Applied Geochemistry 47 (2014) 186–197

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Anthropogenic Rare Earth Element in rivers: Gadolinium and lanthanum. Partitioning between the dissolved and particulate phases in the Rhine River and spatial propagation through the Rhine-Meuse Delta (the Netherlands)

Gerard Klaver [a,b], Marc Verheul [c], Ingrid Bakker [d], Emmanuelle Petelet-Giraud [a,*], Philippe Négrel [a]

[a] *BRGM, Laboratories Division, 3 av. C. Guillemin, BP36009, 45060 Orleans, France*
[b] *Le Studium, CNRS, Orleans, France*
[c] *Deltares, Utrecht, The Netherlands*
[d] *Rijkswaterstaat, Lelystad, The Netherlands*

ARTICLE INFO

Article history:
Available online 9 June 2014
Editorial handling by M. Kersten

ABSTRACT

In this study, we report for the first time lanthanum and gadolinium anomalies at the catchment scale (Rhine-Meuse River system) together with the partitioning of their anthropogenic contents between the dissolved and the particulate phases. We compare the dissolved and total REE patterns of samples taken at 9 locations in the Rhine Branches including Lobith (situated at the German–Dutch border where the Rhine is not yet divided in three Branches), in surface water fed by the Rhine Branches (canals and lake IJsselmeer and Ketelmeer) and 3 locations where the water is derived from the river Meuse (originating from Belgium and France).

We demonstrate that the anthropogenic input of lanthanum in the German part of the Rhine River identified by Kulaksiz and Bau (2011) can be traced in the complex Rhine-Meuse Delta up to the North Sea. In the Dutch Branches of the Rhine River, in contrast to the German part of the Rhine River, the anthropogenic lanthanum (La_{ANTHRO}) is mainly present in the particulate phase (SPM) and not in the dissolved phase (defined as the <0.45 μm fraction). In the Meuse River no anthropogenic lanthanum was found. The amount of La_{ANTHRO} transported by the Rhine River at the Lobith station (German–Dutch border) varies from 2008 to 2010 between 3.7 and 5.2 tons/y in the dissolved phase, and between 28.8 and 37.4 tons/y in the particulate phase. However, a big discrepancy is evidenced when we compare the La_{ANTHRO} load calculated on bases of the total water samples with the La_{ANTHRO} load calculated as the sum of the particulate and dissolved load: the total La_{ANTHRO} load is roughly 2 times larger than the La_{ANTHRO} load calculated as the sum of the dissolved and particulate La_{ANTHRO} load. The difference between the two calculated fluxes is most likely caused by not sampling the finest fraction of the particulate pool in the SPM samples with an overflow centrifuge.

The anthropogenic gadolinium identified by high gadolinium anomalies in the REE patterns originates from numerous point sources (waste water treatment plant effluents) and can thus be considered as diffuse pollution when compared to anthropogenic lanthanum clearly resulting from a single source. The amount of anthropogenic gadolinium measured in the dissolved phase (main carrier of Gd) increases or decreases along the Rhine and Meuse Rivers depending whether or not the mixing water contains anthropogenic gadolinium, i.e. receives waste water effluents.

1. Introduction

The composition of suspended Rare Earth Elements (REE) in river water reflects the rock composition of its drainage basin. The greater the basin dimensions and its rock variation the higher resemblance of the suspended matter (SPM) to that of shale (e.g. Martin et al., 1976; Dupre et al., 1996; Dubinin, 2004). The composition of the dissolved REE in river water is governed by the chemical properties of the REE in solutions rather than the rock composition of the drainage basin (e.g. Goldstein and Jacobsen, 1988; Elderfield et al., 1990; Sholkovitz, 1993, 1995). The higher the pH value, the lesser the content of the dissolved REE and the greater the composition difference relative to that of shale.

