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Arsenic speciation in environmental multimedia samples from the Youngsan River Estuary, Korea: A comparison between freshwater and saltwater

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ABSTRACT

Differences in the distribution, partitioning, and bioaccumulation characteristics of arsenicals between freshwater and saltwater systems remain poorly understood. To determine the characteristics of distribution and behavior of arsenicals, multimedia environmental samples including water, suspended particles, zooplankton, sediments, and porewater were collected from inner (five sites, freshwater) and outer (five sites, saltwater) regions of the estuary dike of the Youngsan River Estuary in South Korea (Nov., 2012). Six organic and inorganic forms of As were separated and measured using HPLC–ICP/MS equipped with an anion exchange column. Concentrations of arsenicals in water samples of the inner region (mean = 1.5 μg As L^{-1}) were significantly lower than in those of the outer region (mean = 5.2 μg As L^{-1}). Conversely, concentrations of As in suspended particles in the inner region (mean = 14 μg As g^{-1}) were much greater than in the outer region (mean = 5.7 μg As g^{-1}). The field-based distribution coefficient (K_d) for As depended strongly on salinity; relatively greater K_d values were found in freshwater compared with saltwater. The As^V was found to be the major form of As in all water and particle samples in both inner and outer regions. The zooplankton species were significantly distinguishable between the inner and outer regions; cladocerans were the most dominant species in freshwater and cyclopoida were predominantly found in saltwater. The As concentrations in zooplankton were shown to be particle-concentration dependent, suggesting that dietary exposure plays a substantial role in the bioaccumulation of As. Inorganic arsenicals, such as As^V and As^{III} were the most dominant forms found in zooplankton. Partitioning behavior of As between porewater and sediments was similar to that in water–particle distributions. The results of the present study enhance the understanding of As biogeochemistry in river and estuarine environments.

1. Introduction

As is a ubiquitous metalloid element found in several organic and inorganic forms in aquatic environmental media, such as water, suspended particulate matter (SPM), sediments, porewater, and various organisms (Azizur Rahman et al., 2012; Cullen and Reimer, 1989). As introduced into the marine environment, primarily via river runoff, originates from natural sources and anthropogenic activities (Balzer et al., 2013; De Gieter et al., 2005; Kitts et al., 1994). The multimedia distributions, fate, and biological effects (e.g., toxicity and/or bioaccumulation) of As are complexly dependent on its form, salinity, and sorption characteristics (Anderson and Bruland, 1991; Azizur Rahman et al., 2012; Hong et al., 2016; Waslenchuk and Windom, 1978). Generally, inorganic forms of As such as trivalent arsenite (As^{III}) and pentavalent arsenate (As^V) are more toxic than organic forms, and As^V is known to be most abundant and stable in the oxic water column (Azizur Rahman et al., 2012).

Forms of As in an aquatic environment are controlled by several biotic and abiotic factors, including redox conditions, pH, salinity, microbial activity, and planktonic communities (Caumette et al.,

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2011; Cullen and Reimer, 1989; Kitts et al., 1994). Inorganic forms of As can be inadvertently uptaken by phytoplankton and macroalgae through phosphate uptake systems (waterborne exposure) (Hellweger et al., 2003). Furthermore, As can be transformed into organic forms within the bodies of phytoplankton, and a proportion of As can be released into the water column (Azizur Rahman et al., 2012). In addition, arsenicals can be transferred to aquatic animals via direct consumption through the food web (dietary exposure) in both freshwater and marine ecosystems. However, studies of the differences in bioaccumulation characteristics of As (e.g., exposure routes, controlling factors, and forms of As) between freshwater and marine organisms are scarce.

Dissolved As can be adsorbed onto SPM and deposited to sediments as a result of changes in physical, chemical, and biological factors within the water column (Yang et al., 2016). The environmental mobility of As in terms of land–ocean connection and global transport pathways is affected mainly by sorption characteristics in estuarine areas (Turner, 1996; Turner and Millward, 2002). For example, particle-adsorbed As is relatively less mobile than freely dissolved forms, because particulate As could be ingested by organisms and/or accumulated in sediments. Thus, the water–particle distribution (partitioning) coefficient (K_d value) is very useful for understanding the multimedia distributions, transport, and fate of arsenicals in an estuarine system. Previous studies have reported that adsorption and desorption characteristics of As in estuaries are dependent primarily on salinity, SPM concentrations and compositions, as well as biological activities (Balzer et al., 2013; Benoit et al., 1994; Hong et al., 2016). Although many previous studies have been conducted to understand the partitioning behaviors of As in freshwater and estuarine environments (Balzer et al., 2013; De Gieter et al., 2005; Hong et al., 2016; Michel et al., 1993, 1999; Millward et al., 1997), the controlling factors have been shown to be site-specific; thus, additional field studies on this subject are needed.

The Youngsan River Estuary is part of one of the largest rivers in South Korea, which flows toward the southwest and discharges freshwater into the Yellow Sea (Hong et al., 2013). An estuary dike was constructed on the river in 1981 for agricultural and flood control purposes. Subsequently, an artificial freshwater lake (the Youngsan Lake) was created upstream of the dike, which is completely separated from the outer estuarine (saltwater) area (Kim et al., 2017; Lee et al., 2009). Based on the elevation of the water level of the inner lake, freshwater is discharged via water gates into the estuarine area (~1.8 billion tons per year). The multimedia distributions and sorption characteristics of land-derived organic chemicals and elements change between the freshwater and estuarine areas because of the drastic change in salinity (Turner, 1996; Turner and Millward, 2002). For example, the adsorption affinities of long-chain perfluoroalkyl acids in saltwater are significantly greater than in freshwater, suggesting that such chemicals could be largely scavenged from the water column (Hong et al., 2013). However, in a closed estuary such as the Youngsan River Estuary, information on comparisons of the distributions, fate, and bioaccumulations of arsenicals between freshwater and saltwater is limited.

In the present study, environmental multimedia (water, SPM, zooplankton, sediments, and porewater) distributions, adsorption characteristics, and bioaccumulations of As were determined, focusing on the differences between freshwater (inner dike) and saltwater (outer dike) regions. The results of this study improve the understanding of As biogeochemistry and fate in estuarine environments.

2. Materials and methods

2.1. Sampling and sample preparations

Overall, 10 sites along the Youngsan River Estuary (distance: ~30 km) were selected as sampling points that included both freshwater artificial lake (inner dike, 5 sites, R1–R5) and estuarine areas (outer dike, 5 sites, E1–E5) in November 2012 (see Fig. 1). Temperature (T), salinity (S), dissolved oxygen (DO), and pH were measured *in situ* at the surface and the bottom layers of the water column using a calibrated multiprobe (YSI 556 MPS, Yellow Springs, OH) (Table S1 of the Supplementary Materials). Four liters of surface water were collected for analysis of SPM, total As, and As speciation using a Van Dorn water sampler. In the laboratory, water samples were filtered as soon as possible using 0.45-μm membrane filters (Nuclepore, Whatman, Maidstone, UK). Filtered water samples for determination of total As and As speciation concentrations were acidified with nitric acid (Ultrapure, Merck, Darmstadt, Germany) and stored at 4 °C prior to analysis. SPM concentrations were determined using a microbalance after freeze-drying, and the filter samples were stored at −20 °C for particulate As analysis.

