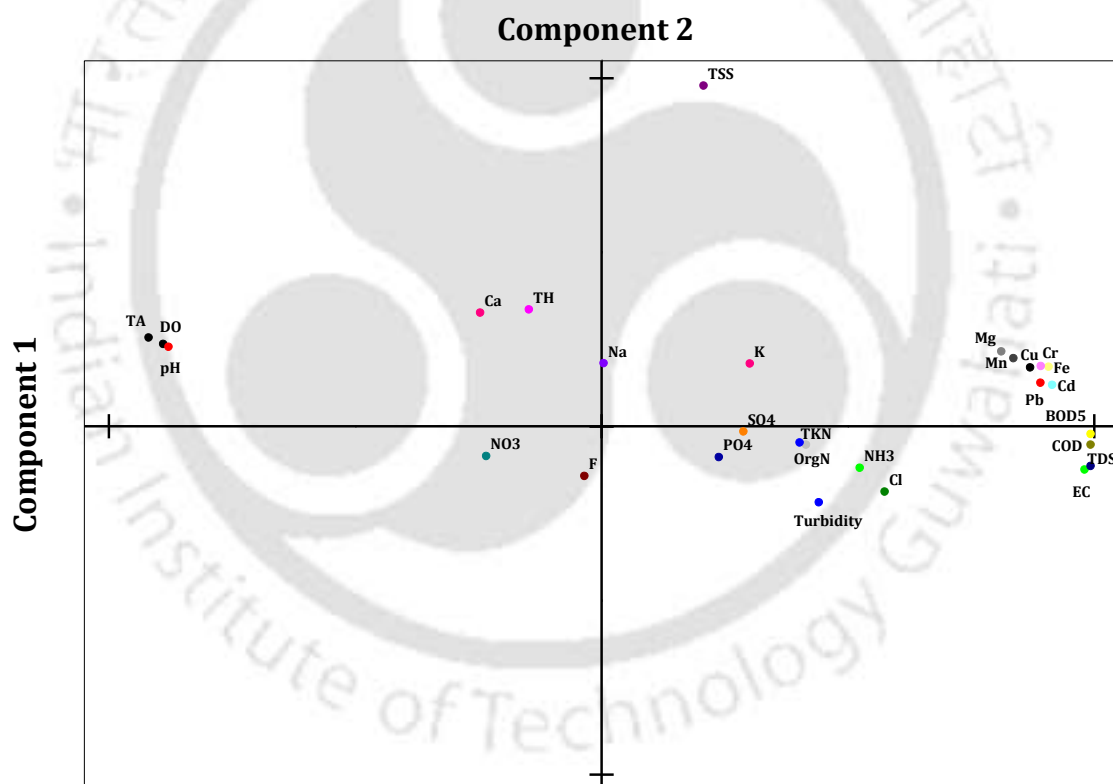
Table 5. 4. The results of KMO and Bartlett's sphericity test (obtained through PCA).

KMO and Bartlett's Test <sup>a</sup>		
Kaiser-Meyer-Olkin Measure of Sampling Adequacy		0.742
	Approximate Chi-Square	3743.387
Bartlett's Test of Sphericity	Degrees of Freedom	253
	Significance level	0.000

<sup>a</sup> Based-on correlations

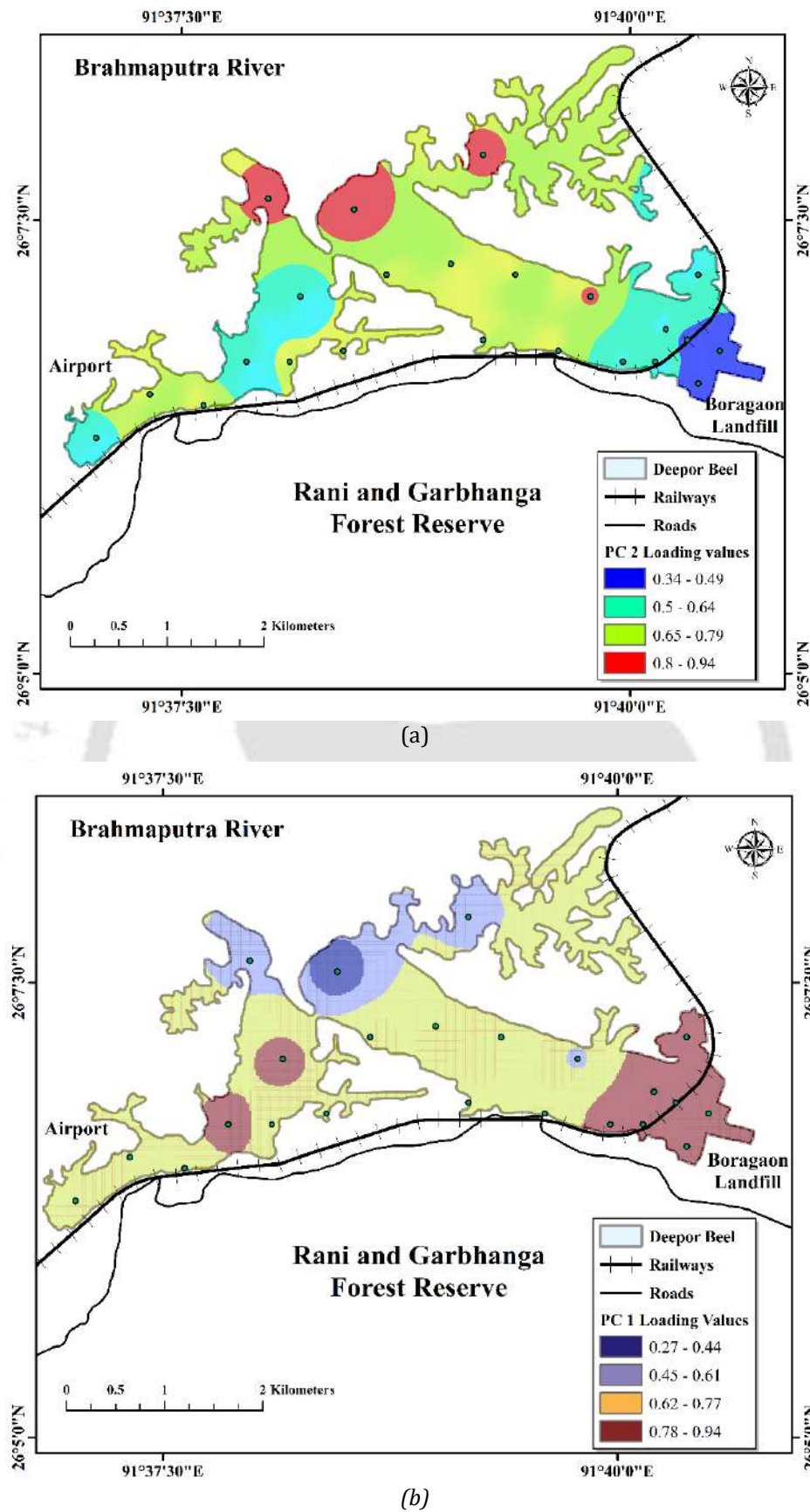
It was clearly observed that COD, BOD<sub>5</sub>, TDS, EC, Cd, Cr, Fe, Pb, Cu, Mn, and Mg exhibited strong positive loadings for PC-1, indicating substantial anthropogenic interference such as the Boragaon landfill and the industries in the wetland. Strong negative loading of DO displayed promising results in PC-1 as the values of DO vary inversely with the BOD/COD values. Furthermore, moderate loading values for Cl<sup>-</sup>, NH<sub>3</sub>, turbidity, TKN, and OrgN indicate a secondary source of organic contamination to the wetland (possibly from the Basistha River, which drains its water primarily composing municipal wastewater into Deepor Beel). PC-2, however, showed a strongly favourable loading for TSS while having moderate loadings for TH and Ca, indicative of a natural surface water runoff being the major probable contributor.

Fig. 5. 4 presents an overall summary of the PCA carried out for the WQ dataset. It provides the parameters (variables) which are associated more with a particular component along with the correlations existing between them.



**Fig. 5. 4.** PCA analysis results showing plot between the two PCs in a rotated space.

For example, it can be observed that BOD<sub>5</sub>, EC, TDS, COD, and all the metals were observed to have a higher affinity towards PC-1. Similar is the case for TA, DO and pH. However, they lie on the opposite quadrant, thus displaying a highly negative correlation. Similarly, TSS, TH, Na<sup>+</sup>, Ca<sup>2+</sup>, NO<sub>3</sub><sup>-</sup>, and F<sup>-</sup> are affiliated more towards PC-2, with F<sup>-</sup> and NO<sub>3</sub><sup>-</sup> being negatively correlated to other variables.



**Fig. 5. 5.** GIS mapping showing the distribution of principal factors (a) PC-1 and (b) PC-2 for each of the sampling locations.

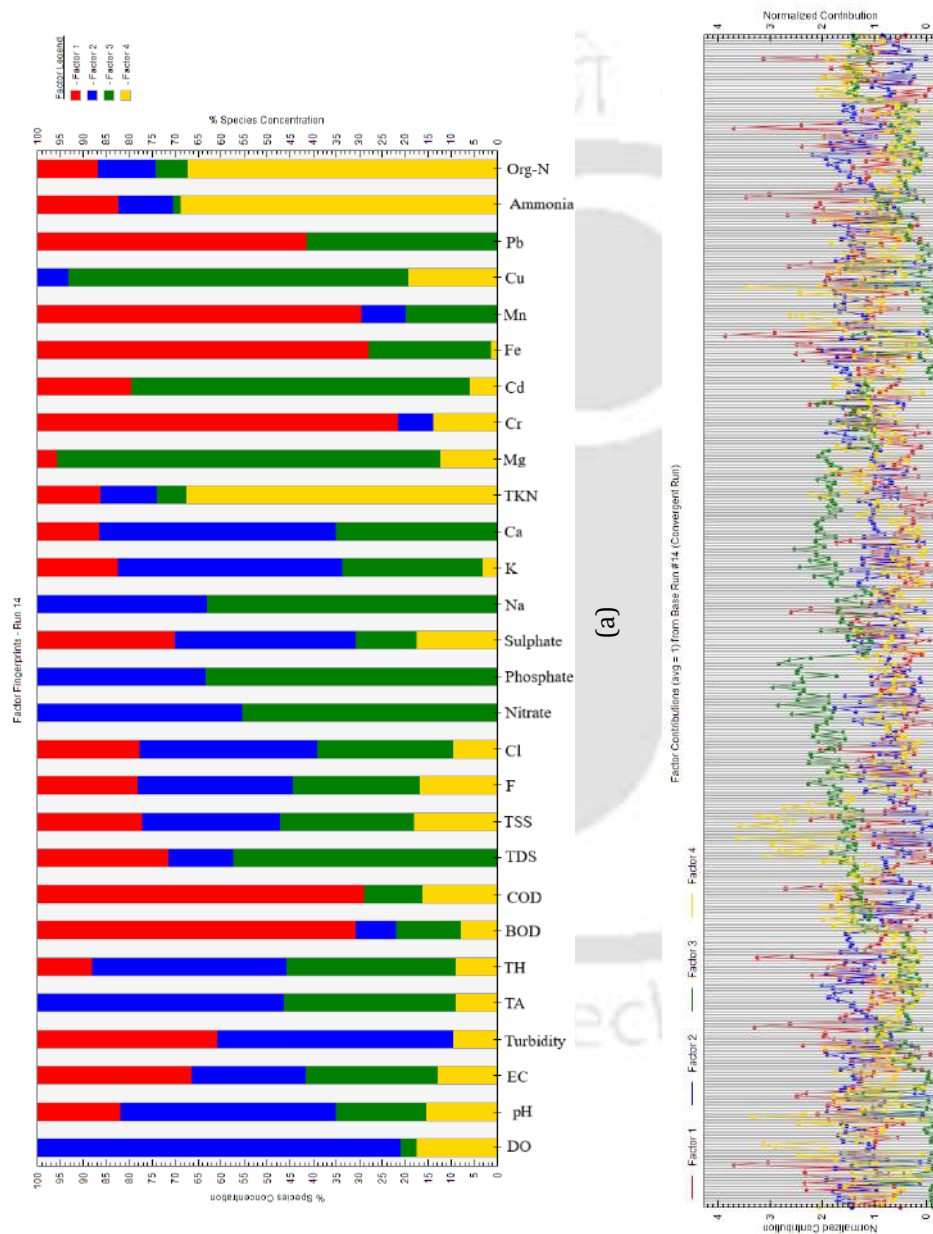
Fig. 5. 5 is a spatial representation of the PC loading values (PC-1 and PC-2). Clearly, PC-1 had higher loading values near the landfill site and the industrial zone, representing sites having higher anthropogenic contamination factors (Fig. 5. 5a). Similarly, PC-2 showed higher values towards the central region of the wetland (Fig. 5. 5b), thus indicating natural factors of contamination of Deepor Beel.

## 5.5. Source apportionment

The source apportionment and various factor contributions were estimated using the EPA - PMF software, which considers the concentration and uncertainty factors as input to the model. The resulting input parameters then generated a signal/noise ratio for each of the WQ parameters. Based on the S/N ratio, the parameters were classified as Strong ( $S/N > 2$ ), Weak ( $0.2 < S/N < 2$ ) and Bad ( $S/N < 0.2$ ) respectively. Four factors; 1, 2, 3, and 4, were considered for the PMF analysis to assess each of their contributions to the water pollution of Deepor Beel, based on the results of the iterations for each factor obtaining the minimum  $Q(\text{Robust})/Q_{\text{exp}}$  value (Table 5. 5). The model was then simulated, considering all the input parameters and the four factors, providing results, as shown in Fig. 5. 6 and Fig. 5. 7. It can be seen that Factor 1 is primarily dominated by  $\text{BOD}_5$  (69.3%), COD (71%), Cr (78.5%), Fe (71.9%), Mn (70.6%) and Pb (58.6%). This indicates a source rich in organic matter, as well as heavy metals. Thus, leaching from the Boragaon landfill site can be considered the major source of contamination for Factor 1 since the municipal landfill site leachates are highly organic due to various organic wastes (e.g. food wastes) being dumped into the landfill. Also, the inorganic wastes rich in heavy metals such as batteries, scrap, and unused metals contribute to the leaching of heavy metals (Chu *et al.* 1994). Furthermore, DO (79.1%), pH (46.9%), TA (53.6%), TH (42.3%), Turbidity (51.4%),  $\text{K}^+$  (48.7%) and  $\text{Ca}^{2+}$  (51.2%) were observed to have significant contribution to water contamination of Deepor Beel pertaining to Factor 2. This is an indicator of a natural cause of pollution, such as surface water runoff. Similarly, for Factor 3, TDS (57.5%),  $\text{NO}_3^-$  (55.4%),  $\text{PO}_4^{3-}$  (63.5%),  $\text{Na}^+$  (63%),  $\text{Mg}^{2+}$  (83.2%), Cd (73.7%), and Cu (74%) were found to be the predominating parameters. Industrial wastewater effluents enriched with contagious trace metal elements along with cations and anions might be the primary factor responsible for this. Finally, TKN (67.6%),  $\text{NH}_3^-$  (68.8%) and OrgN (67.2%) were found to be the parameters affecting Factor 4 the most. This indicates contamination from a source primarily rich in nutrients. Thus, discharge from Basistha River (carrying large concentrations of domestic sewage) might be the primary factor responsible. Fig. 5. 6a and Fig. 5. 6b represent the Factor Figureprints and the normalized contributions for all the 28 WQ parameters, summarising the PMF results.

**Table 5.5.** Summary of PMF and EE diagnostics by a run for water quality data of Deepor Beel.

Diagnostic	2 factors	3 factors	4 factors	5 factors	6 factors	7 factors
Qexp	247.9	358.1	1358.1	2043.1	830.4	375.8
Q(True)	9731.1	7069.0	1566.9	3288.5	3290.6	4023.8
Q(Robust)	9649.1	7017.3	1566.8	3245.3	3300.0	4001.9
Q(Robust)/Qexp	38.92	19.59	1.15	1.59	3.97	10.64



**Fig. 5.6.** (a) Factor Fingerprints and (b) Normalized contribution profile of all the 28 parameters resulted from EPA – PMF model.

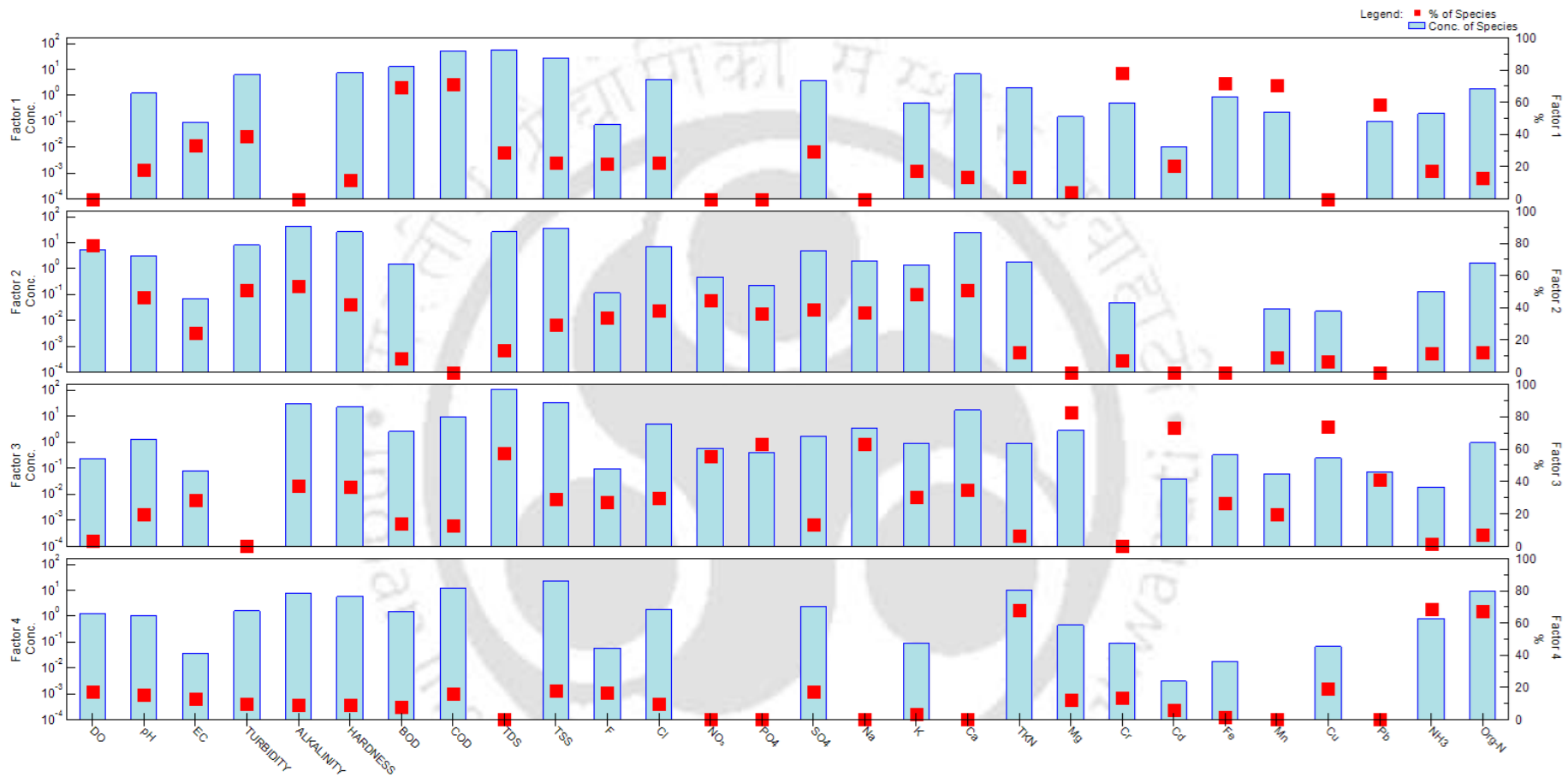


Fig. 5. 7. PMF source profiling of 28 WQ parameters for Deepor Beel.

## 5.6. Summary

This study presented a detailed insight into the geochemistry and assessment of water quality as well as apportioning of various pollution sources contributing to the water contamination of Deepor Beel using different Environmetrics tools. Critical concluding remarks of the study are as follows:

- a. Hierarchical clustering categorized the 23 sampling locations of the study area into three statistically distinct clusters. The clustering process was further validated using the "Stopping Rule". It was observed that the sites closest to the Boragaon landfill, locations present in the central portion and the industrial zone of the wetland formed separate and distinct clusters based on the site similarities. They were considered as sites of high, low, and moderate contaminations, respectively.
- b. The discriminant analysis provided the significance of clustering by discriminating the parameters responsible. Nine (EC, TDS, TSS,  $\text{PO}_4^{3-}$ ,  $\text{Na}^+$ , Mg, Cd, Pb and OrgN) out of 28 parameters were responsible for the discrimination and the spatial variability among the three clusters. Low Wilk's  $\lambda$  values also validated that the groups formed were distinctive with minimum overlapping between them.
- c. The principal component analysis applied to the normalized dataset yielded two principal components, which aided in identifying potential pollution sources. PC-1 indicated anthropogenic contamination as the primary source, while PC-2 suggested natural phenomena such as surface water runoff to be the primary source. Spatial representation of the sites also revealed similar results.
- d. The WQ dataset matrix was finally subjected to factorization generating a model for source apportionment. Leaching from the Boragaon landfill site, surface water runoff, discharge of effluents from the industries in the wetland and discharge from Basistha River were found to be the significant factors for the pollution of Deepor Beel.



We still have too much air and water pollution and we still need to work to reduce it. But we also need to put the problem of pollution into a historical as well as scientific perspective.

- Ronald Reagan

# 6

## Indexing approach to assessing water quality depending on end-use of water

This chapter provides detailed insights into the results obtained for Objective II. The spatio-temporal variations of water quality in Deepor Beel for different end-uses of water have been assessed through two primary indexing techniques, i.e., information entropy and multivariate statistics.

### 6.1. Assessment of overall water quality

For assessment of the overall water quality of Deepor Beel, the entire water quality dataset was divided seasonally into three categories; pre-monsoon (January-March), monsoon (April-September), and post-monsoon (October-December) period.

#### 6.1.1. Modified Entropy-weighted WQI approach

Table 6. 1 and Fig. 6. 1 provide a detailed representation of the Spatio-temporal variability of the MEWQI.

**Table 6. 1.** Percentage distribution (sampling locations) of MEWQI classes across various seasons.

Classes	Pre-monsoon	Monsoon	Post-monsoon
Excellent	0.00	0.00	0.00
Very Good	4.35	0.00	0.00
Good	65.22	0.00	47.83
Fair	21.74	0.00	39.13
Poor	8.70	56.52	8.70
Extremely Poor	0.00	43.48	4.35

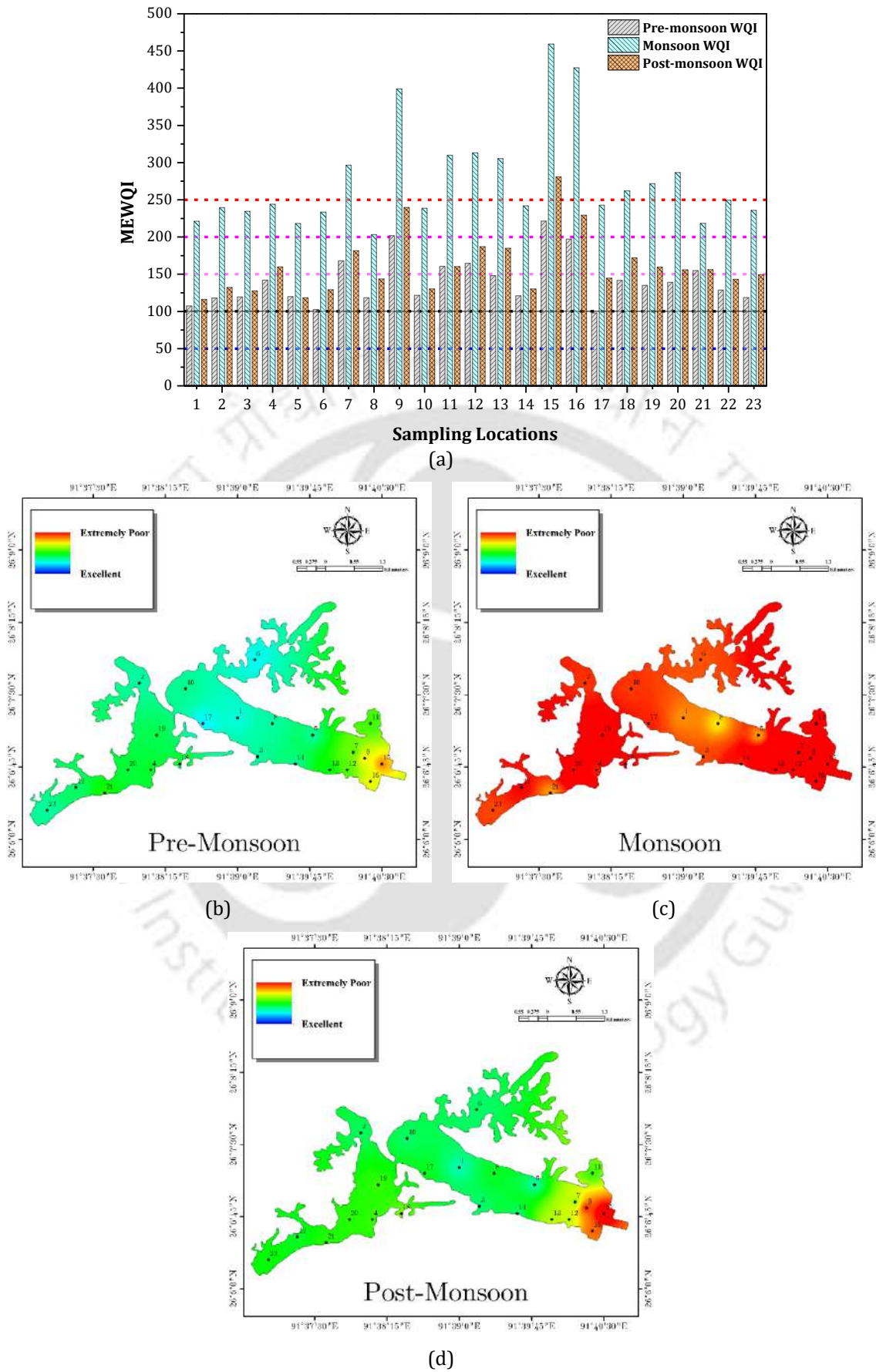


Fig. 6.1. Spatio-temporal variation of MEWQI.

The pre-monsoon period was observed to be the best as far as the water quality of Deepor Beel is concerned, as more than 65% of the sampling locations fell under the "Good" category, while none of the locations was classified as "Extremely Poor". However, the sampling locations 9 and 15 fell under the "Poor" category, while the 16<sup>th</sup> location had a MEWQI value of just less than 200 (197). These locations are the closest to the Boragaon landfill, while site 15 is the confluence point of Deepor Beel and the Basistha River, thereby rendering it very high MEWQI values, even during the lean period. Additionally, site 17 fell under the "Very Good" category, making it the cleanest site.

The monsoon was observed to have the most adverse effect on the water quality of Deepor Beel, as all locations, irrespective of their proximity to any probable pollution source, fell under the "Poor" or "Extremely Poor" category. The MEWQI values varied from a minimum of 203 to a maximum of well over 450, thereby showing the extent of pollution in the entire wetland. This is primarily attributed to large amounts of leaching from the solid waste dumpsite and the discharges from the industries. Also, vast amounts of stormwater runoff from the vicinity of the area, such as the Rani and Garbhanga forest reserve, further enhance water pollution. Significant discharges of heavy metals and organic loadings were found to be the major contributing factor for the degradation of water quality during the monsoon.

For the post-monsoon period, the water quality remains more or less within the "Good" and "Fair" range, while some sites (9 and 16) remained within the "Poor" category. Location 15 fell under the "Extremely Poor" category. This is indicative of the receding monsoon, and with that, the leaching of contaminants from various pollution sources is also reduced to a considerable extent. This makes the wetland less susceptible to water pollution, and thus the water quality starts improving with the advent of the pre-monsoon period.

To understand the proposed method's efficacy, a significantly reliable tool known as the cluster analysis was employed on the water quality dataset, averaged over the entire sampling period. IBM SPSS Statistics (v.25) was used for the computation process. Ward's method employing the Squared Euclidean distance method was employed after the entire dataset was normalized using the Z-scale transformation (Wilks 2011). The clustering process resulted in a graphical interpretation through a dendrogram, which provided information regarding the high intra-cluster and low inter-cluster similarities (Fig. 6. 2a) (Shrestha & Kazama 2007). Clearly, at  $D_{link}/D_{max} = 10$ , the 23 sampling locations were found to be categorized into three clusters; Clusters 1, 2, and 3, the spatial mapping of which as shown in Fig. 6. 2b. It was observed that locations 9, 15, and 16 (cluster 1) displayed similar behaviour, verified by the MEWQI values obtained. These three locations always displayed significantly higher yet numerically closer values even during the lean periods of pre-monsoon and post-monsoon. This

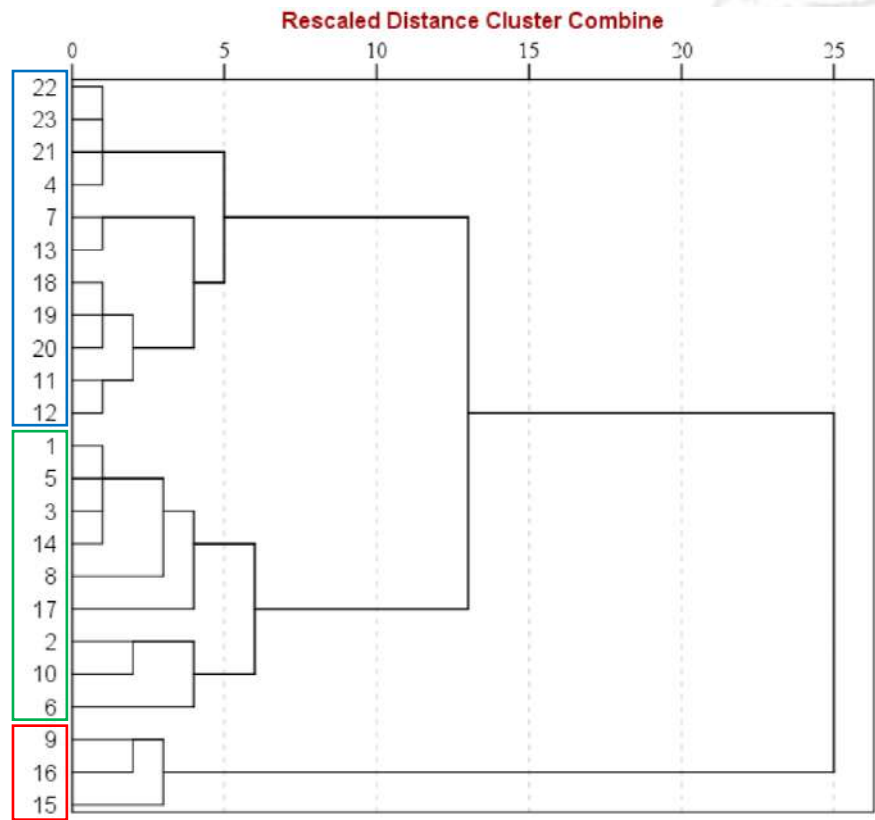
makes them highly polluted (HP) locations. Likewise, cluster 2 (locations 1, 2, 3, 5, 6, 8, 10, 14, and 17) primarily comprise locations with considerably low pollution (LP). This is also reflected in the MEWQI values obtained, as shown in Fig. 6. 1, wherein these locations constituted the minimum MEWQI values, with 17 being the cleanest site, during the pre-monsoon period, having a value less than 100. Lastly, the third cluster (locations 4, 7, 11, 12, 13, 18, 19, 20, 21, 22, and 23) constituted sites of relatively moderate pollution (MP), which is also indicative of the MEWQI values that lied between the HP and LP locations. It is also interesting to observe that sites 7, 11, 12, and 13 acted as a buffer zone between clusters 1 and 2, making it even more convenient to understand the reliability of the use of the proposed MEWQI methodology.

### 6.1.2. PC-weighted WQI approach

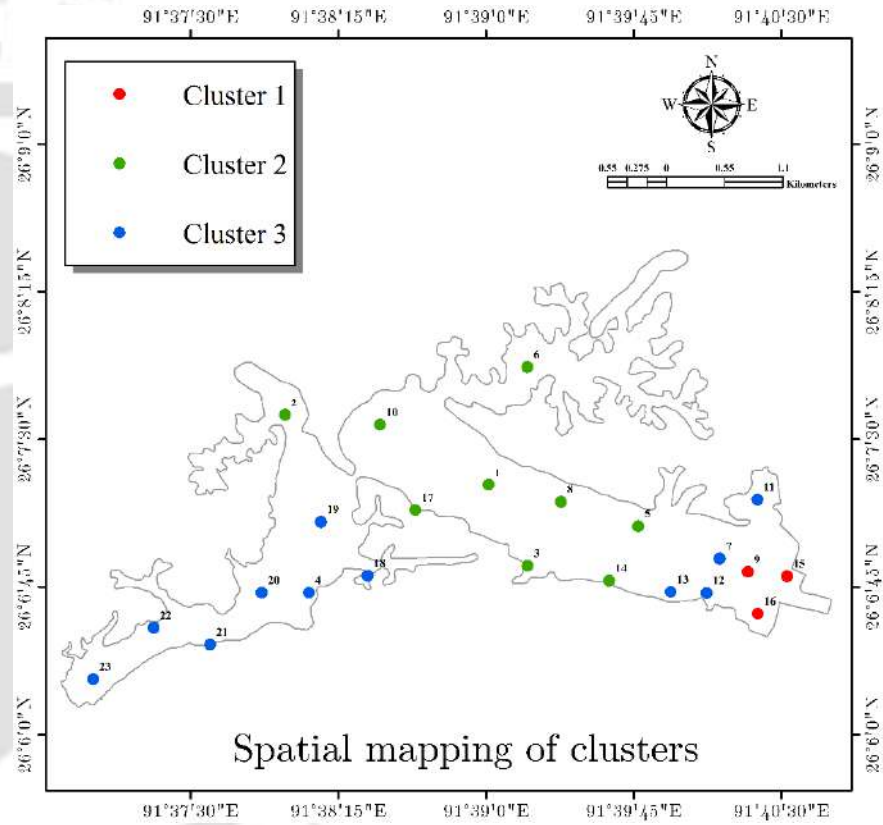
For determining the PCA-WQI values, the first step was to categorize the sampling locations based on their similarities. The HCA classified the sampling locations into three principal categories, as depicted through dendrogram and spatial representation through Fig. 6. 2. Clearly, cluster 1 represents high pollution sites, owing to their proximity to the landfill. Cluster 2 indicates sites receiving the minimum pollution, while cluster 3 represents sites with moderate pollution loadings; the pollution levels lie between clusters 1 and 2. Additionally, as the sites progress from the high pollution to the minimum pollution, a transition occurs between them, represented by sites 7, 11, 12 and 13 (moderate pollution).

Post HCA, PCA on each cluster was carried out, resulting in principal components, i.e., PCs used to estimate sub-index values. The PCs for each cluster are given in Table 6. 2. It is evident that cluster 1 is primarily attributed to the anthropogenic contamination due to the leaching from the Boragaon landfill. This is because PC-1, which contributes to nearly 61% of the variance, is governed by parameters such as DO, BOD,  $PO_4^{3-}$ ,  $SO_4^{2-}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , Cr, Cd, Fe, Mn, Cu, and Pb, which are strong indicators of anthropogenic contamination. Negative DO is attributed to positive BOD, as both vary inversely to each other. Likewise, cluster 2 is primarily attributed to natural contamination and minimum anthropogenic interferences.

This is because PC-1 of cluster 2 that accounts for nearly 54% of the variances are governed by naturally contaminating components, such as pH, EC, Turbidity, TA, TDS, and  $PO_4^{3-}$ . Furthermore, cluster 3 is primarily attributed to heavy metal leaching from the industries located nearby. This is attributed to PC-1 of cluster 3, which accounts for about 50% of the variances and is governed by parameters such as EC, and heavy metals like  $Mg^{2+}$ , Cr, Cd, Fe, Mn, Cu, and Pb.



(a)



(b)

**Fig. 6. 2.** Result of the cluster analysis through (a) a Dendrogram and (b) its spatial extent.

**Table 6. 2.** Varimax-rotated component matrix for different water quality parameters for 23 different monitoring locations of Deepor Beel (Rotation method: Varimax with Kaiser normalization).

<b>(a) Cluster 1</b>		
<b>Eigenvalue</b>	14.627	9.373
<b>Variance (%)</b>	60.945	39.055
<b>Cumulative variance (%)</b>	60.945	100
<b>Principal Component</b>	<b>1</b>	<b>2</b>
DO	-0.994	0.111
pH	-0.952	-0.306
EC	0.932	-0.363
Turbidity	-0.195	-0.981
TA	-0.932	0.363
TH	0.261	-0.965
BOD	0.996	0.087
TDS	0.994	-0.112
F <sup>-</sup>	0.321	0.947
Cl <sup>-</sup>	0.819	-0.574
NO <sub>3</sub> <sup>-</sup>	-0.215	0.977
PO <sub>4</sub> <sup>3-</sup>	-0.818	-0.576
SO <sub>4</sub> <sup>2-</sup>	0.946	0.323
Na <sup>+</sup>	-0.363	0.932
K <sup>+</sup>	0.429	0.903
Ca <sup>2+</sup>	0.958	0.286
Mg <sup>2+</sup>	0.995	-0.100
Cr	0.975	0.224
Cd	0.975	-0.22
Fe	0.892	0.451
Mn	0.985	0.171
Cu	0.999	0.039
Pb	0.966	0.259
NH <sub>4</sub> <sup>-</sup>	-0.293	-0.956

<b>(b) Cluster 2</b>					
<b>Eigenvalue</b>	12.892	4.204	2.445	2.089	1.256
<b>Variance (%)</b>	53.715	17.516	10.186	8.702	5.234
<b>Cumulative variance (%)</b>	53.715	71.231	81.418	90.12	95.354
<b>Principal Component</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
DO	-0.899	-0.318	0.185	-0.018	-0.081
pH	-0.864	-0.294	0.326	0.169	-0.002
EC	0.912	0.382	-0.066	0.072	0.103

Turbidity	0.743	0.555	0.114	0.176	0.041
TA	-0.85	-0.332	0.281	0.007	-0.044
TH	0.111	-0.214	0.943	-0.042	-0.144
BOD	0.877	0.457	-0.073	0.044	0.1
TDS	0.871	0.446	-0.11	0.031	0.099
F <sup>-</sup>	0.015	-0.032	-0.057	-0.992	0.028
Cl <sup>-</sup>	0.155	-0.145	-0.388	-0.576	0.658
NO <sub>3</sub> <sup>-</sup>	-0.55	0.187	0.785	0.164	-0.056
PO <sub>4</sub> <sup>3-</sup>	0.816	0.384	0.378	0.005	0.109
SO <sub>4</sub> <sup>2-</sup>	-0.108	-0.389	-0.14	0.272	0.819
Na <sup>+</sup>	-0.011	0.143	0.648	0.412	-0.142
K <sup>+</sup>	0.201	-0.111	0.064	0.767	0.501
Ca <sup>2+</sup>	-0.238	-0.199	0.937	-0.036	-0.109
Mg <sup>2+</sup>	0.361	0.922	-0.087	-0.046	-0.082
Cr	0.411	0.89	-0.149	-0.033	-0.091
Cd	0.608	0.786	0.014	0.057	0.062
Fe	0.274	0.924	-0.158	-0.058	-0.153
Mn	0.414	0.908	0.022	0.04	-0.008
Cu	0.261	0.961	0.018	0.047	-0.06
Pb	0.565	0.807	0.058	0.084	0.068
NH <sub>4</sub> <sup>+</sup>	0.453	0.233	-0.229	-0.006	0.776
<b>(c) Cluster 3</b>					
<b>Eigenvalue</b>	11.928	4.064	2.607	1.414	1.355
<b>Variance (%)</b>	49.702	16.933	10.864	5.893	5.644
<b>Cumulative variance (%)</b>	49.702	66.634	77.499	83.392	89.036
<b>Principal Component</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
DO	-0.974	0.05	-0.065	0.087	0.096
pH	-0.827	-0.024	-0.363	0.275	-0.078
EC	0.978	-0.006	-0.053	-0.031	-0.039
Turbidity	-0.35	-0.644	0.096	-0.264	0.602
TA	-0.976	0.012	-0.05	-0.086	0.103
TH	-0.289	0.541	0.268	-0.06	-0.646
BOD	0.961	0.011	0.053	-0.129	-0.056
TDS	0.95	0.000	0.008	-0.132	-0.131
F <sup>-</sup>	0.184	-0.197	-0.312	-0.496	-0.31
Cl <sup>-</sup>	-0.253	0.445	0.255	0.287	-0.049
NO <sub>3</sub> <sup>-</sup>	0.265	0.087	0.907	0.249	-0.007
PO <sub>4</sub> <sup>3-</sup>	0.201	-0.271	-0.015	0.914	0.024
SO <sub>4</sub> <sup>2-</sup>	0.038	0.007	-0.077	0.179	0.767

Na <sup>+</sup>	-0.072	0.469	0.786	0.027	-0.314
K <sup>+</sup>	-0.599	0.75	-0.11	-0.14	0.197
Ca <sup>2+</sup>	0.05	0.876	0.339	-0.101	-0.136
Mg <sup>2+</sup>	0.972	-0.102	-0.029	0.175	0.03
Cr	0.971	-0.085	-0.046	0.138	0.099
Cd	0.939	-0.01	-0.096	0.143	0.191
Fe	0.966	-0.142	0.066	0.123	0.066
Mn	0.977	-0.121	0.02	0.116	0.079
Cu	0.912	-0.321	0.117	0.049	-0.045
Pb	0.961	-0.006	-0.033	0.174	0.099
NH <sub>4</sub> <sup>-</sup>	0.163	0.42	0.307	0.631	0.161

The PCs obtained from the PCA for each independent cluster were then used to compute the sub-index values, details of which are represented in Table 6. 3. The weights computed from Table 6. 3 were finally employed to determine the overall PCA-WQI through Eq. 4.37.

**Table 6. 3.** Weights for different variables in water samples from Deepor Beel.

**(a) Cluster 1**

PC	Eigen-value	Relative eigen-value	Variable	Loading Value	Relative Loading Value	Weight
1	14.627	0.609	DO	0.994	0.062	0.038
			pH	0.952	0.059	0.036
			EC	0.932	0.058	0.035
			TA	0.932	0.058	0.035
			BOD	0.996	0.062	0.038
			TDS	0.994	0.062	0.038
			Cl <sup>-</sup>	0.819	0.051	0.031
			PO <sub>4</sub> <sup>3-</sup>	0.818	0.051	0.031
			SO <sub>4</sub> <sup>2-</sup>	0.946	0.059	0.036
			Ca <sup>2+</sup>	0.958	0.059	0.036
			Mg <sup>2+</sup>	0.995	0.062	0.038
			Cr	0.975	0.060	0.037
			Cd	0.975	0.060	0.037
			Fe	0.892	0.055	0.034
			Mn	0.985	0.061	0.037
			Cu	0.999	0.062	0.038
Pb	0.966	0.060	0.037			
			<b>Total</b>	<b>16.128</b>		
2	9.373	0.391	Turbidity	0.981	0.147	0.058

TH	0.965	0.145	0.057
F <sup>-</sup>	0.947	0.142	0.056
NO <sub>3</sub> <sup>-</sup>	0.977	0.147	0.057
Na <sup>+</sup>	0.932	0.140	0.055
K <sup>+</sup>	0.903	0.136	0.053
NH <sub>4</sub> <sup>-</sup>	0.956	0.144	0.056
<b>Total</b>	<b>6.661</b>		

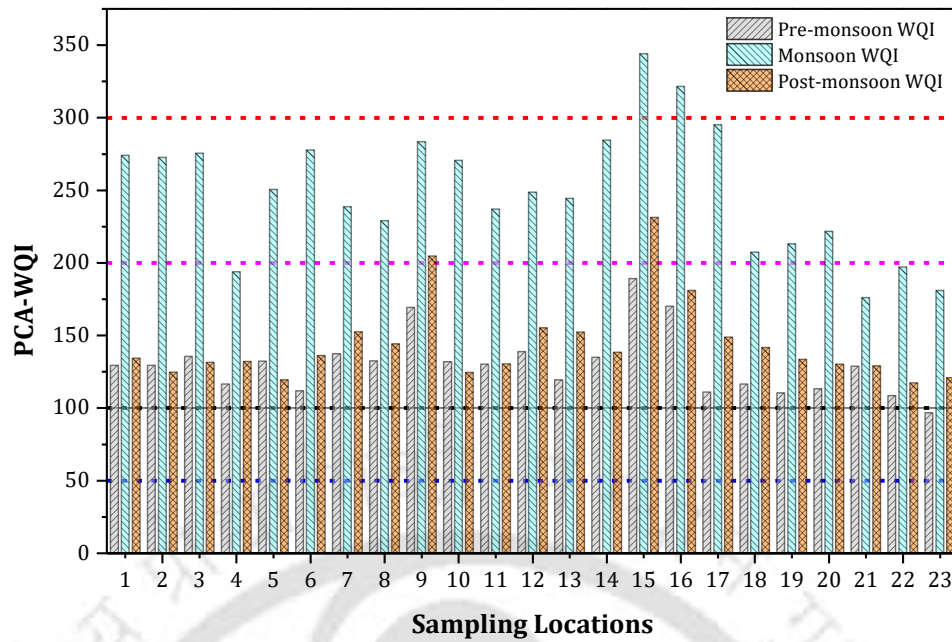
**(b) Cluster 2**

PC	Eigen-value	Relative eigen-value	Variable	Loading Value	Relative Loading Value	Weight
1	12.892	0.563	DO	0.899	0.132	0.074
			pH	0.864	0.126	0.071
			EC	0.912	0.133	0.075
			Turbidity	0.743	0.109	0.061
			TA	0.850	0.124	0.070
			BOD	0.877	0.128	0.072
			TDS	0.871	0.127	0.072
			PO <sub>4</sub> <sup>3-</sup>	0.816	0.119	0.067
			<b>Total</b>	<b>6.832</b>		
2	4.204	0.184	Mg <sup>2+</sup>	0.922	0.149	0.027
			Cr	0.890	0.144	0.026
			Cd	0.786	0.127	0.023
			Fe	0.924	0.149	0.027
			Mn	0.908	0.146	0.027
			Cu	0.961	0.155	0.028
			Pb	0.807	0.130	0.024
			<b>Total</b>	<b>6.198</b>		
3	2.445	0.107	TH	0.943	0.285	0.030
			NO <sub>3</sub> <sup>-</sup>	0.785	0.237	0.025
			Na <sup>+</sup>	0.648	0.196	0.021
			Ca <sup>2+</sup>	0.937	0.283	0.030
			<b>Total</b>	<b>3.313</b>		
4	2.089	0.091	F <sup>-</sup>	0.992	0.564	0.051
			K <sup>+</sup>	0.767	0.436	0.040
			<b>Total</b>	<b>1.759</b>		
5	1.256	0.055	Cl <sup>-</sup>	0.658	0.292	0.016
			SO <sub>4</sub> <sup>2-</sup>	0.819	0.364	0.020
			NH <sub>4</sub> <sup>-</sup>	0.776	0.344	0.019
			<b>Total</b>	<b>2.253</b>		

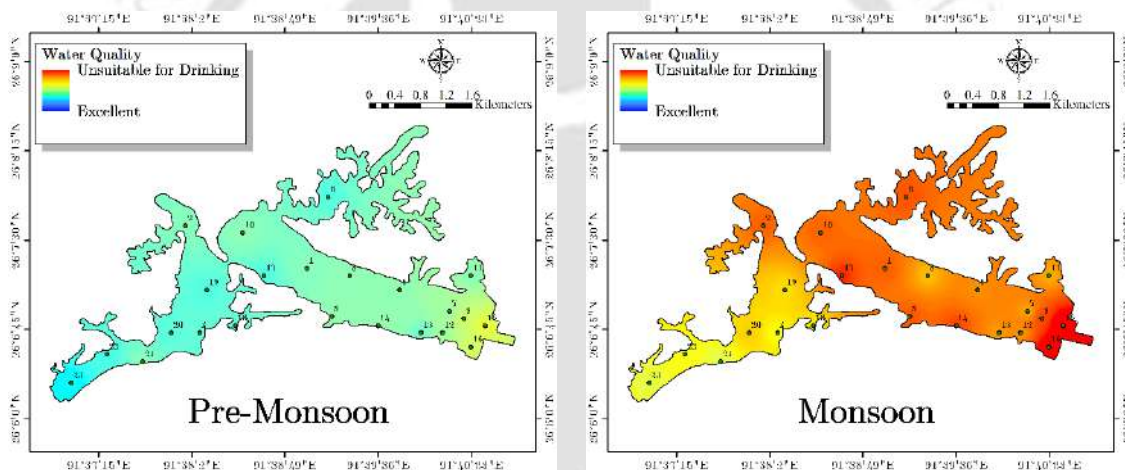
## (c) Cluster 3

PC	Eigen-value	Relative eigen-value	Variable	Loading Value	Relative Loading Value	Weight
1	11.928	0.558	DO	0.974	0.079	0.044
			pH	0.827	0.067	0.037
			EC	0.978	0.079	0.044
			TA	0.976	0.079	0.044
			BOD	0.961	0.078	0.043
			TDS	0.950	0.077	0.043
			Mg <sup>2+</sup>	0.972	0.079	0.044
			Cr	0.971	0.079	0.044
			Cd	0.939	0.076	0.042
			Fe	0.966	0.078	0.044
			Mn	0.977	0.079	0.044
			Cu	0.912	0.074	0.041
			Pb	0.961	0.078	0.043
			<b>Total</b>	<b>12.364</b>		
2	4.064	0.190	Turbidity	0.644	0.237	0.045
			Cl <sup>-</sup>	0.445	0.164	0.031
			K <sup>+</sup>	0.750	0.276	0.053
			Ca <sup>2+</sup>	0.876	0.323	0.061
			<b>Total</b>	<b>2.715</b>		
3	2.607	0.122	NO <sub>3</sub> <sup>-</sup>	0.907	0.536	0.065
			Na <sup>+</sup>	0.786	0.464	0.057
			<b>Total</b>	<b>1.693</b>		
4	1.414	0.066	F <sup>-</sup>	0.496	0.243	0.016
			PO <sub>4</sub> <sup>3-</sup>	0.914	0.448	0.030
			NH <sub>4</sub> <sup>-</sup>	0.631	0.309	0.020
			<b>Total</b>	<b>2.041</b>		
5	1.355	0.063	TH	0.646	0.457	0.029
			SO <sub>4</sub> <sup>2-</sup>	0.767	0.543	0.034
			<b>Total</b>	<b>1.413</b>		

Fig. 6. 3 details the PCA-WQI values obtained for all 23 sampling locations of Deepor Beel for all three seasons. The spatio-temporal maps depicting the variation of water quality in the wetland clearly indicates that the monsoon plays a significant role in the deterioration of the water quality of Deepor Beel. Additionally, the principal governing factor for water pollution remains the Boragaon landfill, which is evident from the pre-monsoon and post-monsoon plots.

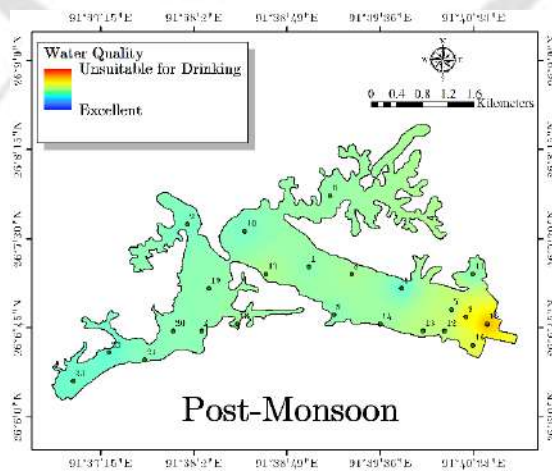


(a)



(b)

(c)



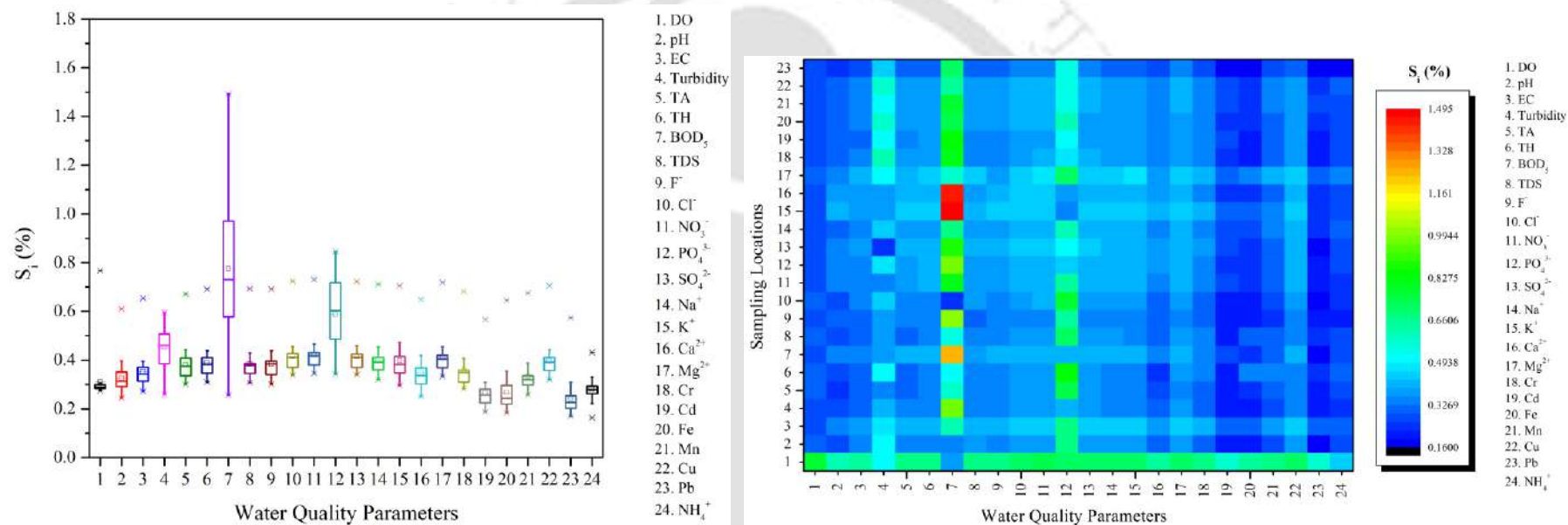
(d)

Fig. 6. 3. Spatio-temporal variation of PCA-WQI.

The results obtained from both the methodologies, i.e., modified entropy weighted method and multivariate statistical method, are found to go hand-in-hand with one another, as is clear from Fig. 6. 1 and Fig. 6. 3. Now, prior to the application of the methods in any monitoring programme, it is essential that we test the reliability of both methods. Hence, sensitivity analyses were conducted to test the reliability of a model and the impact of a particular input parameter on the assessed results.

The effects of removing each physico-chemical parameter on the MEWQI and PCA-WQI score are represented in Fig. 6. 4 and Fig. 6. 5. It was observed that for MEWQI, the overall sensitivity value varied from 0.16 – 1.49%, with an average value of 0.39%. It was further observed from the box-plot that BOD<sub>5</sub> showed the maximum sensitivity at 1.49%, which was followed by PO<sub>4</sub><sup>3-</sup>, while other parameters displayed near similar characteristics in the variability (Fig. 6. 4a). The effects of various parameters on all 23 sampling locations are shown in Fig. 6. 4b, wherein it was observed that BOD<sub>5</sub> was the most sensitive to locations 15 and 16, while PO<sub>4</sub><sup>3-</sup> was the most sensitive to locations primarily in the central portion of the wetland, thus indicating organic contamination and use of agro-based fertilizers to have more impact on the water quality of these locations, respectively. Similarly, for PCA-WQI, the sensitivity values varied from 0.19 – 2.00%, with an average value of 0.63%. In this case, the maximum sensitivity was shown by Cl<sup>-</sup>, which was followed by Na<sup>+</sup> and Ca<sup>2+</sup>. Fig. 6. 5b shows the sensitivity values in pattern plots for all the sampling locations. It was observed that site 6 was the most sensitive towards the three parameters, which shows natural contamination to have played a major role in the impact of water quality in this area.

However, the MEWQI and PCA-WQI values were not found to be sensitive to any particular or a few parameters, thus suggesting that values obtained from both methods did not have a significant impact on the removal of any one or a few parameters. In other words, the developed indices did not possess excessive reliance on a few specific parameters; instead, all parameters played an equal role in assessing water quality (Abtahi *et al.* 2015). This suggests that the development of the proposed MEWQI and PCA-WQI are correct as well as extremely reliable.



(a) Box plot showing statistics of sensitivity values for all parameters

(b) Pattern plot showing spatial extent

**Fig. 6. 4.** Sensitivity analysis of the parameters involved in estimation of MEWQI.

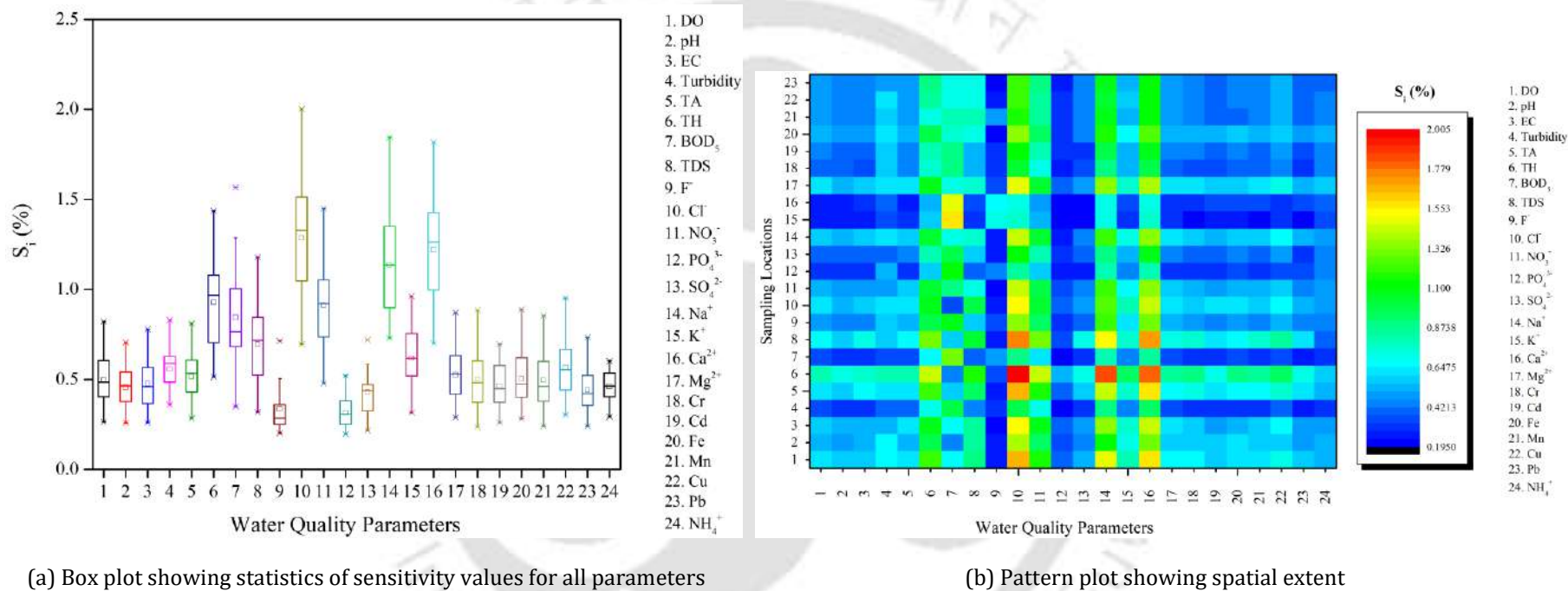


Fig. 6.5. Sensitivity analysis of the parameters involved in estimation of PCA-WQI.

## 6.2. Assessment of water quality for specific end-use

### 6.2.1. Assessment of water quality for heavy metal contamination

Similar procedures to assessing overall water quality were employed to determine the heavy metal contamination in a water body. The results obtained for both methods are discussed herewith.

#### 6.2.1.1. Modified entropy-weighted WQI approach

For modified entropy-weighted heavy metal index (MEHMI), it was observed that monsoon played a crucial role in the heavy metal contamination in the water column of the wetland, particularly in the sites proximate to the Boragaon landfill (Fig. 6. 6). This is followed by the region in the industrial complex (in the western part). Monsoon is followed by the post-monsoon period, while the pre-monsoon period remained the best among the three seasons, as far as heavy metal contamination is concerned. This is primarily attributed to the discharge of heavy metals in significant concentrations from the landfill (in the form of leachates) followed by the small-and-large-scale industries. During the pre-monsoon period, there is minimum leaching from the landfill as well as industrial effluents, which makes it relatively less contaminated.

#### 6.2.1.2. PC-weighted WQI approach

To determine the proposed heavy metal index, HCA was first applied to the raw water quality dataset, which rendered a dendrogram (Fig. 6. 7a), categorizing the 23 monitoring locations into three statistically significant clusters at  $D_{link}/D_{max} < 5$ . Cluster 1 comprised eight sites (1, 2, 3, 5, 6, 8, 10 and 17), which correspond to sites in the mid-zone of the wetland. Similarly, cluster 2 and cluster 3 encompassed 7 (7, 9, 11, 12, 13, 15 and 16) and 8 (4, 14, 18, 19, 20, 21, 22 and 23) sites, respectively. Sites included in cluster 2 were adjacent to the solid waste landfill site and cluster 3 mostly comprised of sites proximate to the industrial zone, except site 14. Based on the average heavy metal concentrations in these clusters, clusters 1, 2 and 3 were assigned as regions of low pollution (LP), heavy pollution (HP), and moderate pollution (MP) sites, respectively. Fig. 6. 7b provides a spatial representation of the sites, classified based on HCA, showing the transition of various locations from one cluster to another.

PCA was then applied independently on the datasets of each cluster, which assisted in data reduction and the identification of various pollution sources. Table 6. 4 summarizes the results obtained from PCA, including eigenvalues, (cumulative) variance and communalities. The loading values were graded as “strong”, “moderate”, and “weak” for values  $>0.75$ ,  $0.50 - 0.75$ , and  $0.30 - 0.50$ , respectively (Liu *et al.* 2003).

