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The potential risk assessment for different arsenic species in the aquatic environment

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ABSTRACT

The different toxicity characteristics of arsenic species result in discrepant ecological risk. The predicted no-effect concentrations (PNECs) 43.65, 250.18, and 2.00×10^3 μg/L were calculated for As(III), As(V), and dimethylarsinic acid in aqueous phase, respectively. With these PNECs, the ecological risk from arsenic species in Pearl River Delta in China and Kwabrafo stream in Ghana was evaluated. It was found that the risk from As(III) and As(V) in the samples from Pearl River Delta was low, while much high in Kwabrafo stream. This study implies that ecological risk of arsenic should be evaluated basing on its species.

Introduction

Arsenic is a toxic element, which occurs naturally in water, soil, and sediment throughout the world (Mandal and Suzuki, 2002; Cullen and Reimer, 1989). Both natural and anthropogenic sources are currently elevating pollution level of arsenic in the environmental matrices (Kim et al., 2009). Because of its toxicity and increasingly widespread occurrence, arsenic pollution has become a serious problem (National Research Council, 1999; Matschullat, 2000; Nordstrom, 2002; Terlecka, 2005). It has been reported that groundwater is contaminated with arsenic in 21 countries, including Argentina, Bangladesh, Chile, China, Hungary, India, Mexico, and the United States (Pearson et al., 2011; Nikolaidis et al., 2004). Bangladesh has the largest population suffering from the heavy arsenic pollution in groundwater supplies. Arsenic concentrations in groundwater of Bangladesh exceed the World Health Organization drinking water guidelines (0.01 mg/L) by more than 10 times (Rahman et al., 2002; Sarkar et al., 2008). Extremely high arsenic concentrations, 3.00 mg/L, have been found in water from the Bravona River, Corsica, France and one of its tributaries (Migon and Mori, 1999). Arsenic concentrations of 1.39–5.65 μg/L and 3.08–10.48 μg/L have been found in water from Taihu Lake and Dianchi Lake, respectively (Zhang et al., 2013). In addition, the pollution of arsenic in sediments should not be ignored because sediment is an important "sink" of pollutants and arsenic in sediment could be released into water and cause "secondary pollution". An average total arsenic concentration of 47.30 mg/kg has been found in surface sediment from Little Lake Jackson, FL, USA (Whitmore et al., 2008). Arsenic concentrations of 17.20–27.90 mg/kg have been found in surface sediment from Taihu Lake, China (Zhang et al., 2013).

The physical consequences of long-term exposure to elevated arsenic concentrations are severe. In addition, arsenic can accumulate in the aquatic environment, which may lead to ecological damage. The potential adverse effects of arsenic on ecological receptors (*e.g.*, mammals, birds, plants, and/or fish) should be evaluated. Up to now, lots of studies on the ecological

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risk assessment of arsenic pollution have been conducted (Zhang et al., 2013; Wang and Mulligan, 2006; Barringer et al., 2011; Peng et al., 2004; Wei et al., 2011; Keimowitz et al., 2005; Jackson et al., 1991; Mazej and Germ, 2009). However, most of the previous studies on arsenic concentrations and ecological risk assessment in sediment and water focused on the total arsenic concentrations, and limited information was available on arsenic speciation. In fact, arsenic can be present as different chemical species, including arsenite (As(III)), arsenate (As(V)), monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA) (Cullen and Reimer, 1989; Francesconi and Edmonds, 1994), depending on the chemical and geological conditions (Arain et al., 2008). The biological availability and toxicological effects of arsenic depend on its chemical forms (Cullen and Reimer, 1989). For example, inorganic arsenic has a high toxicity level and increases risk of cancer, whereas methylated forms of arsenic, such as MMA and DMA, are significantly less toxicity (Nordstrom, 2002). Toxicity of As(III) is about 60 times higher than that of As(V). The total arsenic concentration in water or sediment does not represent the exact biological availability or potential hazards (Jain et al., 2007). Therefore, the different species and toxicity effects of arsenic should be involved in the ecological risk assessment.

The aim of the present study was: (1) to compute the ecological risk thresholds for those predominant arsenic species in the aquatic environment by collecting and analyzing their toxicity data, respectively; (2) to perform ecological risk assessment for different species of arsenic in the studied areas based on the computed risk thresholds of arsenic species. It is expected that the present study would provide useful information for exactly evaluating the potential risk of arsenic in the environment.

1. Materials and methods

1.1. Toxicity data collection and screening

The toxicity data of arsenic were taken from the US Environmental Protection Agency 'ECOTOX' database (http://cfpub.epa.gov/ecotox/) and a number of publications (*e.g.*, research papers and government reports). Data were collected for at least 10 species at three trophic levels (*e.g.*, algae, crustaceans, and fish). The inherent quality (reliability, relevance, and adequacy) of the toxicity data (acute and chronic lethal toxicity data and chronic reproductive toxicity data) were evaluated using standard methods (European Chemical Bureau, 2003; Klimisch et al., 1997). The means of several toxicity data for the species of interest, from the same location and time, were calculated, and a number of indices that express certain toxic characteristics, including mortality, growth parameters, biochemical parameters, and reproductive success, were selected as endpoints. The chronic toxicity data were screened by selecting the observed effect concentration (NOEC) measured using the longest exposure time if several eligible chronic toxicity data were available for the same species. If NOEC data was unavailable for a species, the half of lowest observed effect concentration was used as the NOEC (Balk et al., 1995).

