



Anthropogenic rare earth elements and their spatial distributions in the Han River, South Korea



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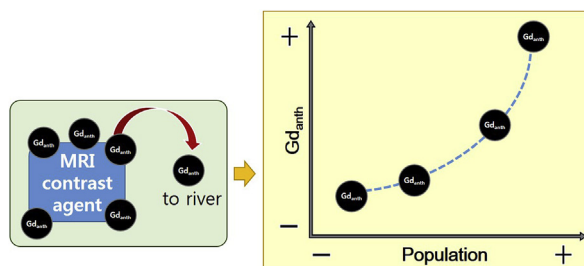
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HIGHLIGHTS

- We collected water samples in the Han River and its tributaries, South Korea.
- We investigated how and to what extent anthropogenic REE anomalies occur.
- Water samples display the pronounced Gd anomaly as well as La and Sm anomalies.
- Total REE_{anth} fluxes are estimated to be 952 ± 319 kg/yr.

GRAPHICAL ABSTRACT



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ABSTRACT

Rare earth elements (REE) consist of lanthanides (from La to Lu), together with yttrium and scandium, in which anthropogenic REE, such as gadolinium (Gd), lanthanum (La), and samarium (Sm), has emerged as micro-contaminants in natural waters in highly developed countries. Here, we collected water samples in the Han River (HR) and its tributaries flowing through Seoul Capital Area, the world's second largest metropolitan area in order to examine how and to what extent anthropogenic REE anomalies may occur. Water samples show higher light REE concentrations than heavy REE concentrations, while wastewater treatment plant (WWTP) samples display much higher heavy REE concentrations due to high Gd concentration. The PAAS-normalized REE patterns indicate that WWTP samples display the pronounced positive Gd anomalies, in which anthropogenic Gd from magnetic resonance imaging (MRI) diagnostic system occurs as a form of Gd complexation with either Cl^- or SO_4^{2-} . Due to the WWTP, both the HR and tributaries show also positive Gd anomalies and the anthropogenic Gd concentrations increase as a function of the distance from the Paldang dam. This result indicates a positive correlation between population, number of MRI instruments, and positive Gd anomaly. Similarly, positive La and Sm anomalies exist in the HR, indicating that the HR is also affected by their point sources. Based on the discharge rate and anthropogenic REE concentrations, their fluxes are estimated to be 952 ± 319 kg/yr, suggesting that this amount of fluxes could disturb REE distribution in the Yellow Sea, and pose harmful effects on aquatic ecosystems.

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1. Introduction

Magnetic resonance imaging (MRI) diagnostic system, as a powerful medical imaging technique, has been used to investigate

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the anatomy and physiology of the body in both health and disease. The Organization for Economic Co-operation and Development (OECD) Health Statistics 2013 reported that the number of MRI units in South Korea is 21.3 per million populations, which is much higher than the OECD average, and that the number of MRI exams is 18.2 per 1000 population, which is lower than the OECD average, in 2011. Because about half of the country's 50 million people reside in the metropolitan area surrounding its capital, the Seoul Capital Area, about 40% of total MRI units are distributed in the metropolitan area.

Gadolinium (Gd)-based compounds, such as gadopentetic acid (Gd-DTPA), are the most commonly used as MRI contrast agents (Bau and Dulski, 1996a). Although recent studies have shown that a portion of Gd chelates broken down in vivo is accumulated in tissue, bone and brain (Darrah et al., 2009, 2013), and that an uptake of Gd by plants and higher organisms occurs in aquatic systems (Lingott et al., 2016), many previous studies have simply assumed that most of Gd used for MRI diagnosis is excreted out of the body within a few hours without any metabolism in body (Kümmerer and Helmers, 2000; Möller et al., 2002) and therefore the same amount of Gd will be directly introduced into water because it cannot be removed during the wastewater treatment (Möller et al., 2003). Since the mid-1990s, many studies have investigated dissolved Gd in populated areas, indicating that Gd can be used to trace MRI-related anthropogenic sources (Bau and Dulski, 1996a; Möller et al., 2000; Lawrence et al., 2009; Rabiet et al., 2009; Kulaksız and Bau, 2011a). Lanthanides comprising the 15 elements from lanthanum (La; $Z = 57$) to lutetium (Lu; $Z = 71$), together with yttrium (Y) and scandium (Sc), are called rare earth elements (REE). They have an essential role in the efficient functioning of the world's economy because they are indispensable for sectors, such as clean-energy, military industry, medicine, agronomy and others (Zhang et al., 1997; Emsley, 2011; Kulaksız and Bau, 2013). With these reasons, recent studies have showed that other REE anomalies, except Gd anomaly, in natural water, such as La and Sm anomalies, are derived from those kinds of point source (Kulaksız and Bau, 2011b; Hissler et al., 2014). Nonetheless, only Gd anomalies have been reported in eastern Asia, such as Japan, China, and Taiwan (Zhu et al., 2004; Ogata and Terakado, 2006; Mao et al., 2014), and none of the studies have been conducted in South Korea yet.

Here, we collected river water samples in the Han River and its tributaries flowing through the Seoul Capital Area, the world's second largest metropolitan area with over 25 million people, in order to investigate how and to what extent anthropogenic REE anomalies may occur. Furthermore, it is examined how anthropogenic REE concentrations will change as river flows and how they will affect the REE distributions in the Yellow Sea. This study will provide the information about the relationship between anthropogenic REE anomalies and their different sources in the HR, South Korea.

2. Study area

The Han River (HR), the largest river system in South Korea in terms of discharge and drainage area, consists of two major tributaries (i.e., the North Han River and South Han River), which join at the Paldang dam to form the main channel of the HR. There are seven tributaries (i.e., Gyeongang, Wangsuk, Tan, Juangnang, Anyang, Gulpo, and Changneung streams) joining at the main channel of the HR (Fig. 1). During June to August 2013, the average discharge rate of seven tributaries ranges from 8.53 to 31.8 m³/s and that in the HR from 1011 to 1051 m³/s (Table 1; Water Information System accessed June 2015). The climate is temperate and has four distinct seasons. The mean annual temperature is 12.5 °C, ranging from

8.7 °C in winter to 16.9 °C in summer. The mean annual precipitation is 1404 mm/year, about two-thirds of which occurs between June and September (Korea Meteorological Administration accessed March 2016).

The HR watershed consists mainly of forest (46.3%), followed by residential and business areas (26.5%) and agricultural area (16.6%). It geographically includes both Seoul and some of Gyeonggi province, where about one-third of population (i.e. over 16 million) in South Korea lives. In particular, more than 50% of total residents live in the Tan, Jungnang, and Anyang watersheds, where most of MRI units are installed and running. In the study area, one or more wastewater treatment plants (WWTPs) have been running at six tributaries except Changneung stream (Fig. 1; Table 1). More detailed information about WWTPs, number of MRI instrument, and population in the study area is given in Table 1.

3. Methods

3.1. Samples collection and field measurements

We collected 20 river water samples in August 2013 from six sites in the HR and two sites in each tributary (Gyeongang; GA, Wangsuk; WS, Tan; TA, Jungnang; JN, Anyang; AY, Gulpo; GP, and Changneung; CN). Also, both influent and effluent of WWTP were collected in July 2014. Due to little difference in the discharge rates of river waters in 2013 and 2014, it can be assumed that the effect of one-year delay between sampling of river water, and both influent and effluent of WWTP on REE concentrations is negligible. The upstream samples in each tributary were collected at the pristine first-order stream, while the downstream samples in each tributary, except for GA, were collected at the site directly affected by the WWTP effluent, in which the downstream sample in the GA could be directly affected by one MRI unit (Fig. 1).