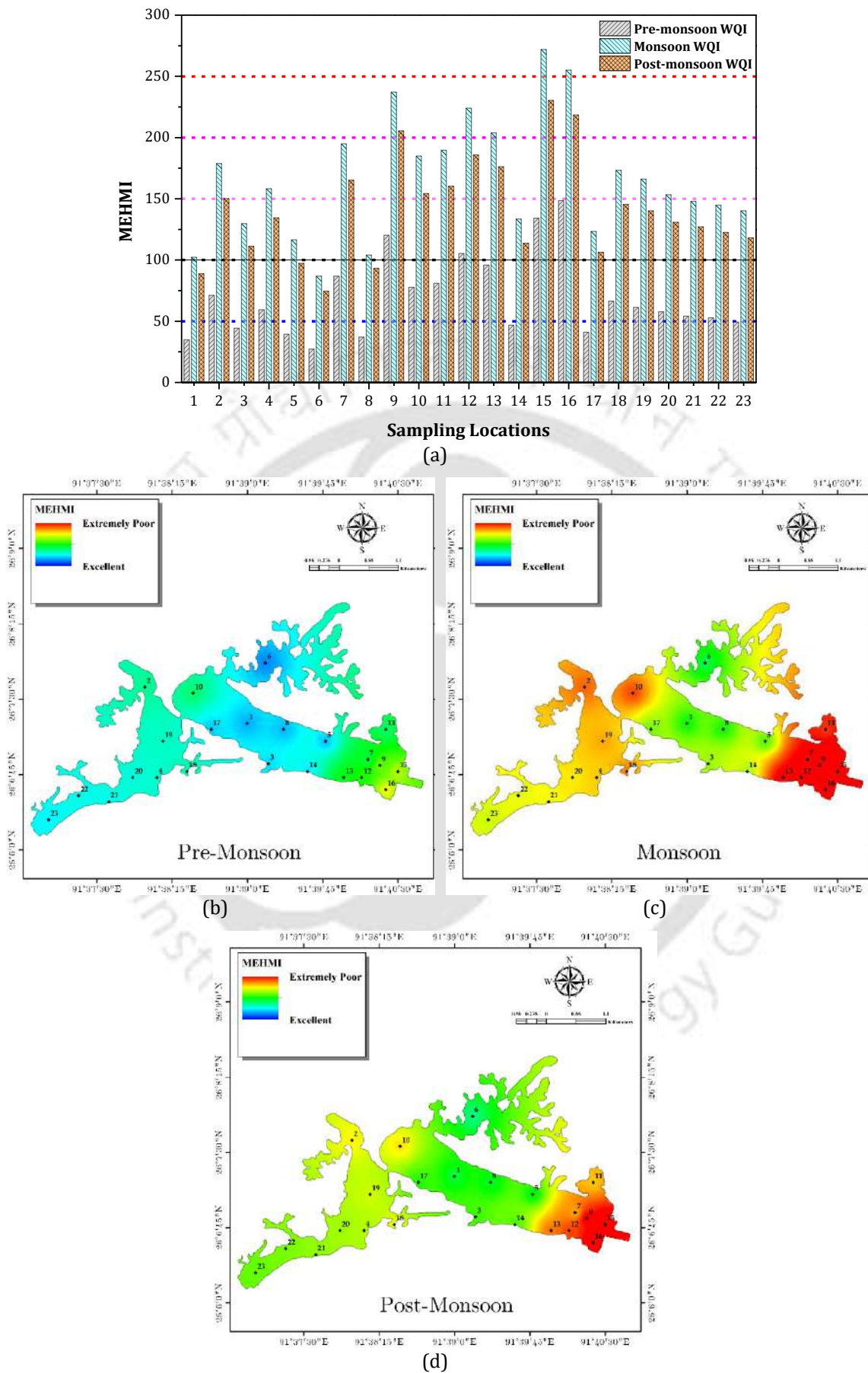
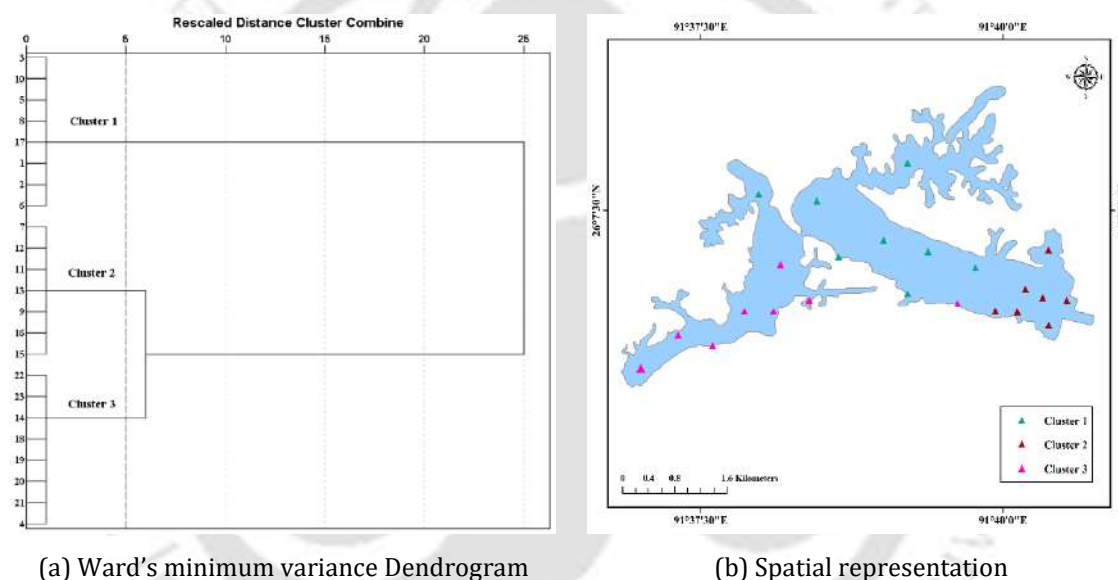


Fig. 6. 6. Spatio-temporal variation of MEHMI.

Three different principal components (PCs), accounting for about 85% of the total cumulative variance, were extracted for the dataset corresponding to cluster 1. Factor 1, accountable for 47.25% of the variance, displayed strong loadings for Cu and Mn, moderate for Fe and Cd and weak loadings for Pb. Similarly, factor 2, accounting for an additional 21.92% of the variance, exhibited strong positive loadings for Cr, whereas weak loading values were found for Mg and Mn. Although Cr shows a strongly favourable loading for cluster 1, it can be observed that the concentration of Cr in these sites are well within the acceptable limits laid down by WHO and IS 10500: 2012 (Annexure A). Finally, factor 3, responsible for 15.86% of the variance, showed a strongly favourable loading on Pb, moderate loading on Mg, and weak loading on Mn. Based on the above analysis, it can be clearly indicated that sites pertaining to cluster 1 primarily represent pollution due to the wearing of rocks and topsoil.



**Fig. 6. 7.** Result of cluster analysis for the estimation of HMI.

Likewise, only one PC was extracted for the datasets pertaining to both clusters 2 and 3. The factor loadings obtained for cluster 2 signified 91.2% of the total variance, whereas cluster 3 accounted for 96.72% of the variance. Both clusters indicated very strong positive loadings for all the heavy metals. Also, the heavy metal concentrations in these sites were higher than the permissible limits for most of the year, suggesting a single pollution source. Sites corresponding to cluster 2 may be presumed to be heavily affected by contamination from the landfill, whereas, on the other hand, effluents from the industries adjacent to the sites of cluster 3 may be the dominant source for the degradation of water quality.

**Table 6. 4.** Varimax rotated component matrix for metals for 23 different monitoring locations of Deepor Beel (Rotation method: Varimax with Kaiser normalization).

<b>(a) Cluster 1</b>				
<b>Eigenvalues</b>	3.308	1.534	1.110	
<b>Variance (%)</b>	47.251	21.919	15.855	
<b>Cumulative variance (%)</b>	47.251	69.169	85.024	<b>Communalities</b>
<b>Variable</b>	<b>Factor 1</b>	<b>Factor 2</b>	<b>Factor 3</b>	
Cu	0.793	-0.510	0.030	0.889
Mg	-0.754	0.278	0.528	0.925
Mn	0.751	-0.379	0.260	0.776
Fe	0.705	-0.142	0.094	0.525
Cr	-0.016	0.941	0.008	0.885
Cd	0.624	-0.750	-0.102	0.962
Pb	0.130	-0.010	0.986	0.989
<b>(b) Cluster 2</b>				
<b>Eigenvalues</b>	6.383			
<b>Variance (%)</b>	91.181			
<b>Cumulative variance (%)</b>	91.181			<b>Communalities</b>
<b>Variable</b>	<b>Factor 1</b>			
Cu	0.935		0.875	
Mg	0.983		0.967	
Mn	0.896		0.803	
Fe	0.956		0.914	
Cr	0.989		0.979	
Cd	0.972		0.946	
Pb	0.949		0.900	
<b>(c) Cluster 3</b>				
<b>Eigenvalues</b>	6.770			
<b>Variance (%)</b>	96.718			
<b>Cumulative variance (%)</b>	96.718			<b>Communalities</b>
<b>Variable</b>	<b>Factor 1</b>			
Cu	0.982		0.965	
Mg	0.998		0.996	
Mn	0.996		0.992	
Fe	0.966		0.934	
Cr	0.996		0.992	
Cd	0.991		0.982	
Pb	0.954		0.909	

**Table 6. 5.** Weights for different variables for determining HMI values.

<b>(a) Cluster 1</b>								
PC (1)	Eigen- value (2)	Relative value (3)	Eigen- value (4)	Varia- ble (5)	Loading value (6)	Relative value (7)	Loading value (8)	Weight (3)×(6)
1	3.308	0.556		Cu	0.793	0.276		0.153
				Mn	0.751	0.261		0.145
				Fe	0.705	0.245		0.136
				Cd	0.624	0.217		0.121
				<b>Total</b>	<b>2.873</b>			
2	1.534	0.258		Cr	0.941	1.000		0.258
3	1.110	0.186		Mg	0.528	0.349		0.065
				Pb	0.986	0.651		0.121
				<b>Total</b>	<b>1.514</b>			
<b>(b) Cluster 2</b>								
1	6.383	1.000		Cu	0.935	0.140		0.140
				Mg	0.983	0.147		0.147
				Mn	0.896	0.134		0.134
				Fe	0.956	0.143		0.143
				Cr	0.989	0.148		0.148
				Cd	0.972	0.146		0.146
				Pb	0.949	0.142		0.142
				<b>Total</b>	<b>6.68</b>			
<b>(c) Cluster 3</b>								
1	6.770	1.000		Cu	0.982	0.143		0.143
				Mg	0.998	0.145		0.145
				Mn	0.996	0.145		0.145
				Fe	0.966	0.140		0.140
				Cr	0.996	0.145		0.145
				Cd	0.991	0.144		0.144
				Pb	0.954	0.139		0.139
				<b>Total</b>	<b>6.883</b>			

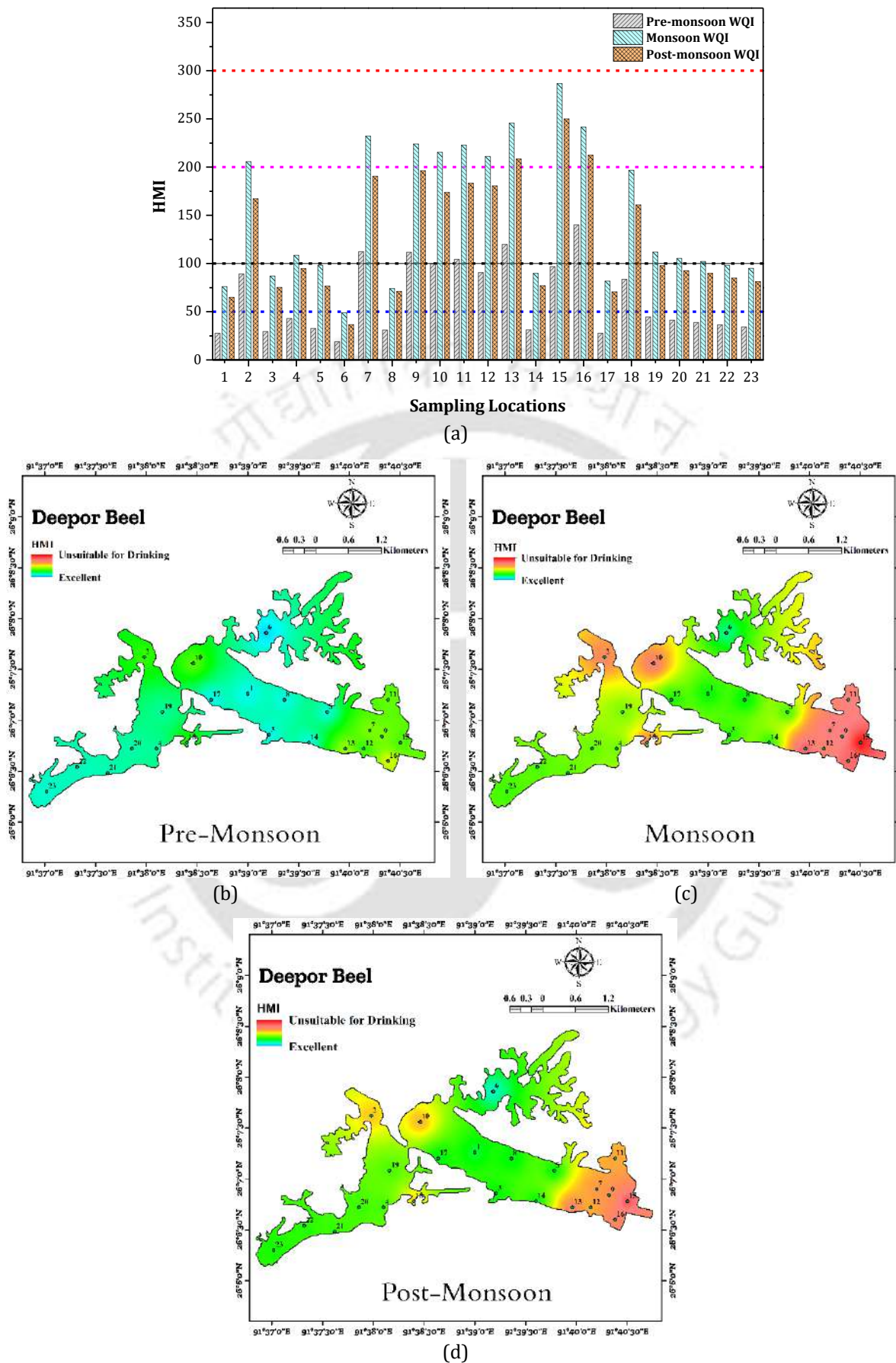


Fig. 6. 8. Spatial variation of HMI values across Deepor Beel stretch.

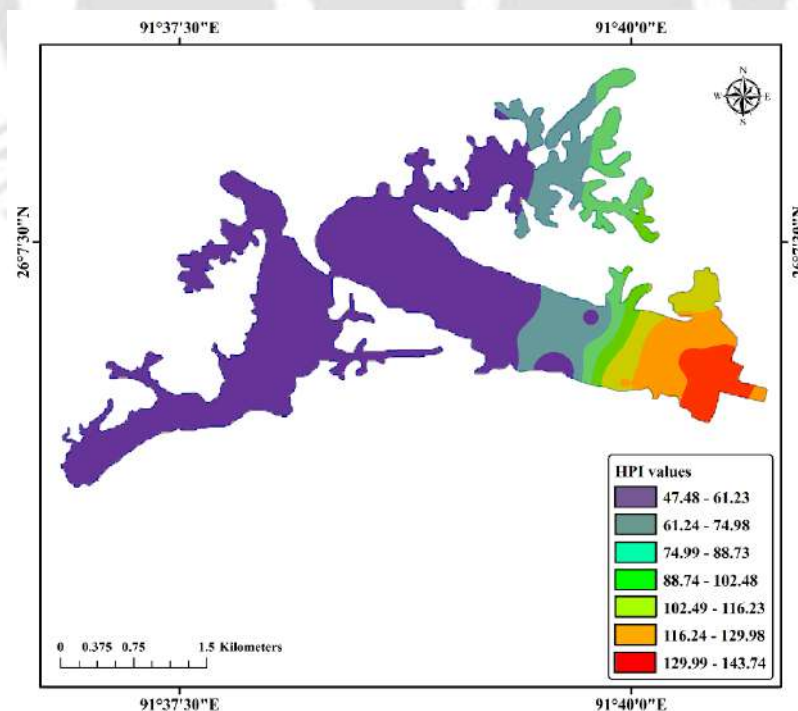
The weight coefficients ( $p_i$ ) assigned for each metal, estimated from PCA, for individual clusters are provided in Table 6. 5. The HMI values for the 23 monitoring locations were evaluated based on equation 5, taking the annual mean concentrations of heavy metals into account. The HMI values ranged from 73.08 to 202.83, with a mean value of 123.52, indicating the water in Deepor Beel to be “Poor”. A spatial representation of the HMI values is shown in Fig. 6. 8, which clearly indicates the sites proximate to the solid waste landfill to be the most contaminated. Leaching from the contaminated landfill, especially during monsoon, might be the possible reason for the degraded water quality.

### 6.2.1.3. Correctness of MEHMI and HMI values

As stated in Chapter 4, the correctness of the proposed indices was checked by comparing them with the already existing indices. The results obtained are described as follows.

#### HPI

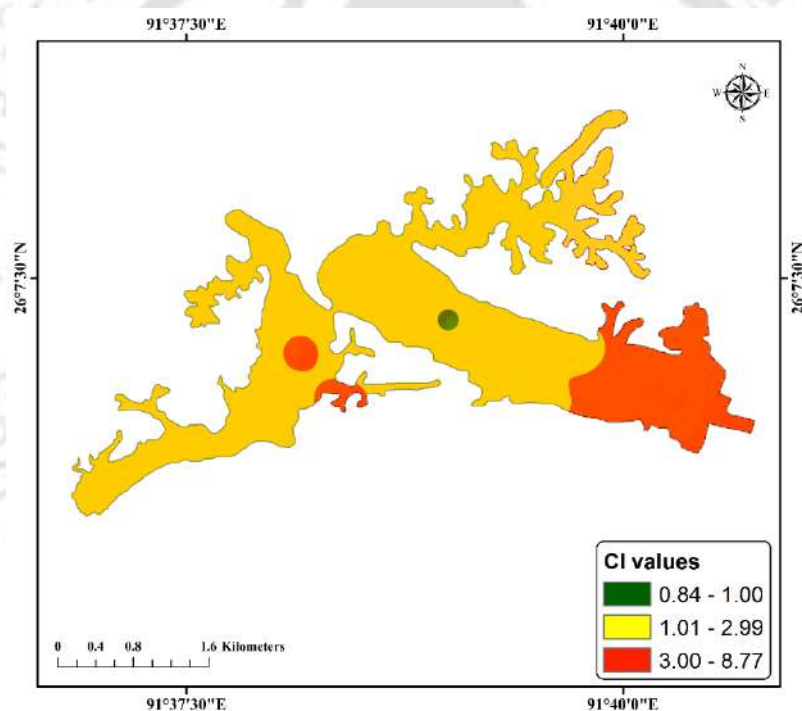
HPI values obtained from Eq. 4.45 and 4.46 have been tabulated in Table 6. 6. A spatial representation of the HPI values is also shown in Fig. 6. 9. It was observed that only 30.4% of the monitoring locations of Deepor Beel exceeded the critical pollution limit. These primarily constitute the sites proximate to the landfill, thus indicating leaching effects as the predominant cause for pollution in the wetland. The mean HPI value of all sites was found to be 75.77, which is well below the critical limit.



*Fig. 6. 9. Spatial variation of HPI values across Deepor Beel stretch.*

## CI

CI values have been calculated using Eq. 4.47, considering the mean annual heavy metal concentrations for each site and the permissible limits as per the guidelines in IS:10500 (2012). Table 6.6 and Fig. 6.10 provide the estimated CI values and a spatial representation, respectively. It was observed that 30% of the sites fall under the “High” contamination group, whereas only 13% constitutes “Medium” contaminated sites. A large percentage (57%) of the sites are still in the “Low” contamination category. The sites which fall under the high contamination category are found to be near the landfill. On the other hand, a large portion of the area close to the industrial zone still comes under the low contamination category. This indicates that the landfill is one major contributor to water pollution in Deepor Beel as far the heavy metals are concerned, whereas the effluents from the industries do not have a similar effect.



*Fig. 6.10. Spatial variation of CI values along Deepor Beel.*

## HEI

HEI values ranged from 5.14 to 14.24, with a mean value of 8.68. The values were divided into three groups based on the multiple of the mean value to differentiate between various pollution levels such as “Low (HEI < 9)”, “Medium (9 < HEI < 18)” and “High (HEI > 18)” (Edet & Offiong 2002). Based on these classification ranges, it was observed that about 70% of the sites fall under the “Low” category, while none are classified to be highly contaminated.

**Table 6. 6.** Values of various indices for sampling stations along Deepor Beel with their descriptive statistics (averaged over the entire sampling period).

Sampling Stations	HPI values	CI values	HEI values	MEHMI values	HMI values
1	51.29	0.84	5.14	56.04	73.08
2	51.35	1.29	5.73	153.93	81.40
3	51.02	1.01	5.42	63.75	77.45
4	52.94	2.89	8.22	81.95	116.71
5	58.89	1.33	5.68	69.05	79.44
6	47.48	1.01	5.42	34.65	77.50
7	127.98	7.78	13.21	178.23	188.15
8	53.37	1.31	5.74	58.64	81.38
9	133.84	8.18	13.62	177.27	194.13
10	54.61	1.26	5.67	162.86	80.26
11	114.63	6.81	12.24	170.05	174.32
12	123.77	7.36	12.80	160.66	182.29
13	116.58	6.57	12.00	191.23	171.21
14	50.84	2.05	6.95	65.85	98.77
15	143.79	8.77	14.24	211.12	202.83
16	139.59	8.66	14.12	197.97	201.11
17	49.84	1.07	5.55	59.91	79.22
18	57.10	3.52	8.92	147.01	126.58
19	55.38	3.20	8.55	84.60	121.37
20	52.69	2.70	7.97	79.50	113.23
21	52.09	2.56	7.74	76.81	110.01
22	51.93	2.41	7.52	73.06	106.84
23	51.68	2.28	7.30	70.00	103.66
<b>Minimum</b>	47.48	0.84	5.14	34.65	73.08
<b>Maximum</b>	143.79	8.77	14.24	211.12	202.83
<b>Mean</b>	75.77	3.69	8.68	114.09	123.52

The major difference between HPI, MEHMI, and HMI can be inferred from Fig. 6. 9, Fig. 6. 8, and Fig. 6. 6. The primary difference lies with sites 4 and 18-23, which show nominal water quality with respect to heavy metal contamination based on HPI values. On the other hand, MEHMI and HMI values categorize these sites between “Poor” and “Extremely Poor”, thereby contradicting it. However, from Annexure A, it can be observed that these sites are heavily contaminated with Cd, Fe, Mn and Pb (concentrations reaching well beyond the permissible limits), although concentrations of Mg, Cr and Cu lie within the permissible limits. This is primarily attributed to the contamination as a result of industrial effluents. Furthermore, the CI

values classify these locations under a “medium” degree of contamination except sites 18 and 19, with a “high” degree of contamination. This infers that the values of the proposed indices resemble a more realistic picture of the water quality compared to the existing indices.

## 6.2.2. Assessment of water quality for examining its irrigation suitability

### 6.2.2.1. Physico-Chemical water quality characterization with respect to irrigation suitability of water

Physico-chemical characterization of the Deepor Beel’s water is represented through spatial distribution maps of all 13 water quality parameters (averaged over the entire sampling period), given in Fig. 6. 11.

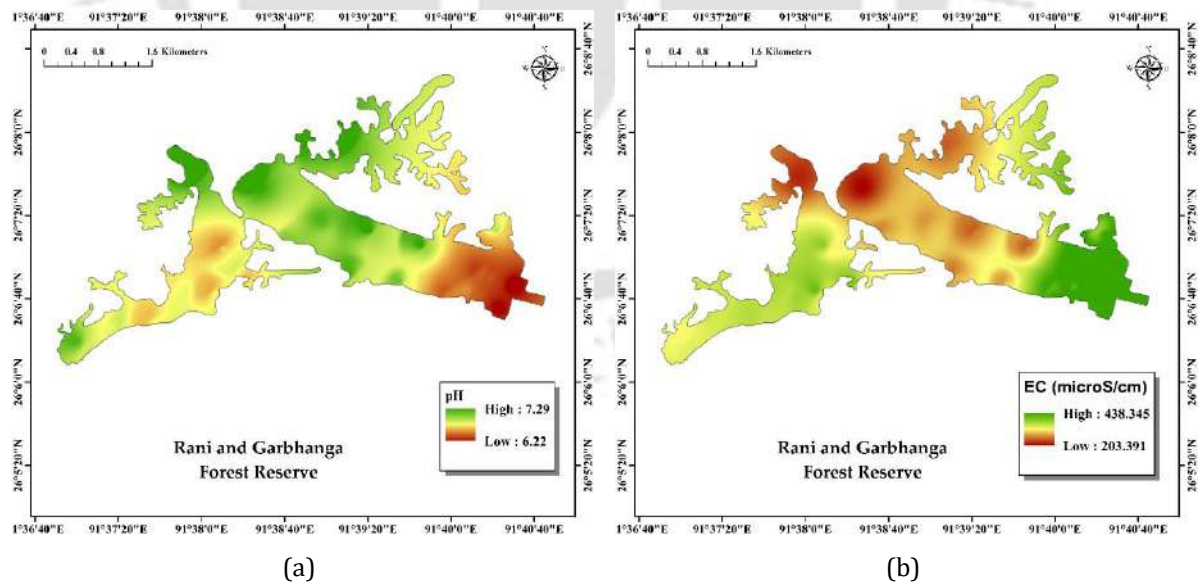
The pH variation (Fig. 6. 11a) shows that most sites, except the locations proximate to the landfill, correspond to values within permissible limits (i.e., 6.5 – 8.5). The pH of the sampling locations near the landfill indicates slight acidic characteristics, primarily attributing to leaching from the landfill. As the landfill comprises various types of wastes, such as lead-acid batteries and plastic stabilizers from several households and industries, there is every chance of acidic leaching from these wastes, eventually entering the Deepor Beel ecosystem and rendering a significant decrease in the pH.

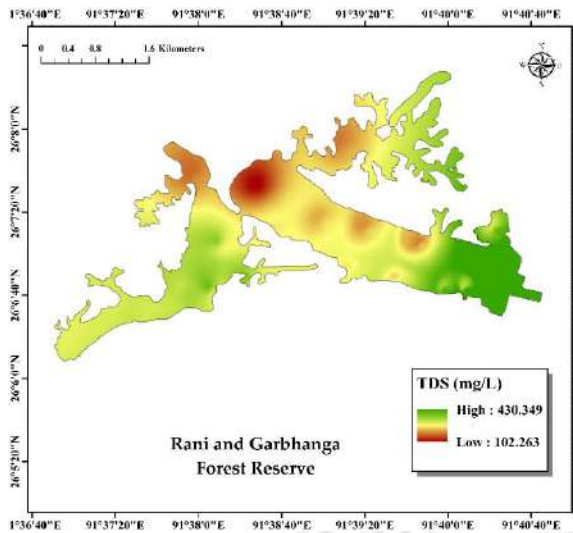
The electrical conductivity (EC) (Fig. 6. 11b) and total dissolved solids (TDS) (Fig. 6. 11c) values for the entire wetland can be seen to vary from 203 to 439  $\mu\text{S}/\text{cm}$ , and 102 to 430  $\text{mg}/\text{L}$ , respectively, which are well within acceptable limits for both drinking as well as irrigation use. Higher EC and TDS values can be observed near the landfill region, followed by the industrial zone, and minimum values were observed in the central region of the wetland. This is indicative of higher ionic concentrations near the landfill and industrial regions compared to the central zone, primarily representing anthropogenic interferences rather than geogenic contributions. Furthermore, there exists a positive correlation between EC and TDS for water in Deepor Beel, thus suggesting TDS to be a significant contributor to the ionic concentrations (Ali *et al.* 2012; Rusydi 2018).

The major anions present in the water follow the order;  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{PO}_4^{3-} > \text{F}^-$ , while all the concentrations were found to be within acceptable limits (Fig. 6. 11d-i). Elevated  $\text{F}^-$  concentrations were observed in a tiny fraction of the wetland (in the central part), primarily owing to many agricultural inputs from the surrounding areas or combustion of coals from the brick kilns present nearby (Gao *et al.* 2016). However, higher levels of  $\text{Cl}^-$  were observed near the landfill, which is also the region where the wetland receives its water from the Basistha River. This is indicative of a significant contribution of domestic sewage into the

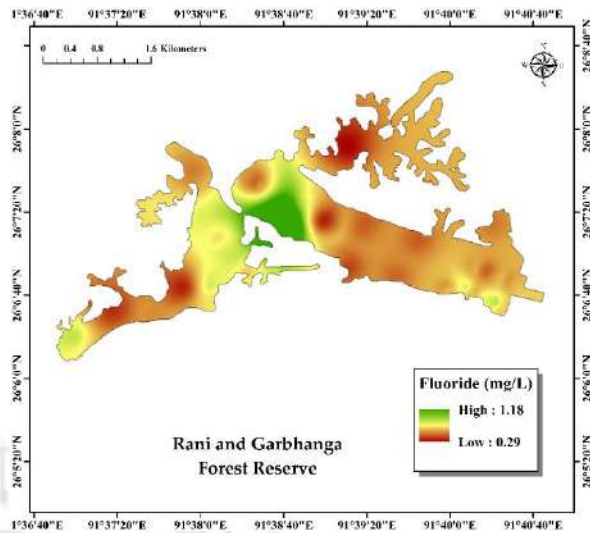
Deepor Beel from the Basistha River.  $\text{NO}_3^-$  concentrations were observed to have lower values near the landfill. This is primarily because of the high organic contamination near the landfill, which renders the oxygen to deplete and convert to ammonium nitrogen ( $\text{NH}_4\text{-N}$ ) due to microbial oxygen demand through the denitrification process (Sørensen 1978; Metcalf & Eddy 2017).  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  display similar spatial variability across the wetland, with higher concentrations in the eastern and northern regions. This is primarily attributed to the phosphate-based fertilizers used by the farmers, household discharge through the Basistha River and the leaching of organic matter from the nearby landfill. Finally,  $\text{HCO}_3^-$  concentration levels are observed to be minimum in the eastern region of the wetland, attributing to the higher acidic levels of the water due to leaching.  $\text{HCO}_3^-$  is a measure of buffering capacity of water. Hence, the drop in pH levels to the acidic range abruptly alters the  $\text{HCO}_3^-$  concentrations, reducing their values as the  $\text{HCO}_3^-$  ions, gaining more  $\text{H}^+$  ions, get converted to  $\text{H}_2\text{CO}_3$  (Tresguerres *et al.* 2010).

Among the cations, the primary pattern of variance observed is  $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$  (Fig. 6. 11j-m). While all the four cations are mostly naturally occurring,  $\text{K}^+$  may be contributed through fertilizer application (in the northern part of the wetland) and  $\text{Mg}^{2+}$  through either fertilizer application (in the northern region) or industrial discharge (in the western region). Leaching from the landfill also contributes to a significant extent to the accumulation of  $\text{Mg}^{2+}$  in the water column of the wetland (eastern portion).

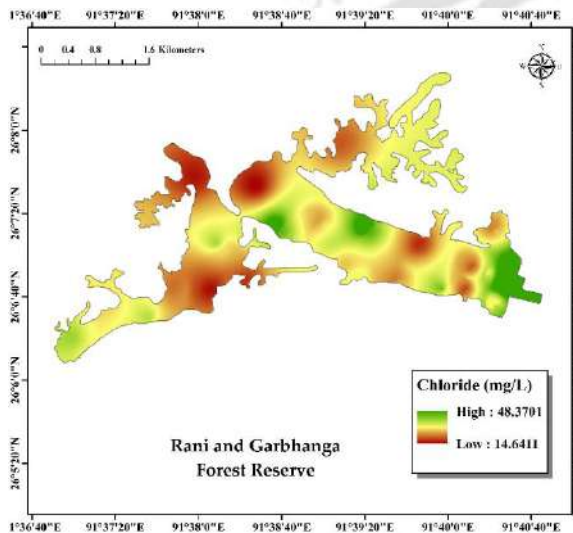




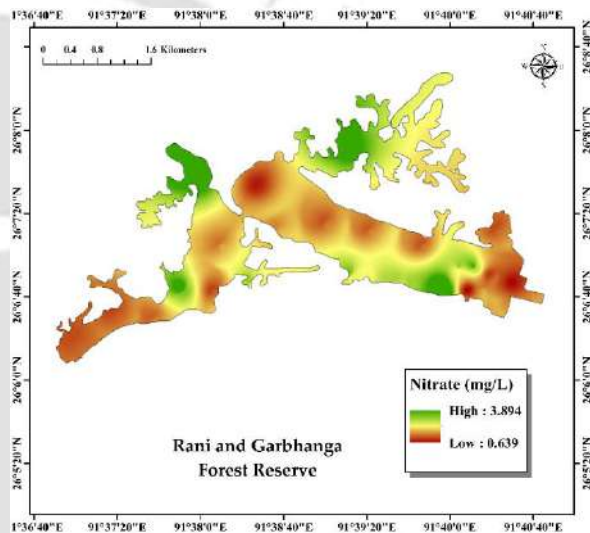
(c)



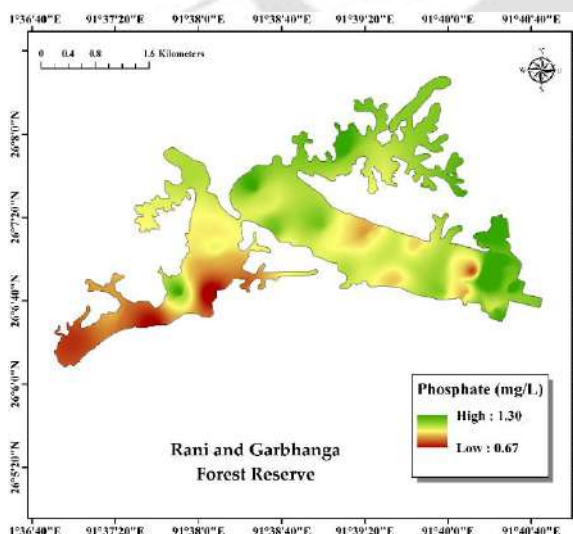
(d)



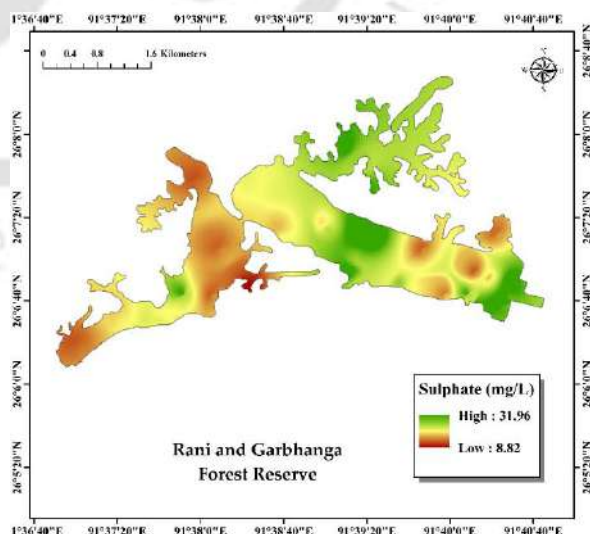
(e)



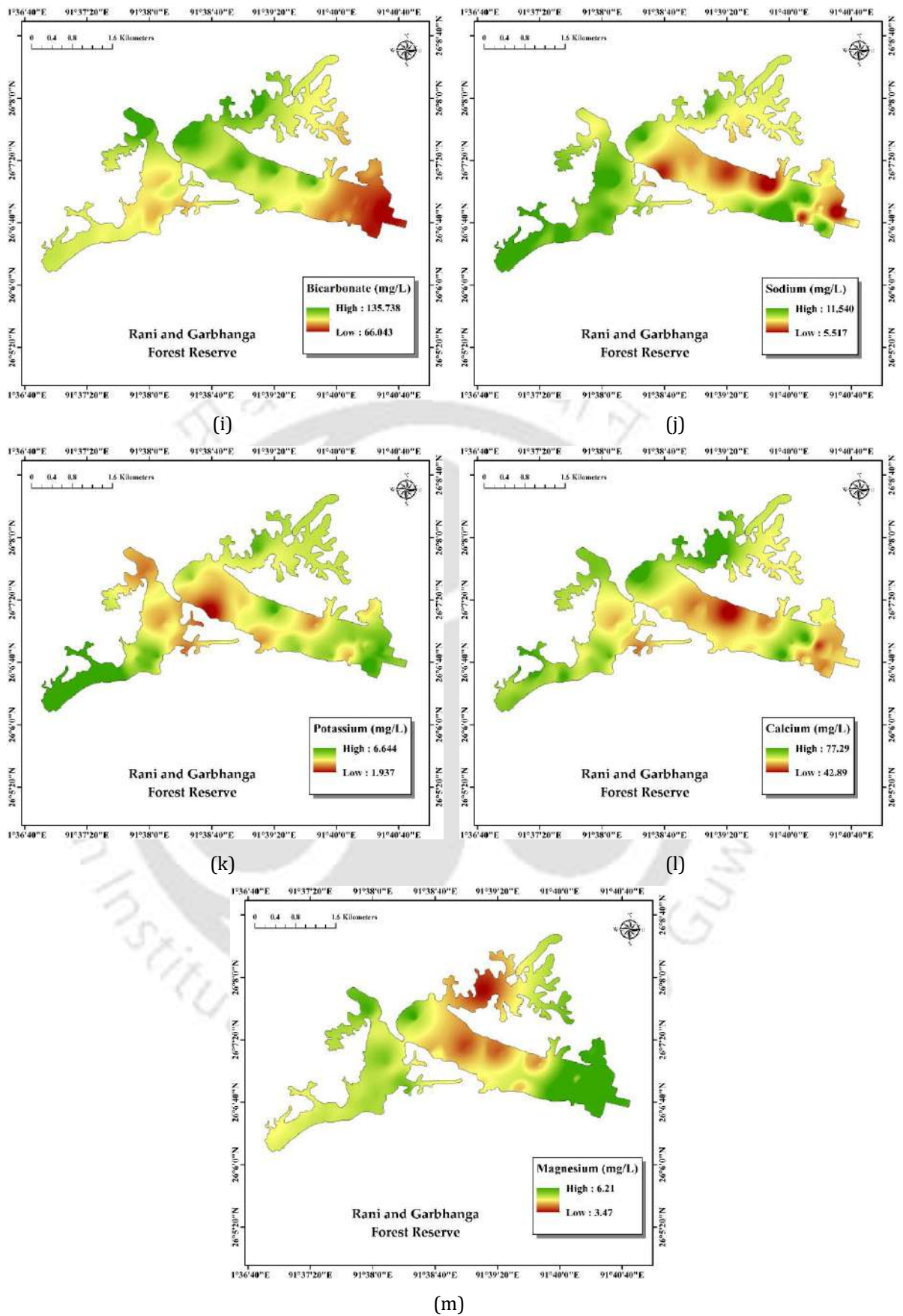
(f)



(g)



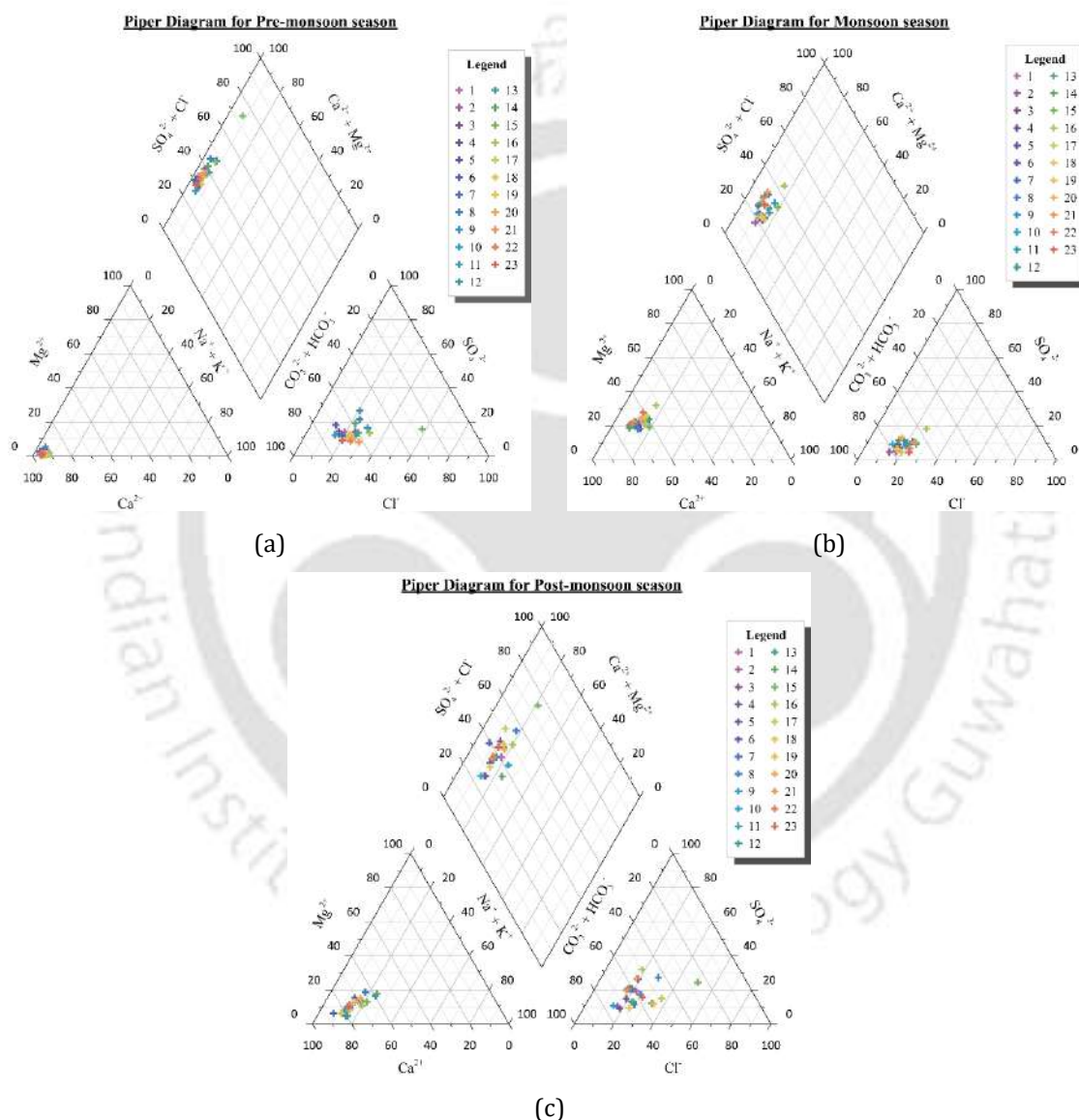
(h)



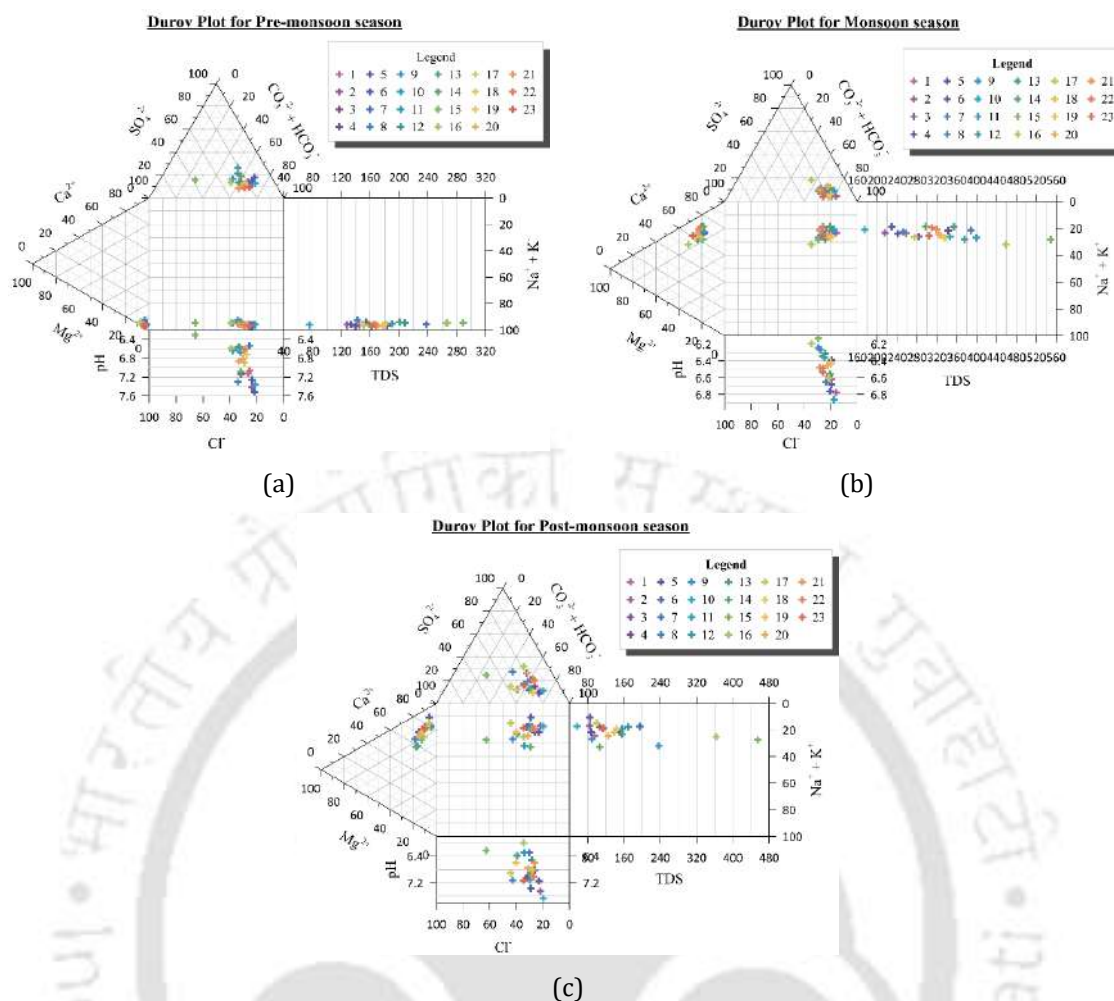
**Fig. 6. 11.** Spatial representation of various water quality parameters (averaged) of Deepor Beel (sampling constituted from Oct'17 to Feb'19).

### 6.2.2.2. Hydrochemical water classification

The hydrochemical classification of Deepor Beel water samples for three seasons; pre-monsoon (Jan-Mar), monsoon (Apr-Sep), and post-monsoon (Oct-Dec), is explained through Piper (Fig. 6. 12) and Durov (Fig. 6. 13) plots. A detailed analysis of the charge balance errors shows the concentration levels of different cations and anions used in the investigation, expressed as meq/L.



**Fig. 6. 12.** Piper diagram showing the major Hydrochemical classifications of Deepor Beel water for three seasons (Langguth 1966).



**Fig. 6. 13.** Durov diagram showing the Hydrochemical processes involved for Deepor Beel water for three seasons (Lloyd & John William Heathcote 1985).

It was observed that the charge balance errors during different seasons of the year varied as; Pre-monsoon (0.026 - 2.319 meq/L; average of 1.492 meq/L) > Monsoon (0.033 - 3.521; average of 1.100 meq/L) > Post Monsoon (0.07 - 1.625; average of 0.842 meq/L). All the values lay within the acceptable error range. Also, the regions near the Boragaon landfill had higher charge balance errors, followed by the industrial and central regions. This is because, during the pre-monsoon period, the concentration levels of different ions remain significantly higher due to dry weather flow conditions, which makes the ionic charge concentrations highly disproportionate. This phenomenon can be clearly verified by referring to the overall spatial distribution of EC ( $\mu\text{S}/\text{cm}$ ) (Fig. 6. 11b), wherein it can be observed that higher EC values are primarily concentrated to the sites proximate to the landfill. Grapher Software (v. 12) was used for plotting both Piper and Durov plots. The Piper diagram involves plotting the major cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) and anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$ ) (all concentrations expressed as mill equivalent percentages, meq %) in separate triangles.

**Table 6. 7.** Hydrochemical analysis of water samples from Deepor Beel (all values are expressed as meq/L).

(a) Pre-Monsoon season

Sampling Locations	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	Σ Cations	Σ Anions	Data Error
1	0.022	0.449	0.011	0.011	0.334	0.079	0.013	3.781	0.111	1.555	3.984	2.382	1.603
2	0.025	0.411	0.023	0.013	0.311	0.029	0.002	3.432	0.215	1.704	3.678	2.488	1.191
3	0.021	0.587	0.039	0.010	0.336	0.150	0.002	3.539	0.148	1.452	3.838	2.444	1.393
4	0.021	0.471	0.001	0.010	0.222	0.038	0.001	3.793	0.184	1.316	4.017	2.040	1.976
5	0.025	0.376	0.008	0.016	0.344	0.031	0.003	3.554	0.132	1.608	3.720	2.377	1.343
6	0.017	0.320	0.011	0.006	0.457	0.027	0.101	4.232	0.101	1.735	4.462	2.546	1.917
7	0.021	0.326	0.013	0.015	0.202	0.038	0.007	3.758	0.236	1.144	4.040	1.721	2.319
8	0.013	0.692	0.023	0.011	0.643	0.080	0.089	2.764	0.117	1.644	3.051	3.025	0.026
9	0.024	0.588	0.027	0.020	0.327	0.033	0.024	3.375	0.258	1.057	3.689	2.043	1.646
10	0.025	0.368	0.002	0.017	0.304	0.038	0.003	3.764	0.222	1.755	4.028	2.472	1.556
11	0.020	0.488	0.024	0.020	0.232	0.046	0.006	3.370	0.234	1.160	3.656	1.945	1.711
12	0.021	0.494	0.024	0.003	0.627	0.049	0.002	2.947	0.246	1.245	3.245	2.413	0.832
13	0.020	0.516	0.023	0.015	0.269	0.076	0.002	3.074	0.240	1.169	3.392	2.012	1.381
14	0.020	0.548	0.021	0.011	0.467	0.061	0.001	3.063	0.150	1.437	3.275	2.503	0.772
15	0.020	1.364	0.004	0.011	0.374	0.058	0.009	3.807	0.321	0.613	4.195	2.386	1.809
16	0.025	0.577	0.042	0.008	0.246	0.056	0.012	3.627	0.284	0.966	3.979	1.864	2.115
17	0.022	0.541	0.021	0.010	0.281	0.060	0.001	3.405	0.141	1.486	3.607	2.360	1.246
18	0.025	0.401	0.001	0.012	0.194	0.034	0.002	2.894	0.206	1.219	3.136	1.853	1.283
19	0.021	0.480	0.002	0.008	0.266	0.017	0.000	3.295	0.197	1.362	3.510	2.139	1.371
20	0.022	0.528	0.001	0.012	0.206	0.013	0.013	4.194	0.177	1.346	4.397	2.114	2.283
21	0.019	0.642	0.001	0.010	0.181	0.057	0.002	3.135	0.172	1.359	3.366	2.212	1.154
22	0.017	0.532	0.002	0.009	0.191	0.051	0.004	3.411	0.162	1.424	3.629	2.175	1.453
23	0.022	0.407	0.002	0.010	0.180	0.034	0.001	3.758	0.157	1.387	3.949	2.008	1.941

(b) Monsoon season

Sampling Locations	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	Σ Cations	Σ Anions	Data Error
1	0.016	0.542	0.016	0.067	0.145	0.672	0.112	2.332	0.455	2.473	3.571	3.259	0.312
2	0.015	0.475	0.139	0.067	0.154	0.881	0.141	2.939	0.548	2.807	4.509	3.657	0.852
3	0.019	0.546	0.016	0.062	0.221	0.596	0.106	2.048	0.503	2.357	3.253	3.221	0.033
4	0.015	0.410	0.034	0.040	0.214	0.732	0.174	3.047	0.528	2.073	4.482	2.786	1.696
5	0.016	0.559	0.015	0.059	0.199	0.504	0.094	2.167	0.483	2.600	3.249	3.447	0.198
6	0.017	0.564	0.144	0.074	0.318	0.880	0.125	3.510	0.429	2.670	4.943	3.787	1.156
7	0.019	0.630	0.099	0.047	0.295	1.024	0.177	3.667	0.568	1.860	5.436	2.950	2.486
8	0.017	0.637	0.015	0.049	0.398	0.498	0.105	2.269	0.458	2.508	3.329	3.625	0.297
9	0.019	0.685	0.009	0.095	0.247	0.667	0.140	2.307	0.596	1.820	3.710	2.874	0.836
10	0.020	0.497	0.027	0.067	0.350	0.893	0.164	3.561	0.558	2.980	5.176	3.941	1.235
11	0.021	0.577	0.016	0.077	0.268	0.681	0.179	2.352	0.564	2.037	3.776	2.996	0.780
12	0.019	0.547	0.003	0.064	0.217	0.682	0.165	2.128	0.585	1.927	3.560	2.778	0.783
13	0.018	0.620	0.151	0.064	0.255	1.142	0.191	4.694	0.575	1.972	6.601	3.080	3.521
14	0.016	0.472	0.063	0.061	0.360	0.842	0.172	3.911	0.507	2.313	5.433	3.285	2.148
15	0.022	0.586	0.016	0.073	0.234	0.459	0.202	2.115	0.648	1.568	3.424	2.500	0.924
16	0.023	0.794	0.014	0.074	0.570	0.926	0.308	2.003	0.617	1.750	3.854	3.225	0.628
17	0.042	0.634	0.029	0.074	0.130	0.555	0.100	1.944	0.500	2.415	3.099	3.324	0.225
18	0.017	0.477	0.085	0.054	0.167	0.840	0.149	2.288	0.542	2.123	3.818	2.922	0.896
19	0.015	0.468	0.049	0.064	0.174	0.859	0.151	2.565	0.535	2.153	4.110	2.921	1.188
20	0.015	0.486	0.109	0.076	0.394	0.811	0.166	2.621	0.523	2.187	4.121	3.267	0.854
21	0.019	0.779	0.027	0.048	0.345	0.862	0.367	3.722	0.518	2.213	5.470	3.432	2.038
22	0.021	0.726	0.036	0.057	0.213	0.914	0.311	4.021	0.514	2.240	5.760	3.293	2.468
23	0.021	0.753	0.029	0.049	0.132	0.927	0.312	2.686	0.511	2.267	4.436	3.251	1.185

(c) Post-monsoon season

Sampling Locations	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	Σ Cations	Σ Anions	Data Error
1	0.012	0.599	0.023	0.009	0.517	0.149	0.139	1.442	0.372	1.602	2.102	2.762	0.660
2	0.018	0.387	0.017	0.004	0.240	0.064	0.089	2.603	0.470	1.690	3.226	2.356	0.870
3	0.013	0.517	0.045	0.013	0.711	0.187	0.140	2.492	0.412	1.476	3.231	2.775	0.456
4	0.033	0.385	0.011	0.013	0.298	0.314	0.176	2.258	0.444	1.345	3.191	2.085	1.106
5	0.014	0.392	0.027	0.007	0.194	0.184	0.143	1.864	0.401	1.536	2.592	2.169	0.423
6	0.012	0.525	0.017	0.015	0.574	0.153	0.121	3.852	0.338	1.695	4.464	2.839	1.625
7	0.020	0.481	0.005	0.010	0.226	0.129	0.137	2.784	0.481	1.252	3.532	1.994	1.538
8	0.024	1.023	0.014	0.017	0.957	0.226	0.184	1.401	0.387	1.536	2.198	3.572	1.374
9	0.013	0.506	0.007	0.009	0.344	0.216	0.155	1.352	0.538	1.156	2.260	2.034	0.226
10	0.011	0.371	0.007	0.008	0.284	0.165	0.145	2.877	0.473	1.942	3.660	2.624	1.036
11	0.016	0.468	0.007	0.008	0.255	0.210	0.097	2.541	0.480	1.268	3.328	2.021	1.307
12	0.030	0.361	0.004	0.012	0.413	0.059	0.097	2.688	0.516	1.230	3.359	2.050	1.309
13	0.022	0.770	0.014	0.008	0.279	0.288	0.128	2.121	0.489	1.261	3.026	2.353	0.673
14	0.019	0.491	0.007	0.008	0.280	0.163	0.147	1.022	0.418	1.377	1.748	2.181	0.433
15	0.017	2.145	0.013	0.011	1.038	0.203	0.153	1.821	0.585	1.064	2.762	4.287	1.526
16	0.023	0.419	0.005	0.007	0.728	0.181	0.135	1.986	0.570	1.121	2.872	2.303	0.569
17	0.123	1.169	0.011	0.004	0.469	0.174	0.048	2.926	0.414	1.532	3.562	3.307	0.254
18	0.025	0.469	0.009	0.008	0.190	0.169	0.081	2.357	0.459	1.370	3.065	2.070	0.995
19	0.031	0.855	0.007	0.009	0.298	0.281	0.105	2.137	0.450	1.344	2.973	2.544	0.429
20	0.013	0.443	0.024	0.005	0.664	0.237	0.146	1.758	0.437	1.358	2.577	2.507	0.070
21	0.020	0.365	0.024	0.008	0.437	0.216	0.142	2.438	0.431	1.410	3.227	2.265	0.961
22	0.013	0.370	0.008	0.009	0.455	0.196	0.133	2.384	0.427	1.379	3.140	2.234	0.906
23	0.028	0.679	0.015	0.011	0.397	0.166	0.161	2.467	0.425	1.462	3.219	2.592	0.627

The plots are then projected to a central diamond region, which provides the overall water classification (Piper 1944). On the other hand, the Durov plot considers a composite plotting of two ternary diagrams wherein the meq % concentration plots of major cations and anions are plotted against each other while considering the TDS concentration (mg/L) and pH values as well (Durov 1948). While the Piper plot provides information regarding the hydro-chemical water classification, the Durov plot provides the processes involved along with the classification.

In the present investigation, it was observed that the Piper and Durov plots showed consistency to the results shown in Table 6. 7. From the Piper plots for three seasons, it is evident that the water characteristics change with seasons. During the pre-monsoon period, the water from all sampling locations except site 15 is observed to belong to  $\text{Ca}^{2+}$  -  $\text{HCO}_3^-$  category, which is also evident from Table 6. 7a. Site 15 particularly belongs to  $\text{Ca}^{2+}$  -  $\text{Cl}^-$  category. This is primarily because of the significant  $\text{Cl}^-$  discharge into the wetland through the Basistha River. The pre-monsoon period is considered to have the lowest flow; hence, with a constant discharge of sewage effluents from the city, the  $\text{Cl}^-$  concentrations (meq %) in the river becomes the most prominent, compared to other anions (Girija *et al.* 2007; Kelly *et al.* 2010). Site 15 is the confluence point of the Basistha River and the input point of Deepor Beel, therefore, displaying higher  $\text{Cl}^-$  content compared to other sampling locations. During the monsoon season, the Deepor Beel water is observed to shift towards the  $\text{Mg}^{2+}$  water range, while site 16 is on the border range of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . This is attributed to leaching from the landfill, carrying considerable amounts of heavy metals, including  $\text{Mg}^{2+}$  (Wu *et al.* 2018). Furthermore, all water samples are found to be in the  $\text{HCO}_3^-$  range, including water from site 15. This is due to heavy stormwater discharge into the Basistha River, diluting the  $\text{Cl}^-$  concentration levels. Finally, for the post-monsoon season, the cationic elements of water decreased for both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , while for the anionic portion, the  $\text{HCO}_3^-$  content declined with an increment for the  $\text{Cl}^-$  content. Again, this is attributed to the increase in the concentration levels of domestic sewage in the Basistha river with the decrement in the stormwater flow (Manna & Aftabuddin 2009).

Similarly, the Durov plot suggests that the water in Deepor Beel has mixed water type characteristics during the monsoon and post-monsoon periods. The water is found to be concentrated primarily near the central region of the square box (Fig. 6. 11b & c), indicating freshwater with simple dissolution and hence, no major cation or anion concentrations (Lloyd & John William Heathcote 1985). For the pre-monsoon season, however, there is a significant amount of  $\text{Na}^+$  and  $\text{K}^+$  concentration levels. This is suggestive of dominant reverse ion exchange of  $\text{Na}^+$  and  $\text{K}^+$  with  $\text{Cl}^-$ , accumulated in the water column through massive discharges

of domestic sewage containing high levels of NaCl (Ravikumar *et al.* 2015). Lastly, higher TDS levels were found to persist in the water column in the monsoon season, compared to the other two seasons, due to an increase in ionic levels due to stormwater intrusion into the wetland. These storm waters carry with them dissolved particles, resulting from weathering of topsoil or rocks in the nearby areas (Bhattacharyya & Kapil 2010; Qiao *et al.* 2017).

### 6.2.2.3. Modified entropy-weighted WQI approach

The MEIWQI values obtained for three seasons and all locations suggested that the water column of Deepor Beel is highly suitable for agricultural purposes (Fig. 6. 14). This is primarily attributed to the discharge of considerable amounts of nutrients, in the form of nitrates and phosphates, from the Basistha River. The results obtained in the current study show excellent correlation to the results obtained wherein the irrigation suitability of the water column was verified using cluster analysis, followed by the USSL (U.S.S.L 1954) and Wilcox (Wilcox 1955) plots (Fig. 6. 18), as shown in the subsequent sections.

### 6.2.2.4. PC-weighted WQI approach

HCA was first employed on the raw standardized (Z-scale transformed) water quality dataset, which resulted in categorizing the 23 sampling locations into three statistically significant clusters. The clustering process is represented through a Dendrogram, given in Fig. 6. 15a. The cluster analysis result was then transferred to a GIS platform for a more comprehensive spatial representation (Fig. 6. 15b). It was observed that cluster 1 comprises the sites, primarily towards the eastern side of the wetland, whereas cluster 2 consists primarily of locations in the central zone. Cluster 3, on the other hand, is mainly concentrated in the western region, near the industrial complex, while including sites 7, 12, and 13. Based on the above observations, it may be presumed that cluster 1 sites are highly polluted (HP) and can be termed HP sites, while clusters 2 and 3 can be considered as low pollution (LP) and moderate pollution (MP) sites. Thus 7, 12, and 13 act as a transition between HP and LP sites.

After grouping all 23 locations into different clusters, PCA was carried out on each independent cluster's datasets. The results of the PCA produced component scores called principal components (PCs). The result of PCA for all three clusters is represented in Table 6. 8. It can be observed that cluster 1 displayed 100% of the total variance through three PCs. pH, EC, TDS, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Mg<sup>2+</sup>, and HCO<sub>3</sub><sup>-</sup> were the primary components of the first PC, accounting for more than 57% of the total variance.

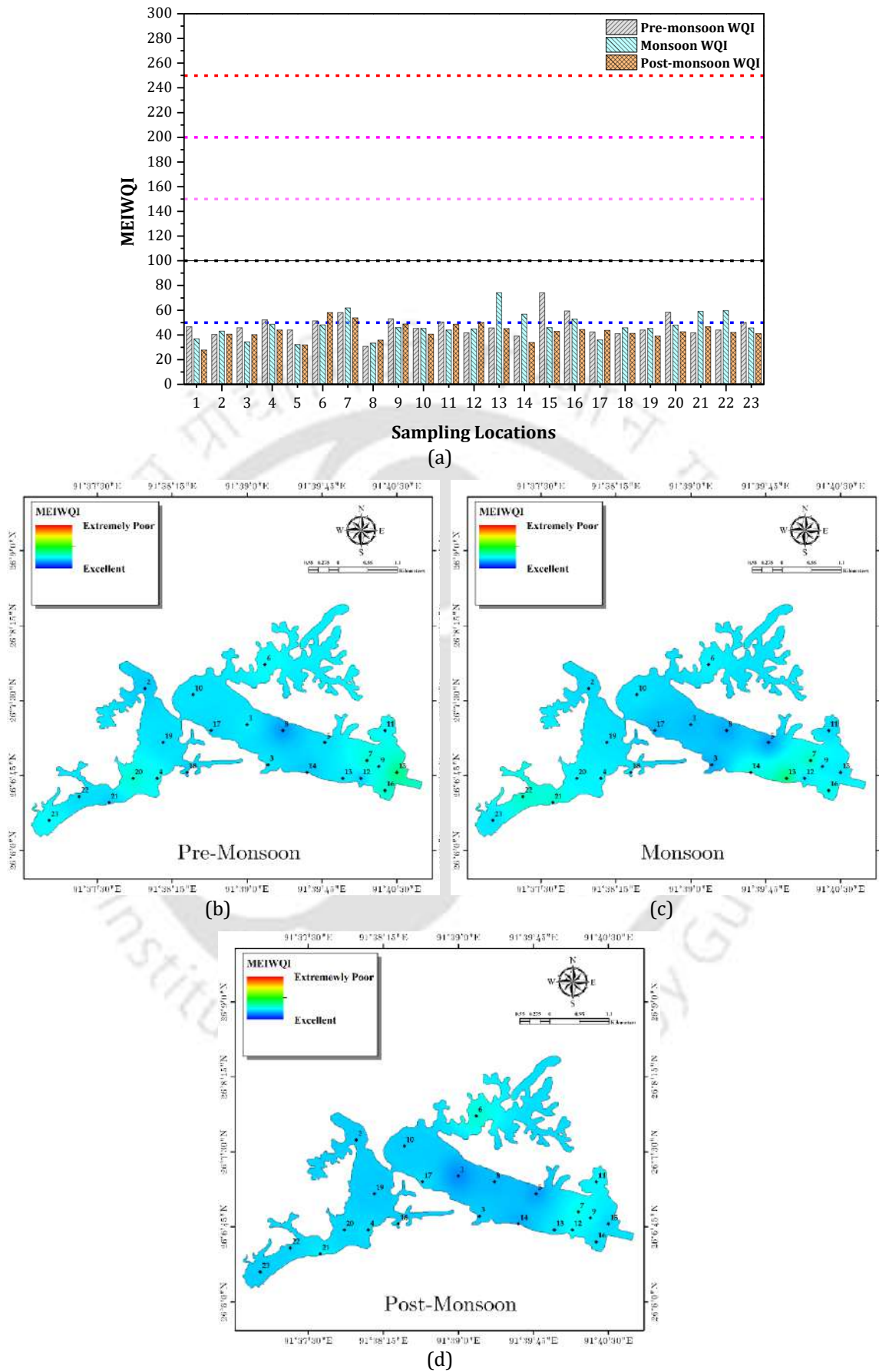
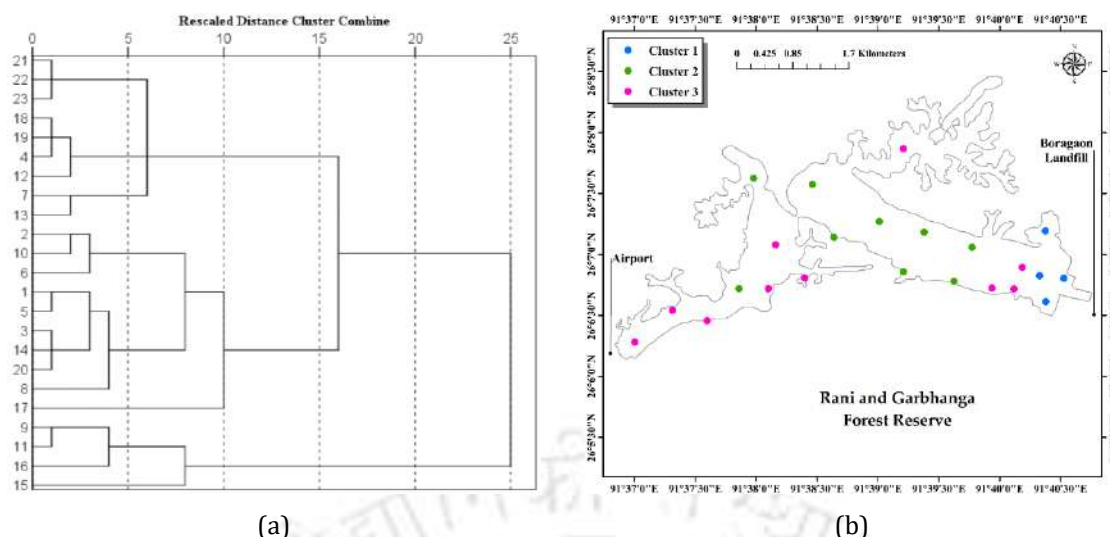


Fig. 6.14. Spatio-temporal variation of MEIWQI.



