Bau, M. & Dulski, P. (1996): Anthropogenic origin of
positive gadolinium anomalies in river waters. – Earth
and Planetary Science Letters, 143 (1-4): 245-255,
6 Abb., 4 Tab.; Amsterdam.

ELSEVIER

Earth and Planetary Science Letters 143 (1996) 245–255

EPSL

Anthropogenic origin of positive gadolinium anomalies in river waters

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Received 29 April 1996; accepted 27 June 1996

Abstract

Positive Gd anomalies in shale-normalised rare earth element (REE_{SN}) patterns of natural waters may provide information on the types of ligands which control surface complexation of REE on particle surfaces. However, REE_{SN} patterns of rivers which drain densely populated and industrialised areas in Central Europe and North America are characterised by pronounced positive Gd_{SN} anomalies, whereas rivers in thinly populated, non-industrialised areas in Värmland and Dalarna, central Sweden, and Hokkaido, Japan, do not show such anomalies. Acidification experiments suggest that, unlike the other REE, the excess Gd found in German rivers is almost completely related to the 'dissolved' REE fraction (< 0.2 μm) in a water sample and not to the acid-soluble particulate fraction, suggesting a negligible particle reactivity of the excess Gd. The positive Gd_{SN} anomalies are of anthropogenic origin and are most likely to result from the application of gadopentetic acid, $Gd(DTPA)^{2-}$, in magnetic resonance imaging (MRI). In MRI, gadopentetic acid, which is an organic aqueous Gd(III) complex with very high stability constant, is used as a paramagnetic contrast agent. Since positive Gd_{SN} anomalies in rivers, lakes, semi-closed sea basins, and coastal seas, which receive riverine REE input from industrialised, densely populated areas may (partly) be of anthropogenic origin, the positive Gd_{SN} anomaly can no longer be used as a natural geochemical indicator.

Keywords: rare earths; surface water; rivers; pollution; gadolinium; drinking water; environmental geology; nuclear magnetic resonance

1. Introduction

In geochemistry and chemical oceanography the rare earth elements (REE) are widely applied as tracers of processes and/or sources because of their coherent behaviour [1–3]. Except for surface waters, seawater in all oceans shows shale-normalized (suffix SN) REE patterns with positive anomalies of La_{SN} and Gd_{SN} [4,5]. These anomalies result primarily from the lower stabilities of surface complexes of La and Gd compared to those of their respective neighbours in the REE series [6,7]. Although the size of the Gd_{SN} anomaly in seawater, which may be quantified by:

$$Gd_{SN}/Gd^{*}_{SN} = Gd_{SN}/(0.33Sm_{SN} + 0.67Tb_{SN}) \qquad (1)$$

is only small ($Gd_{SN}/Gd^{*}_{SN} < 1.2$), it is used as an indicator of the types of ligands that control surface complexation of REE on marine particles [8]. However, it is not known yet, whether the positive Gd_{SN}

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PII S0012-821X(96)00127-6

anomaly is generated entirely within the marine environment or whether it is (at least to some extent) already present in continental run-off. This lack of knowledge partly results from the fact that most REE data for river waters have been obtained by isotope dilution methods which do not provide data for monoisotopic elements such Tb, which is the neighbour to Gd in the REE series. Inductively Coupled Plasma–Mass Spectrometry (ICPMS) allows determination of the concentration of the complete set of REE and is thus more reliable in evaluating anomalous behaviour of an individual REE.

Here we report results of an ICPMS study of REE in river and stream waters and show that pristine rivers do not show Gd_{SN} anomalies, whereas rivers which drain densely populated and industrialised catchment areas are characterised by pronounced positive Gd_{SN} anomalies that are of anthropogenic origin.

2. Sampling, preconcentration, and analyses

The investigated rivers and streams include Rhein, Mosel, Elbe, Sieg, Lippe, Ruhr, Aller, Lenne, Wupper, Dhünn, Sauer, Prüm, Ahr, Wied, Havel, and Spree in Germany, Klarälven, Västerdalälven, and Rottnan in central Sweden, and Toshibetsu and Rawan in Hokkaido, Japan. In this communication we focus on the occurrence of Gd_{SN} anomalies; the full results of this study will be discussed elsewhere.