Temperature, pH, and electrical conductivity (EC) were measured in-situ using an ORION 5-STAR meter equipped with an ORION Combination epoxy pH electrode and DuraProbe 4-Electrode conductivity cells. Total alkalinity was measured using a Mettler Toledo T50A titrator with 0.01 M HCl acidimetric titration to an endpoint of pH = 4.5. Samples for dissolved cations and REE were passed through 0.2 µm filters, collected in I-CHEM LDPE bottles, and acidified to pH = 2 using concentrated, ultrapure HNO₃. Then, about 25 mL samples were dried in Teflon beakers, and the residues were treated with concentrated HNO₃, dried, and then re-dissolved in 5% HNO₃ in order to concentrate REE in samples. Because REE are very surface-sensitive elements and their migration in river waters usually occurs as organically-stabilized Fe-rich colloids (Sholkovitz, 1995; Hannigan and Sholkovitz, 2001), REE data in this study are relative to the dissolved fraction smaller than 0.2 µm. Samples for dissolved anions were passed through 0.2 µm filters and collected in Nalgene LDPE bottles.

3.2. Elemental analysis and the data treatment

Cation concentrations were measured using a Perkin Elmer Optima 8300 ICP-AES at the Korea Basic Science Institute (KBSI). Anion concentrations were measured using a Dionex ICS-1100 ion chromatograph at the KBSI. Rare earth element (REE) concentrations were measured using an iCAP™ Q ICP-MS (Thermo Scientific) interfaced with a seaFAST 2 automated sample introduction system (Elemental Scientific) at the KBSI. Although the CeO generation rate is maintained at less than 2% in order to minimize the oxide and hydroxide interferences during the measurement, the oxide and hydroxide interferences were corrected as following the procedures described in Aries et al. (2000). Furthermore, thallium (Tl) was used as internal standard to correct instrumental mass bias during

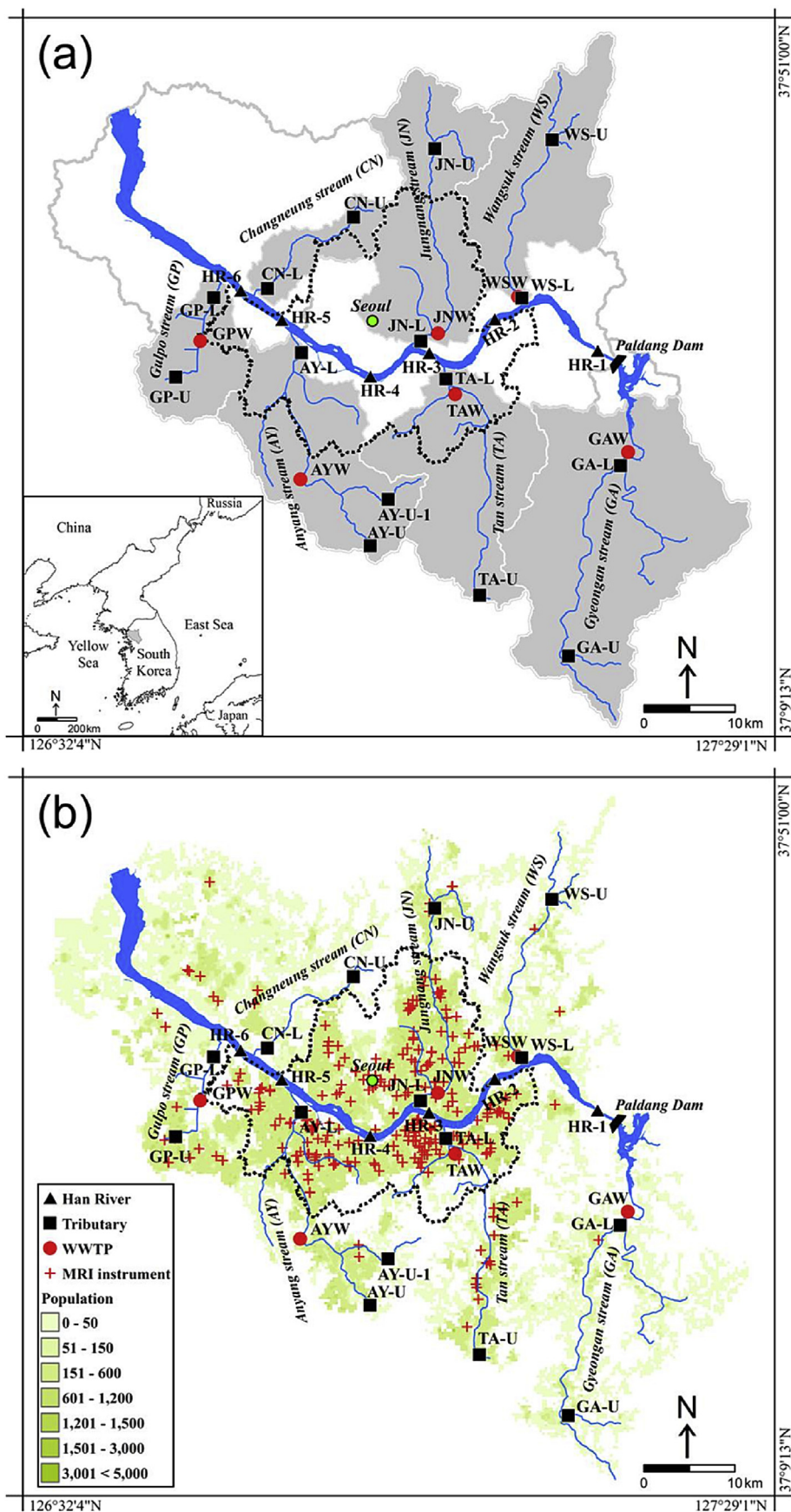


Fig. 1. Map showing the study area and sampling sites (a), and the distribution of population and MRI instruments (b). The colored area and dotted line represents the watershed of each tributary and the boundary of the administrative district in Seoul, respectively.

Table 1
Information about the study area.^a

Tributary	Drainage area ^b (km ²)	Discharge ^b (m ³ /s)	Population ^c (× 10 ³)	No. of MRI instrument ^d	No. of WWTP	Discharge of WWTP (m ³ /s)	Water treatment method ^e
Gyeungan (GA)	551	31.8	387	1	9	0.47	PID, MCF
Wangsuk (WS)	275	22.0	452	3	2	2.03	CNR, MLE, I3, I4
Tan (TA)	303	18.3	1957	45	3	9.01	MLE
Jungnang (JN)	299	16.8	3339	79	3	15.4	CASP, A2O, MLE
Anyang (AY)	281	10.3	3357	43	1	2.68	MLE, CNR
Changneung (CN)	80	—	185	—	—	—	—
Gulpo (GP)	131	11.5	1410	9	1	9.03	HCT

^a The information about WWTP is from Ministry of Environment (South Korea, 2013).

^b Data from Water Information System.

^c Data from Bizgis (www.biz-gis.com).

^d Data from Ministry of Health and Welfare (South Korea).

^e CASP: conventional activated sludge process, CNR: cilium nutrient removal, MCF: micro-chip filter, HCT: high class treatment, MLE: modified ludzack ettinger, PID: phased Isolation ditch.

the measurement. The precision and accuracy has been validated using the international river water standard (SLRS-5), which was in good agreement with reported values (Table 2; Heimbürger et al., 2013).

