

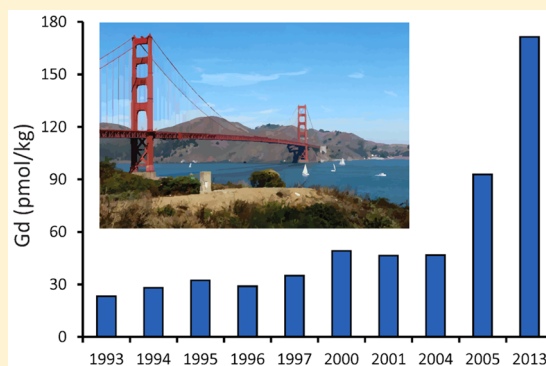
Increases in Anthropogenic Gadolinium Anomalies and Rare Earth Element Concentrations in San Francisco Bay over a 20 Year Record

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ABSTRACT: We evaluated both the spatial distribution of gadolinium (Gd) and other rare earth elements (REE) in surface waters collected in a transect of San Francisco Bay (SFB) and their temporal variations within the Bay over two decades. The REE were preconcentrated using the NOBIAS PA-1 resin prior to analysis by high-resolution inductively coupled plasma mass spectrometry. Measurements revealed a temporal increase in the Gd anomaly in SFB from the early 1990s to the present. The highest Gd anomalies were observed in the southern reach of SFB, which is surrounded by several hospitals and research centers that use Gd-based contrast agents for magnetic resonance imaging. Recent increases in that usage presumably contributed to the order of magnitude increase in anthropogenic Gd concentrations in SFB, from 8.27 to 112 pmol kg⁻¹ over the past two decades, and reach the northeast Pacific coastal waters. These measurements (i) show that

“exotic” trace elements used in new high-tech applications, such as Gd, are emerging contaminants in San Francisco Bay and that anthropogenic Gd concentrations increased substantially over a 20 year period; (ii) substantiate proposals that REE may be used as tracers of wastewater discharges and hydrological processes; and (iii) suggest that new public policies and the development of more effective treatment technologies may be necessary to control sources and minimize future contamination by REE that are critical for the development of new technologies, which now overwhelm natural REE anomalies.



INTRODUCTION

Rare earth elements (REE) constitute a group of critical elements that are of increasing economic importance, because they are used in a number of technological devices (e.g., computer memory, rechargeable batteries, cell phones, fluorescent monitors, catalytic converters, magnets, electric cars, and wind turbines). During the past few decades, there has been an explosion in demand for those items, with a probable corresponding increase in anthropogenic REE discharges to the environment.

We recently reported the initial measurements of REE in the San Francisco Bay (SFB).¹ These measurements demonstrated some REE enrichments, especially for Gd, in the highly industrialized southern reach of SFB and in its plume waters discharging into northeast Pacific coastal waters. These enrichments were associated with increases in anthropogenic Gd anomalies that were consistent with previous reports of similar anomalies in other aquatic systems.^{2–13}

The major source of the anthropogenic Gd anomalies in aquatic systems are water-soluble Gd-based contrast agents, such as Gd(DTPA),² which are used in medical diagnostics in magnetic resonance imaging (MRI) due to the paramagnetic properties of Gd(III) ions. Because free Gd (III) ions are highly toxic, Gd must first be complexed with strong organic chelators (e.g., polyaminocarboxylic acid chelating agents) to be considered safe to be administered to patients undergoing MRI.^{14,15} Its use started around 1988, when Gd-based contrast

agents were first introduced to the market.¹³ The contrast agents are injected into the human bloodstream and excreted via the kidneys. Due to the high stability of these compounds, they readily pass through humans bodies and then through conventional wastewater treatment plants, resulting in positive Gd anomalies in aquatic systems that receive treated effluents.^{2,11,16,17}

As emerging contaminants, there is still relatively little knowledge of the biogeochemical or anthropogenic cycles of REE, including Gd, in the environment. The few studies on the behavior of REE in estuaries have indicated that natural REE, including Gd, behave nonconservatively, are rapidly scavenged in low-salinity regions, and consequently have limited fluxes to marine waters.^{10,11,18,19} In contrast, anthropogenic, strongly chelated, anionic Gd complexes appear to behave conservatively during the estuarine mixing and have a long environmental half-life.^{5,8,10} Anthropogenic Gd is not particle-reactive, and it exclusively partitions into the truly dissolved REE pool.⁵ Consequently, anthropogenic Gd may be decoupled from the natural REE and serves as a conservative tracer of soluble wastewater-derived substances to estuarine and coastal waters.

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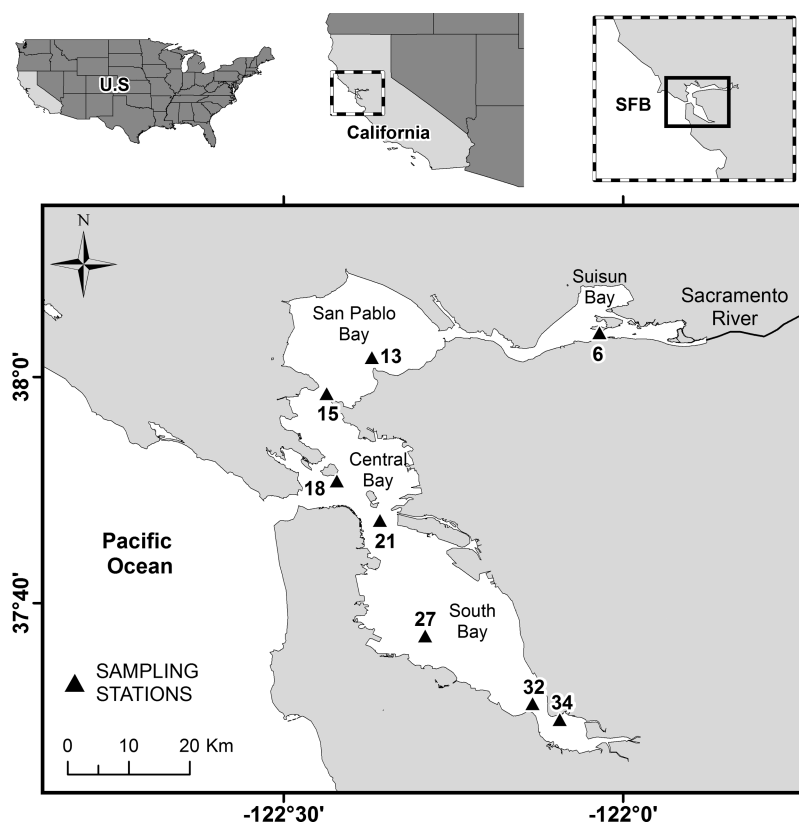


Figure 1. Sample stations along San Francisco Bay, California. For the time-series study, station 34 (Lower South Bay) was used.

