Characterisation of Arsenic Distribution in the Contaminated Sediments Using Principal Component Analysis based on The Four-Step Extraction Protocol

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ABSTRACT

The goal of this work was to characterize the distribution of arsenic in the contaminated sediments using principal component analysis to interpret data generated by a four-step extraction protocol, an operationally defined fractionation procedure used to study the availability and mobility of trace metals available in environmental solid samples. Sediment cores collected from contaminated site of Port Kembla Harbour, Australia were sliced into 2-cm thin layers. Each layer was sieved into three different grain sizes (<63μm, >63 μm and >250 μm) under inert N_2 atmosphere. Redox potential, pH, dissolved As in the interstitial water, exchangeable As, AVS-As, reducible As, and residual As data provided some reliable information concerning the characteristics of As distribution in the contaminated sediments. Principal component analysis indicated As in the fine grain fraction and redox potential developed in the sediment contributed more significantly in controlling the concentration of dissolved As in the sediment interstitial water. It appeared that precipitation-dissolution reaction of As taken place in the sediment involved the fine grain solid phase and occurred actively at redox transition zone at which it changed significantly and the concentrations of dissolved As were high.

Keywords: Four-step extraction protocol, principal component analysis, arsenic, contaminated sediments.

INTRODUCTION

In early investigations the potential effects of metal contaminants on environments were assessed through total concentration in which all forms of a given metal had an equal impact on the environment. It was pointed out that such an assumption was failed to estimate toxicity effects of metal content of sediments (van den Hoop *et al.* 1997). In nature, metals may occur in certain 'pools' of solid. For example, metals that occupy exchangeable sites as outer-sphere complexes are easily exchanged with other dissolved species or available for uptake by organisms, while metals held in the crystal lattices are believed to be less bioavailable and unlikely to be released into the aqueous phase (Poulton & Raiswell 2000). Metals added to the environment through anthropogenic activities however mainly occur in non-lattice sites and are often more reactive than native ones (Gleyzes *et al.* 2002) and thus impose a great potential threat to the environments.

The four-step extraction protocol used in this study is an operationally defined scheme (Keon *et al.* 2001) developed to fractionate of arsenic in environmental solid samples into four fractions (1, 2, 3 and residual). The philosophy is that sample is subjected to the increasingly strong reagents to solubilize four different fractions of the solid thought to be responsible for retaining arsenic in the solid matrices, so from the fractionation patterns of the element one can infer information about mobility, pathways or bioavailability of the studied element or to assess the potential hazard that the sample can pose to the environment (Pardo *et al*. 2004 and Critto *et al*. 2003). In environmental analysis, it is quite common that the data obtained are large and thus application of univariate analysis does not give a clear indication on trends and characteristics of the data or only limited information could be obtained.

Recent studies advice the evaluation of environmental data through the use of multivariate analysis to extract more information and help in data interpretation. For examples, principal component analysis (PCA) was applied to estimate of the source of heavy metal contamination in surface sediments (Loska & Wiechula 2003), to monitor spatial and temporal changes in water quality (Bengraine & Marhaba 2003) and to determine interrelationships of a number of variables affecting arsenic speciation in marine sediments (Villa-Lojo *et al*. 1997).

Others studies were able to interpret of chemical fractionation results obtained by the use of the three-step extraction BCR Procedure (Pardo *et al*. 2004) and to identify the point and non point sources of copper in urban surface water (Sodre *et al*. 2005). These studies show that the application of the PCA to the environmental data set assists the data analysis and enhances the data interpretation.

The goal of this work was to see major trends of arsenic (As) distribution in the contaminated sediments and, at the same time, to identify solid fractions that involved more significantly in controlling the concentration of dissolved As in the interstitial water by applying PCA to the data generated by the four-step extraction protocol.

METHODS

For all procedure described, only analytical grade chemicals were used. Polycarbonate liners (50 cm long, 7 cm id) were used for collecting sediment core samples. PE bottles were cleaned with dilute HCl before use by soaking for a minimum of 24h, and then rinsed with Milli-Q water and dried in open air.

A sediment core sample (~18 cm long) collected from contaminated site of Port Kembla Harbour, Australia was maintained upright position to avoid re-suspension. In the lab, the core was sliced to 2-cm thin layers in inert N_2 atmosphere. Each slice was collected into a 50-ml centrifuge tube and the rest in a small beaker glass. The tube was centrifuged to separate interstitial water which was then acidified and analysed for total As. The remaining solids were wet sieved to separate particles < 63 μm, >63 μm and >250 μm. Redox potential (E_h) and pH for each slice was measured by direct applying the electrodes into the sub sample in the beaker glass, which eventually discarded.

