A risk analysis-based approach for assessing the effects of Pharmaceutical Pollutants (PPs) on river health and options for river health restoration.

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By

Nitin Ranjan

DEPARTMENT OF CIVIL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY (BANARAS HINDU UNIVERSITY) VARANASI- 221005

INDIA

Roll No.: 18061008 **2025**

Chapter 5
Summary and Conclusions

5.1 Summary and Conclusions

River health assessment and restoration has emerged as one of the most fascinating areas of research and development in water sector. Moving beyond the methods already developed using conventional water quality parameters, the present study has attempted to include the effects of Pharmaceutical Pollutants (PPs) in river health assessment framework. The river health condition is presented using a color coded hexagonal map, based on calculation of indicator group score (IGS) and river health index (RHI). It is observed that IGS and RHI can be used as a good scientific tools for identifying the critical indicator group and the current status of river health conditions. The color coded river health condition (RHC) hexagon gives a visual representation of each indicator group to provide insights into areas of required interventions and possible improvements. Once the level of PPs are found above predicted no effect concentration (PNEC), effective management to keep their concentrations within PNEC appears as the first step in achieving acceptable river health conditions. Planning and implementation of such a strategy remains the vital next step toward the objectives of river health restoration.

One of the major objectives of the present study is to include PPs as a component of river health index (RHI) calculation framework. Accordingly, the study followed following sequence:

i. Identification of PPs of major concern
    a. concentration above PNEC and
    b. most frequently reported,
    c. the most vulnerable biotic indicator groups in major rivers worldwide.
ii. Defining ecologically ‘high-risk’ conditions and its classifications

iii. Development of RHI calculation framework, including EPs, to assess the RHC.

iv. Development of strategies for RHC improvement based on three majors' criteria.

- Installation of advanced technology based new STP
- Augmentation of existing STPs for removal of PPs before discharge to rivers.

Although some innovative approach through source separation of urine (to reduce nutrients and PPs in wastewaters have also been discussed, this has not been taken up deeply in this study.

As step 1, an approach for estimating ecological risk to biotic indicators due to PPs based on MEC, PNEC, and RQ_T in rivers has been examined, independent of the actual field measurement of species in aquatic environments. Assuming DORPs and NTs under good conditions (IGS= 60), the specific effect of PPs reported beyond PNEC on RHI has been specifically studied for 7 selected rivers from across the world. The summary of observations and recommendations have been presented.

As a part of the first objective, out of 17 PPs reported in 13 Indian rivers, six PPs are found most frequently above the PNEC. which may be causes of concern for biotic indicators (Algae, MI, and Fish). Expanding our study for the world rivers, an additional 7 rivers from different parts of the world (outside India), it was observed that 5 PPs are causes of concern there, above PNEC causing aquatic imbalances in the river environments.

The following conclusions are drawn from this part of the study:

- Among 17 PPs examined for their presence in 13 Indian rivers, azithromycin, caffeine, diclofenac, naproxen, norfloxacin, and sulfamethoxazole are found in concentrations much above their predicted no-effect concentration (PNEC) values for algae, macroinvertebrates, and fishes in the aquatic environment.

- Caffeine, among the stimulants, is the most frequently recorded pharmaceutical compound in Indian river waters.
- Outside India, from 7 other rivers of the world, amoxicillin, ofloxacin, sulfamethoxazole, triclosan, and acetaminophen are 5 PPs found in concentrations much above their PNEC for biotic indicators.
- Sulfamethoxazole, among the antibiotics class, is the most frequently reported PPs in most rivers worldwide.
- Overall, the present study suggests monitoring and management of 10 pharmaceutical compounds categorized under 3 classes:

  Antibiotics (e.g., amoxicillin, azithromycin, norfloxacin, ofloxacin, and sulfamethoxazole),

  Stimulants (e.g., caffeine), and

  NSAIDs (e.g., acetaminophen, diclofenac, naproxen, triclosan).

Moving to our second, the study defined the ecologically 'high-risk quotient (RQ_h)' condition beyond their PNEC values for concentrations of PPs. Based on analyses, this study proposed an assessment factor (AF) of 10 over PNEC to define the threshold risk quotient (RQ_T) of any polluting chemical in the river environment. Accordingly, the risks with increasing values of RQ_h up to RQ_T (10RQ) on aquatic organisms have been classified into five categories: moderately high, significantly high, critically high, severely high, and impaired condition based on RQ_h values 1-3, 3-5, 5-8, 8-10, and >10, respectively.