Other industrial REE enrichments have also been found in aquatic systems. It has recently been shown that the Rhine River contains substantial amounts of anthropogenic Sm⁵ and La.⁶ Anthropogenic La has also been detected in aerosols.^{20,21} In addition, Lu and Yb anomalies that may also be associated with human activities have been measured in rainwater²² and waters of SFB.¹ However, the sources of those enrichments have not been resolved. The wider impact of the increasing industrial uses of REE on the environment is poorly understood.

The San Francisco Bay area has undergone a substantial population growth over the past few decades, increasing from ~6.0 million people in the 1990s to ~7.5 million people in 2013. Although this region is still adversely impacted by legacy pollutants (e.g., Hg and Pb) dating back one and a half centuries,²³ the potential contamination from REE has only occurred in the past 2 decades with the development of the 'Silicon Valley' around the southern reach of SFB and the development of MRI facilities throughout its watershed.¹ The San Francisco Bay Regional Monitoring Program (RMP) started around that time (in 1993)^{24,25} to systematically measure spatial and temporal variations of water quality in SFB to evaluate the effectiveness of the California Environmental Protection Agency's water quality program in meeting SFB Basin Plan objectives, including the protection of ecological services provided by the bay. The RMP has included collections of surface water samples, using rigorous trace metal clean techniques, throughout SFB,²⁶ and archives from those acidified samples were available for this time-series analysis.

We measured and assessed the spatial distribution pattern of REE in the waters of SFB and also the temporal distributions over a 20-year time period (1993–2013), concentrating on

evolving anthropogenic Gd anomalies during that period. Although samples collected for the RMP were unusually systematic and consistent compared to collections in other estuarine systems,²⁴ there were difficulties in our time-series analysis (i.e., the sample archive was not complete due to logistic reasons or there were no residual aliquots of some RMP samples). Often the analysis of the data is statistically compromised and is hindered by missing data, thus limiting statistical methods that are applicable.²⁷ Moreover, the effects of temporal small-scale and seasonal variability brings confounding factors for large-scale temporal analysis.²⁸ Therefore, we focused on the decadal variations, which correspond with the increasing industrial, and medical uses of REE in the system's watershed. On the basis of those analyses, we believe that REE are emerging technology-critical contaminants in SFB, due to increased mining activities, and increasing in use in a variety of new technological applications, with particular key applications within the energy-related new technologies (e.g., renewable energy and energy-efficient technologies).

Data on coastal waters carrying anthropogenic Gd are scarce, and studies reporting long temporal variation are nonexistent. Therefore, we report for the first time a twenty-year record of REE in a coastal environment demonstrating the contamination of surface waters of San Francisco Bay by anthropogenic Gd as well as the general increase of all REE during the last two decades.

■ MATERIALS AND METHODS

Samples. As previously noted, most of the water samples included in this study represent the long-term regional data collection efforts, which employed trace-metal clean techniques, with rigorous quality assurance and quality control protocols as

part of the San Francisco Bay RMP.²³ These collections included samples from the southern reach of SFB (station BA 30, close to station 34 Figure 1) that were collected during the summer to early fall (June–October) between 1993 and 2005. That sampling period is notable because it was during the region's dry period (Figure 2), when there was essentially no

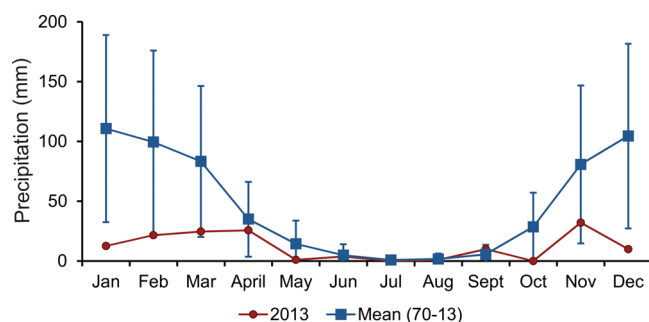


Figure 2. Mean monthly precipitation and standard deviation for the period of 1970–2013 and monthly precipitation for 2013 (data from <http://water.weather.gov/precip/>).

rain, that freshwater discharges were minimal compared to wastewater discharges, hydraulic residence times were longest (i.e., months), and concentrations of industrial discharges in the southern reach were consequently highest.²³ As previously indicated, archives of those RMP collections between 1993 and 2005 were incomplete, and no samples were archived after that. For some years, only unfiltered samples were available. Due to the relatively large amount of suspended particulate material in the southern reach of SFB, these samples were not analyzed, as it would represent a confounding factor in our study.

Details of sample collection, filtration, and storage have been described elsewhere.²⁶ Each filtered (0.45 μm) and acidified (pH 1.8) sample was stored in an acid-cleaned, polyethylene, plastic bottle that was enclosed in two plastic bags. For long-term storage, sample bottles were then stored in a large plastic bag inside a sealed bucket and kept in a dark room with limited access. Consequently, the integrity of those archived samples was preserved.

Additional, contemporary water samples from SFB were collected on a cruise aboard the R/V *Polaris* in December 2013. A total of eight stations, which constitute part of the RMP along a transect from the southern reach or South Bay to the Central Bay and then onto the northern reach (San Pablo and Suisun Bay), were sampled (Figure 1). Although that sampling period was during the region's typically wet period (marked by relatively high precipitation and associated surface runoff and fluvial inputs), an ongoing record drought (Figure 2) made conditions in SFB comparable to those of a normal dry (summer and early fall) sampling period. Samples were collected with a trace-metal clean surface pump system that included a peristaltic pump (Masterflex–Cole Parmer Instrument Company) and PFA Teflon tubing. The sample inlet, mounted on a telescopic rod, was lowered to around 1 m below the water surface at each sample station, and samples were filtered through Calyx capsule filters with 0.45 μm polypropylene membrane and stored in 1 L low-density polyethylene (LDPE) bottles. Sample bottles had been acid-cleaned by soaking in a 6 N HCl (reagent grade) for a week and a 7 N HNO₃ (reagent grade) for a week. The bottles were then stored in a weak HNO₃ (\sim pH 2; trace metal grade) solution for at least 30 days before being used. Sample bottles were rinsed

three times with sample water prior to filling. In the laboratory, the filtrate samples were acidified to a pH of 1.8 (equivalent to 4 mL of sub-boiled, quartz-distilled, 6 M HCl per liter of seawater). Complementary, surface hydrographic data (temperature, salinity, dissolved oxygen, and suspended particulate material) and concentration of nutrients were provided by Jim Cloern's group at the U.S. Geological Survey (<http://sfbay.wr.usgs.gov/access/wqdata/query/easy.html>).

