Rare earth element abundances in some seawaters and related river waters from the Osaka Bay area, Japan: Significance of anthropogenic Gd

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INTRODUCTION

Recently evidence for Gd (gadolinium) contamination of anthropogenic origin has been found in some river waters and some seawaters (Bau and Dulski, 1996; Nozaki et al., 2000; Möller et al., 2000; Kümmerer, 2001; Elbaz-Poulichet et al., 2002; Zhu et al., 2004; Verplanck et al., 2005). Those relatively high Gd concentrations are attributed to the Gd chelates used as Magnetic Resonance Imaging (MRI) contrast agents in medical use (e.g., Bünzli and Choppin, 1989). An important characteristic of the Gd contrast agents is extremely high stability constants of about $10^{17}$ to $10^{23}$, resulting in their rapid elimination from human body and non-reactive nature (e.g., Cacheris et al., 1990; Tang et al., 2003). Given that the anthropogenic Gd sources are restricted to sewage treatment plants (STP), they are expected to become an excellent geochemical tracer of domestic wastewaters in densely populated bay areas. On the other hand, N- and P-compounds from STP are altered by many factors such as biological activities and supply from sediments during the course of their spreading.

In general, the amount of Gd MRI contrast agents drained into natural waters is very small, and it is very difficult to discriminate such anthropogenic Gd from the natural Gd in water samples. However, because Gd is one of the rare earth elements (REEs) that have similar chemical properties, the anthropogenic Gd of extremely low concentrations can be realized as Gd anomaly in the REE patterns. The Gd anomalies in river waters were first reported by Bau and Dulski (1996), and also have recently been found for the river and seawater samples from the Tokyo and Nagoya regions in Japan (Nozaki et al., 2000; Zhu et al., 2004).

Osaka Bay has an oval shape with a length and width of about 60 and 30 km, respectively. The Yodo River together with other relatively large rivers flow into the northeastern and innermost bay area, and thus the area can be considered as an estuary. Osaka City and other satellite cities are located at this side, forming a secondary populated region in Japan. Therefore, the larger Gd anomalies are expected for the seawater samples from the inner part of Osaka Bay.

Some major and trace elements in seawaters and related river waters from the Osaka Bay area, Japan were analyzed in order to examine rare earth element (REE) behaviors, especially the relationship between anthropogenic gadolinium (Gd) and nutrient concentrations. The local silicic rock normalized REE patterns for the seawaters show features of light REE depletion, negative Ce anomaly, and very small Eu anomaly. Moreover, some samples have obvious positive Gd anomalies due to contamination of Magnetic Resonance Imaging (MRI) contrast agents in medical use. We calculated the anthropogenic Gd concentrations by subtracting the assumed natural Gd concentration from the measured one. The anthropogenic or excess Gd concentrations of the seawater samples are well correlated with nutrient concentrations (NH$_4$-N, NO$_2$-N, NO$_3$-N, PO$_4$-P). Because both anthropogenic Gd and nutrients are abundant in sewage treatment plant (STP) effluents and much less abundant in non-contaminated river and seawaters, the observed trends can be explained by dilution of STP effluents with non-contaminated river and seawaters. It was found that the nutrient concentrations for a hypothetical STP effluent calculated by using these correlation lines are consistent with the average nutrient contents for the STP effluents in the study area. Moreover, we made a rough estimation of Gd budget in Osaka Bay. The estimated amount of the Gd MRI contrast agents consumed in the area seems to be consistent with the excess Gd concentrations of river and STP waters. The Gd observations in this study suggest that the Gd anomaly data can be used as a geochemical tracer of wastewater component in urban areas.

Keywords: Gd anomaly, estuary, Osaka Bay, nutrient, rare earth elements, trace elements
Some investigators have focused on the behavior of nutrients in Osaka Bay. The domestic waste waters and other organic matters in this urban area have caused serious water quality deterioration in the area, which has been documented by geographical distribution patterns of nutrient concentrations in Osaka Bay (e.g., Joh, 1986). Stratification of water in summer gives rise to almost anoxic condition in the bottom of the innermost bay area. Decomposition of organic matter in sludge sediments supplies nutrients to water, promoting eutrophication of the inner bay.