In order to characterize of the REE patterns, measured REEs were normalized to the Post-Archean Australia Shale Composition (PAAS; McLennan, 1989) and the REE anomalies were calculated as follows (Bau et al., 2006; Kulaksız and Bau, 2011b, 2013; Möller et al., 2014; Merschel and Bau, 2015):

$$\log(\text{Ce}_{\text{SN}}^*) = [\log(\text{La}_{\text{SN}}) + \log(\text{Pr}_{\text{SN}})]/2 \quad (1)$$

$$\text{Eu}_{\text{SN}}/\text{Eu}_{\text{SN}}^* = \text{Eu}_{\text{SN}} / (Sm_{\text{SN}}^{0.67} \times Tb_{\text{SN}}^{0.33}) \quad (2)$$

$$\text{Gd}_{\text{SN}}/\text{Gd}_{\text{SN}}^* = \text{Gd}_{\text{SN}} / (0.33 Sm_{\text{SN}} + 0.67 Tb_{\text{SN}}) \quad (3)$$

$$\log(\text{La}_{\text{SN}}^*) = 3 \log(\text{Pr}_{\text{SN}}) - 2 \log(\text{Nd}_{\text{SN}}), \quad (4)$$

$$\log(\text{Sm}_{\text{SN}}^*) = [2 \log(\text{Eu}_{\text{SN}}) + \log(\text{Nd}_{\text{SN}})]/3, \quad (5)$$

where the subscript SN denotes normalization to PAAS and the superscript * represents the geogenic background.

The anthropogenic REE, REE_{anth} , was calculated as follows (Lawrence et al., 2009; Kulaksız and Bau, 2013):

$$REE^* = REE_{\text{SN}}^* \times [REE_{\text{PAAS}}] \quad (6)$$

$$REE_{\text{anth}} = REE_{\text{measured}} - REE^*, \quad (7)$$

where REE is either La, Sm or Gd, and $[REE_{\text{PAAS}}]$ is the concentration of the respective REE in PAAS. In case of Gd_{anth} , the factor of 1.1 was multiplied by Gd^* in order to accounts for the natural Gd anomaly (Lawrence et al., 2009).

4. Results

Table 3 reports physical parameters and major ion concentrations for samples. The river water sample ranges in temperatures (T) from 23.2 to 33.2 °C, with mildly acidic to alkaline pH (6.89–9.23), while the WWTP sample in T from 24.1 to 28.3 °C, with mildly acidic to neutral pH (6.57–7.21). The EC of river water sample ranges from 132 to 558 $\mu\text{S}/\text{cm}$, while that of WWTP samples from 471 to 982 $\mu\text{S}/\text{cm}$. The percent charge balance error (CBE), as one measure of the data quality, is given by the equation $[\text{CBE} (\%) = (\text{TZ}^+ - \text{TZ}^-) / (\text{TZ}^+ + \text{TZ}^-) \times 100]$, where $\text{TZ}^+ = 2\text{Ca}^{2+} + 2\text{Mg}^{2+} + \text{K}^+ + \text{Na}^+$, $\text{TZ}^- = \text{Cl}^- + 2\text{SO}_4^{2-} + \text{NO}_3^- + \text{HCO}_3^-$, and is on average better than $\pm 4\%$. On an average molar basis, major cation abundances of the HR and upstream samples follow the order of $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$, and major anion abundances follow the order of $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} \approx \text{NO}_3^-$. On the contrary, those of the downstream and WWTP samples follow the order of $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$, and major anion abundances follow the

Table 2
Concentration of rare earth elements of reference material, SLRS-5.

Elements	Measured value (ppt)	2 σ (n = 10)	Reported value ^a	Recovery rate (%)
La	210	7	196	107
Ce	254	7	236	108
Pr	51.1	1.7	46.9	109
Nd	198	9	185	107
Sm	34.2	1.9	32.4	106
Eu	5.76	0.51	5.6	103
Gd	23.2	1.8	24.9	93
Tb	2.92	0.26	3.2	91
Dy	19.7	0.8	18.2	108
Ho	3.77	0.17	3.6	105
Er	11.5	0.7	10.5	109
Tm	1.21	0.13	1.3	93
Yb	8.49	1.01	9.3	91
Lu	1.63	0.09	1.5	109

^a Data from Heimbürger et al. (2013).

Table 3
Physical parameters and major ion concentrations of samples.^a

Sample ^b	Temperature (°C)	EC (μS/cm)	pH	K (mM)	Ca (mM)	Na (mM)	Mg (mM)	Cl (mM)	SO ₄ (mM)	NO ₃ (mM)	HCO ₃ (mM)
<i>Han River</i>											
HR-1	28.5	132	8.63	0.06	0.35	0.24	0.11	0.15	0.09	0.10	0.71
HR-2	28.7	147	8.25	0.06	0.42	0.29	0.13	0.21	0.11	0.11	0.81
HR-3	26.1	134	7.30	0.06	0.38	0.26	0.12	0.19	0.09	0.11	0.75
HR-4	26.8	164	7.44	0.08	0.43	0.40	0.13	0.28	0.11	0.13	0.82
HR-5	24.8	240	7.48	0.13	0.56	0.85	0.17	0.63	0.18	0.13	1.06
HR-6	28.1	173	7.33	0.09	0.43	0.47	0.13	0.34	0.12	0.16	0.81
<i>Upstream of tributary</i>											
GA-U	25.4	238	7.81	0.08	0.68	0.54	0.22	0.52	0.14	0.12	1.29
WS-U	29.4	295	8.33	0.12	0.71	0.88	0.18	0.69	0.24	0.11	1.21
TA-U	25.5	339	9.12	0.14	0.99	0.75	0.33	0.96	0.25	0.10	1.79
JN-U	28.9	311	8.30	0.12	0.94	0.83	0.20	0.70	0.20	0.10	1.74
AY-U	25.7	284	8.69	0.10	0.83	0.68	0.20	1.01	0.18	0.10	1.15
AY-U-1	29.9	132	8.89	0.05	0.38	0.31	0.09	0.27	0.10	0.10	0.64
CN-U	23.2	149	7.07	0.05	0.40	0.39	0.09	0.28	0.11	0.11	0.77
GP-U	28.7	205	7.93	0.06	0.59	0.53	0.16	0.43	0.14	0.05	1.17
<i>Downstream of tributary</i>											
GA-L	33.2	301	9.23	0.17	0.75	0.97	0.19	0.87	0.25	0.17	1.30
WS-L	24.0	475	7.21	0.27	0.89	1.98	0.25	1.51	0.35	0.42	1.56
TA-L	25.8	194	7.16	0.14	0.44	0.61	0.10	0.51	0.15	0.10	0.79
JN-L	25.8	222	6.97	0.15	0.44	0.74	0.08	0.59	0.14	0.13	0.90
AY-L	32.3	558	8.32	0.29	1.06	2.34	0.32	2.36	0.52	0.29	1.78
CN-L	28.7	400	7.08	0.20	1.14	1.03	0.33	0.88	0.37	0.13	2.10
GP-L	29.2	398	6.89	0.22	0.71	1.65	0.19	1.32	0.36	0.25	1.36
<i>Influent of WWTP</i>											
GAW-I	24.1	648	7.21	0.34	0.92	1.99	0.30	1.93	0.39	n.d.	3.53
WSW-I	25.7	623	7.15	0.35	0.88	2.35	0.27	2.16	0.36	n.d.	2.98
TAW-I	26.7	739	7.05	0.42	0.82	2.78	0.35	2.60	0.30	n.d.	3.61
JNW-I	26.8	690	7.11	0.40	0.75	2.64	0.25	2.17	0.31	n.d.	3.57
AYW-I	28.3	982	7.13	0.45	1.14	4.78	0.37	4.33	0.84	n.d.	3.33
<i>Effluent of WWTP</i>											
GAW-E	26.1	548	7.16	0.40	0.93	2.45	0.30	2.13	0.61	0.39	1.35
WSW-E	26.3	471	6.57	0.33	0.80	2.11	0.22	1.87	0.41	0.74	0.90
TAW-E	27.8	505	6.57	0.39	0.82	2.11	0.25	2.06	0.32	0.70	1.24
JNW-E	26.9	745	7.23	0.48	0.77	2.46	0.28	2.14	0.28	n.d.	4.15
AYW-E	26.2	788	6.95	0.46	1.04	4.20	0.34	4.03	0.74	0.34	1.60
GPW-E	27.8	596	6.70	0.38	0.91	2.83	0.28	2.46	0.57	0.65	1.27

^a n.d.: not detected.