1.2. Calculating PNEC values for arsenic in water phase (PNECwater)

The predicted no-effect concentration (PNEC) is an important index in evaluating potential risk of toxic chemical. The species sensitivity distribution (SSD) and assessment factor (AF) methods, proposed by the European Union, are often used to calculate PNECs (Wu et al., 2011a, 2011b, 2011c). The calculation of PNEC is usually based on the no observed effect concentration (NOEC). However, there are less NOEC data for many compounds, the PNECs for ERA are extrapolated from acute toxicity data, such as the median lethal/effective concentration (LC50/EC50).

1.2.1. Species sensitivity distribution method

The species sensitivity distribution method is usually used when at least 10 toxicity data are available (Jin et al., 2009; Balk et al., 1995). The method was first proposed by Kooijman (1987) and it was improved in subsequent studies (Aldenberg and Slob, 1993; Newman et al., 2000; Wagner and Lokke, 1991). The SSD method involves constructing a curve using the toxicity data that is available for as many species as possible for a specific pollutant. The criterion level is then determined by finding the pollutant concentration on the curve at a predetermined noticeable effect percentage. The criterion level, which is usually labeled HC5, is the pollutant concentration that is hazardous to 5% of the species for which data are available (Van Straalen and Van Rijn, 1998). In general, the reliability of the assessment increases as more data are available. The SSD method uses toxicological data for almost all species and takes into account the uncertainty caused by heterogeneity between species, and it is a direct and reasonable method for assessing the effects of pollutants. The toxicological data used in the SSD method needed to be assessed carefully, and log-transformed when necessary. The data were then sorted and the cumulative probability was calculated by Eq. (1):

$$\text{Cumulative probability} = i/(n+1) \quad (1)$$

where, i is the rank of a species in the data series and n is the total number of species examined (Hall et al., 1998; Schuler et al., 2008). The SSD curve was constructed using the mean toxicity (or the logarithmic value) as the x-axis and the cumulative probability as the y-axis. The HC5 was determined by extrapolating from the curve.

1.2.2. Assessment factor method

The assessment factor method can be applied to compounds for which fewer toxicological data are available, generally no more than 10 datasets, and it was used to supplement the SSD method. There was strong variability in the data when less than 10 toxicity data were available, so the evaluation of the effect endpoint (HC5) may have been unreliable and the AF method was used. However, the AF method has shortcomings because the selection of an appropriate AF is relatively arbitrary, although it is very important to select suitable AF. The principles used to select the most appropriate AF are shown in Table 1. The PNEC is calculated with the ratio of the minimum LC50 (EC50, or NOEC) value to the corresponding AF value.

$$\text{PNEC} = \text{the minimum LC50(EC50, or NOEC)}/\text{AF} \quad (2)$$

1.3. Calculating PNEC values for arsenic in sediment phase (PNECsed)

The ecological risk assessment of contaminant in sediment was performed in a similar way as that in water. The PNEC for each toxic pollutant in sediment was derived using the SSD or AF methods according to its ecological toxicity data. The risk quotient (RQ) was then calculated to characterize the risk level for the toxic pollutant. However, there are relatively scarce toxicity data for most of the toxic pollutants in sediment, and the sediment properties (such as the organic carbon content) are various in different areas, causing difficulty in performing risk assessment for pollutants in sediment. Fortunately, the concentration of a pollutant in the sediment can be indirectly reflected by the concentration in pore water according to the equilibrium distribution model. A risk assessment for the toxic pollutant in the pore water can be achieved using the PNEC for water, and the pollutant concentration in the pore water can be calculated by Eq. (3) (Zhao et al., 2011):

$$C_{\text{porewater}} = C_{\text{sed},i}/K_{\text{oc},i} \times F_{\text{oc}} \quad (3)$$

where, $C_{\text{porewater}}$ (mg/L) is the pollutant concentration in the pore water; $C_{\text{sed,i}}$ (mg/kg) is the pollutant concentration in the sediment, $K_{\text{oc,i}}$ (L/kg) is the equilibrium distribution coefficient (sediment/water) for the pollutant, and F_{oc} (%) is the organic carbon content in the sediment.

1.4. Risk assessment

The most feasible method to characterize the potential risk of toxic pollutant is using the index RQ, which is calculated by Eq. (4) to characterize the ecological risk level. RQ ≥ 1 means a high risk from the pollutant, while RQ < 1 means low risk.

$$\text{RQ} = \text{Environmental concentration}/\text{PNEC} \quad (4)$$

Table 1 – Assessment factor (AF) values used to derive the predicted no-effect concentration (PNEC).

