RESEARCH ARTICLE

# Relationship of metal enrichment with adverse biological effect in the Yangtze Estuary sediments: role of metal background values

**Shou Zhao · Chenghong Feng · Dongxin Wang · Chenhao Tian · Zhenyao Shen**

**Abstract** Exclusive pristine values of As, Cd, Cr, Cu, Fe, Mn, Pb, and Zn in the Yangtze Estuary are calculated using principal components analysis (PCA) to probe the relationship between degrees of metal enrichment and their adverse biological effects. The results show that obvious differences in the degrees of metal enrichment exist when the enrichment factors are analyzed with reference background values on global, national, and local scales. Based on the low variability of aluminum, the exclusive metal background values in the estuary are obtained with PCA and are more likely to reflect the pristine contents of the abovementioned metals in the Yangtze Estuary. For the six most common metals (As, Cd, Cr, Cu, Pb, and Zn), significant correlations exist between the enrichment factors and their adverse biological effects. Arsenic shows the highest potential to cause adverse effects despite its general lack of enrichment. However, Cd is the most conservative element and is not likely to cause biological effects in the estuary.

**Keywords** Heavy metals · Sediments · Risk assessment · Enrichment factor · Yangtze estuary · PCA

## Introduction

Currently, heavy metal pollution caused by human activities is frequently reported, which has attracted considerable concern around the world (Chen 2003; Thevenon et al. 2011; Xia et al. 2011). Unlike organic pollutants, heavy metals in

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aquatic environments cannot be removed by natural degradation processes and can often be enriched in sediments (Lee et al. 2000; Peng et al. 2009). Due to the protracted residence time of metals within rivers and their floodplains (from 10 to 10,000 years), metal-enriched sediments may act as major sources of future contamination and pose an ongoing long-term risk to the environment (Taylor and Hudson-Edwards 2008). Therefore, the investigation of metal enrichment in sediments has become an indispensable part of aquatic environmental assessment.

The evaluation of metal enrichment is often accomplished via element enrichment factors (EFs). EFs were originally put forward to estimate the sources of elements in the atmosphere, precipitation, or seawater (Chester and Stoner 1973; Zoller et al. 1974; Reimann and De Caritat 2005) and have recently become one of the most well-known environmental indicators. To obtain the EF of metals, pre-anthropogenic metal contents are often needed to act as references against which measured values can be compared (Rezaee et al. 2010). Several metal background values of sediments have been developed and employed at different scales, e.g., the metal contents in the Earth's crust on a global scale (Duan et al. 2010); metal background values established by governments on a national scale (Schwartz et al. 2006); or data obtained from cored sediments in pristine areas on a local scale (Abrahim and Parker 2008).

To date, there is still no consensus on the appropriate background values for the calculation of metal EFs, which undoubtedly causes certain discrepancies when different reference values are employed (Rubio et al. 2000). To our knowledge, although some researchers have employed one or two of the abovementioned background values to assess metal enrichment in sediments, few studies have compared the degrees of metal enrichment calculated using the three types of background values described above.

In addition to metal enrichment, adverse biological effects caused by sediment-associated metals are another major concern in aquatic environmental assessment (Christophoridis et al. 2009). Biological risk is likely if the metal contents in sediments are above metal toxicity thresholds (McCauley et al. 2000). Generally, enrichments and biological effects of metal-contaminated sediments are discussed separately or alternatively, with few study combined them together (Birch and Taylor 2002). Furthermore, little attention has been paid to the numerical correlations between the two aspects. However, if some correlations do exist between them, questions such as whether sediment enrichment necessarily indicates biological effect or the degree of metal enrichment for which adverse biological effects is expected to occur could easily be answered. Thus, the numerical relationships between degrees of metal enrichment and biological effects are worthy of study.