^b HR: Han River, GA: Gyeongang, WS: Wangsuk, TA: Tan, JN: Jungnang, AY: Anyang, CN: Changneung, and GP: Gulpo (see Section 3.1).

order $\text{Cl}^- \approx \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$. The high abundances of Na^+ and Cl^- in the downstream and WWTP samples, and the strong correlation between them ($r^2 = 0.98$) suggest that both are contaminants input by anthropogenic activities such as sewage.

Table 4 presents the REE concentrations of samples. As known that the natural REE abundance progressively decreases along the lanthanide series (Taylor and McLennan, 1988), most of samples show the enrichment of light REE (LREE; La to Eu) relative to heavy REE (HREE; Gd to Lu) reflecting the greater abundances of LREE in the bedrock. In the HR, LREE concentrations range from 636 pM to 1499 pM, which are about 10 times as high as HREE concentrations ranging from 120 pM to 345 pM. Similarly, in the tributaries (except for TC-U and AY-L), LREE concentrations are much higher than HREE concentrations. However, WWTP samples display much higher HREE concentrations due to high Gd concentration ranging from 126 pM to 3724 pM.

The PAAS-normalized REE distributions of samples show that river water samples slightly increased from LREE to HREE but two tributaries (i.e., TA-L and GP-U) show a relatively flat pattern (Fig. 2). Due to high HREE concentrations in WWTP samples, WWTP samples have two distinct patterns: 1) the HREE enrichment and 2) the pronounced positive Gd anomaly, which ranges from 4.2 to 297, with an average of 132. The pronounced positive Gd anomaly in WWTP samples results in positive Gd anomaly in both the HR and downstream in tributaries. In the tributaries, upstream samples have Gd anomaly ranging from 1.2 to 2.4 while downstream samples have much increased Gd anomaly ranging from 3.5

to 21.8, indicating the significant influence of WWTP on downstream samples. In the HR samples, the Gd anomaly ranges from 1.6 to 8.2, indicating that Gd anomaly still exists although the tributaries have much lower discharge relative to the HR.

On the contrary, La and Sm anomalies are a little. The La anomaly in the HR samples ranges from 1.03 to 1.24, with an average of 1.11. In the tributaries, both upstream and downstream samples display a little positive La anomaly ranging from 1.00 to 1.64, with an average of 1.23. However, the WWTP samples showed relatively high La anomaly ranging from 0.93 to 2.01, with an average of 1.65, except for AYW-E having extremely high La anomaly of 9.31. Similar with La anomaly, the HR samples show a narrow range of positive Sm anomaly between 1.05 and 1.22 with an average of 1.12. The tributary samples also show a little positive Sm anomaly ranging from 0.78 to 2.28 with an average of 1.16. Interestingly, the WWTP samples display a little Sm anomaly ranging from 0.60 to 1.23 with an average of 0.82.

5. Discussion

5.1. The PAAS-normalized REE pattern

The PAAS-normalized REE patterns of river water are various with either positive Eu and/or negative Ce anomaly, depending on pH and the presence of colloidal particles as well as weathering and riverine processes (Byrne and Sholkovitz, 1996). For example, the PAAS-normalized patterns can show a “bulged” shape centered on

Table 4
REE concentrations of water samples.

