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Arsenic speciation in water, suspended particles, and coastal organisms from the Taehwa River Estuary of South Korea

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ABSTRACT

Water, suspended particulate matter (SPM), and biota samples were collected from the Taehwa River Estuary to determine the distributions, partitioning, and bioaccumulation of arsenicals. Six forms of As were quantitated by the use of HPLC-ICP/MS. As was found mainly near urban and industrial areas, and inorganic As^V was the predominant As form in both water and SPM. Particulate arsenicals were found at the greatest concentrations in coarse particles (>180 μm), followed by medium (30–180 μm) and fine (0.45–30 μm) particles, in freshwater. Arsenical concentrations were similar across the three particle fractions in saltwater. Field-based distribution coefficient (K_d) values for As depended strongly on SPM, with a less robust dependence on salinity. Concentrations of As were greater in macroalgae than in marine animals, such as fishes, bivalves, crabs, shrimps, and gastropods. Overall, the results of the present study provide useful information on the behaviors and fate of arsenicals in an estuarine environment.

1. Introduction

Arsenic (As) is a ubiquitous element with metalloid properties that is widely distributed in the aquatic environment as a result of natural processes and anthropogenic activities (Anderson and Bruland, 1991; Azizur Rahman et al., 2012; Cullen and Reimer, 1989). In particular, anthropogenic activities including mining, smelting, coal combustion, fossil-fuel refinement, use of biocides such as wood preservatives and pesticides, and waste incineration are considered to be major As sources (Cullen and Reimer, 1989). As is introduced into the marine environment primarily through river run-off (Balzer et al., 2013; De Gieter et al., 2005; Kitts et al., 1994). The transport, fate, and biological effects (e.g., toxicity, bioaccumulation, and bioavailability) of As depend strongly on its form (Anderson and Bruland, 1991; Azizur Rahman et al., 2012; Waslenchuk and Windom, 1978).

Inorganic As forms, such as pentavalent arsenate (As^V) and trivalent arsenite (As^{III}), are more mobile and toxic than organic arsenicals, with As^V being the most stable form in an oxic water column (Azizur Rahman et al., 2012). Several factors determine the form in which As occurs in an aquatic environment, including redox conditions (Cullen and Reimer, 1989), salinity (Kitts et al., 1994), turbidity (Sánchez-Rodas et al., 2005), microbial activity (Cullen and Reimer, 1989; Oremland and Stolz, 2003), and the characters of local phytoplankton and zooplankton communities (Caumette et al., 2011, 2012b). Organic forms of As, such as monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA), appear to be produced through biomethylation processes by aquatic microorganisms, such as phytoplankton and zooplankton, to mitigate As pollution stress (Caumette et al., 2014; Franco et al., 2015; Sharma and Sohn, 2009). Dissolved organic arsenicals released from organisms into the water column can be degraded rapidly into inorganic forms (Anderson and Bruland, 1991; Azizur Rahman et al., 2012).

In aquatic environment, As can be adsorbed onto suspended particulate matter (SPM) from aqueous dissolved phase, precipitated, and deposited to sediments as a result of changes in physical, chemical, and biological factors (Yang et al., 2015). The distribution coefficient (K_d) of As between water and SPM has been reported to depend on concentrations and compositions of SPM (e.g., Fe and Mn oxides), salinity, pH, redox condition as well as biological effects (Balzer et al., 2013; Benoit et al., 1994; Turner and Millward, 2002). The K_d values of As are of fundamental significance to geochemical modeling and pollution impact assessment, and are known to be crucial for elucidating the transport and biological effects of estuarine As (Turner, 1996; Turner and Millward, 2002). The fate and behavior of As in estuarine areas fluctuate in response to dynamics of environmental parameters, thus elucidating them should be important for establishing a better understanding of land–ocean interactions and regional to global transport pathways. Although previous studies have examined the partitioning of As in

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estuarine areas around the world (Balzer et al., 2013; Kitts et al., 1994; Michel et al., 1993, 1999; Millward et al., 1997), the environmental factors that control As partitioning are still poorly understood (dos Anjos et al., 2012).

Meanwhile, macroalgae and marine animals such as fishes, bivalves, crabs, shrimps, and gastropods can be exposed to As through waterborne (mostly inorganic forms) and dietary (both inorganic and organic forms) routes and then biotransform and/or retain it in their bodies (Azizur Rahman et al., 2012; Choi et al., 2015; Hong et al., 2014). Uptake, transformation, and excretion of As by aquatic organisms may differ between freshwater and marine organisms. However, the process is not well understood and more field monitoring data are necessary to improve our current understanding for fate of As in estuarine environments.

The Taehwa River runs through Ulsan City, South Korea and reaches the Ulsan Bay of the East Sea. Ulsan Bay is in a highly industrialized region and considered to be one of the most contaminated coastal areas in Korea (Khim and Hong, 2014). Major petrochemical industrial complex development has occurred in Ulsan City since the 1970s, resulting in a deterioration of the Ulsan Bay environment, and various toxic substances, including organic chemicals and heavy metals have been detected widely in water, sediments, and biota (Khim et al., 2001a, 2001b; Koh et al., 2001; Kwon and Choi, 2014; Ra et al., 2014). In 2000, Ulsan Bay was designated as a special management coastal zone (SMCZ) by the South Korean government. Although the water quality of the Taehwa River has been improving in recent years, serious concerns remain regarding the river's sources, occurrences, and bioaccumulation of toxic substances.

In the present study, we investigated the behavior and fate of As in an estuarine system to determine: i) sources and distributions of arsenicals in water and SPM; ii) particle-size distributions of arsenicals in SPM in freshwater and saltwater; iii) field-based distribution coefficients of As in water versus particles; and iv) bioaccumulation features of arsenicals in various marine organisms.

2. Materials and methods

2.1. In situ measurements, sampling, and sample preparation

Water and SPM were sampled and water quality measurements were conducted along the Taehwa River Estuary (~25 km long) from freshwater reaches to the estuarine area in May of 2012 (Fig. 1). Temperature, salinity, dissolved oxygen (DO), and pH were measured *in situ* with a calibrated multi-probe (YSI 556 MPS, Yellow Springs, OH). A total of 20 sites of the Taehwa River Estuary (labelled T1–T20, freshwater and saltwater), including freshwater lakes (T1, T5, and T7) and inland creeks (T15 and T17–T19), were selected as sampling points considering their surrounding anthropogenic pollution activities (details in Fig. S1 of the Supplementary materials (S)). Water samples were collected from suburban (T1–T7), urban (T8–T15), and industrial (T16–T20) areas. In a separate sampling campaign, biological samples of fish, bivalves, crabs, shrimp, gastropods, and macroalgae were collected in urban (B1 and B2) and industrial (B3 and B4) areas in June of 2010.