**Fig. 6. 15.** Results of the cluster analysis represented through (a) a Dendrogram and (b) GIS spatial representation of the points.

This was followed by  $F^-$ ,  $NO_3^-$ ,  $Na^+$ , and  $K^+$  for the second PC (accounting for 29.8% of total variance) and  $PO_4^{3-}$  and  $Ca^{2+}$  for the third PC (accounting for only 12% of the total variance). This attributes to organic loading from the leaching of the landfill and discharges from the Basistha River. Similarly, clusters 2 and 3 comprised 4 PCs each, accounting for 86.3 and 92.8% of the total variance, respectively. For cluster 2, pH, EC, TDS, and  $HCO_3^-$  were the primary pollutants comprising PC 1, accounting for about 37% of the total variance. This is indicative of natural contributions to the water of Deepor Beel. Likewise, for cluster 3,  $Mg^{2+}$ , other than pH, EC, TDS, and  $HCO_3^-$  was found to be a significant contributor, thus suggesting industrial discharge to be a significant factor for water pollution in cluster 3.

**Table 6. 8.** Varimax rotated component matrix for different water quality parameters for 23 different monitoring locations of Deepor Beel (Rotation method: Varimax with Kaiser normalization).

<b>(a) Cluster 1</b>			
<b>Principal Components</b>	<b>1</b>	<b>2</b>	<b>3</b>
<b>Eigenvalues</b>	7.537	3.873	1.590
<b>Variance (%)</b>	57.977	29.794	12.230
<b>Cumulative variance (%)</b>	57.977	87.770	100.000
pH	-0.927	-0.208	0.314
EC	0.983	-0.185	-0.011
TDS	1	-0.004	-0.014
$F^-$	0.4	0.905	0.145
$Cl^-$	0.828	-0.522	0.202
$NO_3^-$	-0.33	0.942	0.053
$PO_4^{3-}$	-0.533	-0.477	-0.699
$SO_4^{2-}$	0.955	0.25	0.163

Na <sup>+</sup>	-0.296	0.953	-0.066
K <sup>+</sup>	0.66	0.751	-0.003
Ca <sup>2+</sup>	-0.256	-0.067	0.964
Mg <sup>2+</sup>	0.997	0.024	-0.08
HCO <sub>3</sub> <sup>-</sup>	-0.984	0.176	0.031

**(b) Cluster 2**

Principal Components	1	2	3	4
<b>Eigenvalues</b>	4.801	2.878	2.236	1.308
<b>Variance (%)</b>	36.933	22.137	17.201	10.063
<b>Cumulative variance (%)</b>	36.933	59.070	76.271	86.334
pH	0.946	0.151	0.215	-0.061
EC	-0.962	0.114	0.07	0.135
TDS	-0.978	-0.045	-0.036	0.14
F <sup>-</sup>	-0.082	-0.059	-0.944	0.084
Cl <sup>-</sup>	-0.2	-0.419	-0.475	0.666
NO <sub>3</sub> <sup>-</sup>	-0.134	0.677	0.188	-0.091
PO <sub>4</sub> <sup>3-</sup>	0.058	0.908	-0.129	-0.017
SO <sub>4</sub> <sup>2-</sup>	-0.135	-0.12	0.414	0.833
Na <sup>+</sup>	0.008	0.716	0.482	-0.197
K <sup>+</sup>	0.069	0.135	0.838	0.452
Ca <sup>2+</sup>	0.415	0.887	0.004	-0.064
Mg <sup>2+</sup>	0.136	0.037	0.028	-0.761
HCO <sub>3</sub> <sup>-</sup>	0.976	0.142	0.031	-0.108

**(c) Cluster 3**

Principal Components	1	2	3	4
<b>Eigenvalues</b>	5.796	3.254	1.614	1.401
<b>Variance (%)</b>	44.587	25.029	12.418	10.781
<b>Cumulative variance (%)</b>	44.587	69.616	82.034	92.814
pH	-0.935	-0.133	-0.147	0.038
EC	0.988	-0.006	-0.069	-0.104
TDS	0.972	-0.012	-0.13	0.017
F <sup>-</sup>	0.013	-0.808	-0.18	0.07
Cl <sup>-</sup>	-0.412	0.323	0.777	0.034
NO <sub>3</sub> <sup>-</sup>	0.515	0.298	0.472	0.598
PO <sub>4</sub> <sup>3-</sup>	0.343	-0.106	0.894	-0.029
SO <sub>4</sub> <sup>2-</sup>	0.217	0.088	0.122	-0.947
Na <sup>+</sup>	0.013	0.568	0.507	0.624
K <sup>+</sup>	-0.652	0.662	-0.14	-0.194

Ca <sup>2+</sup>	0.102	0.945	-0.029	0.198
Mg <sup>2+</sup>	0.933	-0.174	0.24	-0.138
HCO <sub>3</sub> <sup>-</sup>	-0.992	0.006	-0.031	-0.048

The estimation of weights/sub-index values for all parameters and locations is given in Table 6. 9. For determining the weights of each parameter, the absolute values of each component score obtained from the PCA were considered. This is because the negative sign of scores gives the direction of that variable, while the magnitude provides its strength. Also, a strong negative loading implies that the specific parameter is inversely correlated to a factor or variable.

**Table 6. 9.** Weights for different variables in water samples from Deepor Beel.

**(a) Cluster 1**

PC	Eigen-value	Relative Eigen-value	Variable	Loading	Relative loading	Weight
1	7.537	0.580	pH	0.927	0.1389	0.0805
			EC	0.983	0.1473	0.0854
			TDS	1.000	0.1498	0.0869
			Cl <sup>-</sup>	0.828	0.1241	0.0719
			SO <sub>4</sub> <sup>2-</sup>	0.955	0.1431	0.0830
			Mg <sup>2+</sup>	0.997	0.1494	0.0866
			HCO <sub>3</sub> <sup>-</sup>	0.984	0.1474	0.0855
			<b>Total</b>	<b>6.674</b>		
2	3.873	0.298	F <sup>-</sup>	0.905	0.2549	0.0759
			NO <sub>3</sub> <sup>-</sup>	0.942	0.2653	0.0790
			Na <sup>+</sup>	0.953	0.2684	0.0800
			K <sup>+</sup>	0.751	0.2115	0.0630
						<b>Total</b>
3	1.590	0.122	PO <sub>4</sub> <sup>3-</sup>	0.699	0.4203	0.0514
			Ca <sup>2+</sup>	0.964	0.5797	0.0709
						<b>Total</b>

**(b) Cluster 2**

PC	Eigen-value	Relative Eigen-value	Variable	Loading	Relative loading	Weight
1	4.801	0.428	pH	0.946	0.2450	0.1048
			EC	0.962	0.2491	0.1066
			TDS	0.978	0.2532	0.1083
			HCO <sub>3</sub> <sup>-</sup>	0.976	0.2527	0.1081

			<b>Total</b>	<b>3.862</b>		
2	2.878	0.256	NO <sub>3</sub> <sup>-</sup>	0.677	0.2124	0.0545
			PO <sub>4</sub> <sup>3-</sup>	0.908	0.2848	0.0730
			Na <sup>+</sup>	0.716	0.2246	0.0576
			Ca <sup>2+</sup>	0.887	0.2782	0.0713
			<b>Total</b>	<b>3.188</b>		
3	2.236	0.199	F <sup>-</sup>	0.944	0.5297	0.1055
			K <sup>+</sup>	0.838	0.4703	0.0937
			<b>Total</b>	<b>1.782</b>		
4	1.308	0.117	Cl <sup>-</sup>	0.666	0.2947	0.0343
			SO <sub>4</sub> <sup>2-</sup>	0.833	0.3686	0.0430
			Mg <sup>2+</sup>	0.761	0.3367	0.0392
			<b>Total</b>	<b>2.26</b>		

**(c) Cluster 3**

PC	Eigen-value	Relative Eigen-value	Variable	Loading	Relative loading	Weight
1	5.796	0.480	pH	0.935	0.1940	0.0932
			EC	0.988	0.2050	0.0985
			TDS	0.972	0.2017	0.0969
			Mg <sup>2+</sup>	0.933	0.1936	0.0930
			HCO <sub>3</sub> <sup>-</sup>	0.992	0.2058	0.0989
			<b>Total</b>	<b>4.820</b>		
2	3.254	0.270	F <sup>-</sup>	0.808	0.3346	0.0902
			K <sup>+</sup>	0.662	0.2741	0.0739
			Ca <sup>2+</sup>	0.945	0.3913	0.1055
			<b>Total</b>	<b>2.415</b>		
3	1.614	0.134	Cl <sup>-</sup>	0.777	0.4650	0.0622
			PO <sub>4</sub> <sup>3-</sup>	0.894	0.5350	0.0716
			<b>Total</b>	<b>1.671</b>		
4	1.401	0.116	NO <sub>3</sub> <sup>-</sup>	0.598	0.2757	0.0320
			SO <sub>4</sub> <sup>2-</sup>	0.947	0.4366	0.0507
			Na <sup>+</sup>	0.624	0.2877	0.0334
			<b>Total</b>	<b>2.169</b>		

The IWQI values for each sampling location are then computed using Eq. 4.37. Fig. 6. 16 provides the spatio-temporal IWQI representation for Deepor Beel. It was found that all the sampling locations fell under the "Very good" category for all three seasons, making them fit for irrigation use.

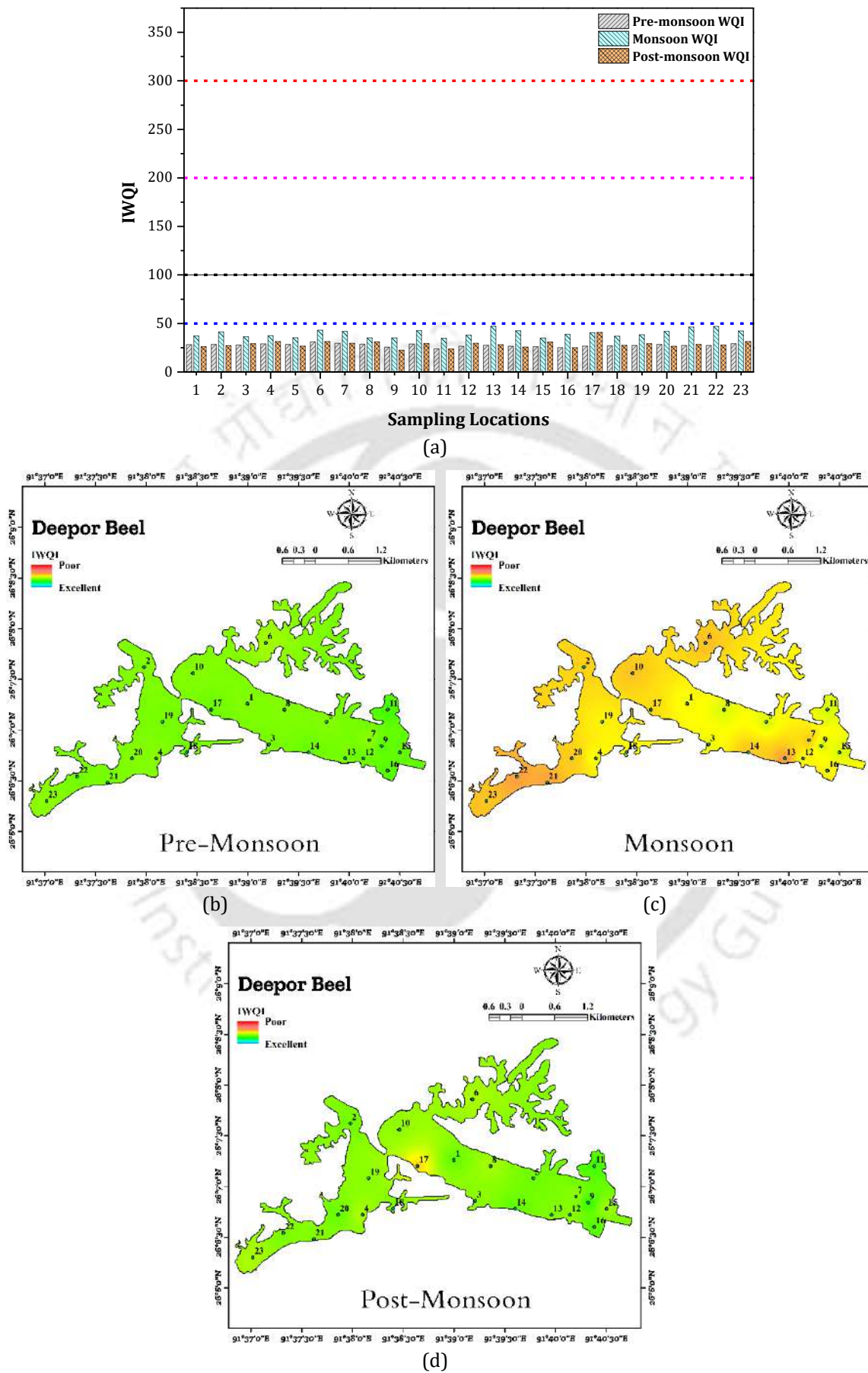


Fig. 6. 16. IWQI values and their spatio-temporal representation.

### 6.2.2.5. Irrigation suitability assessment

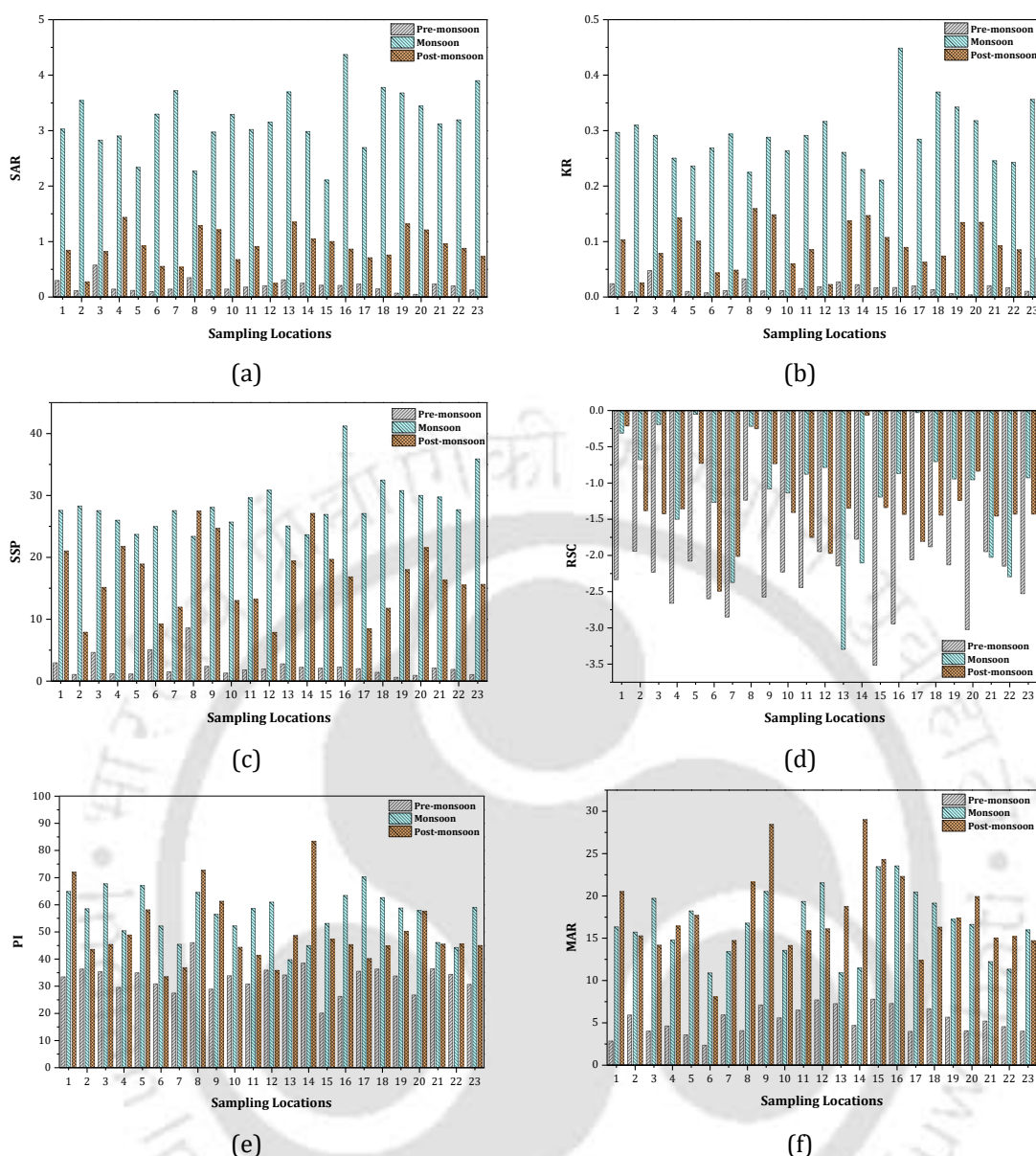
To check the correctness of the proposed MEIWQI and IWQI, the suitability of Deepor Beel water for irrigation use was determined through various irrigation water quality parameters, as depicted in Fig. 6. 17. Table 6. 10 presents the classification of these water quality parameters and the percentage of samples within those classes.

SAR (expressed as meq/L) measures the adverse effects of  $\text{Na}^+$  on the plants and soil in the presence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Values exceeding 20 may have severe implications for soil and plant health. SAR, for Deepor Beel, ranged between 0.45 to 4.37 meq/L, which were well within the acceptable limits (Fig. 6. 17a). These low values of SAR rendered the water of Deepor Beel fit for irrigation for all three seasons. However, it was observed that the monsoon season displayed a considerable surge in the SAR values compared to the other two seasons. This phenomenon can be linked to the weathering of rocks, and topsoil erosion during the stormwater flow into the wetland, increasing the  $\text{Na}^+$  concentrations. The pre-monsoon season displayed the lowest SAR values, making the water the most suitable for irrigation use. Similarly, KR values ranged from 0.003 to 0.448, which were well below the acceptable limit of 1 (Fig. 6. 17b).

SSP (expressed as %) ranged from 0.5 to 41.23, with a mean value of 15.77 (Fig. 6. 17c). Monsoon season was observed to have the most significance, while site 16 showed maximum  $\text{Na}\%$  value. This may have detrimental effects on the soil structure, aeration, and infiltration capacity due to high osmotic pressure (Singaraja *et al.* 2014). This further retards the nutrient absorbing capacity of the crops (Naseem *et al.* 2012).

RSC is rendered a helpful tool in evaluating the irrigation suitability through  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  ratio (Selvakumar *et al.* 2017). A negative RSC value means  $\text{Na}^+$  being a dominant cation. An excess  $\text{Na}^+$  offsets the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions by precipitating them as  $\text{CO}_2$ . However, a positive RSC indicates elevated concentrations of  $\text{HCO}_3^-$  ions through  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in the form of calcium bicarbonate and magnesium bicarbonate (Chitsazan *et al.* 2017). The RSC values of Deepor Beel's water was found to be negative for all seasons, pre-monsoon being the most negative for most of the locations. This indicated the water to be fit for irrigation for all seasons and locations.

The soil's permeability is considerably affected through long-term utilization of water rich in minerals, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{HCO}_3^-$  (Singh *et al.* 2008). Some of them include a reduction in soil aeration, which makes it difficult to sow seeds and retards seeding development.



**Fig. 6.17.** Different irrigation water quality parameters variation through different seasons.

Classification of water for PI was proposed by Doneen (1964), who categorized the PI values into three classes, as given in Table 6. 10. Based on this classification, the water of Deepor Beel was rendered suitable for irrigation as all values fell between 25 - 75%.

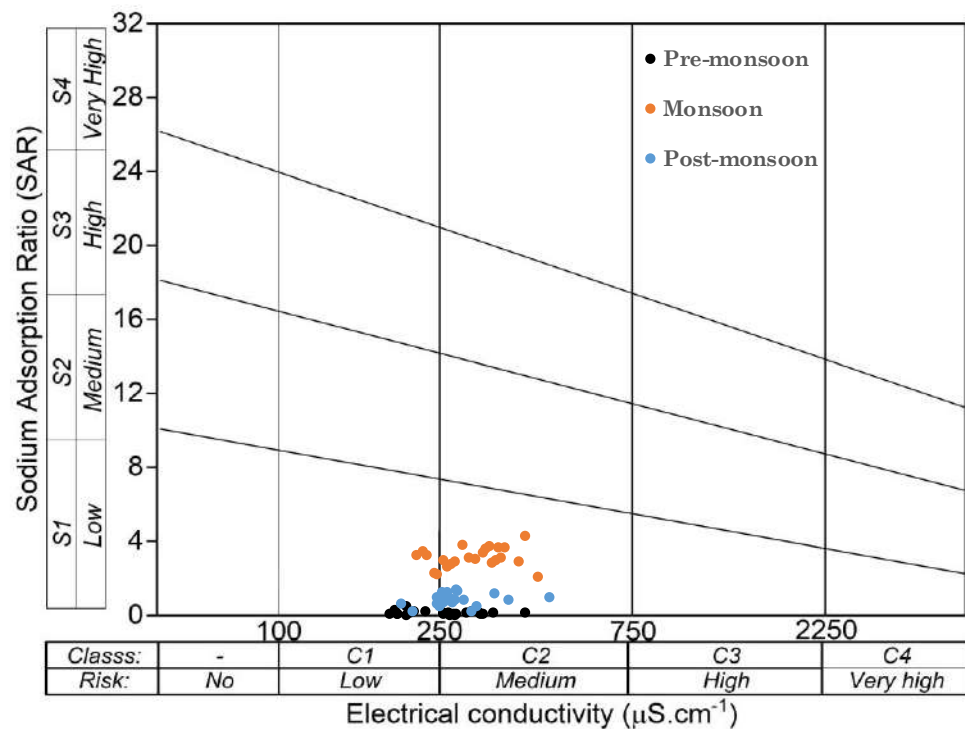
MAR values typically ranged from 2.33 to 29.01, with an average value of just over 13. Based on the water classification for MAR, the water can be deemed fit for irrigation use. High magnesium concentration increases the soil alkalinity, retarding its infiltration capacity (Hussain *et al.* 2017).

**Table 6. 10.** Summary of sample values according to the various specified standards.

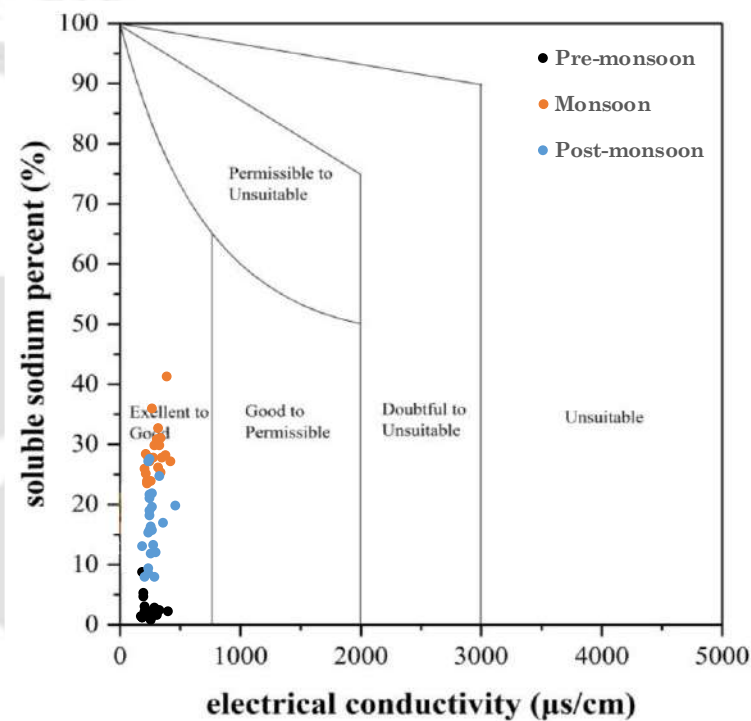
Parameter	Range	Class	% of samples
SAR	≤ 20	Excellent	100
	> 20-40	Good	-
	> 40-60	Permissible	-
	> 60-80	Doubtful	-
	> 80	Unsafe	-
KR	≤ 1	Suitable	100
	> 1	Unsuitable	-
SSP	≤ 50	Suitable	100
	> 50	Unsuitable	-
RSC	≤ 1.25	None	100
	> 1.25-1.70	Increasing	-
	> 1.70-2.10	Significant	-
	> 2.10-2.50	High	-
	> 2.50	Severe	-
PI	> 75%	Excellent	-
	25-75%	Suitable	100
	≤ 25%	Unsuitable	-
MAR	≤ 50	Suitable	100
	> 50	Unsuitable	-

A definite relation exists between the SAR and SSP with EC. This can be reflected through the USSL and Wilcox plots, respectively. The USSL plot considers EC ( $\mu\text{S}/\text{cm}$ ) on a logarithmic scale as the X-axis and SAR as Y-axis. On the contrary, the Wilcox plot uses EC ( $\mu\text{S}/\text{cm}$ ) on a standard scale as X-axis and SSP as Y-axis. Both plots classify the water samples accordingly, as shown in Fig. 6. 18. Keeping view of this, the water samples were plotted for all three seasons. It was observed that the Deepor Beel water, for most locations and sampling periods, fell in the S1-C2, i.e., low sodium and medium salinity category based on the USSL plot. On the other hand, the Wilcox plot showed that all samples fell under the Excellent to Good Zone, indicating their viability for irrigation use.

The results of the proposed MEIWQI and IWQI were thus observed to associate excellently with all the irrigation water quality parameters, thereby reflecting its efficiency and applicability at a global scale.



(a) USSL diagram (U.S.S.L 1954)



(b) Wilcox diagram (Wilcox 1955)

Fig. 6. 18. Rating of water samples to determine irrigation feasibility.

### 6.3. Summary

This chapter provides insights into the results obtained for the proposed methodologies in assessing the water quality of a water body through indexing approaches. Two objective-based methodologies were proposed, and critical concluding remarks from the results obtained are as follows.

- a. The overall water quality of Deepor Beel suggested that the Boragaon landfill plays a significant role in the water quality of Deepor Beel. The contamination levels are more evident during the monsoon, as leaching from the landfill gets directly discharged into the water column of the wetland. This was verified through both the proposed methodologies, which provided a significant correlation with the obtained results.
- b. The efficacy and reliability of the methods were checked through the sensitivity analyses. Both MEWQI and PCA-WQI values were not found to be too sensitive to any particular or a few parameters; instead, all parameters had more or less equal contributions to the assessment of water quality, thus rendering them to be highly effective in the assessment of water quality.
- c. These methods were then employed to assess water quality for specific purposes, depending on the end-use of water. MEHMI and HMI obtained through modified entropy weights and PC-weights, respectively, showed excellent correlation amongst them. Their efficacies were verified through some other indices such as CI and HEI, and the results obtained were compared to the existing HPI. Results indicated a superior correlation for the proposed indices as compared to the existing one. Likewise, MEIWQI and IWQI values were obtained through modified entropy weights and PC-weights, respectively. The results obtained showed that the water in Deepor Beel was rendered suitable for irrigation due to the significant amount of nutrients present in the water column of the wetland. The efficacies of the results obtained for MEIWQI and IWQI were checked using various indicators for irrigation suitability of water. The results showed to correlate excellently with the different irrigation water quality parameters, such as SAR, KR, SSP, RSC, PI, and MAR. Also, validation with USSL and Wilcox plots substantial evidence of the high reliability of the proposed indices.

The results of this study will be of substantial aid to various policy-makers and government or semi-government organizations in taking appropriate steps for improving the health of a water body. This would further aid in properly managing funds allocated for the restoration and rejuvenation of the water bodies. This is because it will help identify the critical pollution limits essential in the restoration process of the water bodies, thereby aiding in updating the regulatory norms for future policies. Additionally, the proposed novel methods are

not limited to any particular water body or geography; instead, they may be universally adopted.



Erosion, desertification, and pollution have become our lot. It is a weird form of suicide, for we are bleeding our planet to death.

- Gerald Durrell

# 7

## Assessment of sediment column quality with respect to heavy metals

The present chapter discusses the results of the III<sup>rd</sup> objective, i.e., assessing the quality of the sediment column of the wetland, including the impacts of sediment contamination on the aquatic ecology. Detailed analyses on specific indices developed for evaluating the sediment quality have also been discussed. Elemental analyses confirming the results obtained have been studied.

### 7.1. Descriptive statistics of the sediment dataset

The basic elaborative statistics (for all three seasons) have been presented in Table 7. 1. Details of the sediment dataset have been shown in Appendix B through the sampling pattern plots. It can be clearly observed that the concentrations of the metals followed the trend; Mg > Fe > Mn > Cr > Pb > Cd > Cu. Most of the maximum concentrations were obtained from the sites close to the landfill, i.e., to the eastern part of the wetland. It can also be observed that the concentrations of Cr, Mn, and Pb were higher during the pre-monsoon period, while Cd, Cu, and Mg showed higher concentrations during the post-monsoon period. Fe, however, displayed relatively greater concentrations during the monsoon as compared to the other two seasons. Significant SD was observed for Cd, Cu, Fe and Mg, indicating high levels of variations in concentrations in the sediment columns of the wetland. Similarly, high CV values for Cd (38.86%), Cu (39.57%) and Mg (24.25%) were also observed from the dataset. All the HMs showed positive skewness, closely to highly positive skewness (skewness  $\geq 1$ ), thereby reflecting a long right-hand tail when normally distributed. Similarly, except Pb (leptokurtic, having a high peak), all the parameters showed platykurtic distribution, thus indicating flatter curves of normally distributed data.

**Table 7. 1.** Statistical summary of the metal concentrations (mg/kg) in sediment samples.

	Cr	Cd	Fe	Mn	Cu	Pb	Mg
Max	240.626	127.055	10197.240	437.648	68.437	264.000	16880.000
Min	137.021	35.071	7503.948	320.616	18.062	150.310	7039.000
SD	28.201	23.543	540.711	25.385	13.039	21.391	2376.720
Mean	172.393	60.576	8061.196	353.692	32.949	169.780	9799.513
CV	16.359	38.866	6.708	7.177	39.573	12.599	24.253
Skewness	0.582	0.941	1.186	1.010	0.879	2.147	0.923
Kurtosis	-0.721	-0.006	1.199	0.388	-0.098	5.315	0.010

## 7.2. Pollution source identification and apportionment

Based on their relative closeness, the raw sediment dataset was then subjected to hierarchical clustering to predict the site similarities. The dendrogram (tree diagram) obtained from the HCA (Fig. 7. 1a) revealed three distinct clusters at  $\frac{D_{link}}{D_{max}} \times 100 \leq 5$ . Cluster 1 comprised sites 7, 9, 11, 12, 13, 15, and 16, whereas cluster 2 comprised sites 4, 18, 19, 20, and 21, and the rest of the sites fell under cluster 3. The three clusters are spatially represented in Fig. 7. 1b, which shows that sites under cluster 1 are mainly proximate to the Boragaon landfill region, while the sites proximate to the industrial zone except sites 22 and 23 were the sites under cluster 2 and the majority of the sites (especially in the central region) were the sites represented by cluster 3. Thus, cluster 1 can be considered to be sites having high pollution, whereas clusters 2 and 3 can be considered as sites of moderate and low pollution, respectively.

PCA was then independently employed on the dataset for all three seasons, thereby producing the principal components for the rotated matrix (Table 7. 2) to determine the probable pollution sources. Eigenvalues  $> 1$  with factor loadings  $> 0.75$  (strong positive loadings) were considered for the analysis. It was observed that the three seasons behaved differently owing to different environmental conditions. The pre-monsoon season accounted for more than 99% of the cumulative variance, with Cd, Cu, Pb, and Mg being the principal components for factor 1, thus suggesting landfill and industrial contribution to the pollution of the sediments of the wetland. Similarly, factor 2 represented the earth's crust, as the major components contributing are Cr, Fe, and Mn. Similar behaviour was observed during the monsoon period except for Pb, which does not have a strongly favourable loading. This might be attributed to the wetland's increasing water levels during this period (Fig. 4. 9).

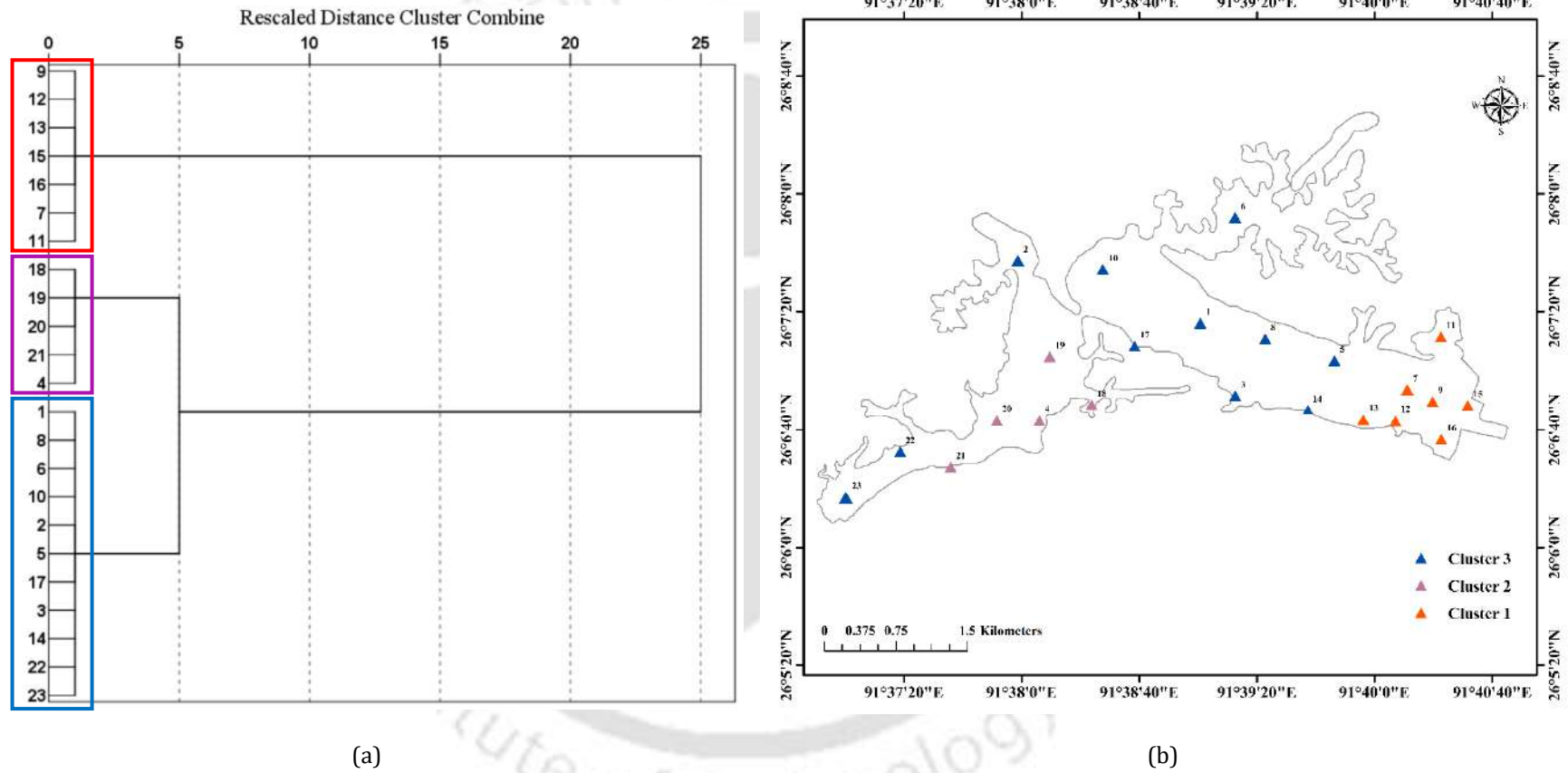


Fig. 7. 1. Hierarchical cluster analysis of the sediment dataset showing (a) Dendrogram and (b) spatial representations of sampling locations.

**Table 7. 2.** Rotated component loadings obtained through PCA for three seasons of the sediment dataset of Deepor Beel.

Rotated Component Matrix <sup>a</sup>						
	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon
<b>Eigenvalues</b>	4.962	4.198	4.202	2.018	2.358	2.448
<b>Variance</b>	70.889	59.969	60.033	28.827	33.681	34.969
<b>Cumulative variance</b>	70.889	59.969	60.033	99.715	93.65	95.002
<b>Heavy Metals</b>	<b>Factor 1</b>			<b>Factor 2</b>		
Cr	0.634	0.119	0.095	0.771	0.993	0.978
Cd	0.998	0.986	0.991	0.059	0.023	0.125
Fe	-0.476	-0.173	0.756	0.877	0.853	-0.652
Mn	0.377	0.274	0.569	0.926	0.922	0.643
Cu	0.998	0.991	0.882	0.054	0.089	0.455
Pb	0.966	0.659	0.187	0.241	0.695	0.968
Mg	0.994	0.991	0.989	0.094	0.105	0.133

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization <sup>a</sup>

a. Rotation converged in 3 iterations.

As a result, the leachates from the landfill (which essentially is the major source of Pb due to the dumping of Pb-acid batteries) remain in the water column rather than getting deposited in the sediment column of Deepor Beel. Furthermore, the post-monsoon season sees a shift in the Pb to factor 2 with Cr. This is indicative of the deposition of Pb and Cr (from industries) into the sediment column of the wetland after the monsoon retreats.

The PMF model assists in quantifying the contribution of each pollution source. The model takes into account the concentration and uncertainty profiles of the monitoring datasets as input files to provide the factor contributions. The uncertainty was determined by  $[0.1 \times \text{species concentration} + (\text{standard deviation}/3)]$ , if the concentration was above the standard deviation (SD), else, the concentration was replaced by  $SD/2$ , and the uncertainty was assumed to be  $(5 \times SD/6)$  (Wang *et al.* 2016). Determining the optimum number of factors for the PMF analysis requires several iterations, and the most optimum number was obtained by readjusting the number of sources till we obtain the value of Q closest to the number of degrees of freedom. In other words, iterations were performed considering the number of factors from 2-7, and the Q values were obtained. The number of factors in the iteration having the minimum  $Q(\text{Robust})/Q_{\text{exp}}$  value was considered as optimum. In the present case, four factors

were considered optimum as the value of  $Q(\text{Robust})/Q_{\text{exp}}$  is minimum for iteration with four factors (Table 7. 3).

**Table 7. 3.** Summary of PMF and EE diagnostics for the sediment dataset of Deepor Beel.

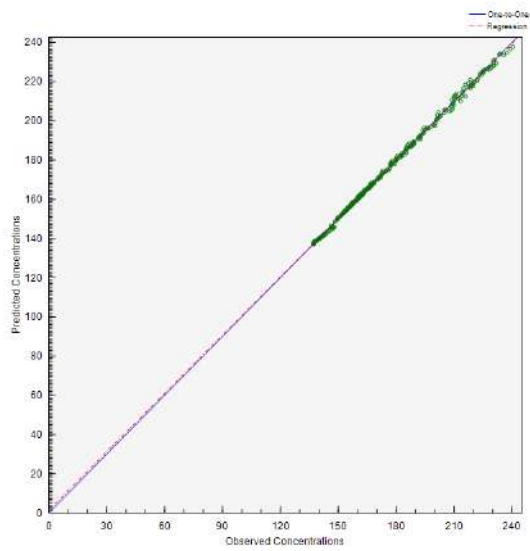
Diagnostic	2 factors	3 factors	4 factors	5 factors	6 factors	7 factors
Qexp	654.3	2712.7	4936.5	3913.7	4783.7	4544.4
Q(True)	2415.2	586.5	217.9	212.9	267.1	283.4
Q(Robust)	3069.5	3299.2	5154.4	4126.6	5050.8	4827.8
Q(Robust)/Qexp	4.691273	1.216205	1.044141	1.054399	1.055835	1.062362

The fitness of the model was tested by comparing the observed versus predicted values of the HMs, thus obtaining the correlation coefficients ( $R^2$ ) (Fig. 7. 2). All the HMs except Fe (0.95) and Mn (0.89) exhibited  $R^2$  values higher than 0.99, thus exhibiting an excellent correlation between the observed and predicted values and indicating high reliability of the model (Table 7. 4). Four factors were considered in the present study for source apportionment of the HMs in sediments of Deepor Beel.

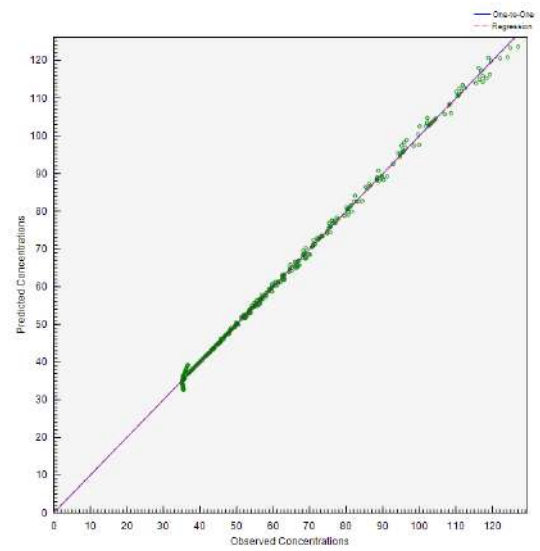
**Table 7. 4.** Correlation coefficients ( $R^2$ ) of different heavy metals in sediment samples collected from Deepor Beel.

Species	S/N	Category	Intercept	Slope	$R^2$
Cr	5.4	Strong	1.451	0.991	0.99
Cd	3.2	Strong	0.201	0.996	0.99
Fe	7.2	Strong	407.264	0.949	0.95
Mn	7.1	Strong	28.967	0.917	0.89
Cu	3.2	Strong	-0.005	0.999	0.99
Pb	6.0	Strong	1.960	0.988	0.99
Mg	4.5	Strong	175.111	0.981	0.99

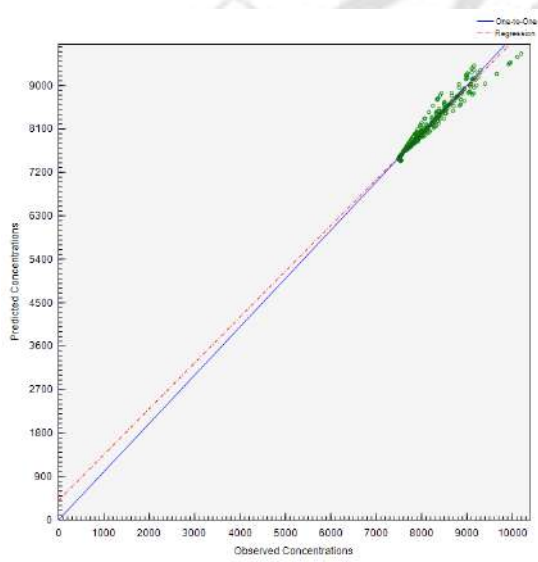
Fig. 7. 3 represents the results of the PMF source apportionment for all the HMs considered in the study. It can be observed that there exist some discrepancies in the concentration profiles and the percentage of HMs occupying various factors. For example, it can be observed that a high concentration of Mg accounted for about only 10% of the total species in factor 1, whereas a low concentration of Cr accounted for more than 60% of the species in factor 4. Similar discrepancies can be seen for all the factors and all the HMs as well. The importance of having more significant percentages of species for a particular HM in a factor is much higher as compared to that of having higher concentrations of a particular HM in a factor, thereby indicating that a factor is majorly affected by the percentage of species rather than their concentration. Thus, the results obtained from the PMF simulations signifying both species concentrations and percentages aid in examining the pollution source apportionment.



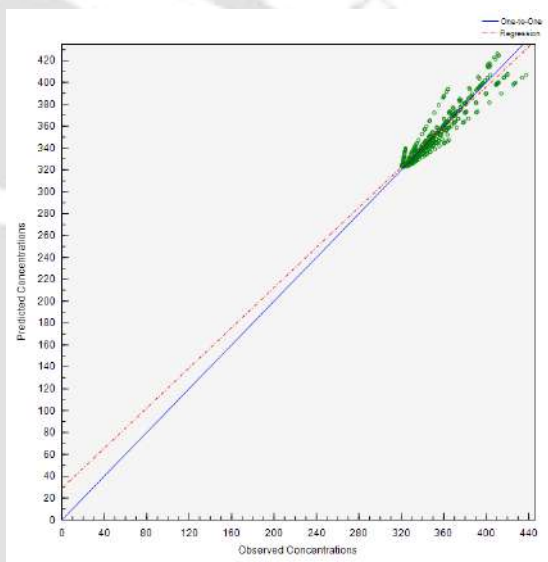
(a) Cr



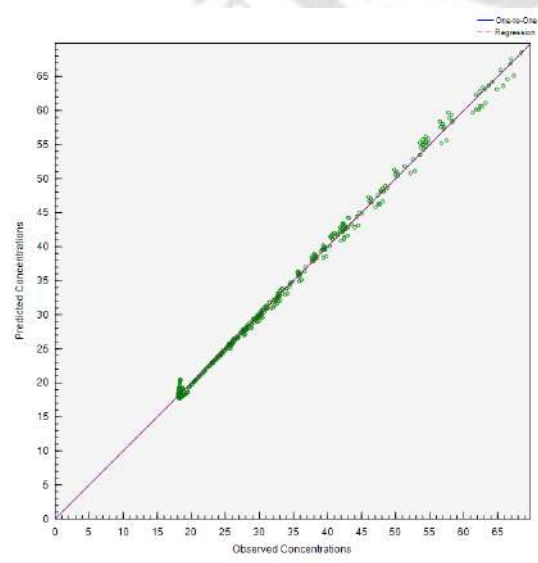
(b) Cd



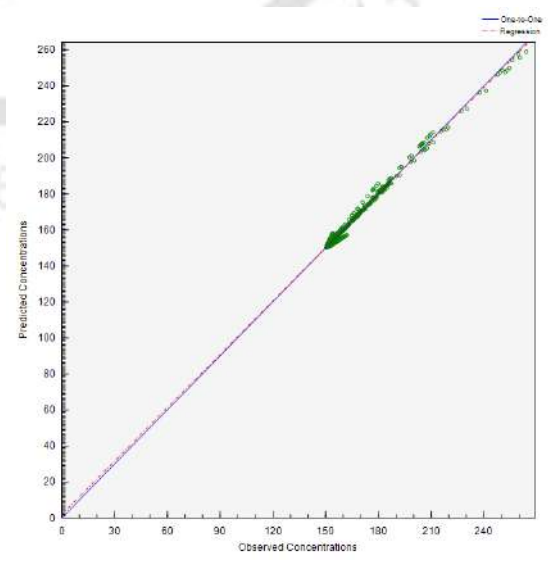
(c) Fe



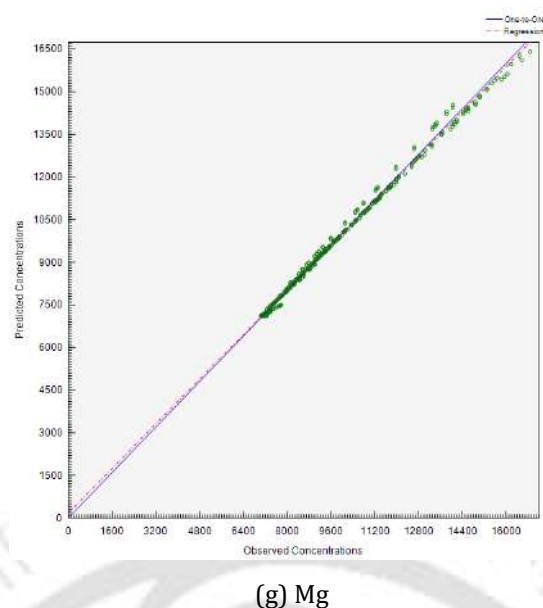
(d) Mn



(e) Cu



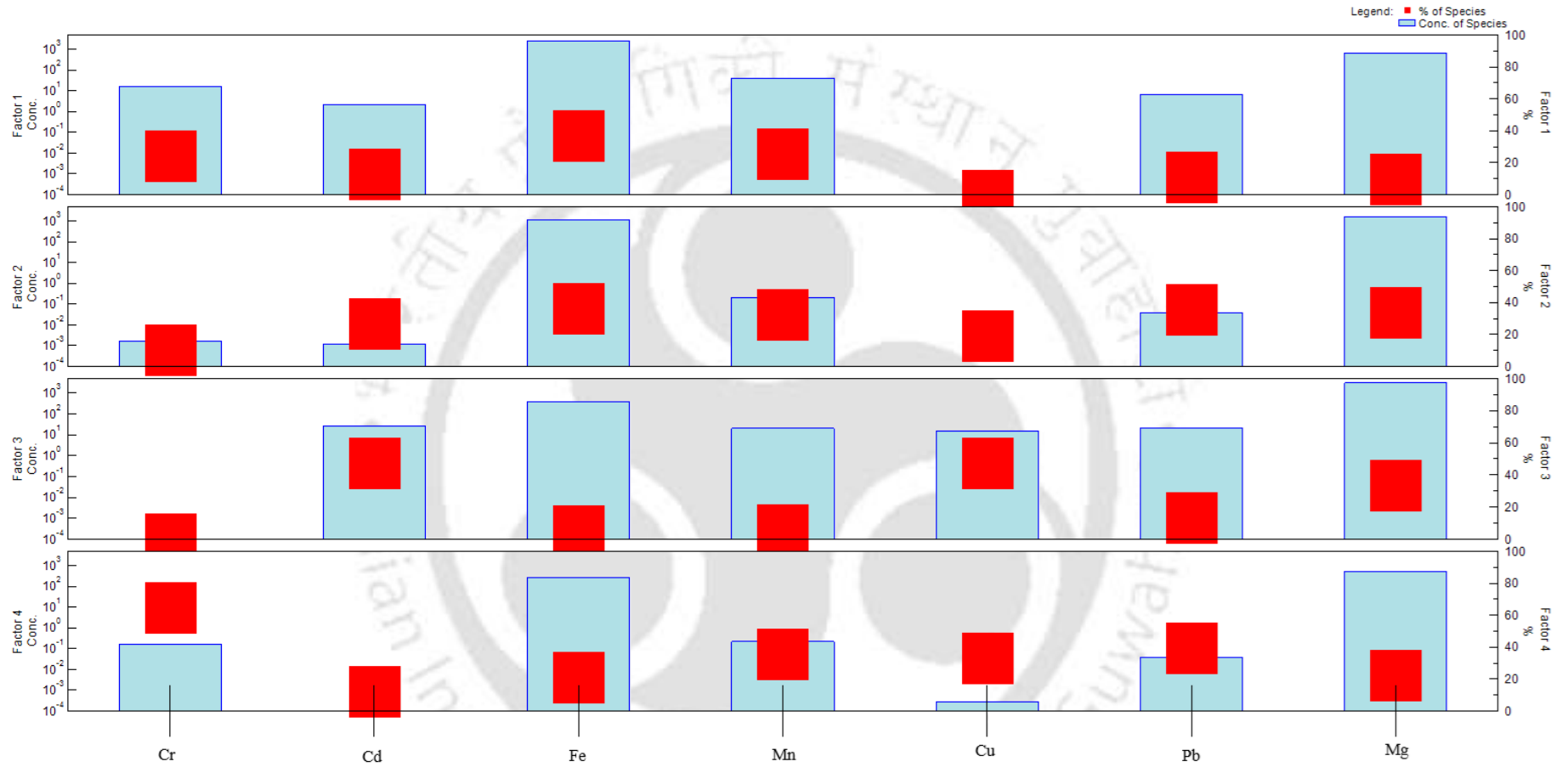
(f) Pb



**Fig. 7. 2.** Correlations between observed concentrations and predicted concentrations of HMs for sediments (mg/kg) of Deepor Beel.

The individual factor source contributions to the pollution of the sediment column of Deepor Beel is shown in Fig. 7. 4 (a and b). Factor 1 primarily constitutes Fe (38.2%) and a lesser portion of Mn (24.6%). This is indicative of the natural parent materials of the soil, deposited in the sediment column through various natural phenomena such as weathering or erosion from nearby areas (Sajn 2003; Acosta *et al.* 2010; Huang *et al.* 2018). Deepor Beel is surrounded by the Rani and Garbhanga forest reserve in the southern part. Inundated runoffs from these hilly regions get discharged into the wetland, especially during the monsoon. These runoffs carry eroded topsoil, which eventually ends up settled at the bottom.

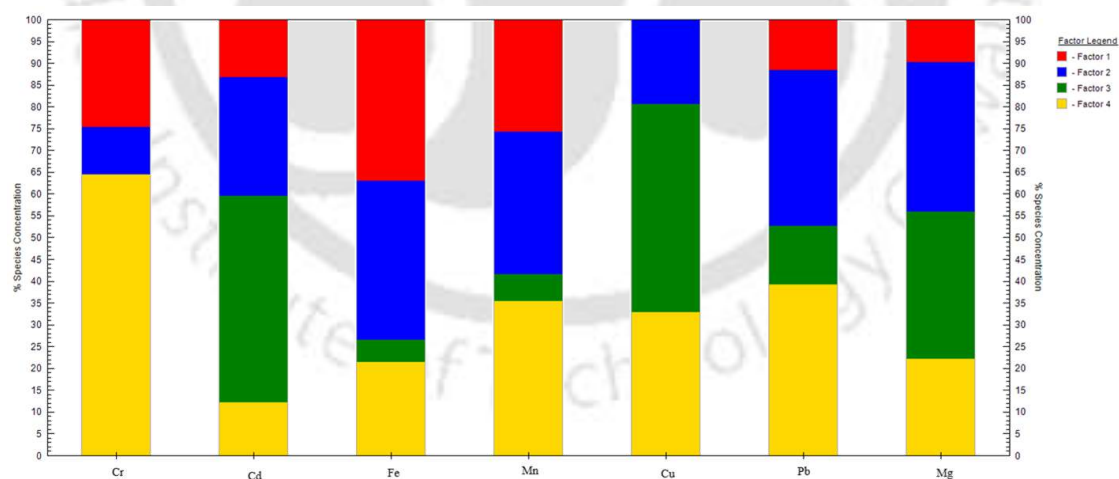
Factor 2 is primarily constituted of contributions from Fe (36.5%), Mn (34.4%), Pb (35.3%), Mg (34.1%) and Cd (28.7%). Factor 2 is likely to originate from the Boragaon landfill site situated in proximity to the wetland (eastern part). Various types of wastes originating from different sources such as domestic, hospitals, small scale industries etc., are being discharged into it. This comprises lead-acid batteries and various plastic stabilizers from households and industries, respectively. Plastic stabilizers (Cadmium Oxide) form a primary source of Cd (Lu *et al.* 2007), while the lead-acid batteries contribute to the Pb contamination. During the monsoon, these metals get leached into the water columns, which eventually end up in the sediments through precipitation.



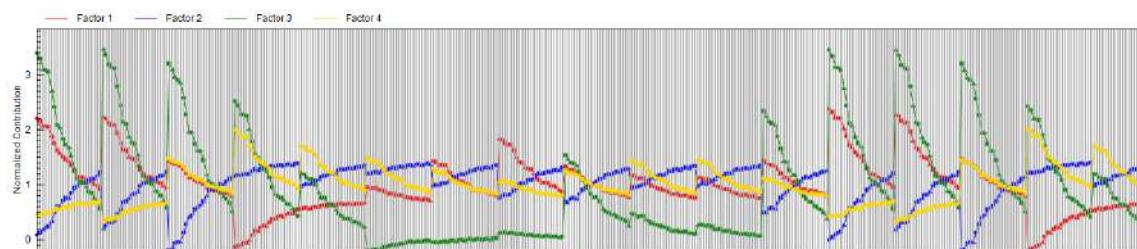
**Fig. 7.3.** Results of PMF source apportionment modelling for heavy metals in sediments collected from Deepor Beel.

Factor 3 comprises Cd (47.5%), Cu (46.6%) and Mg (33.7%), which is a reflection of more on the pollution through agricultural and wastewater runoff (Xiao-Nan *et al.* 2005; Luo *et al.* 2009). The Deepor Beel is susceptible to pollution from the Basistha River, which joins the wetland from its eastern front. The Basistha River carries with it, an accumulation of domestic and agricultural wastes from the city of Guwahati, eventually discharging its water in the wetland. The HMs getting discharged into the wetland is much higher during the dry (low-flow) period. With the advent of monsoon, dilution plays a significant role in reducing pollution levels.

Finally, Factor 4 is constituted of pollution contribution through Cr (64.7%), Cu (34.6%), Pb (39.7%) and Mn (36.2%). Reports have been documented suggesting traffic emissions and discharges of industrial effluents to be the primary factors responsible for soil contamination pertaining to Cr, Cu and Pb (Imperato *et al.* 2003; Li *et al.* 2009). The western zone of the wetland has a cluster of various large and small-scale industries discharging their effluents into the wetland. The wetland is also surrounded by a national highway (NH 37) with continuous flowing traffic. Hence, the continuous emissions from the vehicles on the national highway can be considered to be credible pollution sources. Thus, factor 4 can be primarily attributed to the contributions from industrial effluents and traffic emissions from the highways.



(a)



(b)

**Fig. 7. 4.** (a) Source contributions and (b) normalized contributions to heavy metals of each factor generated by the PMF model.

While the PMF receptor model estimates the sources' contribution to pollution, there is another model which roughly uses a similar technique (least-squares fitting); the Chemical Mass Balance (CMB) method. The major limitation of the PMF receptor model to the CMB technique lies in the error estimation, wherein precise error estimation is usually carried out in the CMB technique as compared to the PMF modelling technique. This is primarily because the CMB analysis is carried out on a sample-by-sample basis. As a result, it becomes possible to assign error estimates to each of the source contribution values. However, this can also lead to some misspecification of the source profiles as there can be errors in the estimated source contributions as a result of changes in the source profiles. Nevertheless, both techniques use similar approaches in estimating the pollution source apportionment. Hence the output from both the models possesses certain similarities, although there also exist specific differences which depend on the input dataset and the estimates of the uncertainties.

### 7.3. Contamination and ecological risk assessment

#### 7.3.1. Contamination Factor and Pollution Load Index

Fig. 7. 5 shows the CF values for all the metals across the three seasons for each sampling location. It can be seen that the CF values mostly lie in the moderate contamination range (1 - 3), except for some metals in certain seasons. Also, the CF values for the post-monsoon season can be observed to have relatively higher values as compared to other seasons. This makes the sediment column of the wetland more susceptible to contamination as the anthropogenic discharges from the surroundings of the wetland can get precipitated or deposited more on the sediment column during this season. Furthermore, the CF values for Cd, Fe, and Mg were found to be slightly less than other metals, thus, suggesting the natural occurrence of these heavy metals. The dominance of Cr, Mn and Pb in the CF values is indicative of anthropogenic involvement in the addition of heavy metals in the sediments of Deepor Beel.

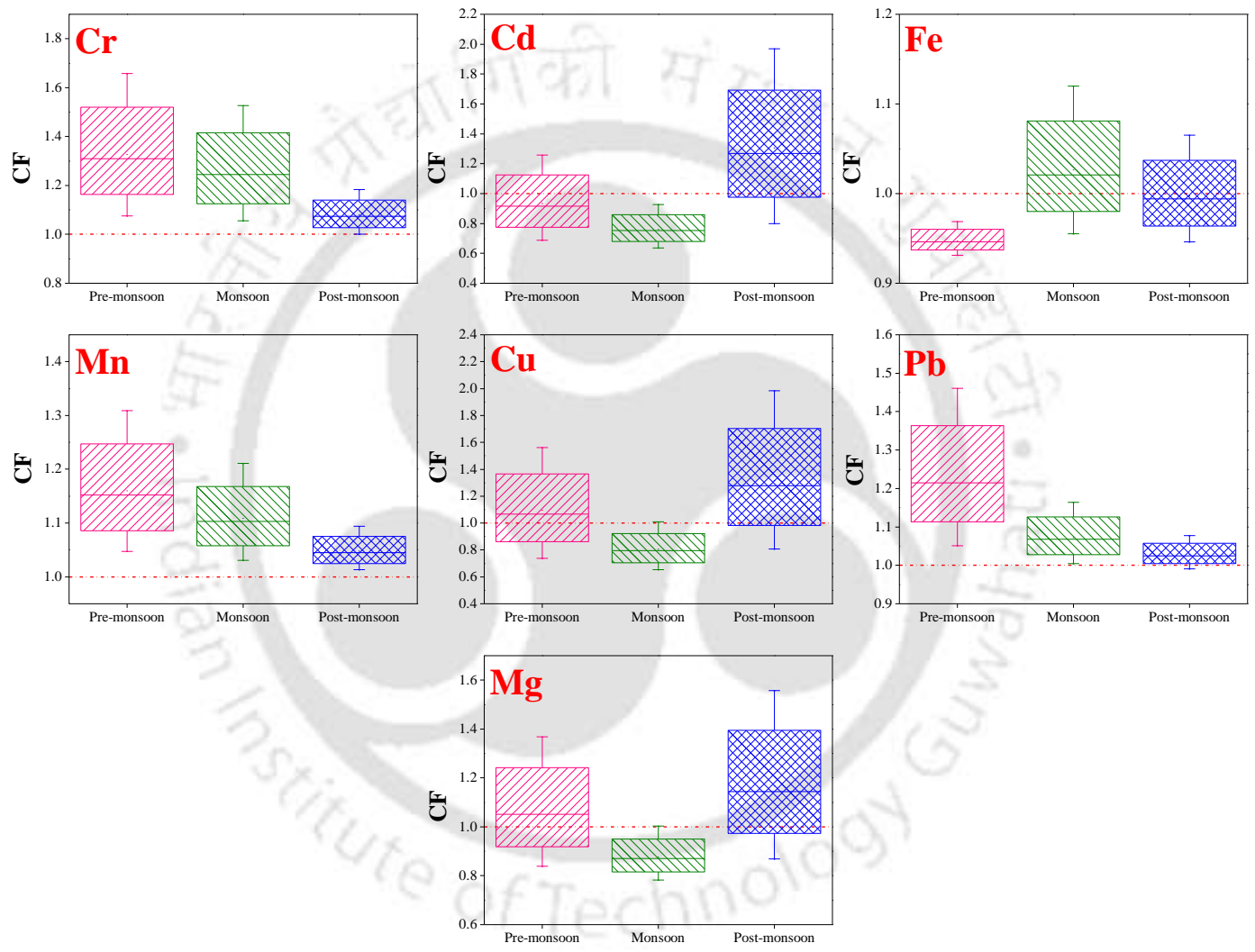
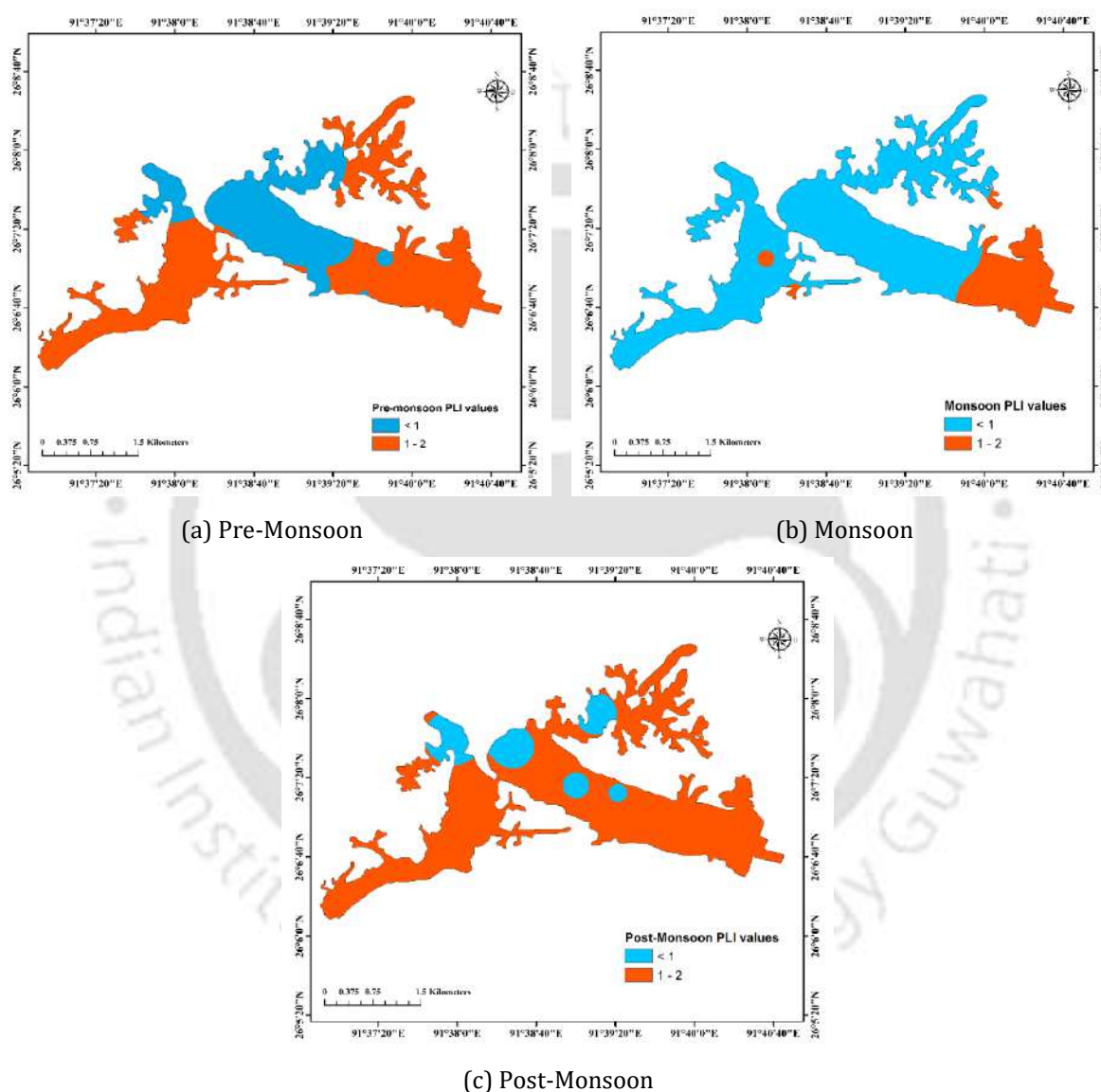


Fig. 7. 5. Contamination factor for sediment samples of Deepor Beel.

