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

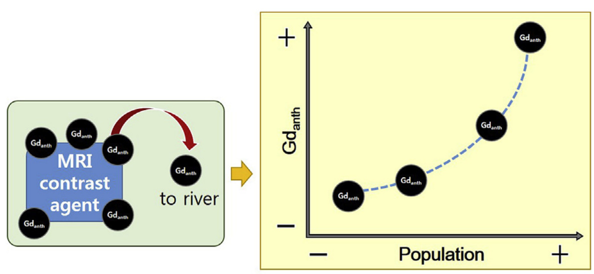
Hyeongseok Song [a, b, 1], Woo-Jin Shin [b, 1], Jong-Sik Ryu [a, b, *], Hyung Seon Shin [b], Heesun Chung [a], Kwang-Sik Lee [a, b]

[a] *Graduate School of Analytical Science and Technology, Chungnam National University, Daejeon 34134, Republic of Korea*
[b] *Division of Earth and Environmental Sciences, Korea Basic Science Institute, Chungbuk 28119, Republic of Korea*

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 populaton, 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.

1. Introduction

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

* Corresponding author. Division of Earth and Environmental Sciences, Korea Basic Science Institute, Chungbuk 28119, Republic of Korea.
E-mail address: jongsikryu@gmail.com (J.-S. Ryu).
[1] Both authors equally contributed to this work as co-first authors.

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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., Gyeongan, 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 m^3/s and that in the HR from 1011 to 1051 m^3/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 (Gyeongan; 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 HNO_3. Then, about 25 mL samples were dried in Teflon beakers, and the residues were treated with concentrated HNO_3, dried, and then redissolved in 5% HNO_3 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