In the laboratory, water samples intended for As analysis were filtered sequentially through prewashed and preweighed 180- and 30-μm nylon net filters (Merck, Darmstadt, Germany) and a 0.45-μm filter

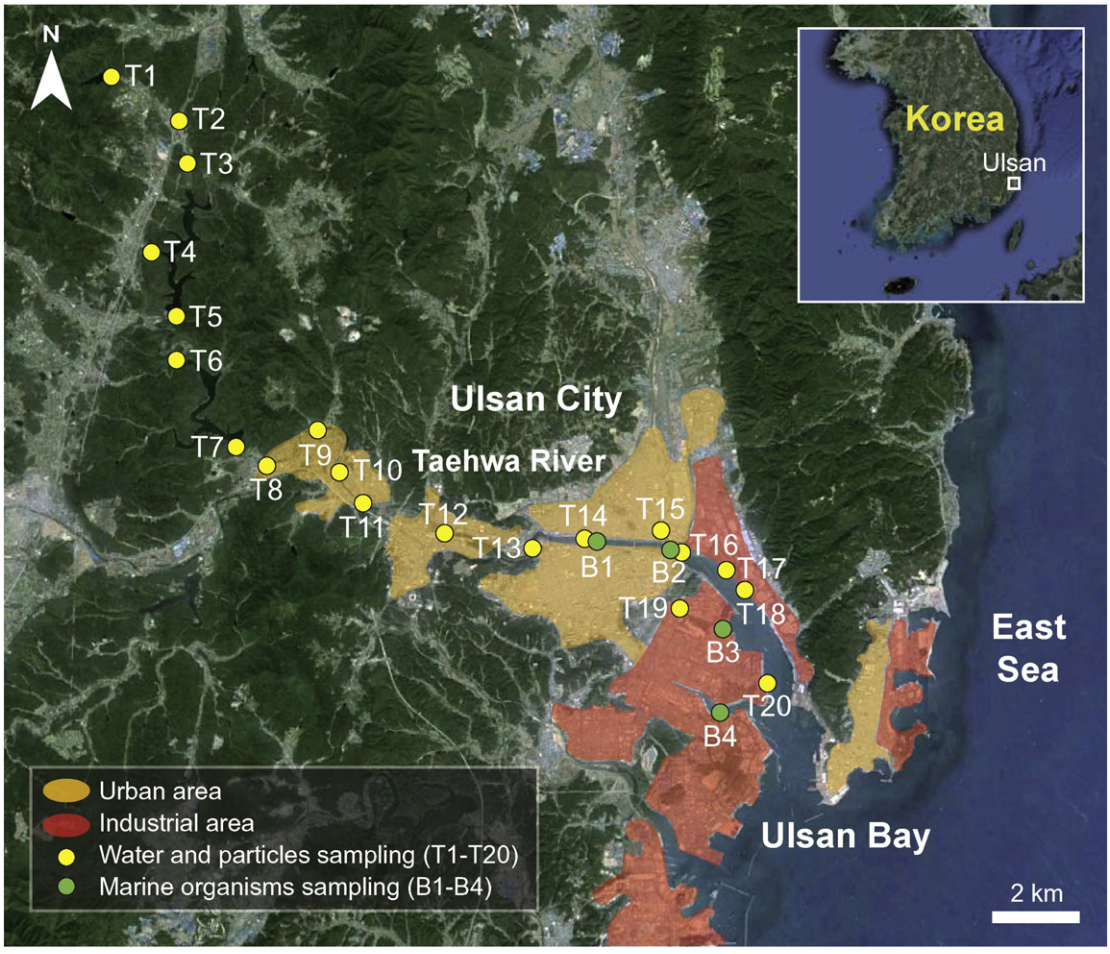

Fig. 1. Sampling sites along the Taehwa River Estuary in Ulsan, South Korea. Water and suspended particle samples were collected from suburban (T1–T7), urban (T7–T15), and industrial (T16–T20) areas. Biological samples were collected from urban (B1 and B2) and industrial (B3 and B4) areas.

(Nuclepore, Whatman, Maidstone, UK). Samples of SPM were divided into three size groups: coarse (>180 μm), medium (30–180 μm), and fine (0.45–30 μm). Concentrations of each SPM were determined by use of a balance after freeze-drying. Finally, dissolved fractions for analyses of total dissolved As and As speciation were collected (<0.45 μm). Samples for the determination of total dissolved As concentrations were acidified (pH < 2) with nitric acid (Ultrapur, Merck) and stored at 4 °C prior to analysis. Apart from the particle size fraction analysis of As, SPM was collected for total particulate As measurement with a 0.45-μm membrane filter. All filter samples were freeze-dried and stored at −20 °C prior to analysis. Biological samples were pooled, freeze-dried, and stored at −20 °C prior to analysis. Total organic carbon (TOC) was analyzed following high-temperature combustion in a TOC analyzer (Shimadzu TOC-VCPH, Shimadzu Co., Japan).

2.2. Total As analysis

Freeze-dried SPM (filter papers) and biota samples were digested with a mixture of concentrated nitric acid and hydrogen peroxide on a heating mantle (120 °C) for 4 h, then evaporated to near dryness and diluted in 1% HNO_3, as described previously (Hong et al., 2014). Unfortunately, total concentration of As in SPM was conducted only in total SPM and could not be determined separately for different size particles due to insufficient amounts of size-fractioned SPM samples. Total concentrations of As in water (dissolved phase), SPM, and biological samples were measured by the use of inductively coupled plasma-mass spectrometry (ICP/MS, Elan DRC II, PerkinElmer, Shelton, CT). Total As concentration was measured as AsO^+ at m/z 91 in dynamic reaction cell (DRC) mode with O_2 as the reaction cell gas (0.6 mL min^{-1}) in order to prevent interference by $ArCl^+$ (m/z 75). The plasma flow was 16.5 L min^{-1}, the nebulizer gas flow was 1.02 L min^{-1}, the RF power was 1200 W, the lens voltage was 6.5 V, and RF power was 1200 W. Total As determination accuracy was assessed in relation to the certified reference material (CRM) MESS-3 (marine sediment, National Research Council (NRC), Canada), and recovery in the range of 93 to 97% of the certified value of As was considered acceptable.

2.3. As speciation analysis

Forms of As in water, SPM, and biota were identified and quantified by previously described methods (Hong et al., 2014; Whaley-Martin et al., 2012a, 2012b) with some modifications. Water samples acidified with nitric acid (2%) were analyzed without any pretreatment. Freeze-dried SPM samples (0.45-, 30-, and 180-μm filters) or freeze-dried and homogenized biota samples (0.1–0.5 g) were transferred to 15-mL polypropylene centrifuge tubes, and extracted with 10 mL of 2% nitric acid solution. Samples were sonicated for 30 min and placed on a water bath shaker for 4 h (60 °C, 120 rpm), then centrifuged for 15 min at 1000 ×g. Supernatants were filtered through 0.22-μm membrane filters (13 mm, MCE filter, Jet Biofil, Guangzhou, China) and kept frozen until they were subjected to instrumental analysis.

Six forms of organic and inorganic As, including arsenocholine (AC, $C_5H_{14}AsO^+$), arsenobetaine (AB, $C_5H_{11}AsO_2$), MMA (CH_5AsO_3), DMA ($C_2H_7AsO_2$), As^{III}, and As^{V}, were separated and quantified by HPLC-ICP/MS (PerkinElmer Series 200 HPLC and ELAN DRC II ICP/MS System) with a Hamilton PRP-X100 anion exchange column (250 mm × 4.1 mm, 10 μm particle, Reno, NV) (Table S1). Detailed instrument conditions for HPLC-ICP/MS are given in Table S2. Mobile phases were (A) 4 mM ammonium nitrate (99.999% purity, 256064 Sigma-Aldrich, Saint Louis, MI) and (B) 40 mM ammonium nitrate in deionized water adjusted to pH 9.5. Our pretest results indicated that ammonium nitrate was the most suitable mobile phase to minimize the effects of background signal drift for As speciation analysis using the HPLC-ICP/MS compared to other mobile phases such as ammonium phosphate (>99.99% purity, 379980 Sigma-Aldrich) and ammonium carbonate (ACS reagent, 09716 Fluka, Buchs, Switzerland) (data not shown). The injection volume was 20 μL with a flow rate of 1.5 mL min^{-1} and the mobile phase sequence was: 100% A 0–3 min; 100% B 3–15 min; 100% A 15–18 min. Chromera Chromatography Data System (Ver. 2.1, PerkinElmer) was used for HPLC-ICP/MS analysis. Of note, determined by the previous studies, the degradation or interconversion of arsenicals did not significantly occur during experiments when applied by 2% nitric acid solution (Caumette et al., 2011; Hong et al., 2014; Whaley-Martin et al., 2012a).