PLI values are spatially represented through Fig. 7. 6. Critical observations can be made from Fig. 7. 6 regarding the spatial and temporal variations of the PLI values. The post-monsoon period has been recorded as the season with maximum effects on the sediment column, while the monsoon season remains the least affected. Leaching from the landfill as well as outlets of various small- and large-scale industries remain the highest in the monsoon season. But these contaminants remain mostly in the water column.



**Fig. 7. 6.** PLI variations for three seasons across Deepor Beel.

It is during the post-monsoon period that the deposition or precipitation of these contaminants on the sediment column from the water column is highest due to less turbulence and disturbances as a result of the stormwater flow into the wetland, which hinders the precipitation process. Also, the water depth during the monsoon is significantly high compared to other seasons. The more considerable water depth also delays the accumulation process of

the heavy metals on the sediment columns. The PLI values, however, lie between 1 and 2, thus indicating moderate contamination in the wetland.

### 7.3.2. Enrichment Factor and Geoaccumulation index

Fig. 7. 7 and Table 7. 5 depict the enrichment factor values for all three seasons and all the heavy metals taken into consideration. It can be observed that the enrichment values do not exceed 2 in any case, thereby indicating that there is minimum enrichment, and thus the contribution of the anthropogenic sources in the heavy metal enhancement of the sediment samples is still in the preliminary stage. Cd is found to be the most enriched among all the heavy metals, especially in the sites close to the landfill and Bharalu river. This can be attributed to the discharge from the agricultural runoff and domestic wastewater entering the wetland, which carries significant Cd with them (El Kammar *et al.* 1999; Faroon *et al.* 2012; Ramadan 2014). Cd is followed by Pb, which is primarily due to the leaching effect from the landfill nearby.

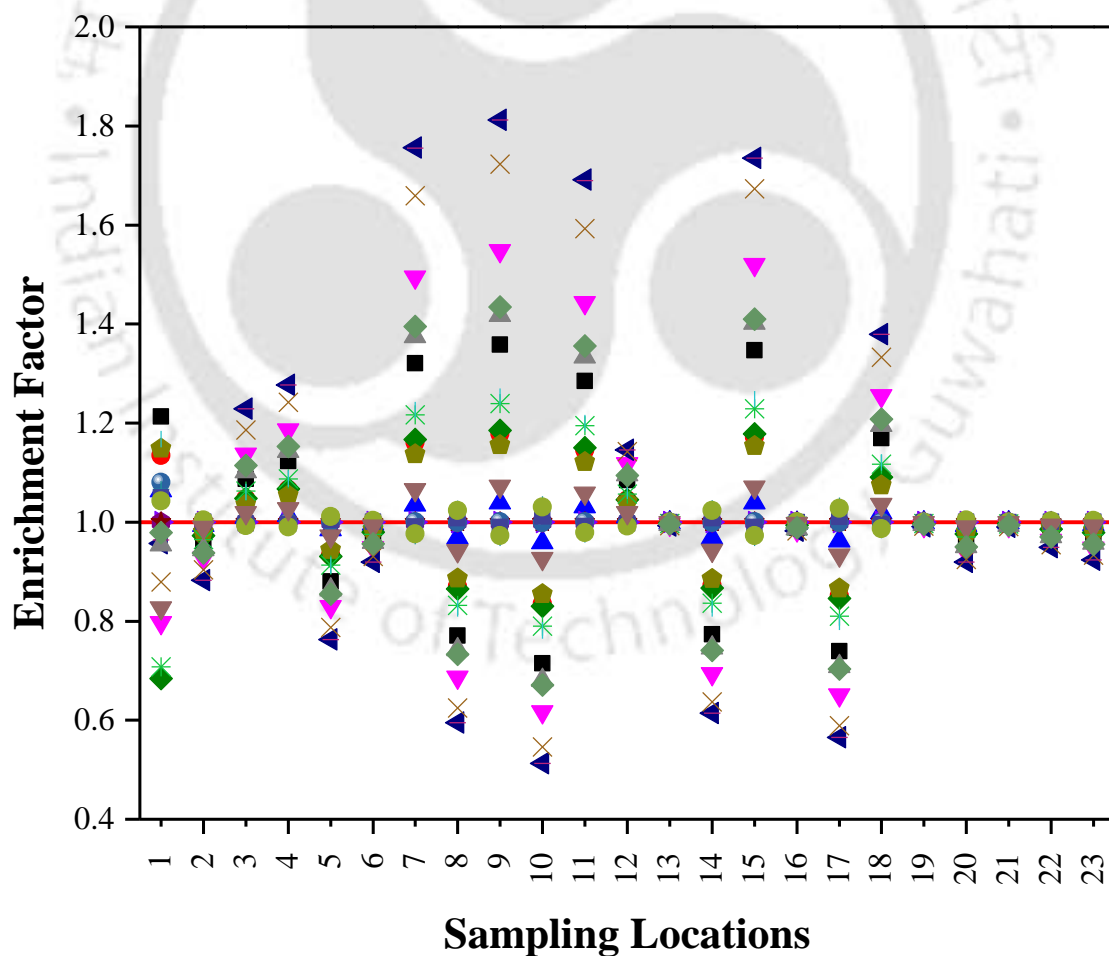


Fig. 7. 7. Enrichment Factor values for all sampling locations across Deepor Beel.

**Table 7.5.** Enrichment factor for sediment samples of Deepor Beel.

Sampling Location	Enrichment Factor																				
	Cr			Cd			Fe			Mn			Cu			Pb			Mg		
	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon
1	1.213	1.134	1.064	0.797	0.684	0.957	1.000	1.000	1.000	1.148	1.080	1.066	0.879	0.708	0.964	1.168	1.050	1.043	0.954	0.827	0.979
2	0.953	0.974	0.994	0.927	0.973	0.883	1.000	1.000	1.000	0.980	1.000	1.004	0.904	0.965	0.883	0.966	1.001	1.004	0.945	0.989	0.938
3	1.087	1.047	1.010	1.137	1.048	1.229	1.000	1.000	1.000	1.036	1.000	0.992	1.186	1.063	1.229	1.061	0.997	0.993	1.102	1.019	1.114
4	1.123	1.065	1.014	1.186	1.067	1.277	1.000	1.000	1.000	1.054	1.000	0.988	1.242	1.087	1.277	1.088	0.996	0.990	1.143	1.027	1.153
5	0.880	0.933	0.985	0.829	0.931	0.763	1.000	1.000	1.000	0.944	1.000	1.013	0.787	0.913	0.763	0.912	1.004	1.011	0.863	0.972	0.855
6	0.965	0.981	0.996	0.948	0.980	0.919	1.000	1.000	1.000	0.985	1.000	1.003	0.931	0.975	0.919	0.975	1.001	1.003	0.960	0.992	0.956
7	1.321	1.161	1.035	1.495	1.167	1.756	1.000	1.000	1.000	1.137	1.001	0.972	1.659	1.217	1.755	1.226	0.991	0.976	1.375	1.065	1.395
8	0.771	0.870	0.968	0.687	0.865	0.595	1.000	1.000	1.000	0.886	0.999	1.027	0.625	0.832	0.595	0.826	1.008	1.023	0.743	0.942	0.733
9	1.358	1.178	1.039	1.548	1.185	1.812	1.000	1.000	1.000	1.155	1.001	0.968	1.723	1.239	1.812	1.253	0.990	0.973	1.418	1.072	1.434
10	0.715	0.835	0.959	0.617	0.830	0.513	1.000	1.000	1.000	0.855	0.999	1.036	0.546	0.790	0.513	0.781	1.011	1.030	0.681	0.926	0.671
11	1.285	1.145	1.031	1.443	1.150	1.691	1.000	1.000	1.000	1.121	1.001	0.975	1.593	1.195	1.690	1.200	0.992	0.979	1.334	1.058	1.356
12	1.085	1.044	1.011	1.118	1.045	1.146	1.000	1.000	1.000	1.041	1.000	0.991	1.142	1.057	1.146	1.064	0.997	0.992	1.096	1.019	1.094
13	0.996	0.998	0.999	0.995	0.998	0.993	1.000	1.000	1.000	0.998	1.000	1.000	0.993	0.997	0.993	0.997	1.000	1.000	0.995	0.999	0.996
14	0.773	0.872	0.968	0.694	0.867	0.614	1.000	1.000	1.000	0.885	0.999	1.028	0.637	0.836	0.614	0.826	1.008	1.023	0.746	0.943	0.741
15	1.347	1.171	1.039	1.520	1.178	1.735	1.000	1.000	1.000	1.154	1.001	0.968	1.673	1.229	1.735	1.248	0.990	0.973	1.402	1.071	1.410
16	0.988	0.994	0.998	0.984	0.994	0.982	1.000	1.000	1.000	0.994	1.000	1.001	0.982	0.992	0.982	0.991	1.000	1.001	0.987	0.997	0.988
17	0.739	0.851	0.962	0.651	0.846	0.565	1.000	1.000	1.000	0.866	0.999	1.033	0.589	0.810	0.565	0.799	1.010	1.028	0.709	0.933	0.703
18	1.169	1.088	1.019	1.255	1.091	1.379	1.000	1.000	1.000	1.074	1.000	0.984	1.333	1.117	1.379	1.120	0.995	0.987	1.196	1.036	1.208
19	0.995	0.997	0.999	0.993	0.997	0.991	1.000	1.000	1.000	0.998	1.000	1.001	0.992	0.997	0.991	0.996	1.000	1.000	0.995	0.999	0.995
20	0.957	0.977	0.994	0.939	0.976	0.919	1.000	1.000	1.000	0.979	1.000	1.005	0.925	0.970	0.919	0.968	1.001	1.004	0.951	0.990	0.950
21	0.995	0.997	0.999	0.993	0.997	0.990	1.000	1.000	1.000	0.998	1.000	1.001	0.991	0.996	0.990	0.996	1.000	1.000	0.994	0.999	0.994
22	0.975	0.986	0.997	0.963	0.986	0.949	1.000	1.000	1.000	0.988	1.000	1.003	0.954	0.982	0.949	0.981	1.001	1.002	0.971	0.994	0.970
23	0.963	0.980	0.995	0.947	0.979	0.924	1.000	1.000	1.000	0.983	1.000	1.004	0.933	0.974	0.924	0.973	1.001	1.003	0.958	0.992	0.955

**Table 7. 6. Geoaccumulation Index for sediment samples of Deepor Beel.**

Sampling Location	Geoaccumulation Index																				
	Cr			Cd			Fe			Mn			Cu			Pb			Mg		
	Pre monsoon	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon
1	-0.404	-0.445	-0.558	-1.009	-1.174	-0.710	-0.682	-0.627	-0.647	-0.483	-0.515	-0.555	-0.869	-1.125	-0.699	-0.457	-0.556	-0.586	-0.750	-0.900	-0.677
2	-0.480	-0.508	-0.584	-1.124	-1.239	-0.906	-0.688	-0.651	-0.665	-0.519	-0.540	-0.566	-1.021	-1.202	-0.896	-0.513	-0.578	-0.598	-0.838	-0.940	-0.787
3	-0.349	-0.399	-0.539	-0.929	-1.128	-0.578	-0.678	-0.608	-0.633	-0.457	-0.497	-0.546	-0.764	-1.071	-0.568	-0.417	-0.539	-0.576	-0.687	-0.871	-0.600
4	-0.165	-0.243	-0.470	-0.666	-0.968	-0.177	-0.662	-0.543	-0.586	-0.365	-0.432	-0.515	-0.436	-0.885	-0.167	-0.280	-0.479	-0.543	-0.478	-0.768	-0.347
5	-0.367	-0.414	-0.545	-0.955	-1.143	-0.621	-0.679	-0.614	-0.638	-0.466	-0.503	-0.549	-0.798	-1.089	-0.610	-0.431	-0.544	-0.579	-0.708	-0.880	-0.625
6	-0.422	-0.460	-0.564	-1.037	-1.190	-0.756	-0.683	-0.633	-0.651	-0.492	-0.522	-0.558	-0.905	-1.144	-0.746	-0.471	-0.561	-0.589	-0.771	-0.910	-0.704
7	0.019	-0.085	-0.396	-0.417	-0.807	0.174	-0.644	-0.472	-0.533	-0.267	-0.361	-0.481	-0.135	-0.700	0.184	-0.138	-0.414	-0.505	-0.272	-0.659	-0.105
8	-0.394	-0.437	-0.555	-0.995	-1.166	-0.687	-0.681	-0.623	-0.645	-0.479	-0.512	-0.554	-0.851	-1.116	-0.677	-0.451	-0.553	-0.584	-0.739	-0.895	-0.664
9	0.093	-0.020	-0.365	-0.319	-0.741	0.305	-0.636	-0.442	-0.511	-0.225	-0.330	-0.466	-0.021	-0.626	0.314	-0.079	-0.386	-0.489	-0.190	-0.613	-0.010
10	-0.441	-0.476	-0.571	-1.066	-1.206	-0.805	-0.685	-0.639	-0.656	-0.501	-0.528	-0.561	-0.943	-1.163	-0.794	-0.485	-0.567	-0.592	-0.793	-0.920	-0.731
11	-0.045	-0.140	-0.423	-0.502	-0.863	0.057	-0.650	-0.498	-0.552	-0.301	-0.386	-0.493	-0.236	-0.764	0.067	-0.187	-0.437	-0.519	-0.343	-0.697	-0.188
12	0.086	-0.026	-0.368	-0.328	-0.747	0.293	-0.636	-0.445	-0.513	-0.229	-0.333	-0.467	-0.031	-0.633	0.303	-0.085	-0.389	-0.491	-0.197	-0.617	-0.019
13	0.080	-0.031	-0.371	-0.336	-0.753	0.282	-0.637	-0.448	-0.515	-0.233	-0.336	-0.469	-0.041	-0.639	0.292	-0.090	-0.391	-0.492	-0.205	-0.621	-0.027
14	-0.331	-0.384	-0.532	-0.903	-1.112	-0.537	-0.676	-0.602	-0.629	-0.448	-0.491	-0.544	-0.731	-1.053	-0.526	-0.404	-0.533	-0.573	-0.667	-0.861	-0.575
15	0.144	0.025	-0.343	-0.252	-0.695	0.393	-0.630	-0.421	-0.495	-0.196	-0.309	-0.455	0.057	-0.574	0.403	-0.038	-0.366	-0.478	-0.133	-0.581	0.055
16	0.125	0.009	-0.351	-0.277	-0.712	0.360	-0.632	-0.429	-0.501	-0.207	-0.317	-0.459	0.029	-0.593	0.370	-0.054	-0.374	-0.482	-0.154	-0.593	0.031
17	-0.358	-0.406	-0.542	-0.942	-1.135	-0.599	-0.678	-0.611	-0.636	-0.461	-0.500	-0.548	-0.781	-1.080	-0.589	-0.424	-0.542	-0.578	-0.697	-0.876	-0.612
18	-0.111	-0.197	-0.449	-0.592	-0.921	-0.070	-0.657	-0.523	-0.571	-0.337	-0.411	-0.506	-0.345	-0.831	-0.060	-0.239	-0.461	-0.532	-0.417	-0.736	-0.275
19	-0.119	-0.204	-0.452	-0.602	-0.928	-0.085	-0.657	-0.526	-0.573	-0.341	-0.414	-0.507	-0.358	-0.839	-0.075	-0.244	-0.463	-0.534	-0.426	-0.741	-0.285
20	-0.189	-0.264	-0.479	-0.699	-0.989	-0.226	-0.664	-0.552	-0.592	-0.377	-0.440	-0.520	-0.476	-0.909	-0.216	-0.298	-0.487	-0.547	-0.505	-0.781	-0.379
21	-0.197	-0.270	-0.482	-0.711	-0.996	-0.242	-0.664	-0.555	-0.594	-0.381	-0.443	-0.521	-0.490	-0.917	-0.232	-0.304	-0.490	-0.549	-0.514	-0.786	-0.390
22	-0.238	-0.305	-0.498	-0.768	-1.031	-0.328	-0.668	-0.569	-0.605	-0.402	-0.458	-0.528	-0.561	-0.958	-0.318	-0.335	-0.503	-0.556	-0.560	-0.809	-0.445
23	-0.297	-0.355	-0.520	-0.852	-1.082	-0.457	-0.673	-0.590	-0.620	-0.431	-0.479	-0.538	-0.667	-1.018	-0.447	-0.379	-0.522	-0.567	-0.627	-0.842	-0.526

Similarly, the geo-accumulation index values show a positive trend for the points lying near the landfill site and during the post-monsoon period (except Cr) (Table 7. 6 and Fig. 7. 8). The  $I_{geo}$  values, however, were in the low to moderate pollution range, i.e., lying between 0 and 1. All the sites displaying positive  $I_{geo}$  values were closer to the landfill, thereby indicating the landfill to have a significant impact on the contamination of sediments in Deepor Beel.

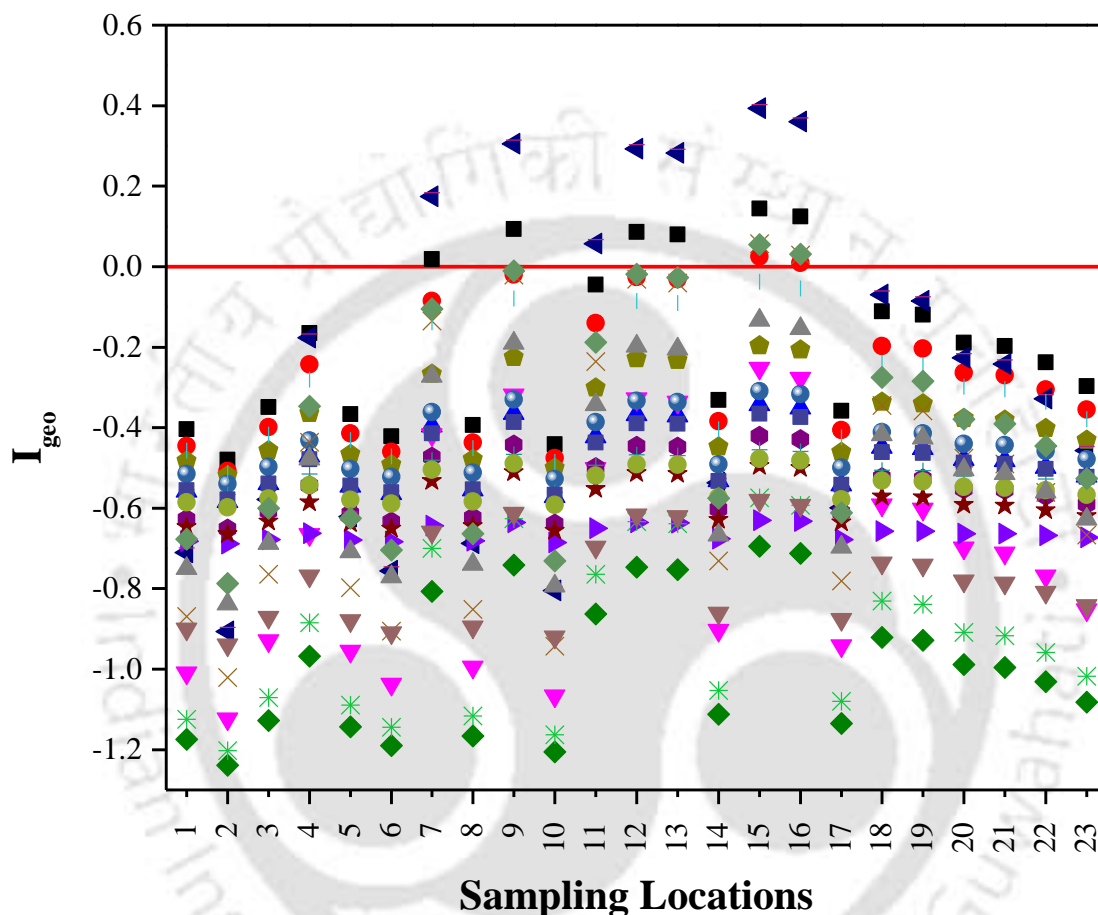
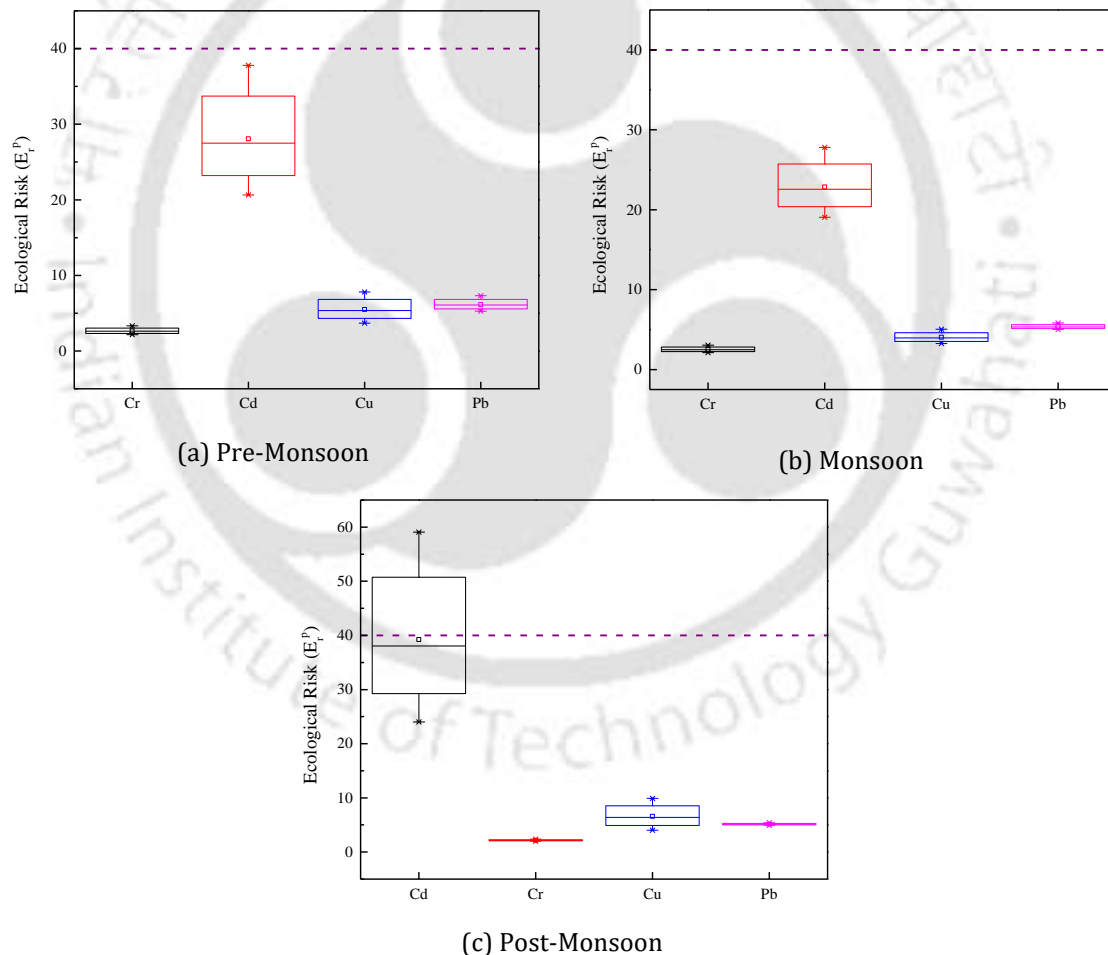


Fig. 7. 8. Geoaccumulation index values for all sampling locations across Deepor Beel.

### 7.3.3. Potential ecological risk

The potential ecological risk was evaluated by estimating the potential ecological risk index (Fig. 7. 9), overall risk index (RI) values (Fig. 7. 10), and the integrated pollution degree and its grade (Fig. 7. 11 and Table 7. 7). All the estimations were carried out across the three seasons to comprehend and understand the temporal variability of the risk involved. It was observed that Cd played a significant role in the contribution of the ecological risk of the wetland (Fig. 7. 9). The post-monsoon period shows the values go above 40, although the values almost reached almost the 40-mark in the pre-monsoon season. This makes Cd a primary contributor to the ecological risk of Deepor Beel, while the contribution of other heavy metals (Cr, Cu and Pb) remains relatively insignificant. This can be attributed to the high availability

of readily exchangeable fraction, as compared to other metals, as shown in Fig. 7. 12. Furthermore, the potential risk lies chiefly in the post-monsoon seasons compared to other seasons. It can also be observed from Fig. 7. 11 and Table 7. 7 that the integrated pollution degree of the sites was relatively higher in the post-monsoon period, with monsoon contributing the least to the ecological risk. Additionally, a higher number of sites were included in the moderate pollution category during the post-monsoon period, while the monsoon season observed all the sites falling under the low pollution category. Finally, the risk index values also depict higher risks involved in the post-monsoon period as compared to other seasons. The sites proximate to the landfill were observed to have higher values, followed by the sites in the industrial complex and the sites in the central portion of the wetland. The RI values, however, remain within the low-risk range for all the sites and seasons, with a maximum value of just above 76.



**Fig. 7. 9.** Potential Ecological Risk Index variations for the heavy metals in sediment samples.

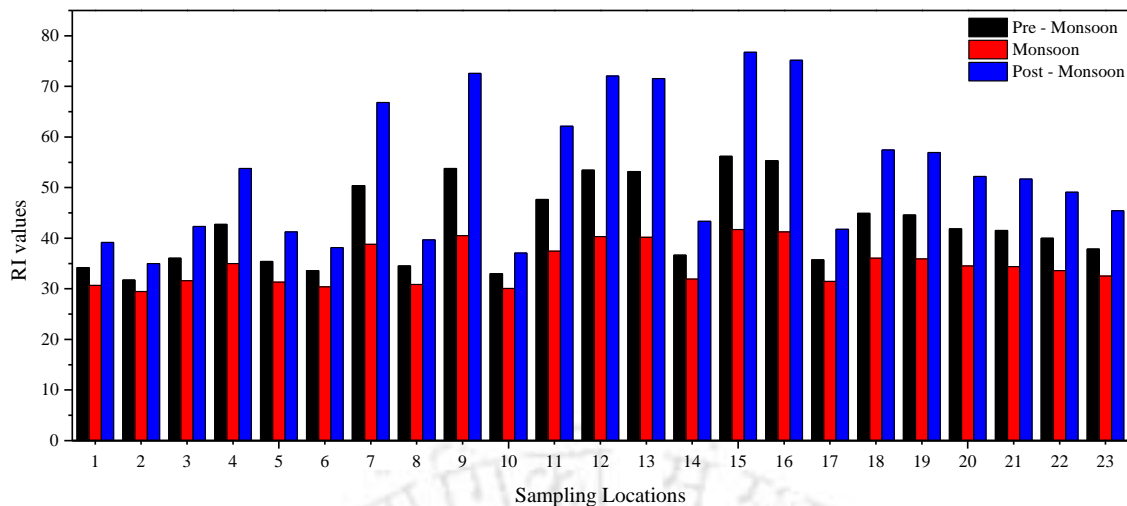


Fig. 7. 10. Seasonal variations of RI values for all the sampling locations across Deepor Beel.

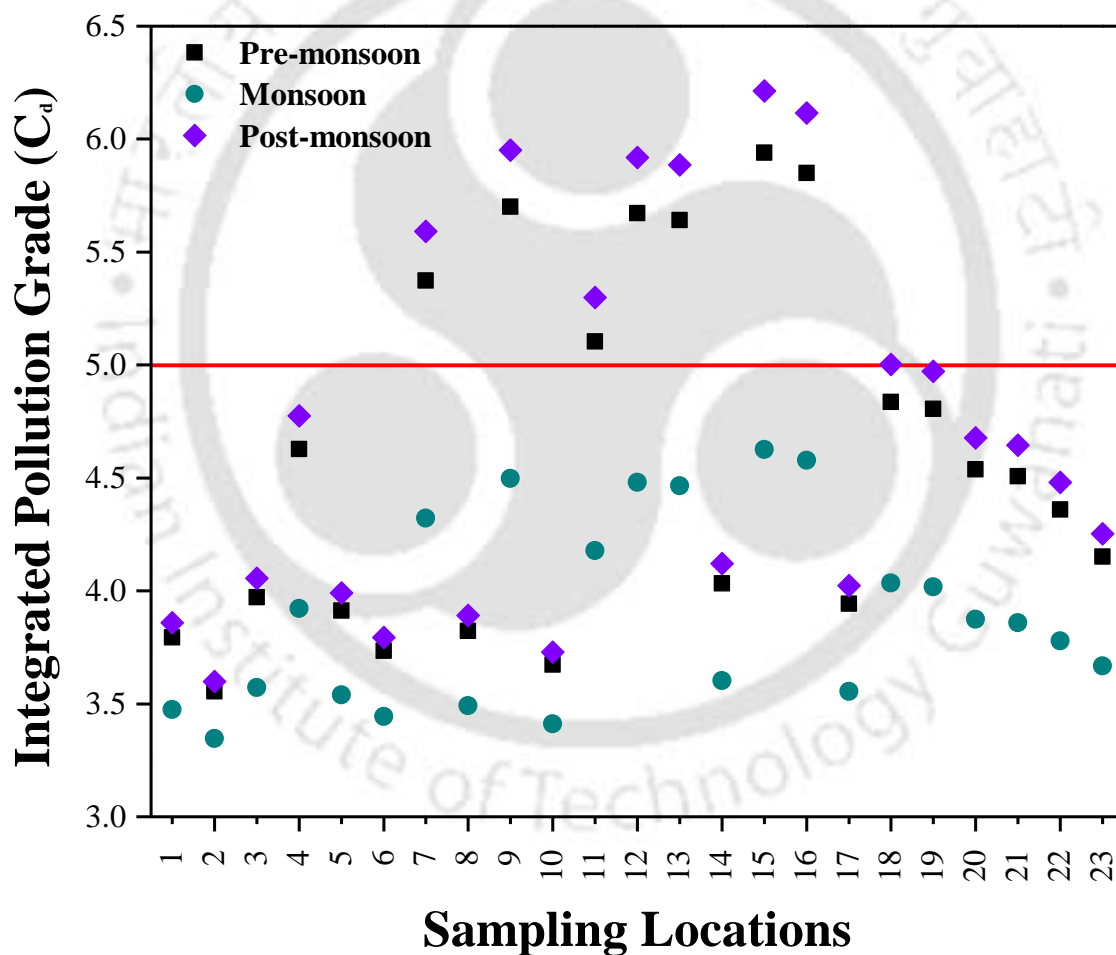


Fig. 7. 11. Spatio-temporal variations of Integrated Pollution grade values in the sediment column of Deepor Beel.

**Table 7. 7.** Results of Single Factor Evaluation on Heavy Metal Pollution in Sediments.

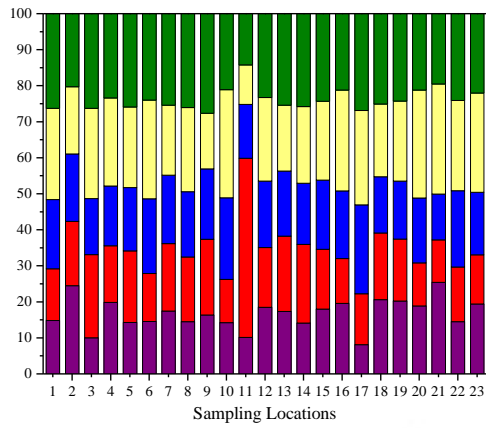
Sampling Location	CF <sup>P</sup> = C <sub>m</sub> /C <sub>b</sub>												C <sub>d</sub> (ΣCF <sup>P</sup> )			Integrated Pollution Grade		
	Cr			Cd			Cu			Pb			Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon
	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon						
1	1.134	1.102	1.019	0.745	0.665	0.917	0.821	0.688	0.924	1.092	1.021	1.000	3.793	3.475	3.859	L	L	L
2	1.076	1.055	1.001	0.688	0.636	0.800	0.739	0.652	0.806	1.051	1.005	0.991	3.555	3.347	3.598	L	L	L
3	1.178	1.138	1.033	0.788	0.687	1.005	0.883	0.714	1.012	1.123	1.032	1.006	3.972	3.571	4.056	L	L	L
4	1.338	1.267	1.083	0.945	0.767	1.326	1.109	0.812	1.336	1.236	1.076	1.030	4.628	3.922	4.775	L	L	L
5	1.163	1.126	1.028	0.774	0.679	0.976	0.863	0.705	0.983	1.113	1.028	1.004	3.912	3.539	3.990	L	L	L
6	1.119	1.090	1.014	0.731	0.657	0.888	0.801	0.679	0.894	1.082	1.017	0.997	3.734	3.443	3.794	L	L	L
7	1.520	1.415	1.140	1.124	0.858	1.692	1.366	0.923	1.704	1.363	1.126	1.057	5.373	4.321	5.592	M	L	M
8	1.141	1.108	1.021	0.752	0.668	0.932	0.832	0.692	0.938	1.098	1.022	1.001	3.823	3.491	3.892	L	L	L
9	1.600	1.480	1.165	1.202	0.898	1.853	1.479	0.972	1.865	1.420	1.148	1.069	5.701	4.497	5.951	M	L	M
10	1.105	1.079	1.010	0.717	0.650	0.859	0.780	0.670	0.865	1.072	1.013	0.995	3.674	3.411	3.729	L	L	L
11	1.454	1.362	1.119	1.059	0.825	1.560	1.273	0.883	1.571	1.317	1.108	1.047	5.104	4.178	5.298	M	L	M
12	1.592	1.474	1.162	1.195	0.894	1.838	1.468	0.968	1.851	1.415	1.146	1.067	5.671	4.481	5.919	M	L	M
13	1.585	1.468	1.160	1.188	0.890	1.823	1.458	0.963	1.836	1.409	1.144	1.066	5.641	4.465	5.886	M	L	M
14	1.192	1.149	1.037	0.802	0.694	1.034	0.904	0.723	1.041	1.133	1.036	1.008	4.032	3.603	4.121	L	L	L
15	1.658	1.527	1.183	1.259	0.927	1.970	1.561	1.008	1.983	1.461	1.164	1.077	5.939	4.625	6.213	M	L	M
16	1.636	1.509	1.176	1.238	0.916	1.926	1.530	0.994	1.939	1.445	1.158	1.074	5.849	4.577	6.115	M	L	M
17	1.170	1.132	1.030	0.781	0.683	0.990	0.873	0.710	0.997	1.118	1.030	1.005	3.942	3.555	4.023	L	L	L
18	1.389	1.309	1.099	0.995	0.792	1.429	1.181	0.843	1.439	1.271	1.090	1.037	4.836	4.034	5.003	L	L	M
19	1.381	1.303	1.096	0.988	0.788	1.414	1.171	0.839	1.424	1.266	1.088	1.036	4.806	4.018	4.971	L	L	L
20	1.316	1.250	1.076	0.924	0.756	1.283	1.078	0.799	1.292	1.220	1.070	1.027	4.538	3.874	4.677	L	L	L
21	1.309	1.244	1.074	0.917	0.752	1.268	1.068	0.794	1.277	1.215	1.068	1.025	4.508	3.858	4.644	L	L	L
22	1.272	1.214	1.062	0.881	0.734	1.195	1.017	0.772	1.203	1.190	1.058	1.020	4.359	3.778	4.480	L	L	L
23	1.221	1.173	1.046	0.831	0.708	1.093	0.945	0.741	1.100	1.154	1.044	1.012	4.151	3.667	4.252	L	L	L

\*\*L and M correspond to Low and Moderate respectively.

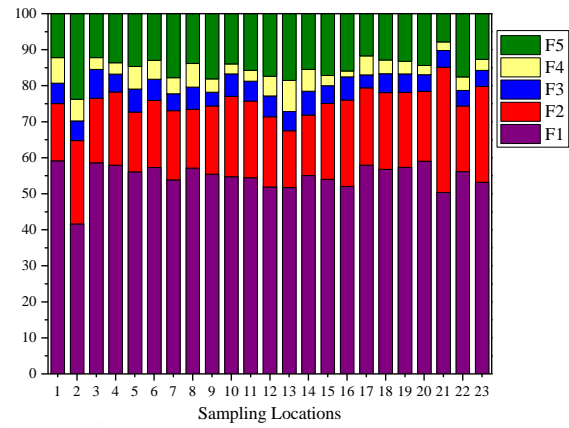
## 7.4. Speciation fraction of heavy metals in sediment samples

The metal speciation analyses carried out in the present study to assess the forms in which each of the heavy metal is present is shown in Fig. 7. 12. All heavy metals have varying behaviours under different environmental conditions. Hence, it is necessary to determine the forms in which they are present to assess their toxicity in the sediment samples (Förstner 1985). Cd, Mn and Mg were found to be primarily in the exchangeable (F1) form for all the sampling locations. This shows that they are readily available for exchange with the water column, thus having greater mobility in the aquatic ecosystem. This proves to be detrimental to various aquatic species as these heavy metals tend to bioaccumulate in their bodies (either through surface adsorption or ingestion into the body).

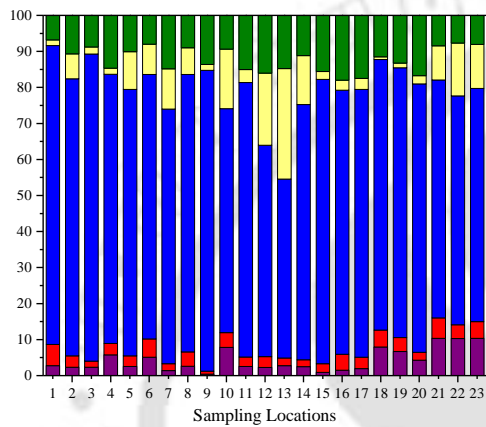
Cr displayed to be found mainly in the reducible (F3) and oxidizable (F4) forms for all the sampling locations with an exception to site 11, which is observed to be bound by carbonates (F2) fraction. This indicates that the release of metals is possible under two conditions; firstly, if the sediment column transforms to anoxic condition from the oxic state (primarily with the increase in the water depths, which will reduce the dissolved oxygen levels) under the microbial influence (F3 fraction) and secondly, under oxidizing conditions such as dredging or transport through water currents, flooding, etc. (F4 fraction). Cr also displayed to possess residual (F5) fraction, especially in the sites in the central portion of the wetland. This indicates that they possess inert characteristics to some extent and are not easily released to the water column, thus making it suitable for the aquatic ecosystem (Morillo *et al.* 2004). Fe was found to be predominantly in reducible (F3) fraction, thus indicating that it is in a highly oxidized state in the sediment samples, i.e., in the form of iron oxides. They are released under controlled conditions under the influence of microorganisms. Cu and Pb displayed typical characteristics of all the fractions in almost equal proportions, thus indicating their complexity in the form they are present in the sediment samples. Finally, Mg was found to be in the F2 fraction, along with being in the F1 fraction, indicating their presence in carbonate forms. This makes them more susceptible to getting transformed into the water column, thereby rendering them dangerous.



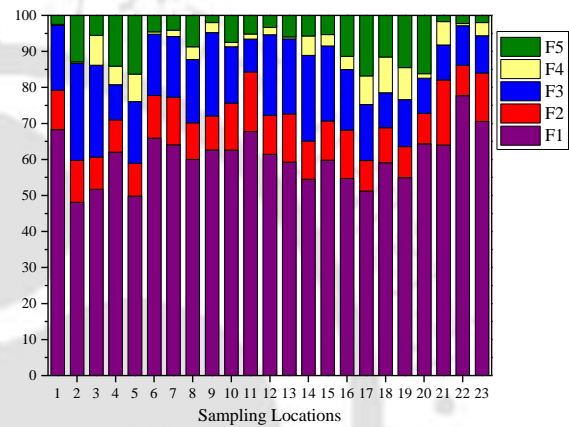
(a) Cr



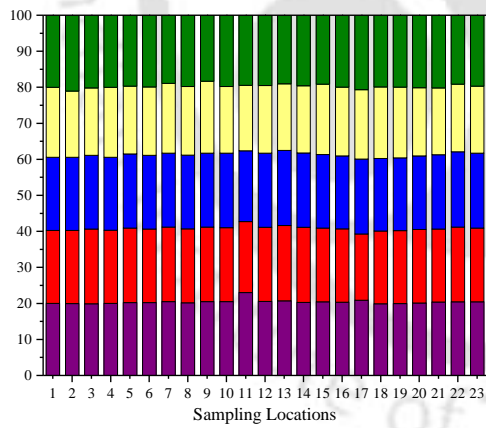
(b) Cd



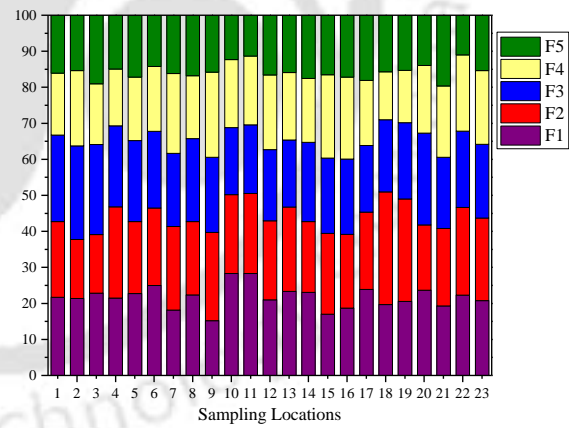
(c) Fe



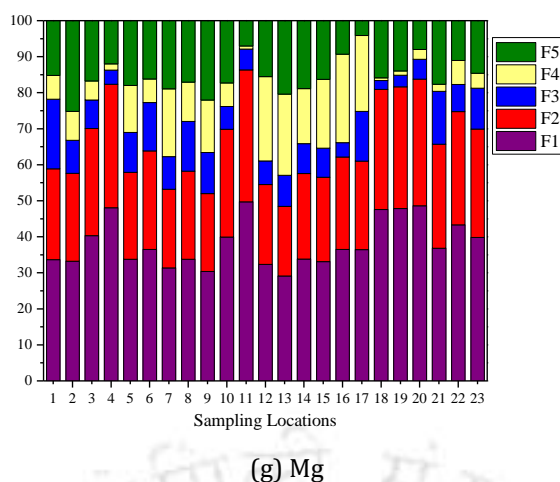
(d) Mn



(e) Cu



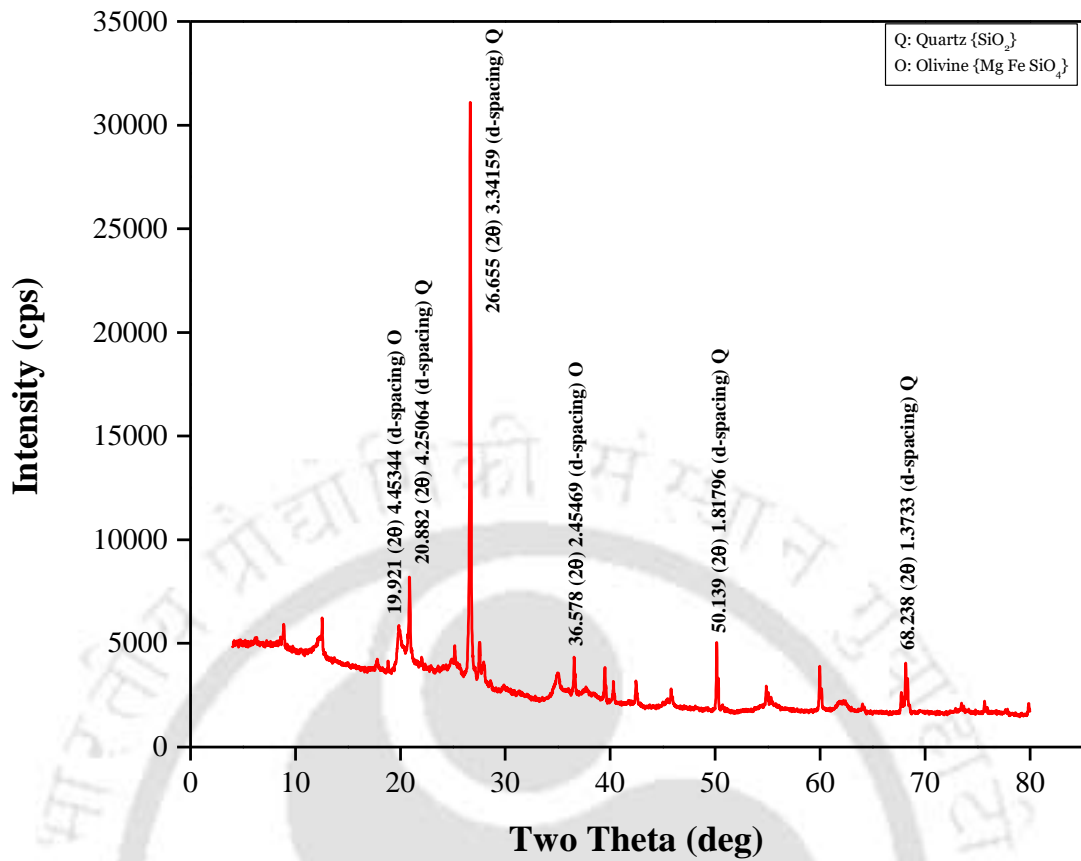
(f) Pb



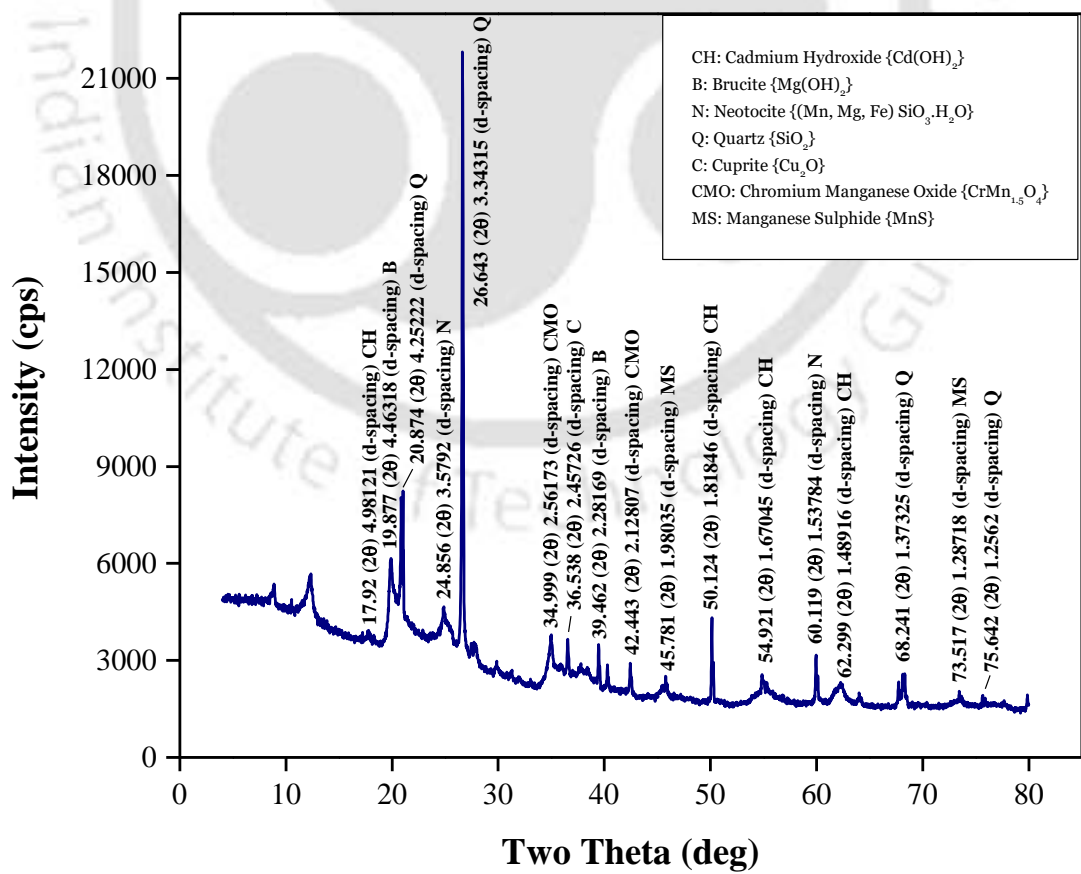
*Fig. 7. 12. Speciation fractions of various heavy metals in sediment samples of Deepor Beel.*

## 7.5. Elemental analyses

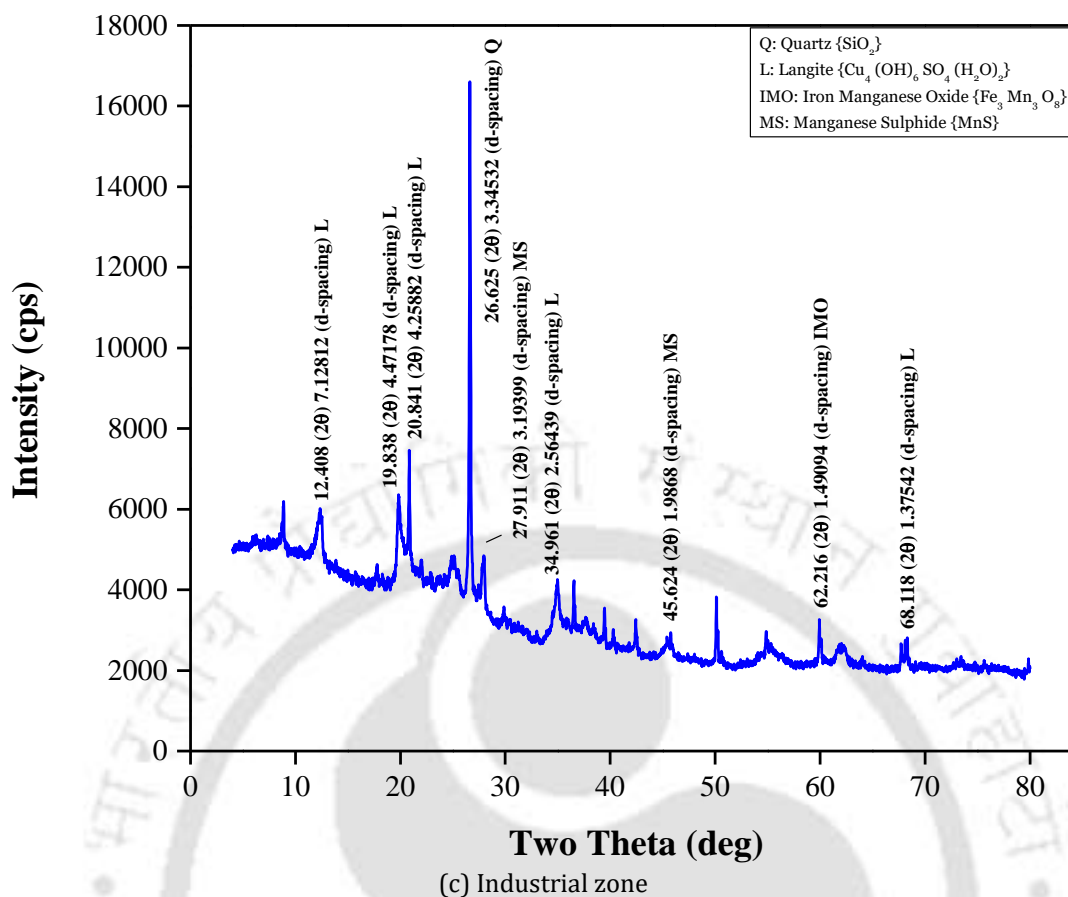
XRD analyses of the powdered sediment samples were carried out for three representative samples; one from the central zone, one from the proximity of the landfill site and one from the industrial zone. The XRD plot between two theta (degrees) and the intensity (cps) is shown in Fig. 7. 13. It can be observed that the central zone of the wetland (Fig. 7. 13a) is comprised of majorly Quartz ( $\text{SiO}_2$ ) and a small amount of Olivine ( $\text{MgFeSiO}_4$ ). These are primarily the naturally occurring elements, which signify that the central portion of the wetland is devoid of any major anthropogenic pollution. Similarly, the sediments from the neighbourhood of the landfill site (Fig. 7. 13b) was found to be heavily contaminated with all HMs such as Cd (Cadmium Hydroxide), Mg (Brucite), Mn (Manganese Sulphide), Cr (Chromium Manganese Oxide) and Cu (Cuprite). This is primarily due to the leaching effects from the landfill entering into the wetland, especially during the monsoon. The Boragaon landfill site is the only landfill site in Guwahati, wherein all the wastes from the entire city are dumped, including industrial as well as domestic wastes. During monsoon, the leachate generated thus, has a huge concentration of HMs, generated as a result of different types of wastes dumped in the landfill. These HMs then get precipitated with time and get deposited into the sediment column. Finally, the XRD analysis of the sediment from the industrial zone (Fig. 7. 13c) also revealed to have been affected by the foreign intrusion of pollution, however with lesser effects as compared to the sediments near the landfill. Cu (Langite), Fe and Mn (Iron Manganese Oxide) were found to be the major pollutants affecting the sediments in the region, which provides evidence of the discharge of HM enriched effluents from various small- and large-scale industries into the wetland. The elemental analysis thus provided significant information regarding the structure and morphology of the sediment samples together with the forms of HMs present in them.



(a) Central zone



(b) Landfill zone



**Fig. 7. 13.** XRD analysis of the sediment samples from various zones of Deepor Beel.

SEM-EDS analysis followed XRD analysis on the sediment samples collected from two points; one from the western zone proximate to the industrial complexes and the other from the eastern zone near the Boragaon landfill. This is primarily because the central portion of the wetland was found to be devoid of any anthropogenic contamination, as obtained from the XRD analysis. The distorted structures of the samples provide an indication of anthropogenic contamination to the sediment column of the wetland. Elemental mapping of both the samples (Fig. 7. 14 and Fig. 7. 15) were also carried out to determine their elemental composition. It was seen that for the sediment sample collected near the industrial zone, Mg (0.3% by weight), Mn (0.2% by weight), Ti (0.1% by weight) and Co (0.1% by weight) were the primary elements found other than Si (13.8% by weight), Al (7.4% by weight) and Fe (3% by weight). Similarly, Cu (1.6% by weight), Zn (1.1% by weight), Ti (0.4% by weight), Mg (0.3% by weight), Pb (0.2% by weight) and Cr (0.1% by weight) were found to be the major contaminants. The weight fractions of the common elements present in both the samples were found to be higher in the Boragaon landfill sample as compared to the sample from the industrial zone. The significant existence of Ti and other metals in both samples indicates high pollution levels in the sediment column of Deepor Beel, which may have occurred as a result of the anthropogenic intervention.

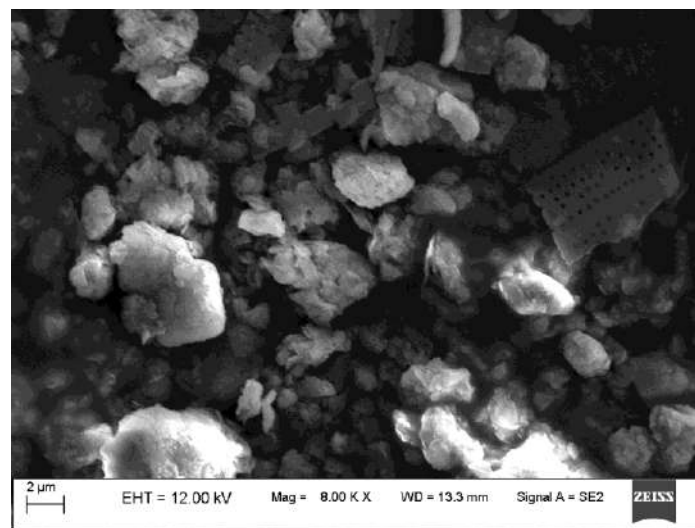
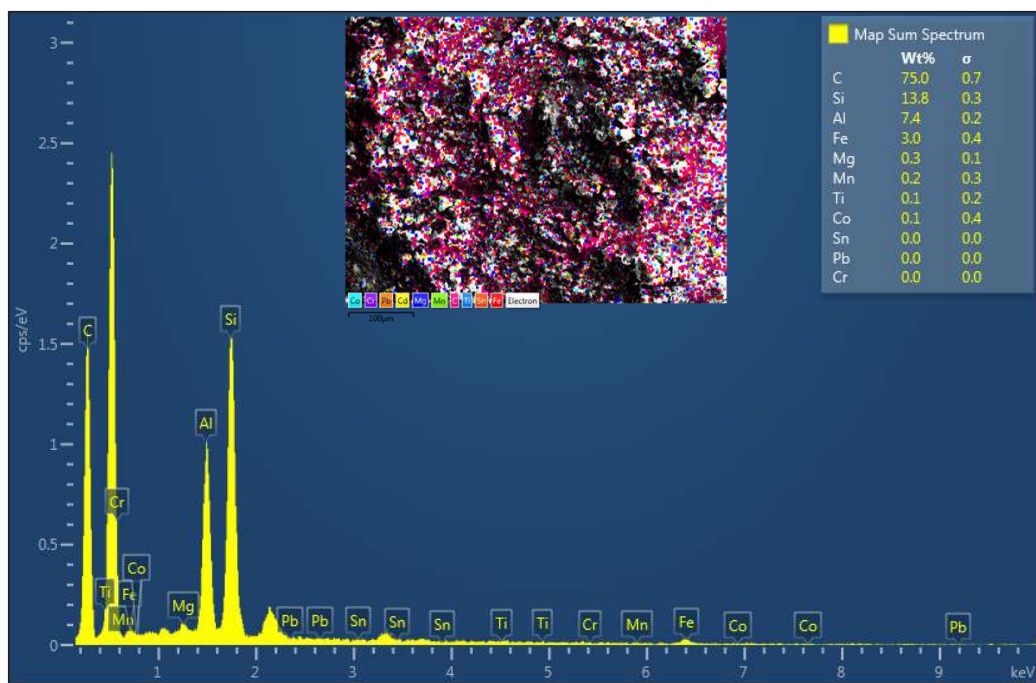
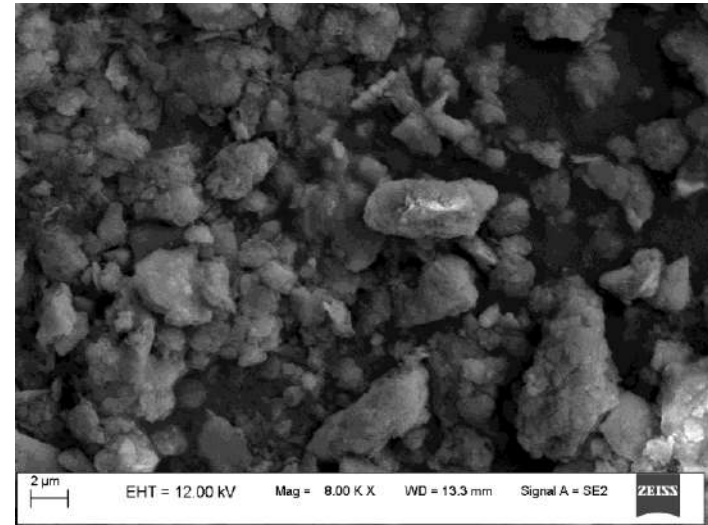
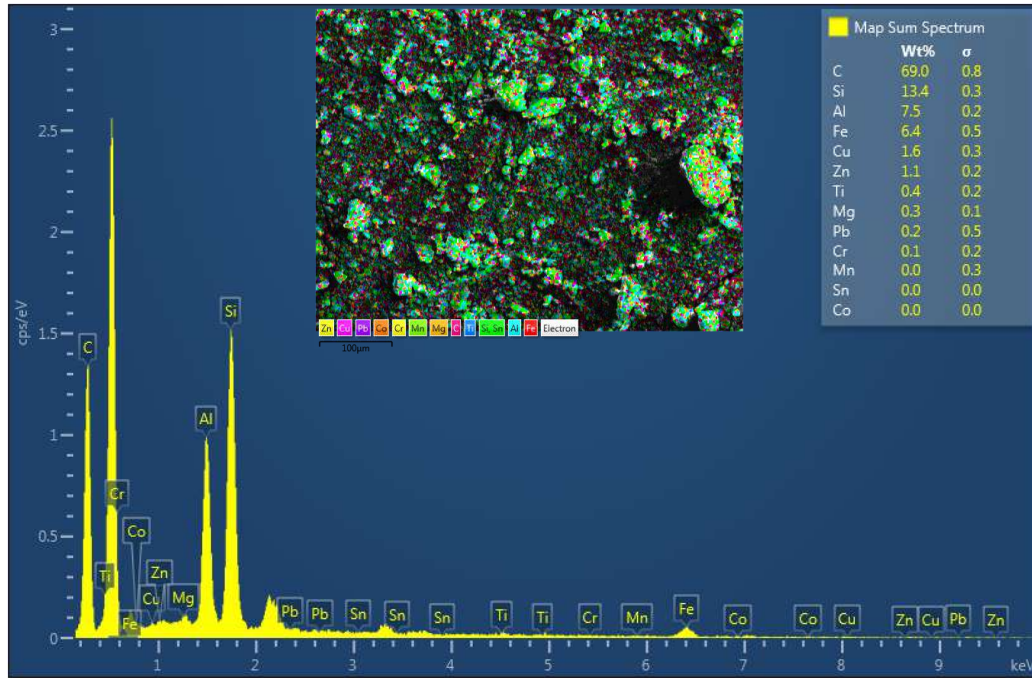


Fig. 7. 14. SEM – EDS analysis of sediment sample near industrial zone.



**Fig. 7. 15.** SEM – EDS analysis of sediment sample near Boragaon landfill.

## 7.6. Summary

The present study provides detailed evidence for the assessment of the sediment quality of a wetland. For the first time, detailed monitoring and assessment of sediment quality were presented for Deepor Beel, Assam. Critical concluding remarks derived from the present study are as follows.

- a. Hierarchical clustering of the sampling locations statistically categorized them into three distinct clusters. These corresponded to the sites of high, moderate, and low contamination, respectively. PCA was then employed on the sediment dataset, which showed a varying response to different seasons, indicating significant temporal changes in the pollution sources in Deepor Beel. PMF receptor model used in the following study for apportionment of pollution sources was simulated considering four factors. The results of the simulation provided natural geogenic parent rock materials as one of the factors (Factor 1), while the other factors being the Boragaon landfill site (Factor 2), agricultural and wastewater runoff (Factor 3) and industrial effluents discharge coupled with traffic emissions (Factor 4).
- b. Various indexing approaches were exercised to determine the level of contamination attributed to various heavy metals, both spatially and temporally. The contribution of the seven heavy metals individually across the 23 sampling locations and three seasons showed that the post-monsoon season had the most significant impact on sediment contamination. Spatial analysis of the various indices also revealed that the sites close to the landfill are most affected, followed by the sites in the industrial complex and the central portion, respectively. Furthermore, the monsoon season had the least effect on the contamination of the sediment column. The significant rise in the water depth was found to be the primary reason for the same. The potential ecological risk assessment also suggested that the post-monsoon season has a relatively higher risk than other seasons. All the sites were found to have lower risk during the monsoon, while maximum sites fell under the moderate risk category in the post-monsoon period. Furthermore, Cadmium was the major contributor to the ecological risk, with its values exceeding 40 during the post-monsoon season. Lastly, the risk index values displayed low risk for all the sites and the three seasons.
- c. The chemical speciation of the heavy metals was carried out to analyze the different forms in which these contaminants exist in the sediment column of the wetland to assess their impacts on the aquatic ecosystem. Cd, Mn and Mg were found to have a profoundly negative impact on the aquatic ecology.

