# Risky Pollution Index: An Integrated Approach Towards Determination of Metallic Pollution Risk in Sediments

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## Abstract

In contrast with Mobility Factor (MF) and Risk Assessment Code (RAC) indices, $I_R$ attributes a risk share to metal species bound to reducible and oxidizable phases which are totally neglected in both of the two above-mentioned indices. In other words, besides the absolutely mobile fractions, the potentially mobile ones are also regarded in risk evaluation process elaborated by $I_R$. The different structure of the newly-developed index may prevent risk level underestimation especially in case where a remarkable percent of bulk concentration is accumulated within reducible and oxidizable phases. The independency of the index value to the bulk concentration makes it possible to discuss the potential risk in different levels of bulk concentration. Furthermore, the index capability in indication of risky pollution, regardless of the pollution source type, may prevent the probable misleading caused by distinct separation of bulk concentration into geopogenic and anthropogenic portion.

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## Introduction

Due to their non-degradable nature, toxic metals are considered among major contaminants in aquatic systems (Nabi bidhendi et al., 2007; Nasrabadi et al., 2009). Regarding the uncertainties of water and biota in monitoring the toxic metals contamination level in aquatic systems, sediment analysis is preferably considered in such studies. The bilateral role of sediments as both sink and source of toxic metal pollution is remarkably of interest. Such a role may be imposed to the sediments by different biological and physico-chemical conditions. Accordingly, the type of metallic analysis plays a significant role in clarification of the toxic metals nature bonded to the sediments. The bulk analysis through which the total concentration of a specific metal is determined in the sediment sample may not envisage the consequent risk regarding bioavailability, bioaccessibility and bioaccumulation. Speciation analysis through which the percent of total concentration incorporated to different loose and resistant bonds is identified may manifest the potential risk of existing pollution. That is why through the last few decades, researchers have followed different sequential extraction techniques to estimate the fractionation of metals in sediments (Chester & Hughes, 1967; Tessier et al., 1979; Horowitz et al., 1999; Stamatis et al., 2006)

The chemical forms of the metal determine the relevant mobility, bioavailability and consequently the entrance potential into the food

chain. The case is more complicated when metalloids like arsenic and selenium are considered. Determination of different metalloid species in water and sediments plays a key role in detecting the environmental risk levels. In geological zones where a natural enrichment of arsenic exists, such studies are mandatory. Sediment and groundwater speciation studies in central and western Iran as geopogenically metalloid enriched zones have been carried out (Keshavarzi et al., 2011; 2012). Accordingly, the need for evaluating the different forms of toxic metals in contaminated soils and sediments has triggered the evolution of metal speciation techniques. A range of relevant extractants in sequential extraction analyses are introduced in Table 1.

**Table1. Relevant extractants in sequential extraction analyses (Ure et al., 1995)**

| Phase extracted or isolated | Extractant |
|---|---|
| Water-soluble | $H_2O$ |
| Exchangeable | $MgCl_2$ |
| | $NH_4OAc$ |
| | $CaCl_2$ |
| | $KNO_3$ |
| | $MgNO_3$ |
| Carbonate | $HOAc$ |
| | $NaOAc$  pH5 |
| | EDTA |
| Mn/Fe oxides | $NH_2OH.HCl$ |
| | Dithionite/Citrate |
| Organically bound/ sulfides | $NH_4P_2O_7$ |
| | NaOCl |
| | EDTA |
| | $H_2O_2/HNO_3/NaOAc$ |
| | $H_2O_2/HNO_3/NH_4OAc$ |
| Residual | $HNO_3/HClO_4/HCl$ |
| | HF |

Although single-step and sequential extraction procedures may be utilized for both soils and sediments, single-step methods are normally considered in soil studies while the sequential methods are preferred in sediment analyses.

Lots of different kinds of indices have been introduced to indicate the contamination level of the sediments regarding toxic metals. Generally, the developed indices may be categorized in three major types: (i) accumulative or comparative indices which simply aggregate the concentration values of different metals in a sample or consider the ratio of the metal concentration value to that of a reference within the study area (normally a clean reference). Pollution index (PI) (Ott, 1978), Index of metals pollution in marine sediments (q) (Satsmadjis and Voutsinou-Taliadouri, 1985), Index for chemistry (ratio-to-reference RTR) of the sediment quality triad component (I) (Chapman, 1990), Metal pollution index (MPI) (Usero et al., 1996), Index for chemistry (new maximum RTR) of sediment quality triad component (NI) (DelValls et al., 1998), Marine sediment pollution index (MSPI) (Shin & Lam, 2001) and Metal enrichment index (SEF) (Riba et al., 2002) are the ones gathered in this category. (ii) enrichment indices which compare the existing metal concentration of the sample to whether its own background level or a baseline that may be utilized in different case studies. A group of the most famous sediment metallic pollution indices like Mueller geoaccumulation index (Igeo) (Mueller, 1979), EF (enrichment factor) (Szefer et al., 1998; Sutherland, 2001), Ipol (index of pollution) (Karbassi et al., 2008), New index of geoaccumulation (NIgeo) (Ruiz, 2001) and Degree of contamination (DC) (Hakanson, 1980; Kwon & Lee, 1998) are attributed to this class. (iii) ecological risk indices which make a

comparison among the measured metal concentrations to the sediment quality guidelines; metrics like ERM (effects range median) and ERL (effects range low) that indicates the concentration of a contaminant that resulted in adverse bioeffects in 50% and 10% of published studies, respectively (Long & Morgan, 1990; Long et al., 1995), PEL (probable effects level) (concentration above which adverse effects frequently occur) and TEL (threshold effects level) minimum concentrations associated with degradation or changes in the quality of the aquatic system (MacDonald et al., 2000), Pollution load index (PLI) (Wilson & Jeffrey, 1987), Mean sediment quality guideline quotient (SQG-Q) (Long & MacDonald, 1998), Logistic regression Models (Field et al., 1999; 2002), Equation sub-index sediment quality (Ferreira, 2000), Mean sediment quality guideline quotient as indicator of contamination and acute toxicity (SQG-Q1) (Fairey et al., 2001) and Potential ecological risk index (ERF) (DelValls & Chapman, 1998) are typical examples in this category.

