



Seasonal variations of rare earths and yttrium distribution in the lowland Havel River, Germany, by agricultural fertilization and effluents of sewage treatment plants



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ABSTRACT

REE and Y (REY) distribution in the lowland Havel River passing the Federal State of Berlin, Germany, depends on contributions of point sources such pharmaceutical and high-tech industries, acid water from the open pit lignite mining, and medical application of very stable organic Gd chelates. Another omnipresent dispersed source of REY are water-soluble Ca-phosphates containing micro-amounts of Eu(II)-bearing barite as components of common agricultural fertilizers. After distribution in the field during the cold season (October through March) these Ca-phosphates dissolve and secondary phosphates and calcite precipitate both being enriched in light REE. Heavy REE are preferably exported by runoff together with part of the micro-contaminant barite leading to high Yb/Nd ratios in the Havel water and REY distribution patterns with only small Eu deficits. During the warm season (April through September) light REE together with phosphate are leached from secondary soil minerals by runoff. The micro-component barite is retained in vegetation-covered soil. Thus, REY patterns of Havel water show significant Eu deficits. The high Gd anomalies result from medical applications of Gd-chelates which after urination pass the sewage treatment plants. The seasonal variations of total Gd in the Havel River are artifacts based on seasonal locally varied discharge of effluents from sewage treatment plants. The natural Gd concentration of 8 pmol/l in the northern Havel is enhanced to 3300 pmol/l, when the Havel River leaves Berlin territory. The elimination of phosphate from Lake Tegel water affects the fractionation of REE but not the concentration of total Gd. Although enhanced in total phosphorus (TP), the REE concentrations in the water from the Spree River and the Teltow Canal are less than in the Havel water before their confluence. Only Yb and Lu do not decrease. The contributors of the Havel River are high in total organic carbon (TOC) and dissolved organic carbon (DOC) compared to the Havel water before their indicating that REY are preferentially sorbed by settling organic matter. Applying PHREEQC and assuming that only 10% of TP is present as ortho-phosphate yields that only carbonate complexes are essential.

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1. Introduction

The naturally occurring suite of the rare earth elements La to Lu is ubiquitous in hydrological systems. Including Y this group of elements is henceforth presented as REY. To a substantial extent their distribution in the hydrosphere depends on (i) formation of soluble chemical complexes, (ii) sorption onto surfaces of crystalline and amorphous matter (Dia et al., 2000; Ingri et al., 2000; Johannesson et al., 2004; Tweed et al., 2006; Tang and Johannesson, 2006; Willis and Johannesson, 2011), (iii) coprecipitation with alteration products, (iv) scavenging by Fe–Al oxyhydroxides (Bau, 1999; Ingri et al., 2000; Ohta and Kawabe, 2001; Quinn et al., 2004, 2006), and (v) concentration in and later release from the biosphere (Stille

et al., 2006a, 2006b; Sun et al., 1997; Takahashi et al., 2005, 2007; Texier et al., 1999). Besides the inorganic ligands such as carbonates and phosphates, humates in vegetation-covered catchments are considered a particularly important category of ligands because of their strong affinity for metals and their ubiquity in soils, sediments, pore-, ground- and surface water (Dupre et al., 1999; Lead et al., 1998; Willis and Johannesson, 2011).

Due to the interaction with bedrocks and sediments (Banks et al., 1999; Johannesson et al., 2000; Zhang et al., 2006) the REY abundance in river and lake water shows seasonal and temporal variations (Goldstein and Jacobson, 1988; Ingri et al., 2000; Leybourne and Johannesson, 2008; Sholkovitz, 1992, 1995). These variations are considered to reflect different types and rates of water/rock interactions. REE patterns of groundwaters from limestones resemble each other (Johannesson et al., 1997, 1999, 2000; Möller et al., 2003; Smedly, 1991). In groundwater from sandstones (Möller et al., 2003), basalts (Möller et al., 2003; Paces

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et al., 2001) and granites (Möller et al., 1997) the REE patterns differ from those of the aquifer rocks because of incongruent dissolution of REE-bearing major, minor and tracer minerals (Möller, 2000).

Anomalous Gd concentrations are recognized worldwide in rivers, coastal seawater, ground- and tap water because very stable organic Gd chelates of various chemical compositions but of similar chemical properties (Brücher, 2002) are applied in hospitals and by private radiologists as contrast enhancement agents in magnet resonance imaging (IMR) of the blood system since 20 years (Bau et al., 2006; Bau and Dulski, 1996; Elbaz-Poulichet et al., 2002; Hennebrüder et al., 2004; Knappe et al., 1999, 2005; Kulaksiz and Bau, 2007, 2011, 2013; Lawrence et al., 2006, 2009; Möller et al., 2000, 2002; Nozaki et al., 2000; Petelet-Giraud et al., 2009; Rabiet et al., 2009; Verplanck et al., 2005; Zhu et al., 2004). These Gd chelates are neither removed during sewage treatment nor by sorption onto particulate matter in surface water. They survive for months unchanged in the hydrosphere (Dulski et al., 2011). Recently anomalous concentrations of La and Sm were reported in the Rhine River, Germany, (Kulaksiz and Bau, 2011, 2013). The usage of REE in the high-tech products and their increase in garbage and industrial effluents will be responsible for long-term increase of REY in the hydrosphere.