Case no.	Existing toxicity data	AF
1	Acute LC50 or EC50 values available for at least one species from three trophic levels (fish, daphnia, and algae)	1000
2	Chronic NOEC values available for one species (fish or daphnia)	100
3	Chronic NOEC values available for two species from two trophic levels (fish, daphnia, and/or algae)	50
4	Chronic NOEC values available for three species from three trophic levels (fish, daphnia, and algae)	10
5	Chronic NOEC values available for three phyla and eight families available using the SSD method	1–5
6	Toxicity data from field observations or ecological system simulation	Depends on the specific circumstances

LC50 : median lethal concentration; EC50 : 50% effective concentration; NOEC : no observable effect concentration; SSD : species sensitivity distribution.

1.5. Sample collection and analysis

Surface water samples (from 0–20 cm deep) and surface sediment samples (from 0–20 cm deep) were collected from seven sites (P-A, P-B, P-C, P-D, P-E, P-F, P-G) in the Pearl River Delta in December 2008 (the dry season) and July 2009 (the wet season). And the sampling sites are shown in Appendix A Fig. S1. The water samples were fixed with 2 mol/L HNO_3 (to adjust pH to 2) and filtered through a 0.7 μm filter (GF/F, Whatman, Maidstone, UK) once they were brought to the laboratory. The sediment samples were collected with a stainless steel sediment sampler and sodium azide was added to the samples to avoid the arsenic chemical speciation changing by microorganisms after the samples had been collected. The sediment samples were transferred to acid-washed dark-colored polyethylene bags and transported to the laboratory within 4 hr, where they were freeze-dried (FD-1; Shanghai Joyn Electronic, Shanghai, China), gently ground, and passed through a 60 mesh sieve; then they were stored at 4°C in aluminum foil (to avoid exposure to sunlight) until analysis.

The concentrations of the different arsenic species in the water and sediment samples were analyzed by liquid-chromatography hydride-generation atomic fluorescence spectrometry (LC-HG-AFS; Beijing Titan Instruments, Beijing, China). Detailed operational parameters of instrumental analysis are shown in Appendix A Table S1. As(III) and As(V) standards were purchased from the National Standard Substances Center (Beijing, China). DMA and MMA were purchased from Sigma-Aldrich (St Louis, MO, USA). All of the reagents used were of analytical grade, and all solutions were prepared using ultrapure water produced by a Milli-Q purification system (Millipore, Bedford, MA, USA).

The water samples were determined directly by LC-HG-AFS after they were filtered through a 0.45 μm filter. Took 0.2000 g of sediment sample and 10 mL phosphoric acid into a 50 mL conical flask, and added 10 mL phosphoric acid. Then the conical flask was immersed and shaken for 1 hr in a water bath at 60°C. After the solution cooled, it was centrifuged at 2500 r/min for 15 min and the supernatant was filtered through a 0.45 μm filter. Then it was determined by LC-HG-AFS (Zhang et al., 2008).

1.6. Quality control

All of the experimental reagents used were of analytical reagent grade. Milli-Q water was used to prepare the extraction solutions. Samples were analyzed in triplicate and one standard sample was analyzed at intervals of 5 experimental samples to ensure the accuracy of the results. Meanwhile, to obtain the accurate experimental data, field blank and lab blank were set as well. The chromatogram of As(III), As(V), MMA and DMA is shown in Appendix A Fig. S2. The calibration curves for four species and corresponding correlation coefficients (R) are shown in Appendix

A Table S2. The relative standard deviations for the analyses were lower than 5%, which means that the results reached the required precision. Standard addition experiments showed that the average recoveries of As(III), As(V), DMA, and MMA were 80%–105%. The minimum detection limits of As(III), As(V), DMA, and MMA in water samples were 0.25, 0.51, 0.36 and 0.39 μg/L respectively. And the minimum detection limits of As(III), As(V), DMA, and MMA in sediment samples were 0.02, 0.03, 0.02 and 0.02 mg/kg, respectively.

2. Results and discussion

2.1. Calculation of PNECs for arsenic species in water

Arsenic trioxide (CAS No. 1327533) and arsenite (CAS No. 7784465) were both treated as As(III) species. A total of 51 toxicity data were selected, in which 49% of them were for vertebrates, 43% for invertebrates, and 8% for plants. Arsenic pentoxide (CAS No. 1303282) and arsenic acid (CAS No. 7778394) were both treated as As(V) species. Totally 22 toxicity data were selected, in which 9% of them were for vertebrates, 14% for invertebrates, and 77% for plants. SSD curves for As(III) and As(V) were constructed using the toxicity data and a log-logistic model. The fitting parameters, test results, and the calculated HC5 values are shown in Table 2. The determination coefficients (R^2) for the two models was all above 0.90, and the variance test (F value) reached a statistically significant level, showing that the SSD curves for As(III) and As(V) (Fig. 1) were constructed well using log-logistic models. The As(III) and As(V) HC5 values were 43.65 and 250.18 μg/L, respectively. Both As(III) and As(V) have previously been found to be teratogenic (IPCS, 1981). Our results show that the toxicity of As(III) is much higher than that of As(V). The possible reason is that As(III) can more easily go through the cell membrane and produce toxic effect to enzyme of organism.

