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
	$NH_4P_2O_7$
Organically bound/ sulfides	$NaOCl$
	$EDTA$
	$H_2O_2/HNO_3/NaOAc$
	$H_2O_2/HNO_3/NH_4OAc$
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$<30^{\circ}$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 $20\pm2^{\circ}$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°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°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:

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

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

Table2. 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)

	a	b	c	d		I_R		MF	RAC
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

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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.

References

1. Adamo P., Arienzo M., Imperato M., Naimo D., Nardi G., "Distribution and partition of heavy metals in surface and sub-surface sediments of Naples city port", *Chemosphere, 61* (2005) 800-809.

2. Bird G., Brewer P.A., Macklin M.G., Balteanu D., Driga B., Serban M., Zaharia S., "The solid state partitioning of contaminant metals and As in river channel sediments of the mining affected Tisa drainage basin, northwestern Romania and eastern Hungary", *Applied Geochemistry, 18* (2003) 1583-1595.

3. Chapman P., "The sediment quality Triad approach to determining pollution-induced degradation", *Sci. Total Environ. 97/98* (1990) 815-825.

4. Chester R., Hughes R. M., "A chemical technique for the separation of ferro-manganese minerals, carbonate minerals and adsorbed trace elements from pelagic Sediment", Chemical Geology, 2 (1967) 249-262.

5. Cuong D.T., Obbard J.P., "Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure", Applied Geochemistry, 21 (2006) 1335-1346.

6. DelValls T.A., Forja J.M., Go´mez-Parra A., "Integrated assessment of sediment quality in two littoral ecosystems from the Gulf of Ca´diz, Spain", Environ. Toxicol. Chem. 17 (1998) 1073-1084.

7. Fairey R., Long E.R., Roberts C.A., Anderson B.S., Phillips B.M., Hunt J.W., Puckett H.R., Wilson C.J., "An evaluation of methods for calculating mean sediment quality guideline quotients as indicators of contamination and acute toxicity to amphipods by chemical mixture. Environ", Toxicol. Chem. 20 (2001) 2276-2286.

8. Ferreira J.G., "Development of an estuarine quality index based on key physical and biogeochemical features", Ocean Coast, Manage, 43 (2000) 99-122.

9. Field L.A., MacDonald D.D., Norton S.B., Ingersoll C.G., Severn C.G., Smorong D., Lindskoog R., "Predicting amphipod toxicity from sediment chemistry using logistic regression models. Environ. Toxicol. Chem. 21 (9) (2002) 1993-2005.

10. Field L A., MacDonald D.D., Norton S.B., "Evaluating sediment chemistry and toxicity data using logistic regression modelling. Environ", Toxicol, Chem. 18 (6) (1999) 1311-1322.

11. Forghani G., Moore F., Lee S., Qishlaqi A., "Geochemistry and speciation of metals in sediments of the Maharlu Saline Lake", Shiraz, SW Iran, Environ. Earth Sci., 59 (2009) 173-184.

12. Galan E., Gomez-Ariza J.L., Gonzalez I., Fernandez-Caliani J.C. Morales E., Giraldez I., "Heavy metal partitioning in river sediments severely polluted by acid mine drainage in the Iberian Pyrite Belt", Applied Geochemistry, 18 (2003) 409-421

13. Guven D.E., Akinci G., "Heavy metals partitioning in the sediments of Izmir Inner Bay", Journal of Environmental Sciences, 20 (2008) 413-418.

14. Hakanson L., "An ecological risk index for aquatic pollution control", A sedimentological approach. Water Res. 14 (1980) 975-1001.

15. Hnatukova, L., Benesova, L. and Kominkova, D., 2009. Impact of urban drainage on metal distribution in sediments of urban streams, Water science and technology, 59 (6), 1237-1246.

16. Horowitz A.J., Meybeck M., Idlafkih Z., Biger F., "Variations in trace element geochemistry in the Seine river basin based on floodplain deposits and bed sediments", Hydrological Process, 13 (1999) 1329-1340.

17. Kabala C., Singh B.R., "Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter", Journal of Environmental Quality, 30 (2001) 485-492.

18. Karbassi A.R., Monavari S.M., "Nabi Bidhendi G.R., Nouri J., Nematpour K., "Metal pollution assessment of sediment and water in the Shur River. Environmental Monitoring and Assessment, 147 (2008) 107-116.

19. Katherine F.M., Christine M.D., "Comparison of original and modified BCR sequential extraction procedures for the fraction of copper, iron, lead, manganese and zinc in soils and sediments", Analytica Chimica Acta, 478 (2003) 111-118.