Analytical Methods. REE were extracted and preconcentrated with the NOBIAS-chelate PA-1 resin using the methodology developed for our preliminary study of REE in SFB.¹ Due to the relatively high level of REE in the Bay, it was possible to use a smaller sample volume (20–30 mL) than previously reported by Hatje et al.¹ A manifold of four columns was used for the simultaneous processing of four samples. The resin was packed into 2 cm long columns with an internal volume of 27 μL (GlobalFIA). Prior to each extraction and preconcentration, the resin was extensively cleaned with the procedures described by Biller and Bruland.²⁹

Although we had not previously found any measurable differences between the recoveries of REE for coastal and ocean samples with and without pretreatment by UV oxidation,¹ we observed that without the UV pretreatment, the resin in some of the columns turned brownish and became less efficient, resulting in poor recoveries of samples from the southern reach of SFB. This region has relatively high amounts of dissolved organic carbon²⁶ that measurably interfere with some metal (e.g., Ag) extractions.³⁰ Therefore, all samples were UV-oxidized using a UVO cleaner (Model 342, Jelight Company, Inc.) with a mercury lamp, which has been shown to be adequate for destroying metal-binding organic ligands for a range of trace metals.^{29,31} The samples were irradiated for 4 h at \sim 16 mW cm⁻² in 90 mL Teflon jars modified with quartz lids imbedded in the caps. With this UV oxidation, no change was observed in the color of the resin and in the REE recoveries after multiple sample loadings.

Details of the sample preconcentration have been described elsewhere.¹ Briefly, immediately prior to extraction, the pH of the samples was adjusted to 4.7 ± 0.2 . The columns were rinsed with 0.05 M NH₄Ac rinse and conditioning solution for 3 min. Samples were then loaded onto the columns at a speed of 0.5 mL min⁻¹ (Dynamax, Rainen peristaltic pump). The columns were then flushed and rinsed with a 0.05 M NH₄Ac rinse and conditioning solution for 3 min. Each column was then eluted with 0.4–0.5 mL of 1N HNO₃ (herein referred to as E-HNO₃; trace-metal grade, Fisher Scientific,) spiked with 10 ppb Rh, using pressurized (5 psi) N₂. The eluate and sample mass were used to calculate the exact concentration factors for each sample. For each batch of samples extracted, at least 1 blank per column was determined. This blank consisted of California Coast (CUTZ II, August 2011) REE-free seawater that was loaded onto a column for 1 min and then eluted in the same manner as the samples. This seawater blank was pH-adjusted to pH 5.0 ± 0.5 and then pre-cleaned using the NOBIAS-chelate PA-1 resin to ensure that this seawater was REE-free. No difference was observed between system blanks on the various columns of the manifold. Reagent blanks were determined by adding double amounts of reagents (i.e., quartz-distilled HCl and sample buffer) in REE-free seawater and comparing to a blank with the normal amount of reagents. Reagent blanks from the quartz-distilled HCl and rinse and conditioning solution were negligible for all REE.

Table 1. Average System Blanks, Detection Limits, and GEOTRACES Reference Samples ($n = 3$)

elements	average blank (pmol kg ⁻¹)	detection limit (pmol kg ⁻¹)	sample GSC (pmol kg ⁻¹)	sample GSP (pmol kg ⁻¹)
¹³⁹ La	-0.004	0.87	16.4 ± 0.48 (99.1%)	4.18 ± 0.29 (115.1%)
¹⁴⁰ Ce	0.039	0.06	14.0 ± 0.11 (98.9%)	2.65 ± 0.02 (109.6%)
¹⁴¹ Pr	0.002	0.04	3.06 ± 0.03 (99.8%)	0.83 ± 0.01 (105.8%)
¹⁴⁶ Nd	0.013	0.09	13.8 ± 0.13 (100.1%)	3.91 ± 0.03 (106.5%)
¹⁴⁷ Sm	-0.019	0.36	3.16 ± 0.08 (96.6%)	1.33 ± 0.10 (104.0%)
¹⁵³ Eu	0.001	0.01	0.62 ± 0.005 (95.3%)	0.17 ± 0.01 (99.2%)
¹⁵⁷ Gd	0.003	0.03	3.32 ± 0.02 (99.0%)	1.22 ± 0.01 (93.7%)
¹⁵⁹ Tb	0.001	0.01	0.54 ± 0.004 (99.5%)	0.20 ± 0.004 (92%)
¹⁶³ Dy	0.002	0.06	3.76 ± 0.01 (97.8%)	1.50 ± 0.02 (106.4%)
¹⁶⁵ Ho	0.005	0.02	1.11 ± 0.01 (109.7%)	0.48 ± 0.01 (119.0%)
¹⁶⁶ Er	0.001	0.05	3.39 ± 0.02 (99.7%)	1.36 ± 0.02 (103.5%)
¹⁶⁹ Tm	0.002	0.001	0.46 ± 0.005 (95.8%)	0.16 ± 0.003 (107.7%)
¹⁷² Yb	0.001	0.02	2.85 ± 0.02 (96.6%)	0.85 ± 0.01 (105%)
¹⁷⁵ Lu	-0.002	0.001	0.46 ± 0.003 (100.2%)	0.13 ± 0.0003 (109.6%)

Values in brackets represent the % recovery in relation to Hatje et al., 2014.¹

A Thermo Element XR Magnetic Sector HR ICP-MS was used for REE analyses. The instrument was optimized for sensitivity while at the same time monitoring for oxide formation by pumping a 1 ppb tune solution (Rh, Ba, La, Ce, Pr, Nd, and Sm).¹ System blanks and the limits of detection (LOD) are listed in Table 1. Replicate analyses of REE in reference samples had relative standard deviations (RSD) of 0.25–2.9%, with the exception of La and Sm that, for unknown reasons, had RSDs around 7.5% for the GEOTRACES Surface Pacific (GSP; SAFE site) reference sample.

