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# High-technology metals as emerging contaminants: Strong increase of anthropogenic gadolinium levels in tap water of Berlin, Germany, from 2009 to 2012

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ABSTRACT

The distribution of rare earth elements (REE) in tap water sampled in December 2012 in Berlin, Germany, is characterized by anomalously high levels of gadolinium (Gd). While the western districts of the city show strong anthropogenic positive Gd anomalies in REE distribution patterns, the eastern districts are (almost) unaffected. This contamination with anthropogenic Gd results from Gd-based contrast agents used in Magnetic Resonance Imaging, that enter rivers, groundwater and eventually tap water via the clear water effluent from wastewater treatment plants. While the spatial distribution of anthropogenic Gd in 2012 confirms results of an earlier study in 2009 (Kulaksiz and Bau, 2011a), anthropogenic Gd concentrations have increased between 1.5- and 11.5-fold in just three years. This confirms predictions based upon the increase of anthropogenic Gd concentrations in the Havel River over the past two decades and the time it takes the water to migrate from the Havel River to the groundwater production wells. Anomalously high levels of anthropogenic Gd in tap water, which are not confined to Berlin but have also been observed in London, U.K., and in German cities in the Ruhr area and along the Rhine River, reveal that high-technology metals have become emerging contaminants. While non-toxic at the observed concentrations, the anthropogenic Gd is a microcontaminant that may be used as a conservative pseudo-natural tracer for wastewater-derived xenobiotics such as pharmaceuticals, food additives and personal care products. Our results suggest that monitoring the concentrations of such substances in Berlin's drinking water can be restricted to a few central and western districts of the city, demonstrating that implementation of anthropogenic Gd as a tracer in monitoring programs can contribute to significant cost savings.


## 1. Introduction

The continuous development of new technologies and new substances has lead to strongly increased release of high-technology metals into natural waters, although their toxicological effects and the potential implications for the ecosystem are often not fully understood. The rare earth elements (REE) are prime examples of this development (Kulaksiz and Bau, 2013).

The REE *sensu strict*u are comprised of the elements from atomic number 57 (lanthanum, La) to 71 (lutetium, Lu) and display coherent geochemical behavior. Small intra-REE fractionation is due to the systematic decrease of atomic radii with increasing REE atomic number, which causes small differences of mineral/liquid partition coefficients and stabilities of chemical complexes. For convenience, REE concentrations of natural waters are commonly normalized to Post-Archean Australian Shale (PAAS, McLennan, 1989; subscript: SN), which produces smooth $REE_{SN}$ distribution patterns. Individual REE may show anomalous behavior in natural waters: redox-sensitive Ce and Eu may show anomalies that may be used as redox- and/or temperature-proxies (e.g., Bau, 1991; De Baar et al., 1988; German and Elderfield, 1989; Michard, 1989), and La, Gd and Lu may show small anomalies due to subtle differences between the stabilities of REE complexes (Bau, 1999; Byrne and Kim, 1990). In addition to these natural anomalies, anthropogenic anomalies of Gd and, recently, La and Sm have been reported from natural waters (e.g., Kulaksiz and Bau, 2013, and references therein).

In this update of the first monitoring study (Kulaksiz and Bau, 2011a; samples taken in 2009) of REE levels in drinking/tap water in the City of Berlin, Germany, we report changes with respect to REE and especially Gd concentrations and distribution in tap water in the eastern and western districts of Berlin between 2009 and 2012, and show a strong increase of the anthropogenic Gd concentration in the western districts of the city.

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## 2. Background

The first evidence of anthropogenic REE input into the hydrosphere was reported by Bau and Dulski (1996) who observed positive Gd anomalies in German rivers and in tap water from Berlin, Germany. Since then, anthropogenic positive Gd anomalies in natural waters have been found in Europe (Elbaz-Poulichet et al., 2002; Knappe et al., 2005; Kulaksiz and Bau, 2007, 2011b, 2013; Massmann et al., 2004, 2008; Möller et al., 2000, 2002, 2014; Morteani et al., 2006; Petelet-Giraud et al., 2009; Rabiet et al., 2006), North America (Barber et al., 2006; Bau et al., 2006; Verplanck et al., 2005, 2010), Australia (Lawrence et al., 2009), and Asia (Nozaki et al., 2000; Zhu et al., 2004, 2005). Furthermore, municipal tap water used as drinking water was investigated by Kulaksiz and Bau (2011a) in the western and eastern districts of Berlin, Germany. They reported strong positive Gd anomalies in tap water from the *western* districts of Berlin (Fig. 1), while tap water from the *eastern* districts did not yield any Gd anomalies. This specific spatial distribution results from the unique history of Berlin, where before the reunification of Germany in 1991, natural and artificial bank infiltration were crucial necessities for sustainable water management in West-Berlin, but unimportant in East-Berlin. While tap water in the eastern districts of Berlin is sourced from deep groundwater wells, around 70% of the total tap water production in Berlin comes from shallow groundwater wells affected by natural and induced bank infiltration (e.g., Massmann et al., 2004; Pekdeger and Sommer-von Jarmersted, 1998). Contamination of tap water with anthropogenic Gd is not confined to Berlin, but is also observed in tap water in London, U.K. (Kulaksiz and Bau, 2011a), and in Cologne, Düsseldorf, and Essen, Germany (Kulaksiz and Bau, unpublished data), for example (Fig. 1).

