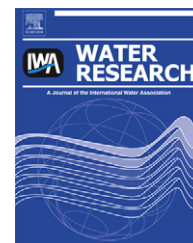


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Dissolved silver in European estuarine and coastal waters

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ABSTRACT

Silver is one of the most toxic elements for the marine microbial and invertebrate community. However, little is known about the distribution and behaviour of dissolved silver in marine systems. This paper reports data on dissolved and sediment-associated silver in European estuaries and coastal waters which have been impacted to different extents by past and present anthropogenic inputs. This is the first extended dataset for dissolved silver in European marine waters. Lowest dissolved silver concentrations were observed in the Gullmar Fjord, Sweden (8.9 ± 2.9 pM; $x \pm 1\sigma$), the Tamar Estuary, UK (9.7 ± 6.2 pM), the Fal Estuary, UK (20.6 ± 8.3 pM), and the Adriatic Sea (21.2 ± 6.8 pM). Enhanced silver concentrations were observed in Atlantic coastal waters receiving untreated sewage effluent from the city of A Coruña, Spain (243 ± 195 pM), and in the mine-impacted Restronguet Creek, UK (91 ± 71 pM). Anthropogenic wastewater inputs were a source of dissolved silver in the regions studied, with the exception of the Gullmar Fjord. Remobilisation of dissolved silver from historically contaminated sediments, resulting from acid mine drainage or sewage inputs, provided an additional source of dissolved silver to the estuaries. The ranges in the log particle-water partition coefficient (K_d) values of 5–6 were similar for the Tamar and Mero estuaries and agreed with reported values for other estuaries. These high K_d values indicate the particle reactive nature of silver with oxic sediments. In contrast, low K_d values (1.4–2.7) were observed in the Fal system, which may have been due to enhanced benthic inputs of dissolved silver coupled to limited scavenging of silver on to sediments rich in Fe oxide.

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1. Introduction

Silver is one of the most toxic elements to bacteria, phytoplankton and invertebrates (Richards, 1981; Bryan, 1984; Luoma et al., 1995; Ratte, 1999), principally by disabling the enzymes Na/K adenosine triphosphatase and carbonic anhydrase in animals (Morgan et al., 2004; Bielmyer et al., 2007), and interacting with thiol groups in enzymes and proteins of micro-organisms (McDonnell and Russell, 1999). Silver is

strongly bioaccumulated by a number of marine phytoplankton, macro-algae and invertebrates (Fisher et al., 1984; Bryan, 1984), and it is known that the degree of silver accumulation by organisms is dependent on its chemical speciation. The monovalent silver ion (Ag^+) is considered the most toxic silver species in aquatic systems and it has been shown that silver toxicity in freshwater phytoplankton is directly related to intracellular accumulation (Campbell, 1995; Lee et al., 2005).

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Whilst it has been predicted that the monovalent silver ion is the main dissolved species in freshwaters, experimental data have shown that in rivers and estuaries dissolved silver associated with colloidal macromolecular organic matter is a significant or dominant fraction of the total dissolved silver pool (Wen et al., 1997, 2002). It was proposed that the silver was bound to organo-thiol (sulfhydryl) groups in this fraction (Wen et al., 1997; Adams and Kramer, 1998). The macromolecular fraction is reported to decrease with an increase in salinity (Wen et al., 1997), perhaps because of flocculation, precipitation or salting out processes. In tandem, silver chloro-complexes (AgCl^0 , AgCl_2^- , AgCl_3^{2-} and AgCl_4^{3-}) appeared to become more important in saline waters, as predicted by speciation modelling (Turner et al., 1981; Cowan et al., 1985). Indeed, Miller and Bruland (1995) could find no evidence for organic complexation of dissolved silver in fully marine waters.

In the estuarine water of Galveston Bay, Wen et al. (1997) observed that most of the particulate silver ($77 \pm 6\%$) was in an Fe/Mn oxyhydroxide/sulfidic phase, and suggested that complexation with thiol groups was again important. However, this predominantly river-borne material was lost from the water column with increasing salinity. In contrast, the solid state speciation of silver became more dominated by a weakly adsorbed phase at higher salinities, suggesting that a dynamic exchange of silver between water and particles occurred in Galveston Bay, even though silver chloro-complexes appear to have limited particle-reactivity at salinities >5 (Luoma et al., 1995). In oxic surface sediments of 17 English estuaries, Luoma et al. (1995) observed that particulate silver was mostly associated with an uncharacterised organic phase, and the authors did not discount the potential importance of sulfide complexation of silver in this phase.