GEOTRACES Surface Coastal (GSC; Santa Barbara Basin Coastal Site) and GSP reference samples were run as a quality-control check (Table 1). Although there are no consensus values for REE concentrations of the GEOTRACES samples, values previously measured in GSC and GSP samples¹ and our new measurements were in good agreement (Table 1).

RESULTS AND DISCUSSION

Surface Transect throughout SFB for 2013. The measured REE data for the 2013 surface transect along SFB are listed in Table 2. The Gd concentrations along the SFB varied by an order of magnitude, from 14.1 pmol kg⁻¹ to 171 pmol kg⁻¹. Most of these values were substantially higher than those observed for the waters of the SFB plume and Central California coastal waters.¹ Nevertheless, according to ecotoxicological tests, the lanthanides seem to be less toxic than other contaminants, such as Cd and Pb.³² At the current level, the concentrations of Gd observed for SFB are well below peak concentrations (362 nmol L⁻¹),³² which could pose harmful effects on aquatic ecosystems. Nevertheless, REE are expected to share common characteristics regarding their toxicity; therefore, their toxicity could be additive and promote an increase of the potential risk in SFB and elsewhere.^{32,33}

There was a sharp decrease in Gd concentrations from the southernmost reach or Lower South Bay (LSB) to the Central Bay and then a small increase toward the northern reach of SFB. There were also similar, albeit smaller, increases in the other REE concentrations in those two SFB extremities. In addition, there was, in general, higher increases in light REE (LREE) than in heavy REE (HREE) in the southern reach of SFB.

Figure 3 illustrates the positive correlation between the Gd concentrations and nutrient (nitrate and nitrite) concentrations

($r = 0.98$; $p < 0.05$). This association is attributed to the relatively large amounts of agricultural and wastewater discharges to the northern reach of SFB and wastewater discharges to the southern reach of SFB that contain high loads of anthropogenic Gd and nutrients compared to those of northeast Pacific coastal waters mixing into the Central Bay. Moreover, the hydraulic residence time of waters in the Lower South Bay extends for months during dry periods, further contributing to the seasonal build-up in REE (Table 2) and nutrient concentrations. As previously noted, although this sampling collection was performed during autumn, a supposed wet season (Figure 2), it was a very atypical period in the midst of one of the longest droughts in the recent history of California, and the hydraulic flushing of the entire SFB system was unusually protracted, as it is during normal dry seasons. Because fluvial inputs and surface runoff to the South Bay are relatively limited, even during wet conditions, due to diversions for agriculture, industries, and municipalities, the highest levels of nutrients and Gd are attributed to the accumulation of wastewater discharges from hospitals, research facilities, and high-tech industries using REE in the South Bay.

To put that spatial disparity in perspective, the shallow waters of the South Bay receive 63% of the total effluents from publicly owned treatment works (POTWs), whereas the North Bay and the Central Bay receive only 20% and 17%, respectively.³⁴ Similarly to Gd, it has been reported that for Pb and Ag the combined loads from POTWs in the northern reaches are between 2- and 3-fold lower than those in the South Bay.³⁵ The differences in concentrations of Gd, and possible other contaminants, between the northern and southern reaches of SFB are not only due to the load of treated effluent inputs but also the hydraulic residence time and the composition of the effluents originated in each region that reflects the complexity and diversity of anthropogenic activities in the South and North reaches of the bay. Marshland, agricultural, and some urban and industrial developments are present in the northern reach, whereas the southern reach is surrounded by a megalopolis that includes San Francisco, Silicon Valley, and San Jose and consists of more than 5 million people. Consequently, it is not surprising that the highest concentrations of REE occur in the southern reach of SFB.

Normalized REE Ratios. REE fractionation, relative to the continental source, is identified by normalizing the REE

Table 2. Salinity and REE Concentrations (pmol kg⁻¹) for the 2013 Surface Transect along San Francisco Bay^a

stations	elements (pmol kg ⁻¹)														ΣREE	Ce/Ce*	Gd _{SN} /Gd _{SN} *	Gd _{anthrop}	Gd#	
	S	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb						Lu
6	19.0	55.2	64.4	11.3	52.9	12.4	3.47	31.8	2.59	18.2	5.28	17.4	2.54	17.1	2.75	297	0.59	2.3	18.2	13.6
13	30.1	52.4	40.7	9.67	46.0	10.4	2.86	20.5	2.25	16.0	4.65	14.2	2.09	14.2	2.30	238	0.42	1.8	9.00	11.5
15	30.7	61.3	53.1	11.9	54.0	11.8	3.15	21.9	2.45	16.6	4.65	14.5	2.11	13.8	2.23	273	0.45	1.7	8.89	13.0
18	32.3	43.3	29.8	7.60	35.5	7.86	2.16	14.1	1.71	12.1	3.40	10.4	1.49	9.75	1.56	181	0.38	1.6	5.37	8.73
21	31.2	47.6	35.3	9.03	42.1	9.52	2.59	18.7	2.13	14.6	4.25	12.9	1.90	12.5	2.05	215	0.39	1.8	8.05	10.7
27	31.6	88.9	118.6	19.8	87.5	19.7	5.26	49.8	3.91	25.9	6.76	22.4	3.36	23.4	4.05	479	0.65	2.5	29.5	20.2
32	30.0	87.3	69.3	21.3	100.2	25.2	7.01	107.2	5.31	36.3	10.1	32.8	4.87	34.5	5.86	547	0.37	3.9	79.9	27.2
34	28.2	195.8	264.8	60.1	267.7	62.8	16.1	171.4	10.8	67.1	15.8	49.8	7.18	48.4	7.88	1246	0.56	2.9	111.8	59.6

^aCe/Ce*, Gd_{SN}/Gd_{SN}*, Gd_{anthrop} calculated using eqs 1 and 2 and a third-order polynomial fit.

