EXTENDED ABSTRACT

In recent years, several frameworks have been developed to calculate the River Health Index (RHI) and classify the River Health Condition (RHC) based on RHI values. While Dissolved Oxygen-Related Parameters (DORPs) and Nutrients (NTs) are two accepted broad groups of indicators in calculating RHI, this study proposes to include Emerging Pollutants (EPs) as the third group of indicators that cause stress on river health. Algae, Macroinvertebrates (MI), and Fish are taken as three biotic indicator groups to reflect the resultant conditions of river health. Pharmaceutical pollutants (PPs) are one of the most prominent groups amongst the EPs being found and reported in river waters worldwide. Due to their persistent nature, bioaccumulation, biomagnification, and toxic effects on aquatic organisms, PPs have drawn the global attention of the scientific community concerned with river health. Wastewater from pharmaceutical manufacturing units, hospitals, and domestic sewage containing excretal matters of medicine-using communities are the prime sources of PPs in natural water bodies. The present study aims to identify PPs of major concern that adversely affect the biotic organisms in aquatic environments, map their concentration levels, and define the threshold concentrations of tolerance to understand the ecological risk. The study also proposes to develop a framework for calculating RHI, including the effects of PPs on the biotic indicators of river health. Finally, it intends to enlist the possible options for river health restoration through supplementation of existing wastewater treatment systems, installation of appropriate new technology, or any other innovative solutions.

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 (NH_3-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 as follows:

$$RHI= [(DORPs \times w_1) + (NTs \times w_2) + (EPs\times w_3) + [(A\times w_4) + (MI \times w_5) + (F \times w_6)] \times 100 \qquad \text{(Eq. 1)}$$

Where DORPs = Dissolved oxygen-related parameters group score, NTs = Nutrients indicator group score, EPs= Emerging Pollutants group score, A= Algae indicator group score, MIs= Macroinvertebrate indicator group score, F = Fish indicator group score, and w_1, w_2, w_3, w_4, w_5, and w_6 are weights assigned to these respective indicator groups.

Based on reasoning and understanding of the cause-and-effect model, in the present study the weights for different groups of indicators have been taken as:

$$w_1=0.10,\ w_2= 0.20,\ w_3= 0.20,\ w_4= 0.20,\ w_5 =0.20, \text{ and } w_6= 0.10$$

The individual values of all water quality parameters are normalized on a 0-5 scale based on acceptable concentration (score 5) and critical concentration (score 0). The arithmetic mean of normalized scores of all parameters in an indicator group is calculated and converted on a 0-100 scale as an Indicator Group Score (IGS). Mathematically,

$$IGS = [\sum \text{Scores of individual parameters} / (5\times\text{No. of parameters in the group})] \times 100 \qquad \text{(Eq. 2)}$$

The presence of PPs poses different degrees of risk on biotic indicators present in river waters. Such associated risks are estimated based on the measured environmental concentration (MEC) and their Predicted No Effect Concentration (PNEC) for different biotic groups. The USEPA Ecological Structure–Activity Relationships (ECOSAR™) QSAR program is used to predict the ecotoxicological effects of pharmaceutical compounds. US ECOSAR and other relevant research papers have been used to ascertain the PNEC values of different pharmaceutical compounds. Based on such values, Algae are found to be the most frequently affected group of biotic indicators, followed by MI and Fish.

Traditionally, the Risk Quotient (RQ), Hazard Quotient (HQ), and Optimized Hazard Quotient (RQ_f) have been used for the risk assessment of PPs on aquatic organisms. As long as MEC ≤ PNEC and RQ ≤ 1, ecologically, there is a 'low risk' to biotic species. When MEC> PNEC and RQ >1 for any biotic indicator, it is defined as a 'high risk' condition. Based on analyses of a large number of data, it was observed that in many cases, MEC ≤ PNEC and RQ ≤ 1; but for several others, RQ is >1, which indicate 'high risk' conditions. Representing RQ>1 as a high-risk quotient (RQ_h), the calculated values were found to range from 1.2 (for MI) to 335 (for Fish). Thus, based on risk condition posed by the presence of PPs on aquatic organisms and calculated RHI, the Ecological Risk Condition (ERC) and River Health Condition (RHC) have been defined and depicted as given in Table 1.