It has been pointed out that more than 75% of nitrogen and phosphorus outflow from Osaka Bay through Tomogashima Strait (Yanagi et al., 1985; Tanimoto and Hoshika, 1997; Hoshika et al., 1999). On the other hand, Fujiwara et al. (1997) has stressed the inflow of nutrient rich relatively deep ocean water from the Kii Channel in conjunction with outflow in the upper layer as estuarine circulation. Such intrusion of nutrient-rich water along the bottom of the Kii Channel from the Pacific Ocean seems to be related to the flow path of the Kuroshio Current (Ozaki et al., 2004). Hayashi and Yanagi (2001) examined phosphorus cycling in the area using a numerical ecosystem model (a box model) consisting of euphotic and aphytic layers and pointed out that DIP (dissolved inorganic phosphorus) in the euphotic layer is mainly supplied by decomposition of DOP (dissolved organic phosphorus) and detritus. Moreover, the ratios of phosphorus and nitrogen originated from land and the open ocean in the Seto Inland Sea were estimated to be 0.28:0.72 and 0.19:0.81, respectively (Yanagi and Ishii, 2004). Moreover, the eutrophication caused by wastewater discharge and the effect of reclamation projects has been argued as an environmental issue in the area (e.g., Ueshima et al., 1999; Sanukida, 2002).

In contrast to these labile nutrients (P, NO₃, NO₂ and NH₄), which are affected by several processes such as biological activities, dissolution of sedimentary components and outflow and inflow through Tomogashima Strait (cf., Takeoka, 2002), the source of Gd contrasting agents is restricted to STP. Despite such simplicity of the Gd contrasting agents as a geochemical tracer, REE data for the area are sparse. In this study, we would like to report concentration data of REEs and some other elements in seawaters together with related river waters from the Osaka Bay area to accumulate fundamental REE data including Gd anomaly and to examine the relationship between the Gd anomaly and nutrient concentrations.

**SAMPLES AND ANALYTICAL METHODS**

The sampling sites for river waters, seawaters and STP...
Rare earth element abundances and anthropogenic Gd in seawaters

The surface seawaters and river waters were collected with a polyethylene bucket. At the sampling positions of I and M, bottom waters were also collected using Bandon Sampler at different seasons (summer and fall). The depths for them were not exactly measured, but were considered to be a few meters above the sediment surface. These water samples were immediately filtered through a 0.45 µm or a 3 µm membrane filters into polyethylene bottles. The filtered samples for REE and other cation analyses were immediately acidified with HCl (20 ml of 6M HCl for one liter sample). For NH4-N, NO2-N, NO3-N, and PO4-P analyses, the filtered samples were immediately frozen using dry ice and stored in a freezer at the laboratory.

Concentrations of Na were determined by the flame atomic absorption (AA) method, whereas Fe and Mn were measured by flameless atomic absorption method with a Hitachi Z-8200 AA spectrometer. For nitrate analyses, samples were passed through copperized Cd reduction columns to reduce nitrate to nitrite. The nitrite was determined by diazotizing with sulfanilamide and coupling with N-1-naphthyl-ethylenediamine to form a purple azo dye that was measured at absorbance of 540 nm using 10 mm length cell. Nitrate was calculated by difference between nitrate plus nitrite and nitrite. Ammonium concentrations were measured by indophenol method. Phosphorus (PO4 3-), and silica were determined by colorimetric methods using the molybdenuim blue complex.

REEs and Ba were measured by mass-spectrometric isotope dilution method using a thermal ionization mass-spectrometer (JEOL 05RB). The REEs and Ba were firstly separated from major elements by coprecipitation with ferric-hydroxide using about one litter sample (e.g., Masuda and Ikeuchi, 1979). The ferric-hydroxide thus formed was separated by centrifuge, and treated with HF-HClO4. After evaporation, the residue was dissolved by HCl, and conventional cation exchange column method was applied for separation of light REEs and heavy REEs. In order to avoid Ba interference to La measurements, nitric acid solutions were used for further elution (Jahn et al., 1980).

For analyses of 3 µm filtration samples, before applying the above procedures, decomposition of particulate matters was performed by conc. HNO3 treatment followed by HF-HClO4 treatment. All of the acids were purified by sub-boiling several times with quartz glass distillation vessel. The total analytical blanks for the REE data were sufficiently low, but in some cases, blank corrections of about 10% were made at a maximum. All of the data listed in Table 3 are blank corrected. Uncertainties for most elements are believed to be less than 3%, but around 5% might occur in some cases of Gd, Dy and Yb.

