



Dispersion and solubility of In, Tl, Ta and Nb in the aquatic environment and intertidal sediments of the Scheldt estuary (Flanders, Belgium)



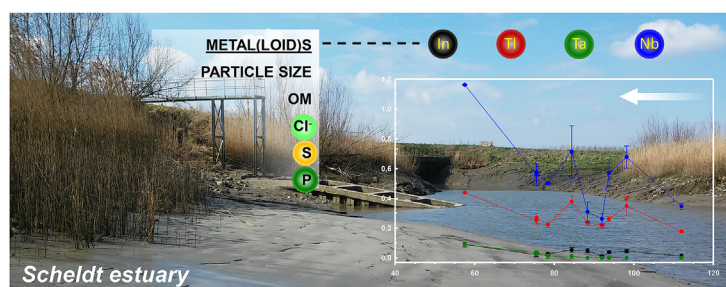
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HIGHLIGHTS

- Indium, thallium, tantalum and niobium is monitored in Scheldt estuary.
- The metal(loid)s correlate with sediment silt fraction, OM, S and P.
- Extreme low elemental solubility is associated to particle size, OM and salinity.

GRAPHICAL ABSTRACT



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ABSTRACT

Certain specialty elements are indispensable in modern technologies for their particular properties. Yet, potential risks associated to the release of these elements at any stage, remains unknown. Therefore, the dispersion of indium (In), thallium (Tl), tantalum (Ta) and niobium (Nb) in the aquatic environment of the Scheldt estuary (Flanders, Belgium) was studied. Maximum concentrations in intertidal sediments of $101 \pm 15 \mu\text{g kg}^{-1}$ for In, $481 \pm 37 \mu\text{g kg}^{-1}$ for Tl, $88 \pm 19 \mu\text{g kg}^{-1}$ for Ta and $1162 \pm 4 \mu\text{g kg}^{-1}$ for Nb appeared on the sampling location closest to the river mouth, i.e. 57.5 km upstream. Their distribution in the intertidal sediments depends on the physicochemical sediment characteristics along the flow of the river Scheldt. The same was the case for most other metals and aluminum as their occurrence also correlated ($p < 0.05$) with the occurrence of In, Tl and Nb. While in general, studied elements correlate to the OM content and sulfur and phosphorus herein included, a relative enrichment of In, Tl and Nb was seen at Rupelmonde (92.0 km from the river mouth). Mainly the intertidal sediment silt fraction is capable of retaining the elements by exchanging with other ions in the mineral interlayer. Increasing salinity towards the river mouth can furthermore induce the formation of insoluble chloride species. Overall, the solubility of In, Tl, Ta and Nb appeared extremely low upon extraction of pore water from intertidal sediments saturated to 100% field capacity.

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1. Introduction

Along with technological developments, the world demand for raw materials has increased exponentially. Not only the quantity, but also the complexity of the extracted minerals is reflected in our

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consumer goods (European Innovation Partnership on Raw Materials, 2016). When assessing the necessary input factors for an envisioned sustainable economy, a list of metals is considered essential. Some of these essential elements are considered critical when evaluating their demand and supply, including the geopolitical risks associated with the supply. The so-called technology-critical elements (TCEs) consist of gallium, germanium, indium, tellurium, niobium, tantalum, tellurium and thallium, besides the platinum group elements and most rare-earth elements (Cobelo-García et al., 2015).

The need for TCEs in specialty applications is related to their unique properties. As niobium and tantalum behave chemically very similar, they are both being extracted from columbite and tantalite minerals (Nowak and Ziolek, 1999). They both possess +V as most stable oxidation state and a molar volume V_m of $10.8 \text{ cm}^3 \text{ mol}^{-1}$ at room temperature. Niobium is, amongst others, used in permanent magnets, as catalyst in various chemical reactions and added to steel for premium applications. Tantalum is mainly employed in capacitors and finds its way to electronics. Indium on the other hand has an electron configuration $[^{36}\text{Kr}] 4d^{10} 5s^2 5p^1$, predicting the principal, non-zero oxidation state of +III. It is used as indium tin oxide in flat-panel displays. As phosphide (InP) or nitride (InN), they are common semi-conductor materials because of the small bandgap of the latter (Veal et al., 2010). Thallium also occurs in the IIIa +group, having oxidation states of +I and +III. Its applications include high-temperature superconductors and crystal filters for light diffraction. The 201 radioisotope of Tl is used in scintigraphy for medicine (Mckillop, 1980).

The use of TCEs in technologic applications rapidly led to a dispersion in the aquatic and terrestrial environment. While in most cases comparison with pre-industrial data is hardly possible, clear anthropogenic enrichment of certain TCEs can be found in nature. Elevated levels of Platinum Group Elements for example have been detected in urban areas all over Europe (Rauch et al., 2005). Table 1 summarizes the concentrations of indium, thallium, tantalum and niobium known in different environmental compartments. Indium was found to concentrate up to 14 times the average earth's crust distribution in an oligotrophic lake of central

Sweden (Tessier et al., 2014). In the direct vicinity (<1.5 km) of former lead and zinc smelters, even higher concentrations were found in the top 0–25 cm soil (Waterlot et al., 2013) or acid mine drainage (White et al., 2017). Less is known on the dispersion of other elements, in particular with regard to the fractionation and mobility. In part, this may be due to the severe analytical challenges in detecting ultra-trace elements at sub part per trillion levels.