## Materials and methods

Several sequential extraction methods are introduced by different researchers all around the world (Chester & Hughes, 1967; Tessier et al., 1979; Kersten & Forstner, 1986). Regarding simplicity of the method as well as its, credibility, sensitivity, robustness and feasibility due to time and cost limitations the three-step sequential extraction method proposed by the European Community Bureau of Reference (BCR) in 1992 (Ure et al., 1993) which has been optimized

during more than a decade (Rauret et al., 1999; Sahuquillo et al., 1999; Ross & Filip, 2002; Katherine & Christine, 2003; Yuan et al., 2004; Adamo et al., 2005; Cuong & Obbard, 2006) is considered in this study. The detailed sequential steps involved in this method may be described as follows (Rauret et al., 1999; Katherine & Christine 2003; Nasrabadi et al., 2010b):

### STEP 1 (Acid-soluble phase)

A representative sample of air-dried (at$<30^{°}$C)$<63$ micron sediment is weighed into a 100 ml centrifuge tube and 40 ml of reagent "A",0.11 mol.l acetic acid is added and the vessel and contents shaken for 16 hours (overnight) in an end-over-end mechanical shaker operating at 30 r.p.m. in a room at $20\pm2^{°}$C. The supernatant is separated by centrifuging at 1500 G and decanting into a polyethylene bottle. This fraction 1 is analysed immediately or stored at $4^{°}$C. The residue is washed by shaking with 20 ml distilled water for 15 minutes, centrifuging and discarding the washings. The residue is retained for step 2.

### STEP 2 (Reducible phase)

40 ml of reagent "B", 0.1 mol.l hydroxyammonium chloride is added to the broken up residue from step 1, above, in the centrifuge tube and again extracted at 20 °C as before for 16 hours (overnight). The supernatant is separated and retained (Fraction 2), as before for analysis. The residue is again washed, the washings separated by centrifugation are discarded. The residue is retained for step 3.

### STEP 3 (Oxidizable phase)

To the broken up residue, in the centrifuge tube, from step 2, 10 ml of reagent "C", 30 mg.g *(*8.8 mol.l) hydrogen peroxide is added slowly, (little by little to avoid violent reaction and consequent losses). The vessel is lightly covered so that gases can escape, and the reaction allowed to proceed, at room temperature, for 1 hour. After digesting at $85^{\circ}$C for a further 1 hour, the cover is removed and the volume reduced to a few (2-3) ml by heating. A second 10 ml aliquot of hydrogen peroxide reagent is added and digestion carried out for 1 hour at $85^{\circ}$C. The volume is again reduced to a few ml. After allowing to cool 50 ml of extracting solution "D", 1 mol.l ammonium acetate, is added and extraction carried out by shaking for 16 hours. Fraction 3, is separated for analysis, as before by centrifugation.

The total metal content may be determined by digesting the samples with a mixture of $HNO_3$–$HClO_4$ in a microwave oven (Kingston & Jassie, 1988; Nasrabadi, et al., 2010a; Nasrabadi et al., 2010b) considering time and cost economization. However, several bulk analysis methods may be used. The residual phase would be determined by subtracting the sum of concentration associated with three acid-soluble, reducible and oxidizable phases from the bulk concentration. Statistical processing of data is performed with SPSS 15 and Excel 2003.

## Results

In all three types of metallic pollution indices (accumulative or

comparative, enrichment and ecological risk indices), the bulk concentration of metals in the sediment sample is considered. Such a point of view indicates that all chemical forms of a given metal have an equal impact on the environment which may not be regarded reasonable. In order to improve such deficiency caused by bulk analysis, several speciation schemes are developed during recent decades through which different forms of a specific metal with different mobility potential are quantified. Although the ecological risk indices seem to imply the bioavailability of metallic pollution through the metrics achieved by a series of bioassay literature, the highly case-specific nature of such indices restrict their versatility.

Few indices have regarded the speciation for interpreting the sediment metallic contamination among which only Risk Assessment Code (RAC) (Ozmen et al., 2004; Singh et al., 2005; Pertsemli and Voutsa, 2007; Sheykhi & Moore 2013) and Mobility Factor (MF) (Salbu et al., 1998; Narwal et al., 1999; Kabala & Singh 2001; Olajire et al., 2003; Forghani et al., 2009) were found in the literature. The mentioned indices indicate the possible risk by applying a scale to the percentage of metals found in exchangeable and carbonate-bound phases. Accordingly, if the sum of species concentration bound to the mentioned phases is below 1%, there is no significant risk for the aquatic system. With percentages between 1 and 10%, a low risk, 11–30% a medium risk, 31–50% ahigh risk, and above 50% a very high risk is reported (Singh et al. 2005). Although these two indices have

incorporated the role of metal species in pollution risk interpretation, they are highly encompassed by specific speciation techniques; RAC (Tessier et al. 1979) and MF (Salbu et al. 1998). Furthermore, addressing the total potential risk exclusively to water-soluble, exchangeable and carbonate-bound phases may be challenged.