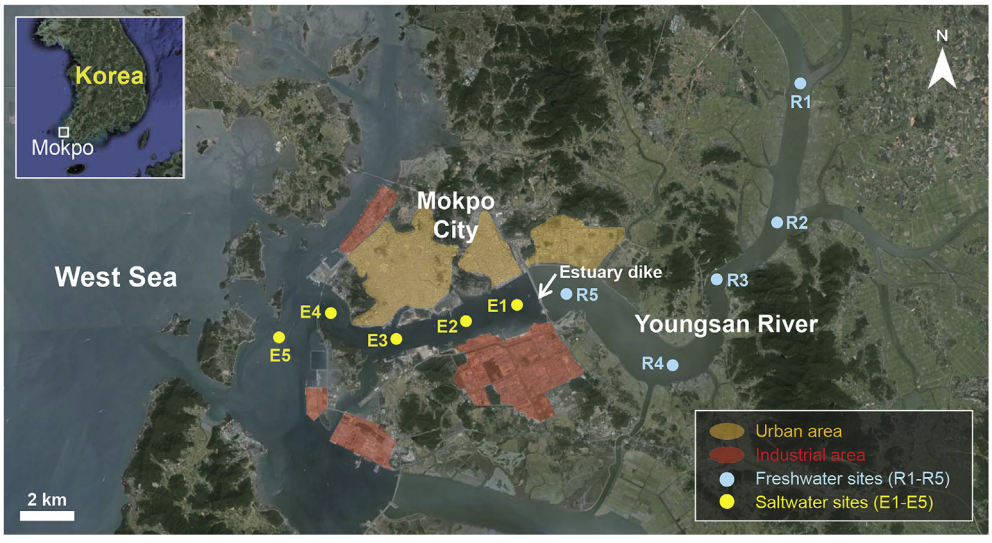

Fig. 1. Map showing the sampling sites (inner: freshwater; outer: saltwater) of the Youngsan River Estuary, Korea (Nov., 2012).

Sediment samples were collected from the 10 sites of the Youngsan River Estuary using a Van Veen grab. Surface sediment samples (0–2 cm) were transferred into pre-cleaned glass jars, and then transported immediately to the laboratory and stored at −20 °C until analysis. Porewater samples were collected using 50-mL Teflon® tubes from the sediment samples. The tubes were centrifuged for 15 min at 3000 rpm, following which the supernatant was decanted into a new 15-mL conical tube. Bulk zooplankton samples were collected from three of the freshwater lake sites (R1, R3, and R5) and three of the estuarine area sites (E1, E3, and E5) using a 100-μm mesh net. Quantitative analysis of zooplanktons could not be conducted. Zooplankton species were qualitatively observed using a stereoscopic microscope, which roughly supported the spatial variability of species composition cross the sampling locations. The species were completely distinguishable between the freshwater and saltwater sites (except for E1), but the internal compositions of the freshwater and saltwater sites were not significantly different (data not shown). Zooplankton samples were kept frozen at −20 °C until freeze-drying and further analyses.

2.2. Total As analysis

Total concentrations of As in the environmental samples were measured using previously described methods (Hong et al., 2014, 2016). Water and porewater samples acidified with nitric acid (2%) were analyzed without any pretreatment. Freeze-dried SPM, sediments, and zooplankton samples were digested with a mixture of nitric acid and hydrogen peroxide on a heating mantle (120 °C) for 4 h. Then, they were evaporated to near dryness and diluted in 1% HNO_3. Total concentrations of As in water, SPM, zooplankton, sediments, and porewater were measured using inductively coupled plasma-mass spectrometry (ICP/MS, Elan DRC II, PerkinElmer, Shelton, CT) as AsO at m/z 91 in DRC mode using oxygen as the reaction cell gas in order to prevent interference by $ArCl^+$ (m/z 75). Detailed operating conditions of the ICP/MS are presented in Table S2. The accuracy of determination of total As was assessed using certified reference material (CRM) MESS-3 (marine sediment, National Research Council (NRC), Ottawa, Canada), and recovery of As was generally acceptable (i.e., 93%–97% of the certified value).

2.3. As speciation analysis

Six organic and inorganic forms of As in the environmental multimedia samples were identified and quantified using previously described methods with minor modifications (Caumette et al., 2011; Hong et al., 2016; Whaley-Martin et al., 2012). Water and porewater samples for As speciation analysis were filtered through 0.22-μm syringe filters (13 mm, MCE filter, Jet Biofil, Guangzhou, China) and kept frozen. Freeze-dried SPM (~0.1 g), sediments (~1.0 g), and zooplankton samples (~0.1 g) were weighed and transferred to 15-mL polypropylene conical tubes and extracted with 10 mL of 2% nitric acid. Samples were sonicated for 30 min and placed on a mechanical water bath shaker for 4 h (60 °C, 120 rpm). Then, they were centrifuged for 15 min at 3000 rpm (1000 × g). Supernatants were finally filtered through 0.22-μm syringe filters and stored frozen.

Six forms of As such as arsenocholine (AC, $C_5H_{14}AsO^+$), arsenobetaine (AB, $C_5H_{11}AsO_2$), monomethylarsonic acid (MMA, CH_5AsO_3), dimethylarsinic acid (DMA, $C_2H_7AsO_2$), As^{III}, and As^V were separated and quantified using HPLC–ICP/MS (PerkinElmer Series 200 HPLC and ELAN DRC II ICP/MS System) with an anion exchange column (Hamilton PRP-X100, 250 mm × 4.1 mm, 10 μm particle, Reno, NV). Detailed instrumental conditions are presented in Table S2. Briefly, HPLC mobile phases were (A) 4 mM ammonium nitrate (Sigma-Aldrich, Saint Louis, MI) and (B) 40 mM ammonium nitrate in milli-Q water adjusted to pH 9.5. Injection volume was 20 μL with a flow rate of the mobile phase of 1.5 mL min^{-1}. Mobile phase gradient program was 0–3 min for 100% A, 3–15 min for 100% B, and 15–18 min for 100% A. Quantifications of arsenicals were conducted using the Chromera Chromatography Data System (Ver. 2.1, PerkinElmer).

2.4. QA/QC

Quality assurance and quality control programs for the As speciation analysis were performed in accord with our previous studies (Hong et al., 2014, 2016). In brief, the method detection limits of the six forms of As using HPLC–ICP/MS were 0.05–0.1 μg L^{-1} in water and porewater, 0.005–0.01 μg g^{-1} in SPM and zooplankton, and 0.001–0.002 μg g^{-1} in sediments (details in Table S3). Detected concentrations in all procedural and instrumental blank samples were less than their corresponding method detection limits. Degradation or interconversion of forms of As did not occur in the 2% nitric acid solution (Hong et al., 2016). Accuracy for concentrations of As forms was assessed using two CRMs, such as DORM-3 (fish protein, NRC) and TORT-2 (lobster hepatopancreas, NRC). Concentrations of the six forms of As in the CRMs were similar to reference values reported previously (details in Hong et al. (2016)).