RESULTS

Nutrients, Fe and Mn

The analytical results for cations along with sample sites are summarized in Table 1. The concentrations of NH4-N, NO2-N, NO3-N, PO4-P and SiO2-Si are presented.
Table 2. Concentrations of nutrient elements

<table>
<thead>
<tr>
<th>Sample name</th>
<th>NH₄-N (ppm)</th>
<th>NO₂-N (ppm)</th>
<th>NO₃-N (ppm)</th>
<th>DIN[2] (ppm)</th>
<th>PO₄-P (ppm)</th>
<th>TP (ppm)[3]</th>
<th>SiO₂-Si (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-7-S-45</td>
<td>0.26</td>
<td>0.019</td>
<td>0.43</td>
<td>0.709</td>
<td>0.052</td>
<td>0.073</td>
<td>1.0</td>
</tr>
<tr>
<td>I-7-B-45</td>
<td>0.17</td>
<td>0.048</td>
<td>0.0028</td>
<td>0.221</td>
<td>0.030</td>
<td>0.043</td>
<td>0.65</td>
</tr>
<tr>
<td>M-7-S-45</td>
<td>0.025</td>
<td>0.0016</td>
<td>0.023</td>
<td>0.050</td>
<td>0.0051</td>
<td>0.011</td>
<td>0.051</td>
</tr>
<tr>
<td>M-7-B-45</td>
<td>0.075</td>
<td>0.014</td>
<td>0.021</td>
<td>0.110</td>
<td>0.030</td>
<td>0.028</td>
<td>0.33</td>
</tr>
<tr>
<td>I-11-S-45</td>
<td>0.29</td>
<td>0.060</td>
<td>0.27</td>
<td>0.620</td>
<td>0.059</td>
<td>0.084</td>
<td>0.97</td>
</tr>
<tr>
<td>I-11-B-45</td>
<td>0.093</td>
<td>0.038</td>
<td>0.069</td>
<td>0.200</td>
<td>0.023</td>
<td>0.044</td>
<td>0.33</td>
</tr>
<tr>
<td>N-7-S-45</td>
<td>0.021</td>
<td>0.0062</td>
<td>0.019</td>
<td>0.066</td>
<td>0.012</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>N-11-S-45</td>
<td>0.14</td>
<td>0.046</td>
<td>0.16</td>
<td>0.346</td>
<td>0.086</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>M-11-S-45</td>
<td>0.33</td>
<td>0.074</td>
<td>0.22</td>
<td>0.624</td>
<td>0.055</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>M-11-B-45</td>
<td>0.12</td>
<td>0.035</td>
<td>1.3</td>
<td>1.46</td>
<td>0.072</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>YO-7-R-45</td>
<td>0.011</td>
<td>0.018</td>
<td>0.60</td>
<td>0.629</td>
<td>0.049</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>MU-11-R-45</td>
<td>0.0063</td>
<td>0.021</td>
<td>0.91</td>
<td>0.937</td>
<td>0.033</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>YO-11-R-45</td>
<td>0.12</td>
<td>0.035</td>
<td>1.3</td>
<td>1.46</td>
<td>0.072</td>
<td>3.0</td>
<td></td>
</tr>
</tbody>
</table>

[2] See explanations in Table 1.
[3] TP was determined for 3 µm filtered samples.

**REE patterns for the seawaters**

The measured REE data are listed in Table 3, and are illustrated in so-called REE pattern diagrams (Fig. 3). The normalizing values used in this study are the average REE abundances of 12 silicic rocks occurred in the Hyogo Prefecture where Osaka Bay is adjoined (Terakado and Masuda, 1988), and are presented in Table 3. The silicic rock data of Terakado and Masuda (1988) are suitable for the normalization, because these rocks can be considered as representatives of crustal rocks in the area around the Seto Inland Sea (cf., Terakado and Fujitani, 1995). Moreover, the average values of these silicic rocks are similar to those of shales such as PAAS (Post-Archean average Australian shale) (Nance and Taylor, 1976) or NASC (North American shales composite) (Haskin et al., 1966). Furthermore, if a systematic error may occur in our measurements, the bias can be cancelled, because the same analytical technique was adopted for both measurements.
for those normalizing values and the present data.