In anaerobic respiration the oxidation of organic matter is coupled with the reduction of alternate electron acceptors such as nitrate (denitrification), ferric iron (iron reduction), sulfate (sulfate reduction), and $CO_2$ (methanogenesis). Anaerobic respiring bacteria use fermentation products, e.g. acids, alcohols, (organotrophic) or inorganic electron donors (lithotrophic) and make energy by electron transport phosphorylation. According to the redox potential ladder, the free Gibbs energy released by reduction of Ferric to ferrous iron is more than that of sulfate, even Nitrate in low pH levels and all kinds of fermentation in pH of 7 (Stumm and Morgan 1996). Such a characteristic makes ferric iron a favorable source of terminal electron acceptor for lots of anaerobic respirating bacteria. Different Mechanisms for respiration of Fe(III)-minerals which include direct contact, electron shuttle and chelation will terminate in reduction of Fe(III) to Fe(II). Such species transformation highly affects the fate and transport of lots of toxic metals and metalloids bound strongly to iron minerals. As Fe(II) is much more soluble than Fe (III) specially in low pH and Eh conditions_favorable in lots of sediments environment_, the formerly-bound metals to Fe (III) minerals would

be deliberated to water column and mobilized due to such transformation. Accordingly, the portion of total metal concentration bound to reducible phase may also be considered in estimating the pollution risk.

A similar case exists regarding the species associated with oxidizable phase. Lithotrophs (Chemoautotrophs) are a large category of bacteria which use carbon dioxide as a carbon source (carbon fixation) and derive their energy (ATP) needs by oxidizing inorganic compounds such as $NH_4$, $NO_2$, $H_2S$, Fe(II) or $H_2$. Sulfur oxidizing bacteria like Thiobacillus thiooxidans and Acidithiobacillus thiooxidans use sulfide ion, elemental sulfur, or thiosulfate as energy sources. They are capable of growth in very acidic environments. Metals bound to sulfide minerals like $Cu_2S$, $CuS$, $ZnS$, $PbS$, $Sb_2S_3$, $FeS_2$, $MoS_2$, $NiS$, $CoS$ may be easily mobilized in case of biochemical reactions rendered by mentioned microorganisms. Furthermore, phototrophic bacteria are another group of microorganisms incorporated in the fate and transport of sulfide ion within sediment-water environments. There are approximately 60 species of phototrophic bacteria broadly grouped into purple and green bacteria. The major genera of Anoxygenic Phototrophic Bacteria may be categorized as; Purple sulfur bacteria (Chromatiaceae and Ectothiorhodospiraceae), Purple nosulfur bacteria (Rhodospirillaceae), Green sulfur bacteria (Chlorobiaceae), Green gliding bacteria (Chloroflexaceae) (Madigan, 2003). These phototrophic bacteria

(e.g., chromatiaceae, chlorobiaceae) use $CO_2$ as a carbon source, light as an energy source, and reduced sulfur compounds (e.g., $H_2S$, $SO$) as electron donors. Such phenomena would highlight the role of metal species bound to sulfide ions in imposing pollution risks to aquatic biota.

In order to contribute the role of metal species bound to different phases in estimating the pollution risk to the biota, developing a risky pollution index ($I_R$) has been considered which is a modified form of geochemical accumulation Index ($I_{geo}$). The geochemical accumulation index is calculated using:

$$I_{geo} = Log_2 [Cn/(1.5 * Bn)] \tag{1}$$

Where Igeo is the geochemical accumulation index, Cn is the sediment metal concentration and Bn is the metal concentration in the shale (Mueller, 1979).

Considering specific weights for the metal concentration in different potentially mobile and mobilizable phases (Acid-soluble, Reducible, and Oxidizable), the new index is defined as (Nasrabadi et al., 2010b):

$$I_R = Log_2 [(R + aAs + bRe + cOx)/R] \tag{2}$$

Where $I_R$ is the risky pollution index, while R, As, Re, and Ox are residual, Acid-soluble, Reducible, and Oxidizable portions of the whole metallic concentration, respectively. The portion attributed to acid-soluble phase (As) may be substituted by the sum of portions bound to water-soluble, exchangeable and carbonate-bound in case of other sequential techniques being used. a, b, and c are constants that

intensify the role of each portion in interpreting the bioavailable risky potential of metallic pollution in sediments and are determined to be 6, 3.5 and 2.5 respectively. In order to quantify a, b and c constants, besides making use of ideas achieved by research team, a data processing mechanism was considered through which the data generated by a group of case studies covering a range of sever to negligible pollution levels was analyzed (Bird et al., 2003; Galan et al., 2003; Guven & Akinci, 2008; Hnatukova et al. 2009; Karbassi et al., 2008; Martínez-Sánchez et al., 2008; Morillo et al., 2007; Nasrabadi et al., 2010b). Considering the percent of bulk metallic concentration bound to different phases and also researchers interpretations of the existent environmental threats, different combinations of a, b and c values by regarding a decreasing order were evaluated and finalized. Accordingly, the finalized formula of the index is developed as:

$$I_R = \text{Log}_2 \left[ (R + 6As + 3.5Re + 2.5Ox)/R \right] \tag{3}$$

In order to interpret the generated values by the index, a ladder similar to that of geoaccumulation index is considered (Table 2).

**Table 2. Risky Pollution Index ($I_R$) interpretation guideline**

| Pollution risk level | $I_R$ Value |
|---|---|
| Negligible | 0 - 1 |
| Low to Medium | 1 - 2 |
| Considerable | 2 - 3 |
| High | 3 - 4 |
| Very high | 4 - 5 |
| Severe | 5 – 9.23* |

**\*In case of ND for the metallic concentration bound to residual phase, 1 is considered for R value in the formula and the maximum possible value of the index would be 9.23.**

In comparison with two structurally similar indices namely mobility factor (MF) and risk assessment code (RAC) which consider only the water soluble, exchangeable and carbonate-bound phases as risky, the newly developed index has the supplementary privilege to avoid risk level underestimation by neglecting potentially risky phases (reducible and oxidizable). Mobility Factor/ Risk Assessment Code interpretation guideline is shown in Table 3.

**Table3. Mobility Factor/ Risk Assessment Code interpretation guideline**

| Pollution risk level | MF/RAC Value |
|---|---|
| No risk | <1% |
| Low | 1 – 10 % |
| Medium | 11 – 30 % |
| High | 31 – 50 % |
| Very high | > 50% |

In other words, MF and RAC indices may be considered as a special case of risky pollution index through which no values have been detected as the species bound to reducible and oxidizable phases. Such comparison has been made between the $I_R$ and MF/RAC interpretation ranges (Table 4).