2.5. Data analysis

During the HPLC-ICP/MS analysis, two unknown peaks of arsenicals were found in SPM, zooplankton, and sediments (peak areas are shown in Table S4). It seemed to be arsenosugar compounds such as glycerol sugar and phosphate sugar in comparison to a previous study (HPLC retention order in anion exchange column) (Caumette et al., 2011). However, these chemicals could not be quantified due to lack of standard materials of arsenosugars. The percentage of identified arsenicals (extraction efficiency) in the environmental multimedia samples was calculated by subtracting the sum of the concentrations of the six arsenicals determined by HPLC–ICP/MS from the total As concentrations determined by ICP/MS. The field-based partition coefficients (K_d in L kg^{-1}) of As between solution (water or porewater) and solid (SPM or sediment) phases were calculated using Eq. (1):

$$K_d = C_{SPM\ (or\ sediment)} \Big/ C_{Water\ (or\ porewater)}, \quad (1)$$

where C_{SPM} is the concentration of As in SPM (μg As kg^{-1}) or sediments and C_{Water} is the concentration of dissolved As in water or porewater (μg As L^{-1}). The bioaccumulation factor (BAF, L kg^{-1}) of As in zooplankton was calculated based on the concentrations of As in both water (C_{Water}, μg As L^{-1}) and zooplankton (C_{Zoo}, μg As kg^{-1}). In addition, the biota-SPM accumulation factor (BSAF) of As was calculated using the concentrations of As in both SPM and zooplankton (Eqs. (2) and (3)):

$$BAF = C_{Zoo}/C_{Water}, \quad (2)$$

$$BSAF = C_{Zoo}/C_{SPM}. \quad (3)$$

Concentrations of As in solid samples such as SPM, sediments, and zooplankton provided here are on a dry weight basis. All statistical analysis such as Pearson correlation analysis and Welch-Aspin test were performed using IBM SPSS Statistics 22 (SPSS Inc., Chicago, IL).

3. Results and discussion

3.1. Multimedia distributions of As in Youngsan River Estuary

Concentrations of dissolved As in water ranged from 1.3 to 1.7 μg As L^{-1} (mean = 1.5 μg As L^{-1}) at the inner lake sites (R1–R5, freshwater) and from 4.6 to 7.2 μg As L^{-1} (mean = 5.2 μg As L^{-1}) at sites in the outer estuarine area (E1–E5, saltwater) (Fig. 2a and Table S5). Significantly greater concentrations of dissolved As were found in the outer regions, while concentrations of particulate As were much greater in the inner region (10–18 μg As g^{-1}; mean = 14 μg As g^{-1}) than in the outer region (4.5–7.7 μg As g^{-1}; mean = 5.7 μg As g^{-1}) (Fig. 2b). Concentrations of As detected in the water samples of the Youngsan River Estuary did not exceed the water quality guidelines (WQGs) for the protection of aquatic life suggested by the Canadian Council of Ministers of the Environment (CCME, 2001). Concentrations of As in the water samples from all sites in the inner region were below the freshwater-WQG (5.0 μg L^{-1}) and those from the sites in the outer region were below the marine-WQG (12.5 μg L^{-1}). The WQGs for As were derived from acute and chronic ecotoxicological data on freshwater and marine organisms (CCME, 2001). Thus, contamination by As in the Youngsan River Estuary does not exceed tolerable levels of ecotoxicological risk.

Distributions of dissolved and particulate As in the water column between the inner and outer regions were clearly distinguished by the boundary of the estuary dike. The zooplankton species were also significantly distinguished; the most dominant species in the freshwater was cladocerans and cyclopoida was predominantly found in the saltwater. Unfortunately, zooplankton density could not be measured in the present study. In general, zooplankton density in the freshwater lake was several orders of magnitude greater compared to that in the estuarine area (Kim & Lee, 2007; Youn et al., 2012). Concentrations of As in the zooplankton ranged from 28 to 33 μg As g^{-1} (mean = 31 μg As g^{-1}) and from 6.3 to 17 μg As g^{-1} (mean = 10 μg As g^{-1}) in the inner and outer regions, respectively (Fig. 2c). Greater concentrations of As in freshwater zooplankton appeared directly affected by the greater concentrations of particulate As. Concentrations of As in the zooplankton were shown to have particle-concentration dependency, suggesting that dietary exposure plays a substantial role in As bioaccumulation in the Youngsan River Estuary, as is discussed further below.

Solid-solution distributions of As between sediments and porewater were similar to those in the water column, indicating that greater concentrations of As were found in the sediments of freshwater (8.1–15 μg As g^{-1}; mean = 12 μg As g^{-1}) than in those of saltwater (4.2–8.7 μg As g^{-1}; mean = 6.2 μg As g^{-1}) (Fig. 2d). On the other hand, relatively greater concentrations of As were found in the porewater in the saltwater area (mean = 46 μg As L^{-1}) than in the freshwater area (mean = 39 μg As L^{-1}) (Fig. 2e). Concentrations of sedimentary As at the sampling sites of both freshwater and estuarine areas obtained from this study did not exceed sediment quality guidelines (probable effect levels (PELs), 17.0 μg g^{-1} for freshwater; 41.6 μg g^{-1} for marine) suggested by the CCME (CCME, 1999). Generally, As contamination levels in the Youngsan River Estuary were comparable with other Korean estuaries, such as the Hyeongsan River Estuary (Hong et al., 2014) and the Taehwa River Estuary (Hong et al., 2016). Furthermore, they were significantly less than in other regions of the world (Mandal and Suzuki, 2002), particularly areas affected by mining activities (Whaley-Martin et al., 2012).

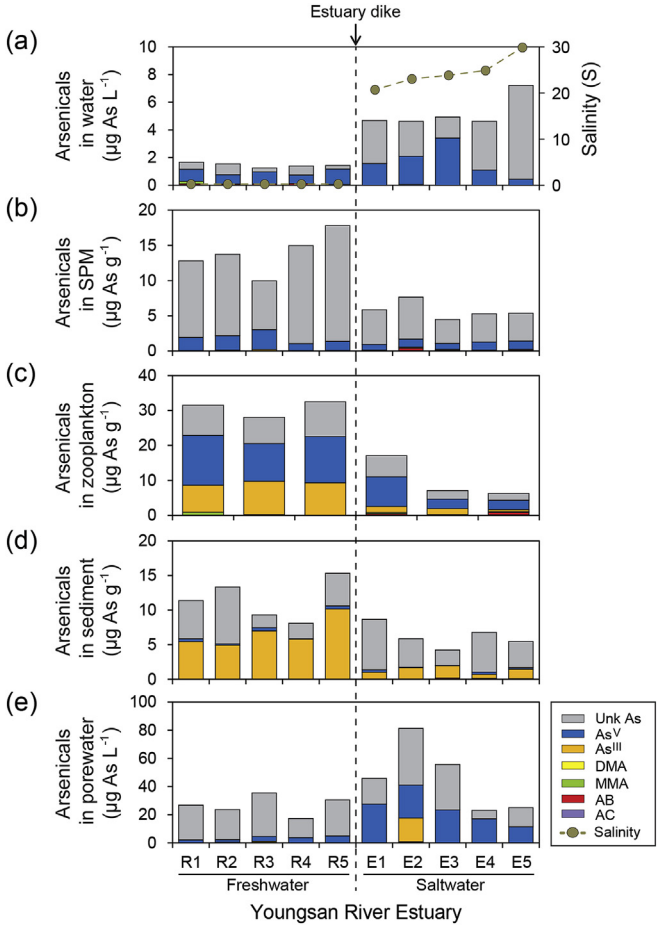

Fig. 2. Concentrations of arsenicals in various environmental samples: (a) water, (b) suspended particulate matter (SPM), (c) zooplankton, (d) sediments, and (e) porewater, collected from the inner and outer regions of the estuary dike in the Youngsan River Estuary, Korea.