The silicic rock normalized REE patterns for the seawaters are characterized by relative depletion of light REEs and negative Ce anomalies. The Eu anomalies are not conspicuous or relatively small. The REE concentrations are not correlated with salinity, but the Lu/La ratios, a measure of the slope of the REE pattern, are broadly correlated with salinity (Fig. 2-I) (detailed discussions about the Gd anomalies will be presented in later sections).

REE patterns of the river and sewage effluent waters

The REE patterns of the Yodo river samples (Fig. 4) show light REE depleted patterns similar to those of the seawater samples, but their Ce anomalies are very small. The smallness of these Ce anomalies is conspicuous when they are compared with those of the stream waters in the Rokko Mountain area (cf., Nakajima and Terakado, 2003). The Yodo river samples are also characterized by obvious Gd anomalies. Note that there exist several wastewater treatment plants along Yodo River.

Two Muko river samples show considerable enrichment of heavy REEs (Fig. 4-A). It is interesting that significant heavy REE enrichments similar to these data were reported for the ground-waters from the western region of the Muku river delta (Otsuka and Terakado, 2003).

The STP effluent samples show overall heavy REE enrichments similar to the seawater and river waters (Fig. 4-B), and their Gd anomalies are obvious. In addition, the Nd points seem to deviate upward from the light REE values. Such Nd anomaly, which is an unusual phenomenon, is considered to be attributed to a pollution of Nd from a factory (Santoku Corporation) which deals with Nd-bearing magnet. It is indeed a rare case that the factory happens to be located in the drainage area of this STP.

Comparison between 3 \( \mu m \) and 0.45 \( \mu m \) filtered samples

The concentration ratios of 3 \( \mu m \) to 0.45 \( \mu m \) filtered samples for each sampling site are illustrated in Fig. 5-a. The 3 \( \mu m \)/0.45 \( \mu m \) ratios tend to be high in the light REE relative to the heavy REE, and the obvious positive Ce and Eu anomalies are seen. The subtracted values (3 \( \mu m \) minus 0.45 \( \mu m \) values), which correspond to the REE abundances contained in the particles between 0.45 and 3 \( \mu m \) sizes, are also plotted in Fig. 5-b. Their overall patterns are relatively flat in the light REE parts and show somewhat heavy REE enrichment without obvious Ce anomalies.

The light REE enriched feature for the 3 \( \mu m \)/0.45 \( \mu m \) filtered samples were observed in the drainage area of the Rokko Mountain area (cf., Nakajima and Terakado, 2003).
ratios indicates that the light REEs tend to be more incorporated into the particulate matters, suggesting that the REEs in seawaters are scavenged in association with precipitation of the particulate matters. Such contention has been documented by the previous investigators (e.g., Byrne and Kim, 1990; Elderfield et al., 1990; Sholkovitz et al., 1994; Byrne and Sholkovitz, 1996; Sholkovitz, 1995; Fu et al., 1997; Tachikawa et al., 1999; Kuss et al., 2001; Arraes-Mescoff et al., 2001). However, silicic rock normalized REE patterns for the 3–0.45 µm size fractions are not so much enriched in the light REE (Fig. 5-b). Moreover, these REE patterns do not show obvious Ce anomalies. Such relatively flat and no-Ce anomaly features suggest that these particles, as a whole, are composed of detritus of crustal rocks that are characterized by flat silicic rock normalized pattern and lack of Ce anomaly.

Ce anomaly
The size of the Ce anomaly is expressed by Ce/Ce*, where Ce is the measured Ce concentration, and Ce* is the interpolated one obtained from the La-Nd linear line on the REE pattern diagram (log-scale in ordinate). In Fig. 6-a, Ce/Ce* values are plotted against Fe contents, and both seawater and river water points fall almost on the trend. Moreover, the Ce/Ce* values of the seawater data are also correlated with Mn contents, though the Mn points for the river waters deviate from the seawater trend (Fig. 6-b). These correlations suggest that Ce⁴⁺ might have been precipitated with Fe-Mn hydroxides as have been discussed by the previous investigators (e.g., Sholkovitz et al., 1978; Elderfield et al., 1990), though detailed discussion on the Ce and Fe-Mn behaviors are beyond the scope of this study.