**Table4. Comparison between MF/RAC and equivalent $I_R$ pollution risk interpretation**

| Pollution risk level (MF/RAC) | MF/RAC Value | Pollution risk level ($I_R$) | Equivalent $I_R$ Value |
|---|---|---|---|
| No risk | <1% | Negligible | <13.3 % |
| Low | 1 – 10 % | | |
| Medium | 11 – 30 % | Low to Medium | 13.3 – 31.5 % |
| High | 31 – 50 % | Considerable | 31.5 – 51.8 % |
| Very high | > 50% | High | 51.8 – 69.7 % |
| | | Very high | 69.7 – 82.7 % |
| | | Severe | > 82.7 % |

A sophisticated synchrony is observed between analogous categories (MF/RAC and Equivalent $I_R$ Values). Such synchrony may be experienced in case studies obeying the above mentioned pattern in bulk concentration distribution among phases like that of Haraz River (Table 5), Vlatava River (Table 6) and Aljesiras Bay sediments (Table 7).

**Table5. Fractionation analysis and pollution interpretation of Haraz River sediments, Iran (Nasrabadi et al., 2010b)**

| Station/ Metal | Sequential speciation phases % | | | | Sum of a,b,c | $I_R$ | $I_R$ interpretation | MF/RAC | MF/RAC interpretation |
|---|---|---|---|---|---|---|---|---|---|
| Co | a | b | c | d | | | | | |
| 1 | 9.5 | 29.3 | 0 | 61.2 | 38.8 | 1.88 | Low to Medium | 9.50 | Low |
| 2 | 13.9 | 29.6 | 0 | 56.5 | 43.5 | 2.15 | Considerable | 13.90 | Severe |
| 3 | 30.3 | 22.1 | 0 | 47.6 | 52.4 | 2.76 | Considerable | 30.30 | High |
| 4 | 25.2 | 23.5 | 0 | 51.3 | 48.7 | 2.54 | Considerable | 25.20 | Medium |
| 5 | 38.6 | 0 | 0 | 61.4 | 38.6 | 2.35 | Considerable | 38.60 | High |
| 6 | 47.7 | 19.5 | 0 | 32.9 | 67.2 | 3.64 | High | 47.65 | High |
| 7 | 58.7 | 14 | 0 | 27.3 | 72.7 | 4.07 | Very high | 58.70 | Very high |
| 8 | 72.7 | 13.7 | 0 | 13.7 | 86.4 | 5.29 | Severe | 72.63 | Very high |
| Pb | | | | | | | | | |
| 1 | 67 | 3.2 | 0 | 29.8 | 70.2 | 4.00 | High | 67.00 | Very high |
| 2 | 40.1 | 24.2 | 0 | 35.7 | 64.3 | 3.42 | High | 40.10 | High |
| 3 | 58.1 | 6.6 | 0 | 35.4 | 64.7 | 3.62 | High | 58.04 | Very high |
| 4 | 27.7 | 21.2 | 0 | 51 | 48.9 | 2.58 | Considerable | 27.73 | Medium |
| 5 | 35.4 | 14.2 | 0 | 50.4 | 49.6 | 2.71 | Considerable | 35.40 | High |
| 6 | 44.2 | 18.9 | 0 | 36.9 | 63.1 | 3.40 | High | 44.20 | High |
| 7 | 44.4 | 13.4 | 0 | 42.2 | 57.8 | 3.16 | High | 44.40 | High |
| 8 | 52 | 0 | 0 | 48 | 52 | 3.01 | High | 52.00 | Very high |
| Cd | | | | | | | | | |
| 1 | 27.9 | 0 | 0 | 72.1 | 27.9 | 1.81 | Low to Medium | 27.90 | Medium |

**Table5. Fractionation analysis and pollution interpretation of Haraz River sediments, Iran (Nasrabadi et al., 2010b)**

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **2** | 15.8 | 36.8 | 0 | 47.4 | 52.6 | 2.56 | Considerable | 15.80 | Medium |
| **3** | 42 | 0 | 0 | 58 | 42 | 2.51 | Considerable | 42.00 | High |
| **4** | 52 | 0 | 0 | 48 | 52 | 3.01 | High | 52.00 | Very high |
| **5** | 60.3 | 0 | 0 | 39.7 | 60.3 | 3.44 | High | 60.30 | Very high |
| **6** | 15.4 | 3.8 | 0 | 80.8 | 19.2 | 1.27 | Low to Medium | 15.40 | Medium |
| **7** | 42 | 0 | 0 | 58 | 42 | 2.51 | Considerable | 42.00 | High |
| **8** | 30.6 | 38.9 | 0 | 30.6 | 69.5 | 3.58 | High | 30.57 | High |
| **Cu** | | | | | | | | | |
| **1** | 19.9 | 3.7 | 0 | 76.4 | 23.6 | 1.52 | Low to Medium | 19.90 | Medium |
| **2** | 22.4 | 6.2 | 4.1 | 67.4 | 32.7 | 1.86 | Low to Medium | 22.38 | Medium |
| **3** | 17.4 | 0 | 4.1 | 78.5 | 21.5 | 1.36 | Low to Medium | 17.40 | Medium |
| **4** | 31.7 | 0 | 10.1 | 58.2 | 41.8 | 2.31 | Considerable | 31.70 | High |
| **5** | 22.7 | 0 | 0 | 77.3 | 22.7 | 1.54 | Low to Medium | 22.70 | Medium |
| **6** | 26.3 | 10.8 | 0 | 62.9 | 37.1 | 2.11 | Considerable | 26.30 | Medium |
| **7** | 32 | 9.2 | 0 | 58.8 | 41.2 | 2.35 | Considerable | 32.00 | High |
| **8** | 15.5 | 0 | 0 | 84.5 | 15.5 | 1.13 | Low to Medium | 15.50 | Medium |

a : Acid-soluble
b : Reducible
c : Oxidizable
d : Residual
$I_R$: Risky Pollution Index
MF: Mobility Factor
RAC: Risk Assessment Code