3.2. As speciation in environmental multimedia samples

Among the identified As forms (extractable arsenicals), inorganic As^{V} was found to be the major form in all water samples from both inner and outer regions of the Youngsan River Estuary (Table 1 and Fig. 2). The quantity of As^{V} accounted for about 57% and 35% of identified As at the freshwater and saltwater sites, respectively. The predominance of As^{V} in the water of the Youngsan River Estuary can be attributed to sufficient levels of DO (aerobic condition) within the water column (Cullen and Reimer, 1989) (Table S1). Organic forms of As, such as AB and MMA, were detected at the freshwater sites, while only small concentrations of AB were detected at the saltwater sites. Different compositions of arsenicals between freshwater and saltwater sites were evidenced which was apparently related to the differences in species composition of planktons, of which results were consistent with the previous findings (Azizur Rahman et al., 2012; Caumette et al., 2011). Unidentified (or unextractable) As explained a large proportion of the total dissolved As. Approximately 64% and 34% of the total As concentrations in saltwater and freshwater sites, respectively, were unknown. These unknown arsenicals seemed to be organic forms of As, such as arsenosugars (e.g., sulfate sugar, phosphate sugar, and glycerol sugar) released from aquatic organisms (e.g., phytoplankton and/or macroalgae) (Caumette et al., 2011).

The forms of particulate As observed were more varied at the saltwater sites, where AB, AC, and As^{III} were detected, than at the freshwater sites where only As^{V} and As^{III} were detected (Table 1

Table 1
Summary of relative compositions of arsenicals in environmental multimedia samples collected from the Youngsan River Estuary (Mean ± SD).

Samples	Regions	Organic As (%)				Inorganic As (%)		Unknown As (%)[a]	Identified As (%)[b]
		AC	AB	MMA	DMA	As^{III}	As^{V}		
Water	Freshwater	[c]	6.3 ± 1.9	2.2 ± 5.0			57 ± 16	34 ± 15	66
	Saltwater		0.21 ± 0.48				35 ± 24	64 ± 24	36
SPM	Freshwater					0.98 ± 0.72	14 ± 8.8	85 ± 9.5	15
	Saltwater	0.19 ± 0.43	2.8 ± 1.3			1.5 ± 0.88	18 ± 3.8	77 ± 3.9	23
Zooplankton	Freshwater			1.2 ± 1.4		29 ± 4.7	41 ± 3.4	28 ± 2.2	72
	Saltwater	0.81 ± 1.4	5.7 ± 4.2	1.5 ± 1.3		15 ± 7.9	44 ± 5.6	33 ± 2.5	67
Sediment	Freshwater					60 ± 16	2.7 ± 1.8	38 ± 17	62
	Saltwater		2.0 ± 1.6	0.20 ± 0.27		23 ± 14	2.6 ± 2.2	72 ± 13	28
Porewater	Freshwater			0.49 ± 0.55	0.72 ± 0.80		13 ± 6.0	86 ± 5.4	12
	Saltwater			0.13 ± 0.20	0.17 ± 0.23	4.2 ± 9.4	50 ± 17	45 ± 13	55

[a] Unknown As = Total As − 6 target arsenicals concentration; Unknown As (%) = (Unknown As/Total As) × 100.
[b] Identified As = Sum of the 6 target arsenicals concentration; Identified As (%) = (Identified As/Total As) × 100.
[c] Blank: below detection limits.

and Fig. 2). As speciation in zooplankton samples had similar trends to those of particulate As. However, greater proportions of unknown arsenicals were found in the SPM samples at both freshwater and saltwater sites. This might have been because of the large amounts of lipid-As in the SPM samples, which cannot be extracted completely, as described previously (Caumette et al., 2011). Inorganic As^{V} and As^{III} were detected mainly in zooplankton common to both freshwater and marine environments, whereas more varied organic forms of As (AB, MMA, and AC) were detected in marine zooplankton. Overall, the results of As speciation of SPM and zooplankton generally had similar patterns to those found in previous studies (Caumette et al., 2011, 2012; Hong et al., 2016), with less contributions from organic forms of As.

In sediments, inorganic As^{III} was the predominant form of As at both the freshwater and the saltwater sites, indicating that reduction of As^{V} to As^{III} under anoxic condition occurred (Chaillou et al., 2003; Langmuir et al., 1999). Organic forms of As such as AB and MMA were detected in estuarine sediments, while inorganic arsenicals were detected only in freshwater sediments. Information on As speciation in porewater samples from previous studies is very limited. The results of the present study indicate that organic forms of As such as MMA and DMA were detected in porewater but that the contributions to the total As were very small. Overall, organic arsenicals contributed less to the total As in the sediments and porewater at the freshwater sites than at the saltwater sites of the Youngsan River Estuary.

3.3. Water–particle partitioning behavior of arsenicals

As described above, distributions of As showed that relatively greater concentrations of dissolved As and smaller concentrations of particulate As were found at the outer estuarine sites. While, smaller concentrations of dissolved As and greater concentrations of particulate As were found at the inner freshwater sites (Fig. 3a). In the Youngsan River Estuary, potential sources of anthropogenic pollutants, such as the industrial complexes and urban areas of the Mokpo City, are located mainly along the outer region (Hong et al., 2013). However, it is unclear whether elevated concentrations of dissolved As in the outer region originate from inland creeks of the outer region or freshwater discharge via the estuary dike. One possible explanation is that particulate As appears to originate from freshwater and it is dissolved into the water column in the estuarine area because of the increased salinity levels. A previous study has suggested that increasing salinity within the water column might alter the sorption characteristics of As in an estuarine system (Chakraborty et al., 2012). Greater concentrations of salt in water result in less adsorption of As into the SPM and sediments because of the formation of weak As complexes.

We calculated the field-based distribution coefficient (K_d) of As between water and SPM in freshwater and saltwater, which reflects short- and long-term reactions such as sorption and precipitation, in the aquatic environment (Balzer et al., 2013; Turner and Millward, 2002). The log K_d values of As in freshwater obtained from this study ranged from 3.88 to 4.10 L kg^{-1} with a mean value of 3.97 L kg^{-1} (Table 2, Fig. 3b, and Table S6). The log K_d values in saltwater ranged from 2.87 to 3.22 L kg^{-1} (mean = 3.04 L kg^{-1}). The K_d values of As were significantly greater in freshwater than in saltwater. Concentrations of As in water tended to increase with increasing salinity, while concentrations of As in SPM showed a decreasing trend (Fig. S1). The log K_d values of As were strongly correlated with salinity, i.e., significantly decreased with increasing salinity ($p < 0.01$). This result indicates that when freshwater discharge to the outer estuarine area occurs, elevated salinity can play an important role in controlling the sorption of As on SPM. Particulate As could be desorbed into the aqueous phase under the elevated salinity conditions within the estuarine area.