Regarding the Yangtze Estuary, over 70 % of the river-derived sediment of the Yangtze River (ca. $4.86 \times 10^8$ tons/year) is deposited in the estuary (Milliman and Meade 1983). Due to intense anthropogenic activities, the riverine loads and compositions into the Yangtze Estuary have been significantly altered (Dai et al. 2010). Additionally, the construction of dams and reservoirs (e.g., the Three Gorges Dam, the largest dam in the world) in the upper reaches of the river have also slowed the tributary flow, which has changed the enrichment environment and pollution level of metals in the estuarine areas (Hu et al. 2012; Stone 2011). Thus, several investigations have reported the enrichment of sediments by several metals (e.g., As, Cr, and Cu) in the estuary (Feng et al. 2004; Fang and Chen 2010; Liu et al. 2011a). Adverse biological effects caused by metal enrichment were also recorded in this area in recent years (Li et al. 2009; Yi et al. 2011). However, little attention has been paid to the effect of the difference in metal background values on the degrees of metal enrichment, and almost no research has focused on the numerical correlations between metal enrichment and adverse biological effect in the Yangtze Estuary.

Thus, in this study, the enrichments of eight metals (As, Cd, Cr, Cu, Fe, Mn, Pb, and Zn) in the sediments of the Yangtze Estuary are comprehensively investigated using background values obtained on the global, national, and local scales. Additionally, the numerical relationships between metal enrichment factors and the corresponding adverse biological effects are also explored to determine the degree of metal enrichment at which biological effects are expected to occur.

## Materials and methods

### Description of sampling sites and sediments

The geographical setting of the study area has been thoroughly described in recent studies (Li et al. 2012; Liu et al. 2011b; Pan and You 2010; Wang et al. 2012; Yang et al. 2011). Figure 1 showed the 30 surface sediment samples collected in pre-cleaned polyethylene bags with a portable Peterson's stainless-steel grab sampler. Each sample was obtained by mixing sediments randomly collected (three times) at each sampling point.

Two sediment cores with lengths of approximately 100 cm (31°22.248 N, 121°57.563E) and 120 cm (31°14.187 N, 122°00.133E) were collected from the Yangtze Estuary (indicated by the ▵ symbols in Fig. 1). The two sites were selected because they were far from the sewage outlets in the upstream within the Yangtze Estuary and were therefore less affected by anthropogenic metal inputs. Sewage input, one of the main sources of river pollution, generally influences the downstream surrounding area more significantly than other remote areas. The sewage outlets in the Yangtze Estuary are mainly located near sites 3, 4, and 10, among others (Fig. 1) (Gu et al. 2013), and most of the discharged pollutants will be carried by water flow through the South Bay. Because of their distance from sewage outlets and the influence of water flow, the two cores are expected to suffer relatively little from human pollution. Moreover, the sediments in this area were relatively coarse, which indicated less potential for scavenging metals (Forstner and Wittmann 1979; Forstner and Patchineelum 1980). Each core was tightly capped and cut along its length in 1 cm intervals. All the samples were brought to the laboratory as soon as possible and preserved at −20 °C.

### Analytical methods

The contents of nine metal species (Al, As, Cd, Cr, Cu, Fe, Mn, Pb, and Zn) in surface and core sediments were measured by inductively coupled plasma mass spectrometry (ICP-MS, Thermo) and inductively coupled plasma optical
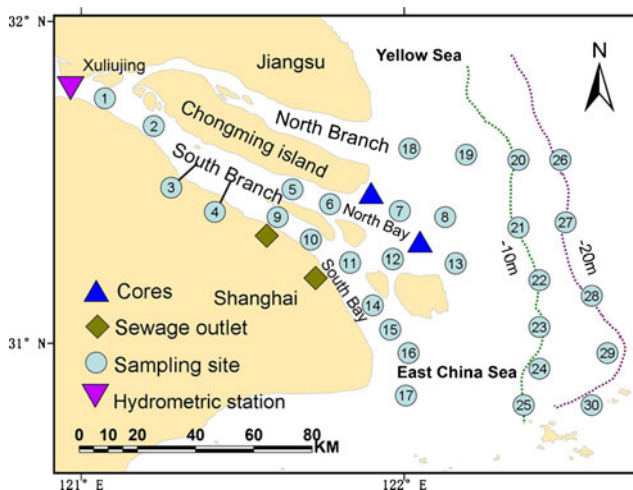