Furthermore, similar synchronies are observed in case studies within Iran where mobility factor is used for sediments of Maharlu Lake (Forghani et al., 2009) and where risk assessment code is considered for sediments of the Kor River (Sheykhi & Moore, 2013). The difference would be arisen when the majority of the bulk concentration is accumulated into two reducible and oxidzable phases. In such case MF and RAC indices would report the no or low

risk level while $I_R$ would interpret the existing risk level among medium to severe depending on the attributed percents to each phase. Such distinct interpretation difference is seen regarding the results achieved in the sediment pollution study of Izmir bay in Turkey (Table8). Minor differences may also be detected through case studies of Tinto River (Table 9) and Lapos River sediments (Table 10).

**Table6. Fractionation analysis and pollution interpretation of Vlatava River sediments, Czech Republic (Hnatukova et al., 2009)**

| Station / Metal Cr | Sequential speciation phases % | | | | Sum of a,b,c | $I_R$ | $I_R$ interpretation | MF/RAC | MF/RAC interpretation |
|---|---|---|---|---|---|---|---|---|---|
| | a | b | c | d | | | | | |
| 1 | 2 | 7 | 16 | 75 | 25 | 1.01 | Low to Medium | 2 | Low |
| 2 | 2 | 7 | 26 | 65 | 35 | 1.36 | Low to Medium | 2 | Low |
| 3 | 1 | 3 | 26 | 70 | 30 | 1.11 | Low to Medium | 1 | Low |
| 4 | 1 | 5 | 18 | 76 | 24 | 0.93 | negligible | 1 | Low |
| 5 | 2 | 5 | 23 | 70 | 30 | 1.17 | Low to Medium | 2 | Low |
| 6 | 2 | 6 | 25 | 67 | 33 | 1.28 | Low to Medium | 2 | Low |
| **Zn** | | | | | | | | | |
| 1 | 17 | 18 | 37 | 28 | 72 | 3.35 | High | 17 | Medium |
| 2 | 20 | 23 | 35 | 22 | 78 | 3.82 | High | 20 | Medium |
| 3 | 19 | 17 | 38 | 26 | 74 | 3.50 | High | 19 | Medium |
| 4 | 33 | 25 | 35 | 10 | 93 | 5.26 | Severe | 33 | High |
| 5 | 38 | 26 | 24 | 12 | 88 | 5.03 | Severe | 38 | High |
| 6 | 40 | 28 | 23 | 9 | 91 | 5.49 | Severe | 40 | High |
| **Cd** | | | | | | | | | |
| 1 | 45 | 22 | 17 | 16 | 84 | 4.66 | Very high | 45 | High |
| 2 | 50 | 30 | 12 | 8 | 92 | 5.79 | Severe | 50 | Very high |
| 3 | 40 | 33 | 17 | 10 | 90 | 5.35 | Severe | 40 | High |
| 4 | 44 | 30 | 16 | 10 | 90 | 5.39 | Severe | 44 | High |
| 5 | 42 | 28 | 20 | 10 | 90 | 5.36 | Severe | 42 | High |
| 6 | 40 | 30 | 21 | 9 | 91 | 5.50 | Severe | 40 | High |
| **Ni** | | | | | | | | | |
| 1 | 12 | 11 | 15 | 62 | 38 | 1.76 | Low to Medium | 12 | Medium |
| 2 | 22 | 16 | 17 | 45 | 55 | 2.61 | Considerable | 22 | Medium |
| 3 | 16 | 11 | 18 | 55 | 45 | 2.09 | Considerable | 16 | Medium |
| 4 | 16 | 7 | 20 | 57 | 43 | 2.00 | Considerable | 16 | Medium |
| 5 | 16 | 14 | 15 | 55 | 45 | 2.11 | Considerable | 16 | Medium |
| 6 | 19 | 13 | 18 | 50 | 50 | 2.35 | Considerable | 19 | Medium |

# Conclusions

In order to contribute the role of metal species bound to different phases in estimating the pollution risk to the biota, developing a risky pollution index ($I_R$) has been considered in this study.

A wide range of sediment metallic pollution case studies from extremely polluted to relatively unpolluted (regarding the pertinent authors interpretation) was considered for index verification.