---

[*] Corresponding author. Tel.: +33 2 38 64 37 75.
E-mail address: e.petelet@brgm.fr (E. Petelet-Giraud).

http://dx.doi.org/10.1016/j.apgeochem.2014.05.020
0883-2927/

Detection of an anthropogenic or natural REE anomaly in water is based on the presence of Rare Earth Elements which are higher or lower than their overall shale normalized geogenic patterns.

The first human impacted REE profiles were reported in German rivers in the mid-1990 by Bau and Dulski (1996) which identified large positive gadolinium anomalies resulting from Gd concentrations up to three orders of magnitude higher than geogenic background values. This positive Gd anomaly is now reported for all rivers worldwide flowing through densely populated areas and is caused by Gd-based contrast agents (Gd-CA) used in magnetic resonance imaging (MRI). Since the first approval of a Gd-CA (Magnevist®) in 1988, more than 100 million Gd contrast enhanced MRI scans are performed. Consequently Gd anomalies have been observed in rivers and lakes (Tricca et al., 1999; Nozaki et al., 2000; Elbaz-Poulichet et al., 2002; Möller et al., 2002, 2003; Knappe et al., 2005; Rabiet et al., 2005, 2006, 2009; Zhu et al., 2004, 2005; Verplanck et al., 2005; Kulaksiz and Bau, 2007, 2011; Lawrence et al., 2006; Petelet-Giraud et al., 2009), estuaries and coastal waters (Elbaz-Poulichet et al., 2002; Zhu et al., 2004; Kulaksiz and Bau, 2007; Lawrence, 2010), groundwater (Möller et al., 2000; Knappe et al., 2005; Strauch et al., 2008; Rabiet et al., 2009) and tap water (Bau and Dulski, 1996; Möller et al., 2002; Kulaksiz and Bau, 2011). Also in the Dutch Rhine-Meuse Delta significantly positive Gd anomalies are observed, showing no exception to these worldwide observations (Petelet-Giraud et al., 2009; Verheul and Klaver, 2011; Klaver et al., 2011; Verheul et al., 2011).

In a recent article, Kulaksiz and Bau (2011) reported dissolved La concentrations in the Rhine River downstream of the city of Worms (Germany) that are up to two orders of magnitude higher than the geogenic background. Kulaksiz and Bau (2011) showed that this strong La enrichment is of anthropogenic origin and traced the source to an effluent from a production plant for fluid catalytic cracking catalysts at Rhine river-km 447.4 (City of Worms, located more than 400 km stream upwards from the German–Dutch boundary, Fig. 1). The effluent is characterized by extremely high dissolved total REE and La concentrations of up to 52 mg L^{-1}. Such La concentrations are well-above those at which eco toxicological effects have been observed (Chen et al., 2003; Slatopolsky et al., 2005; Zhang et al., 2010). Due to the extremely high concentrations of La in the effluent plume relative to that of the Rhine River, the anthropogenic positive La anomaly still persists 400 km downstream near the German–Dutch border (Kulaksiz and Bau, 2011, 2013).

Lanthanum, as all REE, is increasingly used in high-tech products. Therefore, it can be expected that REE anomalies in river water will become more frequent and REE should be evaluated on a regular basis. Rijkswaterstaat, the governmental institute responsible for monitoring water quality in the Netherlands, implemented the REE in their regular monthly or biweekly monitoring program from January 2008 onward (Water Management in the Netherlands, 2009). In 2011 an evaluation of the collected data from 2008 till 2010 was executed together with REE experts from Deltares. Significant positive La anomalies were observed in multiple locations in the River Rhine, sub branches and surface water fed by the Rhine branches during this evaluation. To verify these anomalies, 140 dissolved (defined as <0.45 μm fraction) and total water (=dissolved + suspended matter (SPM)) samples from March and August 2010 were re-analyzed in the Deltares laboratory. The Deltares and Rijkswaterstaat data confirm the observed distinct La-anomalies in the dissolved shale normalized REE patterns of the River Rhine (Kulaksiz and Bau, 2011). In addition, our data show the presence of large La-anomalies in the shale normalized REE patterns of the total water samples (Verheul and Klaver, 2011; Verheul et al., 2011). In total water the REE pattern originates from the SPM fraction, indicating that anthropogenic La is not only present in the dissolved fraction (Kulaksiz and Bau, 2011) but mainly in the SPM fraction (Verheul and Klaver, 2011; Verheul et al., 2011).