There were less than 10 acute and chronic toxicity data for DMA (CAS No. 75605) in algae and fish, so the AF method was used to assess the ecological risk from DMA. According to the toxicity data collected for DMA, and the choosing principles described in Table 1, the AF value should be 50 (Case 3). The lowest NOEC value in the collected dataset was 1.00×10^5 μg/L, which was obtained from the *Chlorella vulgaris* and *Pseudokirchneriella subcapitata* tests. The PNEC value for DMA was therefore 2.00×10^3 μg/L according to Eq. (2), meaning that DMA is less toxic than As(III) or As(V). It has previously been reported that the 50% of lethal doses (LD50) of DMA, As(III) and As(V) which for oral administration to mice, were 7.00×10^2–2.60×10^3, 14.00 and 20.00 mg/kg respectively, and our results are in agreement (Zhang et al., 1996, 2007).

Table 2 – Species sensitivity distribution (SSD) fitting parameters and test results for As(III) and As(V).

As species	HC5 (μg/L)	Goodness of fit test			Models
		R^2	F value	p	
As(III)	43.65	0.97	2354.25	0.001	$y = 1400.89/(1 + e^{-1.19(x - 10.24)})$
As(V)	250.18	0.93	432.89	0.001	$y = 1322.34/(1 + e^{-0.95(x - 13.11)})$

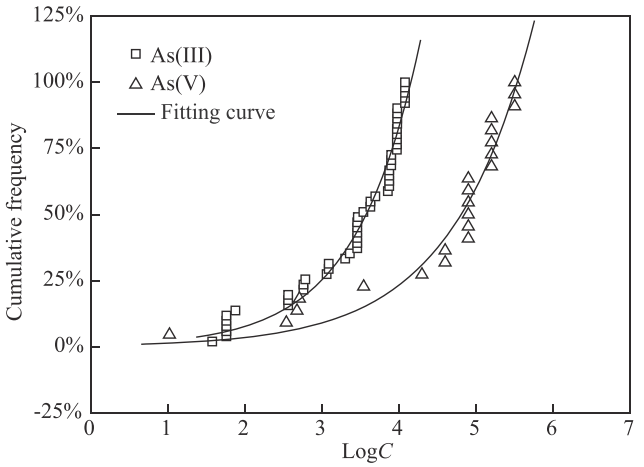

Fig. 1 – Species sensitivity distribution (SSD) curves of As(III) and As(V).

Up to now, almost all assessment on arsenic pollution was based on the concentration of total arsenic without considering the toxicity variation of different arsenic species. For example, the total As concentration was set as 50 μg/L in the Chinese environmental quality standards for surface water (GB3838-2002 Class III), and set as 15 mg/kg in the Chinese environmental quality standard for soils (GB15618-1995 Class I). Although As(III), As(V), and DMA are all toxic, their toxicities are quite different. It is necessary to set limits for different arsenic species in the Chinese environmental quality standards for soils and water, which will be beneficial to evaluate the potential risk accurately.

2.2. Risk assessment of arsenic pollution

2.2.1. Case study in the Pearl River Delta

The As(III) and As(V) concentrations in the samples taken from the seven sites in the Pearl River Delta in the dry season and wet season are shown in Table 3. The total arsenic concentrations in the water samples were much higher in the dry season than those in the wet season. As(V) was the dominant species in the dry season while As(III) was the dominant species in the wet season. Both As(III) and As(V) concentrations in the sediments had no significant changes between the dry season and the wet season, indicating that the arsenic concentrations were much more stable in the sediment phase than in the water phase. DMA and MMA were not found in the 14 samples. The arsenic concentrations in the pore water ($C_{porewater}$) were estimated by Eq. (3), and the results are shown in Table 4. It was found that As(V) was the dominant species in the sediment in both the dry season and the wet season. Ellwood and Maher (2003) reported that the main arsenic species in sediment are As(III) and As(V), especially As(V), and our results are in agreement.

The concentrations of As(III) and As(V) in the water samples collected from the Pearl River Delta were 0.55–27.30 and 0.27–30.10 μg/L, respectively. The RQ values for different arsenic species in water were calculated from their environmental

Table 3 – As(III) and As(V) concentrations in water and sediment samples from seven sites in the Pearl River Delta in the dry season and the wet season.

Sampling sites	Dry season				Wet season			
	Water (μg/L)		Sediment (mg/kg)		Water (μg/L)		Sediment (mg/kg)	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
P-A	9.20 ± 0.31	14.70 ± 0.44	0.07 ± 0.01	6.20 ± 0.33	3.00 ± 0.19	0.90 ± 0.12	0.16 ± 0.01	1.30 ± 0.06
P-B	4.10 ± 0.24	6.30 ± 0.27	0.46 ± 0.03	0.66 ± 0.04	3.10 ± 0.18	0.50 ± 0.04	0.21 ± 0.01	0.60 ± 0.04
P-C	0.55 ± 0.05	7.35 ± 0.31	0.23 ± 0.02	0.39 ± 0.02	27.30 ± 0.49	0.80 ± 0.07	0.49 ± 0.03	0.19 ± 0.01
P-D	3.65 ± 0.21	26.25 ± 0.57	0.75 ± 0.05	0.90 ± 0.11	4.50 ± 0.26	0.30 ± 0.01	0.88 ± 0.05	0.34 ± 0.02
P-E	0.75 ± 0.07	9.05 ± 0.33	0.26 ± 0.02	0.25 ± 0.01	24.90 ± 0.52	1.40 ± 0.07	0.04 ± 0.01	0.13 ± 0.01
P-F	7.30 ± 0.29	12.90 ± 0.41	0.65 ± 0.09	0.54 ± 0.03	5.20 ± 0.33	0.27 ± 0.02	0.35 ± 0.02	0.43 ± 0.04
P-G	14.30 ± 0.41	30.10 ± 0.59	0.07 ± 0.01	ND	2.00 ± 0.16	0.40 ± 0.04	0.67 ± 0.03	0.28 ± 0.02
Total As	7.90 ± 0.36–44.40 ± 1.00		0.07 ± 0.01–6.27 ± 0.34		2.40 ± 0.20–28.10 ± 0.56		0.17 ± 0.02–1.46 ± 0.07	