**Table7. Fractionation analysis and pollution interpretation of Aljesiras Bay sediments, Spain (Morillo et al., 2007)**

| Station/ Metal | Sequential speciation phases % | | | | Sum of a,b,c | $I_R$ | $I_R$ interpretation | MF/RAC | MF/RAC interpretation |
|---|---|---|---|---|---|---|---|---|---|
| Ni | a | b | c | d | | | | | |
| 1 | 38 | 13 | 2 | 47 | 53 | 2.79 | Considerable | 38 | High |
| 2 | 20 | 16 | 24 | 40 | 60 | 2.79 | Considerable | 20 | Medium |
| 3 | 24 | 18 | 19 | 39 | 61 | 2.91 | Considerable | 24 | Medium |
| 4 | 24 | 19 | 4 | 53 | 47 | 2.37 | Considerable | 24 | Medium |
| 5 | 24 | 18 | 2 | 56 | 44 | 2.26 | Considerable | 24 | Medium |
| 6 | 13 | 17 | 16 | 54 | 46 | 2.10 | Considerable | 13 | Medium |
| Cd | | | | | | | | | |
| 1 | 9 | 26 | 8 | 57 | 43 | 1.96 | Low to Medium | 9 | Low |
| 2 | 7 | 24 | 2 | 67 | 33 | 1.56 | Low to Medium | 7 | Low |
| 3 | 18 | 9 | 16 | 57 | 43 | 2.05 | Considerable | 18 | Medium |
| 4 | 2 | 27 | 3 | 68 | 32 | 1.42 | Low to Medium | 2 | Low |
| 5 | 4 | 18 | 2 | 76 | 24 | 1.14 | Low to Medium | 4 | Low |
| 6 | 6 | 17 | 17 | 60 | 40 | 1.72 | Low to Medium | 6 | Low |
| Cu | | | | | | | | | |
| 1 | 27 | 17 | 3 | 53 | 47 | 2.41 | Considerable | 27 | Medium |
| 2 | 10 | 1 | 51 | 38 | 62 | 2.59 | Considerable | 10 | Medium |
| 3 | 10 | 3 | 46 | 41 | 59 | 2.47 | Considerable | 10 | Medium |
| 4 | 20 | 13 | 25 | 42 | 58 | 2.68 | Considerable | 20 | Medium |
| 5 | 27 | 13 | 20 | 40 | 60 | 2.89 | Considerable | 27 | Medium |
| 6 | 18 | 7 | 18 | 57 | 43 | 2.04 | Considerable | 18 | Medium |
| Pb | | | | | | | | | |
| 1 | 20 | 47 | 3 | 30 | 70 | 3.42 | High | 20 | Medium |
| 2 | 30 | 33 | 7 | 30 | 70 | 3.52 | High | 30 | High |
| 3 | 10 | 28 | 24 | 38 | 62 | 2.75 | Considerable | 10 | Medium |
| 4 | 9 | 57 | 4 | 30 | 70 | 3.29 | High | 9 | Low |
| 5 | 27 | 32 | 8 | 33 | 67 | 3.31 | High | 27 | Medium |
| 6 | 30 | 27 | 10 | 33 | 67 | 3.33 | High | 30 | High |
| Cr | | | | | | | | | |
| 1 | 8 | 18 | 8 | 66 | 34 | 1.58 | Low to Medium | 8 | Low |
| 2 | 11 | 27 | 2 | 60 | 40 | 1.91 | Low to Medium | 11 | Medium |
| 3 | 2 | 35 | 4 | 59 | 41 | 1.79 | Low to Medium | 2 | Low |
| 4 | 2 | 30 | 4 | 64 | 36 | 1.58 | Low to Medium | 2 | Low |
| 5 | 4 | 33 | 3 | 60 | 40 | 1.79 | Low to Medium | 4 | Low |
| 6 | 9 | 29 | 2 | 60 | 40 | 1.88 | Low to Medium | 9 | Low |
| Zn | | | | | | | | | |
| 1 | 3 | 39 | 16 | 42 | 58 | 2.49 | Considerable | 3 | Low |
| 2 | 18 | 26 | 20 | 36 | 64 | 2.98 | Considerable | 18 | Medium |
| 3 | 15 | 40 | 12 | 33 | 67 | 3.15 | High | 15 | Medium |
| 4 | 24 | 30 | 8 | 38 | 62 | 3.01 | High | 24 | Medium |
| 5 | 17 | 25 | 23 | 35 | 65 | 3.01 | High | 17 | Medium |
| 6 | 19 | 41 | 12 | 28 | 72 | 3.49 | High | 19 | Medium |

**Table8. Fractionation analysis and pollution interpretation of Izmir Bay sediments (Guven & Akinci, 2008)**

| Station/ Metal Cr | Sequential speciation phases % | | | | Sum of a,b,c | $I_R$ | $I_R$ interpretation | MF/RAC | MF/RAC interpretation |
|---|---|---|---|---|---|---|---|---|---|
| | a | b | c | d | | | | | |
| 1 | 0 | 3 | 72 | 25 | 75 | 3.11 | High | 0 | Low |
| 2 | 0 | 4 | 29 | 66 | 33 | 1.21 | Low to Medium | 0 | Low |
| 3 | 0.5 | 5 | 92.5 | 2 | 98 | 6.99 | Severe | 0.5 | Low |
| 4 | 0 | 5 | 85 | 10 | 90 | 4.58 | Very high | 0 | Low |
| 5 | 0 | 5 | 75 | 20 | 80 | 3.49 | High | 0 | Low |
| 6 | 0 | 3 | 91 | 6 | 94 | 5.35 | Severe | 0 | Low |
| 7 | 0 | 5 | 76 | 19 | 81 | 3.58 | High | 0 | Low |
| **Cu** | | | | | | | | | |
| 1 | 1.5 | 6 | 43 | 49.5 | 50.5 | 1.92 | Low to Medium | 1.5 | Low |
| 2 | 4 | 8 | 65 | 23 | 77 | 3.37 | High | 4 | Low |
| 3 | 3 | 3 | 76 | 18 | 82 | 3.72 | High | 3 | Low |
| 4 | 1.5 | 7 | 87 | 4.5 | 95.5 | 5.83 | Severe | 1.5 | Low |
| 5 | 1.5 | 10 | 78 | 10.5 | 89.5 | 4.57 | Very high | 1.5 | Low |
| 6 | 1 | 20 | 73 | 6 | 94 | 5.46 | Severe | 1 | Low |
| 7 | 1.5 | 7 | 86 | 5.5 | 94.5 | 5.53 | Severe | 1.5 | Low |
| **Pb** | | | | | | | | | |
| 1 | 1 | 36 | 25 | 38 | 62 | 2.61 | Considerable | 1 | Low |
| 2 | 4 | 49 | 23 | 24 | 76 | 3.53 | High | 4 | Low |
| 3 | 8 | 32 | 40 | 20 | 80 | 3.81 | High | 8 | Low |
| 4 | 2 | 63 | 30 | 5 | 95 | 5.97 | Severe | 2 | Low |
| 5 | 2.5 | 57.5 | 37 | 3 | 97 | 6.70 | Severe | 2.5 | Low |
| 6 | 4 | 38 | 51 | 7 | 93 | 5.38 | Severe | 4 | Low |
| 7 | 1 | 32 | 17 | 50 | 50 | 2.07 | Considerable | 1 | Low |
| **Zn** | | | | | | | | | |
| 1 | 46 | 32 | 18 | 4 | 96 | 6.77 | Severe | 46 | High |
| 2 | 29 | 22 | 18 | 31 | 69 | 3.40 | High | 29 | Medium |
| 3 | 23 | 30 | 42 | 5 | 95 | 6.14 | Severe | 23 | Medium |
| 4 | 22 | 32 | 23 | 23 | 77 | 3.82 | High | 22 | Medium |
| 5 | 23 | 46 | 24 | 7 | 93 | 5.71 | Severe | 23 | Medium |
| 6 | 15 | 50 | 29 | 6 | 94 | 5.84 | Severe | 15 | Medium |
| 7 | 9 | 20 | 21 | 50 | 50 | 2.18 | Considerable | 9 | Low |