Field-based K_d values of As between water and SPM in freshwater and brackish water have been found to vary among regions (Table 2). Several previous studies suggested that the major factors controlling the K_d value of As are i) salinity (Balzer et al., 2013; Wang et al., 2016), ii) SPM concentrations (dos Anjos et al., 2012; Faye and Diamond, 1996; Hong et al., 2016; Masson et al., 2009; Yang et al., 2016; Zhang et al., 2009), iii) seasonally varying SPM compositions (Michel et al., 1999), iv) particulate Fe concentrations (Kitts et al., 1994), and v) biological activities (Michel et al., 1993). Adsorptions of As were known to increase with increasing salinity, decreasing SPM concentrations, and increasing particulate iron concentrations. In particular, the K_d values of As generally show a decreasing trend with increasing SPM concentrations, which is called the "particle concentration effect" (Balzer et al., 2013; Benoit et al., 1994; Hong et al., 2016; Wang et al., 2016). However, in the present study, the "particle concentration effect" was not observed. This is one reason why the SPM concentrations in the Youngsan River Estuary were one–two orders of magnitude lower (32–52 mg L^{-1} for freshwater and 12–16 mg L^{-1} for saltwater, Table S1) in comparison with previous studies (Masson et al., 2009; Yang et al., 2016; Zhang et al., 2009) (Table 2). In addition, although the greater concentrations of SPM were found in freshwater areas, the greater K_d values of As were found in inner regions than those in outer saltwater areas.

Concentrations of As in SPM were found comparable with those of sediments, indicating that sedimentary As was dependent on deposition of particulate As. Forms of As in SPM appeared to be changed into reduced forms of As, such as As^{III}, under suboxic and

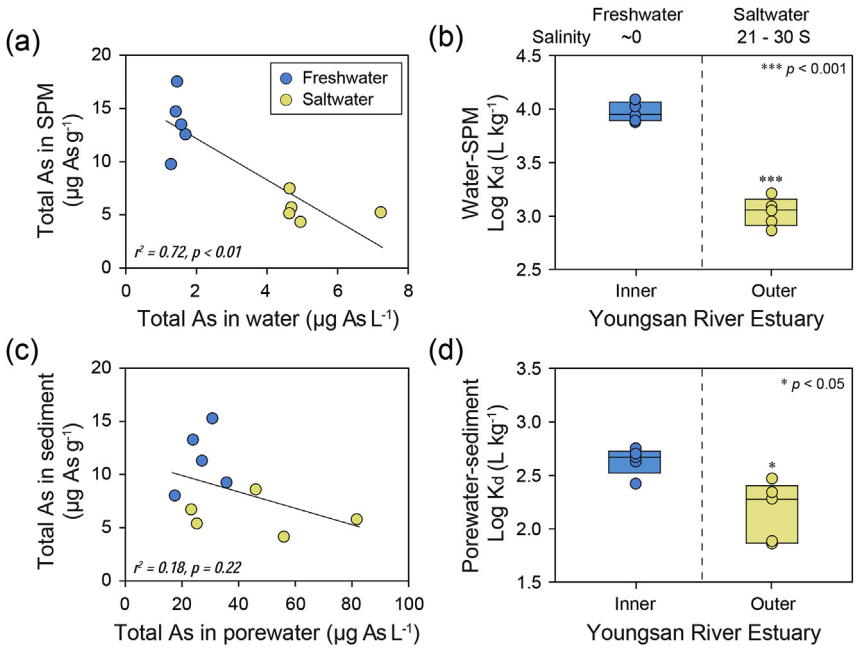

Fig. 3. (a) Scatter plot of concentrations of As in water and SPM, (b) box plot of water–particle distribution coefficient (K_d) of inner (S ~0) and outer regions (S 21–30), (c) scatter plot of concentrations of As in porewater and sediments, and (d) box plot of porewater–sediment distribution coefficient (K_d) of inner and outer regions of the Youngsan River Estuary, Korea. Solid lines represent the linear regression fits (Pearson correlation coefficients and p values are shown). Comparisons between two groups (freshwater vs. saltwater) were determined by the Welch-Aspin test.

anoxic conditions in the sediments. The log K_d values of As between sediments and porewater ranged from 2.42 to 2.75 L kg^{-1} (mean = 2.63 L kg^{-1}) and from 1.86 to 2.47 L kg^{-1} (mean = 2.17 L kg^{-1}) in freshwater and saltwater, respectively (Fig. 3c and d). Sorption characteristics of As between porewater and sediments were similar to the water-SPM partitioning of As that might be due to the salinity effect. Previous studies have reported that As is precipitated with hydrous iron oxides and sulfide to sediments (Fauser et al., 2013; Mandal and Suzuki, 2002). Thus, As mobility increases as the dissolved phase (water and porewater) with increasing salinity of the water column in an estuarine area. Overall, the K_d of As is a crucial factor for predictions of fate, migration ability, and potential risk in estuarine areas (Wang et al., 2016), and it seems to be controlled primarily by salinity in an artificially closed estuary, such as the Youngsan River Estuary. More studies on other potential factors affecting adsorption of As in estuary are needed in the future to fully address biogeochemistry of arsenicals, particularly in the artificially closed estuary system.

3.4. Bioaccumulation of arsenicals in zooplankton

Concentrations of As in freshwater zooplankton were greater than in marine zooplankton species (Fig. 4a). The relationship between As concentrations in zooplankton and in water samples revealed no positive correlation, suggesting that As in zooplankton is affected less by waterborne As exposure. The BAF values

Table 2
Field-based water–particle distribution coefficients of As and its major controlling factors obtained from this study and previously reported data (updated from Hong et al. (2016)).

Regions (Country)	Sample size (n)	SPM (mg L^{-1})	Salinity (psu)	Log K_d values (L kg^{-1}) (min. – max. (mean))	Major controlling factors[a]	References
East-Hainan Estuaries (China)	32	5.3 ± 4.4	ns[b]	4.48–4.81	Salinity	Balzer et al. (2013)
	7	6.1 ± 4.6	~32	4.18		
English Channel (North Sea)	168	ns	ns	4.14	Plankton metabolization	Michel et al. (1993)
Freshwater Lakes (China)	125	1.0–110	ns	4.63–5.20	SPM concentration	Yang et al. (2016)
Gironde Estuary (France)	96	1.0–460	~0	3.70–4.04	SPM concentration	Masson et al. (2009)
Huanghe River Estuary (China)	22	329 ± 56.5	0–29	2.80–4.70	Salinity and SPM concentration	Wang et al. (2016)
Humber Estuary (England)	16	2–80	20–32	3.77–4.97 (4.45)	Particulate Fe concentration	Kitts et al. (1994)
Humber Plume (England)	10	0.6–10	32–35	3.30–4.40 (4.13)	–	Millward et al. (1997)
Moira Lake (Canada)	8	~1 - ~ 8	ns	4.2–4.9	SPM concentration	Faye and Diamond (1996)
Paranaguá Estuary (Brazil)	9	12–62	14–31	3.36–4.26	SPM concentration	dos Anjos et al. (2012)
Scheldt Estuary (Belgium)	11	ns	ns	3.90–4.18	–	De Gieter et al. (2005)
Seine Estuary (France)	34	33 ± 26	0.2–35	3.74–3.99 (3.84)	SPM composition	Michel et al. (1999)
Taehwa River Estuary (Korea)	12	65 ± 92	~0	2.38–3.89 (3.40)	SPM concentration	Hong et al. (2016)
	8	32 ± 7.1	2.9–35	3.12–3.68 (3.42)		
Yata creek and Zhelou River (China)	19	1.3–4220	ns	2.85–6.55 (4.50)	SPM concentration	Zhang et al. (2009)
Youngsan River Estuary (Korea)	5	32–52	0.12–0.16	3.88–4.10 (3.97)	Salinity	This study
	5	12–16	21–30	2.87–3.22 (3.04)		

[a] Major factors controlling partitioning between water and SPM described in the literature.
[b] ns: data not shown.