2.4. Quality assurance and quality control

A mid-concentration calibration standard, procedural blank, and instrumental blank were analyzed after every 10 samples to check for instrumental sensitivity drift and background contamination and/or carryover. Calibration standards of 0.5, 1, 5, 10, 50, 100, and 500 ng g^{-1} of six forms of As were used ($R^2 > 0.998$ for all arsenicals). The method detection limits (MDLs) for the six arsenicals were calculated as: 3.707 × SD (standard deviation, n = 7) for a one-sided 99.5% confidence interval. The MDLs for arsenicals ranged from 0.05 to 0.1 μg L^{-1} for water, from 0.005 to 0.01 μg g^{-1} dw for SPM, and from 0.001 to 0.002 μg g^{-1} dw for biota (Table S3). Accuracy for As speciation was assessed with two CRMs, DORM-3 (fish protein, NRC) and TORT-2 (lobster hepatopancreas, NRC) (Table S1). The results of CRM analysis were consistent with previously reported values (Leufroy et al., 2011; Wahlen et al., 2004). Concentrations in all procedural and instrumental blanks were found to be less than their corresponding MDLs.

2.5. Data analysis

Total concentration of As in water was calculated as the sum of the dissolved As and particulate As concentrations as determined by ICP/MS. The percentage of identified arsenicals (same as extraction efficiency) in water, SPM, and biota was calculated by subtracting the sum of the six arsenicals determined by HPLC-ICP/MS from the total As concentration determined by ICP/MS (Table 1). The field-based partition coefficient (K_d in L kg^{-1}) of As between dissolved phase in water and particle phase was calculated (Eq. (1)).

$$K_d = C_{SPM}/C_W \quad (1)$$

where: C_{SPM} is the concentration of As in SPM (ng kg^{-1} dw) and C_W is the concentration of dissolved As in water (ng L^{-1}).

3. Results and discussion

3.1. Environmental condition

Water quality parameters such as temperature, salinity, DO, pH, SPM, and TOC in water at sites along the Taehwa River Estuary are shown in Table S4. The temperature, salinity, DO, pH, and SPM ranges were 12.5–23.2 °C, ~0–35 S, 5.6–12 mg L^{-1}, 7.3–9.5, and 7.9–330 mg L^{-1}, respectively. The relatively great value of pH 9.48 found at the site T7 (freshwater lake) seemed to be due to excessive primary production by cyanobacteria bloom (López-Archilla et al., 2004) (Fig. S1 and Table S4). In terms of size, the SPM, overall, considered mostly of fine particles (0.45–30 μm, 90%), with minor amounts of coarse (>180 μm, 5.9%) and medium (30–180 μm, 4.3%) particles. Concentrations of TOC in water were greater at industrial area sites (T16–T20, mean = 3.7 mg L^{-1}) than at suburban area sites (T1–T7, mean = 2.17 mg L^{-1}) and urban area sites (T8–T15, mean = 1.7 mg L^{-1}). Total concentrations of As (sum of dissolved and particulate) tended to correlate with water quality parameters such as temperature, salinity, DO, and TOC (Fig. S2). Relatively great As concentrations, for our sample set, were detected at saltwater sites in urban and industrial areas where greater than typical temperature, salinity, and TOC and relatively less DO levels were observed, suggesting that anthropogenic

Table 1
Summary of relative compositions of arsenicals in water, suspended particles, and biological samples collected from the Taehwa River Estuary.

Samples		Salinity[a]	Site (n)	Organic As (%)				Inorganic As (%)		Identified As (%)[b]
				AC	AB	MMA	DMA	As^{III}	As^{V}	
Water	<0.45 μm	Freshwater	12	[c]		1.2			99	42
		Saltwater	8		2.6	1.1	0.21	2.3	94	71
Suspended particles	0.45–30 μm	Freshwater	12			3.3		14	83	24
	30–180 μm	Freshwater	12		0.20			20	80	
	>180 μm	Freshwater	12			2.4		15	83	
	0.45–30 μm	Saltwater	8	0.03	1.4	1.6	0.08	4.14	92	43
	30–180 μm	Saltwater	8		0.33			9.1	91	
	>180 μm	Saltwater	8	0.09	0.45	0.14		9.2	90	
Biota	Fish	Saltwater	2	0.76	72		2.0	19	6.4	54
	Crab	Saltwater	2	0.34	66	0.60	0.38	25	7.9	55
	Bivalve	Saltwater	1	0.94	81		2.3	11	4.6	80
	Shrimp	Saltwater	2	0.41	42		5.6	26	26	45
	Gastropod	Saltwater	2	3.3	57		0.79	39	0.51	43
	Macroalgae	Saltwater	2	0.24	28		1.7	19	52	12

[a] Sampling sites were categorized as freshwater (T1–T12, S ~0) or saltwater (T13-T20, S 2.9–35).
[b] Identified As = Total As − 6 target arsenicals. Percentages of identified As in suspended particles were calculated only for total suspended particles (>0.45 μm).
[c] Blank: not detected.

activities may represent major sources of As in the Taehwa River Estuary.

Additionally, salinity may be a major factor affecting As fate and partitioning between water and SPM (Azizur Rahman et al., 2012). To examine this question, the sites were categorized into freshwater (T1–T12, S ~0) and saltwater (T13–T20, S 2.9–35) groups. Thus, in the following subsections, distributions and concentrations of dissolved and particulate arsenicals and *in situ* partitioning of As are discussed with respect to the sites' surrounding anthropogenic activities and salinity.

3.2. Distributions of dissolved arsenicals

Concentrations of total dissolved As in water ranged from 0.51 to 6.3 μg As L^{-1} (Fig. 2a and Table S5). A clear spatial pattern of As concentrations across the Taehwa River Estuary sampling sites was observed. The mean concentrations of As found in industrial area sites (4.0 μg As L^{-1}) were about double those in urban area sites (1.9 μg As L^{-1}) and about triple those in suburban area sites (1.2 μg As L^{-1}) (Table S6), indicating that point and/or non-point urban and industrial sources affect the spatial distribution of As in the estuary. In particular, industrial activities in several places seemed to be apparent and direct point sources of As in this area. In fact, the greater As concentrations were evidenced in the inland creeks sites (e.g., T19 and T17), which have long been developed a petrochemical industrial complex (Fig. S1). Thus, it is indicated that estuarine As seems to be mainly derived from the upper industrial areas via the inland waterways (creeks) in the Taehwa River Estuary. The As concentration at site T4 was unusually great among the suburban area sites, presumably due to local sources.

Concentrations of As detected in water samples did not exceed the water quality guidelines (WQGs) for protection of aquatic life suggested by the Canadian Council of Ministers of the Environment (CCME, 2001). Concentrations of As in water from freshwater sites (T1–T12) were below the freshwater-WQG (5 μg As L^{-1}) and those from saltwater sites (T13–T20) were below the marine-WQG (12.5 μg As L^{-1}) (Fig. 2a). The WQGs for As were derived from acute and chronic ecotoxicological data on marine and freshwater species (CCME, 2001). Thus, the As pollution in the Taehwa River Estuary does not exceed tolerable ecotoxicological risk levels.