**Fig. 1** Map of sediment sampling sites in the estuarine area of the Yangtze River

emission spectrometer (ICP-OES, Thermo). The detailed analytical procedure can be found in previous studies (Yang et al. 2009). The total organic carbon (TOC) was measured by a total organic carbon analyzer (Elementar, Germany). The detection limits of the ICP-MS are as follows: As, 0.1 mg/kg; Cd, 0.02 mg/kg; Cr, 2 mg/kg; Cu, 0.3 mg/kg; Mn, 5 mg/kg; Pb, 0.5 mg/kg; and Zn, 0.5 mg/kg. The detection limits of the ICP-OES for Al and Fe are 0.1 %, as is the detection limit of the TOC analyzer. Replicate analyses of blanks and reference materials showed good accuracy, and the reference materials contents were within 92–117 % of the certified values for all measured elements. Both the field and laboratory experiments were carefully performed, and all instruments were cleaned with acid or deionized water to prevent contamination.

Metal enrichment and biological effect index

The EF is obtained by the standardization of a measured element against a reference value. The reference element employed in this study is aluminum (Al), which is the most widely used for normalization (Schropp et al. 1990).

The EF is calculated according to the following equation suggested by Buat-Menard and Chesselet (1979):

$$\text{EF} = \left[ C_n(\text{sample}) \Big/ C_{\text{ref}}(\text{sample}) \right]$$
$$\times \left[ B_n(\text{background}) \Big/ B_{\text{ref}}(\text{background}) \right]^{-1} \qquad (1)$$

where $c_n$ (sample) and $c_{\text{ref}}$ (sample) are the contents of the examined and reference metals in the examined sediments, respectively, and $B_n$ (background) and $B_{\text{ref}}$ (background) are the contents of the examined and reference metals in the reference sediments. EF<1 suggests deficient enrichment compared with background values, $1 \leq \text{EF} < 2$ indicates minimal sediment enrichment, and $2 \leq \text{EF} < 5$ indicates moderate enrichment. Finally, $\text{EF} \geq 5$ suggests that the sample is significantly enriched (Sutherland 2000).

Sediment quality guideline (SQG) values were established by Long et al. (1995) to estimate the biological effects of sediments. The SQG involves three concentration ranges: concentrations below effects range—low (ERL) indicate that adverse biological effects are rarely observed, concentrations at or above effects range—median values indicate that adverse biological effects are expected to occur frequently, and concentrations between these values represent a range within which biological effects occur occasionally. In this study, we assume that adverse biological effects can occur if the metal contents in sediments are above the ERL values. Thus, the adverse biological effect (ABE)

indicator was introduced and correlated with the EF. The ABE could be calculated as follows:

$$\text{ABE} = c_n(\text{sample}) \Big/ \text{ERL} \qquad (2)$$

where ABE is the adverse biological effect; $c_n$ (sample) is the content of the examined element in the examined sediment; and ERL is the effects range—low. $\text{ABE} \leq 1$ suggests that adverse biological effects are expected to occur rarely, whereas ABE>1 indicates possible biological effect.

## Results and discussion

### Existing metal background values at three typical scales

The Al, As, Cd, Cr, Cu, Fe, Mn, Pb, and Zn contents in the sediments of the Yangtze Estuary are listed in Table 1. To calculate the enrichment degrees of these metals in the study area more accurately, three typical background values (i.e., global, national, and local) are primarily selected based on the comprehensive investigation of former studies.

Regarding the global background values, the contents of all naturally occurring metals in the Earth's crust, also known as Clark values (Clarke 1924), are often widely used, although the general validity of these reference values has been broadly criticized (Reimann and De Caritat 2000). In this study, the metal contents in the Earth's crust proposed by Taylor and McLennan were adopted (Taylor and McLennan 1995).