- d. The distorted structures of the samples obtained from the SEM-EDS analysis provided significant evidence of anthropogenic pollution. The elemental mapping results depicted various toxic metals in both the samples, one collected from the neighbourhood of the landfill and the other from the western part, i.e., the industrial zone. XRD analysis further revealed that the central portion of the wetland is still untouched and hence devoid of any harmful and toxic metals. Sediments near the landfill site were, however, found to be affected the most due to the leaching effect.

The results of this study would prove to be of substantial help to all the government and semi-government organizations working for the development of the wetland.



Water and air, the two essential fluids on which all life depends, have become global garbage cans.

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- Jacques-Yves Cousteau

# 8

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## Understanding the dynamics of heavy metals in a freshwater ecosystem through their toxicity and bioavailability assay

The current study investigates on correlating the heavy metal contamination, its distribution, and the human health risk associated with all three components of an aquatic ecosystem. For this purpose, water, sediment, and fish samples (three species, notably *Notopterus notopterus*, *Clarias batrachus*, and *Channa striata*) from Deepor Beel were considered, and their heavy metal contamination and distribution were determined. The corresponding health risks were then evaluated for six different heavy metals; Cr, Cd, Fe, Mn, Cu, and Pb. Pb and Mn.

### 8.1. Physico-chemical characterization of water and sediment samples

The heavy metal characterizations of the water samples have been discussed in Chapter 6, while those of the surficial sediments in Chapter 7. It was observed that while the peak concentration values in the water samples were attained primarily during the monsoon season (i.e., April to September), on the other hand, the peak concentrations for sediment samples were attained majorly in the non-monsoon period (October to March). This is attributed to the heavy precipitation of heavy metals during the non-monsoon period, as the monsoon period is linked to strong turbulences due to higher stormwater runoffs, which hinders the precipitation process. Furthermore, the more considerable depth of the wetland during the monsoon (compared to the non-monsoon period) delays the precipitation process of the heavy metals from the water column. However, one common point of observation was deduced from the two plots, i.e., the higher concentrations of heavy metals were observed in the sites close

to the Boragaon landfill, which is followed by the sites proximate to the industrial zone and the least were recorded for the sites in the central portion of the wetland. This is indicative of the landfill being the primary heavy metal contributor to Deepor Beel.

As discussed in the preceding chapter, the sequential extraction procedure carried out for determining the chemical partitioning of heavy metals in the sediment column revealed different behaviours for all the heavy metals. For the risk assessment of various fractionations of heavy metals, a Risk Assessment Code (RAC) was developed by Perin *et al.* (1985) and is widely accepted. The codal provisions classify the risks associated into five different categories based on the sum of exchangeable (F1) and carbonate (F2) fractions available in the heavy metals; No risk, low risk, medium risk, high risk, and very high risk for the sum of F1 and F2 less than 1%, 1 – 10%, 11 – 30%, 31 – 50% and beyond 50%, respectively. Based on the RAC, it was observed that Cd and Mn levels for all the sites, together with Cr levels in site 11, fall under the very high-risk category. On the other hand, Cu and Pb have levels falling under the high-risk category, along with a majority of sites for Cr. Cr levels in sites 1, 6, 10, and 17 are further categorized under the medium risk category, while all the sites corresponding to concentration levels of Fe constitute in the low-risk category. Only one site falls under the no-risk category (Fe level in site 9).

## 8.2. Heavy metals in fish species

For fish samples, their health was verified by the Fulton condition factor,  $K$ , given by Eq. 8. 1 (Piah & Bucher 2014).

$$K = \left\{ \frac{W}{L^3} \right\} \times 100 \quad 8.1$$

where  $W$  and  $L$  indicate the weight (g, wet weight) and the corresponding body length (cm) of the fish specimens, respectively. The statistical values of the Fulton condition factor ( $K$ ) for all three fish species collected from three different zones and three times have been tabulated in Table 8. 1. All the  $K$  values exceeded 1, indicating the wellness in the growth of the fish samples collected each time.

The mean values of heavy metals for the three fish species collected from three different zones of Deepor Beel have been reported in Table 8. 2 (a-c). Different fish organs in the three fish species display different concentrations, primarily due to their ability to absorb and eliminate heavy metals and the variability of the trophic structure (Eneji *et al.* 2011). In the present study, Pb and Cr were found to be the dominant heavy metals in all three species, while Cd exceeding permissible limits was found primarily in the liver and skin. Thus, these fish species were found to be potential bio-accumulators for Pb and Cr pollution in the wetland.

**Table 8. 1.** Descriptive statistics of total body length (cm), wet body weight (g) and Fulton Condition Factor (K) of collected fishes.

	<i>N. notopterus</i>	<i>C. batrachus</i>	<i>C. striata</i>
<b>Body weight (g, wet weight)</b>			
Mean	771.226	921.815	815.354
Min	752.228	896.527	774.355
Max	789.917	935.511	858.971
SD	18.846	21.925	42.369
<b>Body length (cm)</b>			
Mean	39.104	34.257	31.629
Min	38.387	33.384	30.999
Max	39.954	34.941	32.759
SD	0.792	0.795	0.981
<b>Fulton Condition Factor, K</b>			
Mean	1.292	2.299	2.579
Min	1.210	2.188	2.443
Max	1.396	2.514	2.694
SD	0.095	0.187	0.127

The fish samples collected from zone I were found to have higher concentrations than the other two zones, irrespective of the heavy metal and the fish organs. Furthermore, the mean concentration levels of all the heavy metals were significantly high in the liver of all three fish species. This is attributable to the physiological differences in the role of each organ in the bioaccumulation process (Eneji *et al.* 2011). The liver was followed by skin, gill, and muscle. This indicates that the liver and skin have higher metal absorbing capacities than other fish organs, thus having a more active metabolism. This is principally associated with the detoxification process of the heavy metals for living organisms in the liver (Agusa *et al.* 2007; Tyokumbur 2016). As a result, there is a higher tendency for the liver to bioaccumulate heavy metals in them and are thus reflected in their long-term accumulations (Sobihah *et al.* 2018). On the other hand, the concentration levels in the muscle were observed to be the lowest, especially in the samples collected from zone II; the concentrations were found to be below the permissible limits when a majority of the heavy metal concentrations were above the permissible limits (FAO 1983; WHO 2012). Thus, the study reveals that the muscle part of all three fish species is relatively inactive in the bioaccumulation process. It is well-known that heavy metals like Cr and Pb possess carcinogenic characteristics (Malik *et al.* 2010). Hence, their consumption on a regular basis and at higher quantities imply that the human body is under severe risk, which is a matter of grave concern.

**Table 8. 2.** Concentrations of heavy metals (mg/kg, dry weight) in different organs of various fish specimen collected from three different zones of Deepor Beel, India (values are reported as mean; standard deviation).

(a) *Notopterus notopterus*

Heavy metals	Muscle			Liver			Gill			Skin		
	Zone I	Zone II	Zone III	Zone I	Zone II	Zone III	Zone I	Zone II	Zone III	Zone I	Zone II	Zone III
Cr	0.401; 0.033	0.331; 0.034	0.369; 0.040	2.490; 0.235	1.204; 0.194	2.209; 0.061	0.578; 0.031	0.485; 0.014	0.528; 0.011	2.736; 0.037	2.606; 0.025	2.648; 0.045
Cd	0.131; 0.011	0.018; 0.006	0.088; 0.031	1.953; 0.230	1.084; 0.114	1.482; 0.329	0.253; 0.057	0.171; 0.028	0.208; 0.029	0.567; 0.074	0.533; 0.045	0.640; 0.048
Fe	28.155; 1.563	22.822; 2.480	23.162; 1.366	77.664; 1.495	58.093; 2.732	64.917; 0.879	44.499; 3.695	40.449; 0.207	43.297; 5.779	54.589; 4.587	45.607; 2.441	46.679; 1.050
Mn	0.886; 0.0304	0.420; 0.0115	0.704; 0.0676	1.483; 0.0435	0.816; 0.0164	1.221; 0.0969	0.270; 0.0053	0.189; 0.0020	0.238; 0.0119	1.386; 0.0481	0.649; 0.0182	1.097; 0.1070
Cu	1.143; 0.015	0.910; 0.006	1.052; 0.034	4.513; 0.067	3.486; 0.025	4.110; 0.149	3.204; 0.053	2.387; 0.020	2.883; 0.119	2.655; 0.040	2.041; 0.015	2.414; 0.089
Pb	0.557; 0.011	0.383; 0.004	0.489; 0.025	1.329; 0.023	0.970; 0.009	1.188; 0.052	0.982; 0.021	0.655; 0.008	0.853; 0.047	0.645; 0.006	0.547; 0.002	0.606; 0.014

(b) *Clarias batrachus*

Heavy metals	Muscle			Liver			Gill			Skin		
	Zone I	Zone II	Zone III	Zone I	Zone II	Zone III	Zone I	Zone II	Zone III	Zone I	Zone II	Zone III
Cr	0.475; 0.029	0.379; 0.011	0.401; 0.046	3.035; 0.169	1.544; 0.119	2.315; 0.133	0.682; 0.018	0.407; 0.027	0.537; 0.076	2.851; 0.063	2.652; 0.029	2.765; 0.057
Cd	0.175; 0.006	0.097; 0.036	0.131; 0.013	2.132; 0.192	1.265; 0.217	1.611; 0.064	0.273; 0.029	0.164; 0.012	0.197; 0.043	0.583; 0.056	0.511; 0.009	0.638; 0.097
Fe	28.603; 0.869	21.622; 0.973	25.357; 1.645	77.358; 2.374	58.706; 3.522	64.037; 0.714	49.410; 2.062	39.823; 3.813	45.699; 2.251	57.718; 2.198	38.163; 2.572	50.615; 2.983
Mn	0.848; 0.029	0.408; 0.011	0.676; 0.064	1.413; 0.040	0.793; 0.015	1.170; 0.090	0.275; 0.006	0.190; 0.002	0.242; 0.012	1.434; 0.050	0.664; 0.019	1.132; 0.112
Cu	1.124; 0.014	0.904; 0.005	1.038; 0.032	4.405; 0.062	3.451; 0.023	4.030; 0.138	3.248; 0.055	2.401; 0.021	2.916; 0.123	2.695; 0.042	2.054; 0.016	2.444; 0.093
Pb	0.543; 0.011	0.378; 0.004	0.478; 0.024	1.292; 0.022	0.958; 0.008	1.161; 0.048	0.999; 0.022	0.660; 0.008	0.866; 0.049	0.651; 0.007	0.549; 0.003	0.611; 0.015

(c) *Channa striata*

Heavy metals	Muscle			Liver			Gill			Skin		
	Zone I	Zone II	Zone III	Zone I	Zone II	Zone III	Zone I	Zone II	Zone III	Zone I	Zone II	Zone III
Cr	0.369; 0.018	0.321; 0.018	0.353; 0.018	2.490; 0.235	0.666; 0.068	2.334; 0.427	0.382; 0.079	0.359; 0.066	0.360; 0.094	2.741; 0.015	2.602; 0.024	2.576; 0.069
Cd	0.117; 0.033	0.019; 0.006	0.095; 0.029	1.570; 0.479	0.334; 0.072	1.268; 0.094	0.270; 0.007	0.160; 0.006	0.190; 0.010	0.593; 0.085	0.563; 0.045	0.633; 0.044
Fe	28.779; 0.715	21.857; 1.167	25.436; 2.591	74.857; 3.342	50.811; 1.130	65.737; 6.455	45.607; 2.441	42.054; 3.297	42.139; 3.833	53.484; 1.350	44.435; 1.891	47.929; 3.256
Mn	0.842; 0.028	0.406; 0.011	0.671; 0.063	1.328; 0.013	0.766; 0.014	1.107; 0.082	0.279; 0.006	0.192; 0.002	0.245; 0.037	1.354; 0.047	0.638; 0.018	1.073; 0.104
Cu	1.121; 0.014	0.903; 0.005	1.036; 0.032	4.273; 0.056	3.409; 0.021	3.934; 0.125	3.294; 0.057	2.416; 0.022	2.949; 0.128	2.628; 0.039	2.032; 0.015	2.394; 0.087
Pb	0.541; 0.011	0.377; 0.004	0.477; 0.024	1.246; 0.020	0.943; 0.007	1.127; 0.044	1.018; 0.023	0.666; 0.009	0.880; 0.051	0.640; 0.006	0.545; 0.002	0.603; 0.014

Orange highlights represent the samples exceeding the permissible limits.

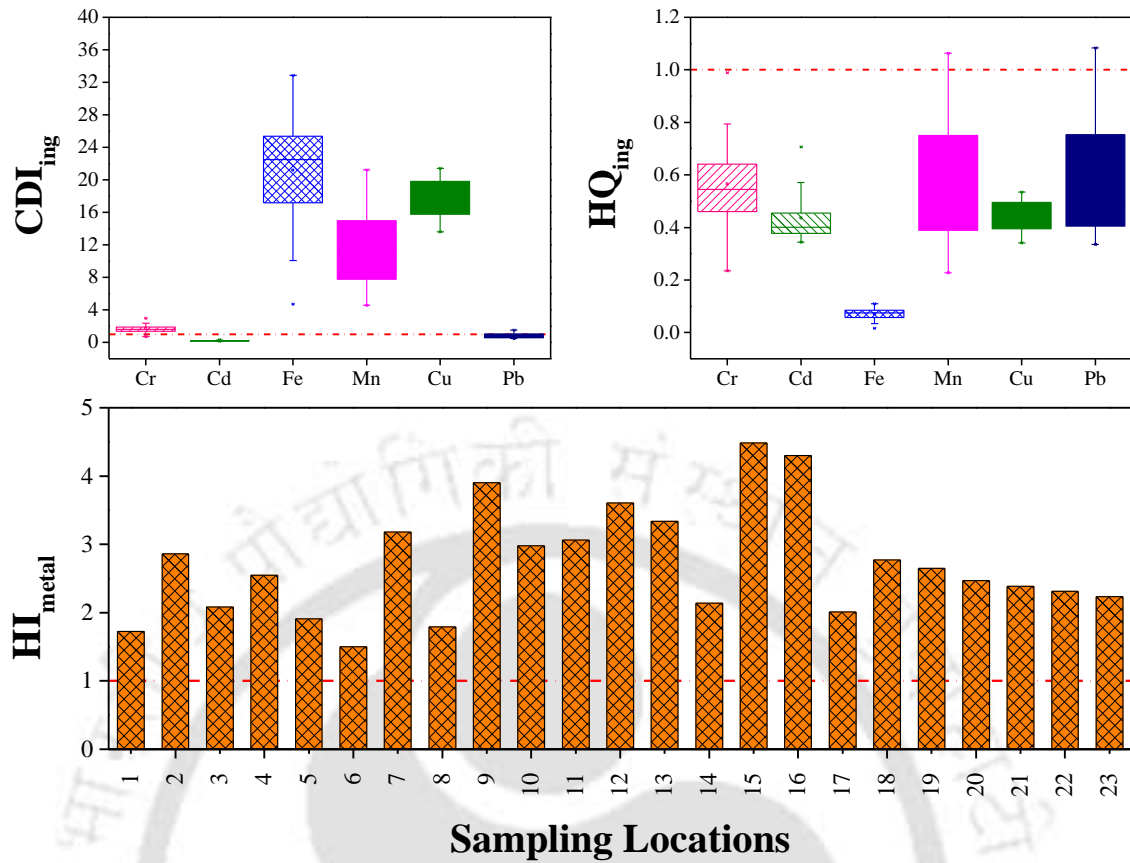
Green highlights represent the samples adhering to the permissible limits.

Furthermore, these fish species also expand their territory to the Brahmaputra River, where significant fishing activities take place. The results obtained from the study were compared with the findings by Gohain & Bordoloi (2017), who carried out a similar study with *Anabas testudineus* from Deepor Beel. Both the findings complemented each other, thereby providing substantial evidence of heavy metal contamination in the fishes of Deepor Beel.

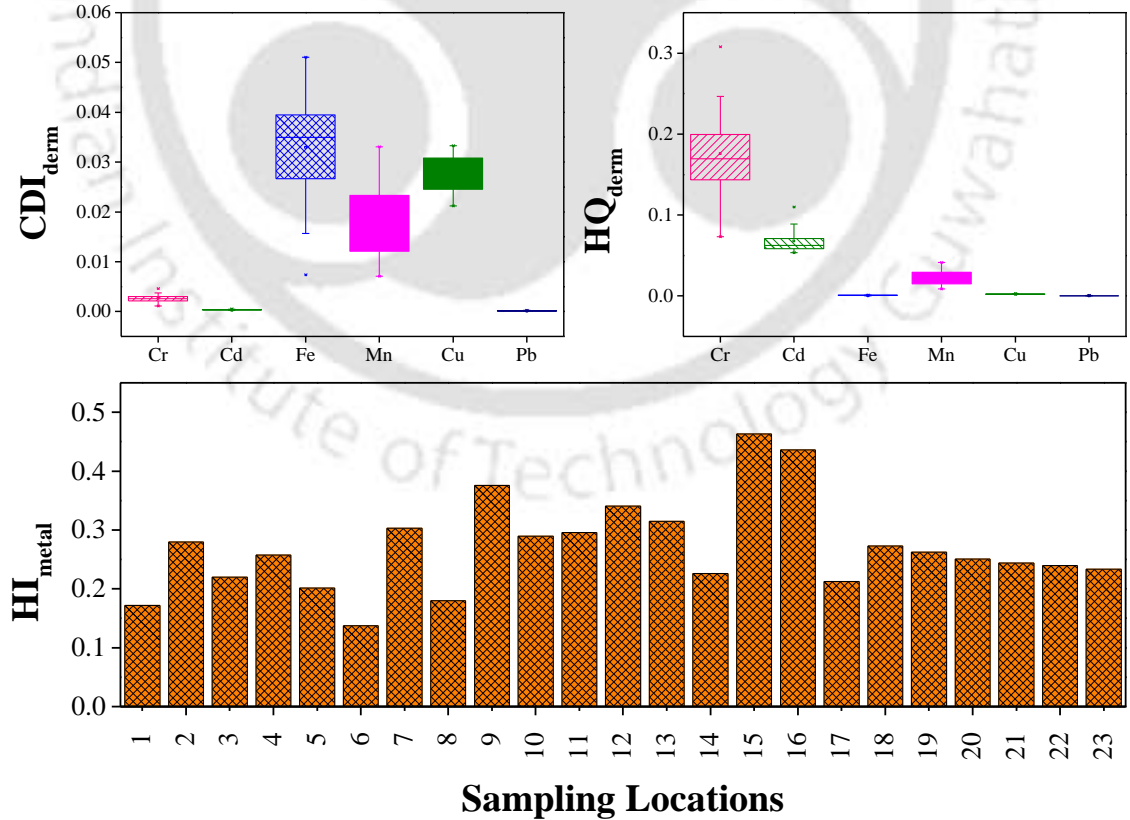
### 8.3. Human health risk assessment

#### 8.3.1. Water environment

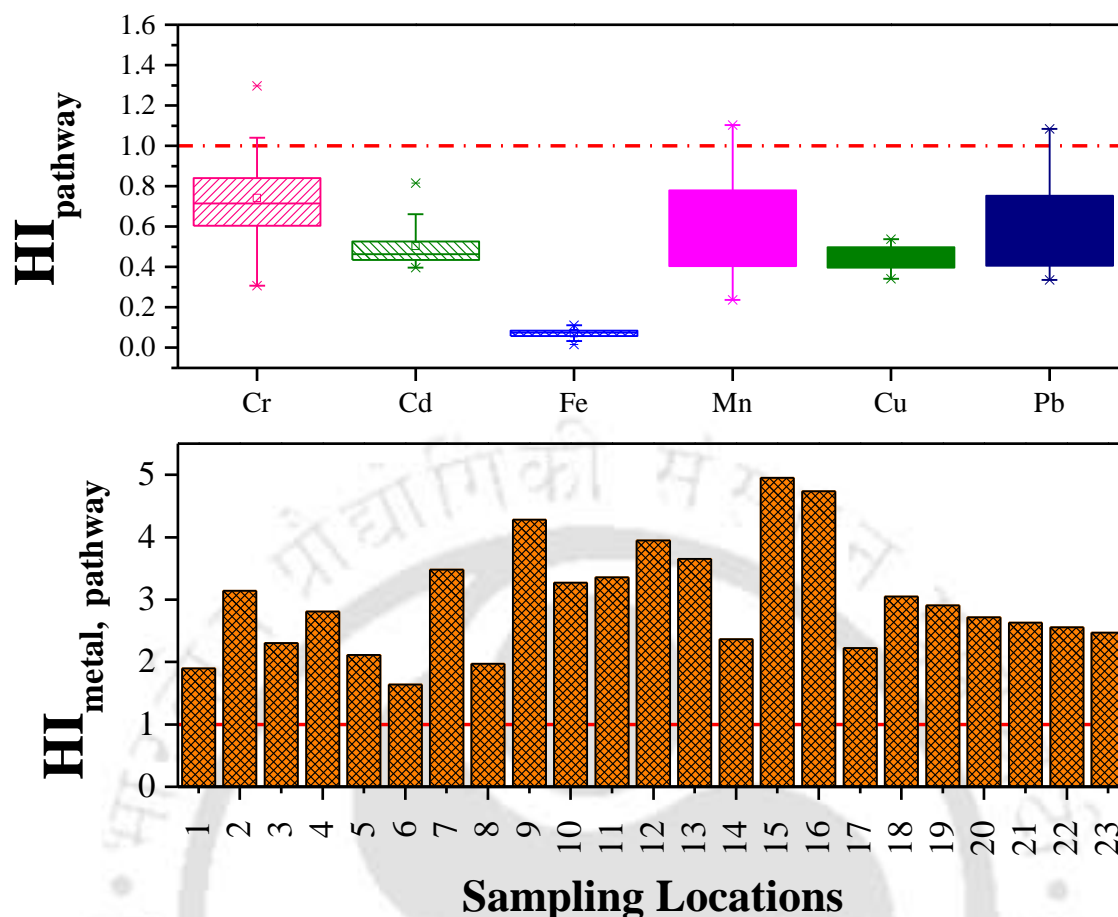
The health risk assessment associated with the water column of Deepor Beel was carried out by estimating the chronic daily intake (CDI) and their corresponding hazard quotient (HQ) values concerning ingestion and dermal adsorption (Fig. 8. 1). It was observed that the  $HQ_{ing}$  values remained mostly below unity for all sites and all heavy metals concerned. Only a few values exceeded one (sites 15 and 16 for Mn and 9, 15, and 16 for Pb). Thus, Pb and Mn are found to be the primary concerning heavy metals in the locations proximate to the Boragaon landfill when it comes to health risks. However, some  $HQ_{ing}$  values, such as those for Cr and Cd near the landfill locations, were approaching unity. This can be attributed to the rising heavy metal pollution levels in the water column of Deepor Beel. Thus, it can be stated that these values may exceed unity in the future, provided, no plausible preventive approaches are undertaken to limit the heavy metal pollution in the wetland. The  $HQ_{derm}$  values for all sites and heavy metals were found to be well below one, indicating that there is no potential threat to the risk of human health due to dermal adsorption. However, when it comes to the cumulative assessment (both pathways combined) of the effects of heavy metals on human health risk, it was observed that the  $HI_{metal}$  values for ingestion exceeded 1 for all the sampling locations, thus indicating that all sites have a potential impact on human health due to cumulative effects on the exposure to all heavy metals combined. Special attention, however, needs to be provided to sites 15 and 16, whose  $HI_{metal}$  values are significantly high (more than four times the critical limit). This may lead to extreme health risks among humans upon exposure to water from these sites. On the contrary, the  $HI_{metal}$  values due to dermal adsorption were still below the critical limit of 1 (Fig. 8. 1c).



(a) Ingestion pathway



(b) Dermal adsorption pathway

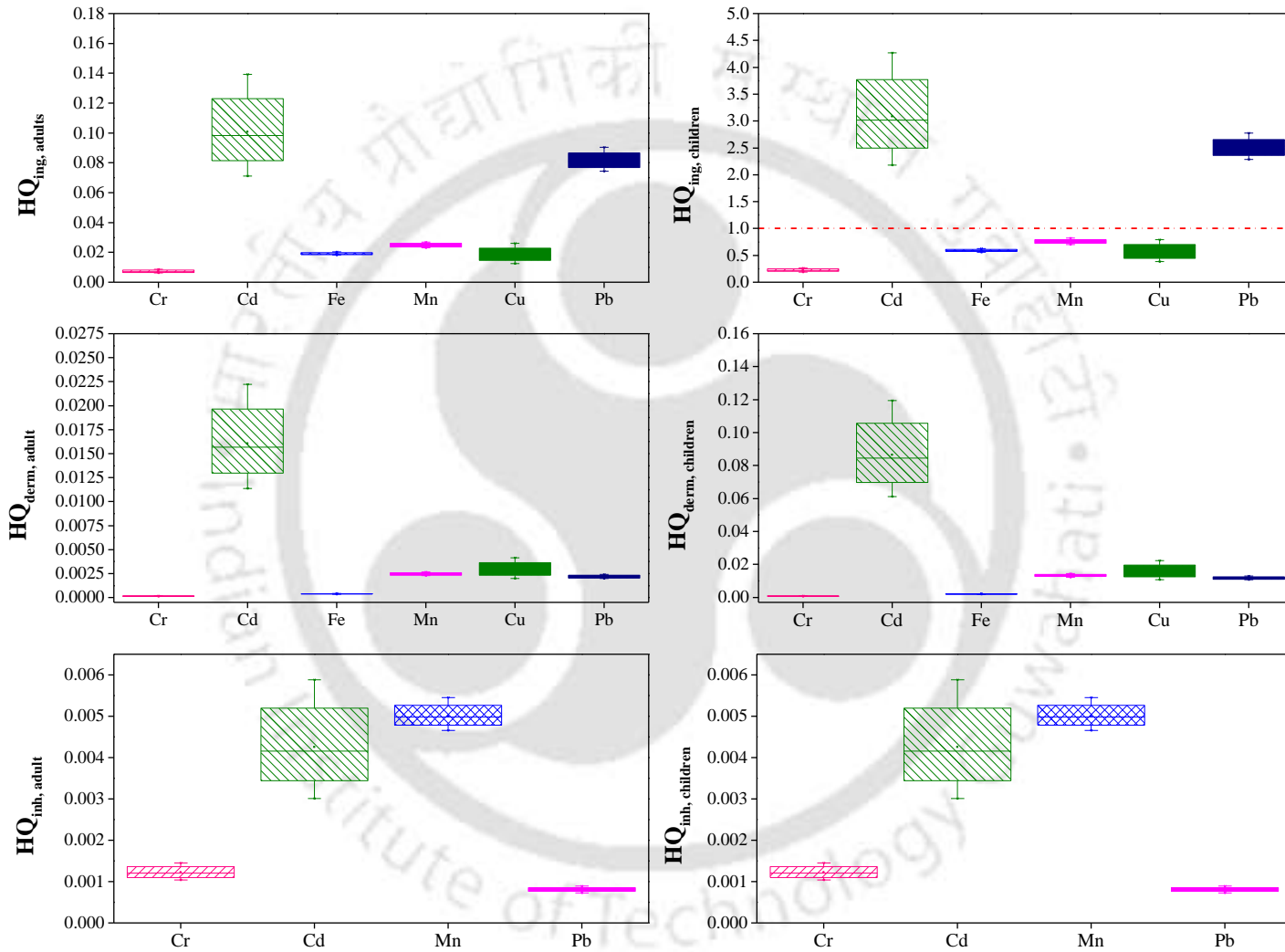


(c) Pathway

*Fig. 8. 1. HRA of water column of Deepor Beel.*

### 8.3.2. Surficial sediments

Heavy metal contamination poses significant threats to human health and the environment as a whole. Elements such as Cr, Cd, and Pb have high toxicity values, even at trace amounts, accounting for multiple organ failures, and therefore, they have been rendered as carcinogens. Hence, the human health risk assessment concerning heavy metals found in the surficial sediments have been presented in the study for both non-carcinogenic and carcinogenic health risks. The non-carcinogenic health risk was assessed by estimating the HQ values. HQ values less than 1 indicate no potential threat to human health, whereas values greater than 1 signify that some degree of non-carcinogenic risk associated with human health can be anticipated. Fig. 8. 2 provides a detailed assessment of the non-carcinogenic risk involved due to the heavy metal contamination of surficial sediments of Deepor Beel. It can be observed that the HQ values for all three pathways and six heavy metals are less than 1 for adults, thus signifying that there is no potential risk to the health of adults as a result of these heavy metals.



**Fig. 8. 2.** Hazard Quotient values for different heavy metals concerning the sediment column of Deepor Beel.

For the health risk of children, it was observed that the HQ values for the ingestion pathway exceeded 1 for Cd and Pb for all the sampling locations. Furthermore, all other metals for all sampling locations and pathways indicated values less than 1. Hence, it can be stated that Cd and Pb displayed significant non-carcinogenic risk resulting in adverse health effects, especially among children. Also, the values of  $HQ_{ing}$  for Cd can be observed to be as high as 4.27, more than four times the desired limits for sites near the landfill, thus suggesting the landfill to be a significant contributor to the health risk.

The HQ values for all heavy metals and, subsequently, the HI values due to dermal adsorption and inhalation were found to be below 1 for both adults and children. The  $HQ_{pathway}$  values, which consider all three pathways and their subsequent HI values, also suggested that children are more significantly affected as compared to the adults (highest HI values for children and adults are 0.36 and 9.73, respectively), with primary contribution from ingestion (Fig. 8. 3). Thus, it can be concluded that Cd and Pb were the primary reason for non-carcinogenic health concerns among the children through the oral intake (ingestion).

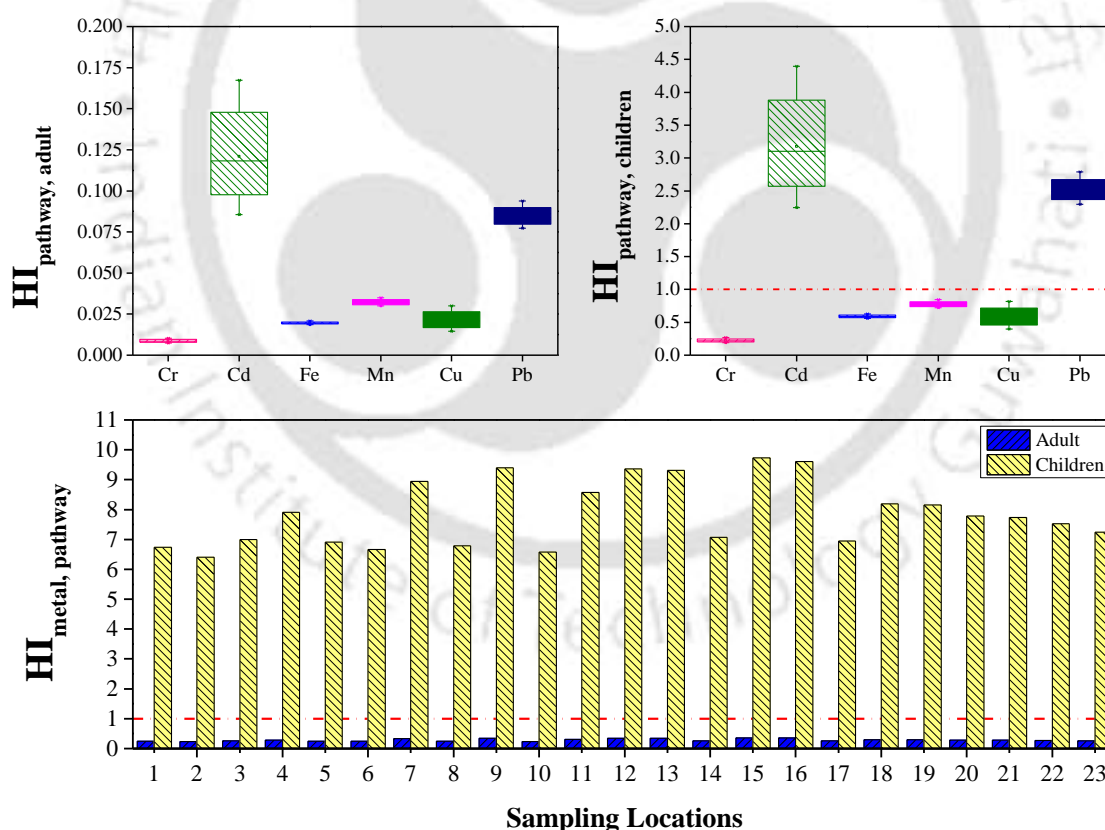
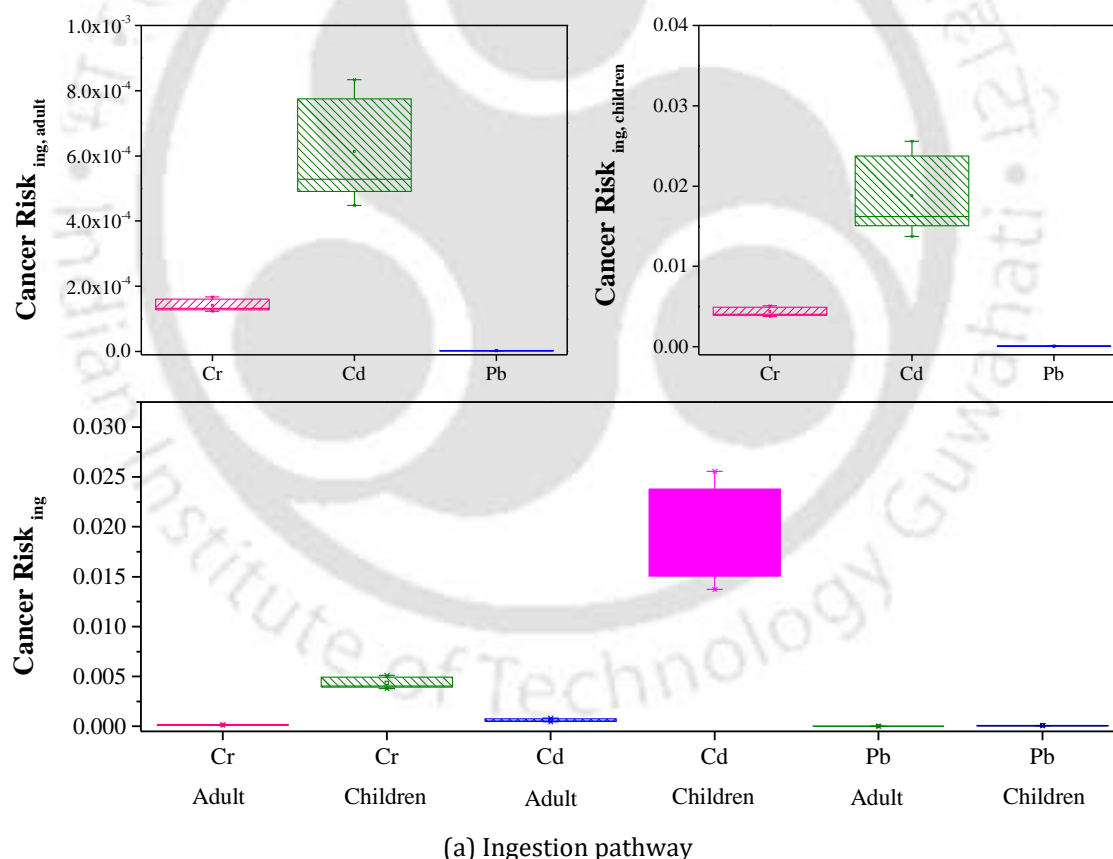


Fig. 8. 3. Hazard Index for all three pathways concerning the sediment column of Deepor Beel.

On the other hand, the carcinogenic health risk assessment carried out for three heavy metals (Cr, Cd, and Pb) and three pathways displayed a much higher potential risk among children compared to that in adults [Fig. 8. 4 and Fig. 8. 5]. The LCR values ranged from  $2.22 \times 10^{-6}$  to  $8.00 \times 10^{-4}$  and  $6.80 \times 10^{-5}$  to  $2.69 \times 10^{-2}$  in adults and children, respectively. Furthermore, it is noticeable that among the metals, the LCR values followed the order;  $Pb < Cr < Cd$ , thereby indicating that Cd has a higher potential for causing a carcinogenic health risk. With the acceptable range lying between  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-4}$ , it was observed that all the sites were rendered to have carcinogenic potential among both adults and children for Cr and Cd. On the other hand, LCR values for Pb fell under the tolerable range; however, it is on the verge of exceeding the acceptable value soon in the absence of any precautionary measures. Regardless of the non-carcinogenic or carcinogenic impact of heavy metals for surficial sediments, the children were more susceptible to health risks as they have more chances for hand-to-mouth or oral ingestion (Luo *et al.* 2012).



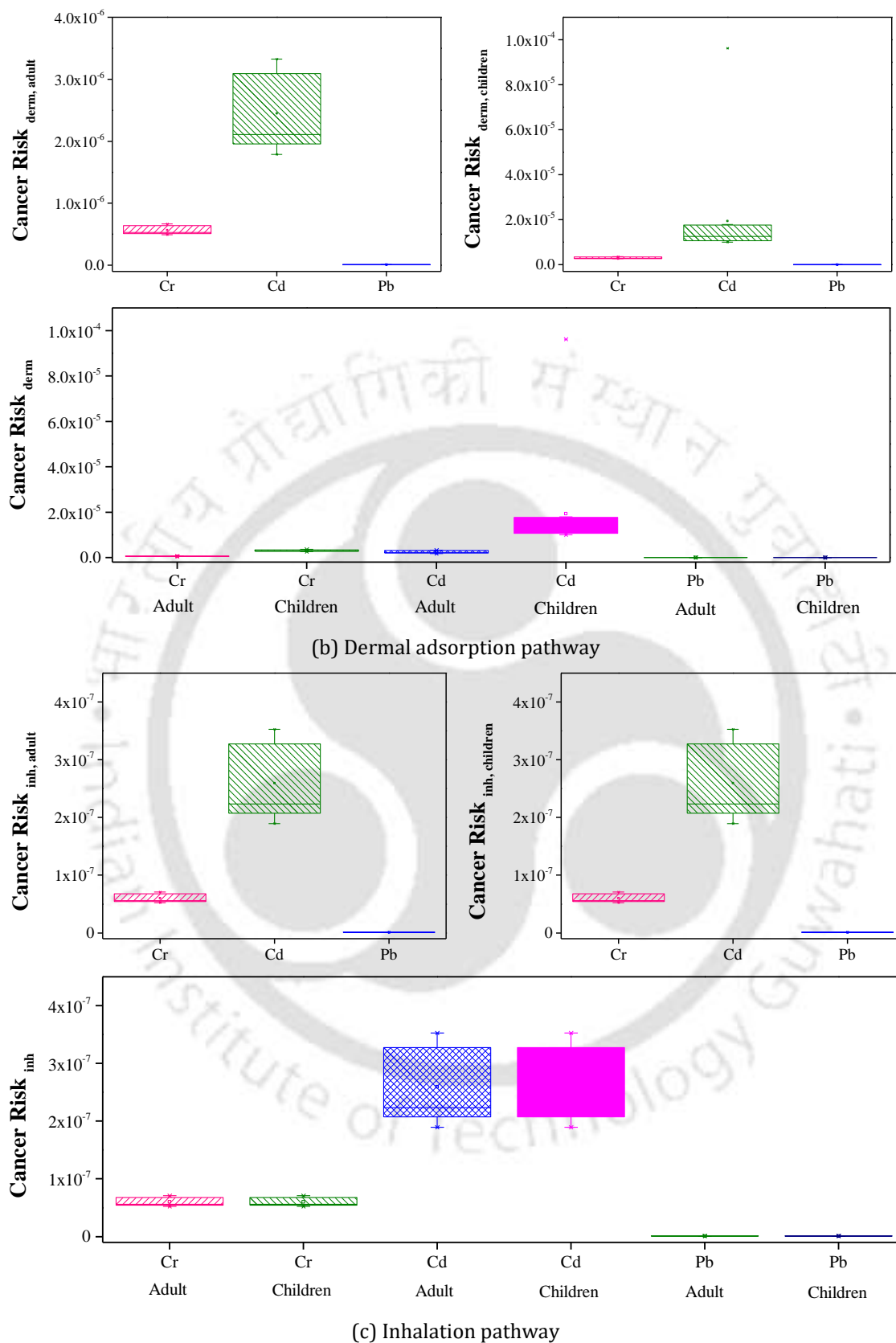


Fig. 8. 4. Cancer risks associated with the sediment column for different heavy metals and pathways.

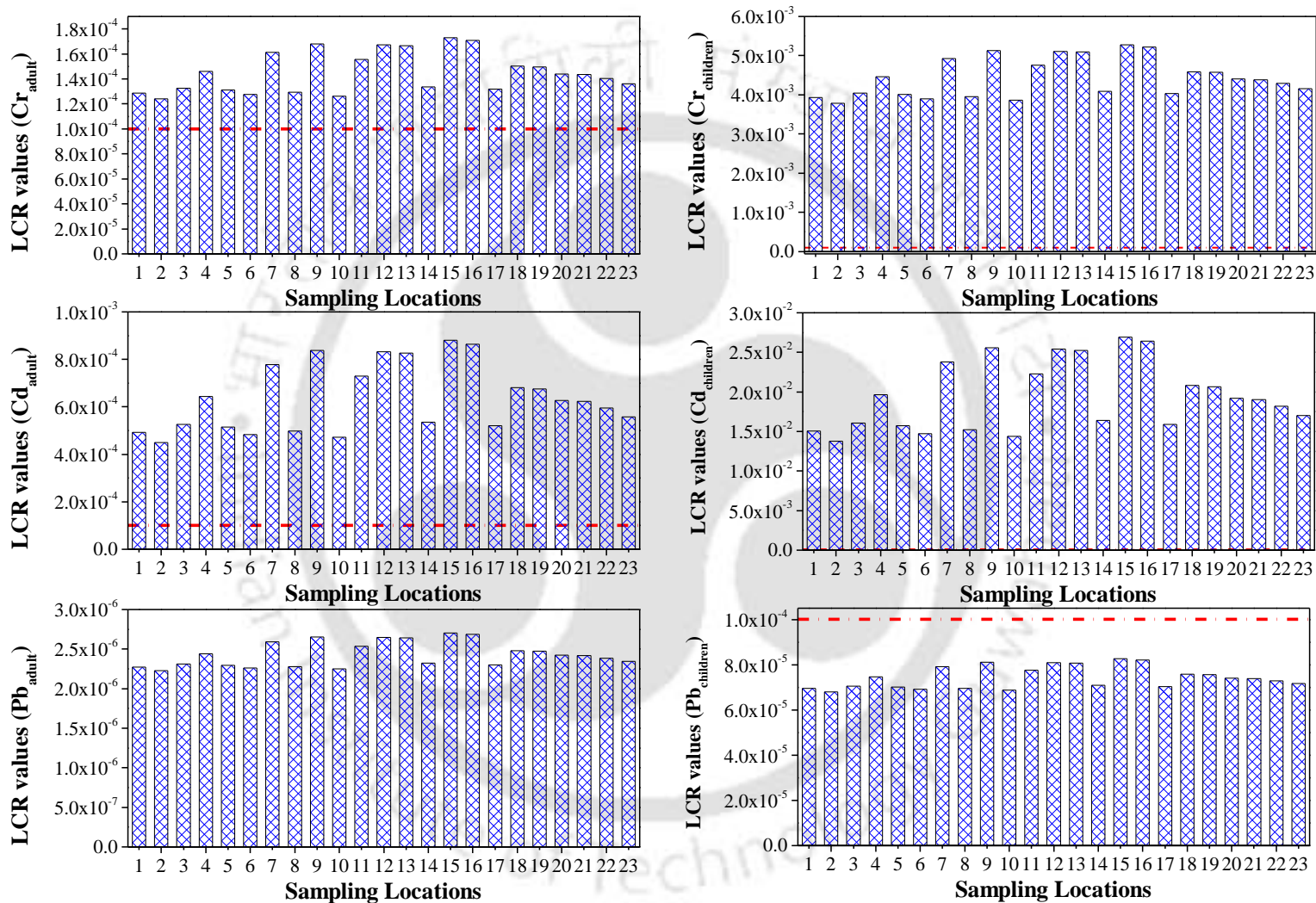


Fig. 8. 5. Lifetime Cancer Risk (LCR) values for different heavy metals associated with the sediment column of Deepor Beel.

### 8.3.3. Fish

The investigation for the assessment of human health risk (non-carcinogenic) as a result of the consumption of three local fish species of Deepor Beel required the estimation of the estimated daily intake (EDI) values, followed by the target hazard quotient (THQ) and the total target hazard quotient (TTHQ). For carcinogenic risks involved, two heavy metals were considered for the analysis, i.e., Cd and Pb, to estimate lifetime cancer risk (TR) values. All calculations were done considering the risk involved in both adults and children for all four organs of the three fish species collected from three different zones of the wetland. Table 8.3 (a-c) provides a detailed estimate of the EDI values for muscle, liver, gill, and skin for *Notopterus notopterus*, *Clarias batrachus*, and *Channa striata*, respectively. All EDI values for Fe, Mn, Cu, and Pb for all organs and three species were found to be within prescribed limits laid down by (FAO 2009); i.e., 2.85 for Cr, 1 for Cd, 800 for Fe, 140 for Mn, 500 for Cu, and 3.57 for Pb. For Cr and Cd, muscle and gills of all three species have values less than the limits, whereas the liver and skin exceeded the limits. Hence, it can be stated that the intake of liver and gill will have adverse implications on human health. Furthermore, the children were found to be affected more than the adults, and fish samples collected from zone II had significantly higher EDI values as compared to the samples collected from the other two zones. To address the non-carcinogenic and carcinogenic health effects upon the consumption of fish species, the target hazard quotient and the lifetime cancer risk values were evaluated, respectively (Fig. 8.6 - Fig. 8.8).

All three fish species displayed similar characteristics and variations of heavy metals in their organs. The THQ values were found to be greater than unity for Cr and Cd in the liver and gill. Also, the THQ values were found to be higher in the samples collected from zone I, as compared to other zones, thus indicating the role of landfill in the bioaccumulation of heavy metals in various fish organs. All other values were observed to be less than one, thus indicating that the resident human settlement near the landfill, consuming these fish species, will face adverse health risks, especially on the consumption of liver and gills. The health risks for Fe, Mn, and Cu were found to be very low, probably owing to their high reference dose values.

The estimation of health risk due to single metal was not sufficient. Therefore, there was a need to determine the cumulative impact of all heavy metals combined on human health, and hence, TTHQ values were obtained for all heavy metals and four organs of the three fish species. TTHQ values greater than unity renders an alarm to public health (Javed & Usmani 2016). The liver was the most affected organ among all, followed by skin, gill, and muscle. Also, *Clarias batrachus* displayed higher values (THQ and TTHQ), with the least being *Channa striata*.

**Table 8. 3.** Estimated daily in-take, EDI ( $\mu\text{g}/\text{kg}$  body weight/day) of the metals from the consumption of various organs of different fish species from the three zones of Deepor Beel in adult people and in children.

(a) *Notopterus notopterus*

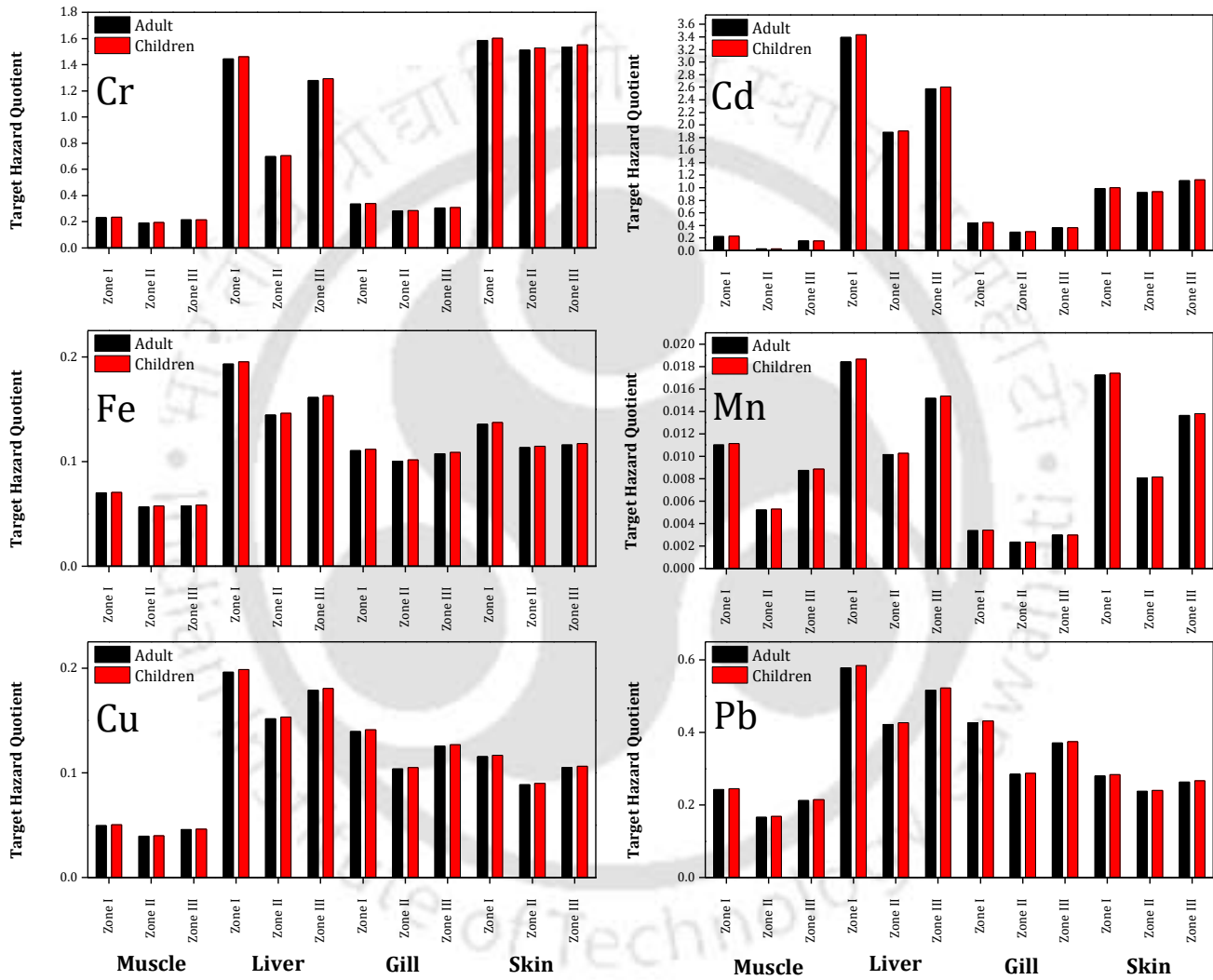
Heavy metals	EDI	Muscle			Liver			Gill			Skin		
		Zone I	Zone II	Zone III	Zone I	Zone II	Zone III	Zone I	Zone II	Zone III	Zone I	Zone II	Zone III
Cr	Adult	0.698	0.575	0.642	4.330	2.093	3.840	1.006	0.843	0.918	4.757	4.531	4.604
	Child	0.706	0.582	0.650	4.379	2.117	3.884	1.017	0.853	0.928	4.810	4.582	4.656
Cd	Adult	0.227	0.031	0.152	3.396	1.884	2.577	0.441	0.297	0.361	0.986	0.927	1.113
	Child	0.230	0.031	0.154	3.434	1.905	2.606	0.445	0.300	0.365	0.997	0.937	1.125
Fe	Adult	48.956	39.683	40.274	135.043	101.013	112.880	77.375	70.333	75.286	94.921	79.302	81.167
	Child	49.508	40.131	40.728	136.565	102.151	114.151	78.247	71.126	76.134	95.990	80.196	82.082
Mn	Adult	1.541	0.731	1.223	2.579	1.418	2.124	0.470	0.328	0.414	2.410	1.128	1.907
	Child	1.559	0.739	1.237	2.608	1.434	2.147	0.476	0.332	0.419	2.438	1.141	1.929
Cu	Adult	1.988	1.583	1.829	7.847	6.061	7.146	5.572	4.150	5.014	4.617	3.548	4.198
	Child	2.010	1.601	1.849	7.935	6.129	7.226	5.635	4.197	5.070	4.669	3.588	4.245
Pb	Adult	0.969	0.665	0.850	2.312	1.687	2.066	1.707	1.138	1.484	1.121	0.950	1.054
	Child	0.980	0.673	0.860	2.338	1.706	2.090	1.726	1.151	1.501	1.134	0.961	1.066

(b) *Clarias batrachus*

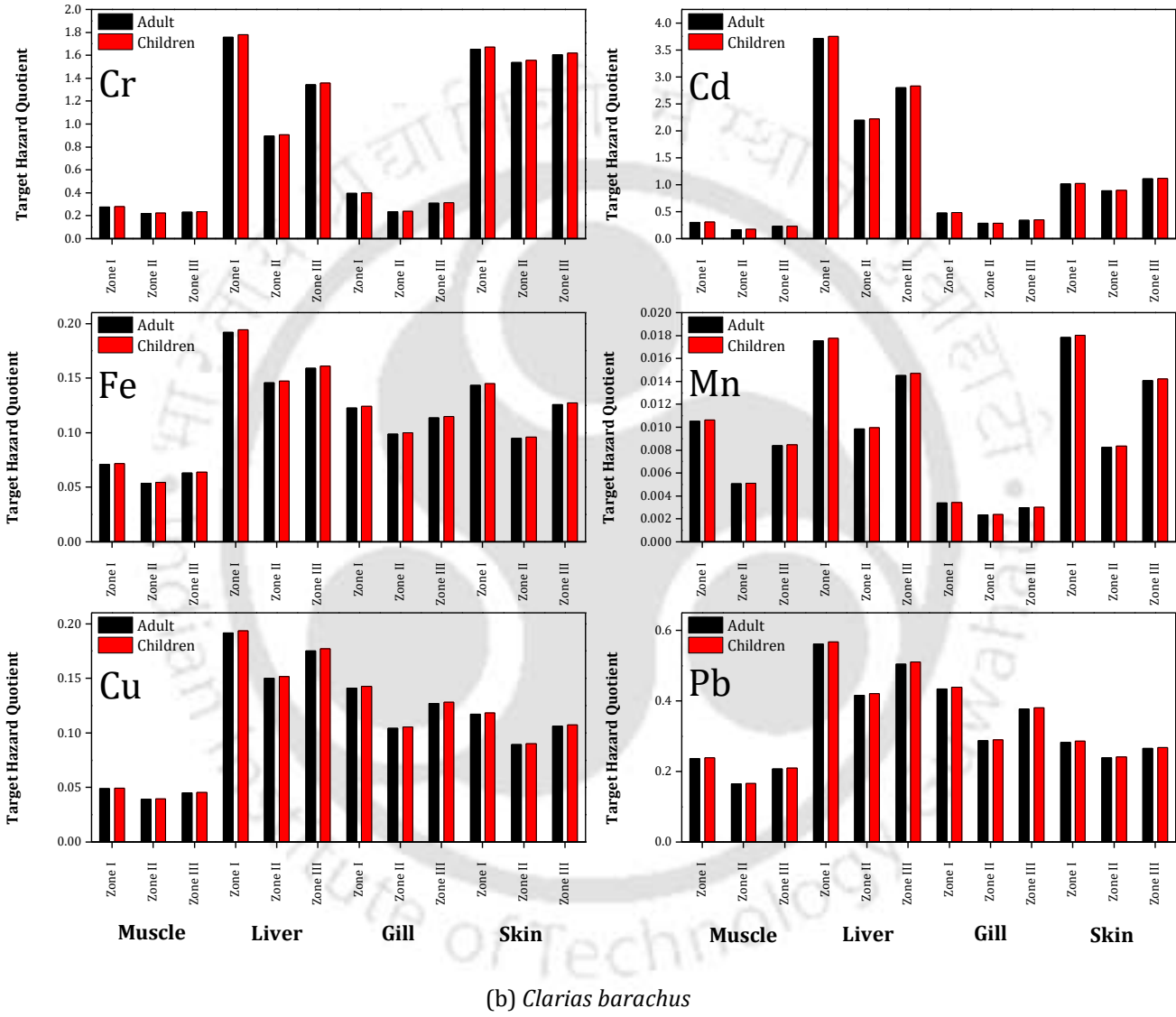
Heavy metals	EDI	Muscle			Liver			Gill			Skin		
		Zone I	Zone II	Zone III	Zone I	Zone II	Zone III	Zone I	Zone II	Zone III	Zone I	Zone II	Zone III
Cr	Adult	0.827	0.659	0.697	5.277	2.685	4.025	1.186	0.707	0.934	4.957	4.611	4.808
	Child	0.836	0.667	0.705	5.336	2.715	4.071	1.199	0.715	0.944	5.012	4.663	4.862
Cd	Adult	0.304	0.169	0.228	3.708	2.199	2.801	0.475	0.284	0.343	1.014	0.889	1.109
	Child	0.307	0.171	0.231	3.749	2.224	2.833	0.480	0.288	0.347	1.026	0.899	1.122
Fe	Adult	49.736	37.596	44.092	134.511	102.080	111.349	85.915	69.245	79.463	100.361	66.358	88.010
	Child	50.296	38.020	44.588	136.027	103.230	112.603	86.883	70.025	80.358	101.492	67.106	89.002
Mn	Adult	1.475	0.710	1.175	2.457	1.379	2.034	0.478	0.331	0.420	2.494	1.155	1.969
	Child	1.491	0.718	1.188	2.485	1.395	2.057	0.483	0.334	0.425	2.522	1.168	1.991
Cu	Adult	1.955	1.572	1.804	7.659	6.001	7.008	5.648	4.175	5.070	4.687	3.571	4.249
	Child	1.977	1.590	1.825	7.745	6.069	7.087	5.712	4.222	5.127	4.740	3.611	4.297
Pb	Adult	0.944	0.657	0.832	2.246	1.666	2.018	1.738	1.148	1.506	1.132	0.954	1.062
	Child	0.955	0.665	0.841	2.271	1.684	2.041	1.757	1.161	1.523	1.145	0.965	1.074

(c) *Channa striata*

Heavy metals	EDI	Muscle			Liver			Gill			Skin		
		Zone I	Zone II	Zone III	Zone I	Zone II	Zone III	Zone I	Zone II	Zone III	Zone I	Zone II	Zone III
Cr	Adult	0.642	0.558	0.614	4.330	1.158	4.058	0.665	0.625	0.626	4.766	4.524	4.478
	Child	0.650	0.564	0.621	4.379	1.172	4.104	0.673	0.632	0.633	4.819	4.575	4.529
Cd	Adult	0.203	0.034	0.166	2.729	0.581	2.204	0.470	0.279	0.330	1.031	0.980	1.101
	Child	0.206	0.034	0.168	2.760	0.587	2.229	0.475	0.282	0.333	1.043	0.991	1.113
Fe	Adult	50.042	38.005	44.229	130.162	88.351	114.305	79.302	73.125	73.271	92.999	77.264	83.340
	Child	50.606	38.433	44.728	131.629	89.347	115.593	80.196	73.949	74.097	94.047	78.134	84.279
Mn	Adult	1.465	0.706	1.167	2.308	1.332	1.925	0.486	0.333	0.426	2.354	1.110	1.866
	Child	1.481	0.714	1.180	2.334	1.347	1.947	0.491	0.337	0.431	2.380	1.123	1.887
Cu	Adult	1.949	1.570	1.801	7.430	5.927	6.840	5.728	4.200	5.129	4.570	3.533	4.163
	Child	1.971	1.588	1.821	7.514	5.994	6.918	5.793	4.248	5.186	4.621	3.573	4.210
Pb	Adult	0.940	0.656	0.829	2.166	1.640	1.959	1.770	1.159	1.530	1.114	0.948	1.049
	Child	0.951	0.664	0.838	2.190	1.658	1.982	1.790	1.172	1.547	1.126	0.959	1.060