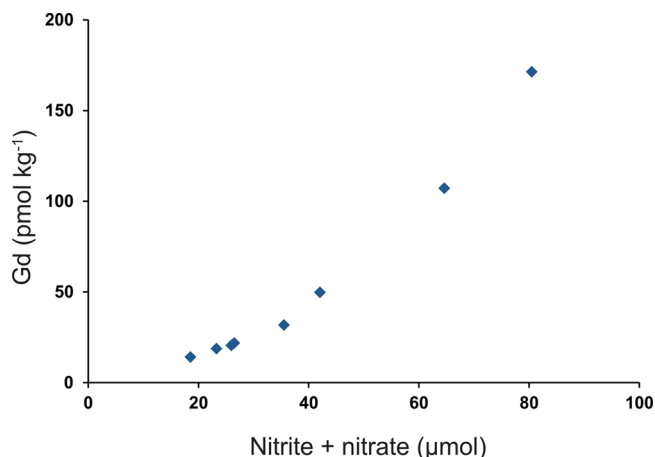


Figure 3. Distribution of Gd vs nitrate and nitrite concentrations for the 2013 surface transect along San Francisco Bay.

concentrations to those of average shale. Most studies have used Post-Archean Australian Shale (PAAS)³⁶ to normalize REE concentrations measured in seawater. This normalization not only helps to eliminate the Oddo–Harkins effect^{36,37} in the natural abundances but also allows an easy comparison with data from elsewhere. The shale-normalized REEs (suffix SN) patterns for the surface transect along SFB (Figure 4a) showed negative Ce anomalies, positive Gd anomalies, and an enrichment of HREE over LREE.

The overall slope of the REE pattern is commonly quantified as the shale-normalized ratio of a HREE to a LREE.³⁸ The relative HREE enrichment in seawater is expected and may be represented by the Er_{SN}/Nd_{SN} ratio, which ranged from 2.6, in

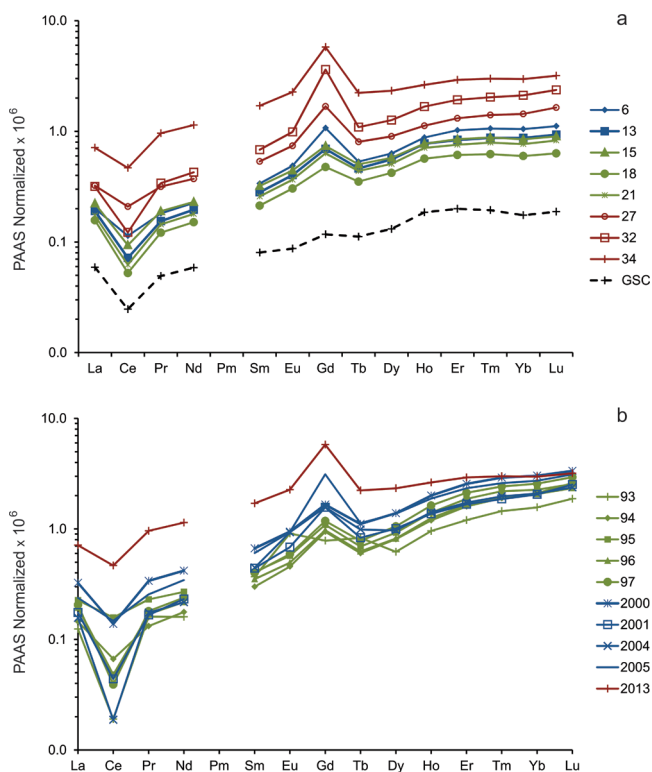


Figure 4. REE abundance normalized to PAAS along San Francisco Bay stations (a) and in the South Lower Bay (b) for the period between 1993 and 2013.

the southern reach, to 4.5 in the northern reach, showing that the fractionation of the REE series differs in both extremes of the Bay. This is consistent with studies that showed that HREE are more strongly partitioned into the complexed fraction versus the ionic state than the LREE.^{37,39} Because the complexed fraction of REE is less reactive to adsorption reactions, the HREE are less readily removed from seawater than are the LREE.

Among the REE, Ce is the only element that can be oxidized to the tetravalent state and fractionated from other trivalent REE in seawater, generating a Ce anomaly in the REE pattern. Anomalies are usually quantified by the ratio of the shale-normalized measured concentration to normalized theoretical concentration, determined by interpolation between neighboring elements. Ce anomalies were quantified with the following equation:⁴⁰

$$\text{Ce}/\text{Ce}^* = \text{Ce}_{\text{SN}} / (\text{La}_{\text{SN}} \times \text{Pr}_{\text{SN}})^{0.5} \quad (1)$$

where SN indicates shale-normalized value of the REE concentration, and * denotes the background interpolated concentration.

The Ce/Ce^* values in SBF varied from 0.4 to 0.7, which is within the range of anomalies observed in Tokyo Bay,¹¹ the high-salinity zone of Weser estuary,⁸ and other coastal areas. The Ce anomaly is a well-established feature in oxic estuarine waters and seawaters and reflect the fact that Ce has a biologically mediated redox cycle (i.e., oxidation of Ce(III) to Ce(IV)), which leads to its preferential removal.⁴¹ The Ce(IV) is present as a solid phase and is very insoluble in seawater. The highest anomalies were observed in the stations that had the highest dissolved Ce concentration, suggesting that it is controlling the Ce anomalies, which tend to decrease from both the northern and southern reaches toward the Central Bay. No significant correlation was observed between dissolved oxygen concentrations (7.2–8.5 mg L⁻¹), salinity (19–32.3), and suspended particulate material (12.9–230 mg kg⁻¹) with Ce/Ce^* ($r = 0.25, -0.46, 0.33; p > 0.05$).

Europium anomalies, when present, were small. Such anomalies are common in reducing environments that allow the presence of Eu^{2+} . However, the subtle presence of a small positive anomaly (when present) of Eu in SFB along a negative Ce anomaly, indicating oxidizing waters, suggest that neither can be solely explained by oxidizing water conditions.⁴²

REE values in SFB (Table 2) were also normalized for REE abundance for GSC reference sample collected in the Santa Barbara Basin, off central California, during an upwelling period (Table 1). The latter REE concentrations are considered comparable to those of coastal seawater off the California coast. This sample presents inter-element concentrations much more similar to those of the SFB waters than PAAS. Consequently, GSC normalization allowed us to evaluate the influence of anthropogenic inputs of REE in the SFB waters relative to the natural REE abundance in coastal waters off California. Besides, it emphasizes subtle differences between samples that might otherwise escape detection. The shale-normalized pattern for GSC waters (Figure 4a) was similar to those patterns observed in the Central Bay. It evidenced a fractionation toward the HREE resulting in an $\text{Er}_{\text{SN}}/\text{Nd}_{\text{SN}}$ ratio of 3.5, a negative Ce anomaly, and no measurable Gd anomaly. There was also a small depression of Tb and Dy in comparison to the HREE. This could be interpreted as the result of subtle tetrad effect, which can cause a separation of REE pattern into four groups, corresponding to the half, quarter, three-quarters, and

completely filled 4f shell, respectively,⁴³ and has been observed in seawater.^{44–46} In this case, we would have in fact a slight enrichment of Ho and Er. This tetrad effect nevertheless remains fairly unexplained.

