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# A new approach for indexing groundwater heavy metal pollution

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ABSTRACT

A new approach has been proposed for indexing heavy metal pollution in groundwater based on highest desirable and maximum permissible concentrations. This new approach aims to address various shortcomings of the existing indexing systems. According to the new indexing system, heavy metal pollution status of any water sample may be expressed by a pair of positive index (PI) and negative index (NI). Positive index reflects heavy metal concentration in water exceeding highest desirable limit, while negative index corresponds to heavy metals within desirable limit. Water quality deteriorates with increasing PI and the pristinity increases with decreasing NI. A comprehensive PI and NI scale has been drawn for labeling the drinking worthiness with regards to heavy metal concentration. When all the constituent heavy metals are less than or equal to prescribed highest desirable limit, PI is assigned a value zero and NI can assume a value less than zero but not less than −1. When all the heavy metals are present below detection limit, the PI of the sample is still zero but NI will be −1. When concentrations of all heavy metals are above the highest desirable limit, its NI will be zero and PI will have some positive value. Heavy metal pollution indices of 100 groundwater samples in the Subarnarekha River Basin (SRB) collected during the pre and post-monsoon seasons have been computed using the proposed new indexing system. The drinking worthiness of all these samples has been discussed in the light of newly proposed indexing system. GIS interpolation maps of new indices, drawn for the pre- and post-monsoon SRB ground waters, clearly reflect the spatio-temporal water quality change pattern. The new indexing system is robust, flexible and may be computed using any water quality standard. It takes care of many of the apparent deficiencies of the existing indexing systems.

## 1. Introduction

Water quality is a function of its constituent matrix wherein each parameter has a limiting value with reference to the intended use and values beyond the limiting ones entail the water sample unsuitable for the designated purpose (WHO, 2006). Since a real life water sample usually comprises an array of elements, the overall quality should ideally be a cumulative effect of all these parameters, though some of them may be present well below the acceptable limiting value. While it is possible to grade a water sample with reference to a particular parameter and its limiting value, it is difficult but desirable to have a comprehensive number which will take into consideration the effects of all the influencing parameters present in the water matrix (Lermontov et al., 2009; Prasanna et al., 2012).

The statement made above may be exemplified as follows. The overall quality of three different water samples is to be graded with reference to five heavy metals present in them. In the first sample three heavy metals are below acceptable limit and two above, in the second four below and one above, and in the third, two below and three above. The grading job is not straight forward as quality not only depends on parameter concentrations but also on their relative toxicity. A comprehensive water quality index would have made the job easier.

Heavy metals are well known for their toxicity towards living beings, especially when dissolved in ionic form in water (Maanan et al., 2015). A highly toxic metal ion present slightly above the permissible level may make the water more hazardous as compared to a relatively less toxic one present well above the acceptable limit. In addition to risk appraisal, an index is also welcome for certifying the drinking worthiness of a water sample. An index would also be user friendly in relatively grading water quality of a set of water samples. The need for a heavy metal pollution index (HPI) was contemplated and visualized in this perspective, which is not only relevant to groundwater but pertinent to any environmental matrix in general that includes soil, sediment, estuarine sediment etc. (Mohan et al., 1996; Liu et al., 2014; Maanan et al., 2015; Caeiro et al., 2005).

HPI in water depends on two factors; number of heavy metal ions

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and their concentrations vis-à-vis permissible levels as per water quality standards. Understandably, HPI being a semi empirical number, many formulations have been proposed by various researchers (Horton, 1965; Mohan et al., 1996; Prasad and Jaiprakash, 1999; Prasad and Bose, 2001; Edet and Offiong, 2002 and cross references therein). Each variant has its own strengths and weaknesses. Two of the mostly used indexing techniques with reference to heavy metal ions in groundwater were the one proposed by Mohan and coworkers based on highest desirable and maximum permissible concentration (Mohan et al., 1996; Prasad and Jaiprakash, 1999; Prasad and Mondal, 2008; Prasad et al., 2014; Herojeet et al., 2015; Mahato et al., 2017; Rezaei et al., 2017; Singh et al., 2017) and the one that uses maximum allowable concentration (MAC) (Edet and Offiong, 2002; Venkatramanan et al., 2014; Singaraja et al., 2015; Rezaei et al., 2017; Singh et al., 2017).

An attempt has been made in this communication to critically examine these two formulations and propose a new indexing system, with the objective to circumvent the identified shortcomings. The new indexing system has been used for calculating quality index of the Subarnarekha River Basin (SRB) groundwater samples and the observed improvements have been highlighted through direct comparison with the existing indexing systems.

## 2. Methodology

### 2.1. Rationale for new approach

Rationale for the new indexing system proposed in the present study has evolved through critical appraisal of the two most popular indexing systems as discussed below.