(a) *Notopterus notopterus*



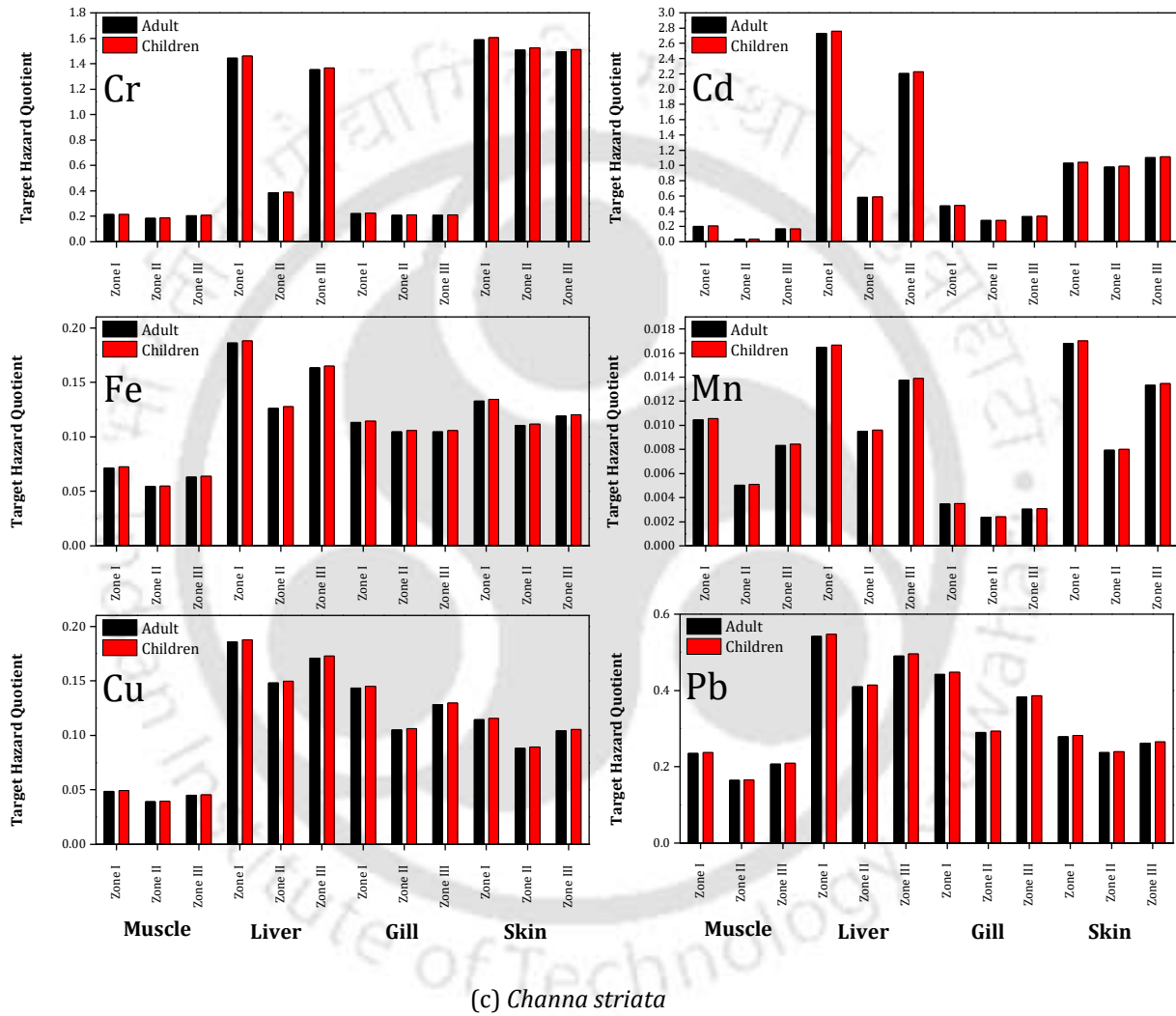
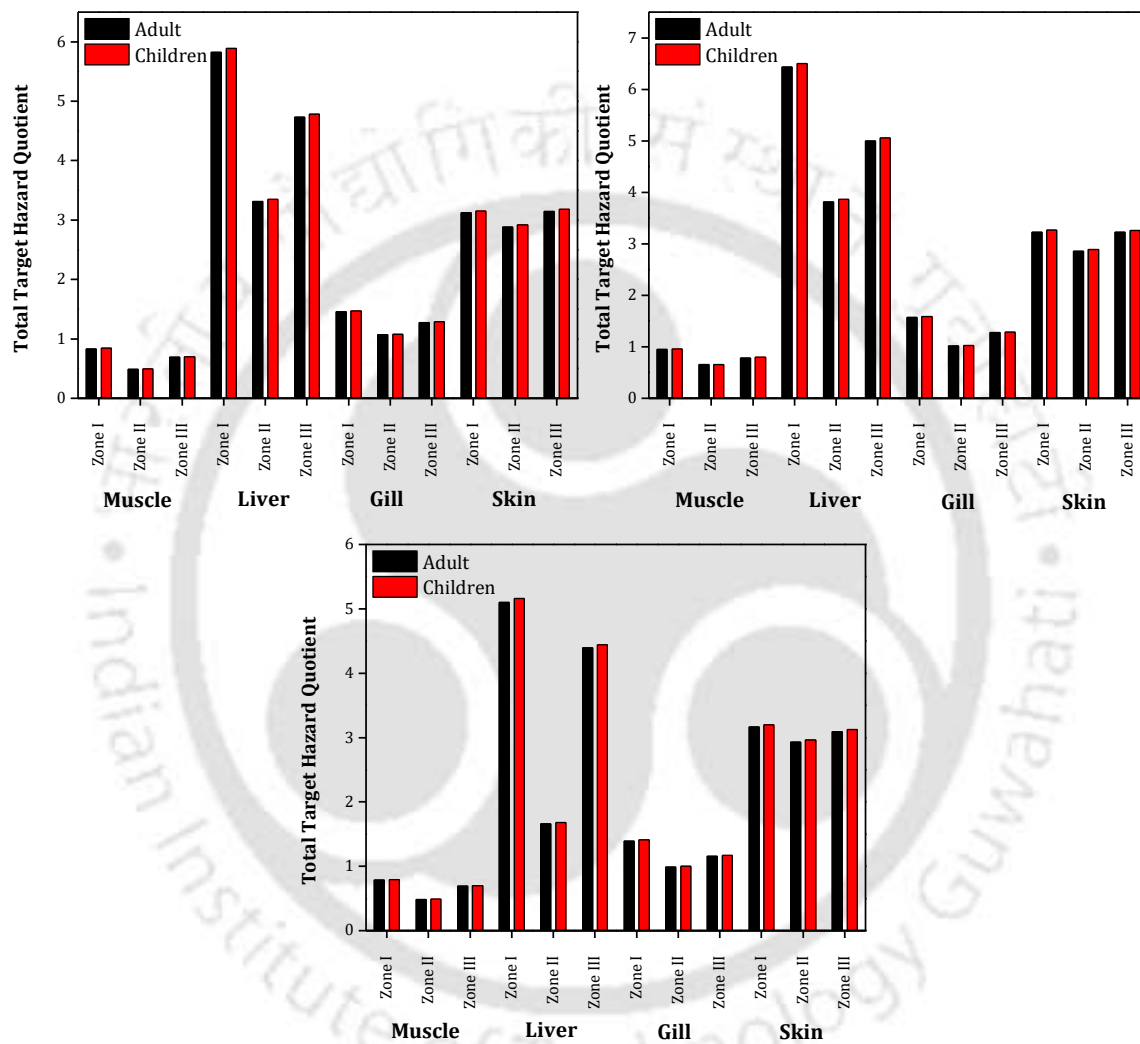
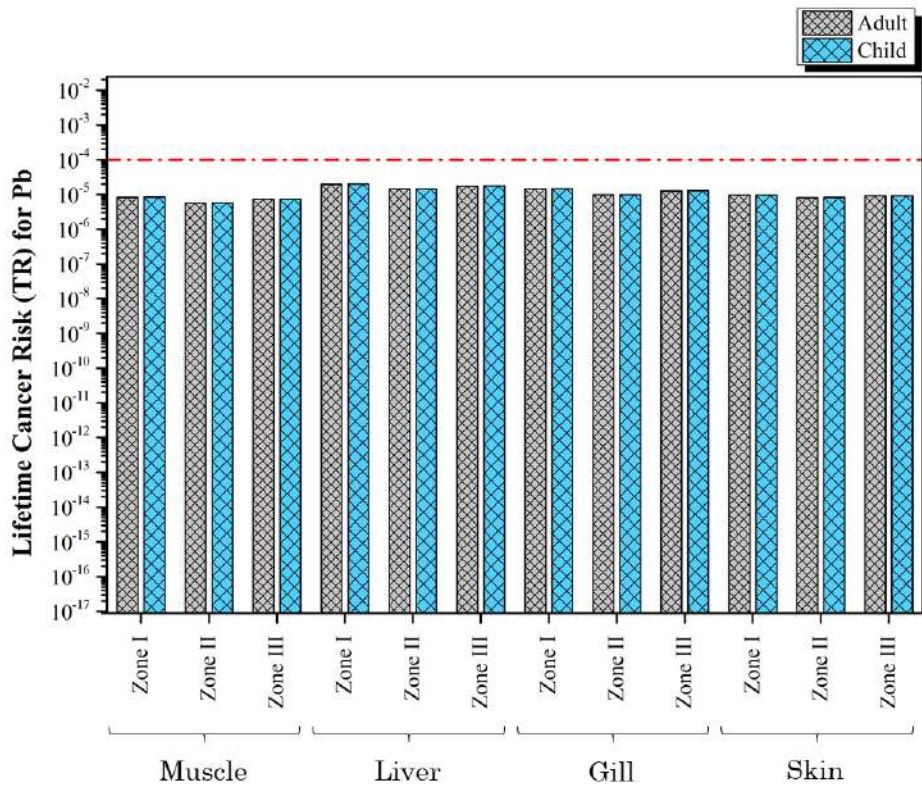
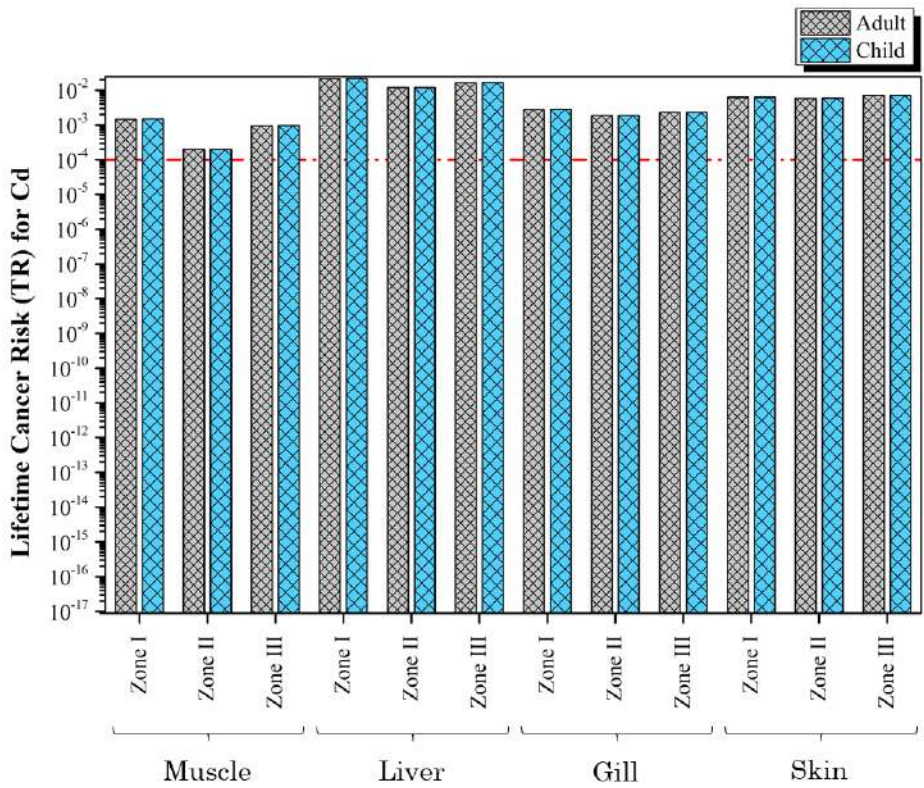


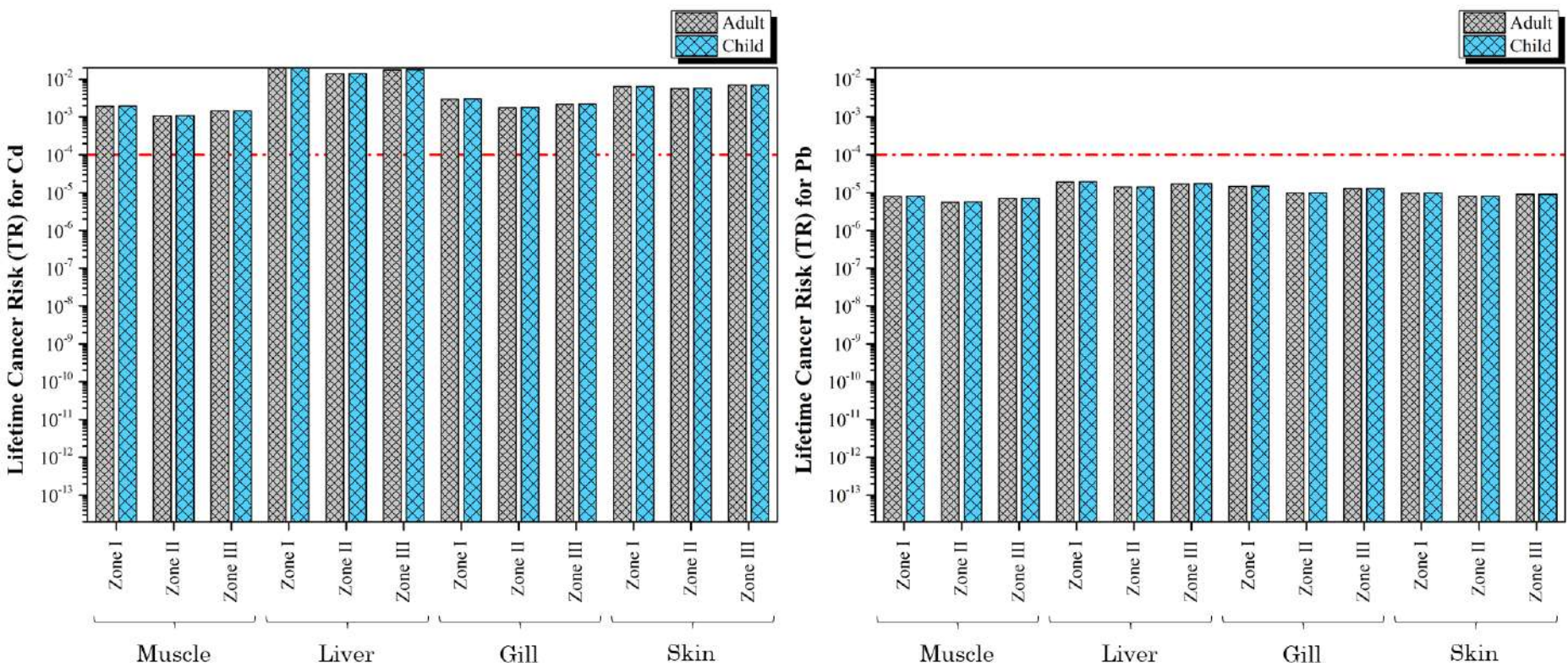
Fig. 8. 6. Estimated target hazard quotient (THQ) for individual metal of various organs of different fish species from the three zones of Deepor Beel.

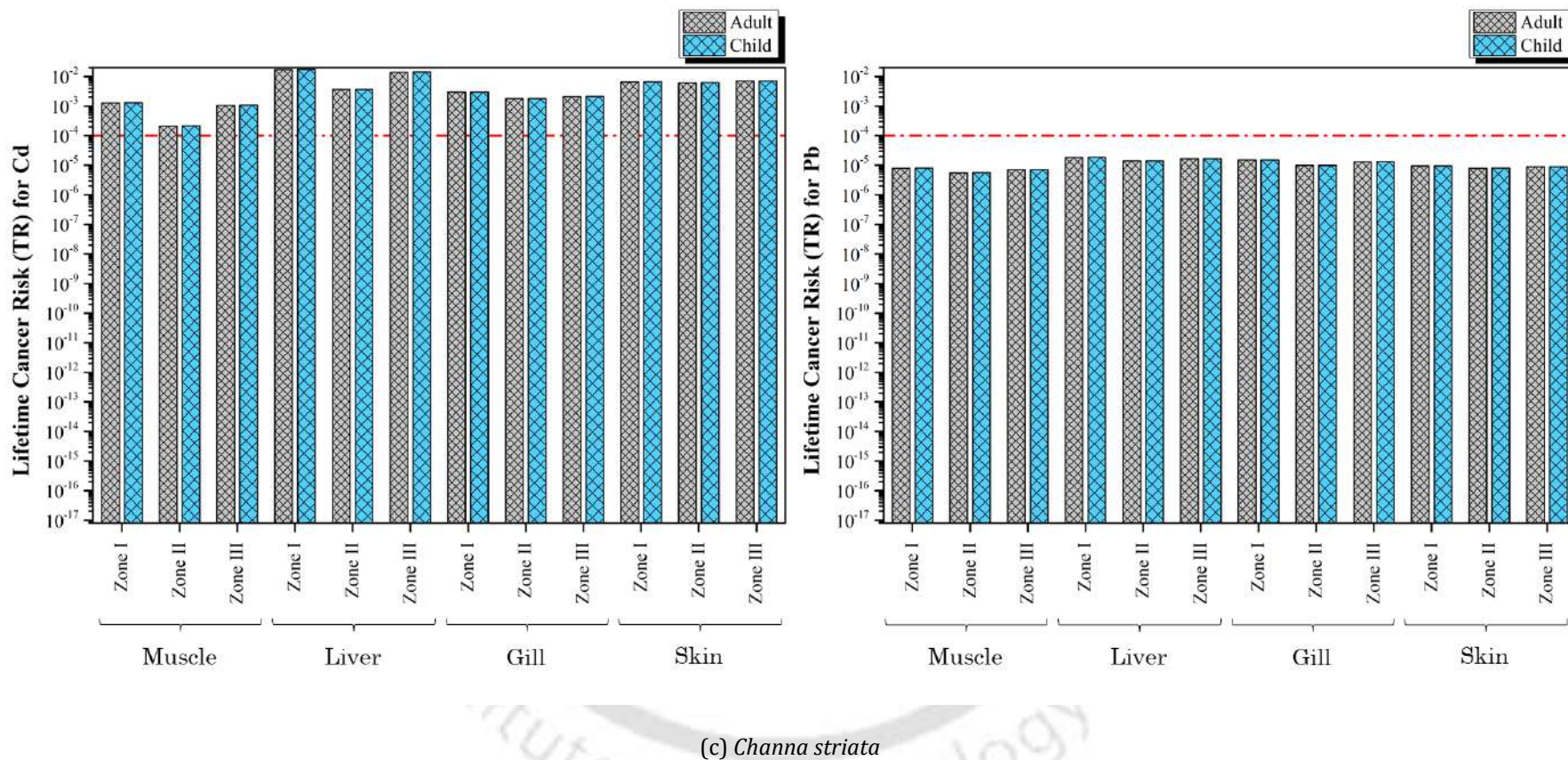


**Fig. 8. 7.** Total target hazard quotient (TTHQ) values for different fish species in Deepor Beel.



(a) *Notopterus notopterus*

(b) *Clarias barachus*



**Fig. 8. 8.** Lifetime cancer risk (TR) for adult and children from the consumption of various organs of different fish species from the three zones of Deepor Beel.

Hence, the liver of *Clarias batrachus* collected from zone I possessed the most non-carcinogenic health impact among the children. On the other hand, the muscle of *Channa striata* collected from zone II has the most negligible impact. The associated cancer risk involved was assessed through the TR values, considering two carcinogenic heavy metals, i.e., Cd and Pb. The desirable and acceptable values are  $1.0 \times 10^{-06}$  and  $1.0 \times 10^{-04}$ , respectively. It was observed that the carcinogenic risk due to Cd was significantly higher for all the organs of the three species. In contrast, the TR values for Pb lay below the acceptable, although more than the desired value. This suggests that Cd has a long-term carcinogenic impact on human health, both for adults and children. Children were found to have a more significant impact on their health on fish consumption from Deepor Beel.

#### 8.4. Bioaccumulation of heavy metals and bioaccumulation factor

The heavy metal fractionation in the sediments determines the extent of bioaccumulation of heavy metals in the biota (Sekhar *et al.* 2004). Based on the binding strength and solubility, the bioavailable fractions of sediments can be classified in the following order;  $F1 > F2 > F3 > F4 > F5$  (Ma & Rao 1997). Both endogenous (environmental factors such as ambient temperature, metal bioavailability, and alkalinity) and exogenous (external factors such as species size, physiological state of the species, etc.) factors control a complicated process like bioaccumulation (Moiseenko & Kudryavtseva 2001). Several factors, such as the proximity of the fish species to the contaminated sediment sites, the magnitude of contamination and their trophic levels, determine the extent of contaminant exposure in the fish tissues. There exist two primary routes of exposure of the contaminants into the tissues of fish; (i) through gills or via ion exchange process of the dissolved chemicals which forms the primary route, and (ii) ingestion of sediment particles or food through the gut, which forms the secondary route of exposure (Burger *et al.* 2002). Among the fish organs, the liver and skin tend to have a higher bioaccumulation tendency than other organs (Agarwal *et al.* 2007; Dhanakumar *et al.* 2015). Hence, an attempt has been made to correlate the heavy metal concentrations in various fish organs to the sediment fractionations available for Deepor Beel to determine their bioaccumulation pattern (Table 8. 4). Since F1 and F2 fractions predominantly aid in the bioaccumulation process; hence, the correlations about these two fractionations have been considered in the following study, although all fractionation correlations are given in Table 8. 4. It was observed that the liver showed significant positive correlations for all metals except Pb and Fe for both F1 and F2, thus indicating the highest bioaccumulation affinity.

**Table 8. 4.** Correlation between metal accumulation in various fish organs and metal fractions in sediments.

Metal	Muscle	Liver	Gill	Skin	Metal	Muscle	Liver	Gill	Skin
<b>Cr</b>					<b>Mn</b>				
F1	-0.2576	<b>0.2535</b>	-0.0415	0.0628	F1	0.2330	0.2517	0.2332	<b>0.2815</b>
F2	0.0022	<b>0.3328</b>	-0.0667	-0.0823	F2	0.3776	0.4056	0.3777	<b>0.4239</b>
F3	0.1094	0.2251	0.0941	<b>0.2773</b>	F3	0.2550	<b>0.2807</b>	0.2553	0.2795
F4	-0.4212	-0.2696	-0.3261	-0.0965	F4	0.3724	<b>0.3911</b>	0.3725	0.3736
F5	0.4366	<b>0.7602</b>	0.5406	0.5795	F5	<b>0.2534</b>	0.2124	0.2534	0.2461
<b>Cd</b>					<b>Cu</b>				
F1	0.4385	<b>0.6260</b>	0.4343	0.3032	F1	0.3838	0.3590	0.3815	<b>0.3951</b>
F2	0.3564	0.1207	<b>0.3944</b>	0.2790	F2	0.4508	0.4616	<b>0.4667</b>	0.4597
F3	0.0624	-0.2922	0.1239	0.0770	F3	-0.5969	-0.6004	-0.5845	-0.5836
F4	-0.0473	0.0024	-0.0615	-0.1384	F4	<b>0.2233</b>	0.2154	0.2032	0.2089
F5	-0.0260	-0.0866	-0.0875	<b>0.2646</b>	F5	<b>0.2887</b>	0.2672	0.2619	0.2756
<b>Fe</b>					<b>Pb</b>				
F1	-0.5027	-0.5319	-0.3984	-0.6238	F1	-0.4284	-0.4265	-0.4267	-0.4281
F2	-0.6784	-0.7534	-0.5590	-0.8354	F2	-0.2001	-0.2019	-0.2037	-0.2031
F3	-0.4522	-0.5404	-0.2373	-0.7373	F3	-0.3899	-0.3850	-0.3883	-0.3930
F4	-0.3475	-0.3787	-0.1803	-0.4771	F4	0.0382	0.0336	0.0375	0.0423
F5	0.2232	0.3702	<b>0.5185</b>	0.1676	F5	-0.0150	-0.0160	-0.0179	-0.0179

Furthermore, muscle displayed no significant correlation for any heavy metal, although a strong correlation was observed for Cd, Mn, and Cu. This shows that muscle has the least tendency for bioaccumulation. Skin showed considerable affinity towards bioaccumulation of Mn and Cu, while moderate and low correlations were observed for Cr and Cd, respectively. Gill displayed low to moderate correlations for Cd, Mn, and Cu, while no correlation existed for other metals. Among the heavy metals, Cd was found to be the best as far as bioavailability is concerned due to its abundance in the readily exchangeable fraction, which is indicated in Fig. 7. 12.

Cu and Mn follow Cd. This indicates that Cd, Cu, and Mn are the predominant metals responsible for bioaccumulation in various organs of fish species, which can be attributable to discharge of water from Basistha River carrying untreated domestic wastewater, industrial effluents from the western part of the wetland and agro runoff. Several studies have also reported the influence of sediment geochemistry due to Cd, Cu, and Mn contamination as a result of untreated sewage, agro runoff, and industrial effluents and have obtained positive correlations between the bioavailable fractions (Sekhar *et al.* 2004; Agarwal *et al.* 2007; Baumann & Fisher 2011; Dhanakumar *et al.* 2015).

Additionally, a correlation analysis carried out between the total metal concentrations in the three fish species and total metal content in sediment (Fig. 8. 9) and water column (Fig. 8. 10) revealed that sediments were more strongly correlated than the water environment for all three species and six heavy metals. This suggests that the sediment column of Deepor Beel contributes to the bioavailability of the heavy metals in the fish species more than the water column.

The bioaccumulation of heavy metals in various organs of fish species is also evaluated using the bioaccumulation factor (BAF) tool. Fig. 8. 11 shows the BAF (in %) for four organs (liver, muscle, gill, and skin) of the three fish species (*N. notopterus*, *C. batrachus*, and *C. striata*) collected from three different zones of Deepor Beel. Critical observations can be made, including the liver having the highest BAFs among all the organs, followed by skin, gill, and muscle. Furthermore, the BAFs in zone I were mostly found to be higher than the other two zones. However, the BAF for Cr in the liver for all three species were higher in zone II, primarily because of the agro discharge from the area. The highest BAF was observed for Cd in liver tissues in *Clarias batrachus* from zone I, while the lowest occurred in Cd concentrations in muscles of *Clarias batrachus* from zone II. This indicated that Cd was regulated in the liver tissue while maintaining a homeostatic status in the muscle. It was also observed that a significant difference in BAF values occurred between the different organs for Cd, Cr, and Mn,

while other metals displayed smaller variations. This can be attributed to the high leachability of Cd, Cr, and Mn due to their high availability of exchangeable fractions.

Hence, the present study indicates that the sites near the landfill plays a critical role in the bioaccumulation of heavy metals in the fishes of Deepor Beel, owing to higher contamination values of sediments in that region.

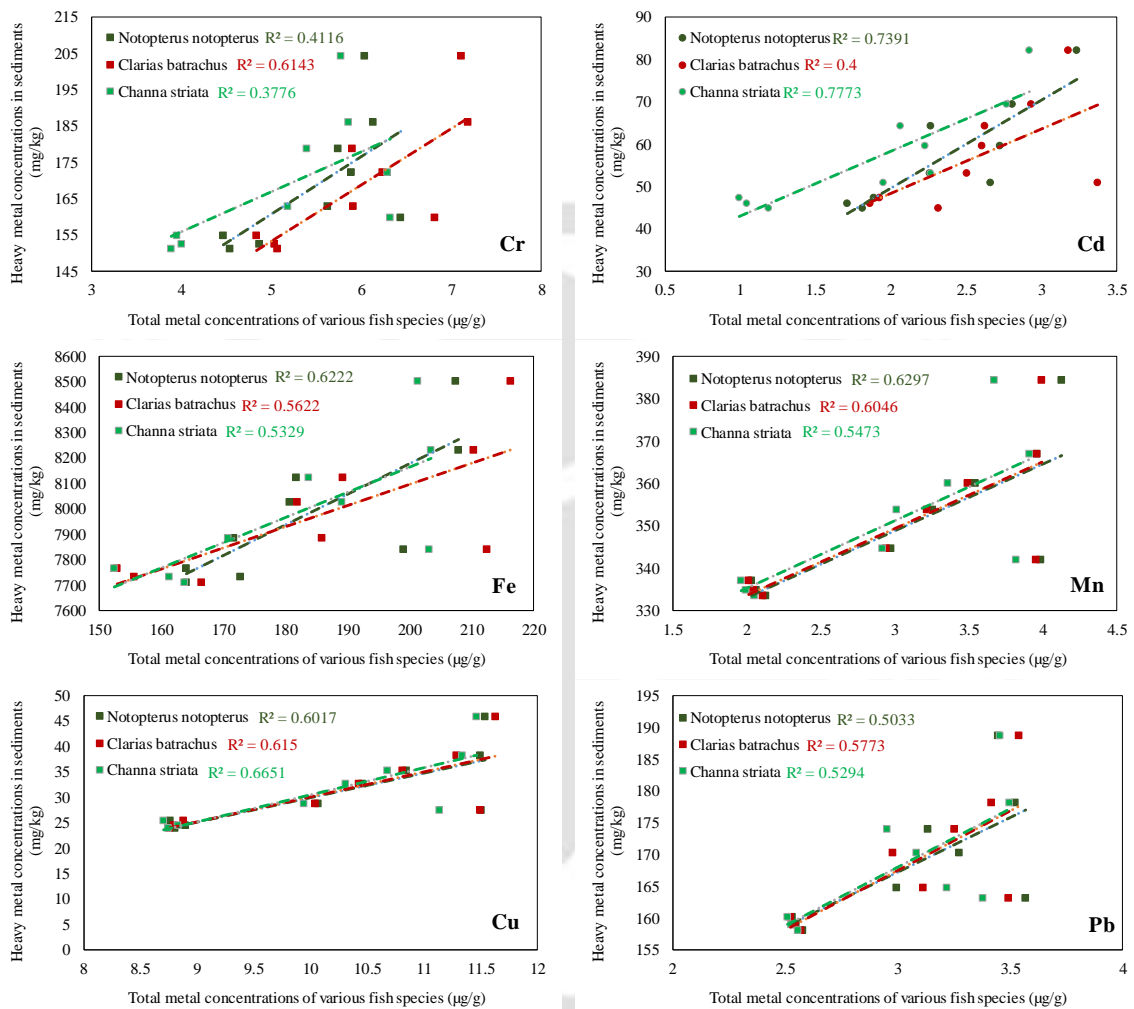


Fig. 8. 9. Significant correlation between various heavy metal contents in fish and sediments.

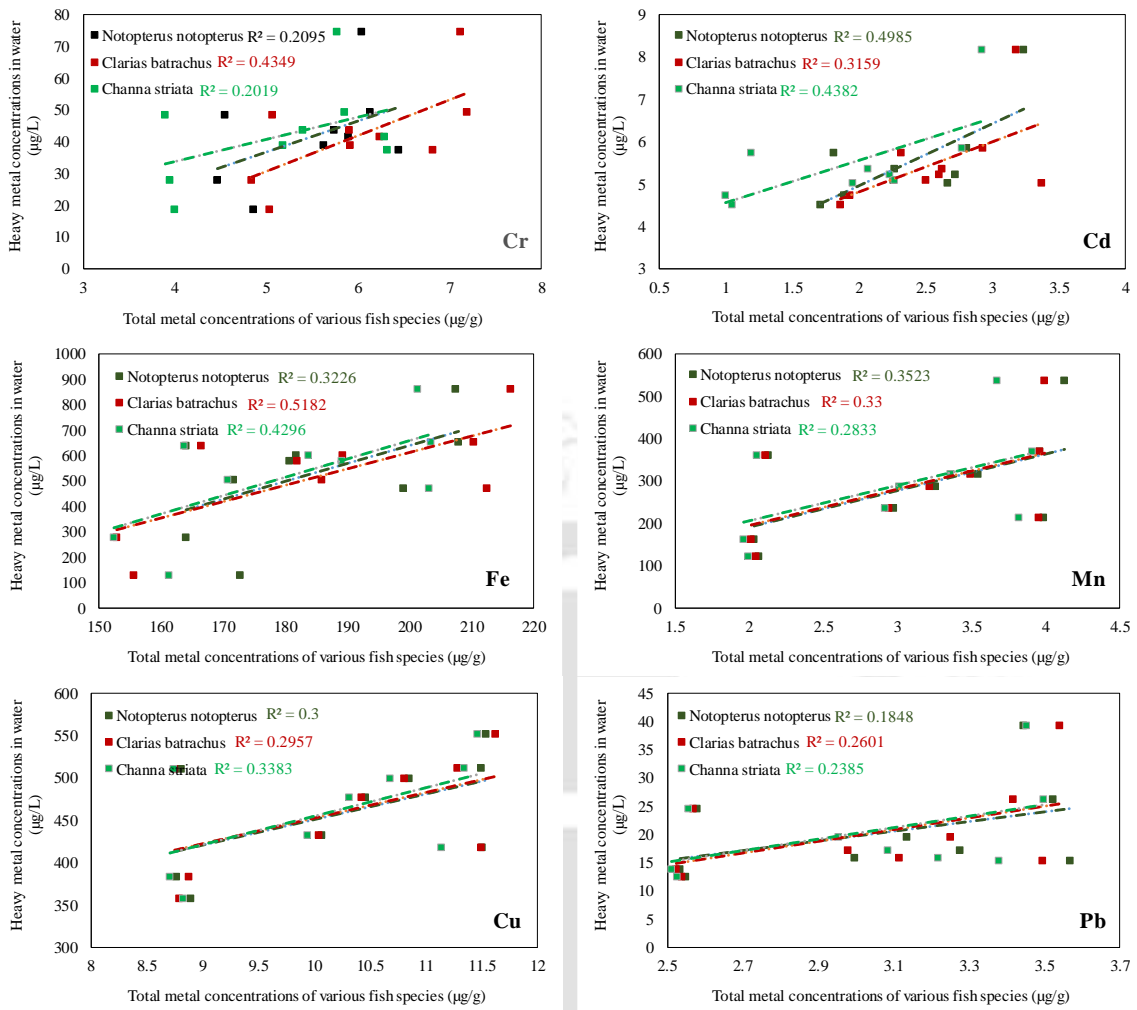
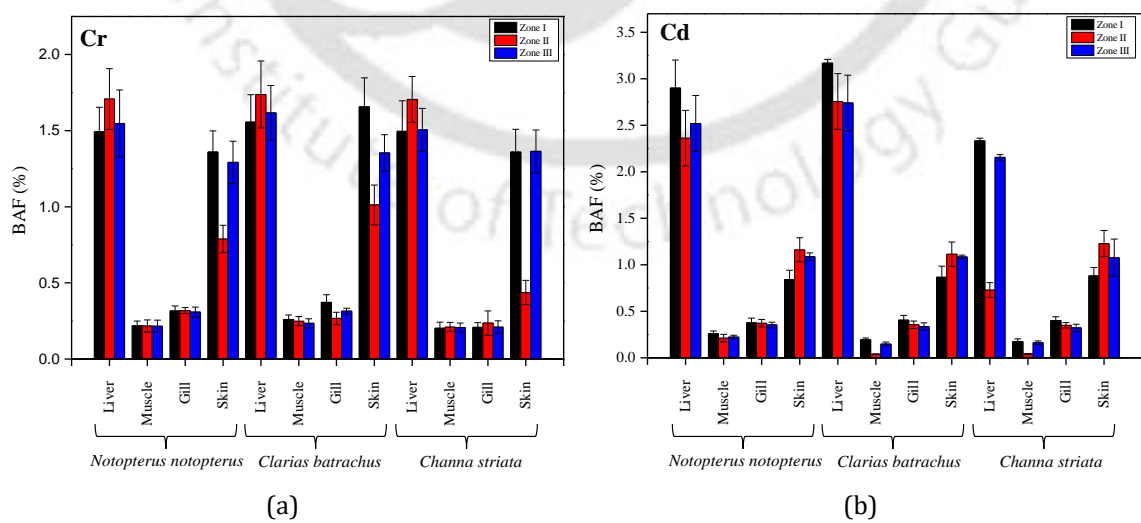
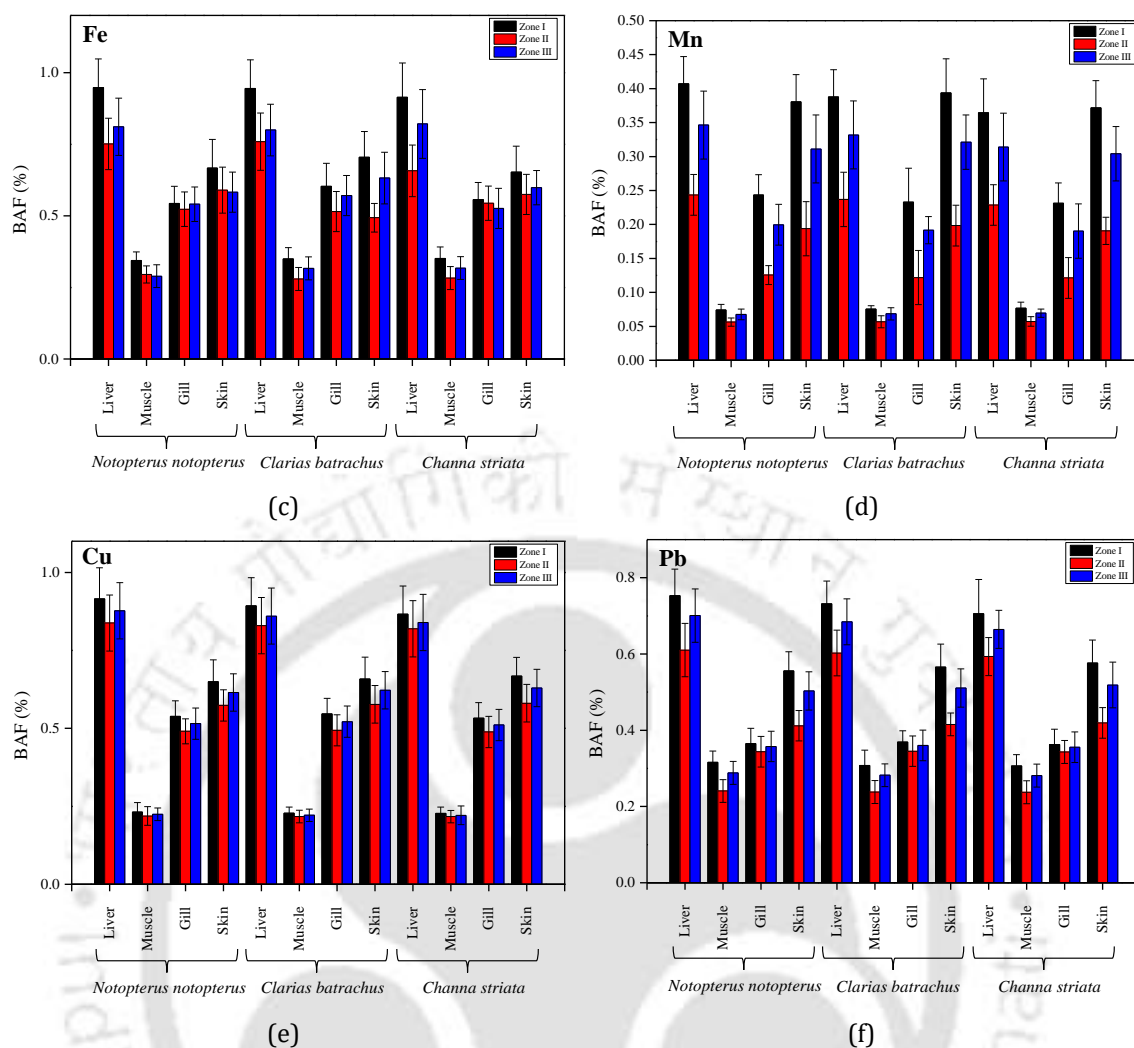


Fig. 8. 10. Significant correlation between various heavy metal contents in fish and water column.





**Fig. 8. 11.** Bioaccumulation factors {BAFs (in percent)} of different heavy metals in various organs of *N. notopterus*, *C. batrachus* and *C. striata* from the three zones of Deepor Beel.

## 8.5. Summary

The present study considered environmental monitoring as a tool for a comprehensive assessment of the dynamics involved with respect to heavy metals in the entire Deepor Beel (wetland) ecosystem considering all three critical components, i.e., water, sediment, and fish. Various critical observations were made, and the following conclusions, listed below, are deduced from the study.

- For the water column of Deepor Beel, the ingestion pathway of exposure is significantly higher than the dermal adsorption. Pb and Mn were found to have a significant contribution to the health risk of humans in the sites adjacent to the Boragaon landfill. However, without proper reclamation policies or planning of the wetland, Cr and Cd may start posing severe health risks shortly.

- b. The non-carcinogenic health risk assessment for the surficial sediments revealed that Cd and Pb have maximum impact for the ingestion pathway for all the sampling locations. The cumulative impact of all the metals for all three pathways combined signified HQ values exceeding nine times the critical limit of 1. On the other hand, the carcinogenic risk assessment indicated Cd to have the highest carcinogenic potential, with its values exceeding the acceptable limits for all sites. Finally, regardless of the carcinogenic or non-carcinogenic potential of heavy metals, children were found to be more susceptible to chronic health effects compared to adults.
- c. The three fish species collected from three different zones of Deepor Beel suggested that all three fish species exhibited higher bioaccumulation of heavy metals in the liver. Furthermore, the samples collected from zone I accumulated considerably higher concentrations of heavy metals, followed by those collected from zone II and III.
- d. Finally, the present study results suggest that the landfill contributes to the heavy metal pollution of the wetland (both water and sediment column), which is further reflected in the fish biota. This involvement of the heavy metals in the aquatic ecosystem's food chain, thus, resulting in their bioaccumulation, may prove detrimental, provided no substantial measures are taken to limit their flow into the aquatic ecosystem.



# 9

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## **Assessment of nutrient (N-P) dynamics in wetlands through a one-dimensional model for assessing the eutrophication levels induced by various pollution sources**

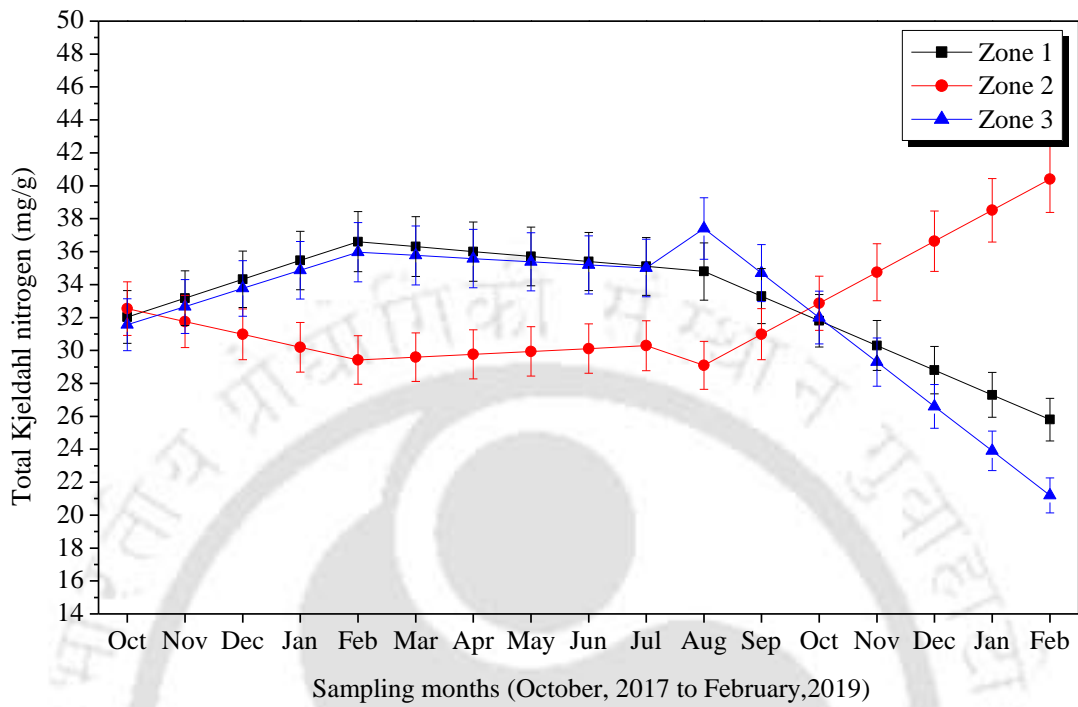
This chapter aims at providing a suitable foundation for the development of a eutrophic-ecological model for Deepor Beel, India. Through this eutrophic model, the nutrient dynamics in the wetland ecosystem was understood and sustainable solutions towards eutrophication abatement in Deepor Beel was proposed.

### **9.1. Spatio-temporal variations of different water quality, plant and sediment samples**

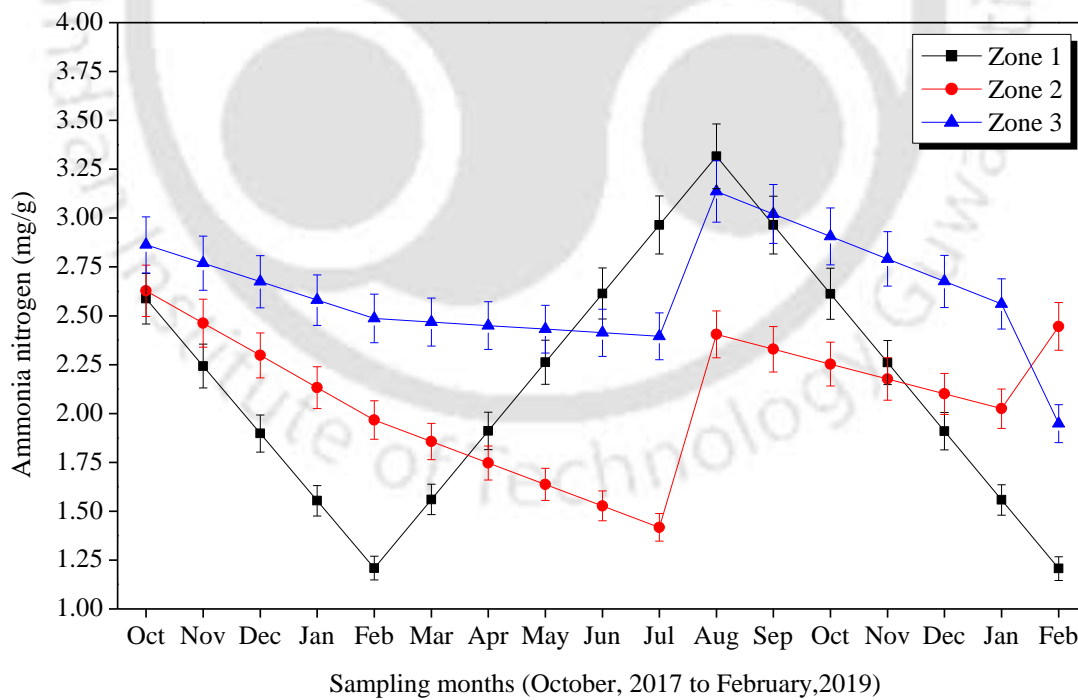
The variations in water and sediment quality have been reported in Appendices A and B, respectively, through pattern plots. For the water samples, alkaline pH values were observed at sampling sites with the substantial presence of water hyacinths, indicating possible role photosynthesis by microorganisms present at the root zone. On the other hand, acidic pH values were observed at sampling points closer to the Boragaon landfill, indicating a probable inflow of acidic surface runoff. Dissolved oxygen showed a wide variation both spatially and temporally across the entire sampling period. It was consistently low for sampling sites 7, 9, 15 and 16, which are located closest to the landfill, occasionally dropping to values lower than 4 mg/L, which is required to support aquatic life. Sampling sites closer to the industrial zone and at the mid-section of Deepor Beel had high dissolved oxygen concentrations for most of

the sampling period. Sampling site 10 showed abnormally high dissolved oxygen concentration in few sampling months, which can be explained by the presence of water hyacinths in that area. The anomalous high value of Total Kjeldahl Nitrogen (TKN) at sampling sites 15 and 16 can be explained by the proximity of those points to the landfill. In fact, the TKN at all the sampling points was relatively high in March 2018. This can be attributed to the fact that the Total Kjeldahl Nitrogen in the inflowing water of the Basistha River was high for that month. The ammonia nitrogen concentration was higher in the winter and pre-monsoon seasons than in the monsoon and post-monsoon seasons. This trend can be attributed to dilution due to increased water volume, higher nitrification rate, higher microbial uptake, etc. It is also interesting to note that most of the high nitrate sampling sites are located close to the banks of the lake, hinting at the possibility of artificial addition of nitrate from the agricultural runoff.

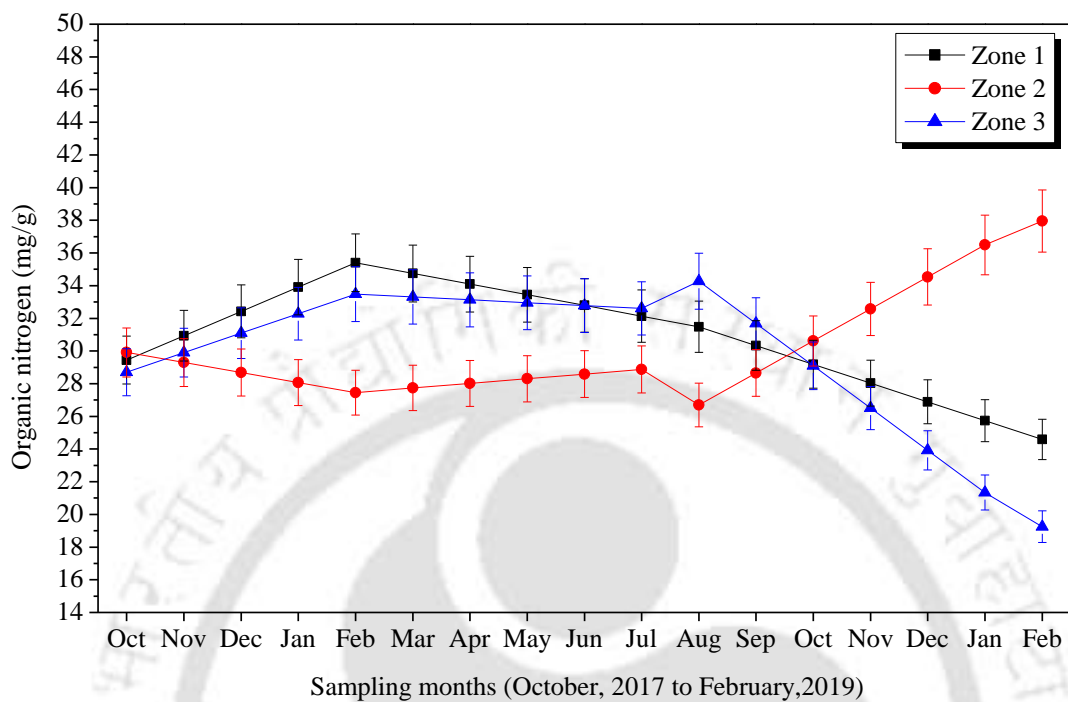
The average temperature of the water in Deepor Beel was higher during the pre-monsoon and monsoon periods (May to September). Higher temperature during this period is a reflection of the high ambient temperature that prevails in the region. Fig. 9. 1 represents the spatio-temporal variation of different nutrients in plants in Deepor Beel. TKN and OrgN show similar trends as indicated by Fig. 9. 1a and c. Water hyacinths in Deepor Beel begin to bloom in the post-monsoon season and attain maturity in the succeeding seasons. This explains the initial rise in TKN and OrgN in zones 1 and 3. The trends then continue to stay mostly constant from February 2018 to July 2018 as most of the water hyacinths during that period in the lake achieve the maturation stage, and hence, lower concentrations are observed in the plant biomass.  $\text{NH}_3\text{N}$ ,  $\text{NO}_3\text{N}$  and PP are found to be present in lower concentrations in the wetland. Similarly, the spatio-temporal variations of the nutrient concentrations in the sediment column of Deepor Beel suggest high concentration in the green zone, which the higher settling rate can explain during that period, which can be validated by the fact that TKN in the water column decreased around the same period. Ammonia nitrogen is present in low concentrations in the sediments as it quickly dissolves into pore water and re-enters the water column under favourable situations. However, on average,  $\text{NH}_3\text{N}$  in the sediments was higher around the same period as TKN, hinting at an increased rate of ammonification of the OrgN present in the sediments.  $\text{NO}_3\text{N}$  is primarily present in trace concentrations in the wetland, while SP varies over a wide range from 0.01-0.6 mg/g.



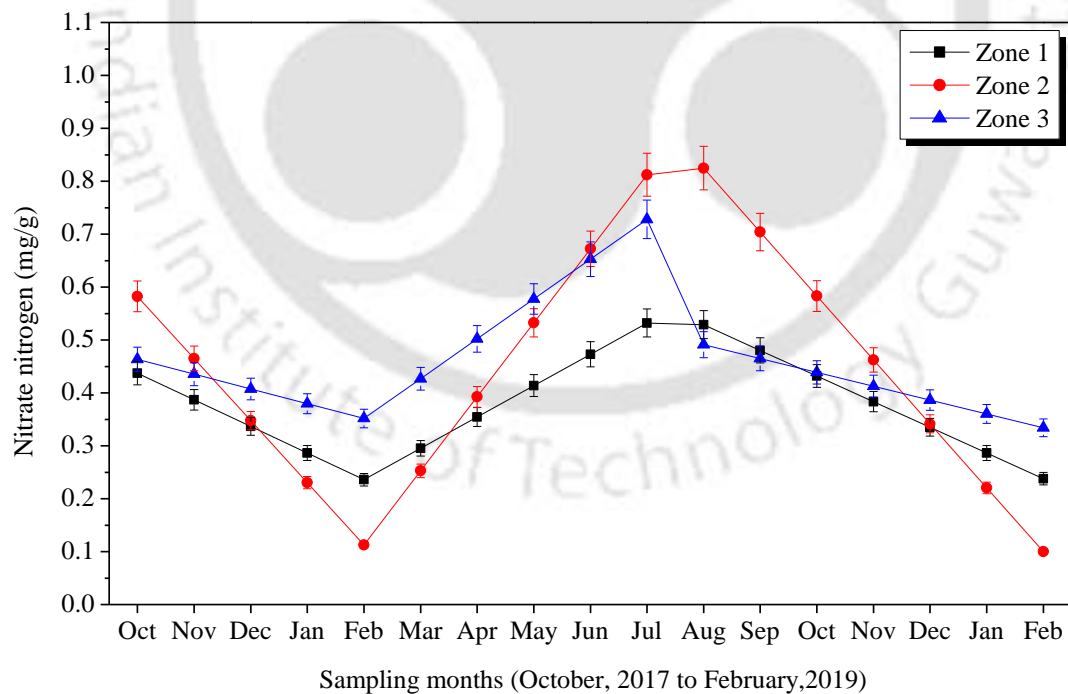
(a)



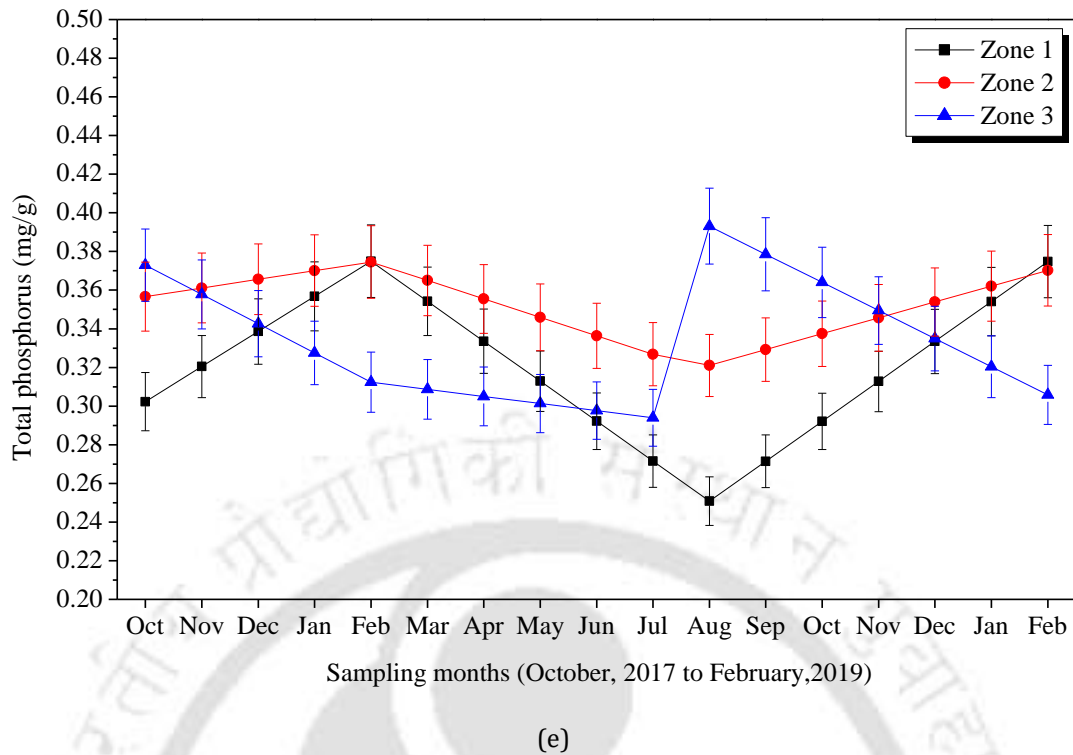
(b)



(c)



(d)



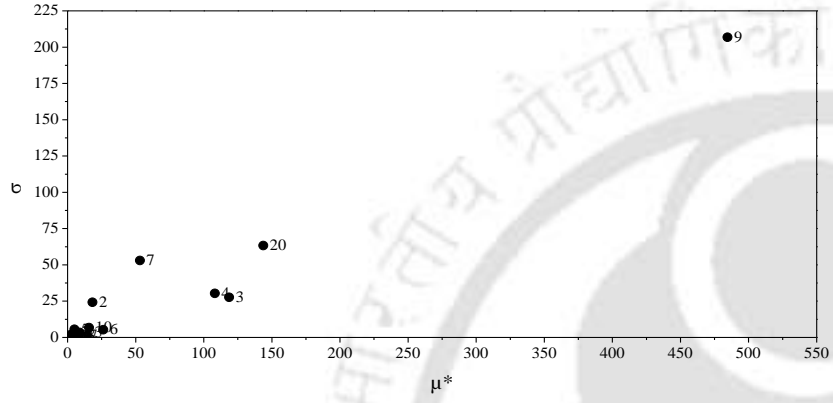
**Fig. 9. 1.** Spatio-temporal variation of various nutrient parameters in plant samples.

## 9.2. Sensitivity analysis

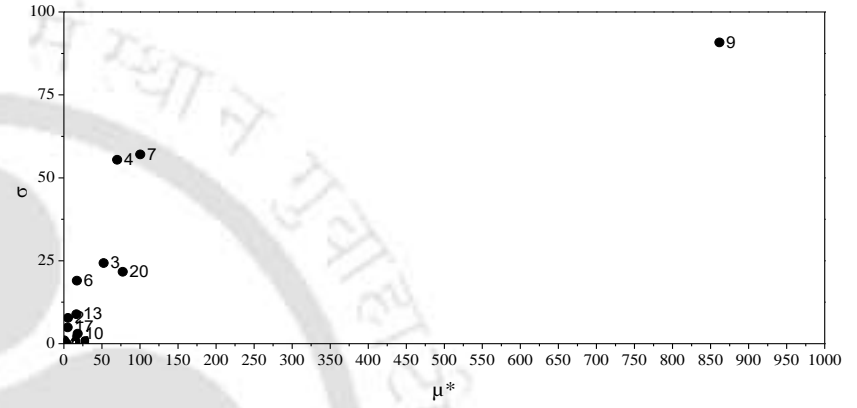
Sensitivity analyses of the elementary effects for different state variables corresponding to different parameters are shown in Fig. 9. 2 a-h. These figures indicate scatter plots between standard deviation ( $\sigma$ ) and absolute mean ( $\mu^*$ ). The plots of these statistical indicators through the Morris method recognizes the input functions having a significant influence with respect to different parameters:

- Low mean and low standard deviation: Negligible
- High mean and low standard deviation: Linear and additive
- High standard deviation: Non-linear or involved in interactions with other input parameters

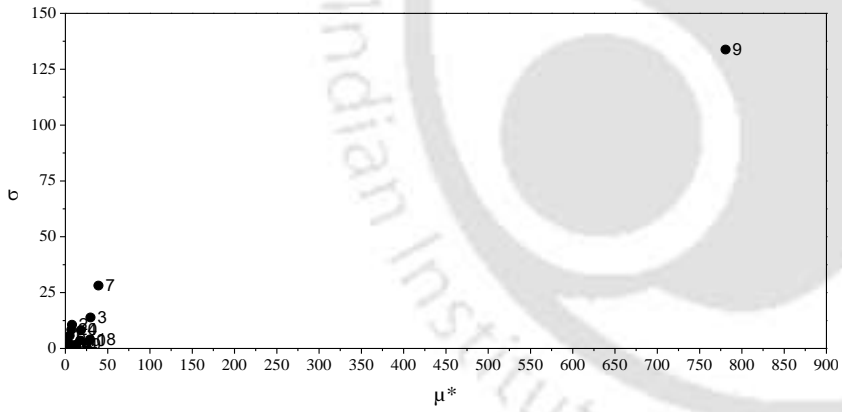
All the plots were constructed for a confidence limit of  $\pm 10\%$ . Clearly, from Fig. 9. 2a,  $\mu_n$  is a dominating factor responsible for the maximum variation of organic Nitrogen in water with respect to other input factors since it has a high standard deviation. Factors such as  $\mu_{\max,20}$ ,  $R_{am}$ ,  $\Gamma_b$  and  $R_{ns}$  have lower standard deviation values, which signifies that they have a linear and additive effect on the other input parameters. Factors other than these have low mean and standard deviation values, suggesting that their effects on the input factors are negligible.



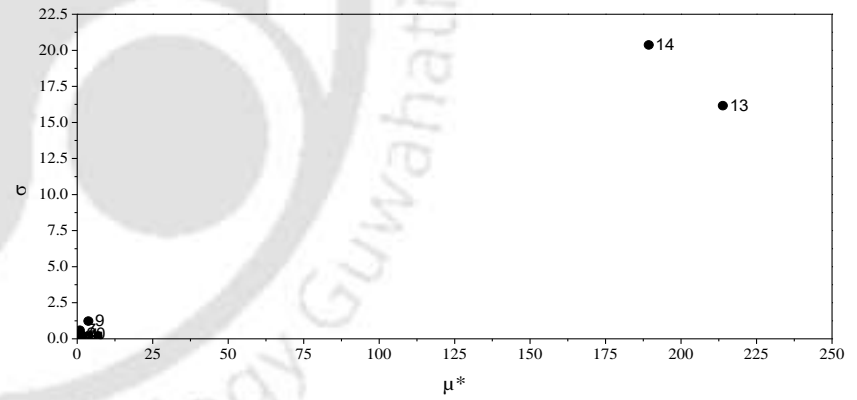
(a) OrgN



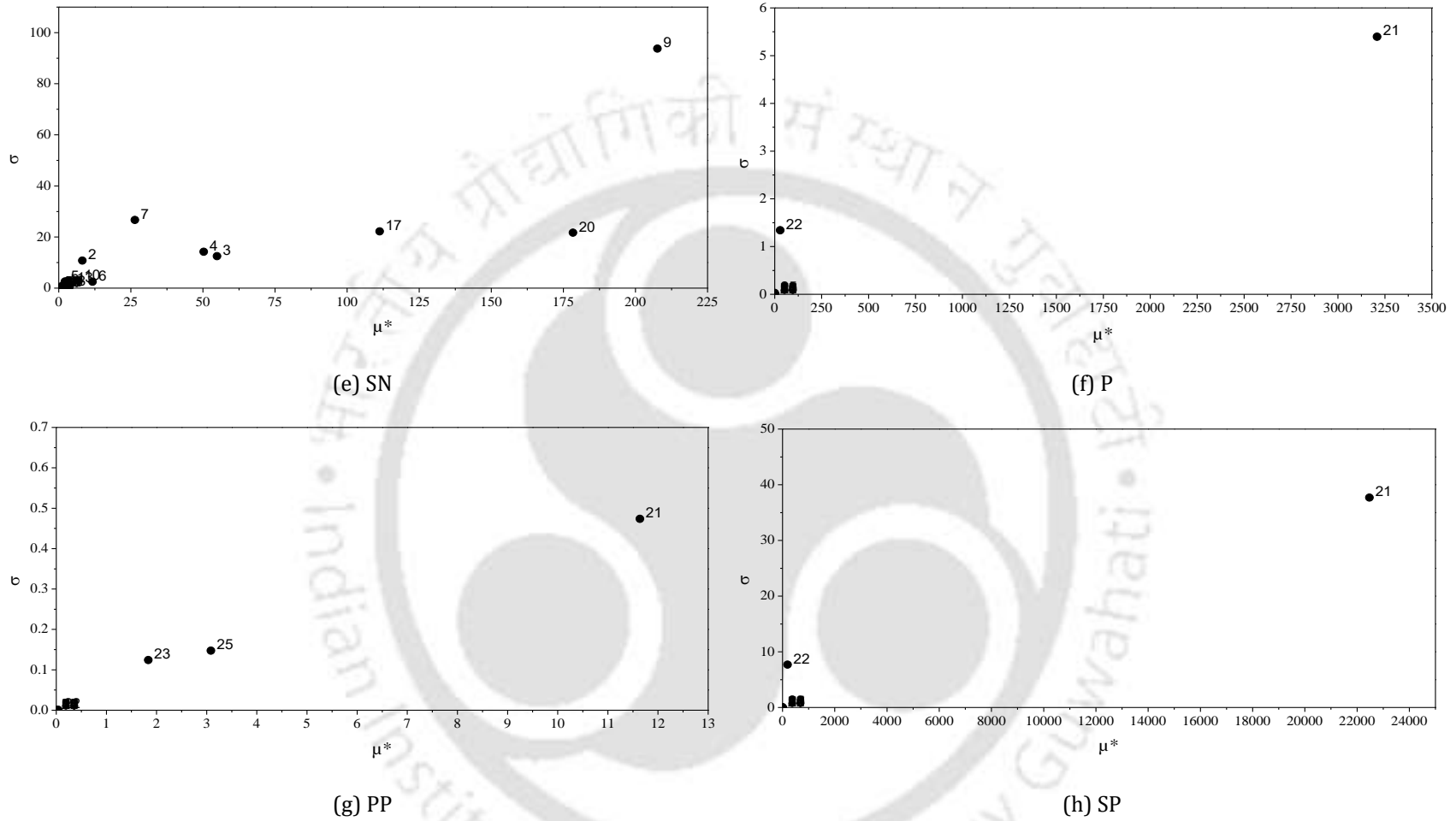
(b) NH<sub>3</sub>N



(c) NO<sub>3</sub>N



(d) PN



- |               |              |                   |                  |               |               |               |                 |                |              |
|---------------|--------------|-------------------|------------------|---------------|---------------|---------------|-----------------|----------------|--------------|
| 1. $K_1$      | 2. $K_2$     | 3. $\mu_{max,20}$ | 4. $R_{am}$      | 5. $\theta_1$ | 6. $\theta_2$ | 7. $\Gamma_b$ | 8. $R_{ndc}$    | 9. $\mu_n$     | 10. $Y_n$    |
| 11. $K_{nh}$  | 12. $K_{no}$ | 13. $\mu_{mpu1}$  | 14. $\mu_{mpu2}$ | 15. $K_{p1}$  | 16. $K_{p2}$  | 17. $R_{nrs}$ | 18. $R_{dn,20}$ | 19. $\theta_3$ | 20. $R_{ns}$ |
| 21. $R_{prs}$ | 22. $R_{ps}$ | 23. $\mu_{mppu}$  | 24. $K_{p3}$     | 25. $R_{pdc}$ |               |               |                 |                |              |

Fig. 9. 2. Analysis of elementary effects of different state variables in relation to different parameters.

Similarly, Fig. 9. 2b suggests that  $\mu_n$  has the highest impact for ammonia nitrogen in the water, accounting for the maximum variability with respect to other parameters. In contrast,  $R_{am}$  and  $r_b$  have a considerably high standard deviation compared to the absolute mean, indicating non-linear behaviour involving interactions with other input parameters. Similar trends are represented for nitrate nitrogen (Fig. 9. 2c), where  $\mu_n$  plays a significant role in the variability of the input parameters, compared to other input factors, while other factors have negligible effects on the variability. However, for plant nitrogen, there exist two factors,  $\mu_{mpu1}$  and  $\mu_{mpu2}$ , which show significant influence as compared to other parameters (Fig. 9. 2d). This shows that the maximum uptake by plants for both ammonia and nitrate respectively play a significant role in the variability of the input parameters, while other factors have negligible influence. Fig. 9. 2e represents the effects of sediment nitrogen in relation to other parameters.  $\mu_n$  is the only parameter that shows a non-linear effect on the variability of the parameter.  $R_{ns}$  and  $R_{nrs}$  show higher mean values with a small standard deviation range, which indicates a linear and additive effect on the variability. Total phosphorus in water and sediment phosphorus (Fig. 9. 2f and g) show similar behaviours for all the corresponding parameters where  $R_{prs}$  significantly influence the variability. On the other hand, the elementary effects on plant phosphorus indicate that  $R_{pdc}$  and  $\mu_{mppu}$  show a linear influence while  $R_{prs}$  shows a non-linear influence with other input parameters.

### 9.3. Calibration and validation of the model

Based on the sensitivity analysis of the one-dimensional ecological model, calibration of different parameters was carried out using the first twelve months of the sampling data. The calibrated model was then validated with the remaining five months of the dataset. The outcomes of the model for both calibration and validation are presented in the subsequent sections.

The initial values of the state variables used in the model during calibration are given in Table 9. 1. The values of the state variables are expressed in  $g\ m^{-2}\ day^{-1}$ . The area of the lake was calculated as 7838389.42  $m^2$  from ArcMap 10.2

#### 9.3.1. Calibration

The calibrated values of the parameters are shown in Table 9. 2, along with the literature range obtained from different sources. The outcomes of the model during calibration are discussed subsequently.