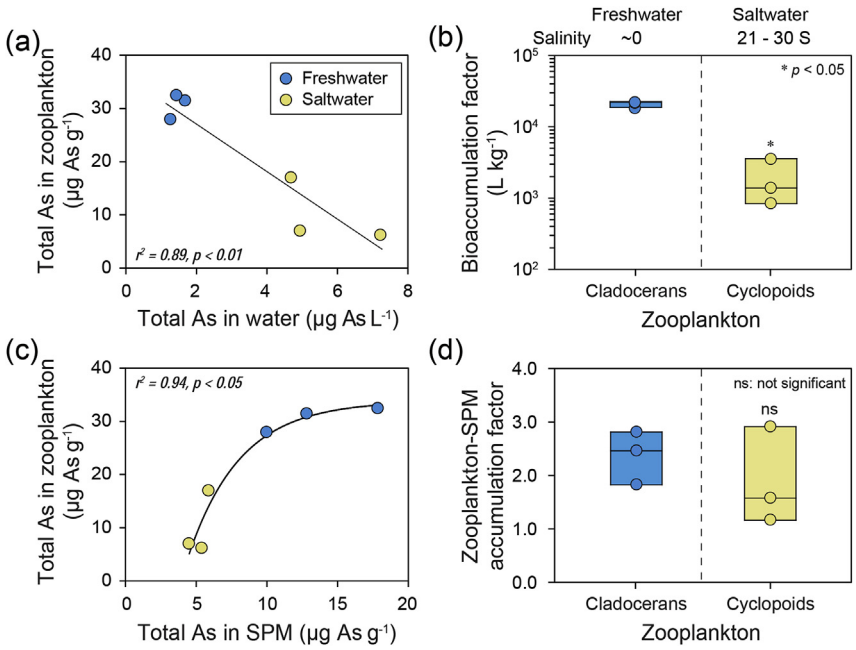

Fig. 4. (a) Scatter plot of concentrations of As in water and zooplankton, (b) box plot of BAF values of inner (S ~0, cladocerans) and outer regions (S 21–30, cyclopoids), (c) scatter plot of concentrations of As in SPM and zooplankton, and (d) box plot of BSAF values of inner and outer regions of the Youngsan River Estuary, Korea. Solid lines represent the linear or exponential regression fits (Pearson correlation coefficients and *p* values are shown). Comparisons between two groups (freshwater vs. saltwater) were determined by the Welch-Aspin test.

calculated based on waterborne As concentrations were about one order of magnitude greater in freshwater zooplankton than in marine zooplankton (Fig. 4b).

Scatter plots of As concentrations in zooplankton as a function of those in SPM showed a linear or exponential regression fit (Fig. 4c). In other words, concentrations of As in zooplankton showed an increasing trend with increasing concentrations of particulate As. BSAF values of As were found to be slightly greater in freshwater organisms than those in marine organisms, but the difference was not significant (Fig. 4d). The results revealed that bioaccumulation potentials of As did not greatly varied between freshwater and marine zooplankton species, say in common pathway of dietary exposure, but relative contribution of surrounding sources to its bioaccumulation slightly varied between them. The values obtained from site E1 (inside the estuary) were comparable with those of freshwater zooplankton because of the freshwater and seawater mixing effects (freshwater zooplankton found in a sample from site E1 under the microscope, data not shown). Overall, As bioaccumulations in freshwater and marine zooplankton was strongly dependent on the concentrations of particulate As, suggesting that dietary exposure plays a substantial role in As bioaccumulation.

Results of As speciation in zooplankton indicated that As^{V}, As^{III}, and MMA were detected mainly in freshwater zooplankton, while more diverse forms of As, including As^{V}, As^{III}, AB, MMA, and AC, were detected in marine zooplankton (Table 1). AB is known to be a biotransformation product which comes from degradation of arsenosugar in zooplankton (Azizur Rahman et al., 2012). AB might accumulate in marine zooplankton via dietary exposure through consumption of phytoplankton (or SPM). AB is well known for acting as a cellular osmolyte because of its structural similarity to glycine betaine during seawater adaptation (Amlund and Berntssen, 2004; Caumette et al., 2011; Whaley-Martin et al., 2012). Previous studies suggested that arsenicals do not biomagnify along the food chain (Azizur Rahman et al., 2012); however, the results of the present study indicate that concentrations of As in zooplankton were greater than those of As in SPM. In the present study, accumulations of As in phytoplankton and higher trophic level organisms could not be observed. Thus, further complementary studies on trophic transfer and biotransformation of As in freshwater and marine food-chains are needed.

Elevated concentrations of As in zooplankton were directly affected by the elevated particulate As in freshwater, which could reflect arsenicals transferred to higher trophic level organisms. However, in the estuarine area, relatively great concentrations of dissolved As (mostly inorganic As^{V}) could be uptaken by marine macroalgae and phytoplankton (e.g., through phosphate uptake systems) (Hellweger et al., 2003). In fact, many previous studies have considered the great concentrations of arsenicals detected in marine macroalgae (mainly non-toxic arsenosugars) (García-Salgado et al., 2012; Hong et al., 2016). Thus, salinity in water and thereby adsorption of As in SPM are crucial factors that affect As biogeochemistry in freshwater and estuarine areas. In a natural estuary, these processes occur gradually from upstream to downstream areas according to the salinity gradient. However, in an artificially closed estuary, such as the Youngsan River Estuary, the freshwater and estuarine ecosystems have completely distinguishable As biogeochemistry because of boundary of the estuary dike (summarized in Fig. 5). When freshwater discharge occurs, according to the amount of rainfall, the As biogeochemistry of the estuarine area could be changed drastically.

4. Conclusions

This is the first study on multimedia distributions of arsenicals that compares freshwater and marine ecosystems. In the present study, several findings on multimedia distributions, adsorption characteristics, and bioaccumulations of arsenicals in the freshwater and saltwater environments of the Youngsan River Estuary were obtained:

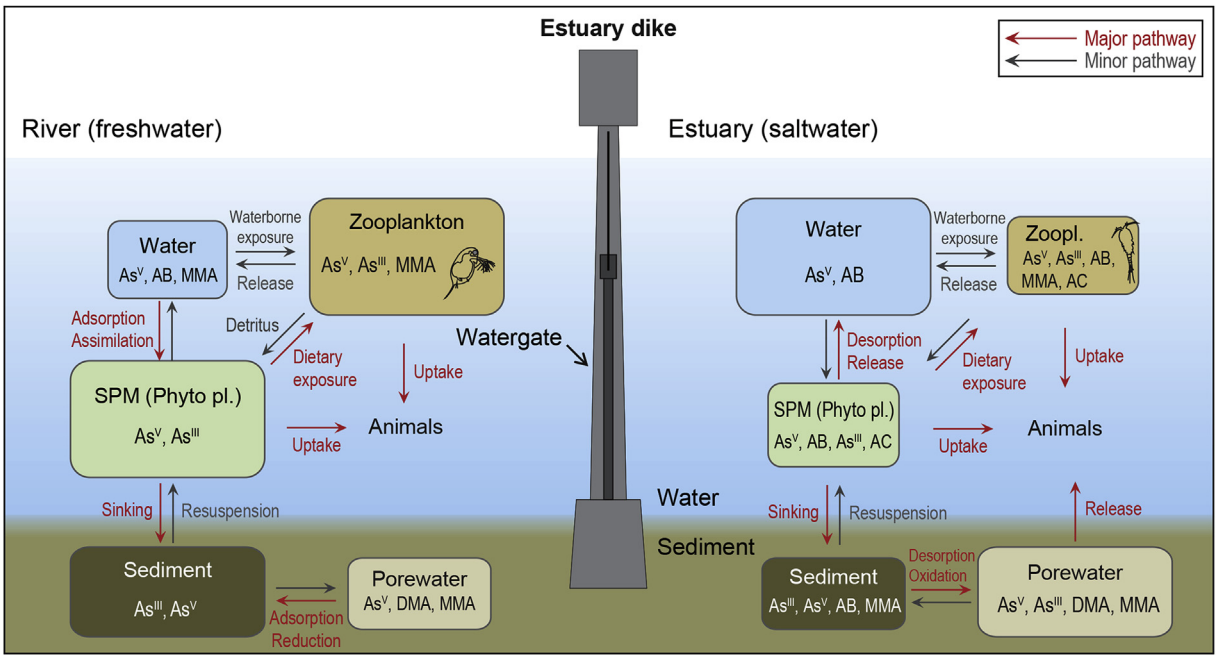

Fig. 5. Biogeochemical cycles of arsenicals in freshwater and saltwater systems. Red and gray arrows indicate major and minor pathways, respectively (relatively and qualitatively). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

- Great concentrations of particulate As were found in the freshwater, while great concentrations of dissolved As were found in the estuarine area.
- Among the six forms of arsenicals, As^{V} was a major form within the oxic water column, while As^{III} was the predominant in the sediments of both freshwater and saltwater sites.
- Field-based K_d values were significantly greater in the freshwater area than in saltwater area because sorption characteristics change as a function of salinity.
- Greater As concentrations found in the freshwater zooplankton compared with those in marine zooplankton, which showed a particle-concentration dependent accumulation, suggesting that dietary exposure is a major pathway.

Overall, the results of the present study enhance the understanding of the biogeochemistry of arsenicals in freshwater and estuarine environments and can be used as baseline information for developing transport and fate models of arsenicals.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2017.11.020.

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<Supplementary Material>

Arsenic speciation in environmental multimedia samples from the Youngsan River Estuary, Korea: A comparison between freshwater and saltwater

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Supplementary Tables

Supplementary Figure

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Table S1. Water quality parameters including temperature, salinity, dissolved oxygen, pH, and suspended particulate matter in surface and bottom water from the Youngsan River Estuary.

Regions	Sites	Depth	(m)	Temperature (˚C)	Salinity (S)	DO (mg L^{-1})	pH	SPM (mg L^{-1})
Freshwater	R1	Surface	0	14.25	0.12	8.80	8.14	50.0
		Bottom	3	13.65	0.13	8.89	7.97	
	R2	Surface	0	16.26	0.12	8.00	8.01	31.6
		Bottom	6	14.55	0.13	7.54	7.85	
	R3	Surface	0	15.92	0.12	7.25	7.99	40.8
		Bottom	15	15.05	0.12	7.49	7.52	
	R4	Surface	0	15.90	0.12	7.74	7.95	52.4
		Bottom	3	15.71	0.12	7.59	7.79	
	R5	Surface	0	15.96	0.16	11.00	7.98	44.4
		Bottom	9	15.64	0.16	8.51	7.77	
Saltwater	E1	Surface	0	17.22	20.65	7.83	7.79	12.4
		Bottom	6	17.72	29.03	6.72	8.24	
	E2	Surface	0	15.06	23.00	9.00	8.39	13.3
		Bottom	11	17.46	29.50	7.01	8.30	
	E3	Surface	0	16.34	23.80	8.25	8.22	13.1
		Bottom	16	16.64	29.41	7.58	8.31	
	E4	Surface	0	16.34	24.85	9.30	8.10	13.8
		Bottom	15	16.11	29.47	7.89	8.31	
	E5	Surface	0	16.25	29.85	8.10	7.96	16.3
		Bottom	11	16.23	30.08	7.91	8.22	

Blank: not analyzed.

Table S2. Instrumental conditions of HPLC-ICP/MS for total As and arsenic speciation analyses.

HPLC system	PerkinElmer 200
Column	Hamilton PRP X-100 (25 cm × 4.1 mm, 10 μm), Anion exchange column
Separation scheme	Gradient: A 100% (0-3 min) → B 100% (3-15 min) → A 100% (15-18 min)
Mobile phase A	4 mM NH_4NO_3
Mobile phase B	40 mM NH_4NO_3 (pH 9.5)
pH adjustment	NH_4OH
Flow rate	1.5 mL min^{-1}
Injection volume	20 μL
ICP/MS system	**ELAN DRC II**
Nebulizer	Quartz concentric
Spray chamber	Quartz cyclonic
Plasma flow	16.5 mL min^{-1}
Nebulizer gas flow	1.02 L min^{-1}
RF power	1200 W for total As; 1500 W for As speciation analysis
Lens voltage	6.5 V
Analytes	AsO (m/z = 91)
Reaction gas	O_2 = 0.6 mL min^{-1}
RPq	0.5
Dwell time	250 ms

Table S3. Method detection limits for arsenic speciation analysis of the environmental multimedia samples.

Arsenicals	Method detection limits				
	Water ($\mu g\ L^{-1}$)	SPM ($\mu g\ g^{-1}$)	Porewater ($\mu g\ L^{-1}$)	Sediment ($\mu g\ g^{-1}$)	Biota ($\mu g\ g^{-1}$)
AC	0.1	0.01	0.1	0.002	0.01
AB	0.05	0.005	0.05	0.001	0.005
MMA	0.05	0.005	0.05	0.001	0.005
DMA	0.05	0.005	0.05	0.001	0.005
As^{III}	0.1	0.01	0.1	0.002	0.01
As^{V}	0.05	0.005	0.05	0.001	0.005

Table S4. HPLC-ICP/MS peak areas of known and unknown arsenicals in the SPM, zooplankton, and sediment samples collected from the Youngsan River Estuary.

Samples and sites			HPLC RT	AC 1.163	AB 1.517	Unknown 1 1.703	As^{III} 2.113	DMA 6.227	Unknown 2 6.771	MMA 7.105	As^{V} 10.278
SPM	Inner	R1				1618	1397				20458
		R2					1122				11630
		R3				826	2529				19628
		R4				225	789				9598
		R5					1178				10505
	Outer	E1			389	233	426				4422
		E2		430	2342		732				5683
		E3			1134		573				4862
		E4			1172						6339
		E5			1597		502				7225
Zooplankton	Inner	R1				1899	15003			3425	18086
		R3				2015	14615			523	11901
		R5				584	9634				10478
	Outer	E1			1102	2022	1138			737	8393
		E3			532	708	1696				4920
		E5		433	4715	4165	884			573	6875
Sediment	Inner	R1					51618				4604
		R2				429	70351				3959
		R3				236	24272				3444
		R4					39604				2892
		R5					48653				4738
	Outer	E1			831	1201	8395				4412
		E2			2579		30380				2843
		E3			2163	1487	8150				2326
		E4			3024	1025	6008		2056	707	4673
		E5			2969	526	19816		661	483	4188

Unknown 1 and 2 peaks seemed to be glycerol sugar and phosphate sugar, respectively according to the previous study (Caumette et al., 2011).