The GSC-normalized REE pattern (Figure 5a) for samples located in the Central Bay and northern reach showed a

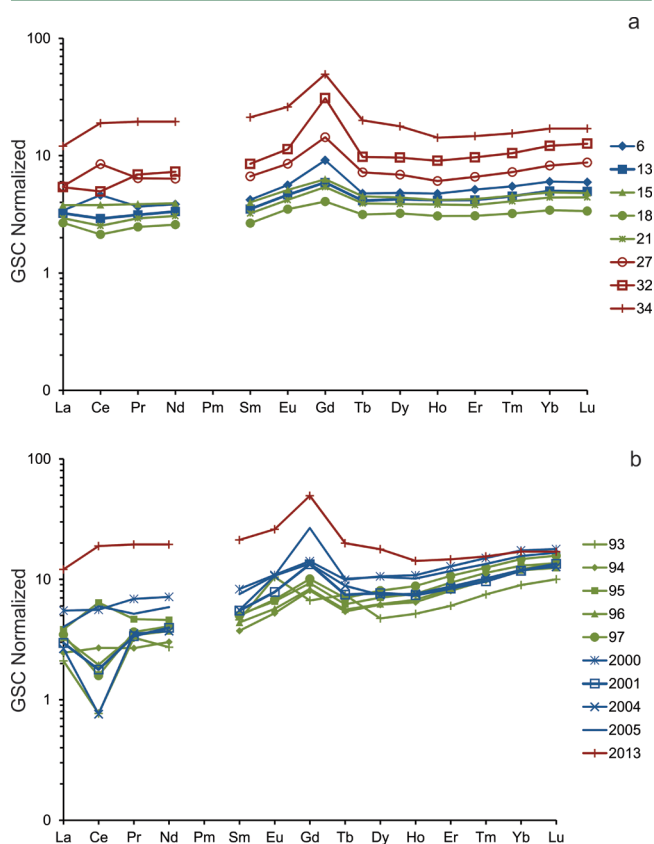


Figure 5. REE abundance normalized to GSC along San Francisco Bay stations (a) and in the South Lower Bay (b) for the period between 1993 and 2013.

relatively flat pattern (i.e., little fractionation) with a slight enrichment of HREE over LREE and clear Gd anomalies. Samples from South Bay presented much higher abundances of REE than those from Central Bay and northern reach in comparison to GSC. Moreover, the slope in the REE pattern observed in the innermost station in the South Bay was quite different from those in the rest of the SFB. Notably, the fractionation of Nd relative to Er, at that site, resembles more the shale ratio than the ocean ratio, suggesting a continental influence on top of numerous wastewater discharges in that region.

The Gd anomaly displayed a consistent behavior. In the GSC normalized REE pattern, the Gd anomaly was smallest in the Central Bay (Figure 5a), a well-mixed region that mediates water exchange between the inner reaches of the bay and the coastal Pacific Ocean. This spatial gradient was consistent with results from our previous study, which showed that a further decrease in the Gd anomaly can be observed along the SFB plume discharging into the adjacent California Current transition zone.¹ The waters in this region are a mixture of the SFB bifurcated estuary and the northeast Pacific coastal waters influenced by upwelling, which dilute the Gd concentrations and its anomaly. In contrast, positive Gd

anomalies systematically increase in both the northern and southern reaches of SFB, reaching maximum values in Suisun Bay, in the northern reach of SFB, and in the Lower South Bay (LSB). Gd normalized concentrations were ~50- and ~5-fold higher, respectively, in LSB and northern reach compared to those in the GSC. The large size of those anomalies precludes the possibility that they result from natural REE fractionation.

As previously indicated, that order of magnitude difference in Gd anomalies between the northern and southern reaches of SFB is attributed to several factors. Firstly, the population density of the southern reach is much greater than that of the northern reach, and the former is the home of “Silicon Valley”, where the use of REE by high-tech industries and hospitals is presumably quite high. (We have been unable to obtain data to substantiate that assumption from the California Environmental Protection Agency, the San Jose Wastewater Treatment Facility, or Stanford University’s hospitals because those measurements are not required by CWC 13267.) Secondly, the southern reach receives less than 10% of SFB’s mean annual river runoff, and POTW discharges are the main source of “freshwater” to that region.³⁵ Third, the hydraulic residence time of water in the southern reach during dry periods, which included most of the 4 years preceding our last collection in December, 2013, is greater than 3 months, compared to that of the northern reach, which ranges from days to weeks.⁴⁷

Positive Gd anomalies are primarily due to the use of relatively refractory Gd complexes (such as Gd-(DTPA)²⁻, where Gd is strongly chelated with DTPA⁵⁻) in MRI, as first revealed by Bau and Dulski.² Due to their exceptionally high stability, these Gd complexes are not removed by commonly used wastewater treatment technologies and pass through conventional wastewater treatment plants into surface waters that reach coastal systems.^{1,4,8,10,11,48}

There are several methods in the literature to predict if Gd has anomalous concentrations. These include linear and geometric extrapolations and interpolations using HREE or LREE^{5,7,8,12,49,50} and modeling the shape of the PAAS-normalized REE pattern using a third order polynomial fit.^{9,51} McLennan clearly stated that the use of arithmetic means, although occasionally used to calculate Gd, Ce, and Eu anomalies, when employing REE concentrations (e.g., Ce/Ce* = 2Ce_{SN}/(La_{SN} + Pr_{SN}) and Gd/Gd* = Gd_{SN}/(0.33Sm_{SN} + 0.67Tb_{SN})) is incorrect, specially for steep normalized REE patterns, because REE patterns are plotted on a logarithmic scale, and it can lead to serious errors.⁴⁰

We tested all of the different approaches cited above and found relatively small variability in Gd/Gd* results (i.e., relative standard deviations between calculations varied between 3 and 11%). The smallest anomalies were obtained by the approach that uses the LREE Eu and Nd.⁵ Europium can be decoupled from other REE due to its redox behavior and, therefore, may show anomalies in REE patterns. It is essential to verify this prerequisite before the quantification of Gd anomalies following this approach; the use of an anomalous element to evaluate the presence of a further anomaly creates an artifact. The highest anomalies were obtained when we used the approach proposed by Ogata and Terakado (i.e., interpolation with Sm and Dy),¹² Møller et al, (i.e., polynomial fit with all REE except Ce and Eu),⁵¹ and Hissler (i.e., interpolation with Nd and Dy).⁵² Despite differences in those approaches and the elements employed, the results did not differ significantly ($p > 0.05$).