More area-specific reference values are obtained at a national scale, with which metal fate and transport over a larger area can be assessed while still providing a detailed description of the enrichment dynamics in an individual region (Woodfine et al. 2002). Because the Yangtze Estuary is a typical water area in China, the national reference values obtained from Chinese Environmental Protection and Geological Mineral Departments might represent the metal background values of the Yangtze Estuary area (Yan et al. 1995).

Moreover, a local baseline established by analyzing comparable local sediments unaffected by anthropogenic activity is considered more reasonable and advantageous because the measured and referenced sediments are texturally, mineralogically, and chemically similar and have experienced similar weathering, erosion, transport, and sedimentation cycles (Abrahim and Parker 2008). As reported in many former studies, the local background values were obtained by taking the average values of several low-content samples selected from the deep, minimally impacted levels of sediment cores (Abrahim and Parker 2008). Thus, in this study, the local background values of the nine metals are obtained from the

**Table 1** Metals contents in sediments of the Yangtze Estuary and their corresponding worldwide, nationwide, local and exclusive background values

| Metal species | Metal contents[b] (mg/kg) | ERL (mg/kg) | Background values (mg/kg) | | | |
|---|---|---|---|---|---|---|
| | | | Worldwide [c] | Nationwide [d] | Local | PCA calculated |
| As | 9.147±2.301 | 8.2 | 1.5 | *9.1* | 5.921 | *9.427* |
| Cd | 0.192±0.121 | 1.2 | 0.098 | 0.14 | *0.148* | *0.169* |
| Cr | 79.17±15.22 | 81 | 35 | 58 | 63.17 | 97.00 |
| Cu | 24.66±9.358 | 34 | 25 | 21 | *18.34* | *16.66* |
| Mn | 772.7±222.9 | – | 600 | 682 | 598.0 | 1145 |
| Pb | 23.77±6.112 | 46.7 | *20* | 25 | 17.12 | *20.74* |
| Zn | 82.97±19.16 | 150 | *71* | 65 | 62.64 | *76.50* |
| Al [a] | 11.82±1.637 | – | 8.0 | 13 | *10.86* | *10.04* |
| Fe [a] | 5.118±1.000 | – | 3.5 | 4.4 | 4.192 | 6.222 |

Calculated metal background values that are similar to worldwide, nationwide, or local reference values are in italics

[a] The unit is %.

[b] Metal contents are expressed in the form of mean±standard deviation

[c] Taylor and McLennan 1995

[d] Yan et al. 1995

bottom sediments of two typical core sediments from the Yangtze Estuary.

Based on the above analysis, the detailed values at the three scales for the nine metals in the Yangtze Estuary were determined and listed in Table 1. The above three types of background values have individual advantages, but it remains unclear which is most suitable for analyzing degrees of metal enrichment in the estuary.

Effect of metal background values on the degree of metal enrichment

The enrichment factors and their percentage distributions in the sediments using the above three background values are shown in Fig. 2. It can be inferred from the figure that, independent of the reference values employed, the EF values of the samples are not higher than 5 for Cd, Cr, Cu, Mn, Pb, Zn, Fe, and generally As (with approximately 10 % exceeding this value), which suggests that these metals are not significantly enriched in the sediments of the Yangtze Estuary.

It can also be seen from Fig. 2 that the global background values often give lower enrichment results than the corresponding national and local values. The majority of the EFs for Cu (93 %), Mn (87 %), Pb (97 %), Zn (97 %), and Fe (73 %) are less than 1 when the global background values are used, indicating deficient metal enrichment compared with background values. However, when national and local reference values are used, the EFs of approximately 73 % of Cu, 74–80 % of Mn, 60–90 % of Pb, 90–97 % of Zn, and 80–97 % of Fe fall between 1 and 2, which is indicative of minimal enrichment.

Arsenic seems to be an exception to the tendency discussed above, with higher levels of enrichment using the average crust values (global scale) than national and local background values. Moreover, in general, arsenic presents the highest EF values, with 100 % of the samples being moderately enriched using global background values, while 70 and 93 % are minimally enriched using national and local background values. As for Cr, the three reference values give similar results, i.e., a small portion (approximate 3 %) is moderately enriched while the majority of the samples are minimally enriched.

