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 (∑REE) 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.

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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...
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.
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<td>28</td>
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REE concentrations in italics are interpolated and not measured (see text). Sample "nanopartic." is the difference between the < 0.2 µm and < 10 kDa fractions (see text).
through a cross-flow ultrafiltration system. 3000 mL of unacidi-
fied sample volume were passed through a Vivaflow 50 unit
(10 kDa MWCO) similar to that described by Schlosser and Croot
(2008), before the ultrafiltrate was processed using the same
separation/preconcentration method employed in analyzing the
other samples.

We report concentrations in the < 0.2 μm REE pool as “dissolved”
(i.e. comprised of REE bound to colloids/nanoparticles, truly dissolved
REE and dissolved chemical REE complexes), while REE concentra-
tions in the < 10 kDa pool are referred to as “truly dissolved”. The
difference between the truly dissolved and the dissolved REE con-
centrations represents the colloid/nanoparticle-bound REE concentra-
tion which we refer to as “nanoparticulate” REE pool for convenience.

2.2. Quantification of REE anomalies

In shale-normalized REE patterns (REE$_{\text{SN}}$, Post Archean Australian
Shale, PAAS, McLennan, 1989) of pristine rivers, the elements from
La to Gd form one coherent group, while Tb to Lu form another one.
The two groups are separated by a small “step” down between Gd
and Tb (Fig. 2, Wiembach Creek). Because of the numerous REE
anomalies in Rhine River water the following equations have to be
used to quantify the anomalies in the REE$_{\text{SN}}$ patterns:

\[
\log \text{La}^{*}_{\text{SN}} = (2 \log \text{Nd}_{\text{SN}} - \log \text{Eu}_{\text{SN}}) \quad (1a)
\]

\[
\log \text{Sm}^{*}_{\text{SN}} = (2 \log \text{Eu}_{\text{SN}} + \log \text{Nd}_{\text{SN}})/3 \quad (1b)
\]

\[
\log \text{Gd}^{*}_{\text{SN}} = (4 \log \text{Eu}_{\text{SN}} - \log \text{Nd}_{\text{SN}})/3 \quad (1c)
\]

where the subscript SN denotes normalization to PAAS, and
the superscript * denotes the geogenic background (extrapolated/
interpolated).

Note that this approach cannot be applied to slightly acidic
rivers rich in organic colloids, such as the Amazon River and other
tropical rivers, as these typically show middle REE-enriched REE$_{\text{SN}}$
patterns and not the subdivision into a La–Gd and Tb–Lu trend
observed in rivers in temperate latitudes. We emphasize that we
use Eu to quantify and/or illustrate the anthropogenic Sm input,
although Eu can be decoupled from the other REE due to its
unique redox behavior and, therefore, may show anomalies in
normalized REE patterns. However, because the major tributaries
to the Rhine River and the main river itself upstream from Worms
do not show any Eu$_{\text{SN}}$ anomaly, this element can be used in the
normalization procedure of these samples. We caution, however,
that this prerequisite has to be verified before Eq. (1b) is applied
to a river water data set.

Fig. 2. REE$_{\text{SN}}$ patterns of pristine Wiembach Creek at Leverkusen showing smooth
REE patterns without any anthropogenic anomalies, the Rhine River at Leverkusen
(Bau and Dulski, 1996) showing a small anthropogenic Gd anomaly, and the Rhine
River at Monheim (2010) showing large positive anthropogenic La and Gd
anomalies.

Fig. 3. REE$_{\text{SN}}$ patterns of the Rhine River sampled during low-discharge periods in 2011 (A) and high-discharge periods in 2012 (B), showing anthropogenic positive La, Sm,
and Gd anomalies.
For each anomalous REE, the anthropogenic component can be calculated using the following equations:

\[
REE^* = REE_{SN} \times \frac{REE_{PAAS}}{REE_{SN}} \quad (2a)
\]

\[
REE_{\text{anthropogenic}} = \frac{REE_{\text{measured}}}{REE_{\text{PAAS}}} - REE^* \quad (2b)
\]

where REE may be La, Sm or Gd, and \([REE_{PAAS}]\) is the concentration of the respective REE in PAAS.

