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Anthropogenic dissolved and colloid/nanoparticle-bound samarium, lanthanum and gadolinium in the Rhine River and the impending destruction of the natural rare earth element distribution in rivers

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ABSTRACT

The strong increase in the consumption of rare earth elements (REE) in high-tech products and processes is accompanied by increasing amounts of REE released into the environment. Following the first report of Gd contamination of the hydrosphere in 1996, anthropogenic Gd originating from contrast agents has now been reported worldwide from river and estuarine waters, coastal seawater, groundwater and tap water. Recently, microcontamination with La, that is derived from a point source where catalysts for petroleum refining are produced, has been detected in the Rhine River in Germany and the Netherlands. Here we report the occurrence of yet another REE microcontamination of river water: in addition to anthropogenic Gd and La, the Rhine River now also shows significant amounts of anthropogenic Sm. The anthropogenic Sm, which enters the Rhine River north of Worms, Germany, with the same industrial wastewater that carries the anthropogenic La, can be traced through the Middle and Lower Rhine to the Netherlands. At Leverkusen, Germany, some 250 km downstream from the point source at Worms, anthropogenic Sm still contributes up to 87% of the total dissolved Sm concentration of the Rhine River. Results from ultrafiltration suggest that while the anthropogenic Gd is not particle-reactive and hence exclusively present in the truly dissolved REE pool (<10 kDa), the anthropogenic La and Sm are also present in the colloidal/nanoparticulate REE pool (between 10 kDa and 0.2 μm). Though difficult to quantify, our data suggest that the Rhine River may carry up to 5700 kg of anthropogenic La, up to 584 kg of anthropogenic Sm, and up to 730 kg of anthropogenic Gd per year toward the North Sea. There exist no regulatory limits for dissolved REE in natural waters, but total REE and Y ($\sum$REY) concentrations of up to 0.14 mg/kg in the plume downstream of and 52.2 mg/kg at the head of an effluent pipe at Rhine-km 447.3 at Worms get close to and well-above, respectively, the levels at which ecotoxicological effects have been documented. Because of the increasing use of REE and other formerly "exotic" trace elements in high-tech applications, these critical metals have now become emerging contaminants that should be monitored, and it appears that studies of their biogeochemical behavior in natural freshwaters might soon no longer be possible.

1. Introduction

The rare earth elements (REE) belong to the group of critical metals that are of strategic importance for the development of key technologies, such as wind turbines, electrical car engines, medical diagnostics and petroleum refining. World demand for REE is projected to increase from 136,000 t per year in 2010 to at least 185,000 t by 2015 (Humphries, 2011), and the rising consumption of REE for high-tech products and processes leads to the release of increasing amounts of REE into the environment, either as solid or as dissolved phase.

The first report of an anthropogenic REE component in natural waters was published in the mid-1990s (Bau and Dulski, 1996) when anomalously high concentrations of Gd were detected in rivers in Germany. The ultimate source of the elevated Gd concentrations are Gd-based contrast agents used in medical diagnostics (magnetic resonance imaging, MRI), which reach surface waters with the clear-water discharge from wastewater treatment plants (WWTP). Since then, anthropogenic Gd has been reported worldwide, from rivers, lakes, ground water, tap water and coastal seawater (Bau and Dulski, 1996; Bau et al., 2006; Elbaz-Poulichet et al., 2002; Knappe et al., 2005; Kulaksız and Bau, 2007, 2011a, 2011b; Lawrence et al., 2006; Lawrence, 2010; Möller et al., 2000, 2002, 2003; Morteani et al., 2006; Nozaki et al., 2000; Petelet-Giraud et al., 2009; Rabiet et al., 2005, 2009; Tricca et al., 1999; Verplanck et al., 2005; Zhu et al., 2004, 2005).

Recently, we have shown that the Rhine River, Germany, carries significant amounts of anthropogenic La and to a lesser extent other light REE (LREE), apparently as a dissolved (<0.2 μm-sized) microcontaminant (Kulaksız and Bau, 2011a). This La contamination has also been observed in the Rhine River in the Netherlands (Verheul et al., 2011). We had suggested that anthropogenic