Water samples were taken with PE bottles from bridges, river banks, or from a canoe, and were filtered through a 0.2 μm membrane filter of 220 mm diameter (Seitz-Filter-Werke, Germany) immediately after sampling. The first 0.5 l of each sample were passed through the filter to allow for equilibration between water sample and filter membrane. The following 2 l were filtered directly into a 3 l PE bottle containing 5 ml 6 M HCl resulting in a final pH between 1.9 and 2.1 for the filtered 2 l sample. A Dy, Tm or Lu spike was added to determine the recovery of REE in the preconcentration procedure. Recoveries were usually well above 90%, and samples giving smaller recoveries (occasionally only 75–90%) were discarded. REE were preconcentrated employing (a slightly modified version of) the method of Shabani et al. [9]. Then 300 ml of a mixture of bis(2-ethylhexyl) hydrogen phosphate (HDEHP) and 2-ethylhexyl dihydrogen phosphate (H_2MEHP) were loaded onto a Sep-Pak® C_{18} cartridge (Millipore Corp., USA). The 2 l water samples (pH 1.9–2.1) were passed through the cartridges at a flow rate of 15–20 ml/min. The REE are quantitatively complexed by the mixture of HDEHP + H_2MEHP, while the major matrix elements, Sr, and Ba are unaffected. The C_{18} cartridges were washed with 15 ml of 0.01 M HCl to remove remaining matrix elements, whereupon the REE were eluted with 40 ml of 6 M HCl at a flow rate of 5 ml/min. The resulting REE-bearing solution was evaporated to incipient dryness. The residue was taken up in 1 ml of 5 M HNO_3 and filled up to a volume of 10 ml with H_2O. Only ultrapure reagents were used throughout the complete procedure. The determination of REE concentrations by ICP–MS has been described elsewhere [10]. Ru and Re were added to the solutions for correction of instrumental drift, and corrections for isobaric interferences and for molecular ions were carried out as described previously [11]. Measured intensities were always more than two orders of magnitude above blank intensities, except for Sm and Eu, for which slightly lower intensities were measured occasionally.

For samples from Lake Värmeln, central Sweden, and the rivers Wupper and Havel, Germany, acidification experiments (similar to the 'whole river pH titration' experiments of Sholkovitz [12]) were carried out. In these experiments 2 l samples were acidified to pH 2 prior to 0.2 μm filtration (filtration was done after 24 h). Further sample treatment was similar to that described above. From the samples filtered prior to acidification we determined the concentration of the so-called 'dissolved' REE (which in fact are the sum of the truly dissolved plus the colloidal REE), and from the samples acidified prior to filtration we determined the sum of the dissolved plus the acid-soluble particulate REE.

In addition to river and stream waters we studied tap water from various parts of the cities of Berlin, Potsdam, and Leverkusen. Furthermore, we sampled the clear water effluent from the sewage treatment plant 'Ruhleben' in Berlin, and took samples from a collecting basin for surface run-off and from a sewer containing sewage from households, metal workings and a hospital in the city of Remscheid, western

Germany. Surface water of the Baltic Sea (as an example of coastal seawater from a semi-closed sea basin) was sampled in the Skagerrak at Koljöfjord, Orust, north of Gothenburg, Sweden. Surface water in the Skagerrak shows a very low salinity and originates in the Baltic Sea (note that for this sample a 0.8 μm filter was used). Unless otherwise noted, the procedures of filtration, preconcentration, and ICP–MS analyses were similar to those described above.

In order to learn about the quality of our data, we did a test study at the River Havel for which preliminary analyses had suggested REE concentrations that were amongst the lowest ever recorded for river waters. To estimate precision, we analysed four samples that were spiked with Tm. As shown in Table 1 and Fig. 1, there is very good agreement between the results even at the low concentrations prevailing in the Havel waters. Relative standard deviations (RSD) are ≤ 2% for most REE, < 2.5% for Eu and Yb, ≤ 4.5% for Sm and Tb, and 6.6% for Ce. Because reference standards for REE in river waters are not available, we estimated the accuracy of our method by determining the REE recovery in analyses of four water samples to which a multi-element spike had been added. This spike contained each REE in an amount that resulted in a concentration in the spiked sample that was between one and two orders of magnitude above the concentration in the original water sample, i.e. still within a concentration range often encountered in filtered river waters. Due to the higher abundances, the precision of these REE deter-

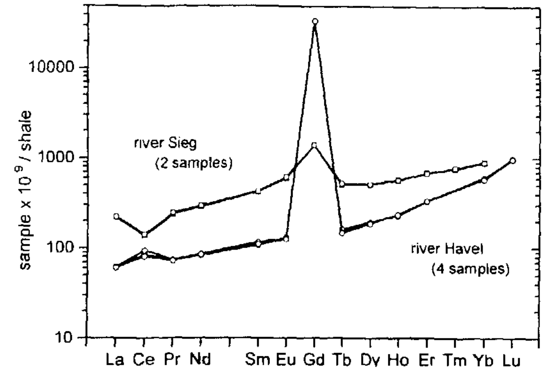

Fig. 1. Shale-normalised concentrations of dissolved REE in four samples of filtered (0.2 μm) water from the River Havel and in two samples from the River Sieg. Note the excellent reproducibility of the data sets.

Table 1

Concentrations of 'dissolved' REE (< 0.2 μm fraction) in four samples (sampling date: 17.06.96) of river water from the Havel, eastern Germany, which had been spiked with Tm, and the mean of four samples spiked with a multi-element spike