Note that positive Sm anomalies which have been observed in international reference standards of seawater and river water, are considered artifacts of standard preparation (e.g., Lawrence and Kamber, 2007; and references therein) or artifacts of sample filtration (Möller et al., 2003), and are not due to an anthropogenic Sm contamination of the water. We reiterate that the lack of any Sm (and La and Gd) anomaly in samples from the pristine Wiembach Creek (Fig. 2), that were processed together with the Rhine River samples, shows that such artifacts did not affect our data.

3. Results

3.1. Dissolved REE

Dissolved concentrations of purely geogenic Yb in the Rhine River samples taken at Leverkusen vary by a factor of 2.4 and cover a rather small range from 1.55 ng/kg (14 May, ‘11) to 3.78 ng/kg (1 January, ’12). This concentration range is similar to previously published REE data for the Rhine River at the same location (3.88 ng/kg, Bau and Dulski, 1996; and 2.44 ng/kg, Kulaksız and Bau, 2011a), and to the general range observed in other European rivers (Gaillardet et al., 2003). The Rhine River samples with highest REE concentrations have been taken during times of high discharge and turbidity in January 2012 (Table 1) and the high concentrations are very likely related to the presence of large amounts of colloids and nanoparticles.

The REE_{SN} pattern of the Rhine River sample taken at Monheim (12.7 km downstream from Leverkusen) in October 2010 (Fig. 3) is characterized by prominent anthropogenic positive anomalies of La (La_{SN}/La_{SN}^g = 30) and Gd (Gd_{SN}/Gd_{SN}^g = 8.5). While the anthropogenic Gd is derived from diffuse sources (WWTP effluents in the catchment of the Rhine River and its tributaries), the anthropogenic La originates from a point source at Rhine-km 447.3, where catalysts for petroleum refining are produced. This particular sample (Monheim, October ’10) carries no other anthropogenic anomalies and confirms the findings of Kulaksız and Bau (2011a).

In marked contrast, all Rhine River samples taken at Leverkusen after October 2010 show anomalously high Sm concentrations (Fig. 3) that are up to 7.7 times higher than geogenic background values, producing a positive Sm anomaly in REE_{SN} patterns (Sm_{SN}/Sm_{SN}^g = 2.1 – 7.7). These samples also show anthropogenic positive La (La_{SN}/La_{SN}^g = 6.0–23) and Gd anomalies (Gd_{SN}/Gd_{SN}^g = 1.4–11).

Similar to the La and Gd anomalies, this positive Sm anomaly still persists at Leerdam (Rhine-km 946), the Netherlands, some 243 km downstream from Leverkusen (Fig. 2). We emphasize that our control sample from Wiembach Creek does not show any positive La, Gd or Sm anomaly (Fig. 2). Our post-October 2010 REE data from the Rhine River at Leverkusen, Germany, represents the first report of dissolved anthropogenic Sm anomalies found in natural waters.

Bulk dissolved REE (\(\sum^*\text{REE}\)) concentrations at Leverkusen range from 45 ng/kg (14 May, ’11) to 179 ng/kg (1 January, ’12). Anthropogenic La accounts for >83% of total La and anthropogenic Gd for >77% of total Gd. This is consistent with previously published data for the Rhine River (Kulaksız and Bau, 2011a).

Anthropogenic Sm concentrations at Leverkusen range between 5.0 and 7.3 ng/kg on top of geogenic background concentrations of 0.96 and 1.1 ng/kg, respectively; the anthropogenic Sm represents 84% and 87% of total Sm.

North of Worms, around Rhine River km 447.3 (Fig. 1b) where industrial effluents from a production facility for catalysts used in petroleum refining enter the river, the anthropogenic REE load changes substantially. From 600 m upstream of the effluent pipe to 1600 m downstream of it, Sm and La concentrations increase strongly from 7.96 ng/kg to 852 ng/kg and from 31.5 ng/kg to 7790 ng/kg, respectively. At a distance of 2 m downstream from the head of the effluent pipe, i.e. within the plume where pure effluent mixes and is already substantially diluted with Rhine River water, REE concentrations are highest (\(\sum^*\text{REE} = 139.8 \mu g/kg\)) with very significant anomalous enrichments of La (115 \mu g/kg) and Sm (13.1 \mu g/kg). While the sample from 600 m upstream of the effluent pipe shows only a strong positive Gd anomaly, the samples from 2 m and 1600 m downstream of the pipe head also display pronounced positive La and Sm anomalies (Fig. 4).