Caumette, G., Koch, I., Estrada, E., Reimer, K.J., 2011. Arsenic Speciation in Plankton Organisms from Contaminated Lakes: Transformations at the Base of the Freshwater Food Chain. Environ. Sci. Technol. 45, 9917-9923.

Table S5. Concentrations of total As and six forms of As in water, SPM, zooplankton, sediments, and porewater collected from the Youngsan River Estuary.

Samples and sites			Arsenicals AC	AB	MMA	DMA	As^{III}	As^{V}	Unk As[a]	sum As	Total As	% identify
Water	Inner	R1		0.096	0.188			0.87	0.52	1.2	1.7	69
(μg As L^{-1})		R2		0.081				0.67	0.80	0.75	1.6	48
		R3		0.10				0.87	0.28	0.97	1.3	77
		R4		0.12				0.62	0.65	0.74	1.4	53
		R5		0.057				1.1	0.25	1.2	1.4	82
	Outer	E1						1.6	3.1	1.6	4.7	33
		E2		0.050				2.0	2.5	2.1	4.6	45
		E3						3.4	1.5	3.4	4.9	69
		E4						1.1	3.5	1.1	4.6	24
		E5						0.45	6.8	0.45	7.2	6.2
SPM	Inner	R1					0.082	1.9	11	1.9	13	15
(μg As g^{-1})		R2					0.14	2.0	12	2.2	14	16
		R3					0.22	2.8	6.9	3.0	10	31
		R4					0.064	0.98	14	1.0	15	7.0
		R5					0.10	1.3	16	1.4	18	7.8
	Outer	E1		0.046			0.097	0.81	4.9	0.95	5.9	16
		E2	0.074	0.33			0.14	1.2	6.0	1.7	7.7	22
		E3		0.14			0.11	0.83	3.4	1.1	4.5	24
		E4		0.14				1.16	4.0	1.3	5.3	24
		E5		0.16			0.080	1.2	3.9	1.4	5.4	27
Zooplankton	Inner	R1			0.88		7.8	14	8.6	23	32	73
(> 100 μm)		R3			0.23		9.5	11	7.5	21	28	73
(μg As g^{-1})		R5					9.3	13	10	23	33	69
	Outer	E1		0.47	0.38		1.7	8.5	6.0	11	17	65
		E3		0.23			1.7	2.7	2.4	4.6	7.1	66
		E5	0.15	0.70	0.14		0.64	2.7	1.9	4.4	6.3	70
Sediment	Inner	R1					5.5	0.40	5.5	5.9	11	52
(μg As g^{-1})		R2					4.9	0.19	8.2	5.1	13	38
		R3					7.0	0.47	1.8	7.5	9.3	80
		R4					5.8	0.044	2.2	5.9	8.1	72
		R5					10.2	0.43	4.7	11	15	69
	Outer	E1		0.051			0.97	0.36	7.3	1.4	8.7	16
		E2		0.064			1.6	0.029	4.1	1.7	5.9	30

		E3	0.20			1.8		2.3	2.0	4.2	47
		E4	0.11	0.038		0.57	0.33	5.7	1.0	6.8	15
		E5	0.092	0.024		1.4	0.21	3.8	1.7	5.5	31
Porewater	Inner	R1					2.1	25	2.2	27	8.0
(μg As L^{-1})		R2		0.22	0.30		1.9	21	2.4	24	10
		R3		0.43	0.65		3.5	31	4.6	35	13
		R4					3.8	14	3.8	17	22
		R5		0.096	0.17		4.7	26	5.0	31	5.4
	Outer	E1		0.096	0.21		27	18	28	46	60
		E2		0.37	0.32	17	23	40	41	81	51
		E3					23	32	23	56	42
		E4					17	6.0	17	23	74
		E5					11	14	12	25	46

[a] Unknown As = Total As – Identified As.
Blank: < MDL.

Table S6. Multimedia distribution coefficients and bioaccumulation factors of As obtained from this study.

Regions and sites		Water-SPM distribution coefficient Log K_d (L kg^{-1})	Porewater-sediment distribution coefficient Log K_d (L kg^{-1})	Bioaccumulation factor (Log BAF)	Zooplankton-SPM accumulation factor (BSAF)
Inner	R1	3.88	2.63	4.28	2.46
	R2	3.95	2.75		
	R3	3.90	2.42	4.35	2.81
	R4	4.03	2.67		
	R5	4.10	2.70	4.36	1.82
Outer	E1	3.10	2.28	3.56	2.91
	E2	3.22	1.86		
	E3	2.96	1.88	3.15	1.58
	E4	3.06	2.47		
	E5	2.87	2.34	2.94	1.16

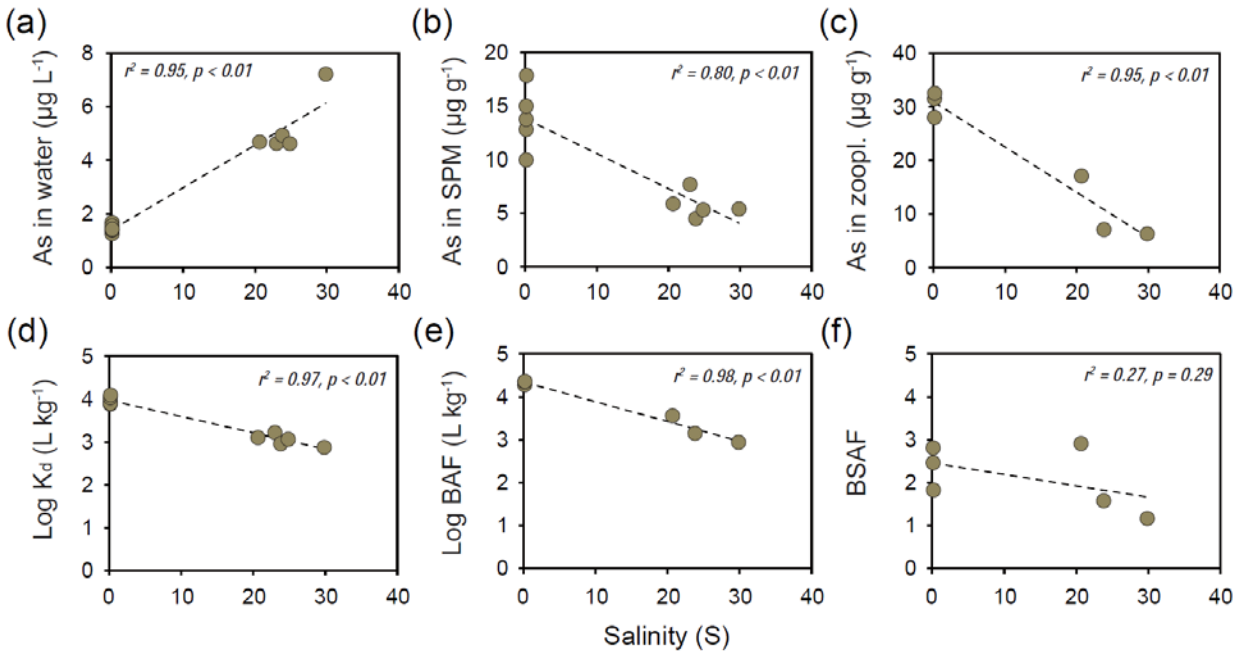

Fig. S1. Relationships between salinity in water and (a) dissolved As, (b) particulate As, (c) As in zooplanktons, (d) log K_d values, (e) log BAF values, and (f) BSAF values. Dashed lines represent linear regressions.