学 位 論 文 内 容 の 要 旨

博士（環境科学）　　　　氏　名　ZAKIA AKTAR

学 位 論 文 題 名

Rare earth elements in treated wastewater and river water in Sapporo, Japan
—emerging micropollutants
（札幌市の下水処理水および河川水中の希土類元素
―新興微量汚染物質として）

A group of 15 elements (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) known as Rare Earth Elements (REEs) have trivalent cations with slightly decreasing ionic radii and atomic numbers from 57 to 71. These REEs are classified as Light REE (La to Sm) and Heavy REE (Tb to Lu). REE concentrations in samples are normalized with a reference material to generate REE patterns, which show fractionation differences and anomalies, reflecting the sample's history. Recently, these elements have gained attention in environmental pollution and toxicological studies, being recognized as emerging contaminants like anthropogenic Gd, La, and Sm in water sources. Few studies have examined REE patterns in treated and river water in Sapporo City, Hokkaido, Japan, which has nine wastewater treatment plants (WWTPs) and two sludge treatment centers. Each WWTP discharges treated water into rivers. This study aimed to analyze REEs in treated and river water, evaluate anthropogenic pollution, estimate behavior, and identify sources.

We used PAAS (Post-Archean Australian shale) and plotted it on a logarithmic scale according to the atomic number from La to Lu, except Pm, producing a smooth, shale-normalized REE pattern. Samples were collected from July 2019 to January 2020 from the Shiroi, Toyohira (at Jozankei bridge), and Ishikari Rivers, where no WWTP discharges occur. Treated water samples were collected from nine WWTPs (A to I) and from upstream and downstream of their discharge points. Additional samples were taken from two WWTPs (C and E) at two discharge points from April to July 2020, mostly on Thursdays. During this period, treated water from one WWTP was sampled every 4 hours over 36 hours. Metals (V, Cr, Co, Ni, Cu, Ga, Ge, As, Se, Rb, Ag, Cd, In, Sn, Cs, Re, Pt, Au, Pb, Th, and U) in treated water were also measured. All samples were analyzed for REEs using the Agilent 8800 triple quadrupole ICP-MS at Hokkaido University.

This study identified anthropogenic REEs in treated water and pollution in river water from upstream to downstream relative to WWTP coverage (chapter 01). Significant positive La anomalies in treated water samples indicated anthropogenic La. The daily discharge of excess gadolinium (Gd) and lanthanum (La) was positively correlated with the number of hospitals in the region. Post-holiday, excess Gd levels were higher at night, while La levels remained stable regardless of the day. The presence of La, particularly in particulate form, suggested that WWTPs' simplified processes are insufficient for removing anthropogenic La. Lanthanum carbonate tablets (e.g., Fosrenol®), prescribed to kidney patients, were identified as the source of excess La. Due to low solubility, most anthropogenic La settled as sewage sludge, with a small percentage released into treated water. Sequential extraction of sewage sludge showed most excess La as a phosphate compound, primarily extractable with citric acid and dilute hydrochloric acid, with a small fraction bound in residues or extractable by ammonium acetate. This raises concerns about alterations to natural REE patterns.

Chapter 02 explains how variations in LREE and HREE concentrations in treated water and upstream and downstream river water reveal anthropogenic REE anomalies. Rivers without WWTPs showed higher LREE than HREE. Farther upstream, the Shiroi and Toyohira rivers exhibited LREE enrichment, while treated water showed HREE enrichment and anthropogenic Gd anomalies, with LREEs removed during treatment. Pronounced positive Gd anomalies in treated water were linked to increased MRI use in Sapporo. Anthropogenic Gd from WWTP effluent raised downstream Gd levels, but excess Gd emissions did not match MRI consumption data, indicating the need for more monitoring. Anthropogenic Gd disrupts natural REE patterns due to its higher water availability than sludge. HREE enrichment in river water may indicate treated water presence, alongside temperature, chloride concentration, and Gd anomalies.

This study examined iodine, metals, excess Gd, and La concentrations in treated water from various WWTPs in Sapporo (chapter 03). It revealed significant spatial and temporal differences influenced by local factors such as hospitals, medical activities, and WWTP schedules. A strong correlation between iodine and Gd suggested common sources, mainly from medical facilities using Gd in MRIs and iodine in CT scans. Temporal analysis showed iodine levels fluctuated significantly, especially increasing at night, reflecting hospital operations starting after weekends. Sewage water with iodine took about 12 hours to be treated, similar to excess Gd. Annual iodine emissions from WWTPs (147.1 tonnes/year) were much higher than estimates based on CT scanner usage (46.7 tonnes/year), indicating additional sources like households and industries. Despite the COVID-19 pandemic, no significant changes in iodine, excess Gd, and excess La concentrations were observed, showing essential medical services continued.

The spatial map for metal distribution in each sewage coverage area showed varying percentages due to local industrial activities (chapter 03). Specific regions showed higher concentrations of certain elements: Area A had high Ni, Ga, and Sn; Area C had high Sn; Area D had elevated Co and Cd; Area E had high Se, Cu, and Pt; Area F had high V and As; Area G had high Cr, Ge, Rb, Cs, Re, Pb, In, Pt, Au, and Th; and Area I had the highest U. The study focused on correlating metals with Gd and La to identify their sources in treated water. A moderate positive correlation between Gd and Cu was attributed to using Cu and Gd contrast agents in MRI procedures.

Advancements in medical facilities suggest future increases in microcontaminants like excess La, Gd, and iodine. Continuous monitoring of REEs in rivers is essential to mitigate environmental impacts. Managing REEs from WWTPs can help control anthropogenic activities in urban areas.