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Octanol-solubility of dissolved and particulate trace metals in contaminated rivers: implications for metal reactivity and availability

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New approaches are presented for fractionating trace metals in natural waters.

Abstract

The lipid-like, amphiphilic solvent, *n*-octanol, has been used to determine a hydrophobic fraction of dissolved and particulate trace metals (Al, Cd, Co, Cu, Mn, Ni, Pb, Zn) in contaminated rivers. In a sample from the River Clyde, southwest Scotland, octanol-solubility was detected for all dissolved metals except Co, with conditional octanol–water partition coefficients, D_{ow}, ranging from about 0.2 (Al and Cu) to 1.25 (Pb). In a sample taken from the River Mersey, northwest England, octanol-solubility was detected for dissolved Al and Pb, but only after sample aliquots had been spiked with individual ionic metal standards and equilibrated. Spiking of the River Clyde sample revealed competition among different metals for hydrophobic ligands. Metal displacement from hydrophobic complexes was generally most significant following the addition of ionic Al or Pb, although the addition of either of these metals had little effect on the octanol-solubility of the other. In both river water samples hydrophobic metals were detected on the suspended particles retained by filtration following their extraction in *n*-octanol. In general, particulate Cu and Zn (up to 40%) were most available, and Al, Co and Pb most resistant ($<1\%$) to octanol extraction. Distribution coefficients defining the concentration ratio of octanol-soluble particle-bound metal to octanol-soluble dissolved metal were in the range $10^{3.3}$–$10^{5.3}$ ml g^{-1}. The presence of hydrophobic dissolved and particulate metal species has implications for our understanding of the biogeochemical behaviour of metals in aquatic environments. Specifically, such species are predicted to exhibit characteristics of non-polar organic contaminants, including the potential to penetrate the lipid bilayer. Current strategies for assessing the bioavailability and toxicity of dissolved and particulate trace metals in natural waters may, therefore, require revision.

Keywords: Trace metals; Octanol; Hydrophobic; Particles; Rivers

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1. Introduction

It is widely recognised that the total concentration of a trace metal in natural waters gives little indication of its environmental reactivity or biological effects (Tessier and Turner, 1995). Various physical and chemical separations and speciation schemes have, therefore, been devised that target particular fractions or species of trace metals. With respect to dissolved trace metals in natural waters, the focus has generally been on the free ion (or other labile species) (e.g. Qian et al., 1998; Mann et al., 2002), the organically-complexed fraction (e.g. Lin et al., 1995; Wu et al., 1997), colloidal forms (e.g. Denaix et al., 2001; Hill and Aplin, 2001), and different valence states of the same metal (e.g. Wuilloud et al., 2002; Smith et al., 2003).

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From a biological standpoint, the free ion is of particular significance as this form of metal is able to interact directly with the cell surface, whereafter it may undergo internalisation (Hudson, 1998). According to the free ion activity model (FIAM), biological response is proportional to the activity of the free ion, and the presence of organic complexing ligands in the bulk solution acts to buffer the free ion activity and reduce these interactions (Roy and Campbell, 1997). However, recent evidence suggests that, in many cases, the uptake of metals may in fact be facilitated in the presence of certain organic complexants (Parent et al., 1996; Carvalho et al., 1999; Parker et al., 2001; Slaveykova et al., 2003). Mechanisms proposed for these observations include modification of cell permeability by adsorbed organic ligands, and passive diffusion of hydrophobic metal species across the cell surface.

The significance of the latter mechanism depends, in part, on the abundance of hydrophobic metal species (alkylated compounds and small, neutral complexes) in the natural environment. Attempts to isolate such from aquatic samples have generally involved reverse-phase HPLC (Riedel and Sanders, 1998; Turner et al., 2001). However, the physico-chemical properties of the non-polar stationary phase (commonly octadecylsilane) are known to be significantly different to those of the lipid bilayer. Moreover, the analyte is prone to interference from non-target, hydrophilic species that undergo adsorption to or entrapment within the matrix of the column support (Batley and Low, 1989). An alternative, more appropriate means of determining a hydrophobic fraction of dissolved trace metals would be to extract the sample in a solvent whose dielectric properties are similar to those of the lipid bilayer. A good surrogate for a generalised lipid phase is *n*-octanol, and the octanol–water partition coefficient is a widely recognised characteristic of organic chemicals that is used for modelling their toxicity and food web accumulation (Sangster, 1997). Accordingly, *n*-octanol would seem a logical solvent for assessing the hydrophobicity of metal species in natural samples.

In a recent paper, we described a "shake-flask" method for the determination of octanol-soluble metal complexes in natural waters and model systems, and examined the hydrophobicity of selected metals in the presence of natural and anthropogenic organic matter and specific organic ligands (Turner and Mawji, 2004). Here, we apply this method to a broader suite of metals in contaminated river waters, and extend the approach to determine the octanol-solubility of trace metals bound to suspended particles retained by sample filtration. We discuss the wider environmental and biological implications of the existence of hydrophobic, and potentially lipophilic metals in aquatic systems, and suggest alternative means of defining and parameterising trace metals in the environment based on our observations.

2. Materials and methods

2.1. Materials

All plastic-ware and glass-ware (sample bottles, pipette tips, centrifuge tubes, filtration unit, flasks) were soaked in 10% v/v HNO_3 (AnalaR grade, BDH, Poole, UK) for 24 h and rinsed with ultra pure water before being used. Centrifuge tubes were also soaked in Decon-90 detergent (Decon Laboratories, Bryn Mawr, PA) for 24 h before being acid-cleaned. HPLC-grade *n*-octanol (Aldrich, Gillingham, UK), and AristaR grade HCl, HNO_3 and NaOH (BDH) were used in the experiments and for sample preservation, and ICP-grade metal standards (BDH) were used for instrument calibration and sample spiking. Precise volumes of samples and reagents were dispensed using a gravimetrically calibrated Gilson micropipette (Anachem Life Sciences, Luton, UK). Milli-Q ultra pure water (resistivity 18 MΩ cm, pH 5.5–6.5) was used throughout, and all laboratory operations were undertaken in a Class-100 laminar flow hood.

2.2. Sampling and sample characterisation

The rivers Clyde (southwest Scotland) and Mersey (northwest England) were sampled for the present study. Both rivers have received domestic and trade wastes from densely populated and highly industrialised catchments for over a century and, despite recent improved legislation, remain considerably contaminated by both trace metals and organic chemicals (Edgar et al., 1999; Fox et al., 1999).

Surface water samples of 1.5 l were collected in high-density polyethylene bottles by hand from the river banks at locations just above the respective tidal limits. Bottles were rinsed several times with river water before being filled and stored cool (4–10 °C). Clyde and Mersey samples were filtered within 120 h and 24 h of collection, respectively, through pre-weighed, 0.45 μm pore size, 47 mm diameter cellulose acetate filters (Millipore) using a Nalgene polysulphone filtration unit connected to a vacuum pump. Filters were dried under laminar flow, re-weighed and stored in a dessicator until further use. The pH and conductivity of a 100 ml aliquot of each filtrate were measured at room temperature (20 ± 2 °C) using calibrated Hanna or YSI electrodes, and the chlorinity and alkalinity of the aliquots were determined by titration with $AgNO_3$ and H_2SO_4, respectively. Remaining filtrates were stored at 4 °C until further use (within 24 h of filtration). For the analysis of dissolved organic carbon (DOC), additional 100 ml aliquots of sample were filtered through 0.7 μm pore size, 47 mm diameter glass fiber filters (Whatman, Maidstone, UK), and were stored frozen in glass vials (for up to four weeks) after being acidified with 100 μl of