In addition to the role of monovalent silver as a toxin, the bioaccumulation of dissolved silver in estuaries may be further enhanced by the formation of the neutral, and potentially lipophilic, species $\text{AgCl}(\text{aq})$ and $\text{AgHS}(\text{aq})$ in low salinity waters (Cowan et al., 1985; Sunda, 1993; Bell and Kramer, 1999; Reinfelder and Chang, 1999). The presence of other, particle-unreactive, chloro-complexed species may also enhance biological uptake. The Criteria Maximum Concentration (CMC) for dissolved silver is 17.6 nM in freshwater and 29.7 nM in salt water (based on CaCO_3 hardness of 100 mg L^{-1}) (USEPA, <http://www.epa.gov/waterscience/criteria/wqtable/index.html#D>, accessed May 2009), although equivalent criteria for particulate silver do not appear to be as well developed (Langston et al., 2003).

Despite the potential environmental impacts of silver, very little is known about the distribution and behaviour of this element in marine waters. This has been largely due to the challenges involved in the accurate and precise analysis of the low levels of dissolved silver that occur in seawater (Barriada et al., 2007). The few data that exist show that in oceanic waters dissolved silver concentrations are in the range $<1\text{--}30 \text{ pM}$; oceanic silver depth profiles indicate low surface water concentrations which increase with depth, indicating a nutrient-type behaviour for this element (Martin et al., 1983; Flegal et al., 1995; Rivera-Duarte et al., 1999; Ndung'u et al., 2001; Ranville and Flegal, 2005). Phytoplankton play a key role in this water column distribution, with silver adsorption to cell surfaces or incorporation in to cells during their growth

in the euphotic zone (Fisher and Went, 1993), and subsequent downward transport and release during re-mineralisation at depth (Martin et al., 1983; Ndung'u et al., 2001). Anthropogenic perturbations of oceanic surface water concentrations have recently been observed in the North Pacific Ocean and tentatively ascribed to industrial aerosol inputs derived from the Asian mainland (Ranville and Flegal, 2005).

Elevated silver concentrations occur in estuarine and coastal waters subjected to anthropogenic inputs, including those from wastewater effluents and acid mine drainage. In San Francisco Bay enhanced concentrations have been reported due to silver-rich wastewater discharges from hospitals, photographic and electronics industries (e.g. Flegal et al., 1991; Sañudo-Wilhelmy and Flegal, 1992; Smith and Flegal, 1993; Stephenson and Leonard, 1994; Flegal et al., 1997; Squire et al., 2002). The introduction of more stringent discharge regulations has resulted in a decrease in silver concentrations over the last two decades in San Francisco Bay (Flegal et al., 2007). Sediments form an important sink of silver under oxic conditions (Luoma et al., 1995), whilst sediment resuspension (Wen et al., 1997) and diffusion of silver-rich porewaters (Rivera-Duarte and Flegal, 1997; Morford et al., 2008) are mechanisms of dissolved and colloidal silver resupply to overlying estuarine and coastal waters.

Previous studies of silver in marine systems in Europe have focused on metal-mine impacted systems in southwest England (Tamar, Looe and Fal estuaries), reporting particulate silver concentrations that were up to 400 times higher than background levels for sediments and bed dwelling organisms (Bryan and Hummerstone, 1977; Bryan and Langston, 1992). This paper reports data on dissolved and sediment-associated silver in a range of European estuarine and coastal systems, and relate the observed distributions to anthropogenic inputs and water column processes.

2. Methods

2.1. Sampling locations

Samples were collected from European estuaries and coastal waters (Fig. 1a) subjected to varying levels of anthropogenic pressures, including discharges from sewage treatment works and drainage from disused mines. The Tamar Estuary, located in southwest England (Fig. 1a, b), extends 31 km from its boundary at Plymouth Sound to the limit of tidal influence. The major freshwater input is from the River Tamar. The estuary is macro-tidal, and maximum suspended particulate matter (SPM) concentrations can exceed 1 g L^{-1} (Uncles et al., 1994); suspended phytoplankton growth is restricted because of the high turbidity. The estuary receives acid mine drainage from numerous abandoned mine workings. The silver-lead mines in the upper estuary are estimated to have produced ca. 28 tons of silver in the seven centuries of operation until the mid 19th century (Booker, 1976). The seaward end of the estuary receives sewage effluent from the city of Plymouth (ca. 240,000 inhabitants), of which until recently (2000), two-thirds was untreated or only partially treated.

The Fal Estuary is situated in southwest England and is comprised of a complex of creeks and tidal rivers extending

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