Four-step extraction protocol

Approx. 0.4 g wet solid sample was taken into a 50 ml Nelgene PE tube and the leaching reagent was added. Suspension was shaken for a given time and filtered through a 0.45 μm before analysis. Detail of the 4-step extraction protocol was given elsewhere (Damris 2005).

Step 1: 40 ml of NaH_2PO_4 1M pH 5 for 18 h, to release exchangeable fraction of As (Ex-)
Step 2: 40 ml of HCl 1M for 1 h, to release As associated with AVS-fraction (AVS-)
Step 3: 40 ml of $NH_2OH.HCl$ 25% in acetic acid for 2 h, to release reducible fraction of As (Red-)
Setp 4: Residual As was released by acid digestion (conc. HNO_3 + conc. H_2SO_4 at 180^0C) (Res-)

Analysis

The concentrations of total As (in the form of As III) in the liquid extracts and interstitial waters were determined by Hydride Generation–Atomic Absorption Spectrophotometry (HG-AAS) method. In this case, As(V) present in the samples was first reduced to As (III) in the present of KI as a reducing agent.

Analytical quality control

Matrix effects on HG were checked by spiked recoveries. The accuracy and precision of the total As analysis were ensured by applying the protocol to the Certified Reference Material for marine sediment CRM-277 for data comparison. Quite good recovery of As was found within 95% confidence limit and RSD did not exceed 10%. Therefore, it is considered to be sufficient accuracy and acceptable precision.

RESULTS AND DISCUSSION

Total As concentrations recovered from three particle sizes as well as dissolved As in interstitial water are shown in Figure.1a, whereas As levels recovered for each of the four solid fractions in the fine grain is shown in Figure 1b.

Solid As levels in the fine grain samples ranged from 140 to 1168 μg/g, whereas in the medium and the large particles between 60 to 263 μg/g and 28 to 187 μg/g, respectively. It is possible to observe that the maximum levels of As in the fine and medium were occurred at the second layer, in which the concentration of dissolved As in the interstitial water was also maximum. The dissolved As concentrations ranged from 33 μg/L to 796 μg/L.

Figure 1b showed the distribution of solid As in the fine grouped according to their respective fraction. It is observed that residual fraction is a major solid for As association followed by the acid soluble fraction (AVS) and the exchangeable fraction (Ex-). The stable fraction recovered in all part of the sediment core, whereas the exchangeable and AVS fractions recovered significant only at top layers. It needs to note that the reducible fraction appeared as a minor component of the sediment core studied.

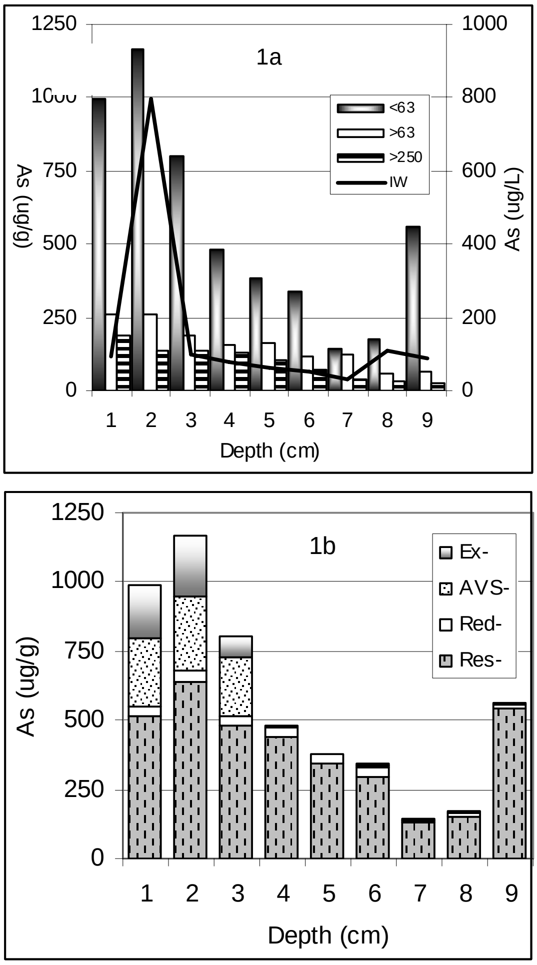
From a close inspection of Figure 1 it is possible to extract only very general conclusion about the mobility of the analyzed element in the sediment. High dissolved As in the interstitial water at sub surface possibly originated from dissolution of unstable fraction of the solid due to onset reducing condition

(Damris *et al*. 2005). Arsenic (As) associated with the solid would be released and dissolved following dissolution of solid Fe as shown by its minimum concentration levels at the same depth (Damris 2005). It can be concluded that the sediment pose a significant hazard to the harbour environment, especially top parts of the sediment. This way of the data analysis does not provide further insight on the fractionation behaviour of arsenic, and does not allow extracting any conclusion about individual fraction either.