	S-1	S-2	*D*	HTm	*SD*	*RSD*	Hme	*RSD*	R-1 *	R-2 *	R-3 *	R-4 *
La	59.8	61.7	3.1	16.9	0.3	1.9	398	1.6	98.9	100	96.2	97.8
Ce	77.9	80.7	3.5	48.5	3	6.6	410	1.8	94.9	99.6	91.8	95.4
Pr	14.8	15.4	3.9	4.63	0.07	1.5	82	1.4	103	107	99.8	104
Nd	66.7	68.8	3.1	19.9	0.3	1.6	383	1.1	97.2	102	96.0	99.4
Sm	15.6	15.9	1.9	4.09	0.2	4.0	73.3	0.8	97.6	101	97.1	97.7
Eu	4.23	4.37	3.2	0.91	0.02	2.4	36.2	1.6	99.3	106	98.5	101
Gd	41.4	41.3	0.2	1013	6	0.6	7839	1.9	101	102	97.8	105
Tb	2.47	2.56	3.5	0.77	0.03	4.5	34.4	1.3	99.5	105	96.1	101
Dy	14.7	14.9	1.3	5.50	0.1	2.0	168	0.8	98.6	103	97.3	101
Ho	3.41	3.48	2.0	1.40	0.02	1.7	33.6	0.7	98.7	99.8	98.4	98.4
Er	11.8	11.6	1.7	5.70	0.03	0.5	161	0.9	96.4	98.1	96.2	96.5
Tm	1.82	1.83	2.2	307 #	4	1.4	33.2	0.8	–	–	–	–
Yb	14.5	14.7	1.4	9.73	0.2	2.2	155	0.9	93.8	94.5	92.4	93.1
Lu	*spike*	*spike*	–	2.43	0.04	1.8	62.6	0.4	97.9	97.7	97.7	98.6

Mean values, relative standard deviations (RSD), and recoveries (R; determined for each of the multi-element spiked samples) indicate good analytical quality. All concentrations in pmol/kg. S = river Sieg with Lu spike; D = difference between S-1 and S-2 (in %); HTm = River Havel with Tm spike (mean of 4); *SD* = standard deviation (1σ); *RSD* = relative standard deviation (in %); Hme = River Havel with multi-element spike (mean of 4); * R = recovery (in %) calculated from multi-element spike Havel water minus mean Tm spiked Havel water; # = Tm spike; recoveries of Tm in the four individual samples are 96, 98, 96, and 95%, respectively.

minations is even better with RSD < 2% for all REE. Recoveries during analyses of these four samples vary between 94 and 103%, 95 and 107%, 92 and 100%, and 93 and 105%, respectively (for more details see Table 1), indicating good quality of our analytical method. The excellent reproducibility is further shown by the close agreement between the results for two samples from the River Sieg (Table 1, Fig. 1) which had been sampled twice within 30 min during a field campaign in spring '95.

Table 2
Concentrations of 'dissolved' REE (< 0.2 μm fraction) in river and stream waters from Sweden, Japan and Germany, in tap water from Berlin–Steglitz, and in the clear water effluent of the sewage treatment plant 'Ruhleben' in Berlin

River	Västerdalälven	Toshibetsu	Rhein	Elbe	Mosel	Wupper	Spree	Havel
Sampling Site	Lima Dalarna, Sweden	Aikappu, Hokkaido, Japan	South of Düsseldorf, Germany	Nienstetten, Hamburg, Germany	Wasser-billigerbrück, Germany	Leverkusen, Germany	Berlin, Germany	Potsdam, Germany
Date	05.05.94	06.11.95	03.05.95	10.05.94	05.05.95	05.08.95	20.07.95	13.03.95
La	1028	173	139	119	57.4	19.7	13.6	15.8
Ce	1672	262	161	177	83.4	32.8	21.7	24.0
Pr	305	57	34.0	26.5	16.4	5.64	3.34	4.08
Nd	1295	255	134	95.6	75.2	32.0	14.8	17.3
Sm	271	63.7	30.2	18.4	17.7	6.12	3.25	4.56
Eu	57	16.3	7.39	4.6	4.21	1.67	0.79	0.91
Gd	265	77.4	54.7	36.0	29.2	207	43.1	675
Tb	39.1	11.7	5.22	3.5	3.01	1.3	0.645	1.02
Dy	236	74	1.7	20.3	20.0	*spike*	4.16	7.43
Ho	49.4	17.2	7.1	4.9	4.96	3.21	1.21	1.96
Er	149	53	2.22	17.5	17.4	14.1	4.64	8.36
Tm	20.5	*spike*	3.21	*spike*	2.72	2.84	1.00	1.49
Yb	135	54.5	22.4	22.4	19.3	24.2	8.80	13.8
Lu	*spike*	9.7	*spike*	4.5	*spike*	5.18	*spike*	*spike*
Gd_{SN}/Gd^{*}_{SN}	1.2	1.2	1.9	1.9	1.7	30	12.4	126

River	Dhünn-UC	Dhünn-LC	Seawater	Tap water	'Effluent'
Sampling Site	Altenberg Germany	Bergisch-Gladbach Germany	Koljöfjord Skagerrak Sweden	Berlin–Steglitz Germany	'Ruhleben' Berlin Germany
Date	03.12.95	03.12.95	22.08.95	20.07.95	14.03.96
La	14.8	27.0	259	6.37	8.70
Ce	40.0	52.3	367	16.1	29.4
Pr	4.87	8.32	58.7	1.86	2.97
Nd	22.5	37.2	217	8.65	18.3
Sm	5.74	10.3	37.4	2.07	3.11
Eu	1.48	2.55	5.96	0.58	0.84
Gd	8.93	71.0	42.1	39.8	7087
Tb	1.04	1.84	5.36	0.69	0.83
Dy	6.23	11.8	*spike*	6.96	6.07
Ho	1.54	2.97	6.81	2.65	1.95
Er	5.27	10.9	20.2	12.9	8.90
Tm	*spike*	*spike*	3.14*	2.47	*spike*
Yb	7.59	15.3	20.0	20.6	13.2
Lu	1.57	3.23	3.44	*spike*	4.82
Gd_{SN}/Gd^{*}_{SN}	1.6	6.9	1.33	12	1681