Table 1: Color Depiction of Ecological Risk Condition (ERC) and River Health Condition (RHC) based on Risk Quotient (RQ) and River Health Index (RHI).

RQ<1 and RQ_h> 1-10	**Level of Ecological Risk**	**Ecological Risk Condition (ERC) (based on RQ and RQ_h)**	**Tool Used**	**RHI**	**RHC**	**Color**	**River Health Acceptance Category**
0	Low Risk	No- Risk	**RHI Calculation Framework**	>80	Excellent	Blue	Acceptable
0.01-0.10		Negligible		70-80	Very Good	Green	
0.10- 1.0		Endurable		60-70	Good	Yellow	
1-3	High Risk	Moderately Stressed		50–60	Stressed	Orange	Poor
3-5		Significantly Stressed		40–50	Overstressed	Grey	
5-8		Critically Stressed		30–40	Critical	Red	
8-10		Severely Stressed		20-30	Sick	Brown	
>10		Impaired Condition		≤20	Dead		

As test check with a data set observed in river Ganga at Varanasi during Jan 15- March 15, 2018, the river health conditions with and without considering the effect of reported concentrations of PPs are found as shown in Fig 1a and 1b.

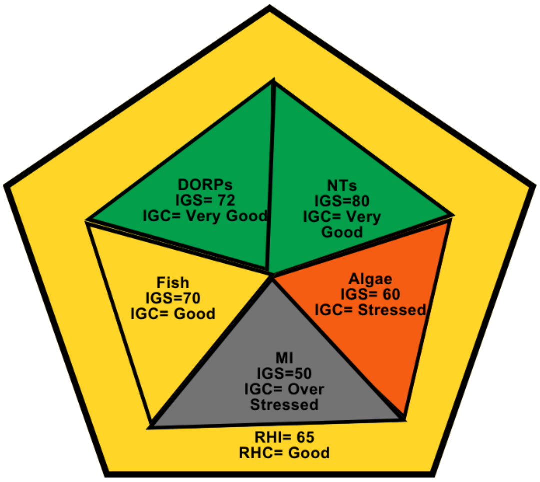

Fig. 1 (a) RHC Pentagon without including PPs

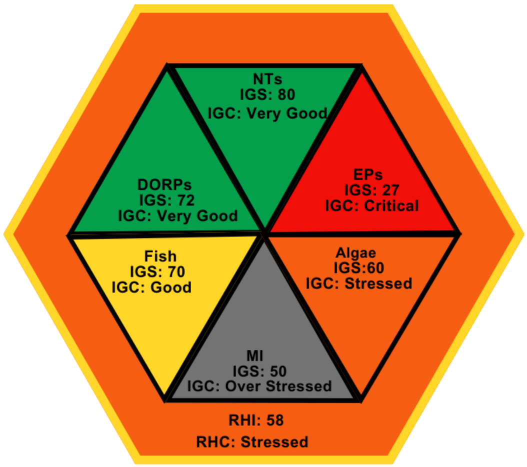

Fig. 1 (b) RHC Hexagon with including PPs

Fig 1: Colored Map of River Health Condition (RHC)

It is seen that with the addition of PPs as the third group of indicators, the shape of the RHC map changes from pentagon to hexagon, RHI reduces from 65 to 58, RHC is found changing from 'Good' to 'Stressed,' and the overall color representing the status of river health changes from 'yellow' to 'orange'. The primary reason for these changes appears the consequential effects of pharmaceutical compounds under PPs group of indicators, whose concentration is greater than PNEC values. It is observed that in the latter case, the Algal group condition changes from the 'Stressed' to the 'Over stressed' category.