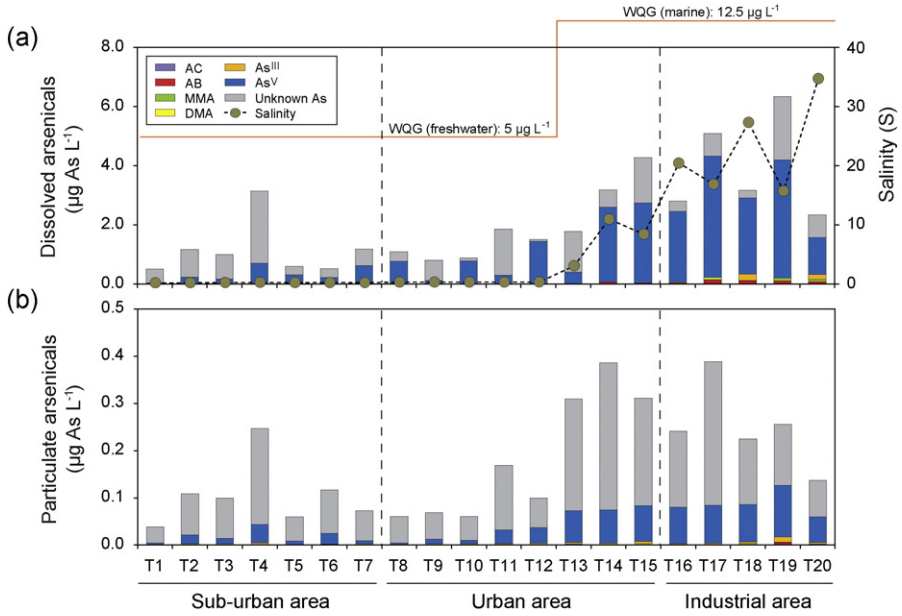

Fig. 2. Concentrations of arsenicals in (a) water and (b) SPM along the Taehwa River Estuary. The horizontal line represents the water quality guidelines for arsenic limits in freshwater and marine environments suggested by CCME (2001).

Speciation analysis results indicated that inorganic As^V was the predominant form of As in the Taehwa River Estuary (Table 1), with As^V accounting for about 94% and 99% of identified As was in saltwater and freshwater sites, respectively. The forms of As observed were more varied at saltwater sites, where AB, DMA, MMA, and As^{III} were detected, than at freshwater sites, where only As^V and MMA were detected. In general, As^V is the most prevalent dissolved form of As in aerobic freshwater and saltwater conditions (Cullen and Reimer, 1989). Thus, the predominance of As^V in water of the Taehwa River Estuary can be attributed to sufficient DO.

Meanwhile, unidentified (or unextractable) As accounted for a large proportion of the total dissolved As. Approximately 58% and 29% of the total concentrations of arsenicals in freshwater and saltwater 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). Various forms of As detected in saltwater sites might be associated with uptake and release of arsenicals by microorganisms such as phytoplankton. Overall, different compositions of arsenicals between freshwater and saltwater sites seemed to be related to differences in plankton species composition.

3.3. Distributions of particulate arsenicals: size fraction analysis

Concentrations (mass per water volume basis) of total particulate As ranged from 0.03 to 0.31 μg As L^{-1} (Fig. 2b and Table S5). Total particulate As concentrations were greater in urban and industrial areas than in suburban areas with similar distributions of dissolved As. Most of the particulate As detected consisted of inorganic forms such as As^V and As^{III}. Meanwhile, particle-size fraction analysis revealed that As adsorption onto fine particles (0.45–30 μm) was the greatest contributor to the total As in SPM, followed by As adsorption onto coarse (>180 μm) and medium (30–180 μm) particles. The size distributions of particle-associated As were due primarily to the large contributions of fine particles to total SPM. The portion of particulate As was relatively minor compared to that of the dissolved phase in the whole-water total As mass (Table S5).

Concentrations of As in SPM (mass per SPM mass basis) differed between freshwater and saltwater sites as well as among particle sizes (Table 1 and Tables S7–S9). Inorganic As forms, such as As^V and As^{III}, were detected mostly in the SPM of freshwater sites, while greater variety of arsenicals was detected in saltwater. Six target arsenicals represented about 24 and 43% of the SPM in freshwater and saltwater samples, respectively, based on the total As in SPM and the sum of arsenicals in the three particle-size fractions. This relatively small percentage of identified As in the SPM of freshwater samples might be due to the large amounts of lipid-As, which cannot be extracted completely, as described previously (Caumette et al., 2011). The concentrations of As in SPM samples (mass per SPM mass basis, several μg g^{-1} level) were significantly greater than those of As measured in water samples (several μg L^{-1} level), suggesting that SPM aggregated with phyto- and zooplankton organisms might accumulate or adsorb As from the water column.

The concentrations of the six primary arsenicals in each of the three size fractions of SPM from freshwater and saltwater sites are shown in Fig. 3. Generally, the coarse-, medium-, and fine-particle fractions included large zooplankton (>180 μm), small zooplankton and large phytoplankton (30–180 μm), and phytoplankton, detritus, and mineral materials (0.45–30 μm), respectively. In freshwater, the greatest concentrations of particulate arsenicals were found in coarse particles, followed by medium and fine particles, while concentrations of arsenicals were similar among the three particle-size fractions in samples from saltwater sites. This result was consistent with a prior report of freshwater phytoplankton and small zooplankton (<180 μm) containing greater levels of arsenicals than large zooplankton (>180 μm) (Caumette et al., 2011). Notwithstanding, the presently reported distributions of particulate arsenicals in relation to size fractions of saltwater samples are a novel observation. Overall, the particulate arsenical concentrations generally elevated in saltwater sites, which suggested the elevated uptake of arsenicals by marine phytoplankton and/or adsorption onto fine particles.

The observed arsenical compositions in SPM indicated that inorganic As^V and As^{III} were the predominant forms of As, while organic arsenicals were minor components (Table 1). These results are somewhat similar in patterns to prior studies, but with lesser contributions of organic arsenicals than those reported for freshwater (Caumette et al., 2011, 2012a) and for marine phyto- and zooplankton (Azizur Rahman et al., 2012; Foster et al., 2008). In general, As^V, a stable and predominant form of As in oxic water columns, is transformed to As^{III} and methylated to MMA and DMA by phytoplankton through metabolic detoxification pathways (Azizur Rahman et al., 2012; Hasegawa et al., 2001; Hellweger and Lall, 2004). Consequently, the organic arsenicals in plankton accumulate in the organisms' bodies or are excreted into the water column. Thus, the small contributions of organic arsenicals in suspended particles containing plankton organisms observed in the present study might be due to the limited As contamination level of the Taehwa River Estuary.

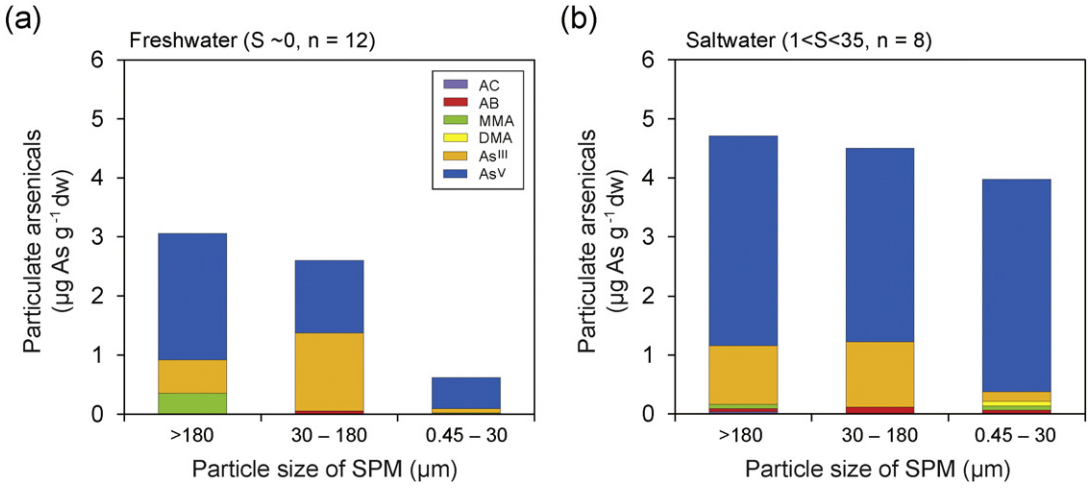

Fig. 3. Mean concentrations of particulate arsenicals for three size fractions (>180, 30–180, and 0.45–30 μm) from (a) freshwater (S ~0, n = 12) and (b) saltwater (S 2.9–35, n = 8) samples of the Taehwa River Estuary.

