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An experimental study on the mixing behavior of Ti, Zr, V and Mo in the Elbe, Rhine and Weser estuaries

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ABSTRACT

Estuaries are important interfaces between land and ocean, in which the input of trace metals into the ocean via the rivers is often significantly modified along the mixing gradient between freshwater and seawater. In the present study we have carried out mixing experiments using river water from the Rhine, the Elbe and the Weser and seawater from the North Sea with the aim of gaining more insights into the behavior of titanium (Ti), zirconium (Zr), vanadium (V) and molybdenum (Mo) and their distribution between dissolved and particulate forms during mixing in the estuaries. Little is known about the modification of their concentrations in estuaries and these metals increasingly enter the rivers and the ocean due to their application as so-called high-tech metals in industrial activities. Such laboratory experiments at controlled conditions allow the systematic investigation of chemical changes related to the mixing ratios, independent of further influence factors occurring in natural systems. Adsorptive stripping voltammetry was used for the analytical determination of the four metals. Although our data largely confirmed a strong particle-reactive behavior of Ti and Zr and a mostly conservative behavior of Mo, our mixing experiments revealed partial deviation from this behavior. Vanadium mostly does not follow a strict conservative mixing trend but shows both small ad- and desorption effects along the salinity transect. Also Mo shows some deviations from conservative mixing at mid-salinities. The enrichment of dissolved Ti and Zr at about 50:50 river: seawater mixtures agrees with recently published data of similar field studies and appears to be a systematic effect possibly related to charge transitions on particle surfaces or change of the dissolved metal speciation. The observed effects partly differed in experiments with filtered and non-filtered river water samples, especially for Ti and Zr, highlighting the role of riverine particulate matter for the modification of dissolved trace metal fluxes in estuaries.

1. Introduction

Rivers are the main contributor of dissolved trace metals into the ocean, with estuaries as important interfaces characterized by steep physico-chemical gradients between the two endmembers. Trace elements originating from weathering of rock minerals but increasingly also man's industrial and agricultural activities (Kabata-Pendias and Pendias, 2001) are transported by river systems in dissolved, colloidal and particulate forms. “Dissolved” trace metals can exist as truly dissolved ions and in association with colloidal humic acids especially in organic-rich rivers (Sholkovitz and Copland, 1981), or bound to colloidal mineral fractions such as Fe-oxyhydroxide colloids. Colloids and particulate matter can sorb large fractions of trace components owing to their surface charge and large surface area exposing numerous potentially reactive functional groups to the solution. Colloids exhibit a tendency to remain in suspension mainly due to their surface charge characteristics and small size. At the same time, a colloidal suspension may change its state of dispersion (aggregating or disaggregating) in response to ambient conditions. Factors commonly affecting the stability of colloidal suspension include solution chemistry, especially pH and ionic strength, mixing conditions,

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number of particles and their size distribution (Lead et al., 1997). This makes estuaries sites of significant colloidal reactions.

The transition metals of the subgroup IV such as zirconium (Zr) and titanium (Ti) are characterized by small ionic radii and charge +4 in marine systems and are grouped as high-field strength elements (HFSE). As these elements have a strong tendency towards hydrolysis, they are highly particle-reactive elements and are rapidly removed from solution by interaction with the surface of sinking particles, unless this is counter-balanced by equally strong chemical complexation with dissolved ligands, e.g. as it occurs for yttrium (Y) and the rare earth elements (REE) by carbonate complexation (Bau et al., 1996; Bau and Koschinsky, 2006). The ultimate consequences of a high reactivity towards particles are 1) very low truly dissolved concentrations of these elements in natural waters and 2) a strong impact of colloids and particles on their distribution (Firdaus et al., 2008).

Different from the HFSE, molybdenum (Mo) and partly vanadium (V) are not considered to be very particle-reactive, and redox conditions of the aquatic environment can influence their dissolved speciation. Molybdenum mostly exists as Mo(VI) in oxic waters at pH above 6 and forms the oxyanion molybdate, MoO_4^{2-} (Turner et al., 1981; Sohrin et al., 1999). Nevertheless, a study found that Mo can also be stable in natural waters as Mo(V) which comprises 0–15% of total dissolved Mo in the estuary of the river Peconic (Wang et al., 2009).