Sample ^a	La (pM)	Ce (pM)	Pr (pM)	Nd (pM)	Sm (pM)	Eu (pM)	Gd (pM)	Tb (pM)	Dy (pM)	Ho (pM)	Er (pM)	Tm (pM)	Yb (pM)	Lu (pM)	Ce anomaly ^b	Eu anomaly ^c	Gd anomaly ^d	La anomaly ^e	Sm anomaly ^f	Anthropogenic Gd (pM) ^g	Anthropogenic La (pM) ^g	Anthropogenic Sm (pM) ^g
<i>Han River</i>																						
HR-1	314	595	65.8	240	42.5	8.04	78.8	4.99	28.8	6.02	18.9	2.65	19.1	3.23	0.96	1.02	2.49	1.03	1.05	44.0	7.88	2.19
HR-2	257	432	53.2	194	34.5	5.81	45.9	4.04	23.9	5.30	16.6	2.55	18.5	3.41	0.85	0.91	1.79	1.04	1.14	17.7	10.7	4.25
HR-3	375	701	77.6	287	50.0	8.77	57.3	5.69	32.4	6.95	21.2	3.00	22.1	3.91	0.95	0.96	1.57	1.07	1.10	17.2	22.9	4.67
HR-4	291	471	58.1	215	37.3	6.96	135	4.45	26.3	5.98	20.5	3.20	26.0	4.95	0.84	1.00	4.82	1.11	1.06	104	29.4	1.97
HR-5	267	483	51.5	198	31.8	5.07	209	4.19	32.4	8.71	33.2	6.17	42.7	8.95	0.95	0.83	8.17	1.24	1.14	181	52.4	3.95
HR-6	170	264	35.6	138	24.9	3.80	138	3.31	20.2	4.87	17.3	2.79	22.4	4.49	0.78	0.79	6.87	1.16	1.22	116	23.3	4.54
<i>Upstream of tributary</i>																						
GA-U	127	146	25.8	105	19.6	3.14	27.6	2.80	19.1	5.26	20.8	3.74	31.3	6.56	0.59	0.81	1.66	1.34	1.20	9.32	32.5	3.24
WS-U	171	158	31.1	120	21.1	6.20	26.0	3.39	19.1	5.10	19.4	3.25	26.4	5.28	0.50	1.43	1.34	1.33	0.78	4.64	42.6	–
TA-U	50.0	40.0	9.08	36.9	7.77	1.18	16.9	1.82	18.0	6.95	35.7	7.36	69.1	15.5	0.43	0.65	1.78	1.46	1.29	6.45	15.7	1.76
JN-U	371	464	64.2	231	38.6	10.7	76.7	5.46	38.8	11.2	46.2	8.15	70.2	15.1	0.69	1.41	2.36	1.21	0.80	41.0	63.7	–
AY-U	167	228	38.5	146	28.7	4.06	37.9	4.77	33.2	8.06	27.1	4.08	30.9	6.11	0.66	0.68	1.40	1.01	1.32	8.19	2.40	7.01
AY-U-1	175	317	37.6	140	27.2	4.02	26.0	3.52	21.8	4.89	16.4	2.56	19.9	3.89	0.90	0.77	1.21	1.05	1.28	2.29	7.56	5.97
CN-U	160	130	36.9	147	31.6	4.05	35.6	4.22	26.1	5.94	18.9	2.86	21.1	3.75	0.39	0.66	1.39	1.11	1.20	7.47	15.4	9.94
GP-U	283	492	50.1	182	33.2	4.61	47.7	4.09	24.3	5.49	17.1	2.46	18.6	3.39	0.95	0.74	1.87	1.21	1.31	19.7	49.3	7.85
<i>Downstream of tributary</i>																						
GA-L	108	124	21.4	84.6	16.9	4.80	141	2.88	23.9	7.65	32.4	6.00	52.5	10.8	0.60	1.36	8.69	1.26	0.83	123	22.5	–
WS-L	117	136	21.2	90.8	17.4	4.44	238	2.48	19.3	6.22	29.2	6.43	58.8	12.0	0.63	1.29	16.1	1.64	0.89	221	45.4	–
TA-L	825	1458	181	680	122	27.8	322	14.1	81.3	17.4	52.5	7.46	53.3	9.44	0.87	1.23	3.59	1.04	0.94	224	28.7	–
JN-L	417	577	80.4	292	52.4	7.76	308	6.75	42.7	10.8	40.2	6.95	59.4	12.2	0.73	0.78	7.44	1.11	1.25	263	41.1	10.3
AY-L	129	202	27.2	98.6	20.0	1.27	448	3.75	29.9	9.04	38.8	7.17	63.8	14.0	0.79	0.29	21.8	1.00	2.28	425	0.50	11.2
CN-L	161	191	27.4	105	19.6	4.52	58.0	2.82	20.6	6.03	25.7	4.79	44.0	9.55	0.66	1.17	3.48	1.41	0.94	39.7	46.9	–
GP-L	119	207	23.2	91.0	18.5	3.80	573	2.85	19.1	5.40	21.9	3.95	33.8	7.69	0.91	1.01	34.8	1.28	1.05	555	26.0	0.81
<i>Influent of WWTP</i>																						
GAW-I	48.5	52.2	7.24	28.6	6.34	1.73	2040	4.1	13.4	7.43	23.9	4.94	49.6	8.70	0.64	0.84	111	1.69	0.89	2020	19.9	–
WSW-I	299	356	49.4	191	35.5	9.60	126	5.07	29.7	7.16	23.3	3.84	28.3	5.45	0.68	1.37	4.19	1.47	0.84	92.8	95.1	–
TAW-I	99.0	143	12.9	51.6	10.5	4.93	3724	2.39	13.0	4.10	16.3	3.14	40.7	5.94	0.92	2.04	297	1.97	0.60	3710	48.7	–
JNW-I	105	124	11.9	44.7	9.14	2.15	815	2.43	18.7	6.67	32.0	6.88	64.4	13.9	0.81	0.97	66.1	2.01	0.96	802	52.9	–
AYW-I	35.8	40.8	6.19	19.5	5.93	1.17	508	3.21	31.7	10.8	48.2	8.99	74.6	16.5	0.63	0.64	34.6	0.93	1.23	491	–	1.11
<i>Effluent of WWTP</i>																						
GAW-E	14.6	21.2	2.41	9.90	2.24	0.90	321	0.83	6.46	3.06	16.0	3.49	31.2	6.21	0.83	1.48	81.0	1.66	0.69	316	5.83	–
WSW-E	23.6	24.4	4.26	17.5	3.91	1.50	272	0.92	5.89	2.14	8.77	1.79	15.1	2.97	0.56	1.65	56.7	1.52	0.71	266	8.06	–
TAW-E	15.6	27.7	3.32	15.1	3.49	1.34	1286	0.94	7.33	2.97	14.6	3.12	31.4	6.40	0.89	1.58	271	1.58	0.72	1281	5.74	–
JNW-E	30.1	33.7	3.57	12.8	2.91	0.71	786	0.84	6.12	2.43	12.6	2.92	31.4	6.64	0.75	0.97	186	1.76	0.97	781	13.0	–
AYW-E	12.2	17.0	1.33	10.6	2.27	0.94	676	0.98	11.0	4.51	23.2	4.74	42.8	9.31	0.98	1.45	147	9.31	0.67	671	10.8	–
GPW-E	22.7	35.1	3.30	13.6	2.66	0.89	760	0.77	6.76	2.86	15.1	3.36	32.8	7.28	0.94	1.33	198	1.88	0.75	756	10.7	–

^a HR: Han River, GA: Gyeongang, WS: Wangsuk, TA: Tan, JN: Jungnang, AY: Anyang, CN: Changneung, and GP: Gulpo (see Section 3.1).

^b $\log(\text{Ce}^*_{\text{SN}}) = [\log(\text{La}_{\text{SN}}) + \log(\text{Pr}_{\text{SN}})]/2$ (see Section 3.2).

^c $\text{Eu}_{\text{SN}}/\text{Eu}^*_{\text{SN}} = \text{Eu}_{\text{SN}}/(\text{Sm}_{\text{SN}}0.67 \times \text{Tb}_{\text{SN}}^{0.33})$ (see Section 3.2).

^d $\text{Gd}_{\text{SN}}/\text{Gd}^*_{\text{SN}} = \text{Gd}_{\text{SN}}/(0.33\text{Sm}_{\text{SN}} + 0.67\text{Tb}_{\text{SN}})$ (see Section 3.2).

^e $\log(\text{La}^*_{\text{SN}}) = 3\log(\text{Pr}_{\text{SN}}) - 2\log(\text{Nd}_{\text{SN}})$ (see Section 3.2).

^f $\log(\text{Sm}^*_{\text{SN}}) = [2\log(\text{Eu}_{\text{SN}}) + \log(\text{Nd}_{\text{SN}})]/3$ (see Section 3.2).

^g $\text{REE}_{\text{anth}} = \text{REE}_{\text{measured}} - \text{REE}^*$. The superscript * denotes the geogenic background (see Section 3.2).