Extending the application of the developed framework for calculating RHI for six Indian Rivers where the presence of PPs have been reported above PNEC values, it was observed that while RHC for four rivers (River Akravati near Bengaluru, RHI=82; River Brahmaputra near Guwahati, RHI=82; River Yamuna at Agra, RHI= 66; and River Ganga near Patna, RHI =66) are found under 'Acceptable' category, two others are found under 'Poor' category. Among the later, River Shipra near Ujjain (RHI 56) is found under

‘Stressed’ condition and the IsakavaguNakkavagu stream of River Godavari (RHI=11) is under ‘Sick’ condition. A deeper look reveals that azithromycin, caffeine, diclofenac, naproxen, norfloxacin, and sulfamethoxazole are six PPs which are most frequently reported (above their PNEC values) in Indian rivers.

In the present study, using RQ_h=10, a Threshold Risk Concentration (RC_T) has been decided, beyond which adverse effects are most likely to have observable manifestations. For RQ_h>10, rivers' ecological condition has been considered ‘impaired.’

Expanding the application of the developed framework further, an additional 7 rivers from different parts of the world (outside India) were selected based on reported concentrations of PPs (above PNEC values for Algae, MI, or Fish). Based on RQ_h (RQ>1), it is observed that all 7 rivers are ecologically in the ‘high risk’ category. Among them, while River Altamaha, USA is under ‘Moderately stressed’ risk category, the other two rivers (Ravi, Lahore, Pakistan; and River Brisbane, Australia) are in the ‘Severely stressed’ category, and four rivers (River Lambro, Milan, Italy; River Nairobi Basin, Kenya; River Wangyang, China; and River Mitheu, Ghana) are in ‘Impaired’ category. For these rivers, assuming that IGSs for DORPs, and NTs group of indicators are in the ‘Acceptable and Good’ condition, and only PPs are considered as reported, RHI calculations suggest that River Lambro, Italy (RHI= 55), River Mitheu, Ghana (RHI= 57), River Nairobi Basin (RHI= 57), and River Ravi, Pakistan (RHI= 57) will be adjudged under ‘Poor and Stressed’ condition. This is primarily due to the presence of PPs having concentrations above PNEC, the river health condition needs improvement to be ‘Acceptable’.

Within the limits of rivers included in this study, analyses indicate pharmaceutical compounds, such as azithromycin, acetaminophen, amoxicillin, caffeine, diclofenac, naproxen, norfloxacin, ofloxacin, sulfamethoxazole, and triclosan are ten most frequently reported chemicals whose concentrations are found above PNEC and create ‘high risk’ conditions for biotic indicators of river health. While most of them affect Algae first, diclofenac and triclosan are found to affect MI and Fish at very low concentrations.

For river health restoration, it is important to identify the critical group of indicators and reduce the concentration(s) of contaminants within that group to under acceptable/ low risk limits. In present practices, conventional wastewater treatment methods generally target DORPs and NTs groups of indicators for pollution load reduction. Mostly they are not very effective in removing PPs from water streams. Activated Sludge Process (ASP), including Sequential Batch Reactor (SBR) based Sewage Treatment Plants (STPs) are the most frequently used options worldwide, including India. Up to the secondary level of treatment, the removal efficiency of PPs through such methods is around 12-20% only, which effectively is not significant enough to improve river health condition. However, addition of tertiary units such as ozonation or ultraviolet (UV) irradiation have been reported to remove PPs more than 65-90% of their original concentrations. If land availability is not a constraint, constructed wetlands (CWs) are observed to be the most economical option for the removal of PPs with improving other water quality characteristics of DORPs and NTs groups of indicators also.

