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Influence of dissolved organic matter on dissolved vanadium speciation in the Churchill River estuary (Manitoba, Canada)

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HIGHLIGHTS

- Temporal and spatial changes in dissolved V speciation using DGT.
- Positive relationship found between protein-like DOM and DGT-labile V.
- Surface sediment is a significant source of DGT-labile V during spring freshet.

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ABSTRACT

Diffusive gradients in thin films (DGT) devices were used to investigate the temporal and spatial changes in vanadium (V) speciation in the Churchill estuary system (Manitoba). Thirty-six DGT sets and 95 discrete water samples were collected at 8 river and 3 estuary sites during spring freshet and summer base flow. Dissolved V concentration in the Churchill River at summer base flow was approximately 5 times higher than those during the spring high flow (27.3 ± 18.9 nM *vs* 4.8 ± 3.5 nM). DGT-labile V showed an opposite trend with greater values found during the spring high flow (2.6 ± 1.8 nM *vs* 1.4 ± 0.3 nM). Parallel factor analysis (PARAFAC) conducted on 95 excitation-emission matrix spectra validated four humic-like (C1–C4) and one protein-like (C5) fluorescent components. Significant positive relationship was found between protein-like DOM and DGT-labile V ($r = 0.53$, $p < 0.05$), indicating that protein-like DOM possibly affected the DGT-labile V concentration in Churchill River. Sediment leachates were enriched in DGT-labile V and protein-like DOM, which can be readily released when river sediment began to thaw during spring freshet.

1. Introduction

Vanadium (V) is a transition metal widely distributed in natural environments (air, water, soil and biota) with potential mutagenic and carcinogenic properties (Stern et al., 1993). Natural sources of V in aquatic environments encompass rock weathering and sediment leaching (Hope, 1997; Rühling and Tyler, 2001; Shiller and Mao, 2000). Vanadium can also be introduced into aquatic environments through industrial activities especially from oil refineries and power plants that are burning V-rich fuel oil or coal (Evans and Landergran, 1975; Moskalyk and Alfanti, 2003; Kirk et al., 2014; Guéguen et al., 2006). Other sources of V to aquatic environments are fertilizers, sewage sludge, and discharge of domestic wastewater (Bhatnagar et al., 2008; McBride and Cherney, 2004). Vanadium is essential for normal cell growth at concentrations below 0.10 μM (Salice et al., 1999) but excessive amounts can cause adverse health effects on human and aquatic species. For example, the total V lethal concentration (LC_{50}) was 37–118 μM for juvenile rainbow trout (*Salmo gairdneri R.*) (Frank et al., 1996), 39–59 μM for zebra fish (*Brachydanio rerio*) (Bishayee et al., 2010), and 65 μM for guppies (*Poecilia reticulata*) (Bishayee et al., 2010). In surface water, V with the oxidation state of +5 is the dominant and most toxic form to cells (Sabbioni et al., 1991) and organisms (Ma and Fu, 2009).

The toxicity of trace metals in aquatic environments is greatly influenced by its chemical speciation and particularly the concentration of its free form and small soluble complexes. On the other hand, metal bound to dissolved organic matter (DOM), iron and aluminum oxyhydroxides are not readily bioavailable (Koukal et al.,

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2007). A change in DOM composition and concentration may affect bioavailability and mobility of metals in waters (Koukal et al., 2003).

The diffusive gradients in thin-films (DGT) technique is a time-integrated, passive sampler technique for the in situ determination of free and weakly bound metals in natural waters (Davison and Zhang, 1994). The DGT device is composed of a diffusive layer, conventionally a polyacrylamide hydrogel, and a binding layer, typically ferrihydrite (Luo et al., 2010; Österlund et al., 2010; Price et al., 2013) or zirconia (Guan et al., 2015) impregnated within the polyacrylamide hydrogel. DGT with ferrihydrite binding gel has been deployed in synthetic and natural freshwater to measure V in his highest oxidation state +5 (Luo et al., 2010; Österlund et al., 2010; Panther et al., 2013; Price et al., 2013).

Despite the fact that spring freshet is characterized by a dramatic increase in flux of dissolved and particulate species (Hölemann et al., 2005; Kuzyk et al., 2008; Mann et al., 2012), it is also the least sampled period. The discharge of Churchill River during freshet periods (up to 1320 m^3/s; Déry et al., 2005) causes significant changes in the estuary including increased stratification and turbidity, reduced marine and freshwater nutrient supply, and supplying the large freshwater pool into the interior ocean (Kuzyk et al., 2008). These conditions suppressed phytoplankton productivity while increasing organic matter supply by the river (Kuzyk et al., 2008). However, DOM concentration and composition as well as V concentration and speciation are still largely unknown during this period.