Therefore, it can be concluded that there are discrepancies in the degrees of metal enrichment when EFs are analyzed using background values on the global, national, and local scales. Significant differences exist between the global background values and the other two, whereas the national and local values give similar information. Overall, the national and local values seem more applicable in the Yangtze Estuary. Caution should be used when applying the crust element values to assess the degrees of metal enrichment in the sediments of the Yangtze Estuary because of the tendency to underestimation.

Exclusive pristine values of metals in the Yangtze estuary with PCA

The discrepancies caused by the usage of different background values motivated us to determine a reliable set of background values exclusive to this area. Principal components analysis (PCA) is a multivariate technique that can be employed to identify dependencies in multivariable data sets

**Fig. 2** Percentage distribution and enrichment classification of metals in sediments of the Yangtze Estuary using worldwide (**a**), nationwide (**b**) and local (**c**) background values
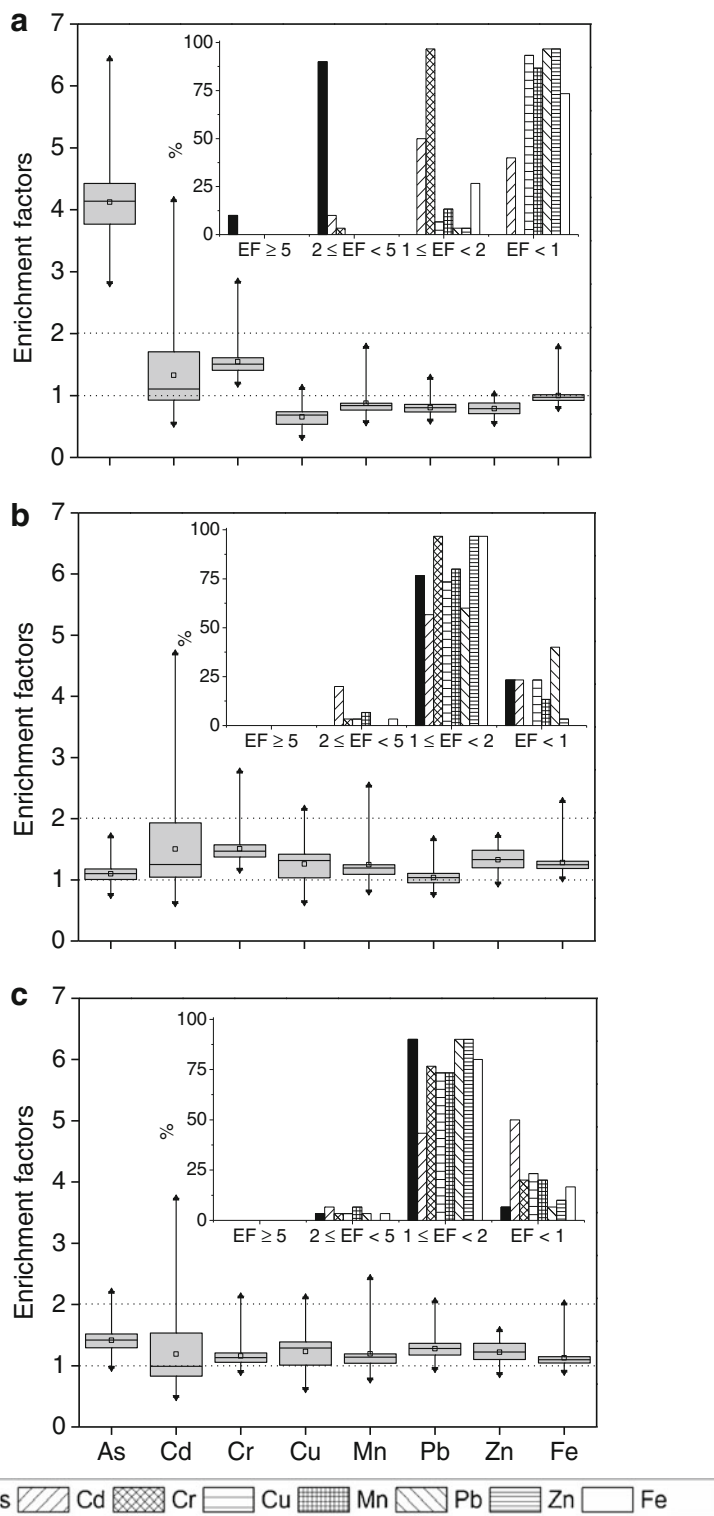