20. Kersten M., Forstner U., "Speciation of trace elements in sediments. In G. E. Batley (Ed.) Trace element speciation: Analytical methods and problems", (1991) (245-317), CRC Press, Boca Raton.

21. Keshavarzi B., Moore F., Mosaferi M., Rahmani F., "The Source of Natural Arsenic Contamination in Groundwater, West of Iran", Water Quality, Exposure and Health, 3(3-4) (2011) 135-147.

22. Keshavarzi B., Moore F., Rastmanesh F., Kermani M., "Arsenic in the Muteh gold mining district, Isfahan, Iran, Environ. Earth Sci., 67 (2012) 959-970.

23. Kingston H.M., Jassie L.B., "In: Introduction to microwave sample preparation", American Chemical Society, Professional Reference Book, Washington DC, U.S.A (1988).

24. Kwon Y.T., Lee, C.W., "Application of multiple ecological risk indices for the evaluation of heavy metal contamination in a coastal dredging area. Sci. Total Environ. 214 (1998) 203-210.

25. Long E.R., MacDonald D.D., "Recommended uses of empirically derived, sediment quality guidelines for marine and estuarine ecosystems", Hum, Ecol, Risk Assess. 4 (1998) 1019-1039.

26. Long E.R., MacDonald D.D., Smith L., Calder F.D., "Incidence of Adverse Biological Effects Within Ranges of Chemical Concentrations in Marine and Estuarine Sediments", Environmental Management, 19 (1995) 81-97.

27. Long E.R., Morgan L.G., "The Potential for Biological Effects of Sediment-Sorbed Contaminants Tested in the National Status and Trends Program. National Oceanic and Atmospheric Administration, Office of Oceanography and Marine Assessment", Seattle WA. NOAA Technical Memorandum NOS OMA 52 (1990).

28. MacDonald D.D., Lindskoog R.A., Smorong D.E., Greening H., Pribble R., Janicki T., Janicki S., Grabe S., Sloane G.,Ingersoll C.G., Eckenrod S., Long E.R., "Development of an ecosystem-based framework for assessing and managing sediment quality conditions in Tampa Bay", Florida, Tampa Bay Estuary Program, Florida, USA (2000).

29. Madigan M., "Brock Biology of Microorganisms", 10th ed., Prentice-Hall, Englewood Cliffs, N.J. (2003).

30. Martínez-Sánchez M.J., Navarro M.C., Pérez-Sirvent C., Marimón J., Vidal J., García-Lorenzo M.L., Bech J., "Assessment of the mobility of metals in a mining-impacted coastal area (Spain, Western Mediterranean), Journal of Geochemical Exploration, 96 (2008) 171-182.

31. Morillo J., Usero J., Gracia I., "Potential mobility of metals in polluted coastal sediments in two bays of southern Spain", Journal of Coastal Research, 23(2) (2007) 352-361.

32. Mueller G. "Schwermetalle in den sediments des Rheins-Veranderungen Seitt" Umschau, 1979, 79 (2007) 778-783.

33. Nabi Bidhendi G.R., Karbassi A. R., Nasrabadi T., Hoveidi H., "Influence of Copper Mine on Surface water Quality", International Journal of Environmental Science and Technology, 4 (1) (2007) 85-91.

34. Narwal R.P., "Singh B.R., "Effect of organic materials on partitioning, extractability and plant uptake of metals in an alum shale soil", Water, Air, Soil Pollut. 103 (1998) 405-421.

35. Nasrabadi T., Nabi Bidhendi G.R., Karbassi A.R., Hoveidi H., Nasrabadi I., Pezeshk H., Rashidinejad F., "Influence of Sungun copper mine on groundwater quality, NW Iran", Environmental Geology, 58 (2009) 693-700.

36. Nasrabadi T., Nabi Bidhendi G. R., Karbassi A. R., Mehrdadi N., "Partitioning of metals in sediments of the Haraz River (Southern Caspian Sea basin)", Environmental Earth Sciences, 59 (2010a) 1111-1117

37. Nasrabadi T., Nabi Bidhendi G.R., Karbassi A.R., Mehrdadi N., "The pollution of Haraz River sediments, southern Caspian Sea basin", Environmental monitoring and assessment, 171(1-4) (2010b. Evaluating the efficiency of sediment metal pollution indices in interpreting) 395-410.

38. Olajire A.A., Ayodele E.T., Oyedirdan G.O., Oluyemi E.A., "Levels and speciation of heavy metals in soils of industrial Southern Nigeria", Environmental Monitoring and Assessment, 85 (2003) 135–155.