DISCUSSION
In this paper, we would like to focus on the anthropogenic Gd concentration and its relation to nutrient concentrations. For this purpose, the characteristics and variations of the REE patterns are discussed firstly.

Difference between light and heavy REE spans
It is interesting that the REE patterns for the 3 µm/0.45 µm ratios (Fig. 5-a) show two separate lines corresponding to the light and heavy REEs. Two typical examples are illustrated in Fig. 7-a. Moreover, the discrete
light and heavy REE discrepancies have also been reported in the studies on hydration-related phenomenon (e.g., Rizkalla and Choppin, 1991; Takeda and Ishida, 2004). Habenschuss and Spedding (1979a, 1979b, 1980) pointed out that the ions La\(^{3+}\) through Nd\(^{3+}\) are nine co-ordinated and those from Tb\(^{3+}\) to Lu\(^{3+}\) are eight co-ordinated in the aqueous chloride solutions. Suzuki et al. (1989) examined the pH values at which the lanthanide (III) hydroxide precipitations from chloride solutions were commenced, and two almost linear lines (La-Nd and Gd-Lu) were recognized on the pH vs. ionic radius diagram. Those data suggest that the light and heavy REE differences seen in Fig. 7 might be related to the change in REE coordination number in seawater.

**Gd anomaly**

As shown in Fig. 7, although a discontinuity exists in a part of the middle REEs, the Gd points fall almost on the heavy REE line. This might be important, because we can practically evaluate a normal Gd position on REE patterns by assuming that the normal Gd exists on the heavy REE line.

Figure 8 shows the average REE pattern for the 0.45 µm filtered seawater samples of this study. It is noteworthy that the Gd point (asterisk) inferred from the heavy REE line falls almost on the Sm-Dy line. On the basis of these observations, we consider that the interpolated value between the Sm and Dy points on the REE pattern diagram is usable as the normal Gd (Gd\(^*\)) position. Therefore, the size of the Gd anomaly (Gd/Gd\(^*\)) is defined as the ratio of the measured Gd value (Gd), to the interpolated Gd value (Gd\(^*\)), i.e.,

\[
\log(\text{Gd}/\text{Gd}^*)_N = (1/2)[\log(\text{Sm})_N + \log(\text{Dy})_N],
\]

where subscript “N” indicates the normalized values.

The Gd anomalies (Gd/Gd\(^*\)) for the 0.45 µm filtered seawater samples together with three river waters and one STP effluent sample are plotted against salinity in Fig. 2-I. Eight seawater samples show a negative corre-
Because "no Gd anomaly" corresponds to Gd/Gd* = 1, it is reasonable that this trend almost passes a lower right end-member of possible non-polluted seawater (Gd/Gd* = 1 and salinity = 35 psu).

Although the Gd/Gd* value might be a measure of the anthropogenic Gd concentration, the excess Gd concentration calculated by subtracting the interpolated Gd concentration (Gd*) from the observed Gd one is preferable for examining anthropogenic Gd component. The excess Gd values (ExGd) for the seawater samples are negatively correlated with salinity (Fig. 9-a). The regression line for eight samples is drawn as an example:

\[ \text{ExGd} (\times 10^{-5}) = -0.0674 \times \text{Salinity} + 2.34 \ (r = 0.91). \]  

Fig. 7. Examples of REE patterns showing discrepancies between light and heavy REE spans. (A) Two examples duplicated from Fig. 5-a. (B) The silicic rock normalized REE pattern for the seawater from Cape Shionomisaki (Data taken from Kamo and Terakado, MS for publication). The dotted lines are intended to show the light and heavy REE spans.

Fig. 8. The REE pattern of the average concentrations of 0.45 µm filtered seawater samples analyzed in the present study. The asterisk indicates the possible normal Gd position, which falls on the Sm-Dy and the heavy REE extensional lines. Thus, the assumed Gd value (Gd*) for the Gd anomaly (Gd/Gd*) was calculated from the interpolation of the Sm-Dy line on this kind of diagram.