All concentrations in pmol/kg; 0.2 μm filter used for all samples, except for Skagerrak seawater (0.8 μm); Skagerrak seawater is coastal surface (0.5 m depth) water originating in the Baltic Sea. * contaminated. 'Effluent' is clear water effluent from sewage treatment plant 'Ruhleben', Berlin. $Gd_{SN}/Gd^{*}_{SN} = Gd_{SN}/(0.33Sm_{SN} + 0.67Tb_{SN})$.

3. Results

The dissolved concentrations of any given REE vary over two orders of magnitude between the different river and stream waters studied. Dissolved Nd, for example, shows a concentration range between 15 and 1225 pmol/kg. While this is compatible with data reported for the < 0.2 or < 0.45 μm REE fraction of other river waters [12–15], the minimum concentrations (determined for the rivers Spree and Havel) are amongst the lowest reported yet. As will be discussed in an accompanying paper, the well known close association of REE with colloidal matter [12–15] suggests that the variable REE concentrations in our sample set are primarily due to variations in the abundances of river colloids.

The shale-normalised REE patterns (shale is Post-Archaean Australian shale, PAAS, from [16]) of all river and stream waters increase from La_{SN} to Lu_{SN} and show no or small negative Eu_{SN}, and no, negative, or even small positive Ce_{SN} anomalies. The majority of German rivers studied (in Tables 1 and 2, and Fig. 1 and Fig. 2a, exemplified by the rivers Sieg, Rhein, Elbe, and Mosel) show positive Gd_{SN} anomalies with Gd_{SN}/Gd^*_{SN} ratios between 1.5 and 3. Even larger positive anomalies have been found for the River Wupper (max. $Gd_{SN}/Gd^*_{SN} = 30$) which flows into the Rhein north of Cologne in western Germany, and for the Spree–Havel river system (max. $Gd_{SN}/Gd^*_{SN} = 240$) in the Berlin/Potsdam area in eastern Germany (Tables

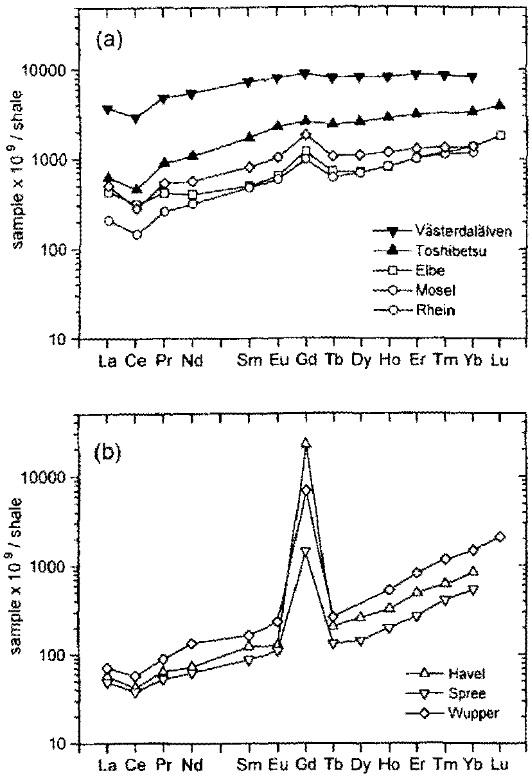

Fig. 2. REE_{SN} patterns of filtered (0.2 μm) river waters. Only rivers draining non-industrialised and thinly populated areas, such as Västerdalälven (Dalarna, Sweden) or Toshibetsu (Hokkaido, Japan), are free from Gd contamination. Almost all German rivers and streams studied so far, exemplified here by the Rhein, Elbe, Mosel, Wupper, Spree, and Havel, display positive Gd_{SN} anomalies of variable size due to anthropogenic Gd input.

Table 3
Gd_{SN}/Gd^*_{SN} ratios of various water samples

Water type	Sampling site	Date	Gd_{SN}/Gd^*_{SN}
River water	Wupper at Leverkussen, Germany	06.05.95	9.1
River water	Wupper at Leverkussen, Germany	05.08.95	30
River water	Wupper at Leverkussen, Germany	05.12.95	10.5
Seawater	Baltic Sea, Koljöfjord, Sweden	22.08.95	1.33
Waste water	surface run-off, Remscheid, Germany	16.04.96	1.28
Waste water	seawage, Remscheig, Germany	16.04.96	3.6
Tap water	Berlin — Steglitz, Germany	20.07.95	12
Tap water	Berlin — Wedding, Germany	04.07.95	22
Tap water	Berlin — Kreuzberg, Germany	04.07.95	19
Tap water	Berlin — Wannsee, Germany	22.10.95	4.9
Tap water	Berlin — Spandau, Germany	15.10.95	1.2
Tap water	Potsdam, Germany	22.10.95	2.3
Tap water	Leverkussen–Opladen, Germany	24.04.95	1.4

$Gd_{SN}/Gd^*_{SN} = Gd_{SN}/(0.33Sm_{SN} + 0.67Tb_{SN})$.