Furthermore, a comparison between the interpretations generated by $I_R$ and those by a couple of structurally similar indices (mobility factor and risk assessment code) was made. In contrast with MF and RAC indices which also consider the role of speciation in interpretation of risk level, $I_R$ attributes a risk share to species bound to reducible and oxidizable phases which are totally neglected in both two above-mentioned indices. In other words, besides the absolutely mobile fractions, the potentially mobilizable fractions are also regarded in risk evaluation process elaborated by $I_R$.  Such a different

**Table9. Fractionation analysis and pollution interpretation of Tinto River sediments, Spain (Galan et al., 2003)**

| Station/ Metal | Sequential speciation phases % | | | | Sum of a,b,c | $I_R$ | $I_R$ interpretation | MF/RAC | MF/RAC interpretation |
|---|---|---|---|---|---|---|---|---|---|
| **As** | a | b | c | d | | | | | |
| 1 | 0 | 95 | 0 | 5 | 95 | 6.08 | Severe | 0 | Low |
| 2 | 10 | 75 | 3 | 12 | 88 | 4.83 | Very high | 10 | Medium |
| 3 | 0 | 92 | 1 | 7 | 93 | 5.57 | Severe | 0 | Low |
| 4 | 0 | 90 | 0 | 10 | 90 | 5.02 | Severe | 0 | Low |
| 5 | 30 | 66 | 0 | 4 | 96 | 6.70 | Severe | 30 | Medium |
| **Cd** | | | | | | | | | |
| 1 | 83 | 0 | 0 | 17 | 83 | 4.92 | Very high | 83 | Very high |
| 2 | 71 | 25 | 1 | 3 | 97 | 7.43 | Severe | 71 | Very high |
| 3 | 81 | 0 | 19 | 1 | 100 | 9.06 | Severe | 81 | Very high |
| 4 | 100 | 0 | 0 | 1 | 100 | 9.23 | Severe | 100 | Very high |
| 5 | 25 | 75 | 0 | 1 | 100 | 8.69 | Severe | 25 | Medium |
| **Cu** | | | | | | | | | |
| 1 | 8 | 82 | 8 | 2 | 98 | 7.48 | Severe | 8 | Low |
| 2 | 80 | 17 | 2 | 1 | 99 | 9.09 | Severe | 80 | Very high |
| 3 | 15 | 50 | 30 | 5 | 95 | 6.11 | Severe | 15 | Medium |
| 4 | 80 | 19 | 0 | 1 | 99 | 9.10 | Severe | 80 | Very high |
| 5 | 0 | 90 | 9 | 1 | 99 | 8.40 | Severe | 0 | Low |
| **Cr** | | | | | | | | | |
| 1 | 0 | 46 | 0 | 54 | 46 | 1.99 | Low to Medium | 0 | Low |
| 2 | 0 | 50 | 0 | 50 | 50 | 2.17 | Considerable | 0 | Low |
| 3 | 0 | 65 | 0 | 35 | 65 | 2.91 | Considerable | 0 | Low |
| 4 | 2 | 18 | 28 | 52 | 48 | 1.92 | Low to Medium | 2 | Low |
| 5 | 4 | 72 | 2 | 22 | 78 | 3.78 | High | 4 | Low |
| **Pb** | | | | | | | | | |
| 1 | 0 | 93 | 2 | 5 | 95 | 6.07 | Severe | 0 | Low |
| 2 | 6 | 75 | 4 | 15 | 85 | 4.43 | Very high | 6 | Low |
| 3 | 23 | 74 | 1 | 2 | 98 | 7.65 | Severe | 23 | Medium |
| 4 | 15 | 85 | 0 | 1 | 100 | 8.60 | Severe | 15 | Medium |
| 5 | 8 | 86 | 4 | 12 | 98 | 4.95 | Very high | 8 | Low |
| **Ni** | | | | | | | | | |
| 1 | 3 | 30 | 9 | 58 | 42 | 1.81 | Low to Medium | 3 | Low |
| 2 | 24 | 27 | 5 | 34 | 56 | 3.07 | High | 24 | Medium |
| 3 | 5 | 63 | 7 | 15 | 75 | 4.24 | Very high | 5 | Low |
| 4 | 0 | 58 | 17 | 25 | 75 | 3.44 | High | 0 | Low |
| 5 | 9 | 53 | 2 | 36 | 64 | 2.96 | Considerable | 9 | Low |
| **Zn** | | | | | | | | | |
| 1 | 66 | 27 | 2 | 5 | 95 | 6.65 | Severe | 66 | Very high |
| 2 | 95 | 3 | 0 | 2 | 98 | 8.19 | Severe | 95 | Very high |
| 3 | 56 | 33 | 10 | 1 | 99 | 8.90 | Severe | 56 | Very high |
| 4 | 65 | 34 | 0 | 1 | 99 | 8.99 | Severe | 65 | Very high |
| 5 | 30 | 64 | 2 | 4 | 96 | 6.69 | Severe | 30 | High |

principle of the newly-developed index may prevent risk level underestimation especially in case where a remarkable percent of bulk concentration is accumulated within reducible and oxidizable phases. Development of the new index is based on the fact that high values of toxic metals/metalloids concentration may be assumed non-risky in case the majority of metals/metalloids bulk concentration is associated

with residual phase and similarly low values of concentration may be interpreted as risky when the majority of bulk concentration is attributed to potentially labile phases (Acid-soluble, Reducible, and Oxidizable according to the BCR sequential extraction method considered in the current study and equivalent phases in case of other methods).

