Substantial gadolinium enrichments in lake and river near metrocities in Korea

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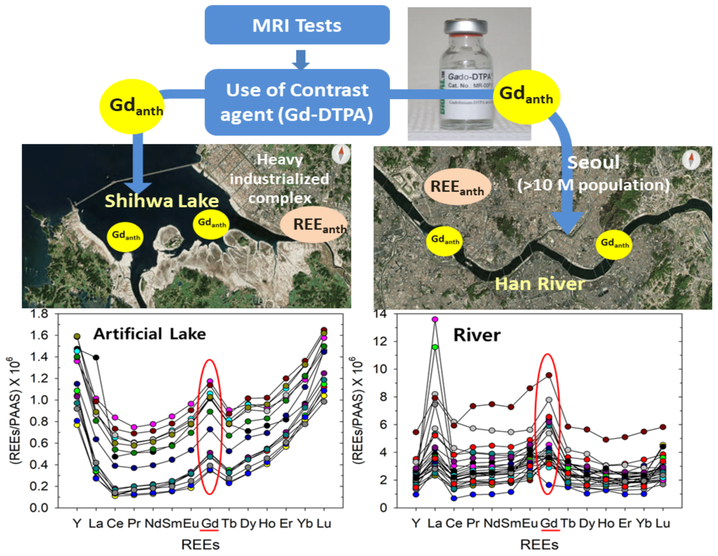
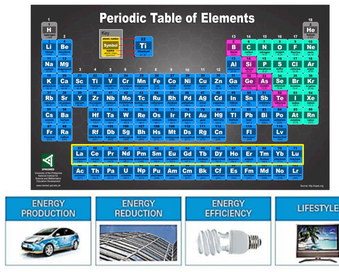
0. Graphical abstract



1. Research Background



motor vehicle, communication device, batteries, LCD, and medical.

- Rare earth elements (REEs) as essential resources for industries, playing critical role in economy and some diplomacy matters.
- Recent increase in anthropogenic REE inputs to the environment.

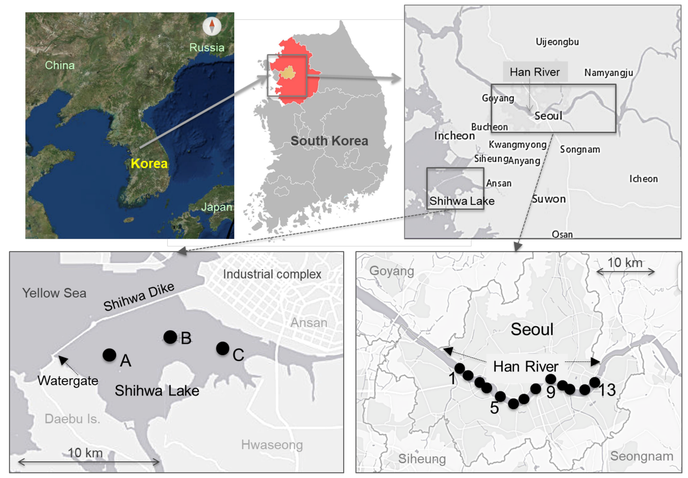
- For example, one of REEs, **anthropogenic gadolinium (Gd)** is in aquatic systems is water-soluble Gd-based complexes, such as Gd-DTPA. Gd-DTPA and other Gd-complexes as been used in **contrast agent of magnetic resonance imaging (MRI)** over three decades.
- With the high stability of Gd complexes in the natural water, the safety of this product for biological toxicity in environmental concentration of artificial Gd has not yet been demonstrated.

- The numbers of MRI facility in Sour Korea is 26.3 per million populations, much higher than that in average number (15.9) in OECD statics in 2017, (5th largest in OECD member countries). More than 1.5M MRI tests were conducted, until now in South Korea.
- However, the impacts of anthropogenic Gd input from MRI test to environments have been rarely studied in South Korea.

2. Research goal

- We hypothesized that natural water systems near large cities in South Korea have been significantly influenced by anthropogenic Gd.
- To assess the impact of Gd e present the REE distributions in natural waters in lake and river in heavily industrialized- and urban areas.