The following risk levels have been derived from the observations:

- Among Indian Rivers, River Ahar, Udaipur (RQ_h= 2.27), River Brahmaputra, Guwahati (RQ_h= 2.73). River Akravati, Bengaluru (RQ_h= 1.65), and River Yamuna, Agra (RQ_h= 2.71) are under 'moderately high-risk conditions due to the presence of azithromycin, caffeine, naproxen, and sulfamethoxazole respectively.

- River Ganga (RQ_h= 4.95), and River Yamuna, Agra (RQ_h= 4.97) are under 'significantly' high risk conditions due to presence of caffeine, and diclofenac respectively for Algae, and Fish.
- Based on RQ_h values, the concentrations of caffeine in River Ahar, Udaipur, India (RQ_h = 24.5) is found under 'impaired condition' category for algae.
- Based on concentrations of PPs reported in rivers in India, the risk quotient (RQ_h) ranges from a modest value of 1.65 with naproxen on macroinvertebrates in river Akaravathi (Bangaluru) to more than 300 with norfloxacin on fish in river IsakavaguNakkavagu, a tributary of river Godavari, near Hyderabad. The concentrations reported indicated 'moderately high' to 'impaired' high risk conditions for biotic indicators.
- Among International rivers, River Altamaha, USA (RQ_h = 1.2 for MI), River Wangyang, China (RQ_h = 2.36 for MI) are 'impaired' high risk conditions due to presence of acetaminophen, and ofloxacin respectively.
- River Ravi, Lahore Pakistan (RQ_h = 10 for Algae) is under 'severely' high risk conditions due to presence of sulfamethoxazole in river.
- River Brisbane, Australia (RQ_h = 7.40 for Algae) is under 'critically' high risk conditions due to presence of sulfamethoxazole in river.
- Concentrations of sulfamethoxazole in River Lambro, Milan, Italy (RQ_h = 17.14), River Ravi, Lahore Pakistan (RQ_h = 10), River Nairobi Basin, Kenya (RQ_h = 51.1 for), River Wangyang, China (RQh = 51), River Mitheu, Ghana (RQ_h = 10.37) appear in similar 'impaired condition' for algae.

Towards developing RHI calculation framework including effects of PPs, with our earlier works as background, in the present study, pH, Electrical Conductivity (EC), Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD), and Chemical Oxygen Demand

(COD) have been considered under DORPs; with Ammonical Nitrogen (NH3-N), Total Nitrogen (TN), and Total Phosphorous (TP) as constituting NTs groups of indicators. In addition, PPs have been considered to constitute the third stressor group under the EPs category. Accordingly, the expression for calculating RHI using six indicator groups is framed, and the application of IGS, IGC, RHI, and RHC have been used to analyse the river health acceptability. The application of a developed framework for RHI calculation including PPs, has been test checked using the dataset for the River Ganga near Varanasi (India). With justifiable results and explanations, the application has been extended to six more Indian rivers to classify the acceptability of RHC as 'acceptable' or 'poor' with PPs reported above PNEC.

Following conclusions are drawn from this phase of the study:

Indian Rivers:

- The RHC for River Akravati, Bengaluru (RHI= 89), River Brahmaputra (RHI= 89), and River Ganga (RHI= 81) is assessed under 'Excellent' condition.
- The RHC for River Ahar (RHI= 73), and River Yamuna (RHI= 73) are classified in the 'Acceptable' category, varying from 'Good' to 'Very good' conditions.
- IsakavaguNakkavagu stream of River Godavari, Hyderabad, India (RHI=27) indicates a 'critical condition', with IGS=0 for all the indicator groups of algae, MI, and fish indicating that under the conditions of the river no- biological life may exist primarily due to high levels of Norfloxacin. In this river, $RQ_h >> RQ_T$.

International Rivers:

Assuming IGS for DORPs and NTs group of indicators in good condition (IGS $\geq$ 60) and considering concentrations of PPs as reported, RHI has been estimated, and the conclusion are detailed below:

- River Altamaha, USA (RHI= 89) is assessed under 'Excellent' condition of river health acceptability.
- River Brisbane, Australia (RHI= 73) and River Wangyang (RHI= 80) are classified in the 'Acceptable' category, varying from 'Good' to 'Very good' conditions.
- River Lambro, Milan, Italy (RHI= 55); River Mitheu, Ghana (RHI= 57); River Nairobi Basin, Kenya (RHI= 57); and River Ravi, Pakistan (RHI= 57) is found under 'Stressed' conditions primarily due to the presence of triclosan and sulfamethoxazole in the aquatic environment.