and has been increasingly employed to discriminate contaminant sources (Reid and Spencer 2009). According to our previous data for the sediment composition in the same sampling sites within the estuary, the sediment contains mainly sand (38.24±38.04 %) and silt (58.30±32.26 %),

with a minor clay content (7.95±7.23 %) (Zhao et al. 2013). Fine-grained sediments tend to have relatively high metal contents due to their high specific surface area and ionic attraction. By comparison, sandy sediments are more likely to reflect the background values. In this study, the

sandy sediments could be discriminated by PCA, and the metal contents in these sandy sites could be used as background values. As shown in Fig. 2, although the three background values give different results for the degrees of metal enrichment, each shows some sampling sites with EFs below 1, representing pristine areas. Rubio et al. (2000) noted that these pristine areas could be identified using PCA, and background values could be defined by calculating the average metal contents of sediments in these sites.

Table 2 and Fig. 3 show that three factors explain a total of 92.56 % of the variation in the data. The first factor accounts for approximately 56.80 % of the data variability and is strongly loaded by Zn, Pb, As, Cu, TOC, and Cd, suggesting that this factor is mainly related to the influence of anthropogenic sources and reflects the complexing nature of the organic matter. The loadings of Cr, Fe, and Mn are associated with factor 2 (25.15 % of data variability), which might represent the lithological inputs because Fe is often considered as a conservative element and is a major constituent of clay minerals. Factor 3 shows a strong loading by Al (10.61 % of data variability), which is also indicative of lithological inputs. Thus, factor 1 is interpreted as anthropogenic inputs, while factor 2 and 3 represent lithological inputs. A plot of the scores (factor score 1 vs. 2, 1 vs. 3), which give the positions of the samples in the coordinates of the principal components, isolates 3 samples as not being affected by pollution (Rubio et al. 2000).

The average metal contents in the sediments of these samples are defined as reference values, which are also listed in Table 1. In Table 1, the calculated contents of Cd, Cu, and Al are very close to the local background values, whereas the calculated Pb and Zn contents match the global reference values well. For national background values, only the content of As is similar to the calculated value. Distinct differences exist between Cr, Mn, and Fe, with the calculated contents greatly exceeding the background values employed in this study.
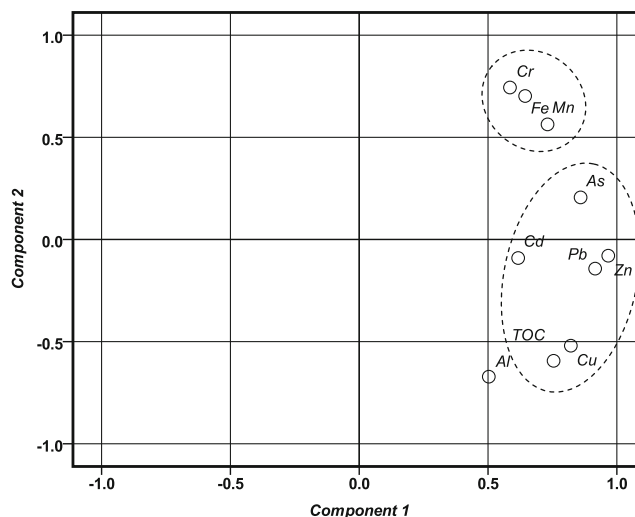


**Fig. 3** Loadings of the first three components obtained from a PCA

**Relationship between metal enrichments and adverse biological effects**

Metal adverse biological effects in sediments are often evaluated using the SQGs developed by the United States Environmental Protection Agency for environmental assessment and pollution prevention and remediation. Because the ERL of Al, Fe, and Mn were not given, only the metal adverse biological effects of As, Cd, Cr, Cu, Pb, and Zn were calculated. The relationships between these metals and the degrees of metal enrichment are investigated (Fig. 4).