Kulaksiz and Bau (2013) report the occurrence of another REE contaminant in the Rhine: in addition to anthropogenic Gd and La, from 2012 the Rhine River now shows also significant amounts of anthropogenic Sm. The anthropogenic Sm enters the River Rhine with the same industrial wastewater that caries the anthropogenic La and can also be traced through the Middle and Lower Rhine to the Netherlands (Kulaksiz and Bau, 2013 and Rijkswaterstaat unpubl. results).

In this paper we compare the shale normalized REE patterns of dissolved and total water. The samples were taken at 9 stations located along the River Rhine branches or surface water (canals and lakes) fed by the Rhine branches and 3 stations located along the River Meuse (Fig. 1). The evaluation of the REE patterns will mainly be based on data from 2010. First the spatial propagation of the La anomaly throughout the Rhine-Meuse Delta in the Netherlands is discussed. Secondly the dissolved and total anthropogenic lanthanum load of the Rhine water in Lobith for 2008, 2009 and 2010 is estimated and compared with the anthropogenic lanthanum load estimated from the REE content measured in the SPM.

2. Study area: the Rhine-Meuse Delta in the Netherlands

The description of the water distribution in the Rhine-Meuse Delta in the Netherlands is adapted from Arnold et al. (2011). An overview map with the major Rhine and Meuse Branches and the sample locations is given in Fig. 1.

The Rhine (average annual discharge at Lobith 2300 $m^3 s^{-1}$; min. discharge 620 $m^3 s^{-1}$ and max. discharge 12 600 $m^3 s^{-1}$) is fed by both rainwater and smelt water and crosses the border in the Netherlands at Lobith (Fig. 1). Stream downwards of Lobith the Rhine is split in 3 branches: Waal, Nederrijn and IJssel. The Waal has the highest discharge of the three and receives about 2/3 of the water. At the North Sea, the Waal and Nederrijn converge with the Meuse and the outflow to the North Sea via the Nieuwe Waterweg (Maassluis, Fig. 1) is regulated by the sluices in the Haringvliet (Scheelhoek, Fig. 1). At Kampen, the IJssel flows into Lake Ketelmeer which is directly connected to Lake IJsselmeer. The general quality of Lake IJsselmeer water is checked in Vrouwenzand and in the drinking water inlet point Andijk (Fig. 1).

Beside the main water systems from the river Rhine (Waal, Lek and IJssel) different canals are constructed to connect these water systems with important cities of the Netherlands. The water of the Amsterdam-Rijnkanaal is used as drinking water and the quality is monitored in Nieuwegein and Niewersluis (Fig. 1).

The River Meuse (average annual discharge at the Dutch-Belgium border 270 $m^3 s^{-1}$; min. discharge <25 $m^3 s^{-1}$ and max. discharge >4000 $m^3 s^{-1}$) crosses the Belgian-Dutch border at Eijsden and is solely fed by rain. At three drinking water inlets the water quality is monitored monthly: Heel, Brakel and Keizersveer (Fig. 1). The Meuse stations are used as control sites.

3. Analytical methods

Rijkswaterstaat lab: Sampling and storage of water and suspended matter samples are carried out according to standard protocols. Suspended matter is sampled with an overflow centrifuge. River water is fed into the centrifuge, equipped with a Teflon sheet onto which suspended matter is collected by centrifugal forces.

Dissolved REE concentrations are analyzed after filtration of the water over a 0.45 μm filter. To 50 ml of the filtered (dissolved) and