As the final step of the sequential program of study, development of strategies for RHC improvement based on three majors' criteria, such as installation of advanced technology based new STP and augmentation of existing STPs for removal of PPs before discharge to rivers have been discussed. The analyses suggest that the conventional technology based STPs, such as ASPs, SBR etc. do not have significant remoal efficiencies for PPs. They need advanced oxidation processes (AOPs) based tertiary treatment for effective removal of PPs for river health restoration.

5.2 Research Contribution to Existing Literature

The scientific community has continuously studied the risk assessment on aquatic organisms due to the presence of PPs. However, an in-depth risk analysis of PPs on different trophic levels of aquatic organisms and their role in developing a framework for river health condition assessment is the need of the hour. This study augments the existing literature as:

- It identifies the concentration at which the presence of PPs causes toxicity to aquatic organisms and normalizes the concentration on a 0-5 scale for the RHI assessment framework.
- It identifies the most vulnerable biotic indicator groups due to the presence of PPs above acceptable concentrations.

- It presents a reviewed PNEC dataset of 17 common pharmaceuticals and defines the threshold risk concentration.
- It defined the ecological 'high risk' conditions (RQ>1) for aquatic organisms.
- It redefined the previous approach for RHI assessment, including the effect of PPS as six indicator groups of river health.
- It reviewed the existing STPs' efficiency in removing PPs and suggested the best possible strategies to reduce the pollutants of concern before reaching the water environment.

5.3 Implications for Practice

This study is among the first to identify the interrelationship between PPs and aquatic organisms in the river environment. The study could also be helpful to the water resource managers in planning the interventions required for pollutants of concern and implementing proper steps for river health improvements. It may also support policymakers in defining the discharge limit of pharmaceutical compounds into river waters concerning ecological health. The study also supports the decision-makers in augmenting existing STPs to take care of pollutants that require tertiary treatment for their removal from the water environment.

5.4 Implications of Research for Policy Formulation

Water Quality Assessment Authority (WQAA), constituted under the Environment (Protection) Act, 1986, suggested that CPCB prepare guidelines for the water quality management plan. In compliance, CPCB (2008) prepared a draft for setting primary water quality goals based on water quality needs for different purposes. Pharmaceutical pollutants and their active ingredients in the water environment pose a great threat to ecological life, and the water environment needs to be intervened by strengthening regulations on pharmaceutical waste management. The need of the hour for policymakers is to establish collaboration between the Ministry of Environment, Forest and Climate Change

(MoEFCC), CPCB, the Ministry of Health, and the Pharmaceutical Industry to define the limit for hospitals and pharmaceutical industries and upgradation of conventional STPs infrastructure before discharging into the river environment.

Progressively, with time, heavy metals and pesticide residues are now being monitored regularly in river water quality monitoring programs to meet drinking water quality standards (IS 10500: 2012) in India. Generally, the acceptable and permissible limits for drinking water quality are based on specifications suggested by the Directives of the European Union (EU), the US Environmental Protection Agency (USEPA), the World Health Organization (WHO), etc. As reported, the EU and USEPA have included pharmaceuticals in their routine monitoring program after observing the presence of PPs in drinking water. In India, there has been no monitoring of pharmaceuticals in surface water resources used for drinking water, and no permissible ambient standards for rivers or effluent standards from sewage treatment plants (STPs) have been set as yet. This appears an imperative need for public and river health protection.

5.5 Limitations

- The present study identified pharmaceuticals as part of emerging pollutants for river health assessment. Under the broad category of EPs, compounds representing EDCs, PCPs, ASs, and other organic pollutants causing ecological imbalances have not been included in the present study.
- This study assessed river health condition based on a risk analysis approach; the RHI framework needs to be validated based on field observed data of water quality and biotic species.
- The study has presented strategic options for river health improvement suggesting application of advanced technologies or application of AOPs, including ozonation as tertiary treatment. This approach needs validation with laboratory and field experiments.

5.6 Scope for Future Studies

Following research and studies can be undertaken to develop the RHI framework for assessing river health worldwide.

- Based on the risk-analysis approach, the RHI framework can be developed based on the cause-and-effect model. The acceptable and critical concentrations of DORPs and NTs indicator groups need to be thoroughly reviewed or developed to assess the threshold level concentration affecting Alge, MI, and Fish biotic indicators.
- The framework can be validated in rivers by analysing the water quality and actual density of aquatic organisms on a given site in such an environment.
- The toxicity of other organic and inorganic pollutants causing ecological imbalances in the water environment should be included in the broad category under emerging pollutants.
- Other treatment technologies, such as adsorption, bioremediation, phytoremediation, etc., should be included to suggest options for augmentation of secondary-level STPs or for suggesting a new installation at the source.