Another important dispersed source are agricultural fertilizers which often contain REY contents of up to 1400 µg/g depending on their source material (Otero et al., 2005). Being produced from marine phosphorites the widespread compound NPK (nitrogen-phosphorus-potassium) fertilizers are rich in REY. The runoff from fertilized areas has to be considered as an omnipresent dispersed source of REY in the countryside. Different from industrial and medical sources, agricultural fertilization is bound to defined seasons of the year. Thus, the pollution by fertilizer is expected to create a seasonal trend of REY in runoff and surface water. The aim of this exemplary study is to search for such seasonal variation of REY abundance in the lowland Havel River when passing the Federal State of Berlin, Germany (Fig. 1). In such a low-flux system the seasonal variations of REE abundance are expected to be higher than in fast running rivers because of enhanced environmental interactions.

2. Hydrology of the study area

The lowland rivers Havel and Spree drain the Pleistocene countryside of Berlin, Germany, under conditions of a continental climate with annual precipitation of 500–600 mm. The Havel River passes the western part of the study area from north to south, whereas the Spree River flows east to west through the City of Berlin (insert of Fig. 1). Both rivers follow glacial troughs filled by Late Pleistocene sediments. Their drainage basins are either covered by mostly pine forests or are used for cattle breeding and agriculture on poor gley and sand-loam soils. Part of the Spree water originates from open pit lignite mining.

Based on different hydrological conditions the Havel River is subdivided into three sections (Fig. 1). The water chemistry of the Havel in Section 1 is dominantly controlled by the drainage basin north of Berlin with its wood-, grass- and farm land and to minor extend by the effluent of the stratified Lake Tegel. Lake Tegel receives contributions from the Nordgraben with its high organic and phosphorus loads from the sewage treatment plant STP-1, the Tegel-Fließ and some Havel water supplied by a pipeline. This water mix passes the phosphate elimination plant (PEP; Fig. 1) which was installed to reduce the eutrophication of the lake. By sorption onto FeOOH precipitates total phosphorus (TP) was reduced to levels of 8–20 µg/l (Schäuser and Chorus, 2007). Due to

abstraction by bank filtration for production of drinking water Lake Tegel discharges less than 0.6 m³/s into the Havel River.

In Section 2 downstream the lock Spandau (S-6; Fig. 1), the Havel water is mixed with a similar amount of Spree water which is strongly affected by effluents from STPs 2, 5, 6 and to a less degree from STP-1, water from the pharmaceutical industries from within the city of Berlin, and water from lignite mining before entering the study area. At the location S-20 the effluent from STP-2 is not included.

In Section 3 the Teltow Canal collects the effluents from STPs 3, 4, 5 and 6, and water from the lignite open pits via the river Spree. STP-2 only discharges its effluent during March through September via a pipe line into the Teltow Canal. In October to March the effluents are discharged into the River Spree (insert of Fig. 1).

3. Sampling

From May 2001 until December 2002 about monthly sampling of surface water was performed at 17 sampling locations (S) along the Havel River and its main contributors (Fig. 1). At all sampling points about 3 l of water were collected in polytetrafluorethylene (PTFE) bottles. Within 1–2 days these samples were filtered through encapsulated cellulose-acetate filter of 0.2 µm (Sartobran®, Sartorius) into PTFE bottles using a peristaltic pump. The filtrate was acidified to pH 2 and spiked with 1 ml containing 100 ng/g of both Pr and Tm. Aliquots of 10 ml of the spiked water were used for direct measurements of the spikes Pr, Tm and of total Gd.

All major and minor dissolved species, total phosphorus (TP), dissolved organic carbon (DOC) and total organic carbon (TOC) were analyzed by the Civil Service of Berlin in separate samples. Samples from Sections 1, 2 and 3 are characterized by numbers S-1 – S-10, S-20 – S-24 and S-30 – S-31, respectively.

4. Analytical procedure of REE

The conditioned water was passed through a Sep-Pac C₁₈® column (Water Corp., USA) preconditioned with a mixture of ethylhexyl-phosphates to collect rare earth elements (REE) and yttrium. The flow rate was 1 l per hour. Later, the columns were washed with 50 ml of sub-boiled 0.01 N HCl. REE were eluted with 40 ml of ultra-pure 6 M HCl. The eluates were evaporated to incipient dryness. Each of the residues was subsequently dissolved in 1 ml of 6 N ultra-pure HNO₃, transferred to a volumetric flask, where 1 ml of 100 µg/g Re and Ru spike were added for internal shift corrections and filled up to 10 ml by 0.5 M sub-boiled HCl. ICP-MS was used to determine REY. The detailed procedure of measurements and the corrections for molecular ion interferences are given by Dulski (1994) and Bau and Dulski (1996).

All samples were measured repeatedly by ICP-MS. Blanks were determined in 0.5 M HCl. The calibration solutions were prepared from stock solutions diluted with ultra-pure water to 0.5 N acidity. All measurements of the 350 water samples were corrected for the recovery of Pr and Tm spikes. The average efficiencies of Pr and Tm in the eluates were (94 ± 6)% and (90 ± 6)%, respectively. The Tm spikes were also high enough to be measured directly with recoveries of (95 ± 6)%, respectively.

5. Distribution of REE

5.1. REE patterns

The PAAS-normalized REE patterns of water from all sampling points along the Havel River (of which only 5 are presented in Fig. 2) show decreasing seasonal variations and declining spread of abundance of light REE downstream. In Section 1 sample S-2

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