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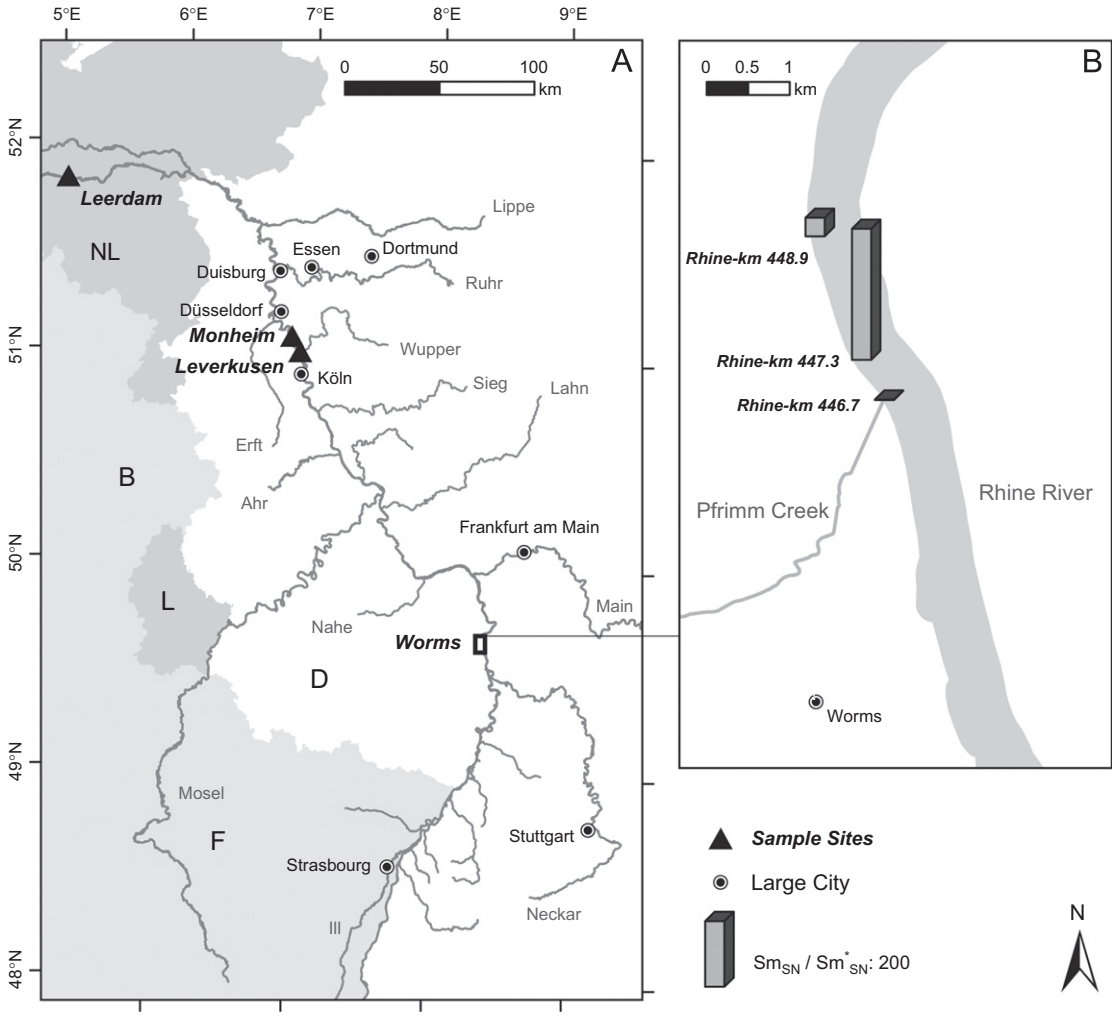

Fig. 1. Simplified map of (A) the Middle and Lower Rhine River and (B) a close-up of the area north of Worms, Germany, showing sampling sites and the location where the anthropogenic Sm anomaly (illustrated as Sm_{SN}/Sm^{*}_{SN}) first occurs. For further explanation see text.

contamination of the hydrosphere with formerly "exotic" trace elements would likely accelerate in the near future and, using the REE as examples, had cautioned that these emerging microcontaminants would likely soon present very severe difficulties for studies of the biogeochemical behavior of these elements in pristine environments.

Only a few months later, this pessimistic view is already confirmed. We here report another anthropogenic REE microcontamination: between mid-October 2010 and mid-May 2011 small but significant amounts of anthropogenic Sm have started to appear in the Rhine River in Germany and the Netherlands. Ultrafiltration revealed that, similar to anthropogenic La and Gd, part of this anthropogenic Sm is truly dissolved. However, in contrast to the anthropogenic Gd that is exclusively present in the truly dissolved REE pool, considerable fractions of anthropogenic Sm and La are also bound to colloids and nanoparticles present in the river water.

2. Methods

2.1. Sampling and analysis

Surface water samples from the Rhine River were collected at Leverkusen (Rhine-km 703), Germany, and at Leerdam (Rhine-km 946), the Netherlands (Fig. 1a). To check for potential analytical artifacts, we also sampled and processed water from the pristine Wiembach Creek at Leverkusen–Opladen, Germany. In spring of 2012 (1 April, '12), we sampled the Rhine River between Rhine-km 446.7 and 448.9 (Fig. 1b), i.e. 600 m upstream and 1600 m downstream from the site where industrial effluent enters the river at Rhine-km 447.3 and causes the previously observed contamination with La (Kulaksız and Bau, 2011a). Unfortunately, the head of the effluent pipe was inaccessible due to high water level of the Rhine River and the sample closest to the pipe could only be taken at about 2 m distance downstream and was already substantially diluted with Rhine River water. Sampling, sample treatment, and chemical analyses followed our routine protocol as described previously (Kulaksız and Bau, 2007, 2011a, 2011b; and references therein), with the exception of the three samples from 1 April, '12, which were analyzed without any preconcentration.

The good overall reproducibility of the method employed is shown by the very close match of measured REE concentrations of two independently processed aliquots of a single Rhine River sample from 14 May, '11 (Table 1). We also emphasize that the pristine Wiembach Creek does not show any anthropogenic REE anomalies (Fig. 2), demonstrating that the anomalies observed in the Rhine River samples do not represent sampling or analytical artifacts.

In addition to the 0.2 μm filtration, one sample from the Rhine River (18 January, '12) was additionally ultrafiltered