3.2. The truly dissolved and nanoparticulate REE pools

In order to investigate the physical speciation of the dissolved anthropogenic La, Sm and Gd, i.e. their association with truly dissolved compounds and/or colloids/nanoparticles, an aliquot of the Rhine River sample from 18 January, ’12, was subjected to ultrafiltration (\(<10\ \text{kDa}\)). Concentrations in the nanoparticulate pool (10 kDa–0.2 \mu m) have been calculated by subtracting concentrations in the truly dissolved pool (\(<10\ \text{kDa}\) ultrafiltrate) from those in the dissolved (\(<0.2\ \mu m\) pool):

\[
REE_{\text{nanoparticulate}} = \text{REE}_{0.2\ \mu m} - \text{REE}_{<10\ \text{kDa}} \quad (3a)
\]

\[
REE_{o.2\ \mu m} \quad \text{Rhine-km 447.3}
\]

\[
REE_{<10\ \text{kDa}} \quad \text{Rhine-km 448.9}
\]

\[
REE_{<10\ \text{kDa}} \quad \text{Rhine-km 446.7}
\]

Fig. 4. REE_{SN} patterns of samples taken 400 m upstream and 2 m and 1600 m downstream of an effluent pipe at Rhine-km 447.3. Note the high REE concentrations and the first appearance of positive La and Sm anomalies downstream of the effluent pipe.
ticulate pools are 3.18, 2.20 and 0.975 ng/kg respectively. Dissolved Yb in the dissolved, truly dissolved and nanopar-ticulate pool. Dissolved Yb in the dissolved, truly dissolved and nanoparticulate pools in Rhine River water (18 January, ‘12). Notice that in marked contrast to Gd, significant La and Sm anomalies are also present in the nanoparticulate pool.

Removal of REE through ultrafiltration, i.e. the percentage associated with nanoparticulates, can be calculated by

$$\%_{\text{removal}} = \left( \frac{\text{REE}_{\text{nanoparticulate}}}{\text{REE} \times 0.2 \mu m} \right) \times 100 \quad (3b)$$

Bulk REE concentration (151 ng/kg $\sum_{\text{REE}}$) in the dissolved pool ($<0.2 \mu m$, 18 January, ‘12) is at the high end of the concentration range of our dataset, but similar to concentrations in the water sampled at Leerdam and Leverkusen in January ‘12, during a time of high discharge and turbidity. After ultrafiltration, the truly dissolved pool ($<10 \mu m$, 18 January, ‘12) carries 46 ng/kg $\sum_{\text{REE}}$, with the difference of 105 ng/kg attributed to the nanoparticulate pool. Dissolved Yb in the dissolved, truly dissolved and nanoparticulate pools are 3.18, 2.20 and 0.975 ng/kg respectively.

Fig. 5 shows the $\text{REE}_\text{SN}$ patterns of the truly dissolved and nanoparticulate REE pools in Rhine River water (18 January, ‘12). While the truly dissolved pool displays anthropogenic positive La ($\text{La}_{\text{SN}}$/La$_{\text{N}}$=8.0), Sm ($\text{Sm}_{\text{SN}}$/Sm$_{\text{N}}$=2.4) and Gd ($\text{Gd}_{\text{SN}}$/Gd$_{\text{N}}$=2.4) anomalies in a $\text{REE}_\text{SN}$ pattern that closely resembles those of the Rhine River during times of low river discharge (Fig. 3a), the nanoparticulates only show positive La ($\text{La}_{\text{SN}}$/La$_{\text{N}}$=5.7) and Sm ($\text{Sm}_{\text{SN}}$/Sm$_{\text{N}}$=2.2) anomalies, but no positive Gd anomaly, in a general $\text{REE}_\text{SN}$ pattern that is slightly enriched in the middle REE.

4. Discussion

4.1. Samarium as another emerging REE microcontaminant

Significant amounts of anthropogenic Sm first appeared in the Rhine River at some time between October 2010 and May 2011 (Fig. 3). The presence of both, anthropogenic Sm and La, in the ultrafiltrate of Rhine River water (Fig. 5) indicates that, similar to anthropogenic La, anthropogenic Sm occurs as a water-soluble Sm compound, and hence there is no obvious reason why its chemical speciation should differ from that of anthropogenic La. The spatial distribution of the anomalous Sm enrichment (Fig. 1b and Fig. 4) clearly demonstrates that the anthropogenic Sm originates from the same industrial cracking catalyst production effluent that causes the La contamination.