Table 2
Field-based water-particle distribution coefficients (log K_d values) of As in freshwater and seawater obtained from this study and previously reported data.

Sampling regions (country)	Samples[a]	Salinity	Particle size (μm)	Sample size (n)	SPM[b] (mg L^{-1})	Log K_d values (L kg^{-1}) Min–Max	Mean ± SD	References
Taehwa River Estuary (Korea)	F	~0	>0.45	12	65 ± 92	2.38–3.89	3.40 ± 0.46	This study
	S	2.9–35	>0.45	8	32 ± 7.1	3.12–3.68	3.42 ± 0.18	
East-Hainan Estuaries (China)	F	ns[c]	>0.4	32	5.3 ± 4.4	4.48–4.81		Balzer et al. (2013)
	S	~32	>0.4	7	6.1 ± 4.6		4.18	
Freshwater Lakes (China)	F	ns	>0.45	125	1.0–110	4.63–5.20		Yang et al. (2015)
Gironde Estuary (France)	F	~0	>0.2	96	1.0–460	3.70–4.04		Masson et al. (2009)
Moira Lake (Canada)	F	ns	>0.8	8	~1–~8	4.2–4.9		Faye and Diamond (1996)
English Channel (North Sea)	S	ns	>1.2	168	ns		4.14 ± 0.24	Michel et al. (1993)
Humber Plume (England)	S	32–35	>0.4	10	0.6–10	3.30–4.40	4.13	Millward et al. (1997)
Humber Estuary (England)	F + S	20–32	>0.45	16	2–80	3.77–4.97	4.45 ± 0.30	Kitts et al., 1994
Paranaguá Estuary (Brazil)	F + S	14–31	>0.45	9	12–62	3.36–4.26		dos Anjos et al. (2012)
Scheldt Estuary (Belgium)	F + S	ns	>0.4	11	ns	3.90–4.18		De Gieter et al. (2005)
Seine Estuary (France)	F + S	0.2–35	>0.4	34	33 ± 26	3.74–3.99	3.84 ± 0.07	Michel et al. (1999)

[a] Samples: freshwater (F) or seawater (S).
[b] SPM: mean ± SD or min–max.
[c] ns: data not shown.

3.4. Water-particle partitioning of arsenicals

Field-based distribution coefficient (K_d) of As between water and SPM reflects short-and long-term reactions, such as sorption and precipitation, in the estuarine environment (Balzer et al., 2013; Turner, 1996). The K_d value is very useful for understanding the fate of chemicals and elements in an estuary. The log K_d values of As were in the range of 2.38–3.89 L kg^{-1} (mean = 3.40 L kg^{-1}) in freshwater and in the range of 3.12–3.68 L kg^{-1} (mean = 3.42 L kg^{-1}) in saltwater sites of the Taehwa River Estuary (Table 2). The K_d values observed in freshwater sites greatly varied with one order of magnitude and were not relatively consistent compared to those found in saltwater (Fig. 4a). This result may imply the compositions of SPM and salinity differ from each other in freshwater and saltwater. Balzer et al. (2013) observed K_d values of As generally decreased with the increasing salinity due to salt effect. However, it should be noted that the K_d values of As obtained from the present study did not show a significant difference between freshwater and saltwater sites. Of note, the freshwater K_d values rather varied compared to saltwater ones, which suggested that salinity is not likely a major factor affecting the As fate in the Taehwa River Estuary. Log K_d values of As correlated inversely with log concentrations of SPM ($R^2 = 0.80$) (Fig. 4b). This tendency, which can be attributed to the so-called particle concentration effect, has been observed in previous studies (Benoit et al., 1994; Faye and Diamond, 1996). The cause of the particle concentration effect is not known with certainty, but it seems to be associated with the existence of colloidal (filter-passing fraction) forms of As (Honeyman and Santschi, 1988).

The log K_d values obtained in the present study were, in general, smaller than those reported previously [e.g., East-Hainan Estuaries (China): 4.48–4.81 L kg^{-1} (Balzer et al., 2013); Gironde Estuary (France): 3.70–4.04 L kg^{-1} (Masson et al., 2009); Humber Plume (England): 3.30–4.40 L kg^{-1} (Millward et al., 1997); Scheldt Estuary (Belgium): 3.90–4.18 L kg^{-1} (De Gieter et al., 2005)] (details in Table 2). Our smaller K_d values of As may be due to: i) greater concentrations of SPM in the Taehwa River Estuary than in other regions, allowing a dilution effect of particulate As; ii) lesser dependence of K_d on salinity, thus showing reactions to occur (Balzer et al., 2013); iii) the presence of phosphate concentrations that are sufficiently great as to prevent inadvertent bio-uptake (Azizur Rahman et al., 2012); and iv) less concentrations of particulate As owing to relatively limited As contamination in the Taehwa River Estuary. More studies on As in SPM, including in plankton organisms, in estuarine environments are needed to clarify the roles of organisms on the partitioning of As between aqueous and particulate phases.

3.5. Bioaccumulation of arsenicals in marine organisms

As were detected in all the biological sample types, encompassing fishes, bivalves, crabs, shrimps, gastropods, and macroalgae, with

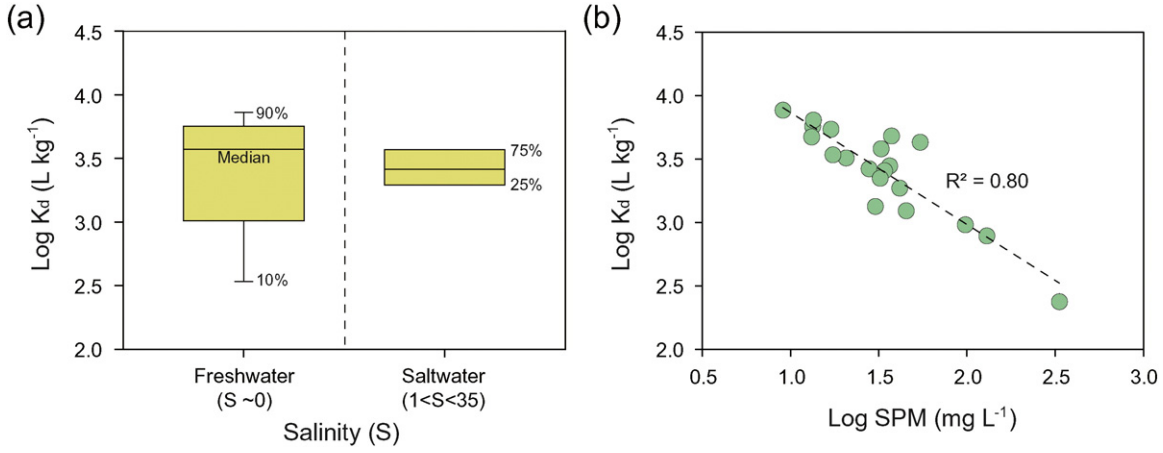

Fig. 4. (a) Boxplot for the log K_d values between water and suspended particles from freshwater (S ~0, n = 12) and saltwater (S 2.9–35, n = 8). (b) Relationship between log concentrations of SPM and log K_d values for Taehwa River Estuary samples.

