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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.

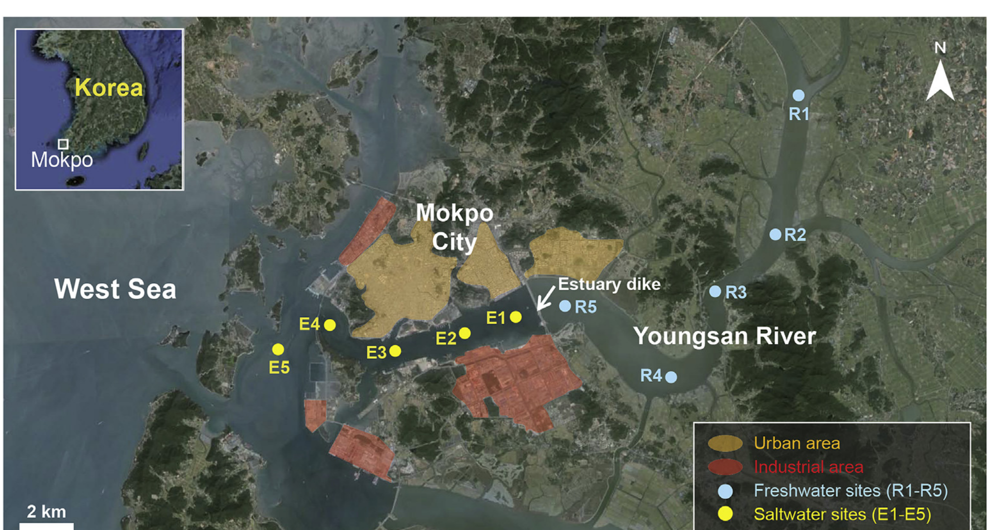

Fig. 1. Map showing the sampling sites (inner: freshwater; outer: saltwater) of the Youngsan River Estuary, Korea (Nov., 2012).

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