**Table 9. 1.** Initial values of the state variables used in the model.

State variable	Description	Value	Units
OrgN	Organic Nitrogen in the water column	22.23	g/m <sup>2</sup> /day
NH <sub>3</sub> N	Ammonia nitrogen in water column	4.27	g/m <sup>2</sup> /day
NO <sub>3</sub> N	Nitrate nitrogen in the water column	0.55	g/m <sup>2</sup> /day
PN	Total nitrogen in plants	1.59	g/m <sup>2</sup> /day
SN	Total Nitrogen in sediments	7.12	g/m <sup>2</sup> /day
P	Total phosphorus in water column	0.48	g/m <sup>2</sup> /day
PP	Total phosphorus in plants	0.02	g/m <sup>2</sup> /day
SP	Total phosphorus in sediments	0.21	g/m <sup>2</sup> /day

- *Organic Nitrogen in the water column*

Observed average organic Nitrogen in the water column decreases in the winter season and rises as the monsoon approaches and peaks in the month of August 2018 (304<sup>th</sup> day). The simulated average organic Nitrogen in the water column has been able to mimic such a trend (Fig. 9. 3a). The reaction rates involved in the sub-model also behave in a similar manner as the simulated average organic nitrogen trend. The decay rate of plant nitrogen has the least effect on the organic nitrogen sub-model, as seen from the figure.

- *Ammonia nitrogen in the water column*

Observed average ammonia nitrogen in the water column reduces to the minimum in the month of May 2018 (212<sup>th</sup> day), beyond which it rises again. The one-dimensional ecological model has been largely successful in following a similar trend (Fig. 9. 3b).

- *Nitrate nitrogen in the water column*

Observed average nitrate nitrogen in the water column remains considerably low until June 2018 (243<sup>rd</sup> day), beyond which it quickly spikes to high values in the months of July and August 2018. The simulated average nitrate nitrogen in the water column mimics this trend for most part of the trend (Fig. 9. 3c). In this state variable, nitrification and inflowing nitrate nitrogen significantly contributed to the simulated data variation, whereas plant uptake played a minimal role.

**Table 9.2.** Calibrated values of various parameters used in the model.

Parameter	Units	Description	Literature range	Source	Calibrated values
$\mu_{\max,20}$	day <sup>-1</sup>	Maximum growth rate of bacteria at 20°C	0.18	Ferrara and Harleman (1980)	0.157
$K_1$	g/m <sup>2</sup> /day	Ammonia uptake half saturation constant	0.32-56*	Mayo and Bigambo (2005)	0.3
$K_2$	g/m <sup>3</sup> /day	Nitrate uptake half saturation constant	2-15*	Mayo and Bigambo (2005)	0.2
$R_{\text{am}}$	day <sup>-1</sup>	Ammonification rate coefficient	0.0005-0.143	Martin and Reddy (1997)	0.125
$\theta_1$	-	Microbial growth temperature coefficient for ammonia	1.08-1.10	Metcalfe (2017)	0.995
$\theta_2$	-	Microbial growth temperature coefficient for nitrate	1.08-1.10	Metcalfe (2017)	0.98
$r_b$	day <sup>-1</sup>	Rate of reaction of plant-biofilm biomass	-	-	0.0168
$R_{\text{ndc}}$	day <sup>-1</sup>	Decay coefficient for plant nitrogen	-	-	0.83
$\mu_n$	day <sup>-1</sup>	Maximum nitrifying bacteria growth rate	0.33-2.21	Jørgensen and Bendoricchio (2001)	0.002
$Y_n$	mg VSS /mg N	Yield coefficient for nitrifying bacteria	0.03-0.13	Charley <i>et al.</i> (1980)	0.095
$K_{\text{nh}}$	g/m <sup>2</sup> /day	Ammonia nitrifying half saturation constant	-	-	0.9
$K_{\text{no}}$	g/m <sup>2</sup> /day	Oxygen half saturation constant	0.13-1.3*	Jorgensen <i>et al.</i> (1991)	1.2
$\mu_{\text{mpu1}}$	day <sup>-1</sup>	Maximum ammonia uptake rate by plants	-	-	0.00106992
$\mu_{\text{mpu2}}$	day <sup>-1</sup>	Maximum nitrate uptake rate by plants	-	-	0.00010962
$K_{\text{p1}}$	g/m <sup>2</sup> /day	Ammonia plant uptake half saturation constant	-	-	0.5
$K_{\text{p2}}$	g/m <sup>2</sup> /day	Nitrate plant uptake half saturation constant	-	-	0.6
$R_{\text{nrs}}$	day <sup>-1</sup>	Sediment nitrogen resuspension coefficient	0.085-0.112	Mayo <i>et al.</i> (2014)	0.0675
$R_{\text{dn},20}$	day <sup>-1</sup>	Rate constant of denitrification	0-1	Bacca and Arnett (1976)	0.05
$\theta_3$	-	Microbial growth temperature coefficient for denitrification	1.08-1.10	Metcalfe (2017)	1.02
$R_{\text{ns}}$	day <sup>-1</sup>	Settling rate coefficient of organic nitrogen	-	-	0.03354
$R_{\text{prs}}$	day <sup>-1</sup>	Sediment phosphorus resuspension coefficient	-	-	0.0001245
$R_{\text{ps}}$	day <sup>-1</sup>	Settling rate coefficient of total phosphorus	0.1-0.5	Lung <i>et al.</i> (1976)	0.000024
$\mu_{\text{mppu}}$	day <sup>-1</sup>	Maximum phosphorus uptake rate by plants	-	-	0.0009285
$K_{\text{p3}}$	g/m <sup>2</sup> /day	Phosphorus plant uptake half saturation constant	-	-	0.585
$R_{\text{pdc}}$	day <sup>-1</sup>	Decay coefficient of plant phosphorus	-	-	0.000645

\* The parameter in literature is reported in g/m<sup>3</sup>

- *Plant nitrogen*

The simulated average plant nitrogen in Deepor Beel showed a high correlation with the observed average plant nitrogen (Fig. 9. 3d). The reaction rates involved in the sub-model are relatively meagre compared to those involved in other sub-models. The decay rate of plant nitrogen appears to be constant compared to ammonia and nitrate uptake rates which dominate the slight variations observed in the simulated data.

- *Sediment nitrogen*

Simulated average sediment nitrogen in Deepor Beel is assumed to be regulated by two reaction rates: settling rate of organic Nitrogen and ammonia regeneration rate. Using this simple assumption, the one-dimensional ecological model has been mostly successful in predicting the variation of observed average sediment nitrogen (Fig. 9. 3e). The reaction rates involved in the sub-model appears to mimic the variation of simulated data.

- *Total phosphorus in the water column*

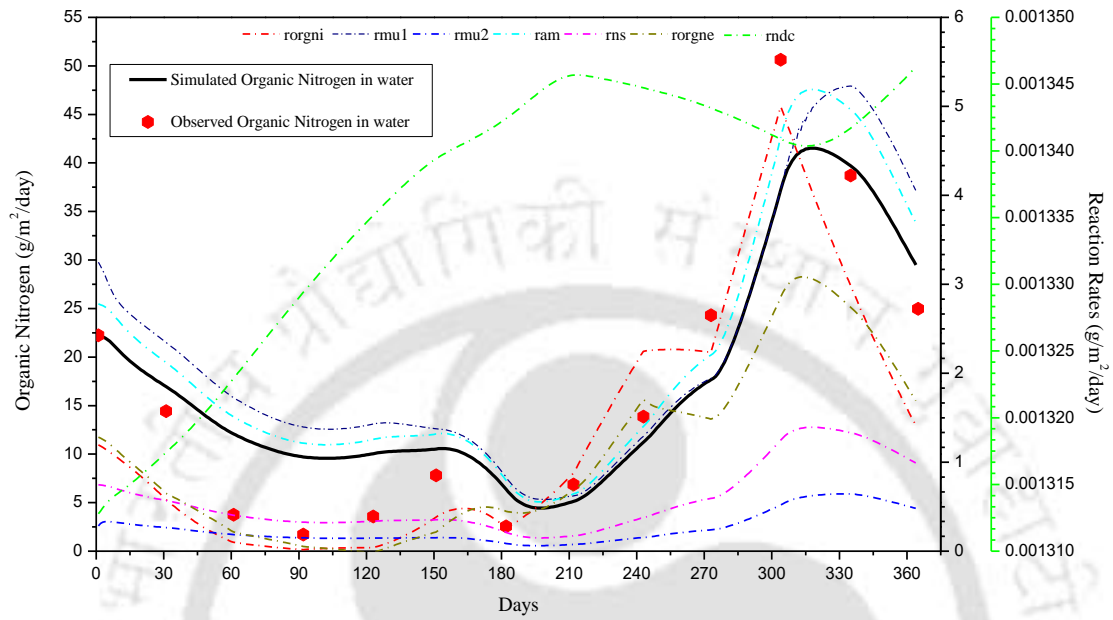
The observed average total phosphorus in the water column remained low in the initial simulation period until May 2018 (212<sup>th</sup> day), beyond which it spiked rapidly to reach the highest observed average total phosphorus concentration in the month of July 2018 (273<sup>rd</sup> day). The simulated average total phosphorus in the water column was able to replicate such variation with decent accuracy (Fig. 9. 3f). This sub-model appears to be primarily affected by the in-flowing and outflowing concentrations of total phosphorus.

- *Plant Phosphorus*

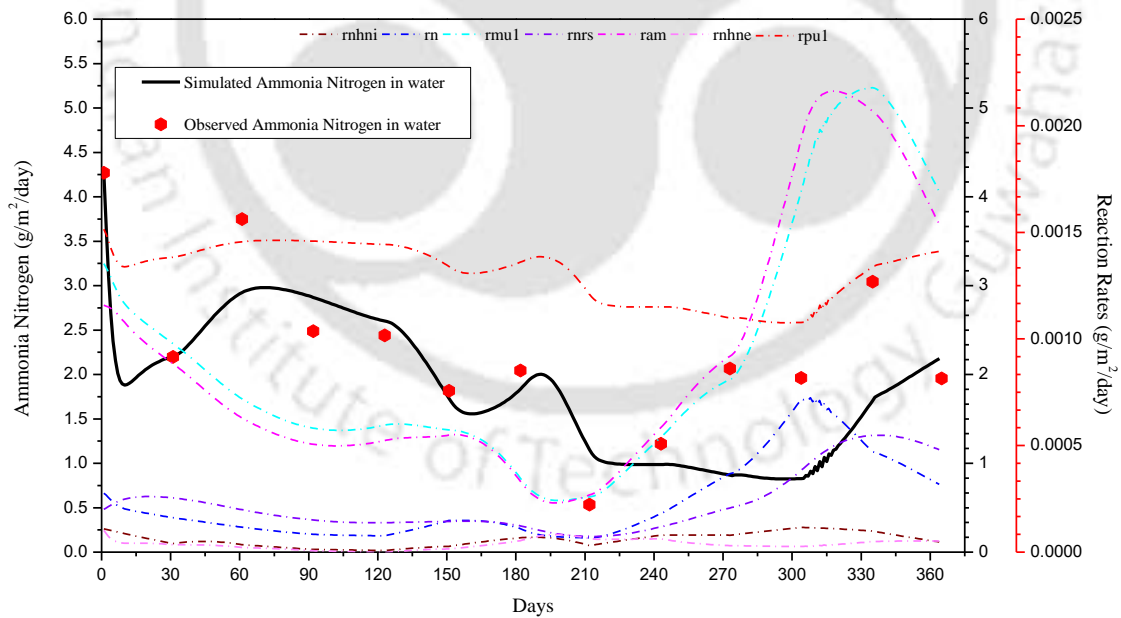
The simulated average plant phosphorus appears to correlate fairly with the observed average (Fig. 9. 3g). The reaction rates involved in the sub-model have very low values, due to which they failed to have any significant impact on other sub-models, but in this sub-model, both the reactions had equal dominance.

- *Sediment Phosphorus*

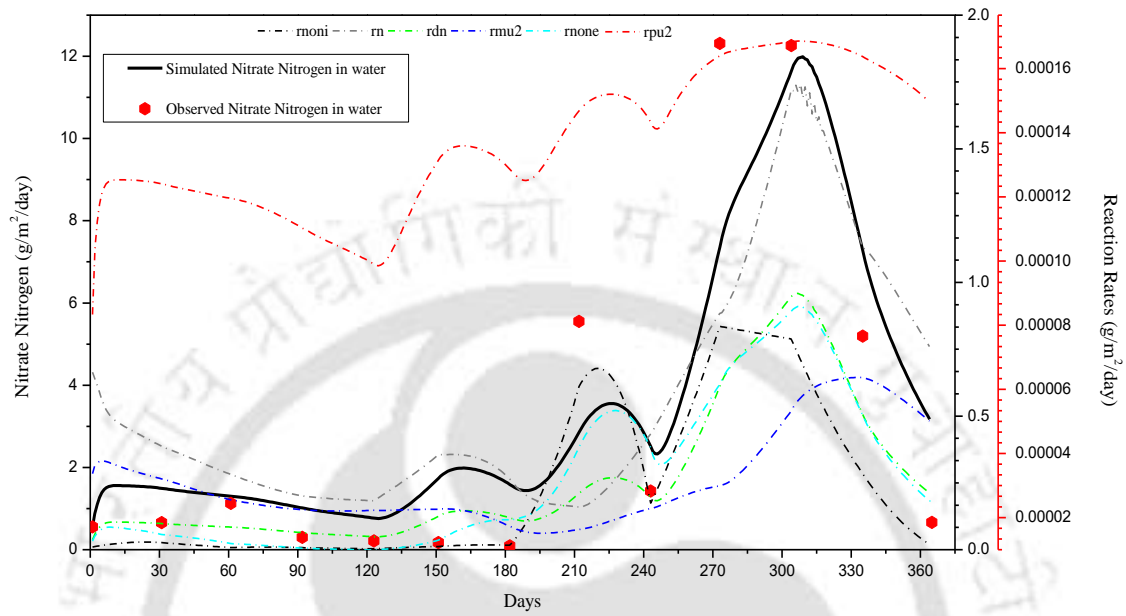
The observed average sediment phosphorus appears to rise rapidly post June 2018 (243<sup>rd</sup> day), successfully simulated by the one-dimensional ecological model (Fig. 9. 3h). In this state variable, the rate of settling of phosphorus plays a significant role in regulating the variation of the simulated data, but the delayed peak in the simulated reflects the considerable effect of sediment phosphorus resuspension rate.



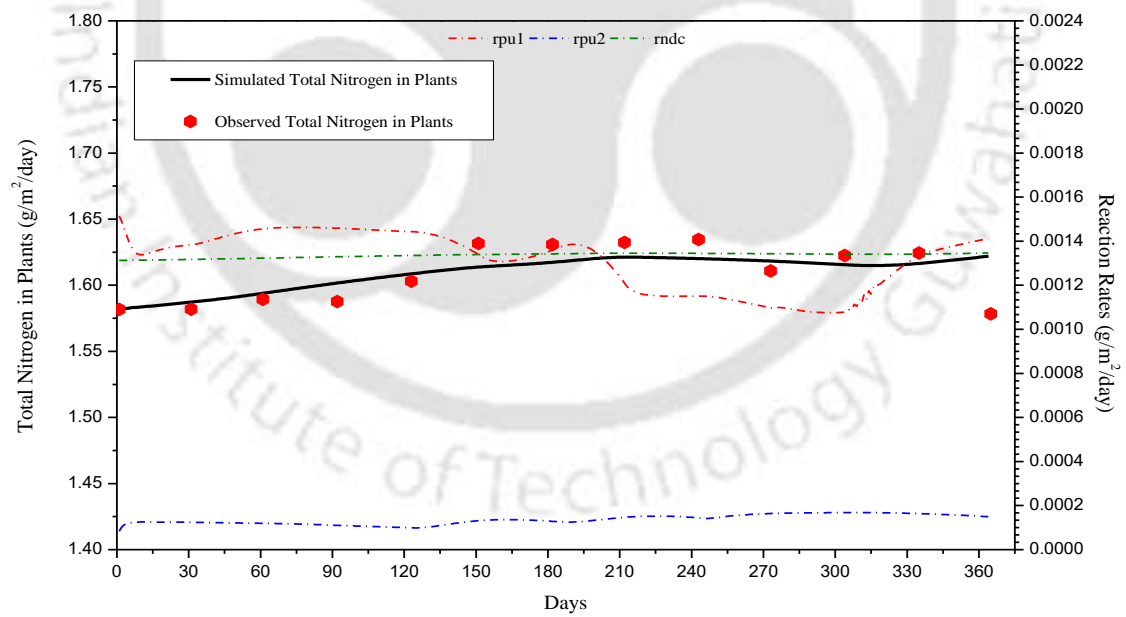
(a) OrgN



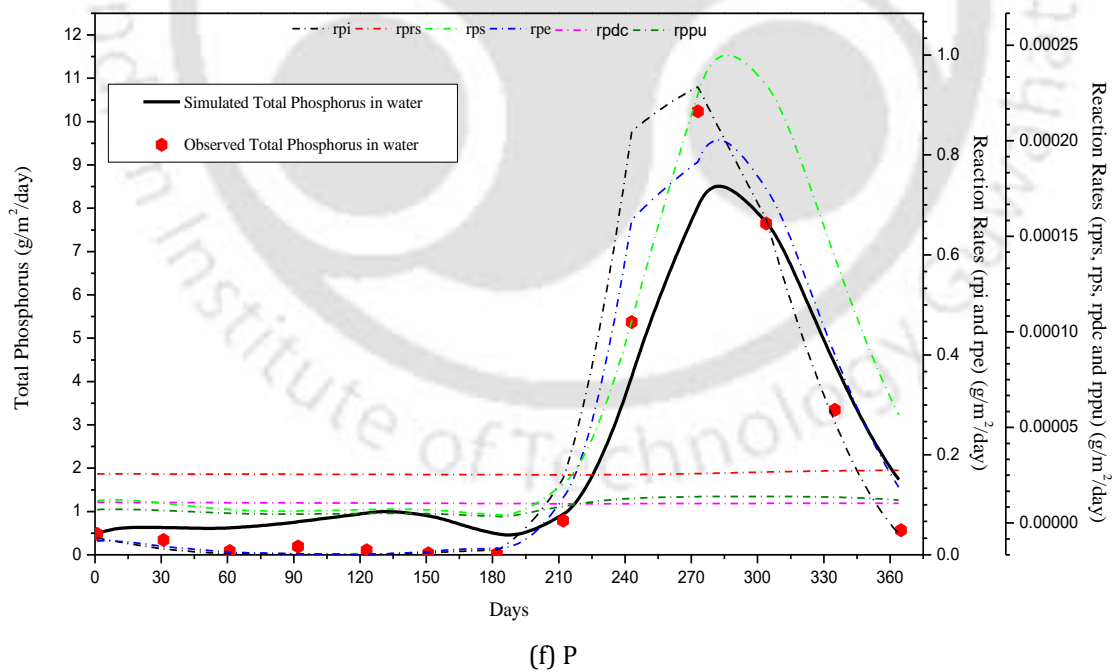
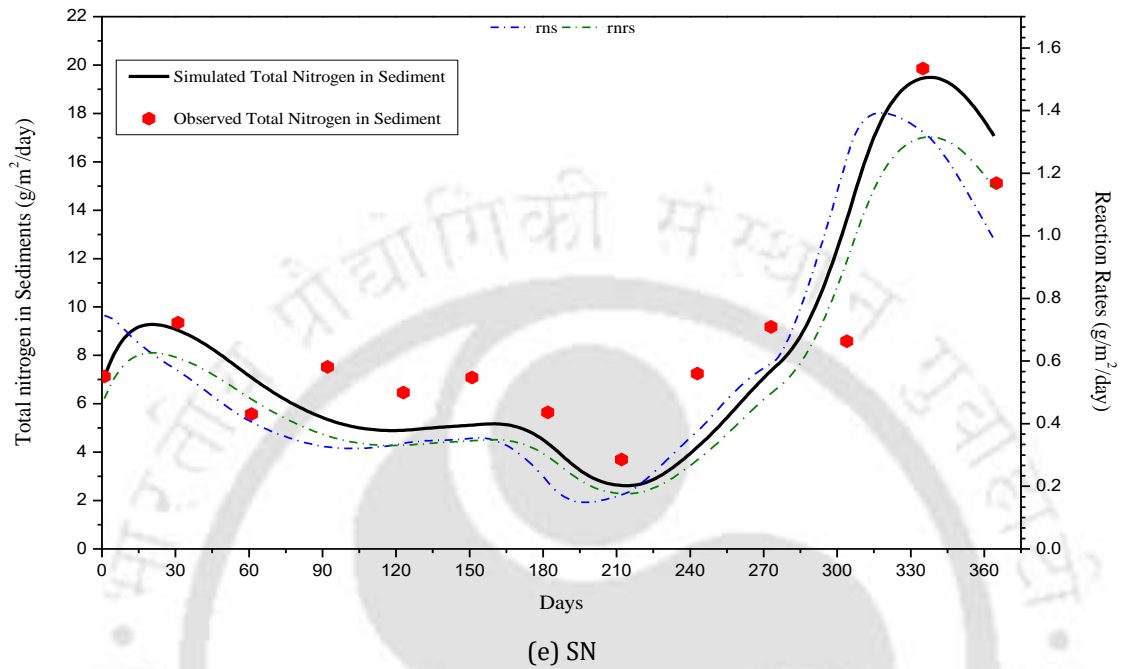
(b)  $\text{NH}_3\text{N}$

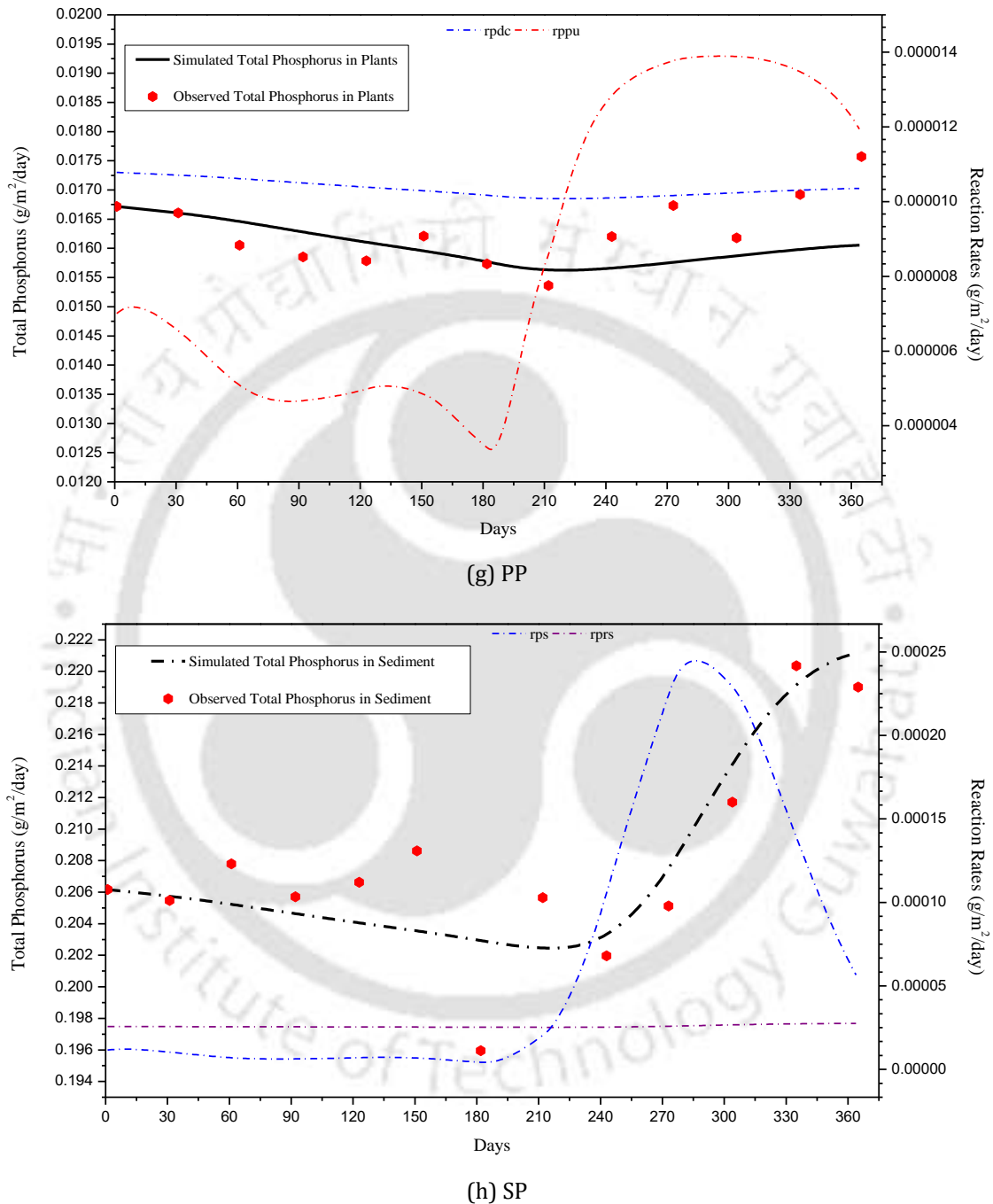


(c) NO<sub>3</sub>N



(d) PN





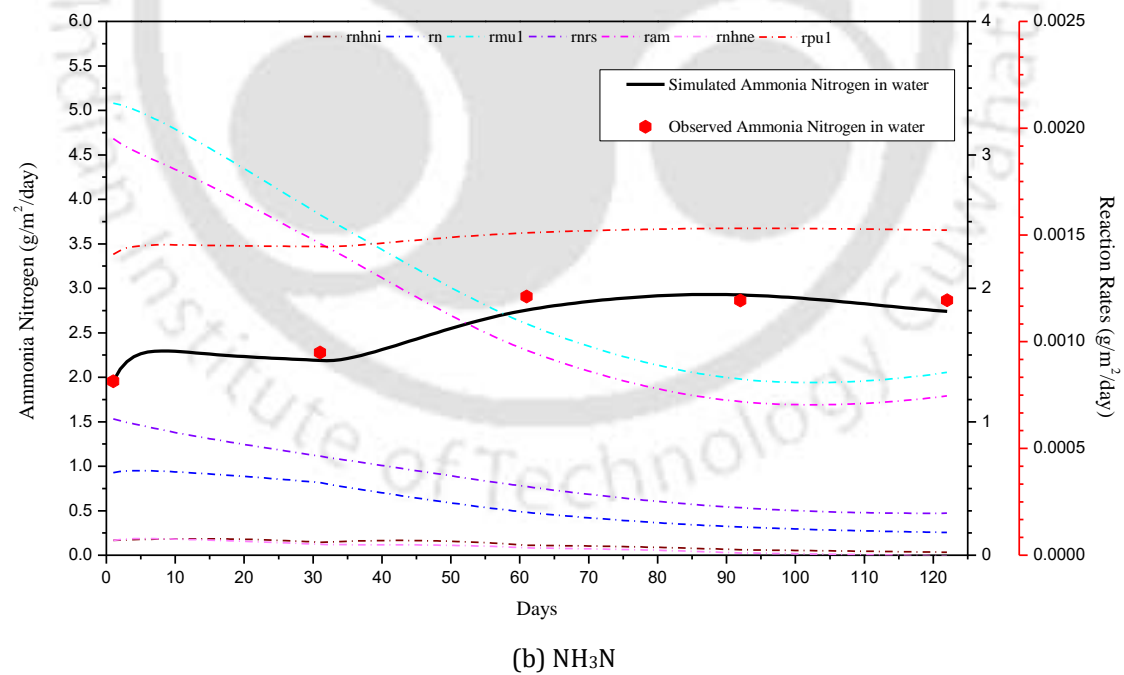
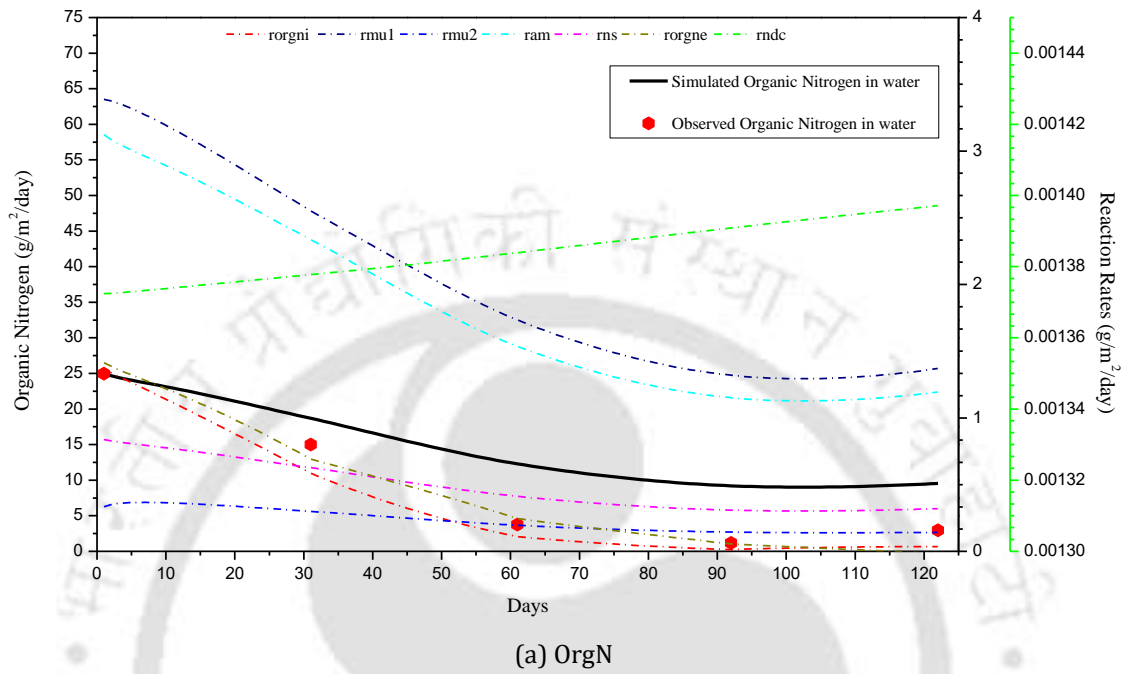
**Fig. 9. 3.** Simulated versus observed values of different parameters along with different reaction rates involved during the calibration of the model.

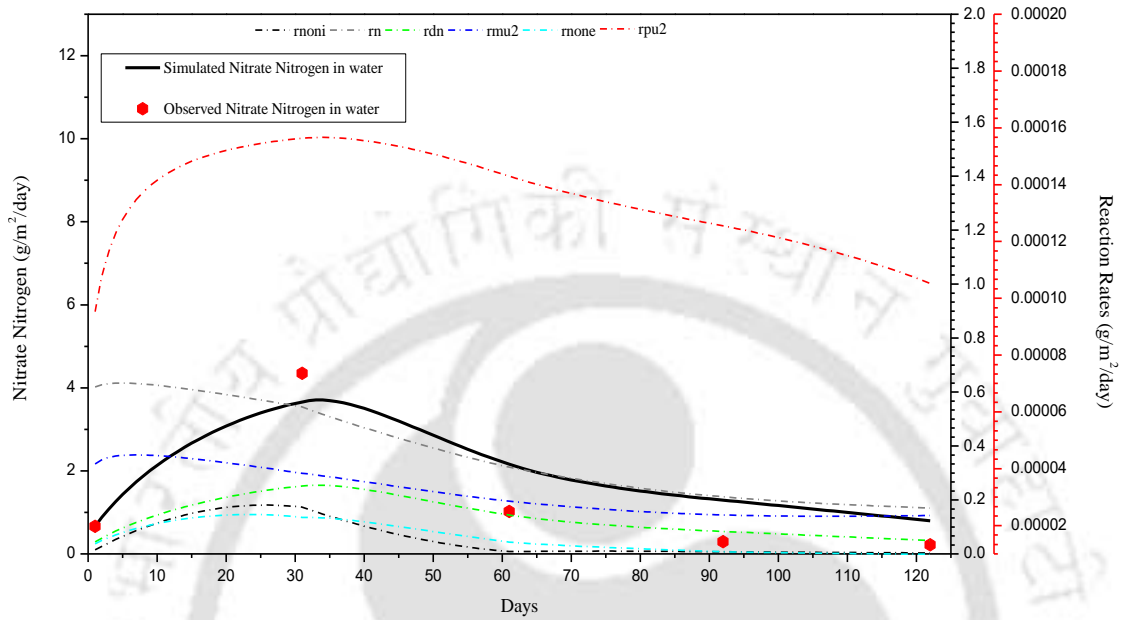
### 9.3.2. Validation

The one-dimensional ecological model was validated using the observed data from the last five months of sampling after the calibration process was completed. The output of the model during validation was then subjected to regression analysis to obtain the RMSE and Coefficient of determination ( $R^2$ ) values for each state variable (Table 9. 3). Good agreement was observed between the simulated data and observed data for all the state variables. Organic Nitrogen, ammonia nitrogen and total phosphorus in water showed a very high correlation ( $R^2 > 0.95$ ), while nitrate nitrogen, sediment nitrogen and plant nitrogen showed a slightly lower correlation ( $R^2 = 0.8$  to  $0.9$ ). Sediment phosphorus and plant nitrogen showed the least correlation among all the state variables ( $R^2 = 0.7705$  and  $0.6260$  respectively), but considering the natural system, such low values of correlation of determination are considered acceptable (Arhonditsis & Brett 2005). The outcomes of the model during validation are present in Fig. 9. 4 a-h.

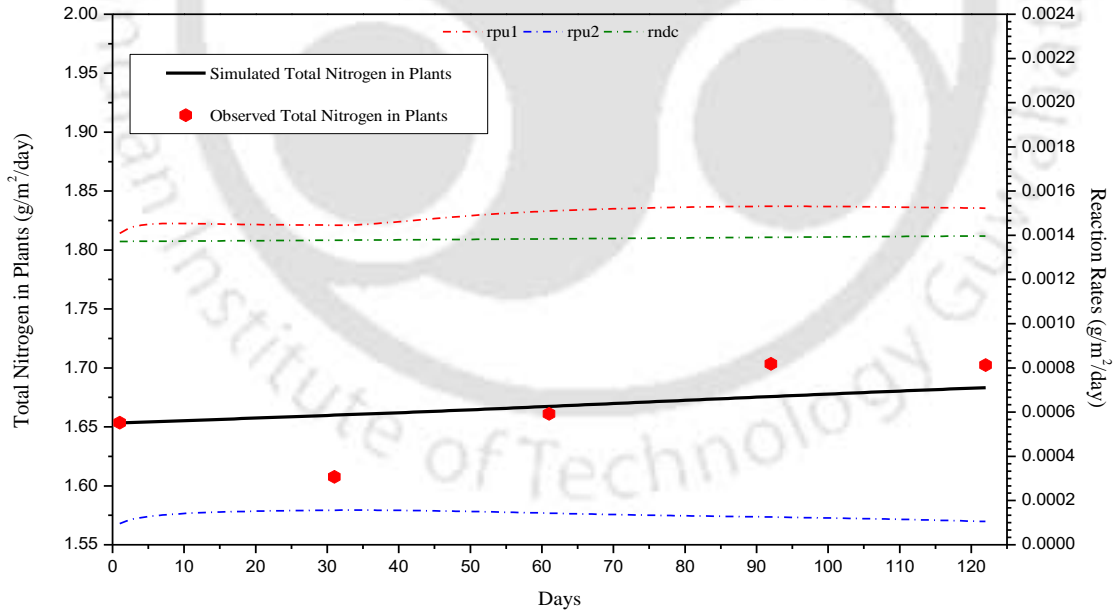
**Table 9. 3.** Goodness-of-fit statistics of the model validation.

State variable	RMSE	$R^2$
Organic Nitrogen in water column	0.9027	0.9867
Ammonia nitrogen in water column	0.1006	0.9563
Nitrate nitrogen in water column	0.5504	0.8515
Plant nitrogen	0.0085	0.6260
Sediment nitrogen	2.0220	0.8378
Total phosphorus in water column	0.0201	0.9979
Plant phosphorus	0.0001265	0.8378
Sediment phosphorus	0.1274	0.7705

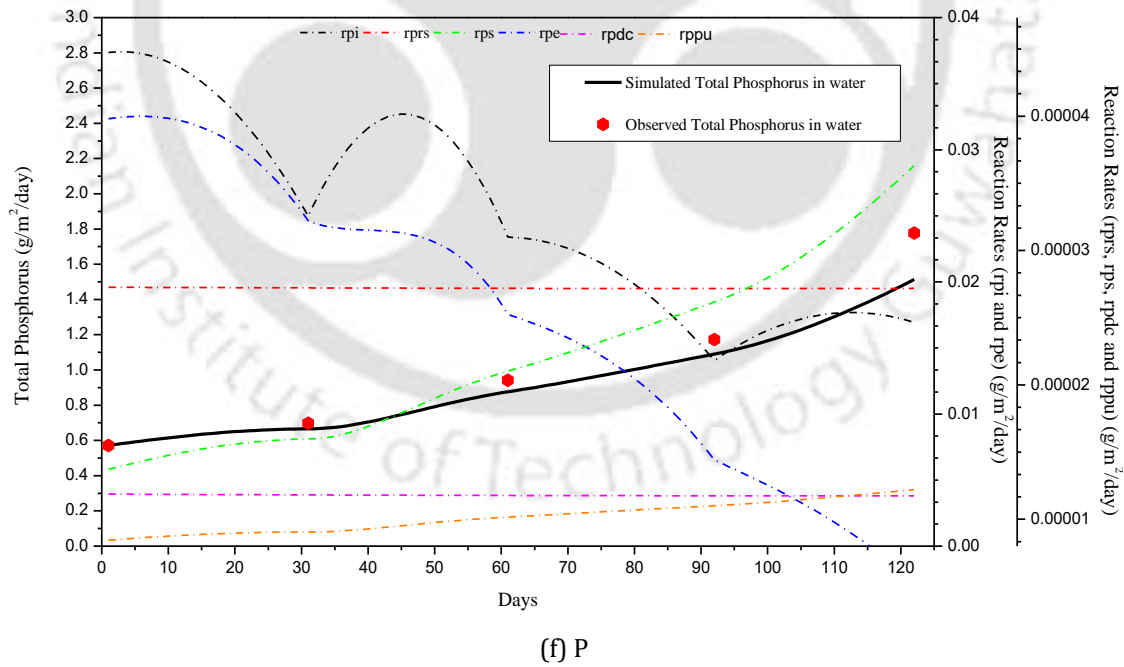
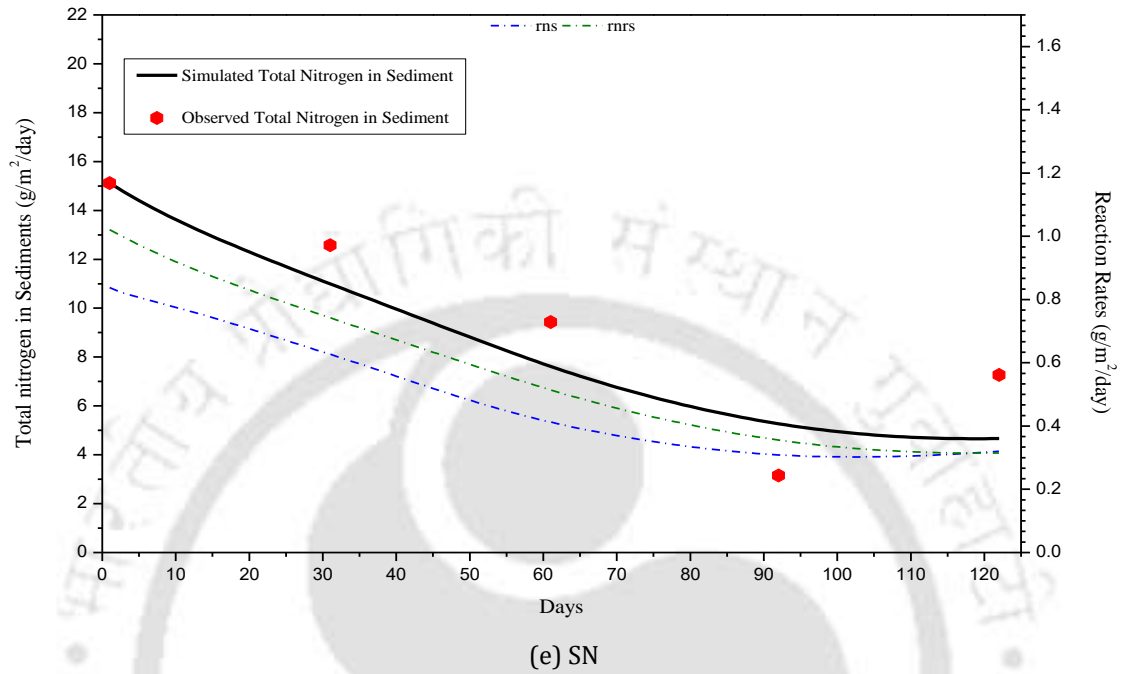


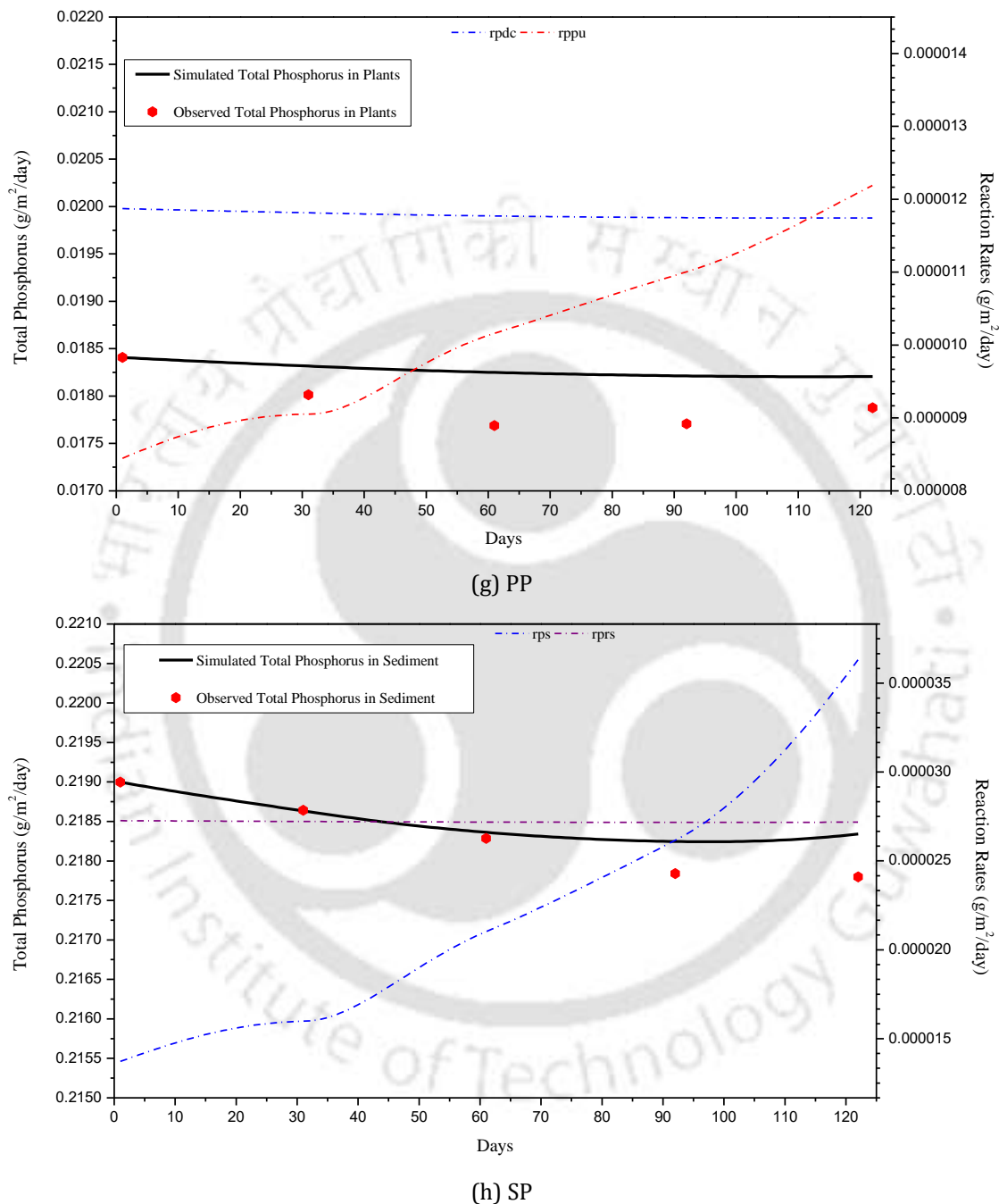


(c) NO<sub>3</sub>N



(d) PN





**Fig. 9. 4.** Simulated versus observed values of different parameters along with different reaction rates involved during the validation of the model.

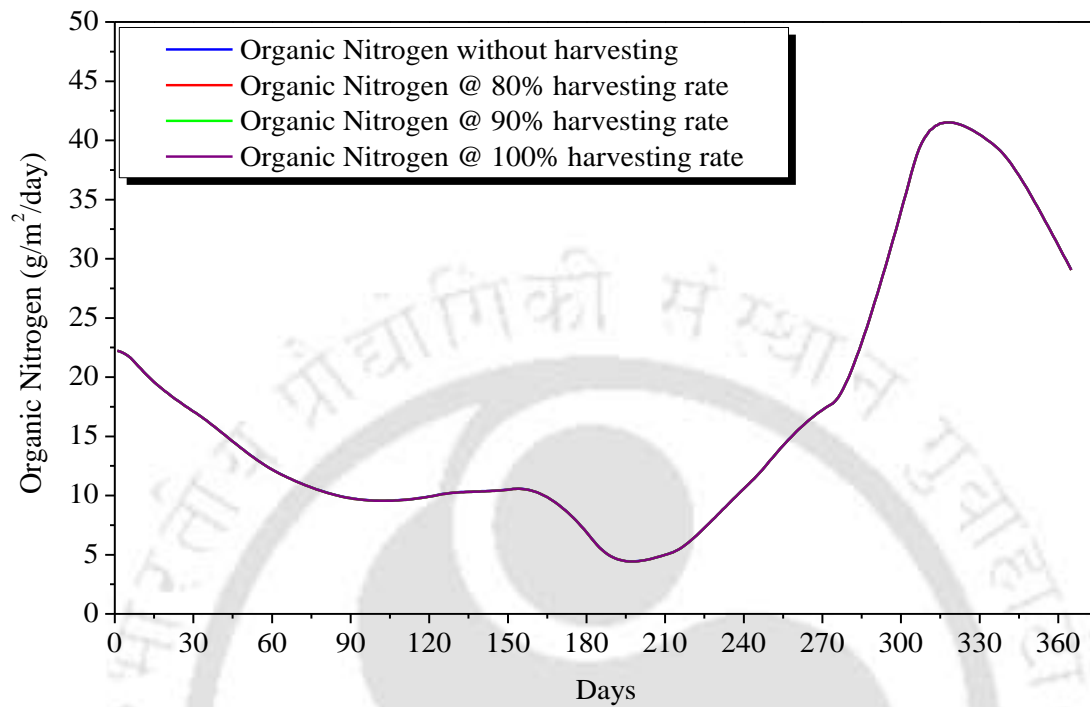
## 9.4. Management options for curbing eutrophication levels

The model validation provided insights regarding the appropriateness of the model; hence, it was thus used for two plausible options which may be regarded as highly likely for curbing the eutrophication levels in the wetland. The details of both the management options are as follows.

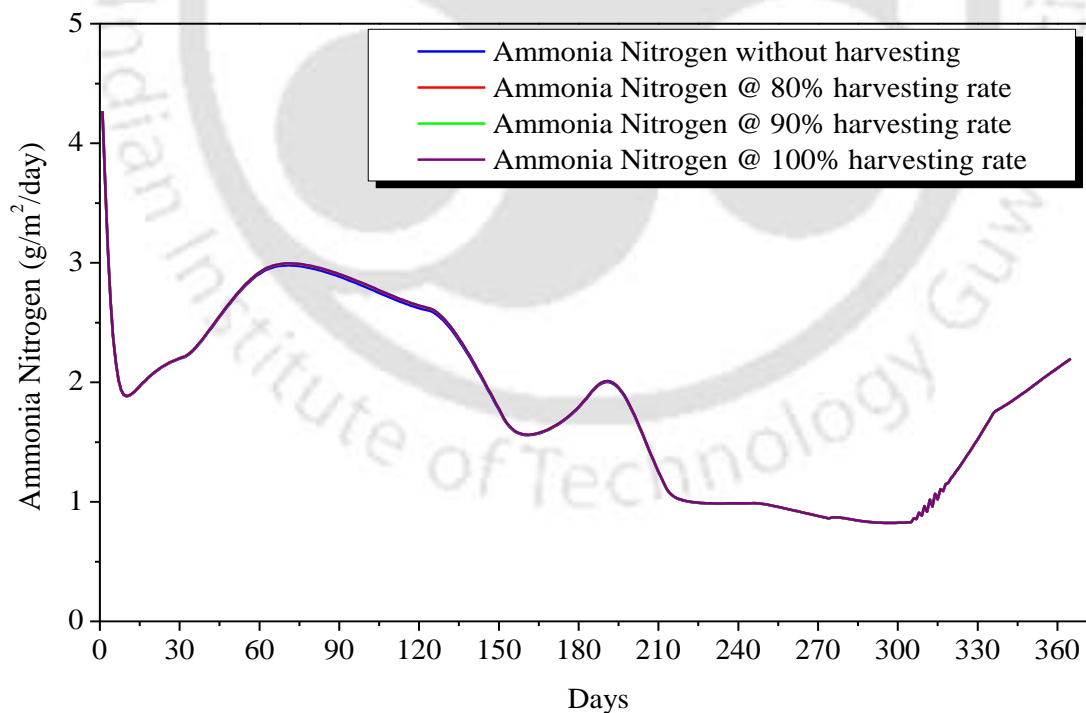
### 9.4.1. Plausible role of harvesting of plants in Deepor Beel

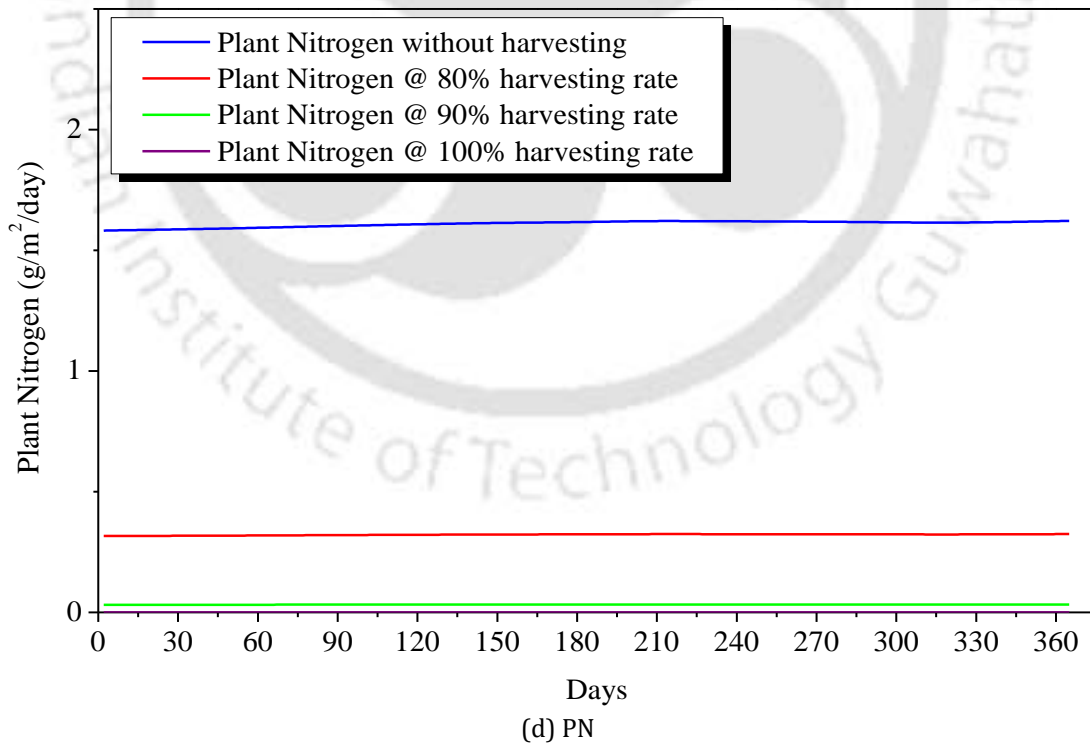
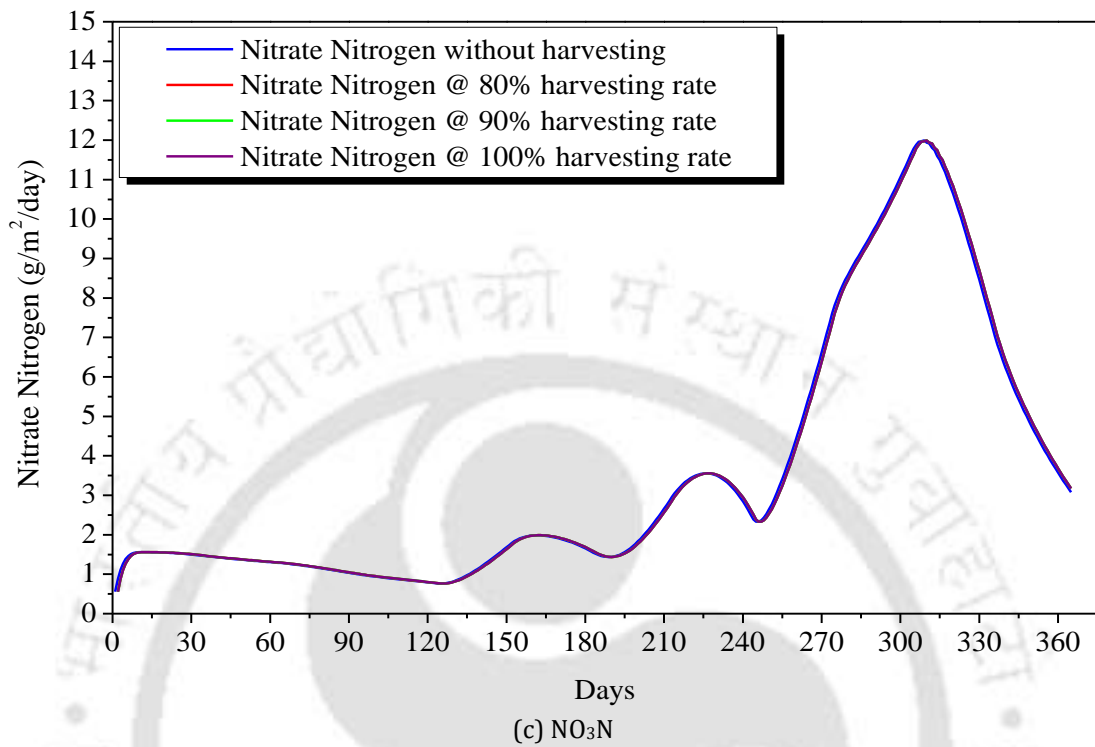
Water hyacinths play an essential role in the ecosystem of Deepor Beel as it controls water currents, partially removes pollutants and serves as food for the aquatic bio-phase. However, the rapid growth of these plants can create several problems such as physical hindrance to fishing and navigation, decrease in the euphotic zone in the lake and increase in the detritus layer. Consequently, harvesting of these plants as an attempt to control their proliferation has been consistently proposed across the globe, but such a method is usually costly and labour intensive (Sarika *et al.* 2014). In fact, harvesting water hyacinths is only a temporary solution, as pointed out by Sarika *et al.* (2014). The one-dimensional ecological model developed in this study is used to investigate the role of harvesting of these plants on the nutrient distribution in Deepor Beel and consequently comprehend the reasons for the transitory nature of harvesting in controlling the water hyacinths.

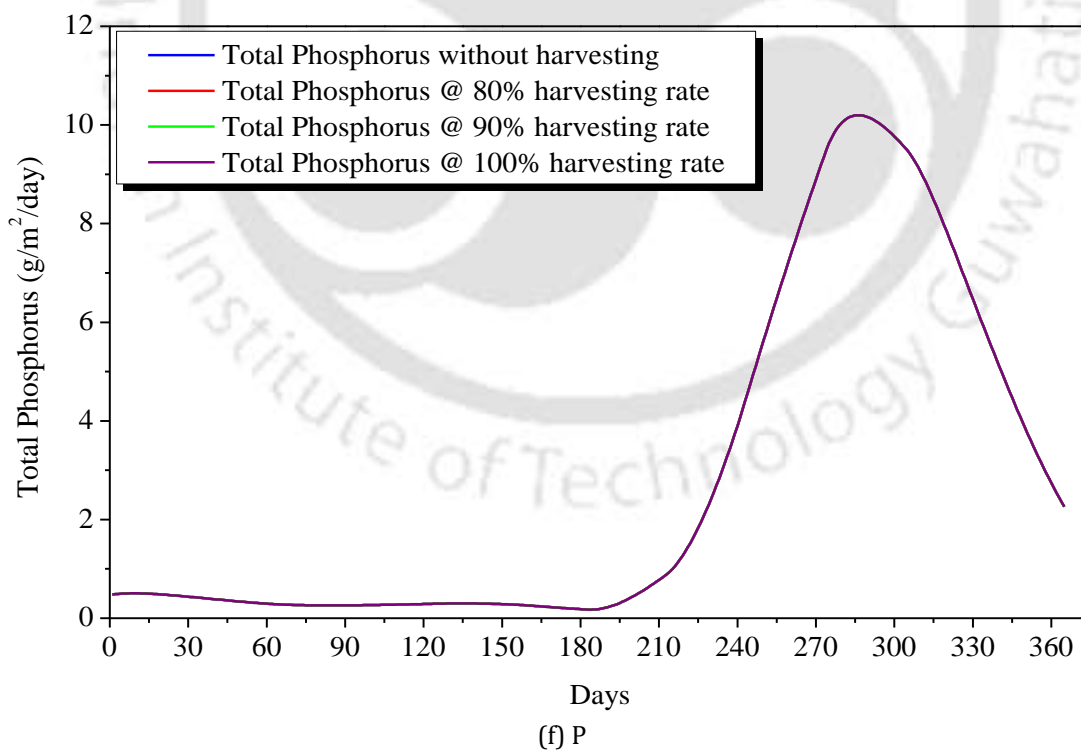
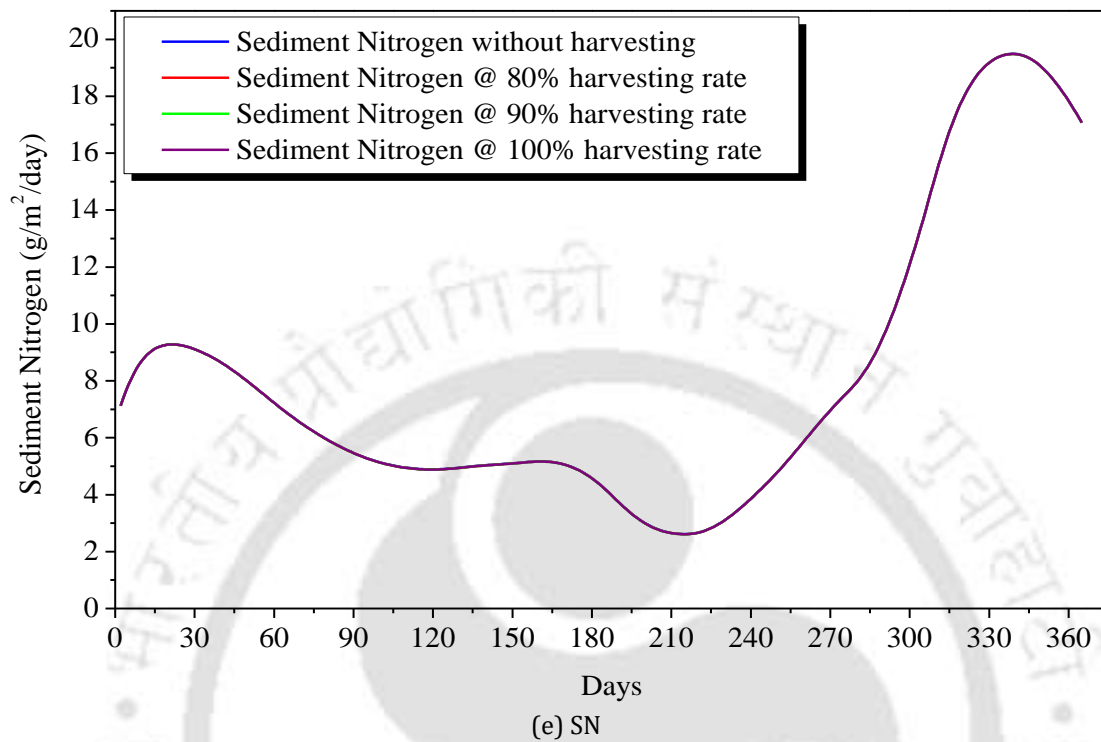
The effects of harvesting of water hyacinths in Deepor Beel on different types of nutrients are shown in Fig. 9. 5 a-h. The model was designed to check the behaviour of all the state variables when the plants in the lake were subjected to no harvesting as well as to three hypothetical harvesting rates of 80, 90 and 100%. As evident from the graphs, harvesting of plants had little effect on the nutrients in different levels except for plant nitrogen and plant phosphorus, which is evident as the removal of plants from the ecosystem will also remove the nitrogen and phosphorus compounds attached to it. The other state variables remain unaffected from harvesting as the rates of ammonia, nitrogen and phosphorus utilization by the plants for growth and rates of plant nitrogen and phosphorus decay are significantly low compared to other reaction rates involved in the respective sub-models. This also explains the temporary nature of the harvesting in weed control of water hyacinth. As the nutrients in the lake remain intact even after harvesting, barely removing the plants from the lake could not prevent the plants from resurfacing in the future. Therefore, harvesting plants in Deepor Beel will not be an effective measure in controlling the eutrophication in the lake.