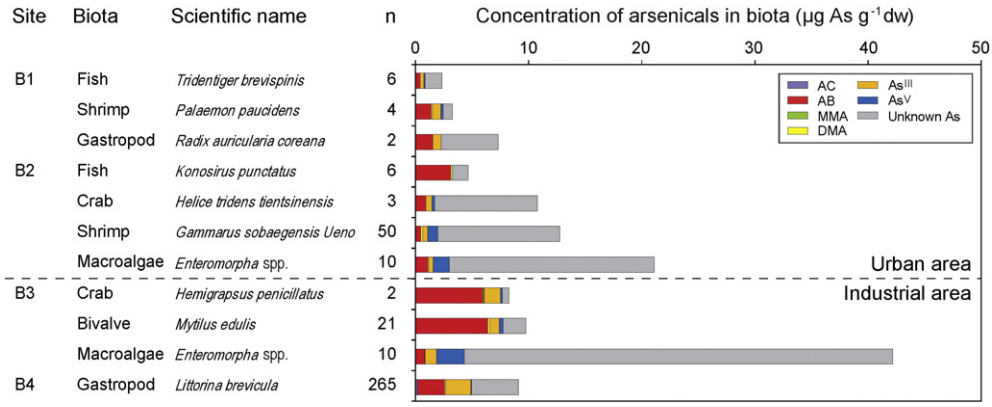

Fig. 5. Concentrations of arsenicals in various aquatic organisms, including fishes, crabs, bivalves, shrimps, gastropods, and macroalgae, collected from the Taehwa River Estuary.

varying concentrations and compositions across phylogenetic groups (Table 1 and Fig. 5). The greatest As concentration was found in macroalgae (*Enteromorpha* spp.), followed by shrimps (*Gammarus sobaegensis Ueno*), crabs (*Helice tridens tientsinensis*), bivalves (*Mytilus edulis*), and gastropods (*Littorina brevicula*), with fishes (*Tridentiger brevispinis*) having the smallest As concentration (Fig. 5). These differences could be due to the organisms' selective food sources, feeding guilds, and metabolic pathways and capacities. In general, As concentrations were greater in biological samples collected from industrial areas (B3 and B4) than in samples collected from urban areas (B1 and B2). For example, As concentrations in macroalgae were 21 and 42 μg As g^{-1} dw in samples collected from sites B2 (urban) and B4 (industrial), respectively. Thus, concentrations of As in biota were dependent on the corresponding waterborne concentrations of As, as we have discussed previously (Hong et al., 2014).

Greater As concentrations were found in macroalgae than in marine animals, suggesting that As accumulates more readily in macroalgae than in marine animals through waterborne exposure to inorganic forms of As in estuarine and coastal environments. Greater As accumulation in macroalgae, relative to in animals, may be due to their inadvertent uptake of As (e.g., through phosphate uptake systems) (Hellweger et al., 2003). The six known arsenicals in this study accounted for only a small portion (~12%) of the total concentration of As in macroalgae, indicating that large amounts of unknown As forms could exist. These unknown As forms might consist of, at least in part, arsenosugars, which are compounds that are commonly found in macroalgae (García-Salgado et al., 2012). Arsenosugars are less- or non-toxic compounds despite being present in great concentrations (Feldmann and Krupp, 2011). Because macroalgae are consumed by humans, great total As levels in macroalgae have the potential to impact human health. However, because the forms of As found in macroalgae are mostly less- or non-toxic organic arsenicals, macroalgae consumption risk for humans and wildlife is likely low.

Six organic and inorganic arsenicals accounted for about over 41% of the total concentrations of As in sampled marine animals (Table 1). The predominant form of As in marine animals was AB, followed by As^{III} and As^{V} (Table S10). The results of our As speciation analysis of marine animals were generally comparable to those in our previous studies (Choi et al., 2015; Hong et al., 2014). AB may accumulate in marine animals due to dietary exposure through consumption of degradable arsenosugars in plankton (Azizur Rahman et al., 2012; Caumette et al., 2012b). Given its structural similarity to glycine betaine, AB might act as a cellular osmolyte (Amlund and Berntssen, 2004; Whaley-Martin et al., 2012b). Thus, accumulated AB in marine animals may play a role in the maintenance of ionic and osmotic homeostasis during seawater adaptation. Overall, the results indicated that bioaccumulation of As was species-specific and salinity would be a key factor affecting bioaccumulation of As in marine animals in an estuarine system.

4. Conclusions

In the present study, several findings on the fate of arsenicals in an estuarine environment including distribution, water-particle partitioning, and bioaccumulation were obtained as delineated below:

- Greater As concentrations were found at sites associated with anthropogenic activities (e.g., sites in urban and industrial areas), with a predominance of dissolved inorganic forms, particularly As^{V} in oxic estuarine waters.
- Inorganic arsenicals could be taken up by marine phytoplankton (e.g., 0.45–30 μm), and then transformed to organic forms under conditions of As pollution stress.
- Field-based water-particle K_d values for As showed no dependence on salinity, but a strong dependence on SPM concentrations.
- Arsenicals can accumulate in various marine organisms, potentially via waterborne and dietary exposure routes.
- Greater concentrations of arsenicals were found in macroalgae than in marine animals, though they were mostly non-toxic organic arsenicals.

Overall, the results of present study enhance our understanding of As behavior, fate, and transport from land to ocean, and boundary zones for differences in these data can be useful as baseline data for developing arsenical fate models for estuarine environments.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.marpolbul.2016.04.035.

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<Supplementary Materials>

Arsenic speciation in water, suspended particles, and coastal organisms from the Taehwa River Estuary of South Korea

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Table of Contents

Supplementary Tables

Supplementary Figures

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Supplementary Tables

Table S1. Information on target chemicals, reagents, and certified reference materials used in this study.

Chemicals	Abbreviation	Concentration	Company
Target compounds			
Arsenocholine bromide	AC	>99%	Wako, Osaka, Japan
Arsenobetaine	AB	>95.0%	Sigma-Aldrich, St. Louis, MO
Disodium methyl arsenate	MMA	~100%	Sigma-Aldrich, St. Louis, MO
Sodium cacodylate trihydrate	DMA	>98%	Sigma-Aldrich, St. Louis, MO
Arsenite	As(III)	1000 ppm	Inorganic Ventures Inc., Lakewood, NJ
Arsenate	As(V)	1000 ppm	Inorganic Ventures Inc., Lakewood, NJ
HPLC Mobile Phase			
Ammonium nitrate	A	4 mM	Sigma-Aldrich, St. Louis, MO
Ammonium nitrate	B	40 mM (pH 9.0)	Sigma-Aldrich, St. Louis, MO
Certified Reference Materials			
Marine sediments	MESS-3	21.2 mg As kg^{-1}	NRC, National Research Council, Canada
Lobster Tissue	TORT-2	59.5 mg As kg^{-1}	NRC, National Research Council, Canada
Fish Protein	DORM-3	6.88 mg As kg^{-1}	NRC, National Research Council, Canada

Table S2. Instrumental conditions of HPLC-ICP/MS for arsenic speciation analysis.

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
RF power	1500 W
Analytes	AsO (m/z = 91)
Reaction gas	O_2 = 0.6 mL min^{-1}
RPq	0.5
Dwell time	250 ms

Table S3. Summary of quality assurance and quality control for arsenic speciation analysis.

Arsenicals	Method detection limits			CRM test			
	Water	SPM	Biota	DORM-3		TORT-2	
	($\mu g\ L^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	Reference values[a] ($\mu g\ g^{-1}$ dw)	This study ($n = 3$, $\mu g\ g^{-1}$ dw)	Reference values ($\mu g\ g^{-1}$ dw)	This study ($n = 3$, $\mu g\ g^{-1}$ dw)
AC	0.1	0.01	0.002	<0.080	<MDL	0.043	0.29 ± 0.072
AB	0.05	0.005	0.001	4.69	4.3 ± 0.32	14.25	14.0 ± 0.89
MMA	0.05	0.005	0.001	0.091	0.064 ± 0.013	0.093	0.06 ± 0.002
DMA	0.05	0.005	0.001	0.459	0.47 ± 0.029	0.84	1.2 ± 0.066
As^{III}	0.1	0.01	0.002	0.085	0.13 ± 0.014	-	<MDL
As^{V}	0.05	0.005	0.001	0.243	0.31 ± 0.015	0.0928	0.89 ± 0.037

[a] Reference values of forms of As in CRMs were presented in previous articles (Leufroy et al., 2011; Wahlen et al., 2004).