The independency of the index value to the bulk concentration makes it possible to discuss the potential risk in different levels of

**Table10. Fractionation analysis and pollution interpretation of Lapos River sediments (Bird et al., 2003)**

| Station/ Metal | Sequential speciation phases % | | | | Sum of a,b,c | $I_R$ | $I_R$ interpretation | MF/RAC | MF/RAC interpretation |
|---|---|---|---|---|---|---|---|---|---|
| As | a | b | c | d | | | | | |
| 1 | 0 | 0 | 95 | 5 | 95 | 5.60 | Severe | 0 | Low |
| 2 | 2 | 0 | 28 | 70 | 30 | 1.12 | Low to Medium | 2 | Low |
| 3 | 0 | 8 | 2 | 90 | 10 | 0.45 | negligible | 0 | Low |
| 4 | 0 | 10 | 5 | 85 | 15 | 0.64 | negligible | 0 | Low |
| 5 | 2 | 28 | 8 | 62 | 38 | 1.63 | Low to Medium | 2 | Low |
| 6 | 0 | 5 | 0 | 95 | 5 | 0.24 | negligible | 0 | Low |
| 7 | 1 | 18 | 3 | 78 | 22 | 0.99 | negligible | 1 | Low |
| Cd | | | | | | | | | |
| 1 | 3 | 0 | 97 | 1 | 100 | 8.03 | Severe | 3 | Low |
| 2 | 75 | 20 | 5 | 1 | 100 | 9.06 | Severe | 75 | Very high |
| 3 | 50 | 25 | 20 | 5 | 95 | 6.47 | Severe | 50 | Very high |
| 4 | 74 | 19 | 7 | 1 | 100 | 9.05 | Severe | 74 | Very high |
| 5 | 70 | 20 | 9 | 1 | 99 | 9.00 | Severe | 70 | Very high |
| 6 | 72 | 20 | 6 | 2 | 98 | 8.02 | Severe | 72 | Very high |
| 7 | 71 | 19 | 7 | 3 | 97 | 7.42 | Severe | 71 | Very high |
| Cu | | | | | | | | | |
| 1 | 2 | 0 | 98 | 1 | 100 | 8.01 | Severe | 2 | Low |
| 2 | 53 | 37 | 10 | 1 | 100 | 8.89 | Severe | 53 | Very high |
| 3 | 20 | 22 | 41 | 17 | 83 | 4.22 | Very high | 20 | Medium |
| 4 | 25 | 28 | 29 | 18 | 82 | 4.23 | Very high | 25 | Medium |
| 5 | 25 | 25 | 40 | 10 | 90 | 5.12 | Severe | 25 | Medium |
| 6 | 12 | 26 | 15 | 47 | 53 | 2.40 | Considerable | 12 | Medium |
| 7 | 11 | 29 | 28 | 32 | 68 | 3.07 | High | 11 | Medium |
| Pb | | | | | | | | | |
| 1 | 4 | 0 | 96 | 1 | 100 | 8.05 | Severe | 4 | Low |
| 2 | 17 | 83 | 0 | 1 | 100 | 8.62 | Severe | 17 | Medium |
| 3 | 5 | 62 | 3 | 30 | 70 | 3.25 | High | 5 | Low |
| 4 | 4 | 71 | 5 | 20 | 80 | 3.93 | High | 4 | Low |
| 5 | 7 | 83 | 2 | 8 | 92 | 5.43 | Severe | 7 | Low |
| 6 | 1 | 51 | 13 | 35 | 65 | 2.85 | Considerable | 1 | Low |
| 7 | 2 | 78 | 5 | 15 | 85 | 4.38 | Very high | 2 | Low |
| Zn | | | | | | | | | |
| 1 | 3 | 0 | 97 | 1 | 100 | 8.03 | Severe | 3 | Low |
| 2 | 62 | 35 | 3 | 1 | 100 | 8.97 | Severe | 62 | Very high |
| 3 | 39 | 28 | 18 | 15 | 85 | 4.71 | Very high | 39 | High |
| 4 | 60 | 25 | 10 | 5 | 95 | 6.58 | Severe | 60 | Very high |
| 5 | 48 | 33 | 14 | 5 | 95 | 6.47 | Severe | 48 | High |
| 6 | 50 | 28 | 7 | 15 | 85 | 4.84 | Very high | 50 | Very high |
| 7 | 32 | 35 | 13 | 20 | 80 | 4.20 | Very high | 32 | High |

bulk concentration. Furthermore, comparing the potentially risky portion of the pollution in a sediment sample with its own background levels (residual phase) instead of a fixed clean case as the concentration in shale (Mueller, 1979) or earth crust (Szefer et al., 1998) may terminate in more realistic conclusions.

On the other hand, classification of the existent metallic pollution into two distinct categories of geopogenic (species bound to residual phase) and anthropogenic (species bound to potentially labile phases) and consequently attributing the risky pollution to the sole anthropogenic portion (Karbassi et al. 2008) may be exposed to as a subtle trap. In other words, geopogenic source depending on several geological textures may also be introduced as the dominant potential risk by extremely fade anthropogenic interventions. The index capability in indication of risky pollution regardless of the pollution source type may prevent the probable misleading caused by distinct separation of bulk concentration into geopogenic and anthropogenic portion.

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