Fig. 9. The excess Gd variation with salinity, DIN and NH₄-N values. The symbols are the same as those used in Fig. 2. A: The excess Gd concentrations for the seawater samples are well correlated with salinity. The regression line excluding I-7-S-45 and MI-7-S-45 and its equation are indicated. The dotted line with an arrow is intended to show the mixing line between the hypothetical STP effluent (ExGd = 3.27. Table 4) and the non-contaminated seawater. B: The excess Gd concentrations are plotted against DIN concentrations. The solid lines indicate the regression lines for the seawaters excluding N-7-S-45. C: The excess Gd concentrations vs. NH₄-N plot. The regression line for the seawaters excluding N-7-S-45 is illustrated.

Fig. 10. The excess Gd variation with NO₂-N, NO₃-N and PO₄-P. The symbols are the same as those used in Fig. 2. The regression lines for the seawater points excluding N-7-S-45 and their equations are indicated.

Although the Gd/Gd* value might be a measure of the anthropogenic Gd concentration, the excess Gd concentration calculated by subtracting the interpolated Gd concentration (Gd*) from the observed Gd one is preferable for examining anthropogenic Gd component. The excess Gd values (ExGd) for the seawater samples are negatively correlated with salinity (Fig. 9-a). The regression line for eight samples is drawn as an example:

\[ \text{ExGd} (\times 10^{-5}) = -0.0674 \times \text{Salinity} + 2.34 \ (r = 0.91). \]
Table 4. Summary of excess Gd and nutrient calculation results

<table>
<thead>
<tr>
<th>Eq. No.</th>
<th>Osaka City data (ppm)</th>
<th>Excess Gd (×10⁻⁵ ppm)</th>
<th>Hypothetical sewage effluent (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIN (2)</td>
<td>(0.89)</td>
<td>11.1 (3.1)</td>
<td>4.33</td>
</tr>
<tr>
<td>NH₄-N (3)</td>
<td>(0.87)</td>
<td>3.96 (4.0)</td>
<td>3.45</td>
</tr>
<tr>
<td>NO₂-N (4)</td>
<td>(0.74)</td>
<td>0.68 (0.76)</td>
<td>2.32</td>
</tr>
<tr>
<td>NO₃-N (5)</td>
<td>(0.76)</td>
<td>6.64 (3.5)</td>
<td>4.03</td>
</tr>
<tr>
<td>PO₄-P (6)</td>
<td>(0.73)</td>
<td>0.66 (0.46)</td>
<td>2.21</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>3.27</td>
</tr>
</tbody>
</table>

(a) Numbers in parentheses indicate r-value (regression coefficient).
(b) Average nutrient concentrations for the STP effluent data reported by Osaka City. Numbers in parentheses indicate standard deviation (STDEV).
(c) Estimation of nutrient concentrations for a hypothetical STP effluent calculated from equations from (2) to (6) and assuming excess Gd = 3.27 × 10⁻⁵ ppm.

The intercept where the line hits vertical axis is 2.34 (×10⁻⁵ ppm), and this value considered to be a possible end-member having highest anthropogenic Gd concentration in the area. This end-member may correspond to a hypothetical STP effluent. Actually, our sewage effluent sample has a lower excess Gd concentration as indicated by a diamond in Fig. 9-a. However, such disagreement is not surprising, because many STP locate in the area and their Gd values might be variable. Such variability is clarified by variable Gd data for the river water samples from Yodo and Syuku rivers (cf., Otsuka and Terakado, 2003).

Excess Gd and nutrient components

It is interesting that the excess Gd and DIN values for the seawater samples show broad trend as shown in Fig. 9-b. Excluding one highest Gd point (N-7-S-45), the regression line for seawater samples gives an equation:

\[ \text{ExGd} (\times10^{-5}) = 0.385 \times \text{DIN} + 0.0605 \quad (r = 0.89). \quad (2) \]

In Fig. 9-b, the river water points excluding one lowest Gd point (MU-7-R-45) fall almost on this line. The reason for such relatively good correlation for both river and seawater points is that uncontaminated possible end-member points for both river and sewaters are considered to be located at the lower left part of this diagram and thus mixing of river and sewaters do not significantly disturb this trend. The other end-member which has high Gd and DIN is considered to be a hypothetical STP effluent.

We calculated an average DIN concentration of the 61 STP effluent data reported by Osaka City (July and November data of 2002 for 16 STP, taken from the Home Page). The average DIN obtained is 11.1 ppm with a standard deviation (STDEV) of 3.1 ppm. If the sewage effluent DIN concentration of 11.1 ppm is adopted, Eq. (2) gives 4.33 × 10⁻⁵ ppm for the excess Gd concentration for the possible STP effluent end-member.