Among the evaluated methods, the third order polynomial fit is the only approach that made no implicit assumption as to whether Gd behaves as LREE or HREE.⁹ As a consequence, the application of this method is more compelling, once it can be employed for the whole range of water samples, from freshwater to seawater to wastewater. Results obtained by this approach also facilitate the comparisons between different studies and geographical areas. Here, we employed a third order polynomial fit⁵¹ to determine the Gd*, where only Eu and Ce were not included, because of their redox chemistry. The background interpolated concentration was then used to determine the anthropogenic component of Gd (Gd_{anthrop}) using the following equation:

$$\text{Gd}_{\text{anthrop}} = \text{Gd}_{\text{measured}} - \text{Gd}^* \quad (2)$$

The anomalies of Gd (Gd/Gd*) varied from 1.6 in the Central Bay to 3.9 at the Lower South Bay (Table 2). Corresponding estimates of anthropogenic Gd concentrations ranged from 5.37 pmol kg⁻¹ (Central Bay) to 111.8 pmol kg⁻¹ (South Bay) and accounted for up to 75% of the total Gd in the southern reaches of the Bay. For the northern reaches, the estimated anthropogenic Gd concentrations (Table 2) were up to 10-fold lower than in the South Bay. Although the sources of anthropogenic Gd are considered smaller in the North than in the South Bay, they are still important and cannot be disregarded. Although there was a marked decrease in Gd anomalies from North and South Bay toward the Central Bay, it is clear that despite dilution and removal processes, the anthropogenic Gd (38% of the total Gd concentration at the Central Bay) from SFB reaches the northeast Pacific coastal waters, as previously shown.¹ These results again attest that anthropogenic Gd complexes exhibit conservative behavior and are not measurably degraded within the SFB estuary. They also indicate that the half-lives of those complexes are at least several weeks, and possibly months, as previously indicated by laboratory experiments.⁵³ Consequently, these data clearly show that anthropogenic Gd can be used as a conservative tracer of soluble wastewater-derived substances^{9,13,50} in estuarine and marine waters and also for hydrological processes.⁵⁴ To summarize, the distribution of anthropogenic Gd along SFB reflects the mixing of three end-members: the northern reach, representing the influx from the Sacramento River basin and the Delta outflow; the South Bay area influx, mainly derived from wastewater effluents from a diverse number of sources, including the “Silicon Valley”; and a number of POTWs and the coastal water entering through the Central Bay.

Time-Series Study. Ancillary variables (<http://sfbay.wr.usgs.gov>) for the studied period varied in relative narrow range, indicating that all samples for the time-series study were collected under similar environmental and hydrological (Figure 2) conditions. Water was well-oxygenated (6.3–7.4 mg L⁻¹) and presented relatively low concentrations of suspended particulate matter (10.3–63.8 mg L⁻¹, respectively, for 2004 and 2013) and high salinities (23.22–31.54, respectively, for 1995 and 1994) during all sampling periods.

The temporal analyses showed a substantial increase for the total dissolved REE content (ΣREE) from 1993 (217 pmol kg⁻¹) to 2013 (1246 pmol kg⁻¹; Table 3). For the time span between 1993 and 2005, all REE distributions exhibited similar enrichment patterns, with peaks in 1995, 2000, and 2005. However, from 2005 to 2013, the increase in REE concentrations was more prominent for the most particle-

Table 3. REE Concentrations (pmol kg⁻¹) at the Lower South Bay for the Period between 1993 and 2013^a

year	elements (pmol kg ⁻¹)														ΣREE	Ce/Ce*	Gd _{SN} /Gd _{SN} *	Gd _{anthrop}	Gd*
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu					
Sep '93	34.1	10.8	10.1	37.6	13.6	6.45	23.2	4.04	17.9	5.76	20.4	3.5	25.5	4.64	217	0.13	1.6	8.3	14.9
Aug '94	39.8	37.7	8.27	41.5	11.1	3.24	28.0	2.94	23.2	7.18	27.2	4.54	34.3	6.42	275	0.48	2.0	14.0	14.0
Aug '95	62.2	89.5	14.4	63.2	15.0	4.06	32.3	3.37	26.6	8.43	31.8	5.25	36.9	6.30	399	0.69	1.8	14.3	18.0
Jul '96	53.2	27.2	10.6	51.1	12.9	3.52	28.9	3.04	23.5	7.52	28.3	4.70	33.8	5.78	294	0.27	1.9	13.5	15.4
Aug '97	56.4	22.2	11.3	56.0	14.8	4.20	34.9	3.80	30.4	9.78	36.2	5.80	41.9	7.28	335	0.20	1.9	16.2	18.7
Aug '00	89.2	78.2	21.2	98.3	24.6	6.72	49.1	5.40	39.9	12.0	43.5	6.98	49.4	8.28	533	0.42	1.7	20.9	28.2
Aug '01	48.1	24.9	10.4	54.4	16.3	4.85	46.3	4.05	29.0	8.21	28.4	4.47	33.5	6.23	319	0.26	2.5	27.6	18.7
Aug '04	43.0	10.6	10.9	51.0	16.5	6.61	46.7	4.81	28.0	8.46	29.5	4.72	34.1	5.89	301	0.11	2.4	26.9	19.8
Aug '05	65.2	83.5	16.0	80.8	22.3	6.65	92.7	5.50	39.5	11.3	39.7	6.22	44.4	7.71	522	0.60	3.4	65.3	27.4
Dec '13 ^b	195.8	264.8	60.1	267.7	62.8	16.1	171.4	10.8	67.1	15.8	49.8	7.18	48.4	7.88	1246	0.56	2.9	111.8	59.6

^aCe/Ce*, Gd_{SN}/Gd_{SN}*, Gd_{anthrop} calculated using eqs 1-2. ^bStation 34 Table 2.

reactive LREE. Lanthanum concentrations, for instance, increased from 65.2 to 195.8 pmol kg⁻¹, whereas Er concentrations only varied only from 39.7 to 49.8 pmol kg⁻¹ (Table 3). These results indicate that there was a change of provenance or processes controlling the inputs of REE to the SFB during this period. Owing to their low dissolved concentrations, the REE can be particularly influenced by chemical transfer between the dissolved and particulate phases during transport, revealing their reactivity during natural processes. Unfortunately, there were no samples available for this time span to evaluate if those temporal changes were continued or specific to a certain period of time.