ND: not detected.

concentrations and the corresponding PNEC values. All of the RQ values for the samples collected from the Pearl River Delta were less than 1 and the results are shown in Table 5, indicating that the potential ecological risk from As(III) and As(V) was low in the studied area. With this method, the ecological risk from different arsenic species could be evaluated. For examples: As(III) and As(V) were 10.00–600.00 and 3.00–200.00 μg/L in the Tinto River cross the Province of Huelva in southwest Spain (Sanchez-Rodas et al., 2005), the RQ values of As(III) and As(V) were 0.23–13.64 and less than 1, respectively. As(III) and As(V) were 0.50–65.00 μg/L and ND-35.00 μg/L in the Odiel River in southwest Spain (Sanchez-Rodas et al., 2005), with corresponding RQ values 0.01–1.48 and less than 1. As(III) and As(V) were 14.00–212.00 and 38.00–125.00 μg/L in the Stuarts Point groundwater system, northern New South Wales, Australia (Smith et al., 2003), their RQ values were 0.32–4.82 and less than 1, respectively. According to the results of examples listed above, the potential ecological risk from As(III) was much higher than that from As(V). And as shown in Table 5, the RQ values of arsenic (As(III): 0.01–0.62; As(V): 0.00–0.12) in this study were relatively low compared with some other lakes around the world (Smith et al., 2003).

Sediment acts like a 'savings bank' of chemical contaminants, so the arsenic saved in the sediment bank would be released into water again, causing the secondary pollution in water phase. In the sediment samples collected from the Pearl River Delta, the concentrations of As(III) and As(V) were 0.04–0.88 mg/kg and ND-6.20 mg/kg, respectively. The RQ values for different arsenic species in sediment samples could be indirectly calculated from their concentrations in pore water and the corresponding PNEC values. The RQs showed that ecological risks from As(III) and As(V) in sediments from the Pearl River Delta were lower than 1, and the results are shown in Table 5. Compared with the previous publications, the As(III) and As(V) contents in sediments in southwestern Ghana (As(III) 190.00–506.00 mg/kg and As(V) 156.00–385.00 mg/kg) (Tulasi et al., 2013), in the Lake Macquarie, NSW, Australia (Ellwood and Maher, 2003) (As(III) 0.23–2.43 mg/kg and As(V) ND-7.93 mg/kg) were much higher than those in the Pearl River Delta. Therefore, the ecological risks of As(III) and As(V) in Ghana and Australia might be much higher than that in the Pearl River Delta.

It is well known that the chemical forms of arsenic can be converted under certain conditions. Therefore, to evaluate the total risk of arsenic at each sampling point, all the RQ values of As(III) and As(V) in both water and sediment samples at the same site were summed up as ΣRQ. The results showed that the ΣRQ values at 7 sampling sites in the studied area were all less than 1, indicating that the total ecological risk of arsenic pollution in the Pearl River Delta was low. However, the ΣRQ values at 2 sampling sites (P-A and P-C) were near 1, the reason may be that there are many mine engineering and spinneries around those sampling sites within the Pearl River basin.

Table 4 – Calculated concentrations of As(III) and As(V) in the pore water ($C_{porewater}$) for the sediment samples from the Pearl River Delta in the dry season and wet season.

Sampling sites	Dry season			Wet season		
	F_{oc} (%)	As(III) (μg/L)	As(V) (μg/L)	F_{oc} (%)	As(III) (μg/L)	As(V) (μg/L)
P-A	1.50	1.52 ± 0.22	1.35×10^2 ± 7.17	4.40	10.20 ± 0.64	82.90 ± 3.83
P-B	2.10	14.00 ± 0.91	20.09 ± 1.22	2.00	6.09 ± 0.29	17.39 ± 1.16
P-C	5.40	18.00 ± 1.56	30.52 ± 1.56	1.30	9.23 ± 0.56	3.58 ± 0.19
P-D	0.20	2.17 ± 0.14	2.61 ± 0.32	1.10	14.03 ± 0.80	5.42 ± 0.32
P-E	0.60	2.26 ± 0.17	2.17 ± 0.09	0.80	0.46 ± 0.12	1.51 ± 0.12
P-F	1.20	11.30 ± 1.56	9.39 ± 0.52	0.30	1.52 ± 0.09	1.87 ± 0.17
P-G	0.40	0.41 ± 0.06	ND	2.10	20.39 ± 0.91	8.52 ± 0.61

$K_{oc,i}$: 0.69 L/kg (Liang et al., 2009); ND: not detected; F_{oc}: organic carbon content in sediment samples.