In Fig. 9-c, the excess Gd values are plotted against NH₄-N, and these data for the sewaters excluding one highest Gd point show almost linear trend:

\[ \text{ExGd} (\times10^{-5}) = 0.86 \times \text{N} + 0.049 \quad (r = 0.87). \quad (3) \]

This relatively good correlation is probably ascribed to the same reason for the DIN-Gd case (Fig. 9-b). Uncontaminated river and seawater components are both located at the lower left corner of the diagram, and the line can be considered as two component mixing line. Therefore, similar to the DIN case, we can calculate the excess Gd concentration using an average NH₄-N concentration of the STP effluent. The average NH₄-N concentration for the STP effluents of the Osaka City data is 3.96 ppm (STDEV = 4.0 ppm). If we adopt this value, Eq. (3) yields an excess Gd concentration of 3.45 × 10⁻⁵ ppm. This value is not so much different from the excess Gd concentration of 4.33 × 10⁻⁵ ppm calculated from Eq. (2).

In Fig. 10, the excess Gd variations with NO₂-N, NO₃-N and PO₄-P are illustrated, and relatively good correlations are observed for seawater samples excluding one highest Gd sample. The trends for them are indicated as follows:

\[ \text{ExGd} (\times10^{-5}) = 3.3 \times (\text{NO₂-N}) + 0.076 \quad (r = 0.74) \quad (4) \]
\[ \text{ExGd} (\times10^{-5}) = 0.59 \times (\text{NO₃-N}) + 0.115 \quad (r = 0.76) \quad (5) \]
\[ \text{ExGd} (\times10^{-5}) = 3.26 \times (\text{PO₄-P}) + 0.063 \quad (r = 0.73). \quad (6) \]

Similarly to DIN and NH₄-N cases, we calculated excess Gd concentrations using Eqs. (4), (5), and (6) and each nutrient concentration data for the Osaka City STP effluents. These data and the calculated results are summarized in Table 4. The average excess Gd concentration for the five cases (i.e., equations from (2) to (6)) is 3.27 × 10⁻⁵ ppm. Using this value and equations from (2) to (6), we calculated each nutrient concentration for a hypothetical STP effluent (see Table 4). These values are almost consistent with the average nutrient concentrations for the Osaka City data.
On the excess Gd vs. salinity diagram, the possible line which passes the intercept value of $3.27 \times 10^{-5}$ ppm is illustrated (dotted line in Fig. 9-a). This line is almost compatible with the observed data points. Therefore, the hypothetical STP effluent values obtained above are roughly consistent with the excess Gd concentrations for the Osaka Bay seawater data. This suggests that the excess Gd can be used as a conservative geochemical tracer.

**Excess Gd budget in Osaka Bay**

We roughly estimated the amount of the Gd MRI contrast agents consumed in the area. It was assumed that the Gd consumption in an area should be proportional to the population in the area, and the total amount of the Gd MRI contrast agents consumed in Japan can be estimated from the production rate of a company and its share in Japan. Necessary data were obtained mainly from one company by fact-finding (personal communication) and from Internet information. The production rate of Gd MRI contrast agent of a company, its share in Japan, Gd concentration in the MRI contrast agent, and the population rate for the related watersheds areas in Japan are $9500 \text{ person/year}$, $60\%$, $0.5 \text{ mol/liter}$, and $16\%$, respectively. The calculated result is that the Gd amount consumed in the area is $2.0 \times 10^5 \text{ g/year}$. This value is almost two times higher than the estimated value based on MRI contrast agent of a company by fact-finding (personal communication) and from Internet information. The production rate of Gd MRI contrast agents in medical use.