Like other REE, Sm finds applications in many different areas, from high-strength permanent magnets to control rods in nuclear reactors. It is used as a catalyst in assisting the decomposition of plastics, the dechlorination of polychlorinated biphenyls (PCBs) (Emsley, 2011), and the dehydration and dehydrogenation of ethanol (Hammond, 2011); Sm(II) iodide is commonly used as a reducing and coupling agent in organic synthesis (Girard et al., 1980).

4.2. Truly dissolved and nanoparticulate anthropogenic REE

Comparison of REE concentrations (Table 1) in the dissolved and truly dissolved pools of Rhine River water (18 January, ‘12) show that removal of geogenic REE by ultrafiltration is most significant for the LREE and decreases systematically with increasing atomic number from 83% for Ce and 66% for Eu down to only 30% for Yb and Lu. This is in line with previous results that have suggested that the heavy REE occur predominantly in the truly dissolved pool, whereas the light REE are more particle-reactive and are rather associated with the nanoparticulate pool (Elderfield et al., 1990; Sholkovitz, 1992, 1995).

The lack of a positive Gd anomaly in the nanoparticulate REE pool (Fig. 5) demonstrates that anthropogenic Gd is not particle-reactive, and that it exclusively partitions into the truly dissolved REE pool. This agrees with previous results (Knappe et al., 2005; Kulaksız and Bau, 2007; Kunnemeyer et al., 2009; Morteani et al., 2006) suggesting that anthropogenic Gd speciation is dominated by highly stable and water soluble chemical complexes with long environmental half-lifes (e.g., Gd-based contrast agents, such as Gd-DTPA). In marked contrast, La and Sm show no clear preference for the truly dissolved or the nanoparticulate pool (Fig. 5), demonstrating that anthropogenic La and Sm are both particle-reactive and behave rather similar to the geogenic REE. For La, this is in agreement with results of Verheul et al. (2011) for the Dutch part of the Rhine River, that demonstrate that the anthropogenic positive La anomaly is also observed in the > 0.45 μm sized particulate REE pool.

4.3. Quantifying anthropogenic REE transport via the Rhine River

The amounts of anthropogenic REE transported via the Rhine River toward the North Sea are difficult to quantify: input of anthropogenic Gd depends on the number of MRI scans in the catchment of a WWTP and on the ratio of Gd-contaminated domestic sewage water relative to uncontaminated industrial sewage and surface run-off, while input of La and Sm depends on the level of catalyst production. There might be loss of anthropogenic REE within the river due to sorption onto settling particles or even bioaccumulation. Rainfall causing increasing river discharge might also affect concentrations because of dilution of the anthropogenic signal, and/or increasing the (colloidal) particulate load of a river.

Hence, depending on the sampling date, anthropogenic REE transport by the Rhine River varies significantly: at Leverkusen, for example, between 0.9–15.5 kg/day for La, 0.4–1.6 kg/day for Sm, and 0.9–2.0 kg/day for Gd. Despite the large range, these numbers suggest that the Rhine River Alone carries every year between 330–5700 kg of anthropogenic La, 146–584 kg of anthropogenic Sm, and 329–730 kg of anthropogenic Gd toward the North Sea. These amounts are not trivial, particularly considering...
that the anthropogenic La and Sm appear to be derived from a single point source.

4.4. Environmental impact of anthropogenic REE

The (eco)toxicity of the REE not only depends on their concentration but also on the mode of administration, with the intraperitoneal route resulting in much higher toxicity levels than the oral route (Bruce et al., 1963; Haley et al., 1961, 1963, 1964a, 1964b, 1966). Since all REE have similar ionic radii and are mostly trivalent, they not only show similar geochemical behavior, but also similar (eco)toxicological behavior. The calcium inhibiting function of La³⁺, for example, is at least qualitatively shared by other trivalent REE (Weiss and Goodmann, 1975). Hence, when discussing (eco)toxicologically effective concentrations, the concentration of bulk REE and Y (ΣREF), i.e. total REE concentration including the concentration of Y (which is the geochemical twin element of Ho and hence shows similar behavior, e.g., Bau, 1996), should be discussed, rather than the concentration of an individual REE. The ΣREF concentration in the truly dissolved, nanoparticulate and dissolved pools of Rhine River water at Leverkusen (18 January, ’12) are 185 ng/kg, 63 ng/kg, and 122 ng/kg, respectively.