Certain numerical relationships exist between the degrees of metal enrichment and adverse biological effects, as exhibited in Fig. 4. The correlation coefficients are 0.84, 0.97, 0.73, 0.97, 0.88, and 0.85 for As, Cd, Cr, Cu, Pb, and Zn, respectively. The horizontal dotted line intersecting the vertical axis corresponds to ABE=1 for a given metal, while the vertical dotted line intersecting the horizontal axis is the corresponding EF value. For any given point in Fig. 4 below

| Component | Initial eigenvalues | | | Element | Component matrix | | |
|---|---|---|---|---|---|---|---|
| | Total | % of variance | Cumulative % | | PC1 | PC2 | PC3 |
| 1 | 5.680 | 56.80 | 56.80 | As | *0.859* | 0.206 | −0.077 |
| 2 | 2.515 | 25.15 | 81.95 | Cd | *0.617* | −0.091 | −0.761 |
| 3 | 1.061 | 10.61 | 92.56 | Cr | 0.585 | *0.744* | 0.103 |
| 4 | 0.323 | 3.225 | 95.79 | Cu | *0.821* | −0.520 | 0.024 |
| 5 | 0.169 | 1.687 | 97.47 | Mn | 0.331 | *0.563* | 0.229 |
| 6 | 0.082 | 0.817 | 98.29 | Pb | *0.916* | −0.143 | −0.244 |
| 7 | 0.061 | 0.609 | 98.90 | Zn | *0.967* | −0.079 | −0.034 |
| 8 | 0.054 | 0.539 | 99.44 | Al | 0.503 | −0.672 | *0.514* |
| 9 | 0.039 | 0.390 | 99.83 | Fe | 0.644 | *0.702* | 0.236 |
| 10 | 0.017 | 0.166 | 100.0 | TOC | *0.754* | −0.594 | 0.176 |

**Table 2** Factor loadings obtained from the PCA of the metal contents in sediments of the Yangtze Estuary

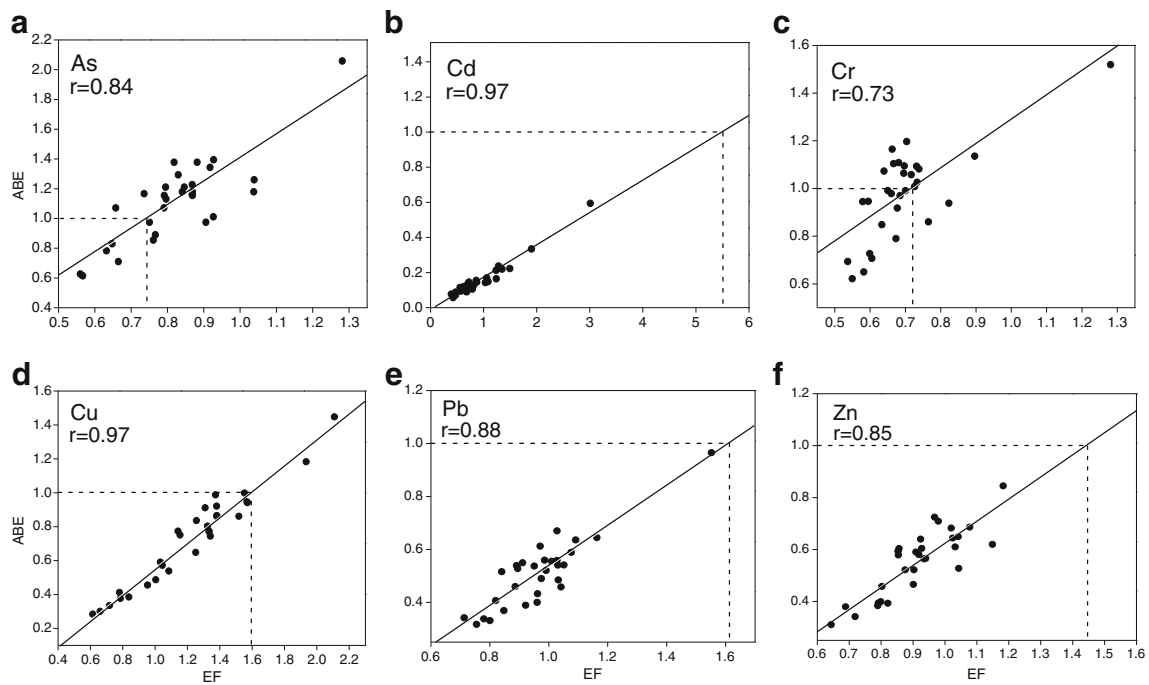The largest positive component loading for each element is in italics