39. OttW.R., "Environmental Indices-Theory and Practice. Ann Arbor Science", Michigan, USA (1978).

40. Ozmen, H., Kulahci F., Ukurovali A. C.¸ Dogru M., "Concentrations of heavy metal and radioactivity in surface water and sediment of Hazar Lake (Elazig, Turkey)", Chemosphere 55 (2004) 401-408.

41. Pertsemli E., Voutsa D., "Distribution of heavy metals in Lakes Doirani and Kerkini", Northern Greece, J. Hazard. Mater,148 (2007) 529-537.

42. Rauret G., Lopez-Sanchez J. F., Sahuquillo A., "Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. Journal of Environmental Monitoring, 1 (1999) 57–61.

43. Riba I., DelValls T.A., Forja J.M., Go´mez-Parra A., "Evaluating the heavy metal contamination in sediments from the Guadalquivir estuary after the Aznalco´ llar mining spill (SW Spain): a multivariate analysis approach" Environ, Monit, Assess, 77 (2002) 191–207.

44. Ross A.S., Filip M.G.T., "Determination of Al, Cu, Fe, Mn, Pb and Zn in certified reference materials using the optimized BCR sequential extraction procedures", Analytica Chimica Acta, 454 (2002) 249-257.

45. Ruiz F., "Trace metals in estuarine sediments from the southwestern Spanish Coast", Mar. Pollut. Bull. 42 (2001) 482–490.

46. Sahuquillo A., Lopez-Sanchez J.F., Rubio R., Rauret G., "Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure", Analytica Chimica Acta, 382 (1999) 317-327.

47. Satsmadjis J., Voutsinou-Taliadouri F., "An index of metal pollution in marine sediments", Oceanol. Acta 8 (1985) 277-284.

48. Salbu B., Krekling T., Oughton D.H., "Characterization of radioactive particles in the environment'", Analyst 123 (1988) 843-849.

49. Sheykhi V., Moore F., "Evaluation of potentially toxic metals pollution in the sediments of the Kor river, southwest Iran", Environ. Monit. Assess, 185 (2013) 3219-3232.

50. S hin P.K.S., Lam W.K.C., "Development of a marine sediment pollution index", Environ, Pollut. 113 (2001) 281-291.

51. Singh K.P., Mohan D., Singh V.K., Malik A., "Studies on distribution and fractionation of heavy metals in Gomti river sediments-a tributary of the Ganges, India", J. Hydrol. 312 (2005) 14–17.

52. Stamatis N., Kamidis N., Sylaios G., "Sediment and suspended matter lead contamination in the gulf of Kavala, Greece", Environmental Monitoring and Assessment, 115 (2006) 433-449.

53. Stumm W., Morgan J.J., "Aquatic Chemistry", Wiley, NY (1996).

54. Sutherland R.A., "Bed sediment-associated trace metals in an urban stream", Oahu, Hawaii. Environmental Geology, 39 (6) (2000) 611-627.

55. Szefer S., Kusak A., Szefer K., Glasby G.P., Jankowska H., Wolowicz M., Ali A.A., "Evaluation of the anthropogenic influx of metallic pollutants in to Puck Bay", southern Baltic, Applied geochemistry, 9 (1998) 293-303.

56. Tessier A., Campell P.G.C., Bisson M., "Sequential extraction procedure for the speciation ofpartition of particulate trace metals", Analytical Chemistry, 51 (1979) 844-851.

57. Ure A.M., Quevauviller Ph., Muntau H., Griepink B., "Speciation of heavy metals in solids and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities", International Journal of Analytical Chemistry, 51 (1993) 135-151.

58. Ure A.M., Davidson C.M., Thomas R.P., "In: Ph. Quevauviller Maier and B. Griepink, Editors, Quality Assurance for Environmental Analysis", Elsevier, Amsterdam (1995).

59. Usero J., Gonza´lez-Regalado E., Gracia I., "Trace metals in the bivalve mollusc Chamelea gallina from the Atlantic Coast of Southern Spain. Mar",Pollut. Bull. 32 (3) (1996) 305-310.

60. Wilson J.G., Jeffrey D.W., "Europe-wide indices for monitoring estuarine quality. In: Kramer, K.J.M. (Ed.)", Biological Indicators of Pollution, Royal Irish Academy, Dublin, Ireland (1987) 225-242.

61. Yuan C., Shi J., He B., Liu J., Liang L., "Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction", Environment International, 30 (2004) 769-783.