Table 5 – Risk quotients (RQs) of As(III) and As(V) in water and sediment samples from seven sites in the Pearl River Delta in the dry season and the wet season.

Sampling sites	Dry season				Wet season			
	Water		Sediment		Water		Sediment	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
P-A	0.21	0.06	0.03	0.54	0.07	0.00	0.23	0.33
P-B	0.09	0.02	0.32	0.08	0.07	0.00	0.14	0.07
P-C	0.01	0.03	0.41	0.12	0.62	0.00	0.21	0.01
P-D	0.08	0.10	0.05	0.01	0.10	0.00	0.32	0.02
P-E	0.02	0.04	0.05	0.01	0.57	0.00	0.01	0.01
P-F	0.17	0.05	0.26	0.04	0.12	0.00	0.03	0.01
P-G	0.33	0.12	0.01	ND	0.04	0.00	0.47	0.03
Total As	0.04–0.45		0.01–0.57		0.04–0.62		0.02–0.56	

2.2.2. Case study in the Kwabrafo stream

Tulasi et al. (2013) measured the distribution of As(III) and As(V) in Kwabrafo stream at Obuasi in southwestern Ghana. The Kwabrafo received effluent from Pompora Treatment Plant area and drains through a network of tailing dam sites in the north–south directions (Appendix A Fig. S3). The water samples were collected from six sites (K-A, K-B, K-C, K-D, K-E, and K-F) along the upstream, midstream, and downstream of Kwabrafo stream. As shown in Table 6, the concentrations of total arsenic, As(III) and As(V) were the highest in midstream, followed by downstream and upstream. The RQs of As(III) and As(V) were calculated for the water samples using the PNEC values of As(III) and As(V) obtained in this study (Table 6). It can be seen that sites K-C, K-D, and K-E (midstream) had high risk from As(III) and sites K-B, K-C, K-D, K-E, and K-F (midstream and downstream) had high risk from As(V). The upstream of Kwabrafo stream was on a higher elevation and As in the upstream could flow downward to the midstream. Otherwise, there was a low land covered with tailings between the heap of tailings (Pompora tailing) and the upper portion of stream, hence most of the water draining from the tailings flows down the midstream section of the Kwabrafo stream, resulting in higher concentration of As in the midstream. Then, the decrease in As level from midstream to downstream might be because As could settle down and be diluted gradually (Tulasi et al., 2013). It has been proved that the gold-bearing ore (rich in arsenopyrite) within the Obuasi region of Ghana is the main pollution source of arsenic. And, mining at Obuasi gave rise to substantial airborne arsenic pollution from ore roasting as well as river-borne As pollution derived from nearby tailings (Asiam, 1996).

Table 6 – Concentrations and RQs of As(III) and As(V) in the water samples from the Kwabrafo stream, Ghana.

Sampling sites	Concentration (mg/L)			RQ	
	Total As	As(III)	As(V)	As(III)	As(V)
K-A	1.15 ± 0.23	ND	ND	<1	<1
K-B	2.40 ± 0.23	ND	0.79 ± 0.08	<1	3.16
K-C	8.34 ± 0.29	0.13 ± 0.02	3.25 ± 0.10	2.95	13.00
K-D	9.20 ± 0.31	0.70 ± 0.13	3.85 ± 0.18	15.91	15.40
K-E	5.00 ± 0.30	0.20 ± 0.04	1.60 ± 0.10	4.55	6.40
K-F	2.50 ± 0.30	ND	0.90 ± 0.10	<1	3.60

ND: not detected.

3. Conclusions

Arsenic can be present as different forms in the environment, and the different arsenic species have quite discrepant toxicity characteristics. It is necessary to determine the concentrations of the different arsenic species in environmental samples and to evaluate their respective ecological risk. The water and sediment samples were collected from the Pearl River Delta, China. The PNECs of As(III) and As(V) were 43.65 and 250.18 μg/L calculated with SSD method, and PNEC of DMA was 2.00×10^3 μg/L using the AF method. The concentrations of different arsenic species were determined, and their ecological risks were respectively assessed. The results showed that the ecological risk from As(III) and As(V) was less than 1. In addition, the ecological risk assessment on different arsenic species in the Kwabrafo stream, Ghana showed that As(III) and particularly As(V) had high potential risk at midstream. We anticipate that this study can provide possibility for accurately evaluating the potential risk of arsenic contamination in the environmental media by considering the respective contribution of different arsenic species.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in online version at http://dx.doi.org/10.1016/j.jes.2014.03.006.

REFERENCES

Aldenberg, T., Slob, W., 1993. Confidence limits for hazardous concentrations based on logistically distributed NOEC toxicity data. Ecotoxicol. Environ. Saf. 25 (1), 48–63.

