Rare earth elements in treated wastewater and river water in Sapporo, Japan—emerging micropollutants

（札幌市の下水処理水とおよび河川水中の希土類元素—新興微量汚染物質として）

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Summary

Rare Earth Elements (REEs), including Lanthanum (La) to Lutatitium (Lu), are crucial components in advanced technologies, with applications ranging from electronics to medicine. These elements are categorized into Light REEs (LREEs; La to Europium (Eu) and Heavy REEs (HREEs; Gadolinium (Gd) to Lu). These REEs are increasingly found as micropollutants in water systems. Wastewater Treatment Plants (WWTPs) have been identified as significant sources of REEs entering the environment, particularly through treated wastewater effluents. These are typically found in water at trace concentrations, ranging from a few nanograms per liter (ng/L) to several micrograms per liter (µg/L). Micropollutants are ubiquitous and conventional processes used in the WWTPs, unable to treat these microcontaminants. Therefore, they can persist in treated wastewater effluent even after treatment. Recent studies have highlighted the growing concern over micropollutants in aquatic environments, especially REEs. Other micropollutants such as artificial sweeteners and iodinated X-ray contrast media (ICM) in treated wastewater discharged in water bodies after the treatment. So, potential anthropogenic pollution is caused by micropollutants as metals gradually enrich in the environment through human activity, although standard and guideline concentrations of these elements are not regulated by environmental quality standards for water pollution. Anthropogenic Gd is a good example of increasing its concentration daily, as recorded for over 20 years in the USA and 27 years in Japan.

Typically, all REEs are stable as trivalent cations, and their ionic radii decrease progressively with increasing atomic number, leading to subtle changes in their chemical properties. This results in REEs forming a cohesive group of elements. When the REE content of a sample is

normalized to standard shale values (from literature) and plotted on a logarithmic scale in order of atomic number from La to Lu, a smooth pattern emerges, known as the REE pattern. Notably, Ce (cerium) and Eu (europium) are exceptions within this group; their redox states allow them to also exist as tetravalent and divalent ions, respectively, creating anomalies in their abundances. These anomalies serve as valuable fingerprints and historical records in the study of natural materials. Anthropogenic influences are significant in studying or identifying the REE pattern of water samples. Despite the growing awareness of the REE contamination, particularly Gd, there is a lack of comprehensive understanding regarding the enrichment of HREEs in river systems. First identified in Germany in 1996, anthropogenic Gd anomalies have since been observed in various locations worldwide. This study focused on the presence of REEs in treated water and river water in Sapporo, Japan, with an emphasis on Gd anomalies and HREE enrichment. The problem revolves around the gradual increase in the concentration of anthropogenic REEs in the environment, particularly Gd, which is commonly used in medical magnetic resonance imaging (MRI) in hospitals. In Sapporo, Japan, the discharge from WWTPs into rivers may contribute to these REEs, but a comprehensive dataset is lacking. The study seeks to address this gap by examining the REE content in river and treated water, exploring the Gd anomalies, and investigating the potential of HREE enrichment as a co-indicator of anthropogenic influence. Furthermore, while anthropogenic Gd has been extensively studied as a pollution tracer, the potential of HREEs remains underexplored. The REEs, especially anthropogenic Gd, have attracted attention as emerging micropollutants in the environment. For example, Gd-based contrast agents used in MRI are highly stable, water-soluble, and are rapidly excreted from the human body after administration without any degradation. Consequently, these Gd contrast agents remain dissolved in treated water as effluents and are eventually released into the environment through sewage systems. This anthropogenic positive Gd anomaly has been recognized as a useful tracer in wastewater studies.

The study area includes various rivers in Sapporo and nine sewage coverage areas with WWTPs (areas A to I) discharging treated water into these rivers. From July 2019 to January 2020, samples were collected from the Shiraigawa, Toyohiragawa, and Ishikarigawa river basins—areas without WWTP discharges. In this study, water samples were collected from upstream, downstream, and discharge points near WWTP plants. Additionally, river water samples were systematically gathered from each sewage coverage area within the city. Physical parameters (temperature and pH) were measured in the field during sample collection. Treated water sampled in the following three modes: a) Thursday around noon from April 16 to June 18 and July 24, 2020 to observe weekly changes by sampling treated water from two areas; b) Weekday daytime, with three times collections from each of the nine WWTPs area to assess facility differences and c) from 6 am Monday to 6 pm Tuesday, treated water was collected every 4 hours from Ca and Cb plants to observe temporal variations over a day and a half. For sample preparation, a 25 ml sample from each 500 ml sampling PET bottle was transferred to 30 ml PP (Polypropylene) and ultrapure HNO_3 acid was added to keep the pH 1 to 2. Samples were prepared without any concentration or condensation method and filtered by a 0.22µm membrane filter before the REE analysis. The REE analysis was performed by ICP-QQQ (Triple Quadrupole) 8800 of Agilent Technologies, Inc. locating in the Open Facility of Hokkaido University. Quantitative calibrations were conducted using the external standard solution (XSTC-1 multi-elements standard, SPEX). The accuracy of determining the REE contents in water and sludge samples was 5% to 25% and 3% to 10%, respectively. Data precision and accuracy were verified by analyzing the reference standard rock samples (JB-2, JB-3, JB-1a, JA-2 and JA-1). No systematic error was observed. All blank sample REE concentrations were below the determination limits. The major anions were measured in filtered water samples without acidification in ion chromatography (IA-300). The REE data were normalized using PAAS (Post-Archaean Australian Shale), a reference material and Gd anomalies were calculated using specific equations. Statistical analysis was conducted using the Kruskal-Wallis rank test.

