

Distribution and geochemical behavior of anthropogenic rare earth elements in two coastal environments

Tomohiro Shimazaki¹, *Hajime Obata¹, Hirofumi Tazoe², Shigeyoshi Ootosaka¹, Shigenobu Takeda³

1. Marine inorganic chemistry division, Atmosphere and Ocean Research Institute, University of Tokyo, 2. Institute of Radiation Emergency Medicine, Hirosaki University, Hirosaki, 3. Graduate School of Fisheries and Environmental Sciences, Nagasaki University

Recently, rare earth elements (REE) are used as high-technology industrial materials in recent years, and are closely tied to modern human life. Because of increasing industrial activities, the demand of REE has been increasing since the 1960s (Zhou et al., 2017). It had been already reported that anthropogenic REE is emitted to aquatic environments (Bau and Dulski, 1996; Nozaki et al., 2000; Elbaz-Poulichet et al., 2002). Among REE, gadolinium (Gd) is used for contrasting agent (for example, Gd(DTPA)) of the magnetic resonance imaging (MRI). By such artificial use, the Gd concentration may be increasing in the aquatic environments in comparison with other REE. This feature is called as “positive Gadolinium anomaly (Gd anomaly) “. However, there are few precedent studies indicating the distribution of anthropogenic REE and Gd anomaly in Japanese coastal areas. In this study we clarified the distribution and the behavior of the anthropogenic REE, especially Gd, in Tokyo Bay and Ariake Sea.

Seawater samples were collected in Tokyo Bay and Ariake Sea, and the samples were collected in the rivers flowing into Tokyo Bay and Ariake Sea. To decompose the organic ligands, the samples were measured after UV-irradiation. Iron hydroxide co-precipitation method was used for collection of REE. To determine REE concentrations in river water and seawaters accurately, we applied the isotope-dilution method. After removing Fe from the anion exchange column, REE concentrations were determined by an inductively coupled plasma-mass spectrometer (ICP-MS). The REE concentration was normalized by using PAAS (Post-Archean Average Australian Sedimentary rock). Moreover, Gd anomaly was calculated by $Gd/Gd^* = Gd_{SN}/(0.33Sm_{SN} + 0.67Tb_{SN})$ (Bau and Dulski, 1996). Gd_{SN} , Sm_{SN} and Tb_{SN} are relative values of gadolinium, samarium (Sm) and terbium (Tb) that were normalized by PAAS, respectively.

Large Gd anomaly was detected in river samples flowing into Tokyo Bay. The vertical distributions of REE were clarified in Tokyo Bay and Ariake Sea. Gd anomaly was detected mainly in Tokyo Bay. The contrasting REE composition implies the anthropogenic REE were supplied to Tokyo Bay. In the area surrounding Tokyo Bay, huge amount of Gd might be released probably because of medical use.

There were no clear differences in REE composition and Gd anomaly in Tokyo Bay between this study and the previous studies, (Nozaki et al., 2000). We will discuss the factors controlling the distribution of REE in these areas.

References

Bau, M. and Dulski, P. (1996) : Anthropogenic origin of positive gadolinium anomalies in river waters, *Earth Planetary Science Letters*, 143, 1-4 : 245-255.

Elbaz-Poulichet, F., Seidel, J.L. and Othoniel, C. (2002) : Occurrence of an anthropogenic gadolinium anomaly in river and coastal waters of Southern France, *Water Research*, 36 : 1102–1105.

Nozaki, Y., Lerche, D., Alibo, D.S. and Tsutsumi, M. (2000) : Dissolved indium and rare earth elements in three Japanese rivers and Tokyo Bay: Evidence for anthropogenic Gd and In, *Geochimica et Cosmochimica Acta*, 64 : 3975–3982.

Zhou, B., Li, Z. and Chen, C., (2017) : Global potential of rare earth resources and rare earth demand from clean technologies, *Minerals*, 7 : 203; doi:10.3390/min7110203.

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