Arain, M.B., Kazi, T.G., Jamali, M.K., Jalbani, N., Afridi, H.I., Baig, J.A., 2008. Speciation of heavy metals in sediment by conventional, ultrasound and microwave assisted single extraction methods: a

comparison with modified sequential extraction procedure. J. Hazard. Mater. 154 (1–3), 998–1006.
Asiam, E.K., 1996. Environmental assessment of gold beneficiation: arsenic audit and impact on the Obuasi environs. GMJ 2 (1), 17–20.
Balk, F., Okkerman, P.C., Dogger, J.W., 1995. Guidance Document for Aquatic Effects Assessment. Organization for Economic Cooperation and Development, Paris, France, pp. 22–28.
Barringer, J.L., Szabo, Z., Wilson, T.P., Bonin, J.L., Kratzer, T., Cenno, K., et al., 2011. Distribution and seasonal dynamics of arsenic in a shallow lake in northwestern New Jersey, USA. Environ. Geochem. Health 33 (1), 1–22.
Cullen, W.R., Reimer, K.J., 1989. Arsenic speciation in the environment. Chem. Rev. 89 (4), 713–764.
Ellwood, M.J., Maher, W.A., 2003. Measurement of arsenic species in marine sediments by high-performance liquid chromatography–inductively coupled plasma mass spectrometry. Anal. Chim. Acta. 477 (2), 279–291.
European Chemical Bureau, 2003. Technical Guidance Document on Risk Assessment—Part II. Institute for Health and Consumer Protection, Ispra.
Francesconi, K.A., Edmonds, J.S., 1994. Biotransformation of arsenic in the marine environment. In: Nriagu, J.O. (Ed.), Arsenic in the Environment, Part I: Cycling and Characterization. John Wiley and Sons, New York, pp. 221–261.
Hall, L.W., Scott, M.C., Killen, W.D., 1998. Ecological risk assessment of copper and cadmium in surface waters of Chesapeake Bay watershed. Environ. Toxicol. Chem. 17 (6), 1172–1189.
IPCS (International Programme on Chemical Safety), 1981. Environmental Health Criteria 18. Arsenic, Geneva, pp. 20–130.
Jackson, L.J., Rasmussen, J.B., Peters, R.H., Kalff, J., 1991. Empirical relationships between the element composition of aquatic macrophytes and their underlying sediments. Biogeochemistry 12 (2), 71–86.
Jain, C.K., Malik, D.S., Yadav, R., 2007. Metal fractionation study on bed sediments of Lake Nainital, Uttaranchal, India. Environ. Monit. Assess. 130 (1–3), 129–139.
Jin, X.W., Lei, B.L., Xu, Y.P., Zha, J.M., Wang, Z.J., 2009. Methodologies for deriving water quality criteria to protect aquatic life (ALC) and proposal for development of ALC in China: a review. Asian J. Ecotoxicol. 4 (5), 609–616.
Keimowitz, A.R., Simpson, H.J., Stute, M., Datta, S., Chillrud, S.N., Ross, J., et al., 2005. Naturally occurring arsenic: mobilization at a landfill in Maine and implications for remediation. Appl. Geochem. 20 (11), 1985–2002.
Kim, Y.T., Yoon, H.O., Yoon, C., Woo, N.C., 2009. Arsenic species in ecosystems affected by arsenic-rich spring water near an abandoned mine in Korea. Environ. Pollut. 157 (12), 3495–3501.
Klimisch, H.J., Andreae, M., Tillmann, U., 1997. A systematic approach for evaluating the quality of experimental toxicological and ecotoxicological data. Regul. Toxicol. Pharmacol. 25 (1), 1–5.
Kooijman, S.A.L.M., 1987. A safety factor for LC50 values allowing for differences in sensitivity among species. Water Res. 21 (3), 269–276.
Liang, C.H., Liu, X., Du, L.Y., Jin, G.Z., Wang, N., Liu, J.J., 2009. The studies on the adsorptive–desorptive behaviour of arsenic in brow soil and its form distribution. J. Henan Agric. Sci. 411 (4), 64–68.
Mandal, B.K., Suzuki, K.T., 2002. Arsenic round the world: a review. Talanta 58 (1), 201–235.
Matschullat, J., 2000. Arsenic in the geosphere—a review. Sci. Total Environ. 249 (1–3), 297–312.
Mazej, Z., Germ, M., 2009. Trace element accumulation and distribution in four aquatic macrophytes. Chemosphere 74 (5), 642–647.
Migon, C., Mori, C., 1999. Arsenic and antimony release from sediments in a Mediterranean estuary. Hydrobiologia 392 (1), 81–88.
Council, National Research, 1999. Arsenic in Drinking Water. National Academy Press, Washington, DC.
Newman, M.C., Ownby, D.R., Mézin, L.C.A., Powell, D.C., Christensen, T.R.L., Lerberg, S.B., et al., 2000. Applying species-sensitivity distributions in ecological risk assessment: assumptions of distribution type and sufficient numbers of species. Environ. Toxicol. Chem. 19 (2), 508–515.
Nikolaidis, N.P., Dobbs, G.M., Chen, J., Lackovic, J.A., 2004. Arsenic mobility in contaminated lake sediments. Environ. Pollut. 129 (3), 479–487.
Nordstrom, D.K., 2002. Worldwide occurrences of arsenic in ground water. Science 296 (5576), 2143–2145.
Pearson, M., Jones-Hughes, T., Whear, R., Cooper, C., Peters, J., Evans, E.H., et al., 2011. Are interventions to reduce the impact of arsenic contamination of groundwater on human health in developing countries effective? A systematic review protocol. Environ. Evid. 1, 1.
Peng, D., Jin, F., Lü, J.J., Li, R.Y., Yang, H., 2004. Study on the content and spatial distribution of organic carbon in the sediment of Dianchi Lake. Soils 36 (5), 568–572.
Rahman, M.M., Mukherjee, D., Sengupta, M.K., Chowdhury, U.K., Lodh, D.C., Roy, S., et al., 2002. Effectiveness and reliability of arsenic field testing kits: are the million dollar screening projects effective or not? Environ. Sci. Technol. 36 (24), 5385–5394.
Sanchez-Rodas, D., Gomez-Ariza, J.L., Giraldez, I., Velasco, A., Morales, E., 2005. Arsenic speciation in river and estuarine waters from southwest Spain. Sci. Total Environ. 345 (1–3), 207–217.
Sarkar, S., Blaney, L.M., Gupta, A., Ghosh, D., Sengupta, A.K., 2008. Arsenic removal from groundwater and its safe containment in a rural environment: validation of a sustainable approach. Environ. Sci. Technol. 42 (12), 4268–4273.
Schuler, L.J., Hoang, T.C., Rand, G.M., 2008. Aquatic risk assessment of copper in freshwater and saltwater ecosystems of South Florida. Ecotoxicology 17 (7), 642–659.
Smith, J.V.S., Jankowski, J., Sammut, J., 2003. Vertical distribution of As(III) and As(V) in a coastal sandy aquifer: factors controlling the concentration and speciation of arsenic in the Stuarts Point groundwater system, northern New South Wales, Australia. Appl. Geochem. 18 (9), 1479–1496.
Terlecka, E., 2005. Arsenic speciation analysis in water samples: a review of the hyphenated techniques. Environ. Monit. Assess. 107 (1–3), 259–284.
Tulasi, D., Adotey, D., Affum, A., Carboo, D., Serfor-Armah, Y., 2013. Speciation of As(III) and As(V) in water and sediment using reverse-phase ion-pair high-performance liquid chromatography–neutron activation analysis (HPLC–NAA). Environ. Monit. Assess. 185 (10), 7979–7991.
Van Straalen, N.M., Van Rijn, J.P., 1998. Ecotoxicological risk assessment of soil fauna recovery from pesticide application. Rev. Environ. Contam. Toxicol. 154, 83–141.
Wagner, C., Lokke, H., 1991. Estimation of ecotoxicological protection levels from NOEC toxicity data. Water Res. 25 (10), 1237–1242.
Wang, S., Mulligan, C.N., 2006. Occurrence of arsenic contamination in Canada: sources, behavior and distribution. Sci. Total Environ. 366 (2–3), 701–721.
Wei, C.Y., Zhang, N., Yang, L.S., 2011. The fluctuation of arsenic levels in Lake Taihu. Biol. Trace Elem. Res. 143 (3), 1310–1318.
Whitmore, T.J., Riedinger-Whitmore, M.A., Smoak, J.M., Kolasa, K. V., Goddard, E.A., Bindler, R., 2008. Arsenic contamination of lake sediments in Florida: evidence of herbicide mobility from watershed soils. J. Paleolimnol. 40 (3), 869–884.
Wu, F.C., Feng, C.L., Cao, Y.J., Zhang, R.Q., Li, H.X., Liao, H.Q., et al., 2011a. Toxicity characteristic of zinc to freshwater biota and its water quality criteria. Asian J. Ecotoxicol. 6 (4), 367–382.
Wu, F.C., Meng, W., Cao, Y.J., Li, H.X., Zhang, R.Q., Feng, C.L., et al., 2011b. Derivation of aquatic life water quality criteria for cadmium in freshwater in China. Environ. Sci. Res. 24 (2), 172–184.