**Fig. 4** Relationship between enrichment degrees and the corresponding adverse biological effects of As, Cd, Cr, Cu, Pb, and Zn in sediments of the Yangtze Estuary

the horizontal dotted line, adverse biological effects are unlikely to occur. In contrast, points above this line indicate likely adverse biological effects.

Among these metals, arsenic in Fig. 4a shows the highest potential to provoke adverse effects, with 70 % of the samples having ABEs above 1. Moreover, to cause an adverse effect, the enrichment factor of arsenic needs only to exceed 0.75, suggesting that As could impose an adverse biological effect despite not truly being enriched. Considering its high potential to cause adverse effects and the frequent reports of its enrichment in the Yangtze Estuary (Chen et al. 2001; Yang et al. 2004), more attention should be paid to arsenic during environmental assessment and remediation.

However, arsenic is not the only element that could cause biological effects despite not being enriched. The relationship between the ABE and EF of Cr in Fig. 4c shows that adverse biological effects are likely to occur if the sediment enrichment factor reaches 0.73. However, unlike arsenic, Cr seems to be more conservative, with only 27 % of samples having ABEs above 1.

Compared with abovementioned As and Cr, there is little probability of toxic effects under similar enrichment degrees when Cd, Cu, Pb, and Zn are taken into consideration. Cd seems to be the most conservative element among all the metals. On the one hand, the highest ABE value of Cd is approximately 0.59, which is far less than 1. On the other hand, Cd would not cause adverse biological effect unless its enrichment factor is above 5.43, which is far higher than that of other metals. As mentioned before, a sample is significantly enriched if its EF is above 5. From this aspect, even though Cd

is significantly enriched, it would still cause no biological effect in the Yangtze Estuary, which offers important information for environmental management and assessment.

The ABE values of all of the samples are below 1 for Pb and Zn (Fig. 4e, f), indicating that the enrichment of these two metals is not enough to induce toxic effects, which would require the EFs to be 1.62 and 1.44 for Pb and Zn. For Cu, a stronger relationship exists between the EFs and ABEs ($r^2$=0.97). The high EF and ABE ratio (1.58:1) suggests that a Cu enrichment factor above 1.58 could result in toxicity (Fig. 4d). This phenomenon also makes it difficult for Cu to cause adverse effects, and only 2 samples exhibited ABE>1 in this study.

## Conclusions

The difference between metal background values greatly influences the interpretation of degree of metal enrichment. The global background values often give lower enrichment results than the corresponding national and local values. Exclusive background values obtained with PCA for the metals in the Yangtze Estuary can synthesize the advantages of the other three background values and better reflect the pristine metal contents in the estuary. Significant relationships exist between the degrees of metal enrichment and adverse biological effects. Biological toxic effects of As and Cr could be incurred even if they were not truly enriched in the sediments. Cd, Cu, Pb, and Zn were more conservative.

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