Molybdenum is known as a biologically essential trace metal. However, its distribution in the ocean is nevertheless largely conservative. Concentrations of Mo in surface seawater remain relatively high, because Mo is characterized by its high solubility in seawater and the concentrations clearly exceed biological requirements (Collier, 1984). Conservative-type trace-elements like Mo show weak interactions towards particles leading to relatively high dissolved concentrations. Furthermore, Mo is expected to vary nearly linearly with salinity; its residence time in the oceans is longer than 10^5 years which exceeds the mixing time of the oceans. Molybdate (MoO_4^{2-}) has a residence time of ca. 8×10^5 years (Elderfield, 2006) and is known to have rather low affinity towards particles, especially at slightly basic pH such as that of seawater (Emerson and Huested, 1991; Collier, 1985; Sohrin et al., 1987; Algeo and Tribovillard, 2009). Nevertheless, recent studies showed that also other patterns of Mo behavior occur in natural waters. Dellwig et al. (2007) showed that Mo behaved non-conservatively in coastal waters and was related to a tight coupling of geochemical, biological, and sedimentological processes. Rahaman et al. (2010) found that dissolved Mo is removed at lower salinity ranges in the Hooghly estuary in the Bay of Bengal and the Mandovi estuary along the coast of the Arabian Sea, both in India, and this loss was associated with mangrove swamps present in the estuaries. Another study, in the Narmada and the Tapi estuaries in the Gulf of Cambay in India, showed that the distribution of Mo with salinity does not follow the theoretical mixing line between river and seawater endmembers suggesting its non-conservative behavior (Rahaman et al., 2014).

For V, only the oxidation state +5 is stable in oxic waters at neutral pH (Wang and Sañudo-Wilhelmy, 2009). Vanadium, like Mo, is present in fresh water as an oxyacid, and vanadate V(V) species (HVO_4^{2-}, $H_2VO_4^{2-}$, HVO_4^{2-}, VO_4^{2-}) dominate, depending on pH (Turner et al., 1981; Sohrin et al., 1999). In seawater, the anion vanadate species, which are totally hydrolyzed, such as HVO_4^{2-}, $H_2VO_4^-$ and the complex $NaHVO_4^-$ are the dominant forms (Middelburg et al., 1988). The vanadate ion is assumed to show relatively low reactivity towards the majority of particles. Complexation with organic matter seems to have no significant effect on its behavior (Jeandel et al., 1987). In coastal water, dissolved V can be influenced by processes like scavenging, redox changes and adsorption onto Fe- and Mn-oxides (Beck et al., 2012).

The natural mixing behavior of Ti, Zr, Mo and V in estuaries is not yet fully studied and already nowadays an anthropogenic input is not negligible any more in many estuarine systems. The metals studied here are used in a number of industrial applications, e.g., vanadium molybdenum mixed oxides are used for the technical production of acrylic acid and can be released from fuel combustion (Adams et al., 2004; Pacyna et al., 1984). However, the major use of V is in ferrous and non-ferrous alloys (Moskalyk and Alfantazi, 2003). Titanium alloys are used e.g. in the energy, car or aerospace industry (Schutz and Watkins, 1998; Boyer and Briggs, 2005) and Zr oxides are, e.g., often contained in catalysts (Ozawa, 1998). These anthropogenic components will be enhanced in the future and therefore processes in estuaries, in which river discharge containing anthropogenic components of these metals enters the ocean, require further monitoring. Their discharge may modify and overprint the geogenic background distribution of these metals, before it is fully understood.

In our study we used laboratory mixing experiments to simulate estuarine mixing of river water from the Rhine, the Weser and the Elbe (Germany) along with surface seawater from the North Sea in order to investigate chemical processes of transition elements from subgroups IV, V and VI (Ti, Zr, V and Mo). We used both filtered and non-filtered water in most experiments to investigate the role of particles on the adsorption and desorption of the metals during the mixing process. The advantage of such laboratory experiments is that mixing effects can be investigated systematically along the mixing gradient between the two endmembers, river water and seawater. In nature, these specific effects are often overprinted by influx of different water masses from tributaries or groundwater discharge, sediment resuspension, rainfall, etc. While mixing experiments have already been carried out by other researchers as well, e.g. by Duinker and Nolting (1978) studying the mixing behavior of trace metals in the Rhine estuary, to our knowledge no such study has focused on the four elements we have selected for our work. Our mixing experiments have produced some new results that may help interpreting field data from previous and future studies more systematically and help predicting the impact of future changes (both natural and anthropogenic) on riverine fluxes of Mo, V, Ti and Zr into coastal waters.

2. Materials and methods

2.1. Chemicals

All chemicals used for the preparation of stock solutions were of analytical reagent grade obtained from the chemicals suppliers Merck (Darmstadt, Germany) or Sigma–Aldrich (Buchs, Germany). Zirconium, vanadium, titanium and molybdenum stock standard solutions (1000 mg kg^{-1}) produced respectively from ZrO_2 with traces of HF, V_2O_5 in 2% HNO_3, Ti metal in 2% HNO_3 and $(NH_4)MoO_4$ were obtained from Inorganic Ventures™ (Canada).

2.2. Apparatus

Differential pulse (DP) voltammograms were recorded using a 693 VA Processor and a 694 VA Stand and 757 VA Computrace (Metrohm AG), including a regular mercury multi-mode electrode (MME) from Metrohm. A glassy carbon electrode was used and all the potentials were quoted against an Ag/AgCl (3 mol L^{-1} KCl) reference electrode. Voltammetric measurements were performed in a conventional voltammetric cell (5–50 mL). The standard addition method was used to evaluate analyte concentrations through peak current measurements. A UV-irradiation device (UV digester 705, Metrohm AG) combined with a 500 W high pressure