Overall the condition analyses suggest that in order to improve in IGS and make RHC under the 'Acceptable' category, there seem three possible approaches: i. augmentation of existing conventional technology-based STPs with tertiary units, ii. installation of advanced technology-based new STPs, such as Membrane bioreactor (MBR)/ Moving Bed Biofilm Reactor (MBBR) with a proven record of removal of PPs as well as improving DORPs and NTs group quality characteristics, and iii. the application of new and innovative options, such as urine separation at the source, which is likely to reduce PPs substantially from wastewater streams. It is encouraging to observe that a growing number of STPs in India and across the world are following chlorination/ ozonation/ UV radiation to disinfect treated effluent to meet biological water quality requirements before discharging to natural water bodies. In addition to its intended objectives, augmentation of treatment systems with such advanced oxidation processes (AOPs) as tertiary unit also helps in oxidising organic substances of calcitrant nature, including pharmaceutical compounds, which effectively reduces the concentrations PPs, thereby reducing the ecologically high risk conditions towards safer side for biotic indicators of river health.

For new installations near the outfall from pharmaceutical industry or hospital wastewater discharges, treatment systems based on MBR or MBBR have been reported to have high efficiencies for removing PPs. Such units will substantially reduce the outgoing concentrations and risks associated with biotic indicators. A more fundamental and new innovative approach to reduce the risk due to PPs is to separate the urine stream from human waste at the source itself. Urine carries around 70-80% of pharmaceutical compounds and more than 50% of nutrients discharged in the water environment. Source separation of urine and diversion from mixing with domestic wastewaters reduces more than 50% of PPs and NTs load, resulting in improved IGS, RHI, and better RHC.

Using the option of adding tertiary treatment units such as ozonation as AOP at STPs at Agra whose effluents discharge in the River Yamuna (India) as an example, the scenario

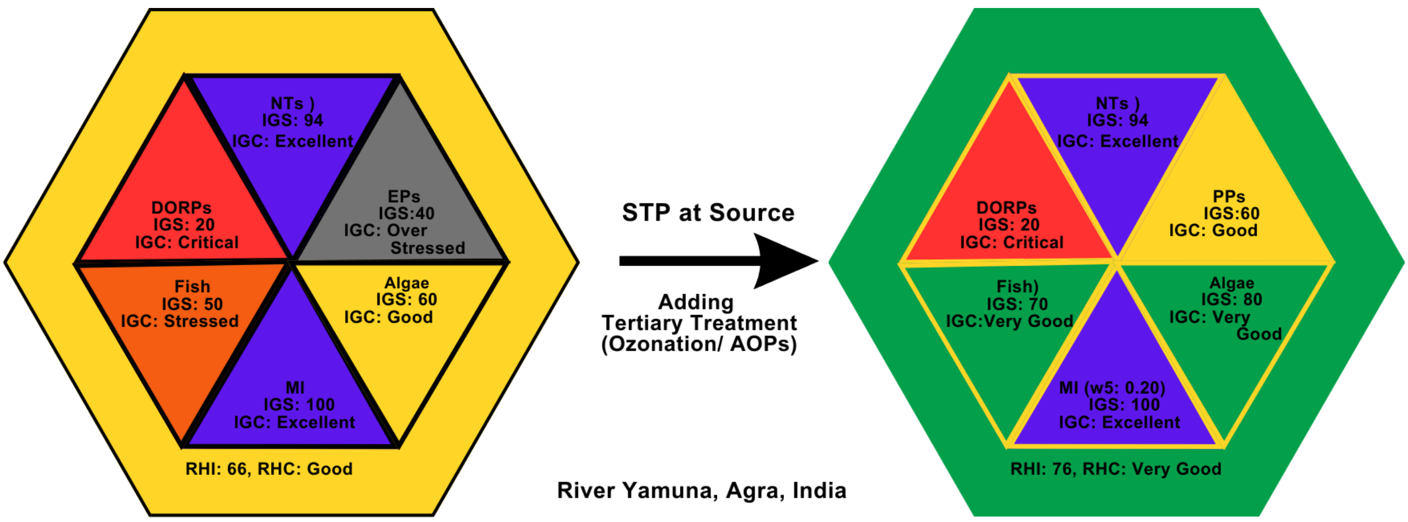

Fig. 2: Possible health conditions improvement plan for River Yamuna at Agra (India)

analysis suggests that the IGC for PPs is likely to change from 'Over Stressed' to 'Good', thereby improving the RHI from 66 to 76 and RHC from 'Good' to 'Very Good' (Fig 2).