While all TCEs are non-essential, they can have a severe impact on biologic processes (Harris and Messori, 2002). In this context, concerns on the effects of exposure on humans are rising. Since the metal toxicity is complex and hard to predict from individual properties (Okamoto et al., 2015), toxicological testing is required. Ralph and Twiss (2002) revealed that thallium was most toxic with Tl^{3+} being 50,000 times more toxic in comparison to Tl^+ . Tl^{3+} shows however a strong oxidation potential and is easily transformed to the more stable Tl^+ oxidation state (Sadowska et al., 2016), that resembles K^+ in physiologic processes (Peter and Viraraghavan, 2005). While intrinsically less toxic, In^{3+} is able to bind human serum transferrin, facilitating the transport through the blood stream and concentrate in tissues (Zhang et al., 2004; Harris and Messori, 2002). Besides, the toxicity of Nb(V) in terms of lowest-observed-effect concentration was found below the aqueous solubility and no effects were observed unless high doses are applied orally (Haley et al., 1962). Hence, an overall ranking of toxicity towards *Daphnia Magna* increases in the order of $\text{Nb} < \text{Ta} < \text{In} < \text{Tl}$, with the latter having the highest toxicity.

Information on the exposure is however incomplete to fully comprehend the associated risks (Filella et al., 2014). The current massive expansion of TCEs in a large number of technologies will certainly influence their environmental distribution as at any stage of the product lifetime, release in the biosphere is possible (Cobelo-García et al., 2015). This study monitored, on the one hand, the dispersion of In, Tl, Ta and Nb in the aquatic environment of the Scheldt estuary, in particular concentrations in surface water and intertidal sediment samples, and on the other hand determined the solubility of these elements. Along the Scheldt, the harbor of Antwerp, one of the major European harbors, and main industries of Flanders (Belgium) are located. Accordingly, sediments of the Scheldt estuary were previously already found to be polluted by other metals (Du Laing et al., 2009).

Table 1

Comparative overview of the presence of indium, thallium, tantalum and niobium in different environmental compartments.

Element concentrations	Indium	Thallium	Tantalum	Niobium
Sediments ($\mu\text{g kg}^{-1}$)	14.9 ± 6.9 ^b 72.3 ± 2.3 ^b 50–220 ^f 960 ^g	506–770 ^d 170–700 ^f 1760 ^g 330–14,000 ^e		
Soils ($\mu\text{g kg}^{-1}$)	17 ^h 51.7 ^b 80–1,560 ⁱ	20,840 ^k 940–2650 ^l 370–1180 ^m		19,000–24,000 ^j
Groundwater ($\mu\text{g L}^{-1}$)	9.3 ^c 20.1 ^b			
Surface water ($\mu\text{g L}^{-1}$)	0.0000–0.0004 ^b		0.0001 ^a	0.0004–0.0007 ^a

^a Firdaus et al. (2008).

^b Tessier et al. (2014).

^c Chen (2006).

^d Duan et al. (2012).

^e Ospina-Alvarez et al. (2014).

^f Grahn et al. (2006).

^g NCS DC 73310 Certified Reference Material.

^h Ladenberger et al. (2015).

ⁱ Waterlot et al. (2012).

^j Scansetti (1992).

^k Woch et al. (2013).

^l Gomez-Gonzalez et al. (2015).

^m Vaněk et al. (2016).

2. Materials and methods

2.1. Sampling site

Water ($N = 30$) and intertidal sediment ($N = 60$) samples were collected along the Belgian part of the Scheldt estuary. In total, 10 locations at the left bank between Kastel ($N 51^\circ 2' 25'' E 4^\circ 9' 56''$) and Doel ($N 51^\circ 22' 6'' E 4^\circ 15' 3''$) were considered (see Fig. 1); the latter being closest to the river mouth (57.7 km) and the Belgium–Dutch border. The exact geographic coordinates of all 10 locations and their distance to the river mouth are given in Table S1. The locations consist of marshes influenced by tidal movement, flooded by river water only at high tides. Surface water was collected by a sampling pole in 1 L quantity and in triplicate at a distance of 2 m from the river bank. All surface waters were stored at 4 °C in PTFE bottles with minimal headspace volume prior to analysis.

Intertidal sediment samples were taken during low tide in duplicate with 1 m spacing. For each replicate, at least 1 kg was collected using an auger at depths of 0–5 cm, 5–15 cm and the zone of 80 cm. The sediments were stored in PE bags for transport and opened to allow air drying at the laboratory.

To study the solubility of the selected elements as well, the pore water was successively collected from the 0–5 cm intertidal

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