1–3, and Fig. 1 and Fig. 2b). Repeated sampling of the River Wupper in May, August, and December, 1995, showed a maximum Gd_{SN}/Gd^*_{SN} ratio in summer (Table 3), indicating that the size of the positive Gd_{SN} anomaly is largest at times of low water discharge. In marked contrast to the German rivers, with their densely populated and industrialised catchment areas, rivers in Värmland and Dalarna, central Sweden, and Hokkaido, Japan, which drain only thinly populated and non-industrialised areas do not show positive Gd_{SN} anomalies (as is exemplified in Table 2 and Fig. 2a by the rivers Västerdalälven, Sweden, and Toshibetsu, Japan). For the Dhünn, a stream in western Germany that had been sampled in both its upper and lower course, the Gd_{SN}/Gd^*_{SN} ratio was found to increase downstream from 1.9 to 6.9 (Table 2, Fig. 3).

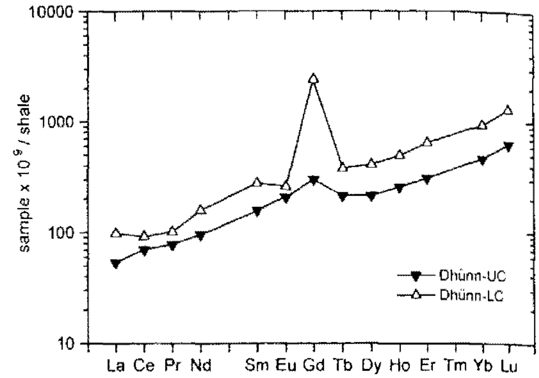

Fig. 3. REE_{SN} patterns of filtered (0.2 μm) waters from the upper (Dhünn-UC) and lower course (Dhünn-LC) of the River Dhünn. Note that the pristine waters of the Dhünn's upper course do not show a positive Gd_{SN} anomaly, but a smooth trend for the LREE from La to Gd and another smooth trend for the HREE from Tb to Lu. In contrast, the sample from the lower reaches of the stream yields a strong positive Gd_{SN} anomaly.

Due to access of surface water to groundwaters in the Berlin area, the positive Gd_{SN} anomaly is transferred to tap water (Fig. 4) which in some parts of Berlin shows Gd_{SN}/Gd^*_{SN} ratios of up to 22 (Table 3). The largest positive Gd_{SN} anomaly recorded so far has been found in the clear water effluent of the sewage treatment plant 'Ruhleben' (Fig. 4) which is the largest waste water treatment plant in Berlin, with a capacity of 240,000 (dry weather) to 600,000 m^3/day (rainy weather), corresponding to a population equivalent of 1.6 million. The clear water efflu-

Table 4

Concentrations of 'dissolved' REE (< 0.2 μm fraction) and dissolved plus acid-soluble particulate REE in samples from Lake Värmeln, central Sweden, and the rivers Wupper and Havel, Germany

	Lake Värmeln		River Wupper		River Havel	
	Värmskog Värmland, Sweden, 04.06.94		River mouth Leverkusen, Germany, 06.05.95		Glienicker Brücke Potsdam, Germany, 17.06.96	
	D	D + ASP	D	D + ASP	D	D + ASP
La	1825	3249	38.7	281	17.0	561
Ce	1873	4004	49.0	470	48.5	1130
Pr	414	742	10.7	77.7	4.63	135
Nd	1623	2768	50.8	328	19.9	496
Sm	275	456	12.9	74.4	4.09	93.5
Eu	42.2	72.4	3.26	17.3	0.91	17.2
Gd	232	396	120	163	1013	1143
Tb	30.0	51.4	2.39	11.2	0.77	11.7
Dy	173	289	15.9	62.1	5.50	64.4
Ho	37.5	57.9	4.26	12.9	1.40	12.6
Er	111	169	17.0	39.2	5.70	34.9
Tm	15.2	22.6	3.01	5.64	*spike*	*spike*
Yb	99.2	145	24.3	40.9	9.73	33.6
Lu	*spike*	*spike*	*spike*	*spike*	2.43	5.98

All concentrations in pmol/kg. D = dissolved REE (< 0.2 μm fraction: dissolved + colloidal REE); D + ASP = dissolved REE plus acid-soluble particulate REE (samples acidified to pH 2 prior to < 0.2 μm filtration).