PCA analysis

Based upon the parameters listed in table 1, a 15 × 9 matrix was built. This matrix was corresponded to the fifteen parameters and the nine slices of the sediment.

The number of the principal components is equivalent to the number of variables involved in the data analysis. However, the first component contains more information than the second, and the second component contains more the information than the third, and so on. Thus the first several components (usually 2 or 3 components) may have contained all information required to explain the data tendencies and patterning. The component should account for at least 75% of the total variance, and relevant components are those whose eigenvalue is higher than 1 (Loska & Wiechula 2003).



(a) (b)

Figure 1. Fractionation pattern of As in the different sediment grain sizes and dissolved As interstitial water (a). Fractionation pattern of solid As in the fine grain size (b).

Table 1. Chemical and physical parameters used in the principal component analysis.

Parameters	**Acronym**	**Unit**
Reduction-Oxidation Potential	Eh	Millivolt
pH	pH	pH Units
Dissolved As in sediment interstitial water	IW	μg/L
Exchangeable fraction of As in the fine grain size < 63 μm	Ex-1	μg/g
Acid soluble fraction of As in the fine grain size < 63 μm	AVS-1	μg/g
Reducible fraction of As in the fine grain size < 63 μm	Red-1	μg/g
Residual fraction of As in the fine grain size < 63 μm	Res-1	μg/g
Exchangeable fraction of As in the medium grain size >63 μm	Ex-2	μg/g
Acid soluble fraction of As in the medium grain size >63 μm	AVS-2	μg/g
Reducible fraction of As in the medium grain size >63 μm	Red-2	μg/g
Residual fraction of As in the medium grain size >63 μm	Res-2	μg/g
Exchangeable fraction of As in the large grain size >250 μm	Ex-3	μg/g
Acid soluble fraction of As in the large grain size >250 μm	AVS-3	μg/g
Reducible fraction of As in the large grain size >250 μm	Red-3	μg/g
Residual fraction of As in the large grain size >250 μm	Res-3	μg/g

Based on the above mentioned criteria, the first two principal components alone explain over 84 % of the total data variance. It is also possible to observe that only the first component was responsible for the 46 % captured variance. Taking complexity of a natural sediment system into account, the fact that only two principal components were able to explain 84% of the data variance represents satisfactory result. Generally, while dealing with complex data such as environmental ones, the distribution among components is relatively spread-out (Pardo *et al*. 2004).

From Figure 2 it is possible to observe that the first PC is correlated to a group parameter in which As associated with potentially mobile fractions i.e. exchangeable (Ex-1, Ex-2, Ex-3) and acid soluble sulfide (AVS-1, AVS-2 and AVS-3) together with pH and Eh. Dissolved As in the interstitial water (IW), however, does not contribute significantly to this PC. Note that As associated with reducible fraction (Red-1) also presents a high loading value for this PC. The PC2 is however mostly correlated to more stable fractions (Red-1, Red-2, Res-1, Res-2, Res-3), IW, pH and Eh and also potentially mobile fractions (Ex-1, AVS-1 and AVS-3). It needs to emphasize that four parameters of the PC1 (Ex-1, AVS-2, AVS-3 and pH) also contributed strongly to the PC2.

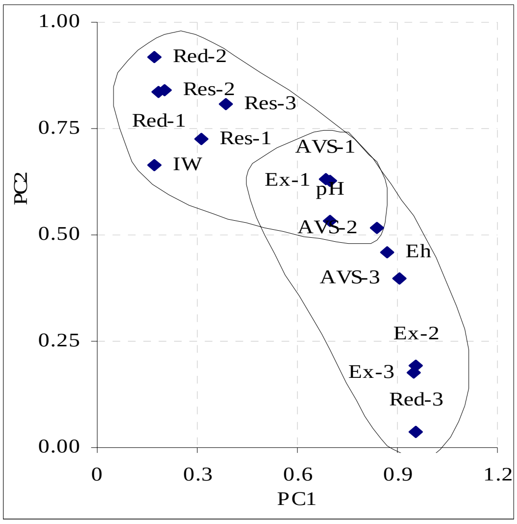


Figure 2. Scores graph for the first two components.