On the other hand, we also estimated the Gd influx amount into Osaka Bay by using the Yodo River data. It is known that the flux of Yodo River is $1.66 \times 10^3 \text{ t/sec}$, and the total flux of river water to Osaka Bay in the whole area is $4.18 \times 10^5 \text{ t/sec}$ (cf., Joh, 1986). This, the contribution of Yodo River to total freshwater flux into Osaka Bay is about $40\%$. The excess Gd concentration of one Yodo River sample (YO-7-R-45) was used (1.14 $\times 10^{-8}$ g/l), yielding $1.5 \times 10^5 \text{ g/year}$ for the total influx amount. This value is somewhat lower than the above estimate ($2.0 \times 10^5 \text{ g/year}$), but can be considered as relatively good agreement. Because the Yodo River Gd concentration is relatively low, we also attempted the hypothetical STP effluent value of $3.27 \times 10^{-8}$ g/l (Table 4), giving $4.3 \times 10^5 \text{ g/year}$. This value is almost two times higher than the estimated value based on MRI contrast agent consumption. However, given that these estimates involved many uncertainties, these disagreements are not serious.

Moreover, we intriguingly estimated the residence time of apparent anthropogenic Gd in Osaka Bay. As mentioned above, the total anthropogenic Gd influx into Osaka Bay was calculated ($2.0 \times 10^5 \text{ g/year}$). The average excess Gd concentration for two seawater samples from the middle bay sampling site was used for the average excess Gd concentration in Osaka Bay (i.e., $0.95 \times 10^{-7}$ ppm). The total excess Gd in Osaka Bay should be calculated by multiplying $0.95 \times 10^{-7}$ ppm by water volume in Osaka Bay (i.e., $42 \text{ km}^3$; ca. $4.2 \times 10^{15}$ g), and the result is $3.99 \times 10^5 \text{ g}$. Comparing this value with $2.0 \times 10^5 \text{ g/year}$, the assessed influx values mentioned above, we obtain mean residence time of 0.02 year (ca. one week) for the apparent anthropogenic Gd in Osaka Bay. This value is almost one order of magnitude lower than the previously reported residence time of about two months for both DIN and DIP in Osaka Bay (Hoshika et al., 1999). Such discrepancy may be attributed to uncertainties in the estimations of the Gd influx and the average excess Gd concentration in Osaka Bay, but the detailed discussions about residence time is beyond the scope of this study.

**CONCLUSIONS**

(1) The silicic rock normalized REE patterns for the seawaters are characterized by light REE depletion, negative Ce anomaly, and very small Eu anomaly. Moreover, most samples have obvious positive Gd anomalies. These positive Gd anomalies are attributed to the contamination of the MRI contrast agents in medical use.

(2) We found that the sizes of the Gd anomalies for the seawater samples are well correlated with salinity, and such correlation is relatively good in comparison with other correlations seen in other components vs. salinity plots. Moreover, the anthropogenic Gd concentrations represented by the excess Gd concentrations are well correlated with DIN, NH$_4$-N, NO$_2$-N, NO$_3$-N and PO$_4$-P concentrations. Such good correlations can be explained by considering that the abundant nutrients and anthropogenic Gd both originated from the STP are mixed with the river and seawaters whose nutrients and anthropogenic Gd concentrations are relatively low.

(3) The estimated concentrations of DIN, NH$_4$-N, NO$_2$-N, NO$_3$-N and PO$_4$-P for the hypothetical STP effluent calculated by using the observed correlation lines are almost consistent with the average concentrations for the STP effluent data published by Osaka City. Such consistency suggests that the Gd anomaly persists conservatively during the mixing processes.

(4) The estimated amount of Gd MRI contrast agents used in the related area is almost consistent with the observed excess Gd amount. Moreover, the residence time of the hypothetical excess Gd in Osaka Bay was estimated to be about one week. This value is considerably lower than the previously reported residence time of about two months for both DIN and DIP in Osaka Bay (Hoshika et al., 1999). As for such discrepancy, further investigations are necessary.

(5) These Gd related observations suggest that the Gd anomaly data are usable for a tracer of urban wastewater.

(6) In addition to Gd, we have briefly examined REE patterns for the seawaters and related river waters. The differences of the REE patterns between the $3 \mu m$ and...
0.45 μm filtered samples suggest that most of the REE contained in the 3-0.45 μm particulate matters reflect the REE patterns of the detrital materials derived from crustal rocks. Moreover, it was found that the sizes of the Ce anomalies are well correlated with Fe and broadly with Mn contents. These trends can be explained by the combined effect of the simple mixing of river and open-sea water and the coprecipitation and/or sorption of Ce⁴⁺ ions with the Fe-Mn-bearing materials, though further studies are necessary to obtain comprehensive understandings.