Leufroy, A., Noël, L., Dufailly, V., Beauchemin, D., Guérin, T., 2011. Determination of seven arsenic species in seafood by ion exchange chromatography coupled to inductively coupled plasma-mass spectrometry following microwave assisted extraction: Method validation and occurrence data. Talanta 83, 770-779.

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Table S4. Water quality parameters including temperature, salinity, dissolved oxygen, pH, and suspended particles in the Taehwa River Estuary.

Sites	Type	Temperature	Salinity	DO	pH	Suspended particles (size: μm)				TOC
						>180	30-180	0.45-30	Total	
		(°C)	(S)	(mg L^{-1})		(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})
T1	Freshwater lake	19.4	0.02	9.24	7.70	0.90	0.25	12	13	1.54
T2	River	17.2	0.04	7.58	7.78	1.3	0.55	96	98	1.34
T3	River	17.9	0.07	10.9	7.90	1.1	0.55	130	130	1.44
T4	River	18.9	0.10	9.40	7.81	1.5	1.3	330	330	3.46
T5	Freshwater lake	19.3	0.06	9.50	7.91	1.2	0.95	34	36	2.44
T6	River	12.5	0.07	10.7	8.15	1.0	0.75	53	54	2.00
T7	Freshwater lake	21.2	0.06	11.9	9.48	1.3	0.95	11	13	2.99
T8	River	19.3	0.14	7.87	7.90	0.90	1.2	43	45	1.73
T9	River	20.0	0.15	9.27	8.03	1.2	0.75	12	14	1.53
T10	River	19.4	0.15	7.02	7.78	1.7	0.95	6.4	9.1	1.09
T11	River	19.7	0.15	8.27	7.37	1.6	2.8	13	17	1.41
T12	River	19.2	0.16	7.51	7.60	2.0	0.15	19	21	1.16
T13	Estuary	20.0	2.92	7.40	7.44	1.1	1.4	35	37	1.99
T14	Estuary	20.2	10.9	5.99	7.32	1.4	1.2	30	33	2.15
T15	Inland creek (urban)	23.2	8.28	8.29	8.00	0.70	1.2	6.0	7.9	2.55
T16	Estuary	20.4	20.4	7.12	7.89	0.60	0.25	33	34	2.27
T17	Inland creek (industrial)	21.4	16.8	5.64	7.71	1.1	0.50	40	42	6.89
T18	Inland creek (industrial)	20.3	27.3	8.26	8.15	1.8	1.1	29	32	2.40
T19	Inland creek (industrial)	22.0	15.6	5.92	7.80	2.1	1.3	27	30	4.61
T20	Estuary	18.8	34.7	7.63	8.15	2.0	0.75	15	17	2.48

Table S5. Concentrations of total As in water samples from the Taehwa River Estuary.

Sites	Dissolved total As		Particulate total As		Total
	Concentration	%	Concentration	%	As
T1	0.51	94	0.031	5.7	0.54
T2	1.2	93	0.087	6.9	1.3
T3	1.0	93	0.080	7.4	1.1
T4	3.2	94	0.20	5.9	3.4
T5	0.60	93	0.048	7.4	0.64
T6	0.52	85	0.094	15	0.62
T7	1.2	95	0.058	4.7	1.2
T8	1.1	96	0.049	4.3	1.2
T9	0.81	94	0.055	6.4	0.86
T10	0.89	95	0.049	5.2	0.94
T11	1.9	93	0.13	6.8	2.0
T12	1.5	95	0.080	5.0	1.6
T13	1.8	88	0.25	12	2.0
T14	3.2	91	0.31	8.8	3.5
T15	4.3	94	0.25	5.5	4.5
T16	2.8	94	0.19	6.4	3.0
T17	5.1	94	0.31	5.8	5.4
T18	3.2	95	0.18	5.4	3.4
T19	6.3	97	0.20	3.1	6.6
T20	2.3	96	0.11	4.5	2.5

Unit: μg As L^{-1}.

Table S6. Concentrations of dissolved As in the Taehwa River Estuary.

Sites	Organic As				Inorganic As		Unk	Total
	AC	AB	MMA	DMA	As^{III}	As^{V}	As [a]	As
T1						0.05	0.46	0.51
T2						0.24	0.94	1.2
T3						0.18	0.82	1.0
T4						0.71	2.4	3.2
T5			0.03			0.29	0.28	0.60
T6						0.23	0.30	0.52
T7			0.04			0.59	0.55	1.2
T8						0.78	0.32	1.1
T9						0.12	0.69	0.81
T10						0.78	0.11	0.89
T11						0.31	1.6	1.9
T12						1.4	0.06	1.5
T13						0.40	1.38	1.8
T14		0.07				2.5	0.58	3.2
T15		0.05				2.7	1.53	4.3
T16		0.05	0.02			2.4	0.36	2.8
T17		0.13	0.02	0.071		4.1	0.76	5.1
T18		0.11			0.22	2.6	0.26	3.2
T19		0.11	0.10			4.0	2.1	6.3
T20		0.07	0.08		0.18	1.2	0.77	2.3

[a] Unknown As = Total As – Identified As.
Blank: <MDL.
Unit: μg As L^{-1}.

Table S7. Concentrations of particulate As (>180 μm) in the Taehwa River Estuary.

Sites	Organic As				Inorganic As		Sum of 6 ΣAs
	AC	AB	MMA	DMA	As^{III}	As^{V}	
T1					0.84	0.85	1.7
T2						0.48	0.48
T3			0.30		0.34	1.9	2.5
T4						0.18	0.18
T5			0.12			2.2	2.3
T6			0.65			8.2	8.9
T7						2.3	2.3
T8							
T9							
T10					0.64	0.37	1.0
T11						3.2	3.2
T12					0.44	1.7	2.2
T13						2.4	2.4
T14						1.2	1.2
T15					1.7	4.2	5.9
T16						1.3	1.3
T17						6.9	6.9
T18		0.033	0.069		1.0	5.0	6.1
T19	0.037	0.094			0.68	4.6	5.4
T20		0.044			0.52	2.9	3.5

[a] Unknown As = Total As – Identified As.
Blank: <MDL.
Unit: μg As g^{-1} dw.

Table S8. Concentrations of particulate As (30-180 μm) in the Taehwa River Estuary.

Sites	Organic As				Inorganic As		Sum of 6 ΣAs
	AC	AB	MMA	DMA	As^{III}	As^{V}	
T1						1.5	1.5
T2						1.4	1.4
T3						0.39	0.39
T4						0.36	0.36
T5						1.1	1.1
T6						3.9	3.9
T7						0.37	0.37
T8							
T9		0.052			2.0	0.56	2.6
T10							
T11					0.37	1.5	1.9
T12					1.6		1.6
T13						1.5	1.5
T14						4.1	4.1
T15					0.96	1.1	2.1
T16						0.79	0.79
T17						7.1	7.1
T18						5.7	5.7
T19		0.12			1.3	3.2	4.6
T20						2.6	2.6

[a] Unknown As = Total As – Identified As.
Blank: <MDL.
Unit: μg As g^{-1} dw.

Table S9. Concentrations of particulate As (0.45-30 μm) in the Taehwa River Estuary.

Sites	Organic As				Inorganic As		Sum of 6 ΣAs
	AC	AB	MMA	DMA	As^{III}	As^{V}	
T1					0.068	0.12	0.19
T2			0.008		0.025	0.18	0.21
T3			0.003		0.017	0.068	0.087
T4			0.003		0.010	0.12	0.13
T5			0.011			0.12	0.19
T6			0.004		0.022	0.22	0.25
T7			0.064		0.17	0.34	0.58
T8					0.023	0.087	0.11
T9			0.021		0.094	0.82	0.94
T10			0.012		0.21	1.1	1.3
T11			0.066		0.083	1.6	1.7
T12			0.018		0.076	1.6	1.7
T13			0.052		0.11	1.8	2.0
T14		0.011	0.021		0.091	2.1	2.3
T15		0.031	0.31	0.078	0.51	12	3.0
T16		0.016	0.021		0.048	2.3	2.4
T17		0.011	0.005		0.079	1.7	1.8
T18		0.049	0.079		0.038	2.2	2.3
T19		0.19	0.028		0.32	3.5	4.1
T20	0.008	0.085	0.061		0.13	3.2	3.5

[a] Unknown As = Total As – Identified As.
Blank: <MDL.
Unit: μg As g^{-1} dw.