Similarly, for health restoration of River Ravi at Lahore (Pakistan), which is currently assessed under 'Stressed' condition (RHI=57), the addition of Ozonation/ AOPs as tertiary treatment is likely to reduce the concentrations of PPs present by 60-70% and change the IGC from 'Sick' (IGS=0) to 'Good' (IGS=60), thereby increasing the RHI from 57 to 78 and changing the RHC to 'Very Good' category.

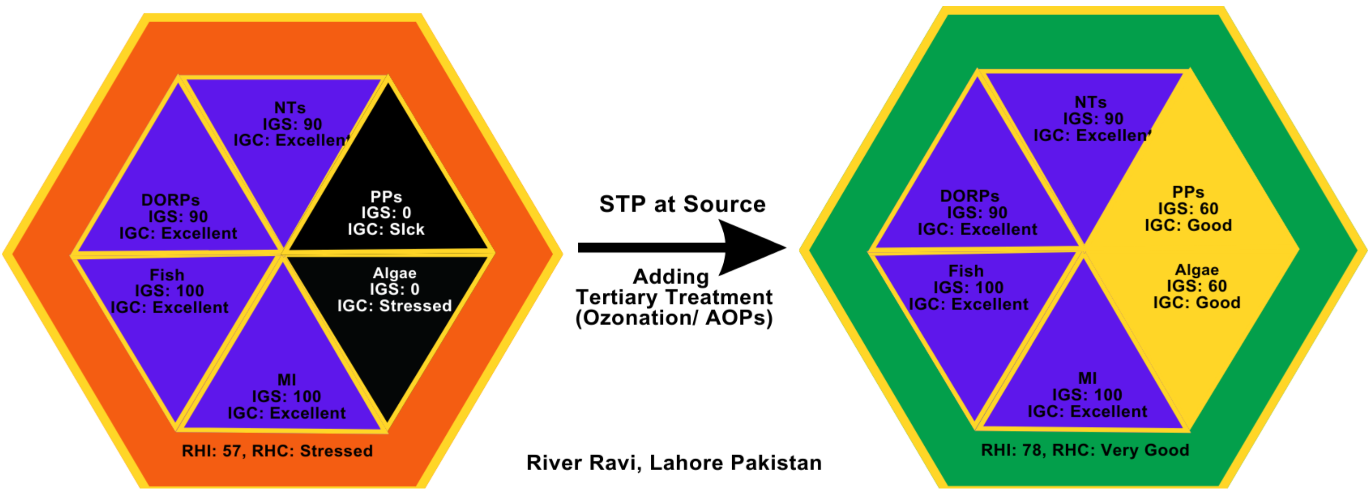

Fig. 3: Possible health conditions improvement plan for River Ravi, Lahore (Pakistan)

With PPs as target indicator group of interest in the present study, these examples adequately establish that IGS and IGC along with RHI and RHC can be used as scientific tools for identifying the critical indicator group of concern and priority for river health restoration.

The IGS and RHI based selection of color to represent indicator group health condition and river health condition provides greater clarity and visual insights into areas of required interventions and possible improvements.

As established through literature review in this study, it appears that at present there is no method of classifying the ecological risk level beyond identification of 'low risk'

(RQ<1) and ‘high risk’ (RQ>1) conditions based on the predicted no-effect concentration (PNEC) of PPs for biotic indicators. Defining a threshold high risk quotient (RQ_h=10), and threshold risk concentration (RC_T) for PPs of concern, the present study has put forward a fresh classification system of ecologically ‘high risk’ conditions.

A color-coded map in the form of a river health hexagon, including the effects of PPs as developed in the present study, may be used as a decision-making tool to identify areas of intervention, possible improvements, and the expected river health condition after implementation of the proposed restoration plan.

Keywords: Emerging Pollutants (EPs), Pharmaceutical Pollutants (PPs), Risk Quotient (RQ), River Health Index (RHI), River Health Condition (RHC).