Unfortunately, the bulk REY concentration (ΣREF) is usually not considered and existing experimental studies have focused on individual REE instead. Shi et al. (2006a, 2006b), for example, reported pathological effects in the kidneys and livers of rats subjected to Sm nitrate at Sm concentrations in the mg/kg range and demonstrated degradation in learning and memory functions in populations exposed to low Sm (3.0 mg/kg) and intermediate Sm (4.5 mg/kg) concentrations. Liver damage in rats occurs at La concentrations of 20 mg/kg (Chen et al., 2003), and Zhang et al. (2010) have shown significant adverse effects on the growth and reproduction of worms (Caenorhabditis elegans) at La concentrations above 1.39 mg/kg. Moreover, Sun et al. (1996) have also shown that bioaccumulation of LREE occurs in internal organs of carp (Cyprinus carpio L.).

Concentrations of dissolved Sm and ΣREF in the lower reaches of the Rhine River at Leverkusen are below concentrations found to be toxic in these studies. However, the highest dissolved Sm concentration in the effluent plume (sampled on 1 April, ’12) is 13.1 μg/kg at Rhine-km 447.3 and still 0.85 μg/kg some 1600 m downstream at Rhine-km 448.9. The dissolved ΣREF concentration at Rhine-km 447.3 is 140.1 μg/kg. The purest effluent sampled to date (sampled during a low-discharge period on 27 October, ’10 (Kulaksız and Bau, 2011a), i.e. before the occurrence of an anthropogenic Sm anomaly in the Rhine River) shows a dissolved ΣREF concentration as high as 52.2 mg/kg (Table 1). Nevertheless, considering the exact sampling point, even this sample was diluted by “normal” Rhine River water, suggesting that the concentrations observed are below those of pure effluent.

We emphasize that the dissolved ΣREF concentrations detected are up to 50 times above the concentration levels at which ecotoxicological effects have been observed. Considering that bioaccumulation of REE has been observed in carp (Sun et al., 1996) and that the river bank close to the effluent pipe is a popular fishing spot, a study focusing on the potential effects of this REE (micro)contamination on the local fish population seems warranted.

5. Conclusions

This study of the REE distribution in the Rhine River, Germany, is the first report of an anthropogenic Sm anomaly in natural waters. The anthropogenic Sm enters the Rhine River at the same site at Worms, Germany, via the same industrial effluent from a facility producing catalysts for petroleum refining, that causes the La contamination in the Rhine River. Similar to anthropogenic La, but in marked contrast to anthropogenic Gd, this Sm originates from a point source. Anthropogenic dissolved Sm concentrations (in the < 0.2 μm filtrate) are as high as 7.30 ng/kg and constitute up to 87% of the total dissolved Sm. Even at Leerdam (at Rhine-km 946, some 240 km downstream of Leverkusen and 500 km downstream of the point source), 3.1 ng/kg of anthropogenic Sm is observed, which represents 37% of the total dissolved Sm. All anthropogenic elements (La, Sm, and Gd) taken together constitute up to 82% of ΣREF in the Rhine River at Leverkusen. While these concentrations are well-below the threshold of about 1 mg/kg at which ecotoxicological effects have been observed, REY concentrations are significantly higher in the effluent plume downstream of the effluent pipe at Rhine-km 447.3 (ΣREF up to 52 mg/kg) and exceed the above mentioned ecotoxicological threshold by one and a half orders of magnitude.

The addition of anthropogenic Sm anomalies to the already severely distorted REE pattern of the Rhine River signals once again the immediate danger that is ahead both for the quality of natural waters and for our ability to study them using REE. With the rapidly increasing demand for REE and the rising number of applications, more anthropogenic REE are expected to enter the environment in the near future. Hence, the fate and pathways of anthropogenic REE should be thoroughly studied, including any potential (and synergetic) toxicity, while distribution and behavior of the natural REE in different compartments of the environment should be closely monitored. The former is essential from a health point of view, and the need for the latter is acute, as establishing REE background concentrations in industrialized countries will soon no longer be possible due to widespread contamination. Considering that the increasing use of formerly exotic high-tech metals is not confined to the REE, the situation regarding the rare earths is just the prelude of what may soon happen with other trace elements that are destined to become emerging contaminants.

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