Table S10. Concentrations of As in marine organisms from the Taehwa River Estuary.

Organisms	Scientific name	Sites	Sample number	Organic As				Inorganic As		Unk As [a]	Total As
				AC	AB	MMA	DMA	As^{III}	As^{V}		
Fish	*Tridentiger brevispinis*	B1	6	0.006	0.43		0.001	0.34	0.11	1.5	2.4
	Konosirus punctatus	B2	6	0.029	3.2		0.12			1.4	4.7
Bivalve	*Mytilus edulis*	B3	21	0.074	6.4		0.18	0.84	0.36	2.1	9.8
Crab	*Helice tridens tientsinensis*	B2	3	0.009	0.94			0.55	0.23	9.1	11
	Hemigrapsus penicillatus	B3	2	0.013	6.0	0.092	0.059	1.4	0.20	0.58	8.3
Shrimp	*Palaemon paucidens*	B1	4	0.021	1.4		0.080	0.75	0.18	0.86	3.3
	Gammarus sobaegensis Ueno	B2	50		0.51		0.16	0.45	0.90	11	13
Gastropod	*Radix auricularia coreana*	B1	2	0.066	1.5			0.75		5.1	7.4
	Littorina brevicula	B4	265	0.189	2.5		0.080	2.2	0.051	4.4	9.2
Algae	*Enteromorpha spp.*	B2	10	0.004	1.1		0.079	0.41	1.4	18	21
	Enteromorpha spp.	B3	10	0.015	0.83		0.036	1.0	2.5	38	42

[a] Unknown As = Total As – Identified As.
Blank: <MDL.
Unit: μg As g^{-1} dw.

Supplementary Figures

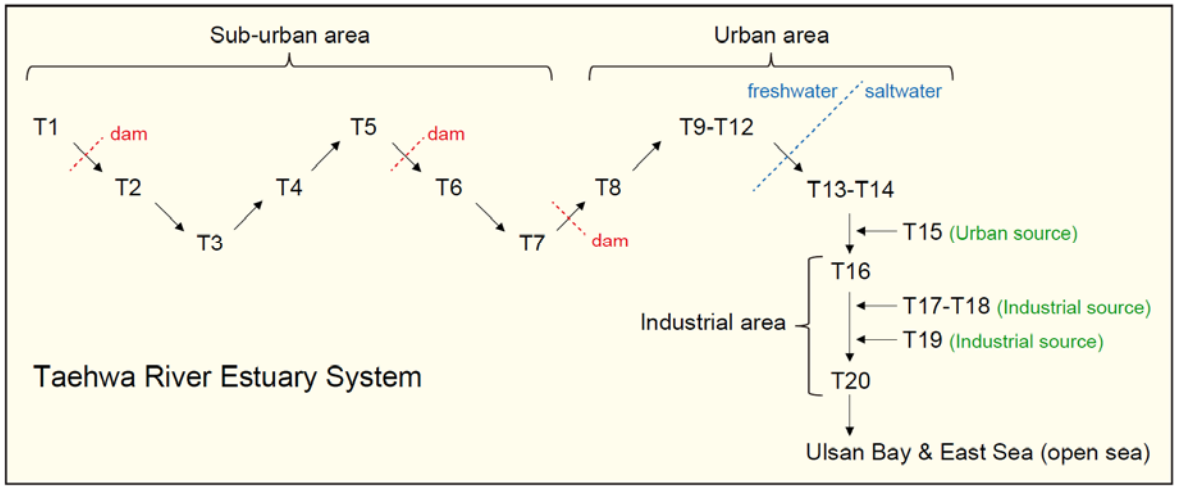

Fig. S1. Water flow, locations of dams, and surrounding activities in the Taehwa River Estuary area.

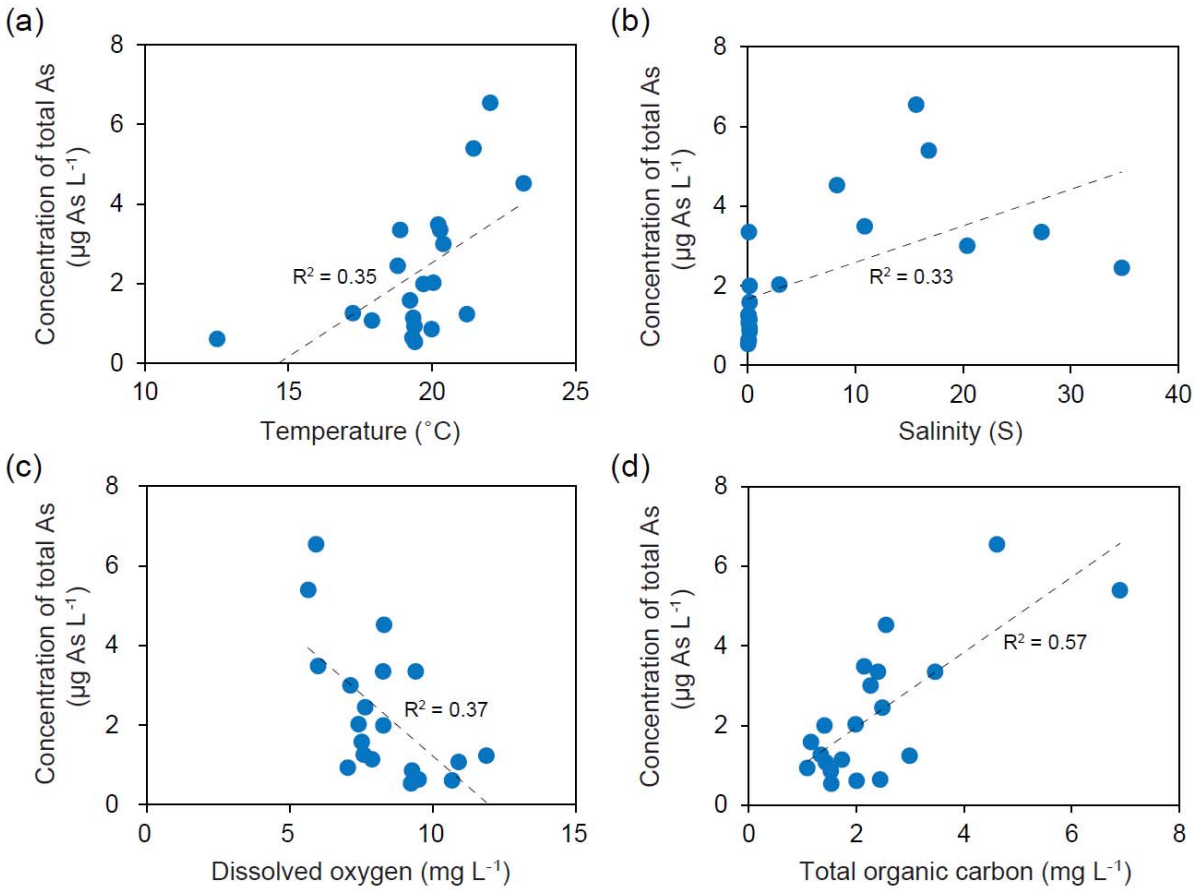

Fig. S2. Relationships between total As concentrations in water and (a) temperature, (b) salinity, (c) dissolved oxygen, and (d) total organic carbon in the Taehwa River Estuary.