The sediment core studied in this work was collected from a highly contaminated site where high concentrations of As in the sediment are evidenced. From this reason, it was expected that a significant amount of arsenic is actively recycled and concentrations of dissolved As in the interstitial water are high. It appears that PC1 explains the distribution of As at the uppermost layers of the core, particularly at top 6 cm. A significant change of the Eh and pH values were observed at this part of the sediment core. In response to the change of Eh and pH values, As associated with exchangeable and AVS fractions are possibly recycled and exchanged with other dissolved species or dissolved into interstitial water (Keon *et al*. 2001). So, PC1 most likely represents the fraction of As that involves in dissolution-precipitation processes under a strong influent of the change of the Eh and pH values.

PC2 is characterized by high loading values for the more stable solid fractions (Red-1, Red-2, Res-1, Res-2, Res-3) and potentially mobile fractions (Ex-1 and AVS-1) as well as IW and pH. It accounted for 38 % of the total variance. It needs to emphasize that Eh is not as a major factor of PC2. It is possible to observe that PC2 was responsible for the distinction among the solid fractions under which As distributions are not under strong influence of the Eh change. Under this condition As is most likely to associate with more stable solid sediments such as pyrite (Berner 1984). This fraction is considered as a residual and mostly found at a bottom part of the sediment core.

Figure 2 is also showed that the exchangeable and AVS fractions of As from the medium and large sizes (Ex-2, Ex-3, AVS-2, and AVS-3) are unlikely involved in controlling the concentrations of dissolved As in the sediment interstitial water. Any exchange between these fractions does not affect the concentrations of dissolved As in the interstitial water. This is probably supported by the fact that the concentrations of potentially mobile As in the medium and large grains are much lower then in the fine. For comparison, the concentrations of As associated with exchangeable and AVS fractions in the fine are approx 40 and 120 times higher than that of in medium and large grain sizes, respectively.

Figure 2 also showed that arsenic in the sediment interstitial water (IW) has a close association with the fine grain from the Ex-1, AVS-1 and Res-1, while the other solid fractions of arsenic are not closely associated with it. The concentration of dissolved As in the sediment interstitial waters is not only controlled by PC2, but also some loading factors of PC1. This probably indicates that there are different solid fractions responsible for dissolved As in the interstitial water at the top and bottom part of the sediments. PC1 is responsible for the dissolved As at top layers, especially from Ex-1 and AVS-1 fractions, while PC2 is responsible for the dissolved As at bottom part of the sediment core under which a strong reducing condition developed. In this case As may be released to the interstitial water following reductive dissolution of more resistant solid As in the presence or absence of sulphide (Mucci *et al.* 2002). The later scenario would explain why As associated with exchangeable and acid soluble sulfide fractions are not recovered at the bottom part of the sediment core, while a significant amount of the dissolved As was found.

Most interestingly, as can be observed from Figure 2, dissolved As in the sediment interstitial water appears to be a transfer medium for As from potentially mobile fractions (Ex-1 and AVS-1) at the top to the more stable residual (Res-) fraction at the bottom. This could proceed only through diffusion mechanisms due to concentration gradient. However, the potentially mobile As associated with larger particle (Ex-2 and AVS-2, and Ex-3 and AVS-3) is not contributed significantly. This is in line with a high concentration of As associated with Ex-1 and AVS-1 at top 6 cm and thus will desorb more readily into interstitial water.

Any increase in the concentration gradient of dissolved As in the interstitial water with depth must result from either consumption at the bottom, i.e. transferred to more stable solid As, or production at the top due to dissolution, i.e. reductive dissolution e.g. Fe oxyhydroxides in the fine grain fractions at sub surface.

CONCLUSION

PCA proved to be effective for risk assessment characterisation of arsenic in sediment system since significant additional information was extracted after its application. Dissolved As in the sediment interstitial waters is most likely controlled by the exchangeable and AVS fractions from the fine grain particle at the top part of the sediment core, but it is also controlled by the more stable solid fraction in the bottom part of the sediment core. Interstitial water appears to act as a transfer medium among solid fractions, but it does not necessarily change the concentrations of dissolved As. The change of redox potential is an important parameter for arsenic exchange between solid fractions at upper part, but less significant for the bottom.

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