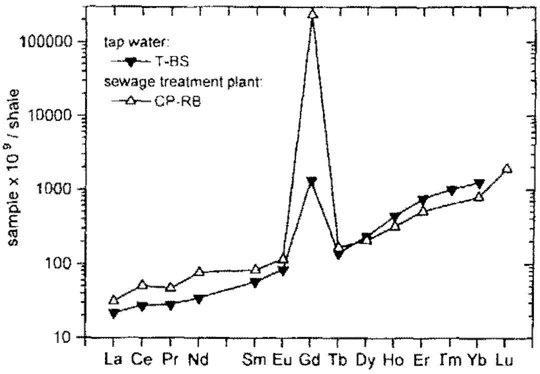

Fig. 4. REE_{SN} patterns for filtered (0.2 μm) tap water from Berlin — Steglitz (T-BS), and for the filtered (0.2 mm) clear water effluent of the sewage treatment plant 'Ruhleben' in Berlin (CP-RB). The pronounced positive Gd_{SN} anomalies in both samples show that there is significant Gd input from anthropogenic sources into surface waters, and that the Gd_{SN} anomaly is even transferred to tap water. Apparently, no or only part of the anthropogenic Gd is removed during sewage treatment and tap water purification.

ent shows a Gd_{SN}/Gd^*_{SN} ratio of 1680 and a Gd concentration of 7000 pmol/kg. In contrast to the surface run-off from a collecting basin in Remscheid that does not show a positive Gd_{SN} anomaly, sewage comprising waste water from households, metal workings and a hospital in the same city yields a Gd_{SN}/Gd^*_{SN} ratio of 3.6 and a positive Gd_{SN} anomaly (Table 3).

As expected, the samples from Lake Värmeln and the rivers Wupper and Havel, which had been acidified prior to filtration (acidification experiments), show higher REE abundances compared the other samples (Table 4).

The sample of coastal surface water of the Baltic Sea yields relatively high REE concentrations (e.g., 217 pmol/kg Nd; Table 2). This may in part be due to the 0.8 μm filter used, but is still within the range reported for coastal seawater elsewhere [14]. Its REE_{SN} pattern shows a negative Ce_{SN} and a positive Gd_{SN} anomaly.

4. Discussion

4.1. Gadolinium in pristine rivers

The quantification of Gd_{SN} anomalies by equations such as Eq. (1) is based on the assumption that normalised REE concentrations vary smoothly with atomic number. However, the REE_{SN} patterns of pristine rivers, such as Västerdalälven, Toshibetsu (both Fig. 2), and in particular the upper course of the Dhünn (Fig. 3) show a smooth trend for the light REE (LREE) from Pr to Gd, and another smooth trend for the heavy REE (HREE) from Tb to Lu. However, although there is no specific Gd_{SN} anomaly in these pristine river waters, calculated Gd_{SN}/Gd^*_{SN} ratios of 1.2 (Västerdalälven and Toshibetsu) and 1.9 (Dhünn) suggest the occurrence of positive Gd_{SN} anomalies in these samples. Hence, Gd_{SN}/Gd^*_{SN} ratios above unity do not necessarily imply the presence of positive Gd_{SN} anomalies, and consideration of the complete REE_{SN} pattern is essential. That, in our pristine river waters, Gd belongs to the LREE is an interesting observation because from studies of organic REE complexes it was suggested that in outers phere complexation Gd behaves as an HREE, and in inner sphere complexation as a LREE [17]. Thus, future studies of pristine river waters, that use ultrafiltration techniques to distinguish between the truly dissolved and the colloidal REE, may study the behaviour of Gd to learn more about the types of ligands that dominate REE solution and surface complexation.

4.2. Origin of positive gadolinium anomalies

In natural substances, such as minerals and waters, the lanthanides always occur as a group, due to their similar physicochemical properties, and hence coherent behaviour in biogeochemical processes. The fact that in the river waters anomalous enrichment is confined to Gd, coupled with the extreme size of the Gd_{SN} anomalies found for some rivers, strongly suggests that the excess Gd is of anthropogenic origin and derived from a synthetic compound. This is supported by the analyses of waste waters from the city of Remscheid: the sewage from households, metal workings, and a hospital yields a positive Gd_{SN} anomaly, but surface run-off sampled from a collecting basin does not (Table 3). Furthermore, there is significant Gd output (7000 pmol/kg) with a pronounced positive Gd_{SN} anomaly from the sewage treatment plant 'Ruhleben' in Berlin, which is more than three orders of magnitude higher than the background concentration of ≈ 4 pmol/kg estimated for non-contaminated Spree–Havel waters. Moreover, pristine water from the upper course of the Dhünn, which was sampled at a location where the stream had not yet received input from farms, towns or industry, does not show a Gd_{SN} anomaly, whereas the sample from the stream's lower reaches yields a strong positive one (Fig. 3), which also points towards an anthropogenic origin of the Gd.

The fact that the positive Gd_{SN} anomaly in the River Wupper is most pronounced at times of low water discharge suggests that the size of the anomaly in the river waters is primarily controlled by the ratio of Gd-contaminated anthropogenic input to input from non-contaminated rain and ground waters. Of course, the impact of Gd-contaminated input is most pronounced if the natural background concentration of the REE in a river is very low (as in the case of the rivers Havel and Spree).