Though unnoticed before the mid-1990s, the release of anthropogenic Gd into surface waters probably started already in 1988, when Gd-based contrast agents for use in magnetic resonance imaging (MRI) were first introduced to the market. These water-soluble and highly stable chemical complexes which ensure complete removal of toxic $Gd^{3+}$ from the body, are injected into the bloodstream of patients, and excreted via their kidneys within 24–48 h. However, due to their high stabilities, these complexes cannot be removed by commonly used wastewater treatment technologies and, hence, pass the wastewater treatment plants unaffected and are released into rivers and lakes. Eventually, they reach coastal seawater (Kulaksiz and Bau, 2007; Nozaki et al., 2000), groundwater and tap water (Kulaksiz and Bau, 2011a). Therefore, anthropogenic Gd is a pseudo-natural tracer for wastewater-derived substances in natural waters, including tap water used as drinking water.

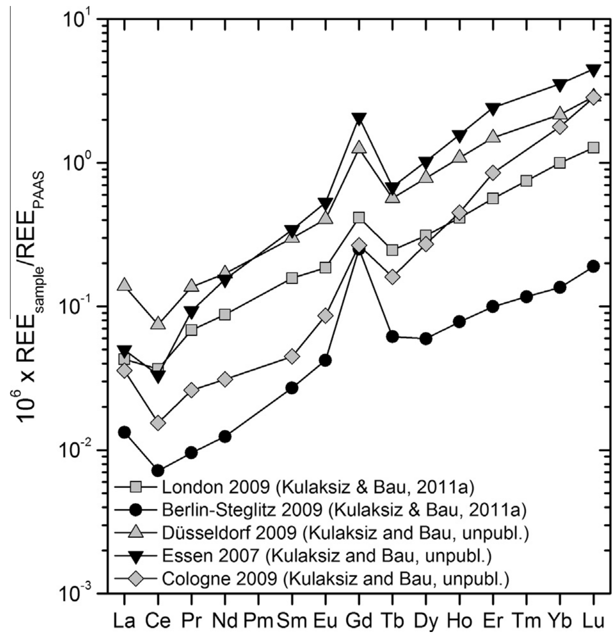


**Fig. 1.** $REE_{SN}$ patterns of tap water samples from London (U.K.), Berlin-*Steglitz*, Cologne, Düsseldorf and Essen (all Germany), showing large positive Gd anomalies due to anthropogenic Gd input.

Kulaksiz and Bau (2011a) reported $REE_{SN}$ patterns of Havel River water and tap water from the western districts of Berlin with

**Table 1**
ICP-MS data for tap water sampled in Berlin in December 2012. All concentrations in ng/kg unless otherwise noted.