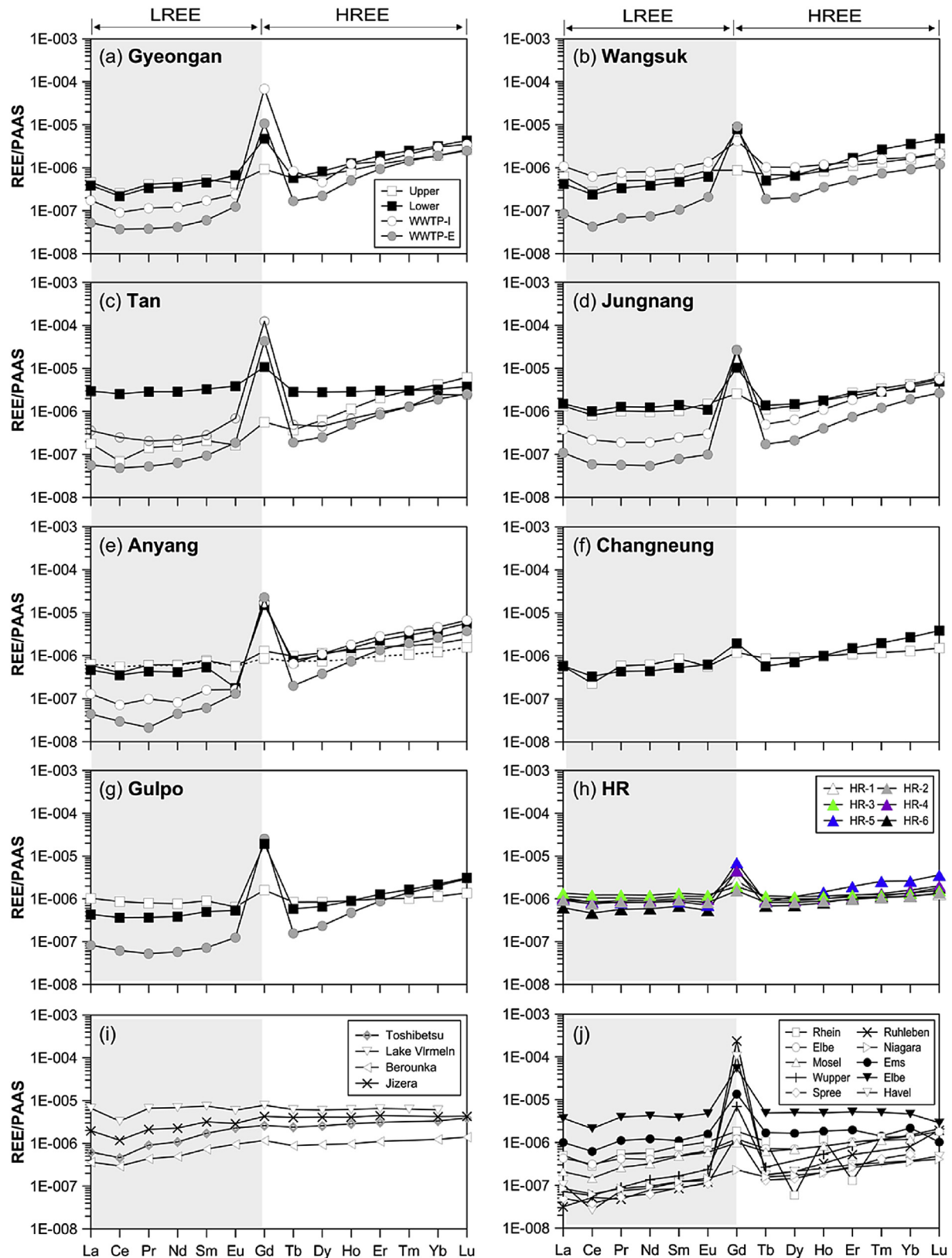


Fig. 2. The PAAS-normalized REE patterns of samples. The data of water samples without (i) and with (j) anthropogenic Gd input are from [Bau and Dulski \(1996a\)](#), [Alibo and Nozaki \(1999\)](#), [Möller et al. \(2002\)](#), [Bau et al. \(2006\)](#), and [Kulaksız and Bau \(2007, 2011a\)](#).

MREE (from Sm to Ho) due to the dissolution of different materials outcropping in the watershed ([Hannigan and Sholkovitz, 2001](#);

[Censi et al., 2007](#)) or can show the HREE enrichment due to the REE adsorption onto river particle surfaces with increasing pH

(Sholkovitz, 1995). Furthermore, the oxidation of Ce(III) to Ce(IV) promotes an adsorptive removal of Ce from the dissolved pool, resulting in negative Ce anomaly (e.g., Goldstein and Jacobsen, 1988), while positive Eu anomaly results from either the reduction of Eu(III) to Eu(II) or the dissolution of minerals, such as plagioclase due to the Eu^{2+} substitution for Ca^{2+} and phosphate rich sedimentary rocks (Kidder et al., 2003). In this study, river water samples display a little negative Ce anomaly and either negative or positive Eu anomaly, and have patterns that are depleted in the LREE with $(\text{La/Yb})_{\text{SN}} < 1.0$ (Table 4; Fig. 3). Interestingly, the effluents of WWTP (WWTP-E) are significantly depleted in the LREE relative to river water and the influent of WWTP (WWTP-I) samples. It could be due to the fact that oxidative removal of Fe during water treatment results in preferential LREE removal (Leybourne and Johannesson, 2008; Verplanck et al., 2010). The $(\text{La/Yb})_{\text{SN}}$ value in upstream samples ranges from 0.04 to 0.52, which is similar to that in WWTP-I samples, indicating conservative behavior of REE before water treatment. However, after water treatment, the $(\text{La/Yb})_{\text{SN}}$ value in WWTP-E samples is abruptly decreased to less than 0.09, consistent with previously reported values in WWTP-E and tap water samples (Bau and Dulski, 1996a; Lawrence et al., 2009; Kulaksiz and Bau, 2011a). Due to the input of WWTP-E with the depleted $(\text{La/Yb})_{\text{SN}}$ value, the $(\text{La/Yb})_{\text{SN}}$ value in downstream samples is also abruptly decreased compared to upstream samples. However, there is little effect of the input of WWTP-E on the $(\text{La/Yb})_{\text{SN}}$ value in the HR samples because the discharge of the HR is much higher than its tributaries and WWTP-E. This suggests that when REEs are used as a geochemical tracer in the environment, especially river waters affected by the effluents of WWTP, it should be dealt with a caution.

5.2. Positive Gd anomaly and its spatial distribution

In pristine river waters that are unaffected by anthropogenic REE input, only negative Ce anomalies and, occasionally, Eu anomalies are common (Lewis et al., 1997; van Middelworth and Wood, 1998; Kidder et al., 2003; Kulaksiz and Bau, 2011b). Also, the occurrence of small positive Gd anomaly (less than 1.4) is a common feature in seawater due to “tetrad effect”, which is resulted from the half-filled 4f electron in its orbital shell,

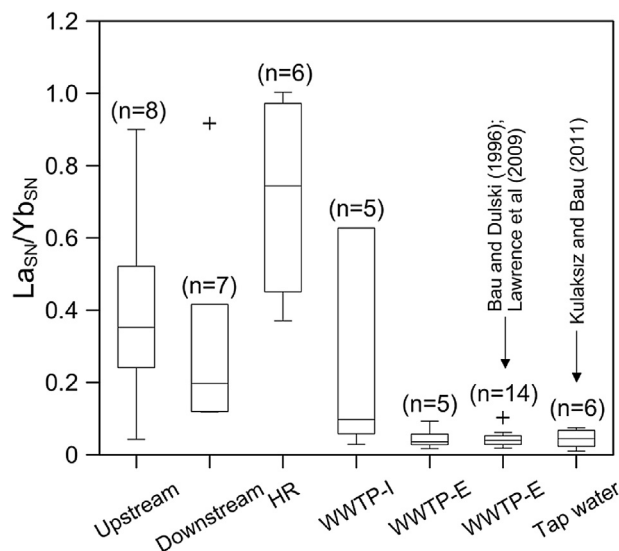


Fig. 3. A box plot of the ratio of La_{SN} to Lu_{SN} . The subscript SN denotes normalization to PAAS. The data of WWTP-E and tap water are from Bau and Dulski (1996a) and Lawrence et al. (2009), and Kulaksiz and Bau (2011a), respectively.

irrespectively of normalization problem (e.g., Bau and Dulski, 1996b; Alibo and Nozaki, 1999). However, since the mid-1990s, a large positive Gd anomaly (i.e., anthropogenic Gd anomaly), ranging from 1.5 to 240, has been reported in terrestrial waters, such as rivers, lakes and groundwater, due to anomalously high concentrations of Gd mainly derived from MRI diagnosis (e.g., Bau et al., 2006; Rabiet et al., 2009). Given that pristine water has the Gd anomaly of less than 1.5 in this study, only three upstream samples in the tributaries (WS, AY and CN) have a Gd anomaly value of less than 1.5, indicating that they are representative of pristine water. Contrary, other four tributaries with the Gd anomaly of higher than 1.5 are already affected by anthropogenic effects even at the upstream.

Mobility and bioavailability of REE are influenced by various factors such as pH, concentration and type of organic and inorganic ligands, and temperature (Sholkovitz, 1995; Byrne and Sholkovitz, 1996). For example, the nitrates, chlorides, and sulfates of REE are soluble, while their carbonates, phosphates, and hydroxides are insoluble (Wells and Wells, 2001). Fig. 4 shows a positive correlation between Gd anomaly and major anions, in which Cl^- and SO_4^{2-} are normalized by HCO_3^- to minimize the effect of riverine processes, such as evaporation and dilution on water chemistry. This result indicates that the WWTP releases anthropogenic Gd as a form of Gd complexation with either Cl^- or SO_4^{2-} . However, two WWTP samples (JNW and TAW) display large Gd anomaly with lower Cl/HCO_3 and SO_4/HCO_3 ratios, indicating that high discharge rates of WWTP with high Gd anomaly could directly affect riverine REE chemistry regardless of major ion chemistry.