The ability of excess Gd to escape removal during sewage treatment and tap water purification suggests that Gd is bound in a very stable aqueous complex. This is in agreement with the results of the acidification experiments. Fig. 5 shows the percentage of each REE that is related to the 'dissolved' REE fraction in a water sample. This is calculated from:

$$(REE_{DISS}/REE_{DISS+ASP}) \times 100\ (\%) \qquad (2)$$

where REE_{DISS} is the concentration of a given 'dissolved' REE (determined from the $< 0.2\ \mu m$ fraction of a water sample), and $REE_{DISS+ASP}$ is the dissolved plus the acid-soluble particulate concentration of this REE. For Lake Värmeln — a lake in Värmland, central Sweden, which does not show a positive Gd_{SN} anomaly — the percentage of dissolved REE increases slightly from La (56%) to Yb (68%) without showing any anomalous deviation from the general trend for Gd. A similar, though stronger, increase from La (14% and 3%, respectively) to Yb (59% and 29%, respectively) is observed for the rivers Wupper and Havel which are two of the German rivers yielding a strong positive Gd_{SN} anomaly. In marked contrast to the non-contaminated Lake Värmeln, however, 74% of Gd in the Wupper is related to the dissolved pool, compared to only 19% of Eu and 21% of Tb, which are next to Gd in the REE series. For the River Havel the difference is even more pronounced, with 89% of Gd in the dissolved fraction compared to 5% for Eu and 7% for Tb. This suggests that in contaminated waters Gd is less particle-reactive than in non-contaminated waters, and that the excess Gd shows a speciation in the waters which is different from that of the 'natural' REE.

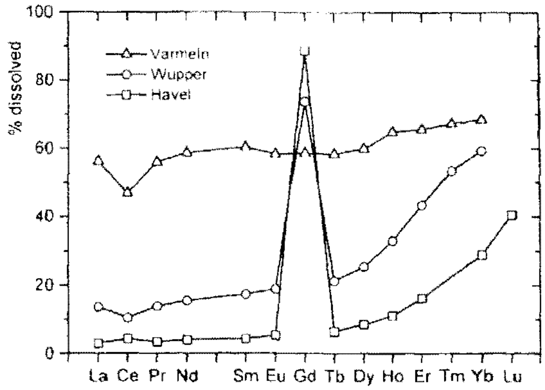

Fig. 5. Percentage of 'dissolved' REE in non-contaminated Lake Värmeln, central Sweden, and in the Gd-contaminated rivers Wupper and Havel, Germany. The anomalously high amounts of 'dissolved' Gd in Wupper and Havel indicate that the anthropogenic Gd is considerably less particle-reactive than the 'natural' REE, and suggests that the anthropogenic Gd is bound to a very stable aqueous chemical complex.

The most likely source of the anthropogenic Gd is gadopentetic acid, $Gd(DTPA)^{2-}$, which has been used since the late 1980s as a paramagnetic contrast-enhancing agent in nuclear magnetic resonance imaging (MRI). Gd(III) is used in MRI because of its large magnetic moment and long electron spin relaxation times [18]. Because the free Gd^{3+} metal ion is toxic, the Gd(III) compound used in medical diagnostics must be in the form of a very stable ($\log K_{Gd(DTPA)} = 22.5$ [19]), almost inert chemical complex to ensure complete excretion from the human body. Although research focusing on the design of macrocyclic Gd(III) complexes as contrast agents is in progress [18], $Gd(DTPA)^{2-}$ is still the most widely distributed contrast agent in MRI.

A conservative estimate, based on information provided by radiologists who use MRI, suggests that in the Berlin area, with its population of more than 4 million, the Gd consumption and disposal which is due to application of $Gd(DTPA)^{2-}$ in medical diagnostics may be in the order of 100 kg/a. A rough estimate based on the dry and rainy weather capacities of the sewage treatment plant 'Ruhleben' (given in Section 3 and the Gd concentration of 7000 pmol/kg Gd determined for its effluent (Table 2) suggests a Gd disposal between 96 and 240 kg/a. These two estimates are in reasonable agreement. Assuming Gd disposal between 100 and 200 kg/a (636 and 1272 mol/a), and an average water discharge of the River Havel of 72.04 m^3/s (average for 1987 [20]), suggests that input from the 'Ruhleben' plant alone might generate Gd concentrations in the Havel between 280 and 560 pmol/kg. The actually determined concentrations in March and June 1996 are 675 and 1143 pmol/kg (Tables 1 and 2); additional data (M. Bau, unpubl. data) indicates that the latter value is exceptionally high. Considering the large uncertainties involved in the above calculations and considering that 'Ruhleben' is not the only sewage treatment plant in Berlin that may supply Gd, these results are in reasonable agreement, and support the hypothesis that anthropogenic input of Gd used for medical diagnostics is the cause of the positive Gd_{SN} anomaly in the Havel.

Recently, Roth et al. [21] reported on the use of the Pr(III) complex Pr[MOE–DO3A] as an in vivo thermometer in nuclear magnetic resonance spectroscopy. Widespread application of this agent may in the future lead to the presence of anthropogenic Pr_{SN} anomalies in surface waters in addition to the Gd_{SN} anomalies already observed today.