Earlier studies on dissolved V speciation showed the DOM adsorption effect was significant in river and estuary (Shiller and Mao, 2000). Lu et al. (1998) found that aquatic humic substances strongly complexed vanadate and VO_2^+. Excitation-emission matrix (EEM) fluorescence spectroscopy and parallel factor analysis (PARAFAC) have been used to assess the composition (e.g. protein- and humic-like based on peak position in the EEM; Coble, 1996) and origin of DOM in natural waters (e.g. Dainard and Guéguen, 2013; Kothawala et al., 2013; Walker et al., 2013). Recent advances in ultra-high resolution mass spectroscopy allowed the identification of structural composition of DOM (e.g. D'Andrilli et al., 2013; Hertkorn et al., 2008; Mangal et al., 2016), a prerequisite for exploring the relationship between DOM and metal complexation. In this paper, the objectives were (1) to determine the concentration of dissolved and DGT-labile V in the Churchill estuary system during spring freshet and at base flow regime; (2) to assess the impact of DOM on V speciation. The influence of DOM concentration and fluorescence composition (Coble, 1996) on V speciation will be discussed; (3) to determine dissolved V speciation in sediment leachate in the Churchill River. Although Shiller and Mao (2000) showed that sediment leaching and rock weathering were important sources of fluvial dissolved V, it is not clear how it would affect its dissolved speciation (i.e. DGT-labile concentration).

2. Materials and methods

2.1. Site description and sampling

The Churchill River, with an average discharge of 1200 m^3/s (Déry et al., 2005), drains a portion of the Canadian Shield and empties into western Hudson Bay. The drainage basin (288880 km^2; Déry et al., 2005) is dominated by flat muskeg plains and shallow lakes. Since 1977, about 90% of the river flow upstream of Southern Indian Lake (~320 km above the Bay) is diverted into the Nelson River to generate power. Ten study sites (R1-R7, E1-E3; Fig. 1) located in the enclosed estuary (approximately 13 km long and up to 3 km wide) in the lower end of the Churchill River were sampled in 2013–2015.

Triplicate DGT units were deployed in the Churchill River estuary system (Fig. 1A) from August 23 to August 27, 2013 (summer base flow; Fig. 1B) and from May 8 to May 16, 2014 (spring pre-freshet; Fig. 1B) and from May 12 to May 21, 2015 (spring freshet). Mean water level in the Churchill River was 22.51 ± 0.02 m in late August 2013, 24.07 ± 0.31 m pre-freshet and 23.90 ± 0.19 m freshet (Government of Canada (2015)). Due to site accessibility in spring, all sites could not be monitored at all seasons. The estuarine DGT units (E1-E3) were deployed in summer 2013 for 4–5 h during high tide over a 6-day period for an overall accumulation period of 24–30 h in order to assess the influence of marine-derived DOM. The prefreshet (R1 and R5) and freshet DGT units (R2-R3 and R6) were deployed for 2–4 d in moving waters (300–350 m^3/s) after drilling a hole through the river ice. The diffusive boundary layer was assumed to be negligible (Denney et al., 1999; Gimpel et al., 2001). R2 was the only site in the vicinity of a shallow wetland.

Water samples were daily collected at each site during the time of DGT deployment and immediately filtered through a pre-combusted, 0.7 μm glass fiber filter (Whatman) (Dainard and Guéguen, 2013) and a 0.22 μm nitrocellulose filter (Millipore) for DOM analysis. Dissolved V samples were obtained after filtration through 1 μm Nuclepore membrane filter (Whatman) and stored at 4 °C until analysis. Temperature of river was measured daily using a digital thermometer (Accumet AP85; ThermoScientific).

2.2. DGT preparation

Each DGT unit was composed of a 0.5 mm precipitated ferrihydrite binding gel layer (Luo et al., 2010), a 0.8 mm diffusive acrylamide-based gel layer and a 0.45 μm cellulose nitrate filter (Zhang and Davison, 1999). The binding and diffusive gels were casted using 0.25 and 0.5 mm thick, acid-bathed, polystyrene spacers, respectively. The binding gel was composed of a 0.5 mm diffusive gel immersed in 1 M iron nitrate solution for 12 h and in 2-*N*-morpholino ethanesulfonic acid (MES buffer) solution between 10 and 40 min (Luo et al., 2010). No significant difference in accumulated V was found in the 10 min soaked gel ($p > 0.05$). The binding gel was then rinsed with Milli-Q water (MQW) for 24 h and stored in MQW. The gel thicknesses (i.e. 0.5 and 0.8 mm for diffusive and binding gels, respectively) were verified using a digital caliper to an accuracy of 0.02 mm. The DGT preparation was conducted in metal-free 10,000 class clean room to minimize metal contamination. Blank concentrations were assessed by measuring the mass of metal present in binding gels on unit brought to the field but not deployed. The field blank of binding gels ($n = 3$) was 0.37 nM, which was much lower than the lowest DGT-labile V concentrations measured in the Churchill River (i.e. 4.3 nM). Binding gels was eluted by 1 M nitric acid (HNO_3; metal-free) for 24 h before ICP-MS analysis (XSeries II, Thermo). Indium and rhodium were used as internal standards. The accuracy of the ICP-MS measurements was assessed using SLEW-3 and SLRS-5 reference water (National Research Council, Canada). The measured V concentrations were within 5% of the certified values.

The time-integrated concentration of DGT-labile V in the bulk solution, C_{DGT} was calculated based on Fick's First Law of Diffusion (Zhang and Davison, 1995):

$$C_{DGT} = (M^* \Delta g)/(t^*A^*D)$$

where M is mass of V accumulated in the binding gel, Δg is thickness of diffusive gel and filter membrane, t is deployment time, A is sampling area exposed to bulk solution and D is diffusion coefficient of vanadium in diffusive gel and filter membrane ($D = 6.26 \times 10^{-6}$ cm^2/s at 25 °C; Luo et al., 2010). The D values were corrected to in situ average temperatures using the Stokes-Einstein relation (Li and Gregory, 1974).