Although recent studies have shown that a portion of Gd

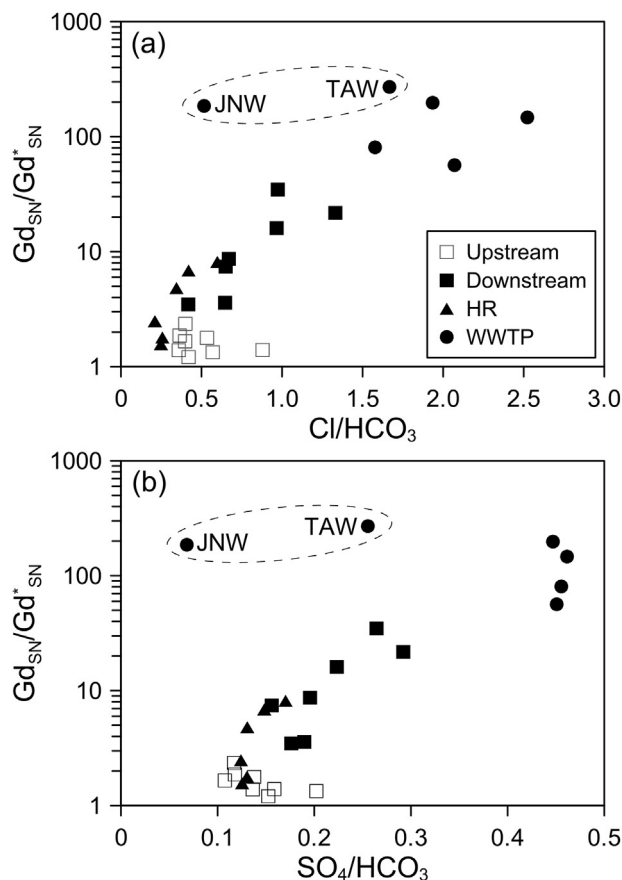


Fig. 4. Plots of $\text{Gd}_{\text{SN}}/\text{Gd}^*_{\text{SN}}$ versus Cl/HCO_3 (a) and SO_4/HCO_3 (b). The subscript SN denotes normalization to PAAS and the superscript * represents the geogenic background.

chelates broken down in vivo is accumulated in tissue, bone and brain (Darrach et al., 2009, 2013), and that an uptake of Gd by plants and higher organisms occurs in aquatic systems (Lingott et al., 2016), many studies have simply assumed that most of Gd used during MRI diagnosis is excreted out of the body (e.g., Kümmerer and Helmers, 2000; Möller et al., 2002). Because there is a positive correlation between population and MRI instrument (Fig. 5a), it can be assumed that positive Gd anomaly in samples also correlates with population. Although upstream samples positively correlate with population (Fig. 5b), there is no clear correlation between downstream samples and population (Fig. 5c), indicating that WWTP may disturb the correlation between them.

Furthermore, there will be the variation of the Gd anomaly as a function of the distance from upstream because anthropogenic Gd

sources are correlated with population. In order to investigate the spatial variation of anthropogenic Gd with the downstream distance, it is assumed that the value of Gd anomaly in upstream samples is an initial value. Although four upstream samples (i.e., WS, TA, JN and AY) have a positive Gd anomaly of higher than 1.5, the spatial variation of Gd anomaly can be easily shown because Gd anomalies in WWTP-E samples are extremely high, up to 155 times. The results indicate that although the Gd anomalies in downstream samples increase to up to 16-folds compared to upstream samples due to the input of WWTP-E, the effect of WWTP-E on the Gd anomaly in downstream samples is not so significant as expected because the discharge of WWTP-E is relatively small compared to tributaries (Table 1).

Because anthropogenic Gd is not easily removed in traditional WWTPs and therefore behaves conservatively in river waters, the anthropogenic Gd, Gd_{anth} , in each tributary should be maintained in the HR. The Gd_{anth} concentrations in downstream samples except CN sample increase from 123 pM to 555 pM as flowing through the area with the high density of MRI instruments (Table 4). Similarly, the Gd_{anth} concentrations in the HR samples slightly decrease to about 17 pM and then abruptly increase to 181 pM as a function of the distance from the Paldang dam (Fig. 6a). It could be due to either relatively low discharge of tributaries flowing into the upper HR and/or the weirs constructed at the upper HR. The results indicate that the HR is significantly contaminated by anthropogenic Gd sources, which are contrast agents from MRI. Therefore, it is expected that micro-contaminants, such as pharmaceutical compounds, also occur in the HR because they are not completely removed during water treatment (Ternes, 1998). It has been shown that pH, colloids and salinity control the fractionation of REE in river and estuarine waters (Sholkovitz, 1995). For example, with increasing pH the order of REE adsorption onto suspended matter is LREEs > MREEs > HREEs. The coagulation of colloidal REE due the addition of seawater accompanies the fractionation (LREEs > MREEs > HREEs). Nonetheless, the conservative behavior of Gd relative to other REE in estuarine water has been reported (Nozaki et al., 2000; Censi et al., 2010), indicating that the tetrad effect results in relatively passive scavenging of Gd over other REE, leaving Gd behind in solution (Alibo and Nozaki, 1999). Therefore, although we did not collect samples at the estuary, it can be assumed that the Gd_{anth} is conservative during estuarine mixing of river and seawater, and the REE distribution will be disturbed in coastal waters and semi-closed sea basins (Bau and Dulski, 1996a). Based on the discharge rate and Gd_{anth} concentrations, the annual Gd_{anth} fluxes in the HR range from 600 kg/yr to 918 kg/yr with an average of 759 kg/yr, which could disturb the REE distribution in the Yellow Sea, and pose harmful effects on aquatic ecosystems.

5.3. Other REE anomalies and their spatial distributions

Positive La and Sm anomalies can occur in river water given that there are point sources, such as industrial facilities for petroleum refining and chemical reactions because La and Sm are used as catalysts (Krishnamurthy and Gupta, 2004; Hajra et al., 2007). For example, emissions highly enriched in La and Sm from fluid catalytic converters (FCC) cause positive La and Sm anomalies in river waters (e.g., Kulkarni et al., 2006; Moreno et al., 2008). Contrary to the Gd anomaly, most of water samples do not display significant La and Sm anomalies, which ranges from 0.93 to 9.31, and from 0.60 to 2.28, respectively. Although La anomalies are mostly shown in the WWTP samples, Sm anomalies are scarce in most of samples. Because anthropogenic La and Sm are easily bounded to colloids and nanoparticles in water, they can be also removed together during oxidative removal of Fe in WWTP (Leybourne and Johannesson, 2008; Verplanck et al., 2010; Kulaksız and Bau,