These positive Gd_{SN} anomalies are by no means confined to Central Europe but are also observed in North American rivers. Data reported for the dissolved REE in the Hudson and Connecticut rivers, USA [12], for example, suggest the presence of significant positive Gd_{SN} anomalies in both rivers (Fig. 6). The Gd_{SN}/Gd^*_{SN} ratios vary between 1.30 and 1.47 for the Connecticut and 1.64 for the Hudson River (note that Gd_{SN}/Gd^*_{SN} had to be calculated as $Gd_{SN}/(0.5Sm_{SN} + 0.5Dy_{SN})$, because no Tb data are available). Meanwhile, strong positive Gd_{SN} anomalies have also been determined for the River Etsch in northern Italy (P. Möller, 1996, pers. commun.). Hence, Gd contamination of surface waters may be a problem in most (if not all) of the densely populated and industrialised parts of the world.

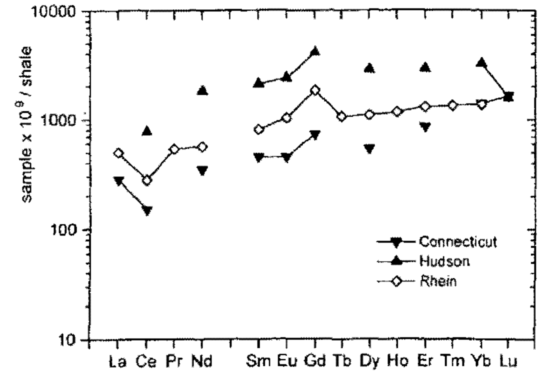

Fig. 6. REE_{SN} patterns of filtered (0.2 μm) waters from the Connecticut and Hudson rivers, eastern USA (data from [12]), and from the River Rhein, western Germany (this study). The data suggest that Gd contamination of surface waters is not confined to Central Europe but is also a problem in other (probably all) densely populated and industrialised parts of the world.

The positive Gd_{SN} anomalies in river waters indicate that even the distribution of rather 'exotic' elements, such as the rare earth elements, may be strongly affected by anthropogenic contamination. While even in the contaminated rivers the observed Gd concentrations are probably too low to induce severe health risks (although nothing is known yet about possible long-term effects), the anthropogenic Gd input limits the use of the Gd_{SN} anomaly as a natural geochemical indicator. It cannot be ruled out that a positive Gd_{SN} anomaly observed in lakes, coastal seas, or semi-closed sea basins, to which REE are predominantly supplied by rivers draining densely populated and industrialised areas, may (in part) be of anthropogenic origin. Because the anthropogenic Gd is considerably less particle-reactive than the 'natural' REE, Gd removal during estuarine mixing of river and seawater can be expected to be minor to negligible compared to removal of the other REE. This further increases the Gd_{SN}/Gd^*_{SN} ratio of the riverine REE input into seawater and amplifies the impact of contaminated river water on the REE distribution in coastal waters and in semi-closed sea basins. One example for such a contamination may be the Baltic Sea: the only complete REE data set available (Table 2) shows a positive Gd_{SN} anomaly ($Gd_{SN}/Gd^*_{SN} = 1.33$), although a 0.8 μm filter was used. Thus, future studies of the REE distribution in natural waters should take possible anthropogenic contaminations into account, and should be restricted to pristine rivers and estuaries.

5. Conclusions

Rivers draining densely populated and industrialised areas show pronounced positive Gd_{SN} anomalies which may reach a size of more than two orders of magnitude. In contrast, rivers in thinly populated and non-industrialised areas, such as Värmland and Dalarna, central Sweden, and Hokkaido, Japan, do not show positive Gd_{SN} anomalies. In the Berlin–Potsdam area, eastern Germany, where the most prominent Gd_{SN} anomalies have been found, the anomalies can be traced back to the clear water effluent from a sewage treatment plant, indicating that the anomaly is due to anthropogenic contamination. The source of the Gd is most likely gadopentetic acid, $Gd(DTPA)^{2-}$, which is applied as a contrast agent in magnetic resonance imaging.

Acidification experiments suggest that the excess Gd occurs in the form of a very stable aqueous complex, leading to a particle reactivity of Gd which is considerably lower than that of the other, 'natural' REE. Hence, REE input from Gd-contaminated rivers may amplify or even generate positive Gd_{SN} anomalies in coastal waters and semi-closed sea basins. In these environments, therefore, Gd_{SN} anomalies can no longer be used as natural geochemical indicators.

Acknowledgements

The help of A. Usui, Geological Survey of Japan, and B. Pracejus, Free University of Berlin, during river water sampling in Japan is gratefully acknowledged. Thanks are due to R. Pepelnik, GKSS Forschungszentrum Geesthacht, G. Altmann, Berliner Wasserbetriebe, and U. Dreesen, REB Remscheid, for providing samples from the river Elbe, the 'Ruhleben' sewage treatment plant, and the waste waters of Remscheid. Further thanks go to B. Richert, GFZ Potsdam, for laboratory assistance. The paper benefited from comments by reviewers E. Sholkovitz, P. Stille, and V. Ragnarsdottir. *[UC]*

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