| District | Post code | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Y | Ho | Er | Tm* | Yb | Lu | ΣREE | ΣREY | pH | Conductivity (μS/cm) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Spandau* | 13597 | 2.63 | 1.50 | 0.26 | 1.15 | 0.34 | 0.10 | 1.06 | 0.10 | 0.77 | 7.68 | 0.20 | 0.75 | 0.14 | 1.05 | 0.22 | 10.28 | 17.96 | 7.10 | 820 |
| *Jungfernheide* | 10589 | 1.21 | 1.32 | 0.24 | 1.14 | 0.35 | 0.10 | 4.01 | 0.11 | 0.91 | 9.97 | 0.26 | 1.03 | 0.20 | 1.60 | 0.34 | 12.82 | 22.79 | 7.15 | 778 |
| *Wedding* | 13347 | 0.69 | 0.82 | 0.15 | 0.69 | 0.22 | 0.07 | 16.76 | 0.07 | 0.68 | 6.26 | 0.24 | 1.24 | 0.27 | 2.41 | 0.51 | 24.83 | 31.09 | 7.15 | 697 |
| *Alt-Tegel* | 13507 | 0.82 | 1.02 | 0.18 | 0.98 | 0.36 | 0.11 | 25.05 | 0.12 | 1.02 | 7.46 | 0.32 | 1.50 | 0.33 | 2.86 | 0.60 | 35.28 | 42.74 | 7.06 | 784 |
| *Wittenau* | 13437 | 0.82 | 1.06 | 0.20 | 1.06 | 0.41 | 0.12 | 26.21 | 0.14 | 1.18 | 8.75 | 0.36 | 1.58 | 0.35 | 2.99 | 0.60 | 37.07 | 45.82 | 7.05 | 768 |
| *Buch* | 13125 | 3.44 | 2.34 | 0.41 | 1.96 | 0.58 | 0.15 | 1.01 | 0.14 | 1.12 | 10.80 | 0.31 | 1.11 | 0.20 | 1.44 | 0.29 | 14.49 | 25.29 | 7.00 | 701 |
| *Pankow* | 13187 | 1.61 | 2.98 | 0.45 | 2.04 | 0.57 | 0.14 | 0.92 | 0.14 | 1.03 | 8.20 | 0.26 | 0.96 | 0.17 | 1.23 | 0.25 | 12.77 | 20.97 | 7.11 | 704 |
| *Friedrichshagen* | 12587 | 0.71 | 0.95 | 0.16 | 0.85 | 0.26 | 0.07 | 0.58 | 0.07 | 0.56 | 5.01 | 0.15 | 0.57 | 0.11 | 0.80 | 0.17 | 6.02 | 11.02 | 7.18 | 820 |
| *Marzahn* | 12679 | 0.85 | 0.90 | 0.20 | 1.00 | 0.34 | 0.08 | 0.67 | 0.09 | 0.70 | 5.29 | 0.18 | 0.62 | 0.12 | 0.88 | 0.19 | 6.81 | 12.11 | 7.25 | 834 |
| *Kaulsdorf* | 12621 | 0.59 | 0.84 | 0.15 | 0.74 | 0.26 | 0.07 | 0.53 | 0.07 | 0.53 | 3.85 | 0.14 | 0.53 | 0.10 | 0.76 | 0.18 | 5.49 | 9.34 | 7.13 | 803 |
| *Friedrichshain* | 10243 | 0.65 | 0.76 | 0.15 | 0.74 | 0.25 | 0.06 | 0.54 | 0.07 | 0.53 | 3.98 | 0.14 | 0.50 | 0.10 | 0.73 | 0.16 | 5.37 | 9.35 | 7.09 | 828 |
| *Neukölln* | 12055 | 0.68 | 0.81 | 0.15 | 0.79 | 0.30 | 0.08 | 7.71 | 0.09 | 0.74 | 5.97 | 0.21 | 0.88 | 0.18 | 1.53 | 0.34 | 14.51 | 20.48 | 7.11 | 842 |
| *Schöneberg* | 10829 | 0.77 | 0.95 | 0.19 | 0.95 | 0.31 | 0.09 | 11.37 | 0.10 | 0.84 | 7.26 | 0.24 | 1.08 | 0.23 | 1.88 | 0.39 | 19.40 | 26.66 | 7.12 | 780 |
| *Zehlendorf* | 14169 | 0.92 | 0.83 | 0.15 | 0.68 | 0.19 | 0.05 | 2.24 | 0.05 | 0.41 | 3.31 | 0.11 | 0.43 | 0.08 | 0.56 | 0.11 | 6.82 | 10.13 | 7.11 | 756 |
| *Steglitz* | 12165 | 0.44 | 0.48 | 0.10 | 0.43 | 0.14 | 0.04 | 2.23 | 0.05 | 0.34 | 2.28 | 0.09 | 0.35 | 0.07 | 0.50 | 0.11 | 5.35 | 7.63 | 7.20 | 754 |
| *Kurfürstendamm* | 10789 | 0.93 | 1.16 | 0.20 | 1.03 | 0.37 | 0.11 | 15.81 | 0.12 | 0.96 | 6.69 | 0.29 | 1.26 | 0.26 | 2.18 | 0.44 | 25.09 | 31.78 | 7.12 | 790 |
| *Zoologischer Garten* | 10623 | 1.36 | 1.28 | 0.22 | 1.15 | 0.40 | 0.11 | 17.73 | 0.13 | 1.01 | 6.55 | 0.29 | 1.32 | 0.27 | 2.21 | 0.46 | 27.94 | 34.49 | 7.20 | 776 |
| *Mitte* | 10117 | 0.81 | 1.12 | 0.20 | 1.06 | 0.41 | 0.12 | 27.33 | 0.14 | 1.13 | 6.27 | 0.34 | 1.58 | 0.34 | 2.86 | 0.58 | 38.02 | 44.29 | 7.47 | 790 |
| *Hauptbahnhof* | 10557 | 0.77 | 0.90 | 0.17 | 0.84 | 0.29 | 0.08 | 22.61 | 0.09 | 0.78 | 4.66 | 0.25 | 1.33 | 0.29 | 2.46 | 0.51 | 31.37 | 36.03 | 7.05 | 782 |

Tm* = Tm concentrations interpolated using $Er_{SN}$ and $Yb_{SN}$.
ΣREE = Total REE concentrations including Tm*.
ΣREY = Total REE concentrations including Tm* and Y.
$Gd_{SN}/Gd^*_{SN}$ = Gadolinium anomaly calculated according to Eqs. (1) and (2) in Kulaksiz and Bau (2011a).
$Gd_{anthr}$ = Anthropogenic Gd concentration according to Eqs. (1)–(3) in Kulaksiz and Bau (2011a).
% $Gd_{anthr}$ = Anthropogenic Gd content as a percentage of total Gd.