#### 2.1.1. Heavy metal pollution index (HPI) using highest desirable ($I_i$) and maximum permissible ($S_i$) concentration (Mohan et al., 1996)

If the water sample contains n number of different parameters, composite heavy metal pollution index (HPI) may be calculated as:

$$\Sigma_{i=1}^{n} HPI^{i} \quad (1)$$

Where $HPI^i$ is the pollution index corresponding to the $i^{th}$ heavy metal ion and may be calculated as,

$$\mathrm{HPI}^{i} = \omega_i . Q_i \quad (2)$$

$\omega_i$ is the relative weightage factor defined as,

$$\omega_i = \frac{W_i}{\sum_{i=1}^{n} W_i} \quad (3)$$

Where, $W_i$ is the unit weightage factor which is inversely proportional to the maximum permissible concentration $S_i$, and defined as,

$$W_i = \frac{1}{S_i} \quad (4)$$

The proportionality constant (Mohan et al., 1996; Prasad et al., 2014) is considered as 1 for all the parameters.

A sub index $Q_i$ for $i^{th}$ parameter is calculated as,

$$Q_i = \frac{|M_i - I_i|}{(S_i - I_i)} \times 100 \quad (5)$$

$M_i$ = Measured concentration of the $i^{th}$ parameter, $I_i$ = Highest desirable concentration of the $i^{th}$ parameter, $S_i$ = Maximum permissible concentration of the $i^{th}$ parameter

#### 2.1.2. Heavy metal evaluation index (HEI) using maximum admissible concentration (MAC) (Edet and Offiong, 2002)

Assuming water sample contains 'n' number of parameters,

$$\mathrm{HEI} = \sum_{i=1}^{n} HEI^{i} \quad (6)$$

Where, $HEI^i$ is the pollution index corresponding to the $i^{th}$ heavy metal ion and may be calculated as,

$$\mathrm{HEI}^{i} = \frac{M_i}{H_{mac}^{i}} \quad (7)$$

Where, $H_{mac}^{i}$is the maximum allowable concentration of the $i^{th}$ parameter with reference to WHO (2011) and $M_i$ has been defined in 2.1.1.

Normally, HEI is calculated using World Health Organization (WHO) water quality standard.

The formulations shown above suffer from two major shortcomings. In the expression for sub-index $Q_i$ shown in Eq. (5), the numerator comprises absolute of the difference between measured concentration, $M_i$ and highest desirable concentration, $I_i$ of the $i^{th}$ parameter. Since HPI is inversely related to water quality, higher HPI implies poorer water quality. Interestingly, absolute of the $I_i$ difference between $M_i$ and $I_i$, in Eq. (5), adds to HPI even when $M_i$ is less than

As per Eq. (5), arsenic concentrations of 5 and 15 $\mu g\,L^{-1}$ should impact the HPI in the same manner though in reality they do not. The limiting value ($I_i$) for arsenic being 10 $\mu g\,L^{-1}$, the first sample should pass the quality test and the second should fail.

Secondly, the denominator in Eq. (5) is the difference between $S_i$ and $I_i$. In many water quality standards, only highest desirable value is permitted for some parameters and no relaxation is accorded even in the absence of alternate sources. For example, parameters like Cr, Ni, Se, Ba etc., have only the highest desirable value ($I_i$) specified in the drinking water standard under IS 10500 (BIS, 2012). In WHO (2006) standard, most of the parameters have been assigned only maximum allowable concentration (MAC) and no window of upper and lower limit. This makes BIS and WHO standards not suitable for calculating HPI using Eqs. (4) and (5). It is intriguing that in many of the recent publications, a lower version of IS 10500 (BIS, 2003) standard was used for calculating HPI even when a higher version was available, ostensibly because in the higher version many of the parameters had only the lower limiting value and no relaxation for the upper limit (Prasad et al., 2014; Varghese and Jaya, 2014; Tiwari et al., 2015; Tiwari et al., 2016).

Yet another tentative area of heavy metal pollution index (HPI) is their linking with water quality. Different HPI ranges have been assigned to classify water quality as 'poor', 'good', very good' and 'excellent'. While an important function of HPI is to indicate the water quality, there is no sound theoretical basis of assigning HPI ranges corresponding to the water quality. Also, these assignments do not clearly identify drinking worthiness of a water sample. These shortcomings make these indexing systems somewhat empirical in their basis and restrict their field of application. Ideally an indexing system should be flexible enough to accommodate any water quality standard and should be able to tell unequivocally if the water is drinkable.

In view of these apparent shortcomings, a modified formulation for heavy metal pollution index (m – HPI) has been proposed in the present work, which maintains the philosophy of HPI or HEI but varies in its workings. This new approach is based on two basic premises. The number of heavy metals to be considered for calculating the m – HPI should be decided apriori. Any comparison between two indices (two samples) is meaningful only when the same set of parameters is considered for calculating the indices. Secondly, any formulation for calculating metal pollution index should be applicable to all water quality standards. The details of the new approach, which henceforth will be called as modified heavy metal pollution index (m – HPI), may be found as follows.

### 2.2. Modified heavy metal pollution index (m – HPI) using highest desirable concentration ($I_i$)

Assuming the water sample contains 'n' number of heavy metal ions,

$$\mathrm{m} = \mathrm{HPI} = \sum_{i=1}^{n} m - HPI^{i} \quad (8)$$

Where, $m-HPI^i$s the modified heavy metal pollution index