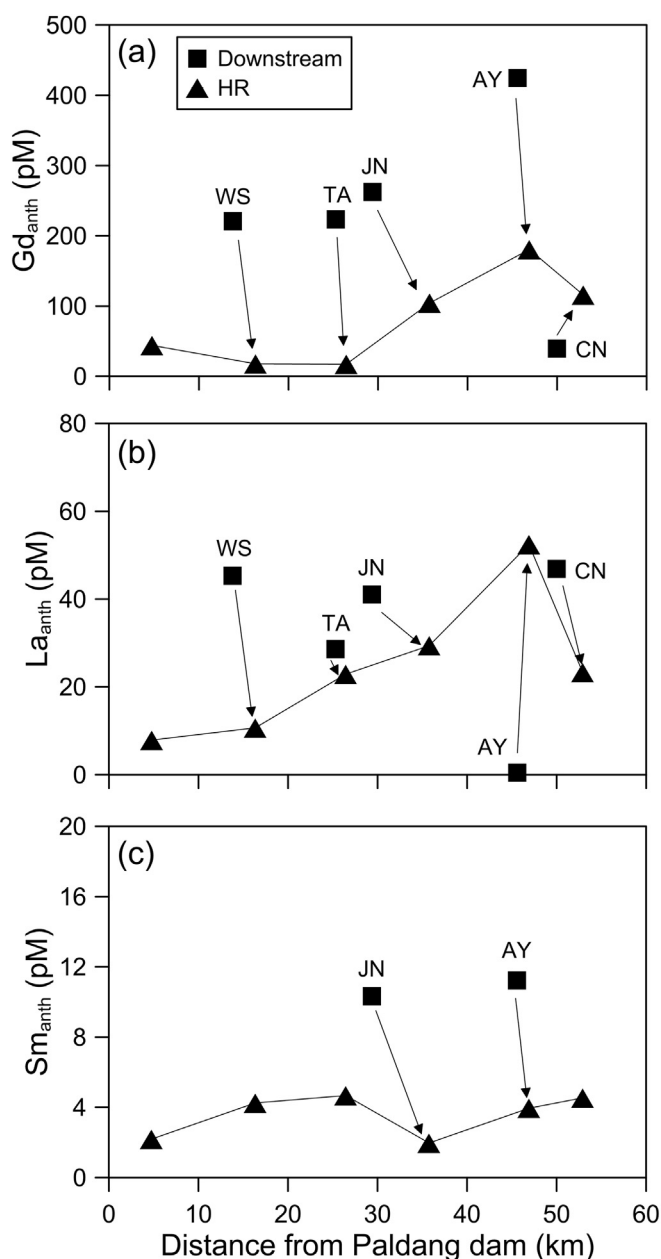


Fig. 5. Plots of population versus number of MRI instruments (a), Gd_{SN}/Gd^*_{SN} in upstream samples (b), and Gd_{SN}/Gd^*_{SN} in downstream samples (c). The subscript SN denotes normalization to PAAS and the superscript * represents the geogenic background. The value of 1.5 accounting for geogenic Gd anomaly is from Bau et al. (2006).

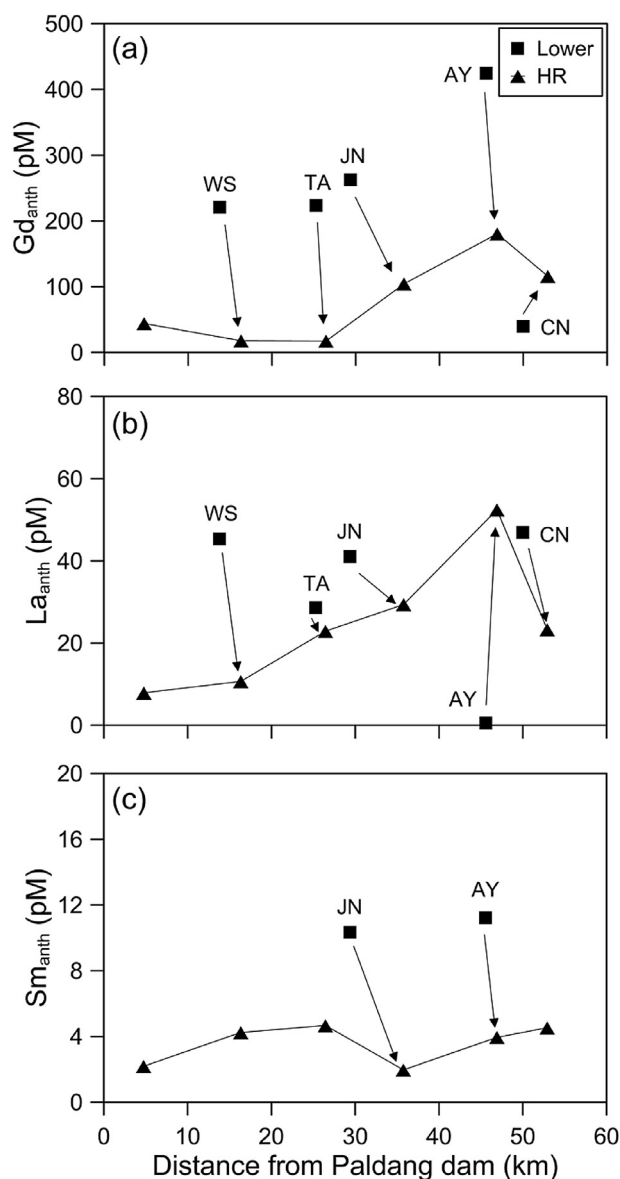


Fig. 6. Variations of anthropogenic Gd (a), anthropogenic La (b), and anthropogenic Sm (c) as a function of the distance from Paldang dam.

2013). Nonetheless, the results show that positive La and Sm anomalies occur in the HR (Table 4), indicating that the HR is affected by point sources releasing anthropogenic La and Sm. The La_{anth} concentrations in the HR samples, ranging from 7.88 pM to 52.4 pM, gradually increase as a function of the distance from the Paldang dam (Fig. 6b), while the Sm_{anth} concentrations are consistent (Fig. 6c). It implies that point sources of anthropogenic La would be scattered in the study area. Therefore, further studies are needed to explore more in details what kinds of point source exist in the HR basin. Furthermore, as discussed above, although WWTP could remove amount of anthropogenic La and Sm, remained La and Sm in river water also cause the REE distribution be disturbed in coastal waters and semi-closed sea basins as anthropogenic Gd. Based on the discharge rate, and La_{anth} and Sm_{anth} concentrations, the total annual fluxes of them range from 127 kg/yr to 260 kg/yr, with an average of 193 kg/yr, suggesting that this amount of the fluxes in the HR could affect REE distribution in the Yellow Sea, and pose harmful effects on aquatic ecosystems as

the Gd_{anth} mentioned above. Therefore, further studies are needed to investigate the REE distribution in the Yellow Sea in order to evaluate the effects of anthropogenic REEs.

6. Conclusions

We collected water samples in the Han River (HR) and its tributaries flowing through the Seoul Capital Area, the world's second largest metropolitan area with over 25 million people, in order to investigate how and to what extent anthropogenic REE anomalies may occur. River water samples have LREE concentrations, ranging from 145 pM to 3294 pM, are about 3 times as high as HREE concentrations, ranging from 99 pM to 668 pM, with the enrichment of LREE, while wastewater treatment plant (WWTP) samples display the HREE enrichment due to high Gd concentration and the LREE removal during water treatment process. The PAAS-normalized REE patterns indicate that water samples display the pronounced positive Gd anomalies, ranging from 1.2 to 297, suggesting that anthropogenic Gd is derived from magnetic resonance imaging (MRI) diagnostic system. Due to the input of WWTP effluent, anthropogenic Gd concentrations increase as a function of the distance from the Paldang dam, indicating a positive correlation between population, number of MRI instruments, and positive Gd anomaly. Similarly, positive La and Sm anomalies also occur in the HR although positive La and Sm anomalies are not as high as Gd anomaly. Total fluxes of anthropogenic REEs in the HR range from 727 kg/yr to 1178 kg/yr, indicating that this amount of anthropogenic REEs could disturb the REE distribution in the Yellow Sea, and pose harmful effects on aquatic ecosystems.

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