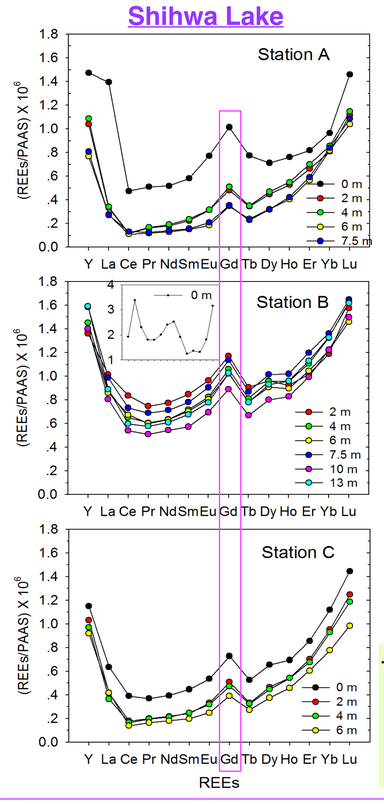
3. Study area

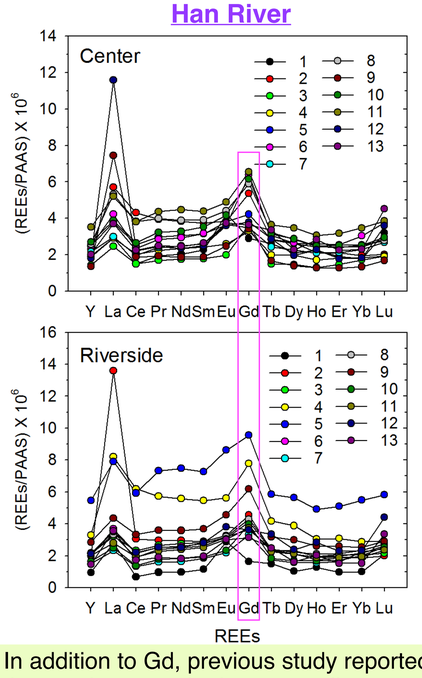


- Shihwa Lake (SL) (left) and the Han River (HR) (right), representing lakessurrounded by heavily industrialized areas and urban river, respectively.
- SL is surrounded big cities with more than one million inhabitants with many industrial cities, complex and ports. The HR is also surrounded by big cities, Seoul and Gyeonggi Prov.. >45% of the total population of South Korea lives near these sites (>10M in Seoul and >13M in Gyeonggi Province).

4. Results

- PAAS-normalized (SN) patterns of dissolved REEs in natural water





- In addition to Gd, previous study reported that anthropogenic La anomalies were found in aquatic system, due to effluent from a production plant for fluid catalytic cracking catalysts in the River water.

- The REE_{SN} patterns in the HR showed a "flat" type REE pattern, with an Yb_{SN}/Nd_{SN} r~1. This type of REE_{SN} pattern indicates a more continental source (rock or soil-like feature) because of the widespread distribution of sedimentary rocks in the drainage area and chemical weathering.
- The **significantly enhanced Gd** anomaly ($p<0.00$) for all 41 samples in both SL and HR , which is also **due to an artificially-derived.**

5. Discussion

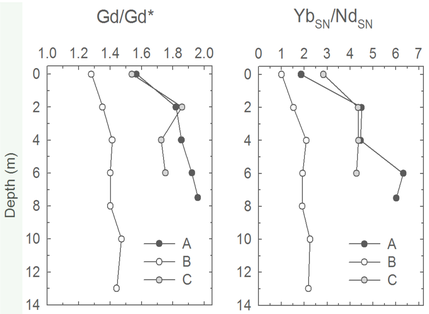
- Gd enrichments in SL and HR based on Gd anomaly (Gd/Gd*)

- In general Gd anomaly (Gd_{SN}/Gd_{SN}^*) is mathematically expressed by linear or geometric extrapolations between Gd_{SN} and neighbor REE_{SN}, such as Sm_{SN}, Eu_{SN} and Tb_{SN} (Hereafter, Gd/Gd*).

Gd anomaly, $Gd/Gd^* = 3\times Gd_{SN}/(Sm_{SN} + 2\times Tb_{SN})$ (1)

	Shihwa Lake (this study)	Han River (this study)	Coastal groundwater	Coastal seawater	East/Japan Sea	Stream
Gd anomaly Gd/Gd*	**1.48±0.14**	**1.63±0.31**	**1.27±0.18**	**1.23±0.15**	**1.21±0.08**	**1.20±0.20**
Sample types	Brackish lake water (N=15)	River water (N=20)	Brackish /fresh-groundwater (N=69*)	South Sea coastal water (N=121*)	Offshore seawater (N=96*)	Stream/river (N=22*)

- In SL, the Gd/Gd* increased with increasing depth/ The higher Gd anomaly in deep water in SL was probably because the stratified deep water was staying much longer than the newly introduced fresh surface water (right Fig.).
- In the HR, the Gd/Gd* were notably higher than those in SL and varied more than in SL, probably because of higher levels of anthropogenic contaminant inputs as a result of the much longer watershed area surrounding large cities in contrast to the enclosed SL. .



- Impact of anthropogenic Gd in Shihwa Lake and Han River

- In this study, we attempted to determine the amount of anthropogenic Gd in SL and the HR. First, we calculated the anthropogenic components (Gd_{anth}) in the water samples using the below equation as previously suggested:

$Gd_{anth} = Gd_{measured} - Gd^*$ (2)

- The calculated inventory of Gd_{anth} in SL and HR were estimated to be 190±80 g Gd_{anth} and 680±360 kg Gd_{anth},respectively, during our sampling period.
- In addition, considering the discharge rate in the HR during our sampling period (950±120 $m^3\ s^{-1}$), the mean flux of Gd_{anth} to the coastal ocean in the HR downstream/ estuary was estimated to be 530±330 g $Gd_{anth}\ day^{-1}$ in summer.
- This Gd_{anth} flux from HR is one order of magnitude higher than that in the Allegheny- (83 g $Gd_{anth}\ day^{-1}$) and Monongahela rivers (33 g $Gd_{anth}\ day^{-1}$) and similar to that of (330 g $Gd_{anth}\ day^{-1}$) the Ohio River.

- Environmental significance statements

This study presents that Gadolinium (Gd), one of rare earth elements (REEs) are noticeably enhanced in the lake and river water near big cities where over 10 million population live. This enhanced Gd, not likely the other 14 REEs are seems to be due to the use of Gd-based contrast agents for MRI tests from a number of hospitals and medical institutes surrounding big cities. This study, therefore, imply that future impact of these artificially derived Gd and some other REEs should be significant in natural waters in polluted area. Overall, **these results suggest that quantitative evaluation of man-made REEs for associated human risk assessments are needed, because considerable amounts of REEs are now used in high-tech industries.**

The details of methods used in this work, sampling and chemical analyses, are not included in here, so please refer to the published paper (Kim et al. 2019, in press,). This research was supported by KIOST project titled "Biogeochemical cycling and marine environmental change studies" (PE99712)

Kim, I., Kim, S. H., & Kim, G. (2019). Anthropogenic gadolinium in lake and river near metrocities in Korea. Environmental Science: Processes & Impacts., doi: 10.1039/C9EM00304E