Wu, F.C., Meng, W., Zhang, R.Q., Li, H.X., Cao, Y.J., Xu, B.B., et al., 2011c. Aquatic life water quality criteria for nitrobenzene in freshwater. Environ. Sci. Res. 24 (1), 1–10.

Zhang, H., Wang, Y.F., Shi, Y.Z., Chen, Y.H., 2007. Application of high performance liquid chromatography and hyphenated techniques in analysis of arsenic species. Spectrosc. Spectr. Anal. 27 (2), 386–390.

Zhang, J., Liu, X.D., Jiang, L., 2008. Speciation analysis of arsenic in soil samples. Rock Miner. Anal. 27 (3), 179–183.

Zhang, N., Wei, C.Y., Yang, L.S., 2013. Occurrence of arsenic in two large shallow freshwater lakes in China and a comparison to other lakes around the world. Microchem. J. 110, 169–177.

Zhang, X.R., Cornelis, R., Kimpe, J.D., Mees, L., Vanderbiesen, V., Cubber, A.D., et al., 1996. Accumulation of arsenic species in serum of patients with chronic renal disease. Clin. Chem. 42 (8), 1231–1237.

Zhao, J.L., Ying, G.G., Wei, D.B., Ren, M.Z., 2011. Ecological risk assessment methodology of toxic pollutants in surface water and sediments: a review. Asian J. Ecotoxicol. 6 (6), 577–588.

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