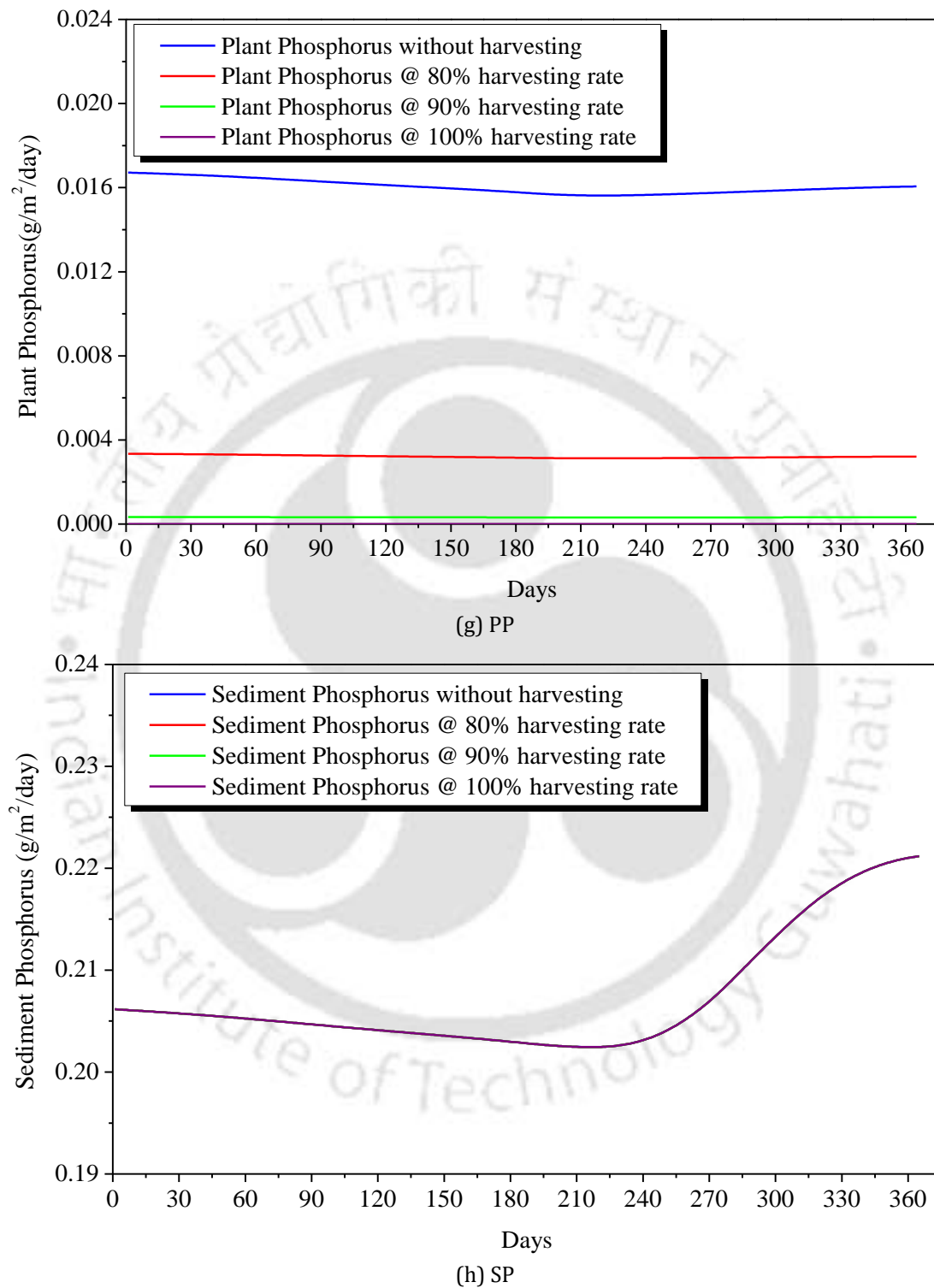


(a) OrgN

(b) NH<sub>3</sub>N







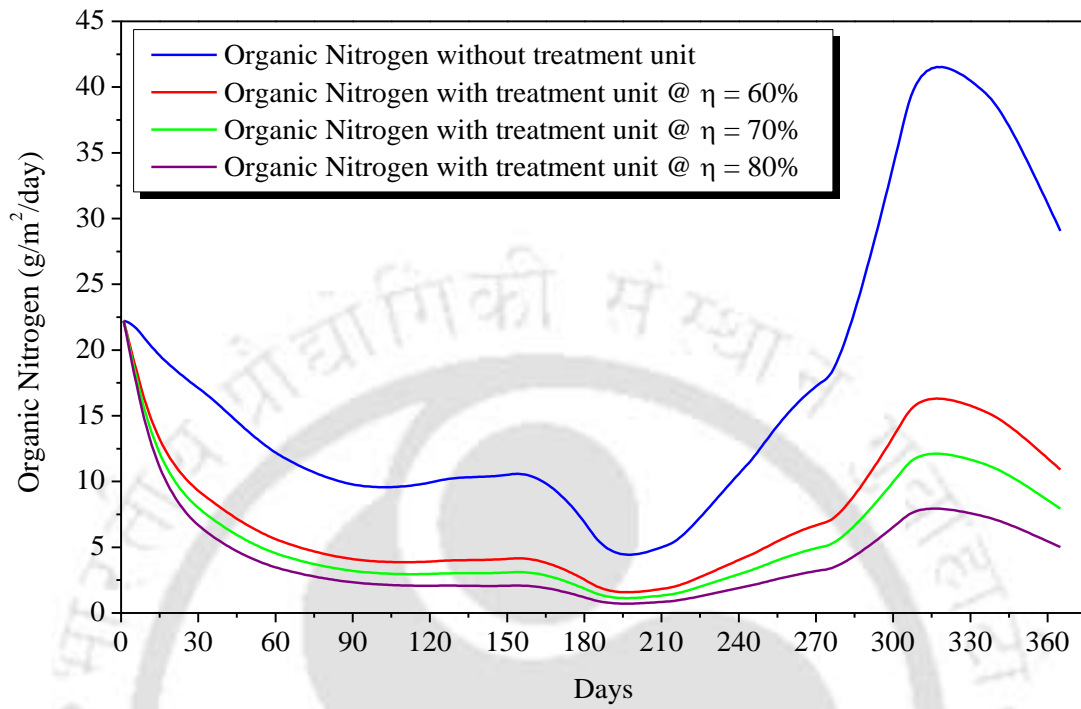
**Fig. 9. 5.** Plausible effects of harvesting at different harvesting rates on various parameters of the model.

#### 9.4.2. Plausible role of a treatment unit at the inlet of Deepor Beel

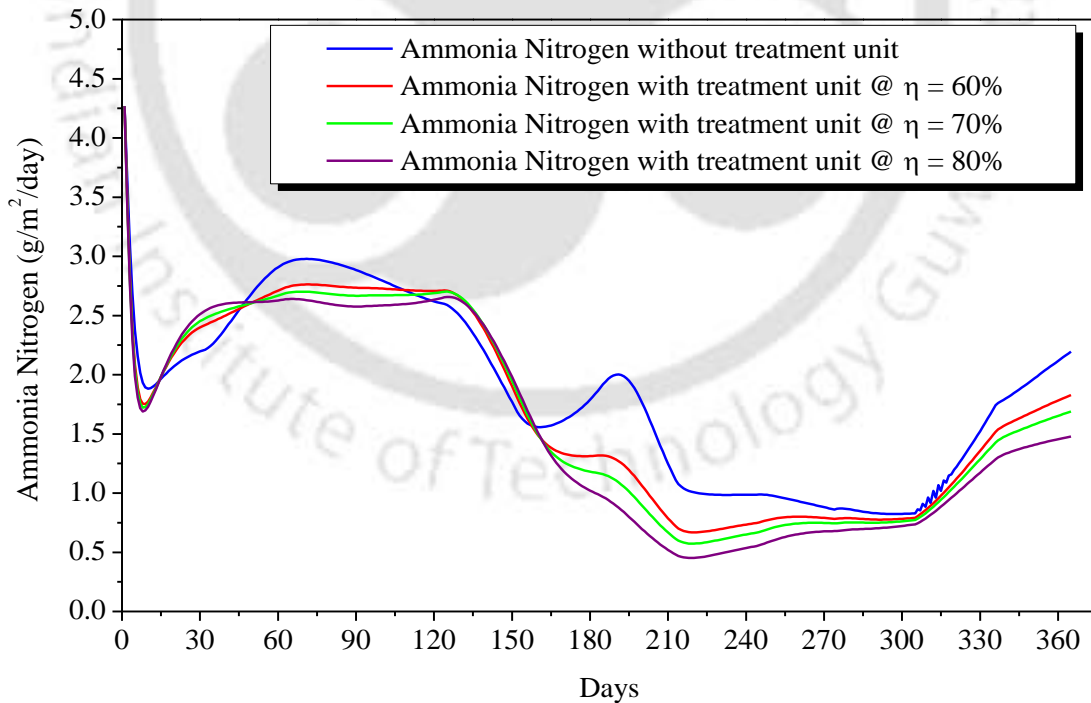
Eutrophication in Deepor Beel can be reduced if the nutrients flowing into the lake are reduced sufficiently to prevent excessive plant growth. One such way to reduce nutrients is by setting up a treatment unit that partially removes the nutrients from the water of the Basistha River. However, the efficiency of the treatment unit should be such that nutrients in the lake are not reduced beyond an optimum value resulting in poor functioning of the wetland. The one-dimensional ecological model developed in this study is used to inspect the effects of introducing a treatment unit in Deepor Beel as well as the role of treatment efficiency on all the state variables.

The treatment of inflowing water to Deepor Beel has a significant impact on the state variables of the one-dimensional ecological model (Fig. 9. 6 a-h). Organic Nitrogen in the lake rapidly decreases on introducing a treatment unit in the lake, and reduction further intensifies with higher treatment efficiencies (Fig. 9. 6a).

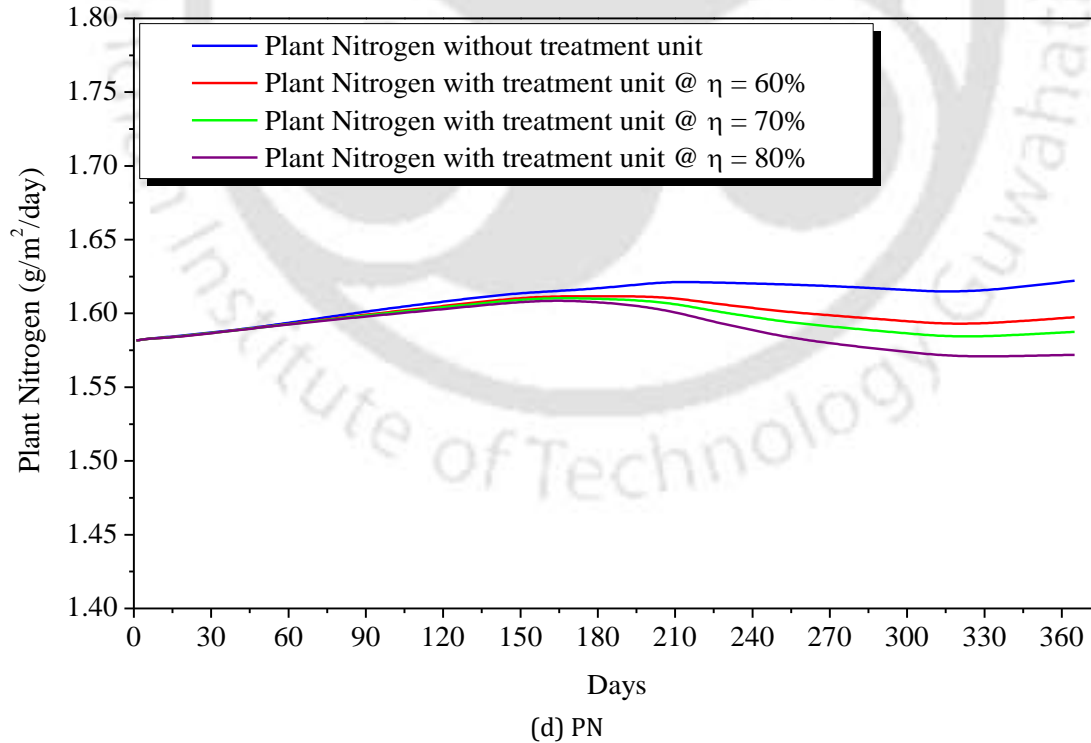
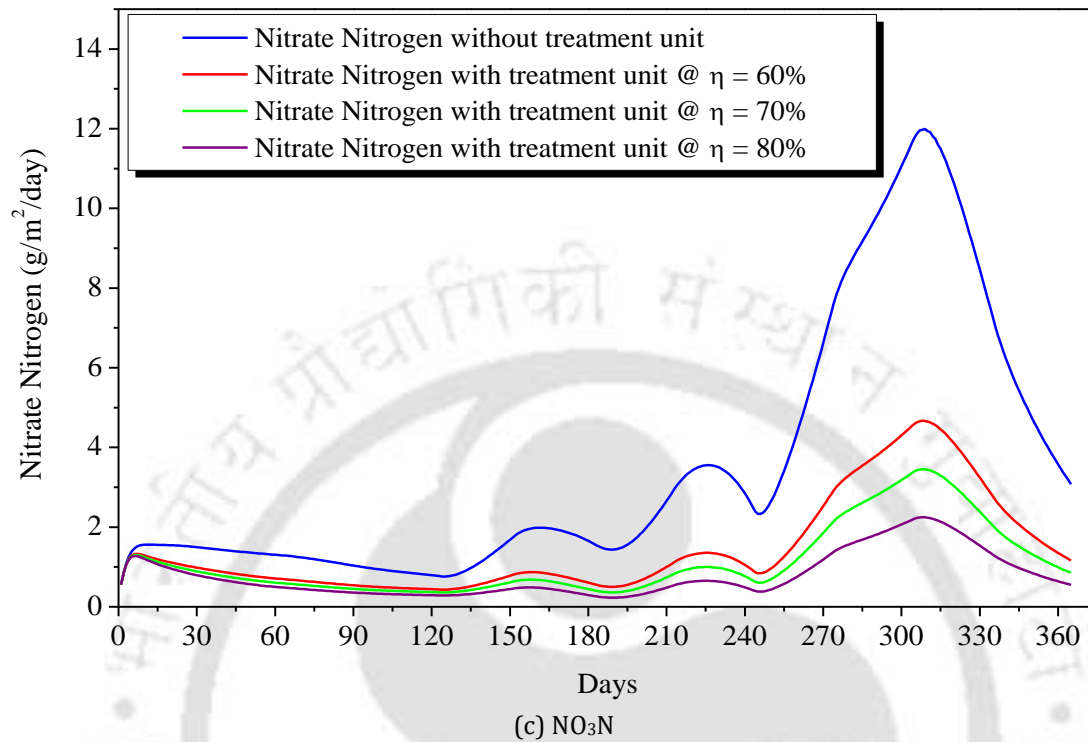
Ammonia nitrogen in the lake also decreases, but such decreases are not as drastic as organic nitrogen (Fig. 9. 6b). However, similar to organic nitrogen, ammonia nitrogen decreases more with an increase in treatment efficiency. Nitrate nitrogen in Deepor Beel also decreases rapidly, and increasing the treatment efficiencies leads to smoothening of the temporal variation of average nitrate nitrogen in Deepor Beel (Fig. 9. 6c). The treatment unit does not have any significant effect on plant nitrogen initially, but in the later part of the simulation, plant nitrogen shows a considerable incremental decrease with an incremental increase in treatment efficiency (Fig. 9. 6d). The widening gap between the trends of plant nitrogen without treatment and with treatment in the later simulation stages indicates a possibility of a permanent decrease in plant nitrogen in the future. The sediment nitrogen in Deepor Beel also decreases when a treatment unit is introduced in the lake, and further smoothenes when the treatment efficiency increases (Fig. 9. 6e). The phosphorus components also behave similarly to the nitrogen counterparts when a treatment unit is introduced in Deepor Beel (Fig. 9. 6 f-h).

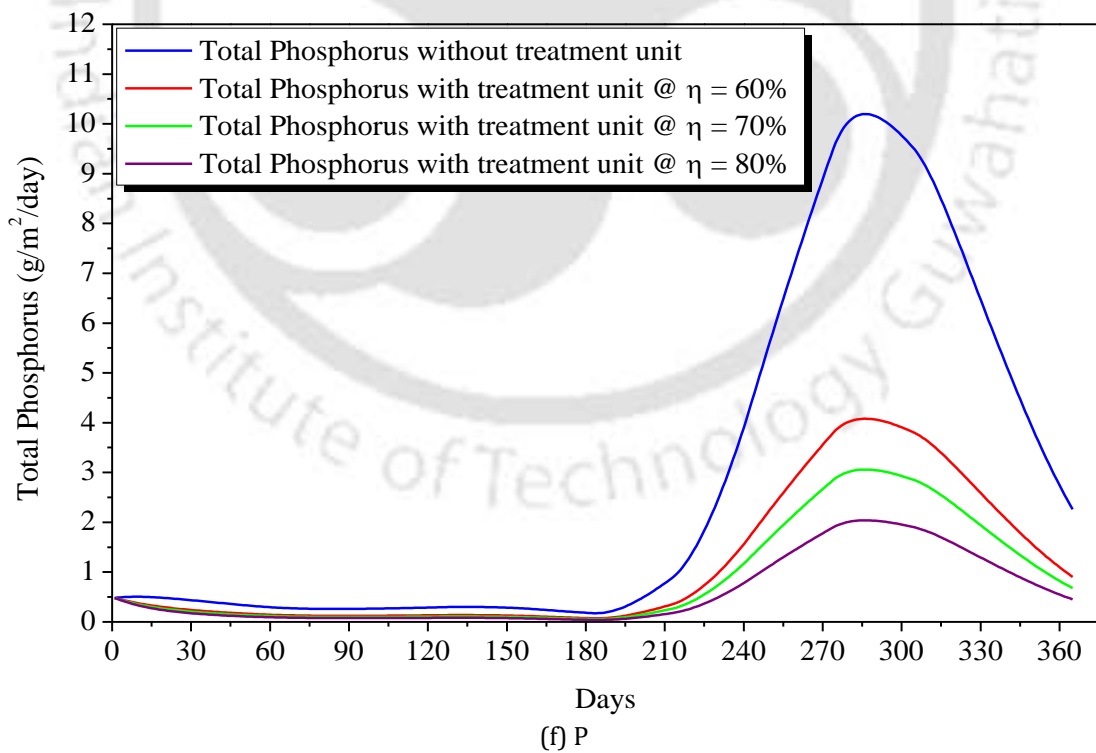
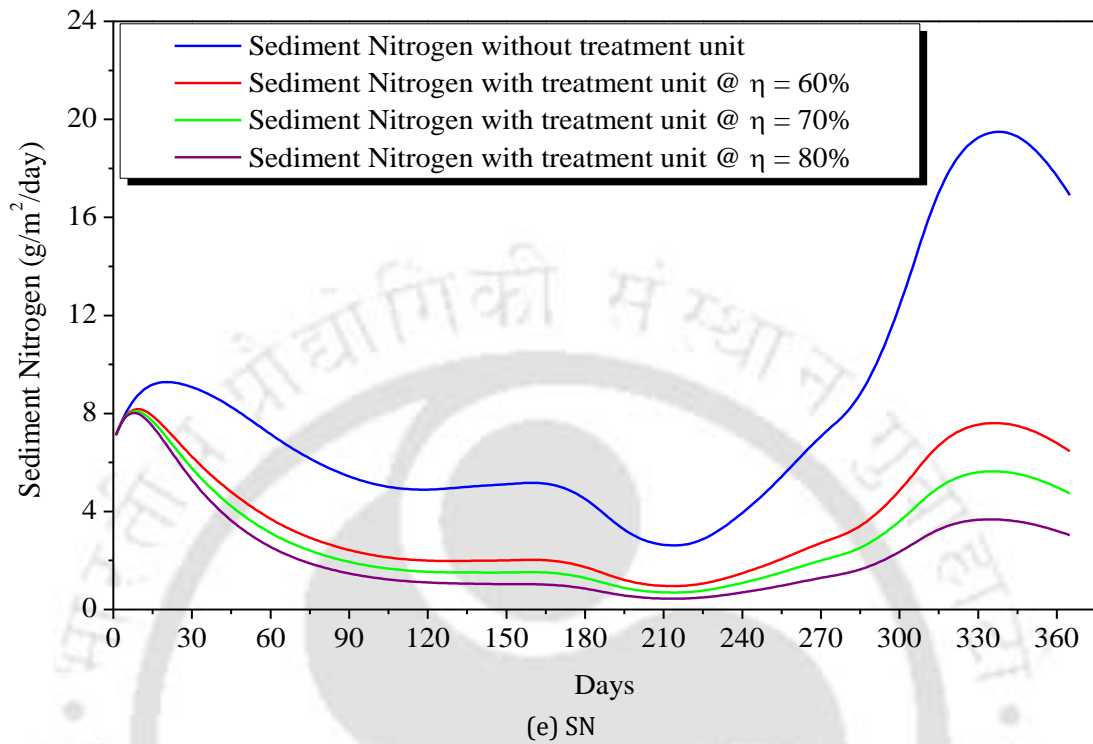


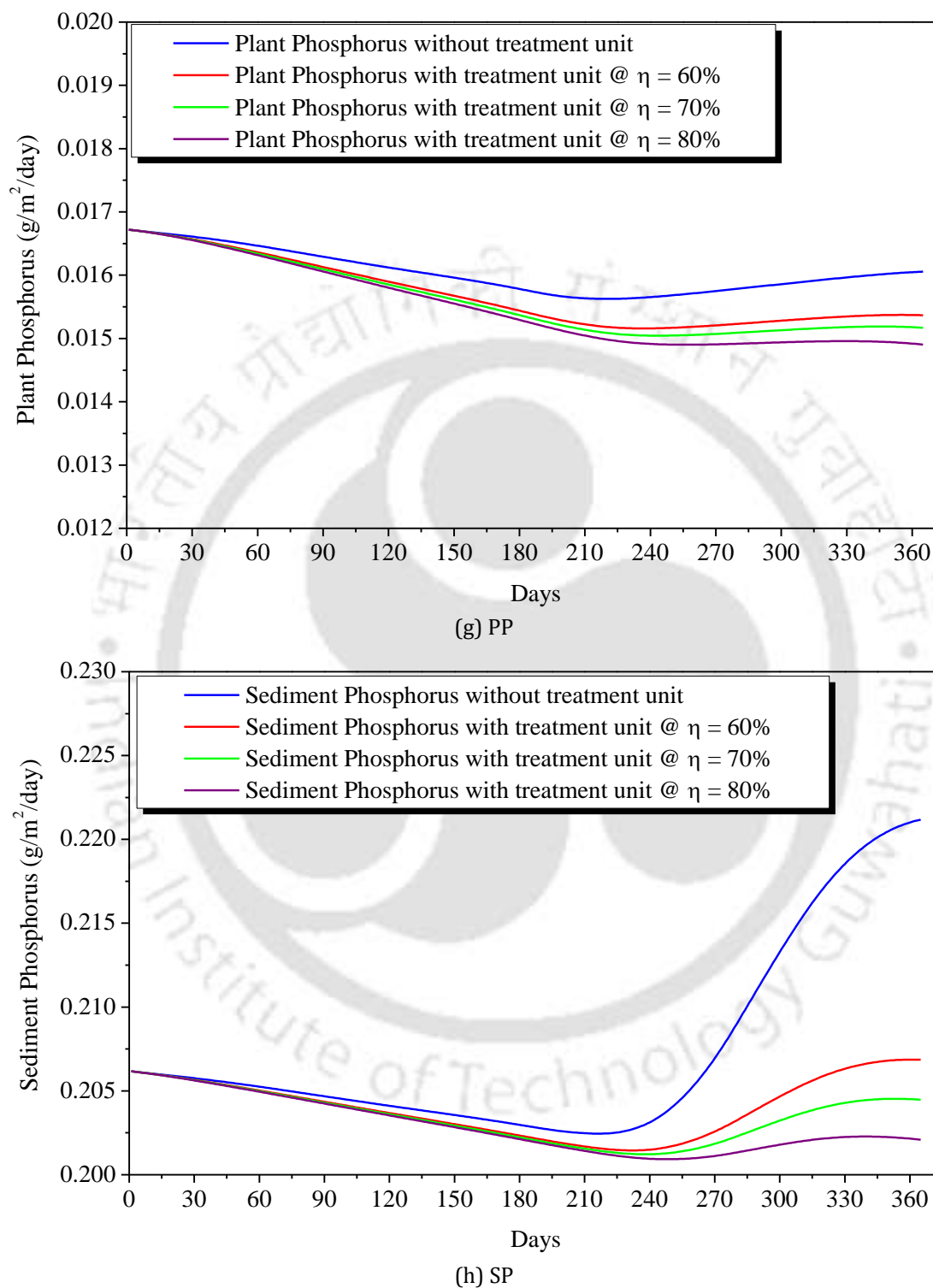
(a) OrgN



(b)  $\text{NH}_3\text{N}$







**Fig. 9. 6.** Plausible effects of a treatment unit at different removal efficiencies on various parameters of the model.

## 9.5. Summary

The present study was conducted to develop a one-dimensional ecological model for Deepor Beel to understand the fate of nutrients, thereby developing a better understanding of the eutrophication process in the wetland. The significant outcomes of this study are listed as follows:

- a. The one-dimensional ecological model developed in this study has successfully predicted the distribution of nutrients in different state variables identified in Deepor Beel. The RMSE and  $R^2$  values of all the state variables lay in the range 0.0001265-2.0220 and 0.6260-0.9979, respectively, during model validation and thereby substantiating the successful behaviour of the model.
- b. The calibrated model provided interesting insights into the behaviour of the state variables. It has eloquently highlighted that the rates of nutrient uptake by plants are considerably low to have any effect on the behaviour of the state variables other than those related to plants. The model has also explained the lesser dependence of the ammonia nitrogen state variable on the inflowing and outflowing ammonia nitrogen for variation. It has also revealed the dominant role of the rate of nitrification as well as the inflowing and outflowing concentration of different nutrients on different state variables.
- c. Applying the model to study the effects of harvesting the plants from Deepor Beel at different harvesting rates has successfully corroborated that harvesting plants is merely a temporary solution to the eutrophication problem as the nutrients in the water column remain nearly intact during harvesting simulation.
- d. Finally, the model predicted that introducing a treatment unit to Deepor Beel such that the water entering the lake is partially treated before entry can be very effective in eutrophication abatement in the lake. The nutrient concentration significantly decreased in the water column during simulation, and the growth of plants also decreased. The diverging trends of plant nitrogen without harvesting and harvesting indicated a possible decrease in the plant population if the treatment unit is operational for an extended period.





Look deep into nature, and then you will understand everything better.

- Albert Einstein

# 10

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## Concluding Remarks and Scope for future research

This chapter provides the overall concluding remarks from the entire research. It also discusses directions for future plausible research in this domain.

### 10.1. Overall concluding remarks from the thesis

A comprehensive study was conducted to understand the dynamics of a wetland ecosystem and the responses of their biotic and abiotic components to various anthropogenic pollutions. For this purpose, four components were chosen, and their characterization was studied in detail. Critical observations were noted during the course of the research. Objective-wise summary of the acquired results are discussed, as follows.

- The I<sup>st</sup> objective constituted the handling of the big dataset. For this purpose, different Environmetrics tools were employed. It was observed that all the tools, i.e., hierarchical cluster analysis, discriminant analysis, principal component analysis, and positive matrix factorization model, provided reliable information regarding the identification and quantification of the pollution sources without losing significant information. The clustering process helps in sites' characterization; Discriminant analysis provides evidence of the highly discriminating parameters responsible for site characterization; PCA helps identify latent pollution sources; while PMF models quantify the contribution of different pollutants from different sources.
- The II<sup>nd</sup> objective dealt with evaluating the water quality status of the wetland. Two novel objective-based indexing techniques were proposed, i.e., employing multivariate statistics and information entropy. These methods helped remove the prejudiced nature of the subjective-based approaches. Both the methods were employed for three distinct water us-

ages; domestic, assessing heavy metal contamination, and determining irrigation suitability. It was observed that both methods were highly reliable and correct. For short monitoring programs, the use of multivariate statistics for computing WQIs proved to be more viable, while for large monitoring programs, information entropy proved to be more helpful. The reliability and correctness were checked through sensitivity assay and compared with correlating with the original dataset.

- The sediment column was assessed for heavy metal contamination—this required identification and apportionment of the probable pollution sources. Hence, the multivariate statistical tools and the PMF model were employed. Both provided excellent correlation with the observed dataset and were thus found to be highly effective. Thereafter, different factors and indices were employed to check the health of the sediment column of the wetland. Potential ecological risks associated with each heavy metal contributing to the sediment contamination were also evaluated. In addition, metal speciation analyses were carried out for each heavy metal to comprehend the available fractions in the sediment column. The results were finally validated through elemental analyses, i.e., XRD and SEM-EDS. The results showed that the sediment column of Deepor Beel was the most affected near the land-fill region, while the central zone remains devoid of any anthropogenic contamination.
- The IV<sup>th</sup> objective concluded the II<sup>nd</sup> phase. Here, we tried understanding the heavy metal dynamics of the entire wetland ecosystem. This constituted the heavy metal concentration values and their distribution in different aquatic components. Also, non-carcinogenic and carcinogenic risks pertaining to long-term exposure to these components were measured. In addition to this, the three different fish samples collected were also assessed for their bio-accumulation potential of heavy metals, thereby providing insights into the health risks involved at higher trophic levels.
- The final objective dealt with the nutrient (N & P) dynamics in the wetlands that result in eutrophication. This was undertaken through a eutrophication-based ecological model, wherein three different components, i.e., water, sediment and water hyacinth, were bound together through a conceptual boundary. Different state variables were employed in the model to visualize the factors primarily responsible for eutrophication in Deepor Beel. The model was calibrated using 12 months' dataset, while the validation was performed with additional five months' dataset. The calibrated results showed excellent validation output. Additionally, the correctness of the model and sensitivity of each parameter was analyzed through sensitivity analysis via the Morris method. The model was finally employed to find plausible options for curbing eutrophication in the wetland. Two different options were chosen, i.e., harvesting water hyacinths and setting up a treatment unit at the mouth of

Basistha River. The later was a more promising option as far as a sustainable and effective measure to curb eutrophication.

The results of this study will be of substantial aid to various policy-makers and government or semi-government organizations in taking appropriate steps for improving the health of a water body. This would further aid in properly managing funds allocated for the restoration and rejuvenation of the water bodies. This is because it will help identify the critical pollution limits essential in the restoration process of the water bodies, thereby aiding in updating the regulatory norms for future policies.

## **10.2. Scientific Contributions from the research and their practical applicability**

On a local scale, the study is a first of its kind extensive monitoring and assessment study carried out on Deepor Beel. Since its inception into the list of Ramsar sites, there has been little or no care taken to preserve its rich biological diversity. Several measures were undertaken in the past, but they were highly unsuccessful due to lack of prognosis. The study provides detailed information regarding all four components of Deepor Beel's ecosystem, i.e., water, sediments, flora and fauna. Sources of pollution have been identified, their contribution to the contamination of the wetland's ecosystem has been quantified. Additionally, the health status with respect to all four components has been presented in detail. The risks associated with long-term exposure to water, sediment and intake of the locally available fish (which the local people are often found to be ingesting) are presented. This will help aware the people living in the region and are dependent on the wetland for their survival about the seriousness of the damages incurred through large-scale anthropogenic interventions. Finally, since eutrophication is one of the primary concerns relating to Deepor Beel's existence, the study proposes management options for curbing the levels of eutrophication through a scientific approach of a eutrophication-based ecological model. Therefore, the results of this study can be utilized on a large scale to restoring the wetland back to its original and natural state before it becomes too late.

On a global scale, firstly, the study provides novel methods to assess water quality involving objective-based approaches, taking into account all the limiting factors in the existing usages. This removes the possibility of any prejudice evolving due to the experts' opinions, thus providing a more realistic picture of water quality. For assessing water quality, this study also presents cases for both short term and long term monitoring programs, which will be helpful for all types of water bodies. In addition to this, the applicability of the proposed methods is not limited to any particular water body or geography; instead, it may be universally adopted.

This study also provides detailed information on assessing the sediment quality in a surface water body and measures to assess their contamination levels. The dynamics of heavy metals (one of the primary pollutants in any water body) through their occurrence, concentrations, and distribution across the entire ecosystem is presented, which can be used for all types of surface water bodies, including rivers. Finally, the model developed is highly scientific and thus can be used for other lakes and wetlands, although the calibrated values of the parameters involved will vary, given the dynamic nature of different natural ecosystems.

### 10.3. Limitations of the study

Although this study provides detailed research on the limnology of wetlands, there are certain limiting aspects to this. They are listed as follows:

- The standard considered in assessing the water quality for the present study is the Indian Standard, which may not deem suitable for other countries (since all countries have their prescribed standards). However, researchers worldwide are at liberty to consider their respective countries' standards or adopt the World Health Organization (WHO).
- The ecological model developed in this study to understand the dynamics of the nutrients in the wetland considers the dataset obtained from the monitoring program conducted on Deepor Beel. Although the overall concept and applicability of the model codes do not change, to carry out similar studies on another water body, one has to carry out similar extensive monitoring for that particular body to simulate the model as per their requirements.

### 10.4. Recommendations for future research

The results of this study are very promising to have a deep understanding of the limnology of the wetlands. However, it is recommended that future research be undertaken in the following areas to improve and extend the findings of this thesis.

- The hunt for the development of new and more efficient water quality indices is far from over. The present study discusses the application of different novel Environmetrics tools for assessing the water quality of a particular water body. Although the indices have proved to be highly effective and correct, newer methods such as fuzzy logic, predictive models like artificial neural networks, wherein the water quality can be best predicted through a set of raw datasets, may be tried and tested. Furthermore, research on improving the proposed models is also highly welcome.

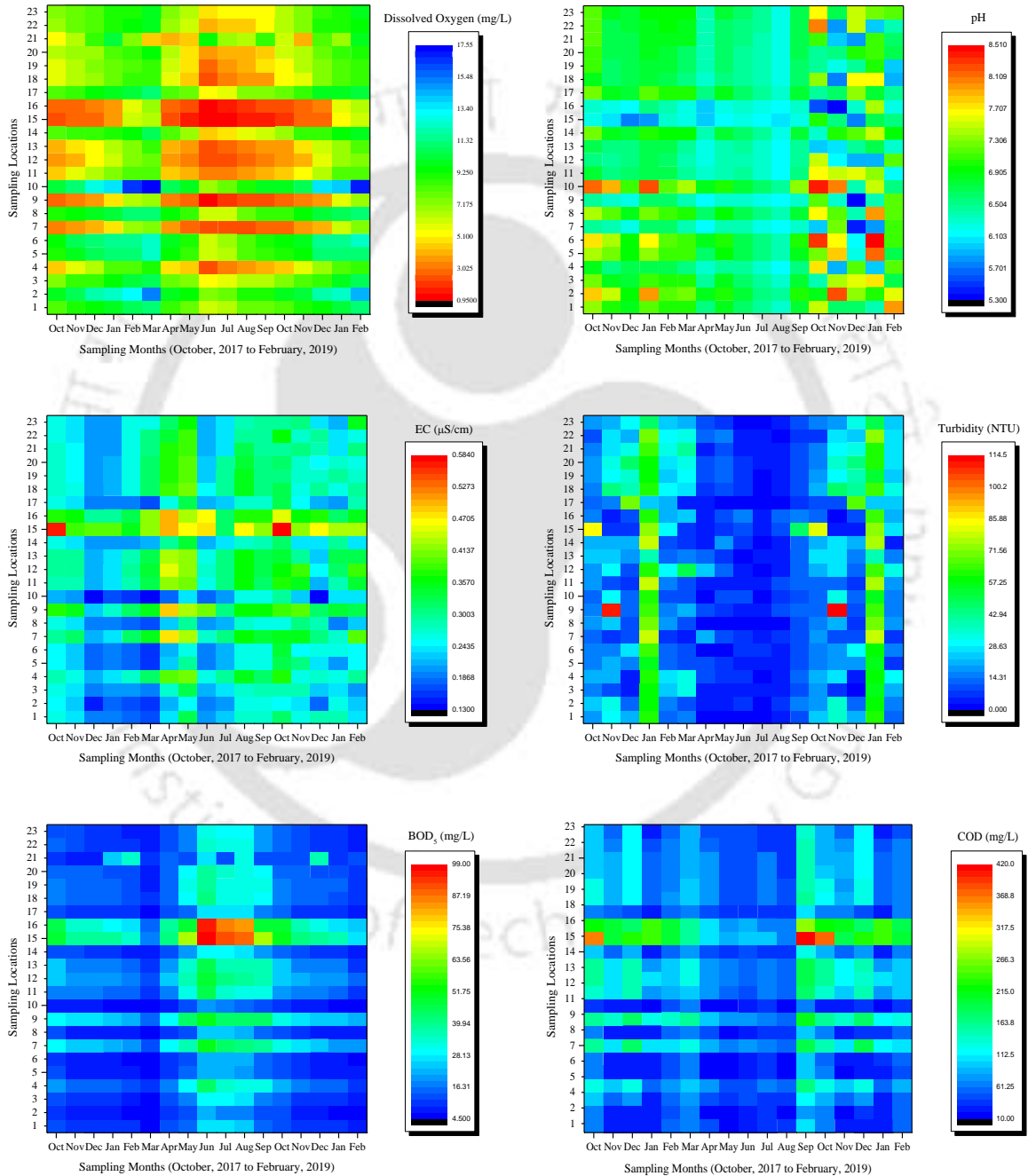
- In the present study, seven different heavy metals were considered for research. Many persistent inorganic heavy metals cause severe impacts on long-term exposure to human health. A detailed study involving such heavy metals is highly recommended.
- Studies on the optimization of water quality monitoring stations can be an excellent future prospect in this regard.
- The one-dimensional ecological model was developed in this study to serve as a stepping-stone to the development of more sophisticated ecological models in Deepor Beel that lend a better understanding of the existing ecosystem and help in formulating effective management strategies for the entire wetland. In fact, the present ecological model can be improved in several ways, which are mentioned below.
  - ✓ The number of state variables in the model can be increased by incorporating additional state variables such as chlorophyll-a, phytoplankton, zooplankton, fish, etc., into the model. The array of forcing functions can also be increased by considering solar radiation as it plays a crucial role in the photosynthesis process and, thereby, in the eutrophication process. Such additions to the ecological model will improve its descriptive capacity.
  - ✓ A hydrological model of the Basistha River can be developed and incorporated into the ecological model to use the one-dimensional model as a predictive tool.
  - ✓ The one-dimensional ecological model can be expanded to two-dimensional and three-dimensional models to grasp the spatiotemporal variation of the nutrients in the Deepor Beel. Such multi-dimensional models can predict the advection and diffusion patterns of nutrients in the lake.
  - ✓ Other species of plants along with water hyacinths, can be added to the representative plant samples to improve the prediction of the nutrient concentration in plants by the ecological model.

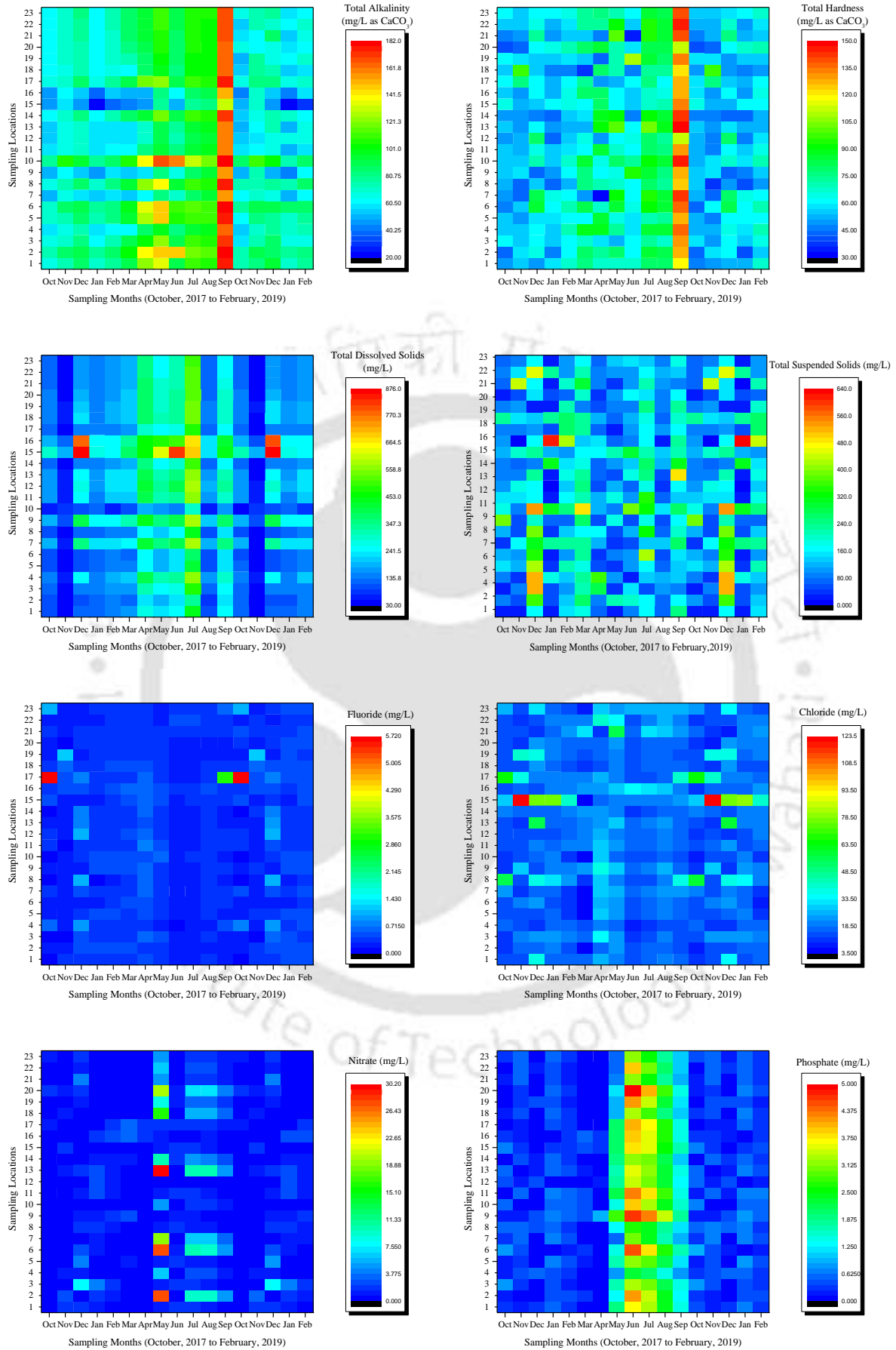


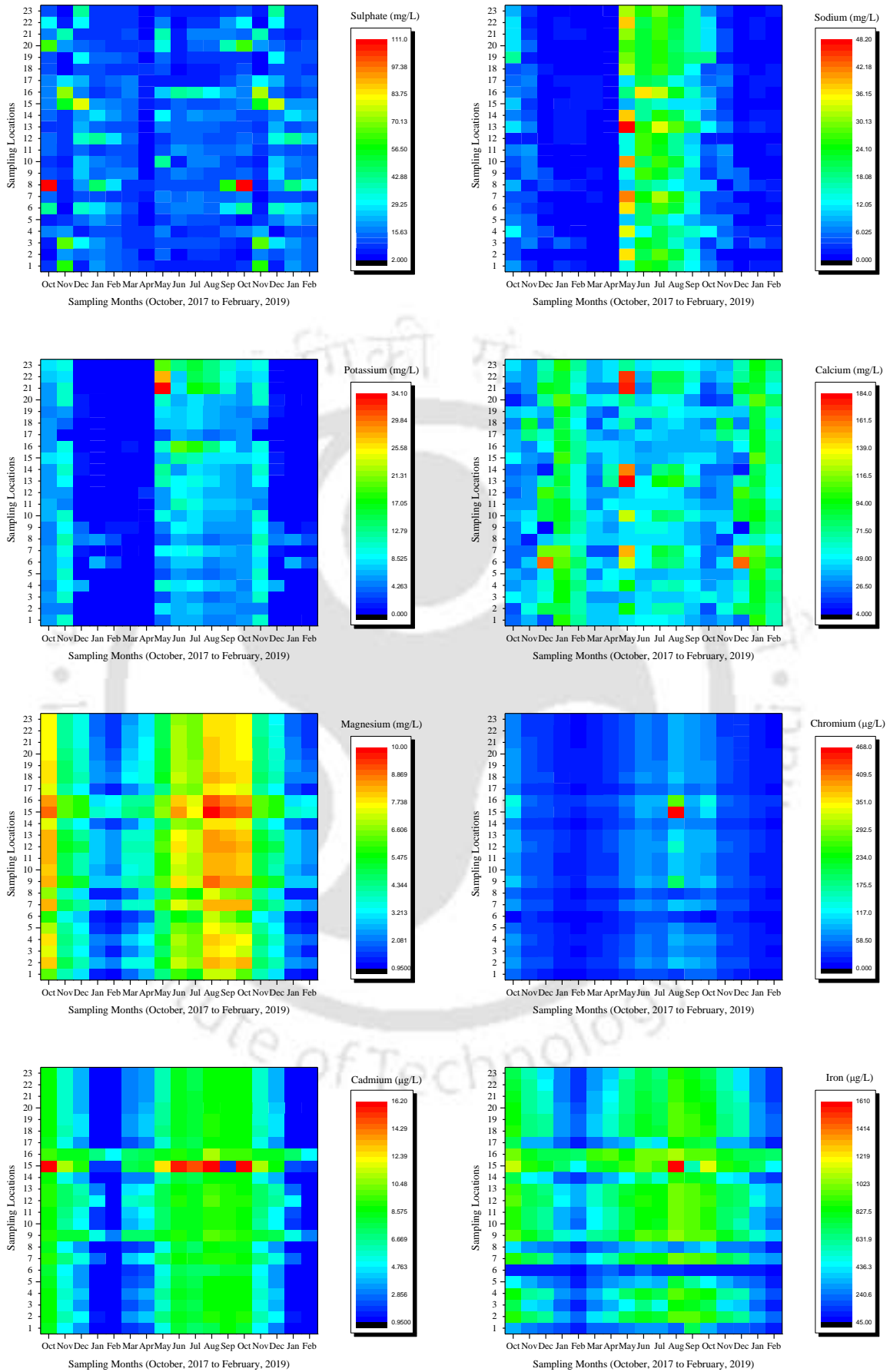


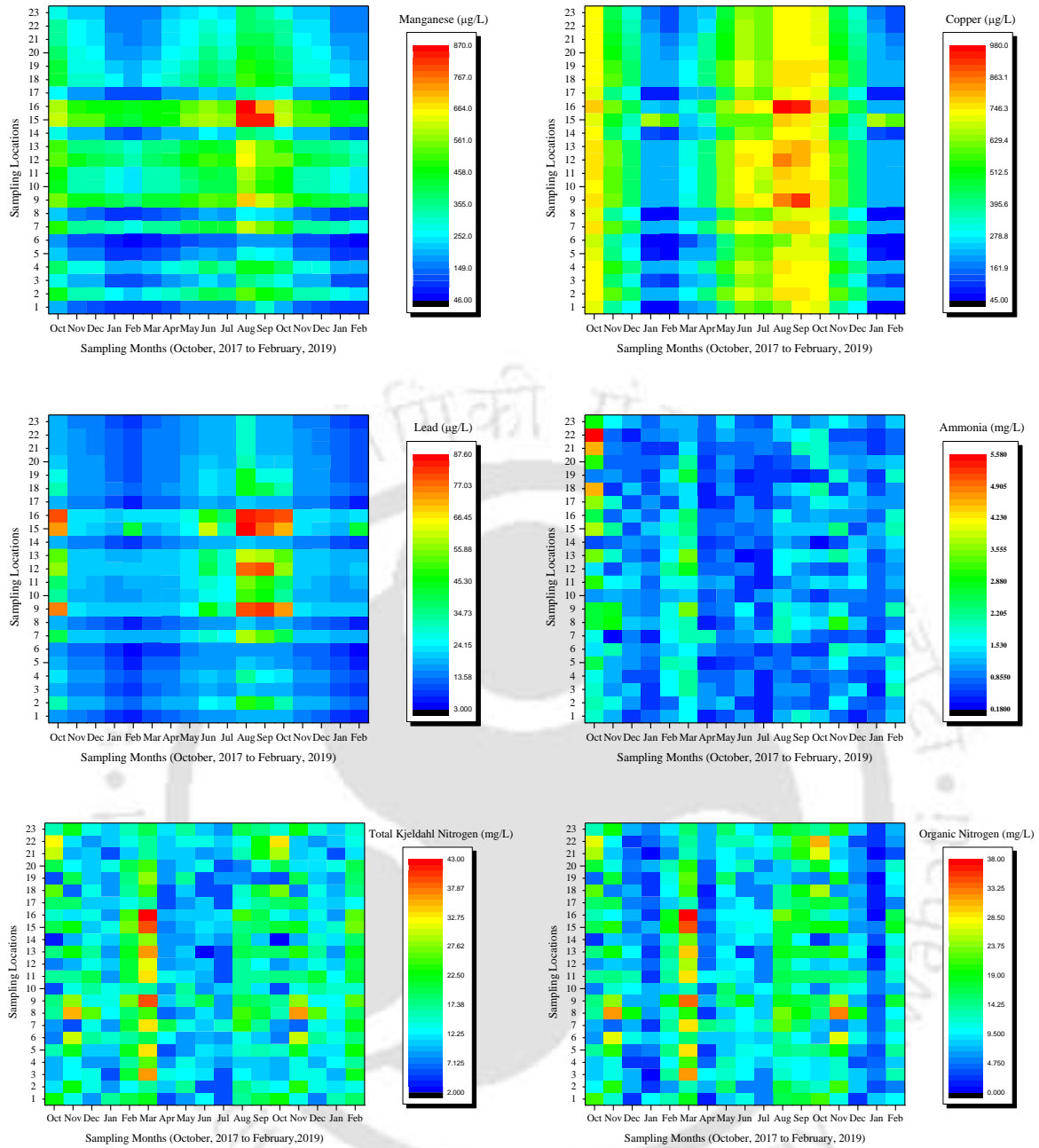
# Appendix A

## Spatio-Temporal Pattern plots for water column of Deepor Beel





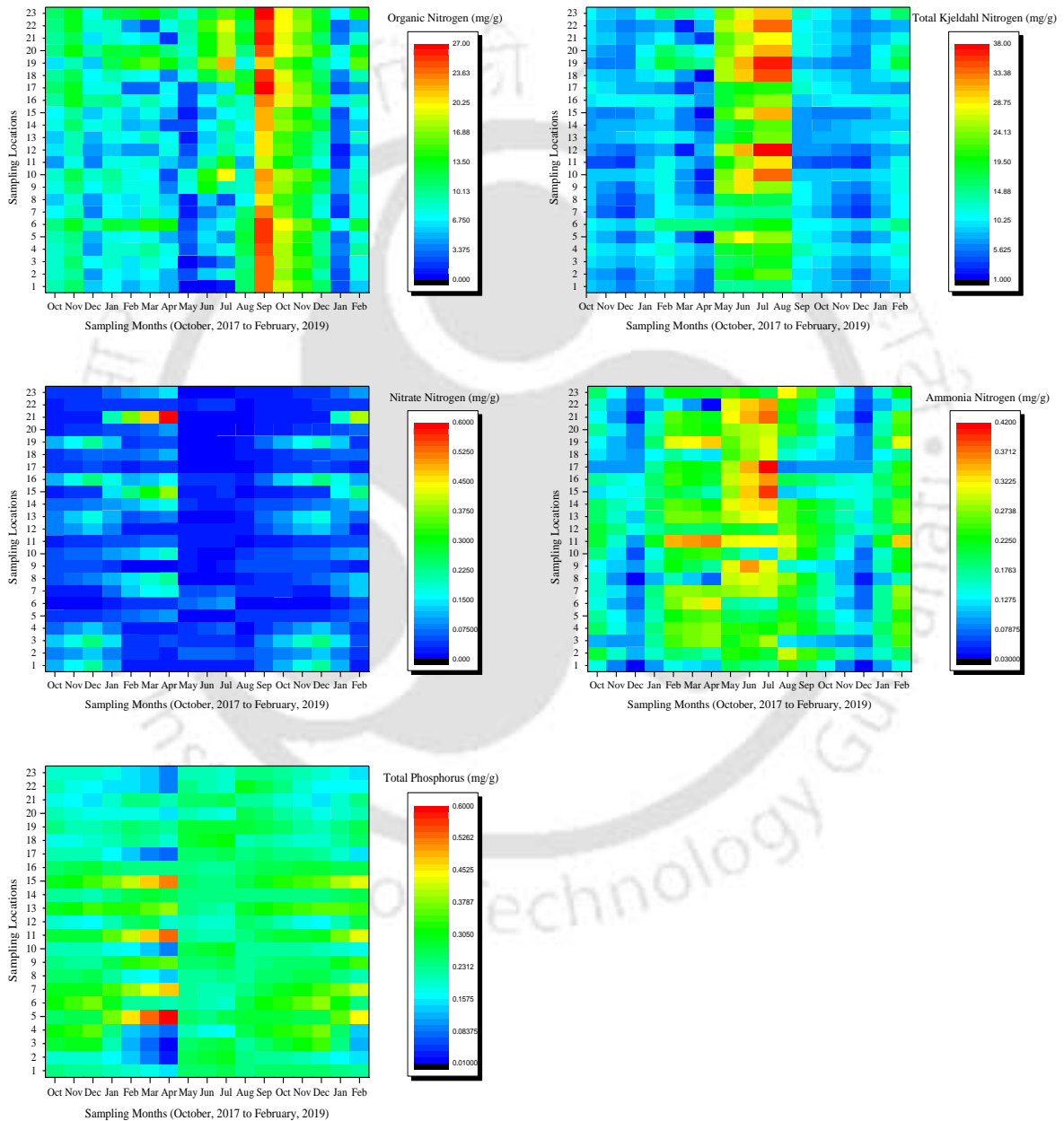




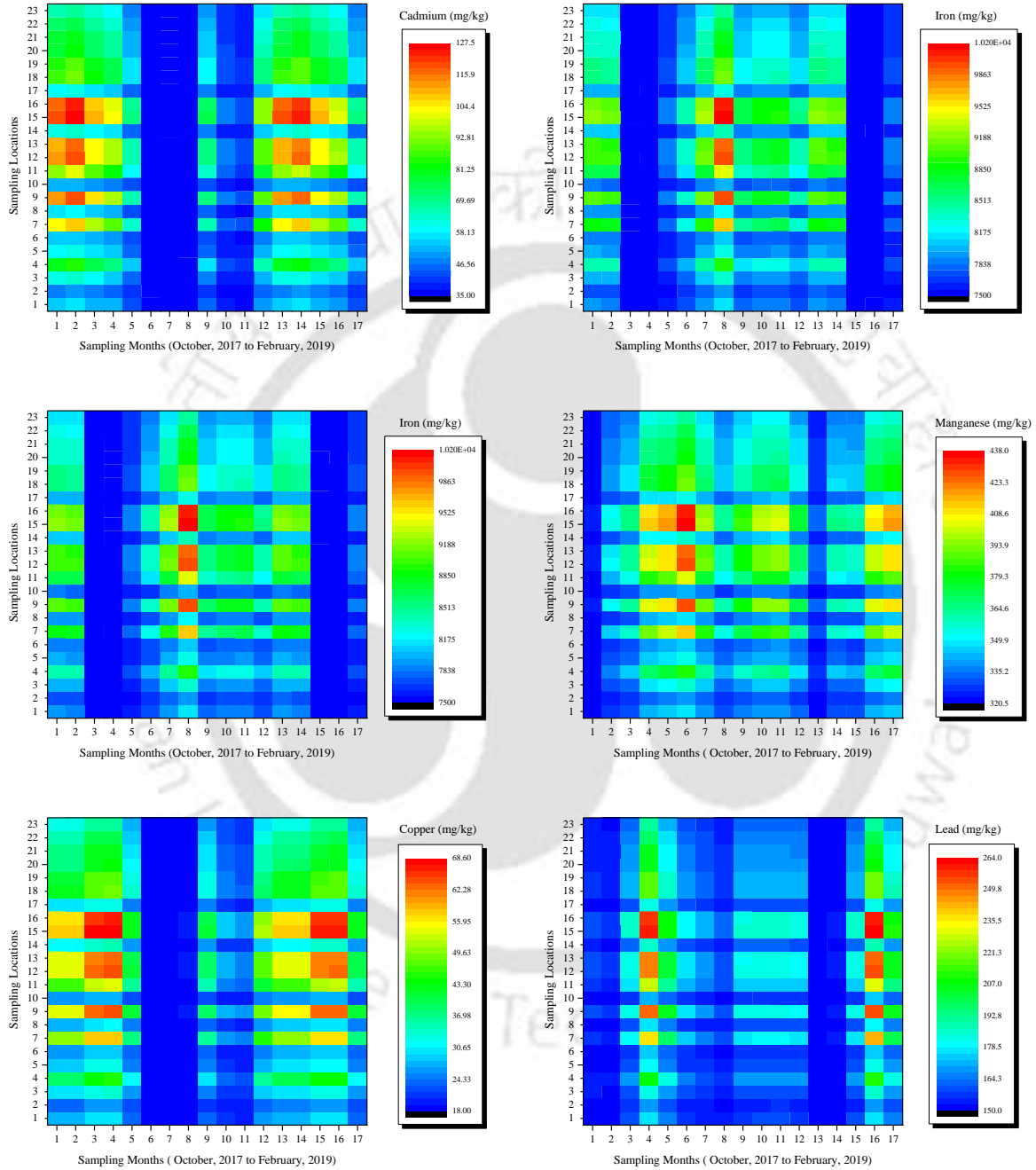
# Appendix B

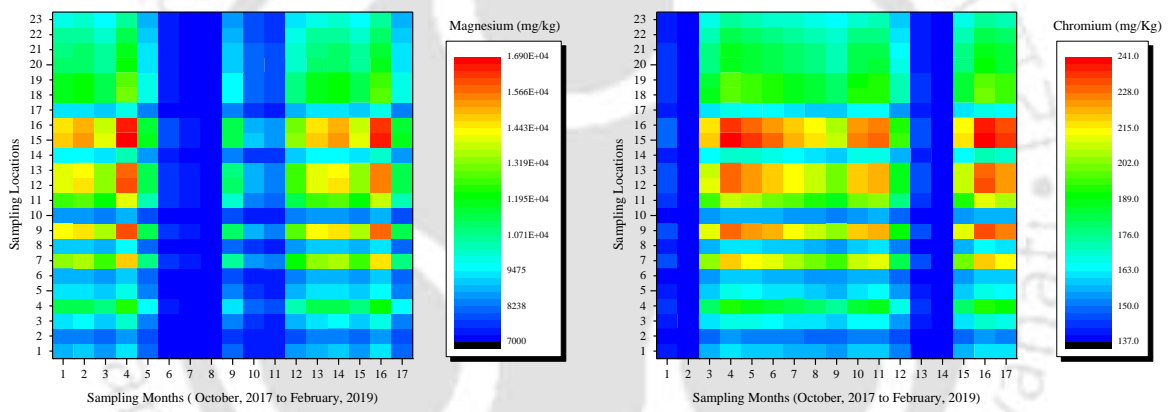
## Spatio-Temporal Pattern plots for sediment column

### B1. Nutrients in sediments



**B2. Heavy metals in sediments**







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# Research Outputs

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## Journal Publications

### Published articles

1. **Dash, S.**, Borah, S. S., & Kalamdhad, A. (2018). Monitoring and assessment of Deepor Beel water quality using multivariate statistical tools. *Water Practice & Technology*, 13(4), 893-908. [I.F.- 0.780, Q3]  
DOI: <https://doi.org/10.2166/wpt.2018.098>
2. **Dash, S.**, Borah, S. S., & Kalamdhad, A. (2019). A modified indexing approach for assessment of heavy metal contamination in Deepor Beel, India. *Ecological Indicators*, 106, 105444. [I.F.- 4.958, Q1]  
DOI: <https://doi.org/10.1016/j.ecolind.2019.105444>
3. **Dash, S.**, Borah, S. S., & Kalamdhad, A. S. (2020). Study of the limnology of wetlands through a one-dimensional model for assessing the eutrophication levels induced by various pollution sources. *Ecological Modelling*, 416, 108907. [I.F.- 2.974, Q2]  
DOI: <https://doi.org/10.1016/j.ecolmodel.2019.108907>
4. **Dash, S.**, Borah, S. S., & Kalamdhad, A. S. (2020). Application of positive matrix factorization receptor model and elemental analysis for the assessment of sediment contamination and their source apportionment of Deepor Beel, Assam, India. *Ecological Indicators*, 114, 106291. [I.F.- 4.958, Q1]  
DOI: <https://doi.org/10.1016/j.ecolind.2020.106291>
5. **Dash, S.**, Borah, S. S., & Kalamdhad, A. S. (2020). Application of Environmetrics tools for geochemistry, water quality assessment and apportionment of pollution sources in Deepor Beel, Assam, India. *Water Practice and Technology*, 15(4), 973-992. [I.F.- 0.780, Q3]  
DOI: <https://doi.org/10.2166/wpt.2020.078>
6. **Dash, S.**, Borah, S. S., & Kalamdhad, A. S. (2021). Heavy metal pollution and potential ecological risk assessment for surficial sediments of Deepor Beel, India. *Ecological Indicators*, 122, 107265. [I.F.- 4.958, Q1]  
DOI: <https://doi.org/10.1016/j.ecolind.2020.107265>

7. **Dash, S., & Kalamdhad, A. S. (2021).** Hydrochemical dynamics of water quality for irrigation use and introducing a new water quality index incorporating multivariate statistics. *Environmental Earth Sciences*, 80(3), 1-21. **[I.F.- 2.784, Q2]**  
DOI: <https://doi.org/10.1007/s12665-020-09360-1>
8. **Dash, S., & Kalamdhad, A. S. (2021).** Understanding the dynamics of heavy metals in a freshwater ecosystem through their toxicity and bioavailability assay. *Environment, Development and Sustainability*, 23(11), 16381-16409. **[I.F.- 3.219, Q2]**  
DOI: <https://doi.org/10.1007/s10668-021-01349-5>
9. **Dash, S., & Kalamdhad, A. S. (2021).** Discussion on the existing methodology of entropy-weights in water quality indexing and proposal for a modification of the expected conflicts. *Environmental Science and Pollution Research*, 28(38), 53983-54001. **[I.F.- 4.223, Q2]**  
DOI: <https://doi.org/10.1007/s11356-021-14482-5>
10. **Dash, S., & Kalamdhad, A. S. (2021).** Science mapping approach to critical reviewing of published literature on water quality indexing. *Ecological Indicators*, 128, 107862. **[I.F.- 4.958, Q1]**  
DOI: <https://doi.org/10.1016/j.ecolind.2021.107862>

### **Articles under consideration**

1. **Dash, S., Kalamdhad, A. S.** A systematic bibliographic research on eutrophication-based ecological modelling of aquatic ecosystems through science-mapping. *Ecological Modelling*. **(Under Review)**.
2. **Dash, S., Kalamdhad, A. S.** Development of specific indices for assessing water quality based on the proposed modifications of the expected conflicts on existing information entropy weights. *Environmental Monitoring and Assessment*. **(Under Review)**.
3. **Dash, S., Kalamdhad, A. S.** Employing multivariate statistics to address the pollution loadings of an aquatic ecosystem. *Environmental Earth Sciences*. **(Under Review)**.

## Book chapters

1. **Dash, S.**, Borah, S., Singh, K. R. & Kalamdhad, A. S. (2020). Seasonal and Spatial Variation of DO and BOD for Assessment of the Water Quality of Brahmaputra River. In: A. Kalamdhad (eds.) *Recent Developments in Waste Management*, Lecture Notes in Civil Engineering, vol. 57 (pp. 473-483), Springer, Singapore.  
DOI: [https://doi.org/10.1007/978-981-15-0990-2\\_37](https://doi.org/10.1007/978-981-15-0990-2_37)
2. **Dash, S.** & Kalamdhad, A. S. (2021). Monitoring heavy metals concentrations in a natural wetland and aquatic plant *Eichhornia crassipes* for assessment of its biomonitoring potential. In: B. Laishram and A. Tawalare (eds.) *Recent Advancements in Civil Engineering*, Lecture Notes in Civil Engineering, vol. 172, Springer, Singapore.  
DOI: [https://doi.org/10.1007/978-981-16-4396-5\\_34](https://doi.org/10.1007/978-981-16-4396-5_34)
3. **Dash, S.**, Borah, S. S, Kalamdhad, A. S. (2020). Application of Multivariate Statistics as a Tool for Development of Water Quality Index (WQI) For Water Quality Assessment of Deepor Beel, Assam, India. In: A. Kalamdhad *et al.* (eds.) *Environmental Degradation: Monitoring, Assessment and Treatment Technologies*, published with Springer-Nature in collaboration of Capital Publishing Company, India.  
DOI: In Press


## Proceedings in different Conferences

1. **Dash, S.**, Borah, S. S., Singh, K. R. & Kalamdhad, A.S. (2018). Seasonal and Spatial Variation of DO and BOD for assessment of the Water Quality of Brahmaputra River. *Proc. International Conference on Waste Management - Recycle 2018*, Apr 1-2, IIT Guwahati, Guwahati, India. (Abstract No. 220).
2. **Dash, S.**, Borah, S. S. & Kalamdhad, A.S. (2019). Assessment of Heavy metal contamination using Indexing approach for Deepor Beel, Assam, *Proc. National Environmental Conference (NEC - 2019)*, Jan 31-Feb 2, IIT Bombay, Mumbai, India. (Abstract No. 149).
3. **Dash, S.** & Kalamdhad, A.S. (2020). Monitoring heavy metals concentrations in a natural wetland and aquatic plant *Eichhornia crassipes* for assessment of its biomonitoring potential. *Proc. International Conference on Advances in Civil Engineering*, Nov 5-7, VNIT Nagpur, Nagpur, India. (Abstract No. ACE011).

## Awards received

1. Recipient of the prestigious **Water Advanced Research and Innovation (WARI) Fellowship Program** supported by the Department of Science and Technology, Govt. of India, the University of Nebraska-Lincoln (UNL), the Daugherty Water for Food Institute (DWFI) and the Indo-US Science and Technology Forum (IUSSTF) for the year 2019-2020.

*The objectives of this program are to provide an opportunity to the best and brightest Indian students to gain exposure and access to world-class research facilities at the University of Nebraska-Lincoln and the Daugherty Water for Food Institute; promote research and capacity building in the area of water; encourage and motivate outstanding students to take up research as a career; and, pave way for the next generation scientists and technologists from India to interact with their American peers, thus helping to build long-term R&D linkages.*

  
Indo-US Science & Technology Forum  
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**Water Advanced Research and Innovation (WARI) Fellowship Program**

The Department of Science and Technology (DST), Govt. of India, the University of Nebraska-Lincoln (UNL), the Daugherty Water for Food Institute (DWFI) and the Indo-US Science and Technology Forum (IUSSTF) are pleased to announce the list of candidates selected for the prestigious *Water Advanced Research and Innovation (WARI) Fellowship Program 2019-20*.

**WARI INTERNS**

S. No.	Name of Applicant	Affiliation
1.	Arun Karthick	Birla Institute of Technology and Science, Pilani
2.	E Jackcina Stobel Christy	Gandhigram Rural Institute, Gandhigram
3.	Jaladhi Sanjaykumar Trivedi	CSIR - Central Salt and Marine Chemicals Research Institute, Bhavnagar
4.	M Raj Kumar	Indian Institute of Technology, Kharagpur
5.	Maliqa Majid	Sher-e-Kashmir University of Agricultural Sciences and Technology, Kashmir
6.	Nitin Kumar Khandelwal	Indian Institute of Science Education And Research (IISER), Kolkata
7.	Preety Kumari	Indian Institute of Technology, Bombay
8.	Rajeev Meora	Alagappa University, Karaikudi
9.	Rao Nargis Jahan	Jamia Hamdard University, New Delhi
10.	Santosh Ravichandran	Anna University, Chennai
11.	Siddhant Dash	Indian Institute of Technology, Guwahati