Gadolinium concentrations exhibited a gradual, consistent increase similar to those of the LREE. A minimum concentration for Gd was observed in 1993 (23.3 pmol kg⁻¹); it doubled in 2000 (49.1 pmol kg⁻¹) and reached a maximum of 171 pmol kg⁻¹ in 2013. Cerium also exhibited a large temporal variation, but due to its redox behavior, we cannot compare its temporal changes with the other REE. The Ce/Ce* values varied from 0.1 to 0.7. The minimum values were observed in 1993 and 2004, indicating that Ce (III) may have been more intensely oxidized during the summer of those years. The levels of suspended particulate material at these occasions were not particularly high enough (i.e., 11.9 and 10.3 mg L⁻¹, respectively, for 1993 and 2004) to suggest that particles had an important role controlling Ce concentrations.

Normalized REE Ratios. The shale-normalized REE patterns for the time-series study are illustrated in Figure 4b. There was a gradual increase in all REE_{SN} patterns from 1993 to 2005, followed by a larger increase in 2013 for the LREE, Gd, Tb, and Dy ratios. No clear anomaly was observed for the REE_{SN} pattern, contrary to Gd (Figure 4b), indicating that natural sources play an important role in the cycling of these elements in SFB.

Shale-normalized patterns were strongly LREE-depleted between 1993 and 2005, with Er_{SN}/Nd_{SN} ratios that ranged from 6.1 to 9.0. In marked contrast, REE_{SN} pattern in 2013 exhibited a different slope, with Er_{SN}/Nd_{SN} ratio at least two times smaller than in previous years. There was a clear fractionation of REE at the southernmost station at the South Bay between 2013 and preceding years, as well as in the transect performed in the Bay (Figure 4a). That fractionation is even clearer for the GSC normalized REE pattern (Figure 5b). Data from 1993 to 2005 presented a relatively flat distribution, with only a small enrichment of HREE over LREE compared to GSC. The temporal trends in LREE concentrations were very similar to that of Gd.

There was a large increase of Gd normalized concentration over time. It was assumed that this increase reflects the large number of MRI examinations in the SF Bay area. Data on the use of MRI are available for only a small number of countries. For the United States, it has been shown that between 1997 and 2006, the number of applications has increased dramatically.⁵⁵ There are no available data for the number of MRI units and applications for the SFB area. However, the United States, considered a supersaturated market, is responsible for around 46% of worldwide sales of MRI, and the number of machines in the United States jumped from 12 units in 1995 to 11 000 units in 2012 (<http://www.magnetic-resonance.org/ch/21-01.html>). The high increase in MRI units and applications observed for the United States, in general, has also occurred in the Bay area, but surprisingly, the data does not reflect such a high increase. The anthropogenic anomaly of Gd

is possibly a common feature of the REE distribution of other coastal systems along the coast of the United States that are subject to receiving wastewater enriched in Gd due to high-tech industrial and, especially, medical applications.

The anomalies of Gd (Gd_{SN}/Gd_{SN}^* ; Table 3) ranged from 1.6 in 1993 to 3.4 in 2005. Estimated anthropogenic Gd concentrations jumped from 8.27 pmol kg⁻¹ in 1993 to 27.6 pmol kg⁻¹ in 2001, and it then nearly doubled from 65.3 in 2005 to 112 pmol kg⁻¹ in 2013. Although anthropogenic concentrations increased over 1 order of magnitude over a 20 year period, the proportion of anthropogenic Gd in the total concentration increased only from 36% to around 70% for 1993 and 2005–2013, respectively. Despite the increase in anthropogenic Gd over time, the natural component of the Gd concentration still represented at least one-third of the total Gd concentrations in SFB from 2005 onward, which may account for the similar temporal distribution patterns of Gd and the LREE.

In summary, the waters of SFB contain substantial positive anomalies of Gd. The maximum concentrations of Gd were observed in the southern and northern reaches of the SFB and were positively correlated with nutrient (i.e., nitrate and nitrite) concentrations. Although the Gd concentrations constituted up to 20% of the ΣREE, they were well below the threshold of ecotoxicological effects.^{32,33} Corresponding Gd anomalies are, like elevated nutrient concentrations, primarily attributed to wastewater treatment plant discharges of refractory MRI contrast agents used in hospitals and medical research centers. This usage presumably accounted for the marked increase of anthropogenic Gd in the southern reaches of SFB between 1993 (8.27 pmol kg⁻¹) and 2013 (112 pmol kg⁻¹). It is unlikely that this increasing trend will be broken any time soon. Because MRI is a modern technique still in expansion, it is expected that the concentration of $Gd_{anthrop}$ in coastal systems will also increase in the future. These increases may possibly be accompanied by increases of other REE concentrations in the environment, due to their growing applications in new high-tech products and processes. Although we observed temporal trends in the distribution of the LREE La, Sm, and Pr similar to that of Gd, these elements did not show positive anomalies, and at the present, we cannot state that their increases were related to anthropogenic activities as previously reported elsewhere.^{5,6}

Finally, the temporal $Gd_{anthrop}$ distribution in SFB is a clear example of the changing scenario of REE cycles in estuarine and coastal environments. A few years ago, REE were only used as tracers of natural processes in aquatic systems. However, their concentrations and ratios in those systems may now be measurably impacted by the rapidly expanded use of REE, as we observed in SFB. Consequently, anthropogenic Gd complexes, with their relatively conservative behavior and long half-lives in estuarine and marine waters,⁸ now constitute a unique tracer of wastewater inputs and the dispersion of wastewater-derived contaminants in SFB and other coastal systems. However, there are currently substantial gaps in our knowledge of REE, from their anthropogenic levels and fate to their biogeochemical or anthropogenic cycling and their individual and additive toxicological effects. Consequently, the adoption of new public policies and the development of more effective treatment technologies will determine the future adverse impacts of REE in aquatic systems.

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Author Contributions

V.H. and K.B. conceived, designed, and analyzed the data. V.H. performed the 2013 fieldwork and all analyses. A.R.F. provided the time-series acidified samples. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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