The river water in Sapporo typically exhibits a concave REE pattern, with the exception of the Barato River. This river has REE concentrations an order of magnitude lower than those found in other rivers such as the Ishikari, Toyohira (Jozankei and inside the city), and Shiroi rivers. The Barato River's unique REE pattern, including a Gd anomaly, is influenced by its connection to WWTPs and its oxbow-like shape. The Gd anomaly is linked to anthropogenic sources from the WWTPs. In contrast, the Toyohira River shows a negative Ce anomaly beyond Jozankei bridge, likely due to natural Ce oxidation during water transport. Ce and Eu anomalies can arise from redox behavior, with negative Ce anomalies often seen in undisturbed water systems. HREE enrichment ratios vary across rivers in the Toyohira, Shiroi, and Ishikari rivers. The Ishikari River exhibits the lowest HREE enrichment, influenced by its larger size and higher volume of water flow. The gradual decline in REE concentrations in downstream river results from adsorption, complexation, and precipitation processes.

In areas with WWTPs, the REE patterns reflect the influence of treated wastewater. One area with Sosei River (a distributary of the Toyohira) exhibits sudden HREE enrichment and positive Eu anomalies in upstream water, likely linked to wastewater discharge. The presence of a positive Eu anomaly and elevated HREE enrichment indicates anthropogenic influences, particularly near WWTP outlets. All treated water samples exhibit Gd and La anomalies, generally showing higher HREE enrichment than river water. The observed Eu anomalies are likely due to lithology rather than anthropogenic sources, although specific cases suggest potential anthropogenic contributions. The study found that the concentration of excess Gd and Gd anomalies varied significantly across different areas in Sapporo, primarily influenced by the number of hospitals and the usage of MRI machines. The highest anthropogenic Gd anomaly and excess Gd concentration were observed in one area related to the highest number of hospitals, close to Sapporo rail station. The total estimated anthropogenic Gd (Gd_{anth}) release in Sapporo, based on the number of hospitals, alignes with the high solubility and long half-life characteristics of Gd-contrast agents, making them challenging to treat effectively at WWTPs. The annual output of Gd_{anth} in Sapporo was estimated with the highest levels found in three areas near the area with high number of hospitals and Sapporo rail station. However, this estimate was significantly lower than the expected based on the number of MRI machines, suggesting the need for more frequent sampling and better data on Gd-contrast agents in MRI facilities across this city. The discrepancy indicated the necessity for further research and monitoring of Gd emissions from different WWTPs.

The conservative nature of anthropogenic Gd makes it a reliable tracer for monitoring treated water discharge into rivers, which could help track the movement and impact of treated water in the environment. In addition to Gd, the study observed a significant enrichment of HREEs in treated water, particularly in one area where the Sosei River received effluent from a nearby WWTP. The sudden rise of HREE enrichment in upstream suggested the presence of an additional, previously unidentified discharge point. This enrichment was linked to the treatment processes employed at the WWTP, where LREEs were more effectively removed, leaving higher concentrations of HREEs in the treated water. The study compared the HREE enrichment in Sapporo with similar findings from other countries, revealing that the enrichment is a consistent phenomenon regardless of the treatment methods used. The high stability and solubility of HREEs in treated water were attributed to their unique chemical properties, particularly their smaller ionic radii and electronic configurations, which make them more resistant to removal during wastewater treatment.

Much is still unknown about La anomalies, including the natural variation of this element. La plays a crucial role in aerobic methane-oxidizing bacteria, and microbial enzymatic activity may contribute to the development of La anomalies. Since 2011, significant La contamination has been reported in the lower Rhine River in Germany, affecting both river water and shellfish samples. This contamination is linked to a spill from a plant that produces petroleum-refining catalysts containing La-based zeolite. These La anomalies are increasingly linked to human activities, including the use of lanthanum carbonate in medical treatments and its application in advanced technologies. Despite the growing evidence of La contamination, particularly in urban environments, there is a significant gap in understanding the specific sources and temporal variations of these anomalies. Previous research has not been sufficiently investigated the contributions from hospital effluents, where lanthanum carbonate is used to treat renal patients, potentially leading to consistent anthropogenic La anomalies in treated wastewater. Moreover, the correlation between La anomalies and hospital density, as well as the variation in La levels between weekdays and holidays, remains unexplored. This study aims to address the gaps in understanding the sources and patterns of anthropogenic La anomalies in Sapporo, Japan's water systems. Specifically, the objectives are to investigate the extent and temporal variation of La anomalies in river waters and treated wastewater, as well as to determine the correlation between La anomalies and the density of hospitals in areas with wastewater treatment plants (WWTPs). This study also examines differences in REE concentrations in treated water samples collected on weekdays versus holidays and identifies primary sources of La anomalies, focusing on the use of lanthanum carbonate medication. This research provides a comprehensive understanding of La contamination in urban water systems.

The results showed that the concentration of La did not vary significantly between workdays and holidays, as evidenced by a Kruskal–Wallis one-way analysis yielding a p-value above 0.05. This suggests that La concentrations were not dependent on the day of the week. However, the abundance of Gd was directly linked to MRI diagnostic activities in hospitals, particularly on weekdays, as shown by significantly higher concentrations of Gd during these periods. This was confirmed using the same statistical approach, with a p-value below 0.05. The temporal variations of La and Gd concentrations were further analyzed from Monday morning to Tuesday evening. Gd concentrations peaked at 10 pm on Monday, likely due to the injection of Gd-based contrast agents during MRI procedures earlier in the day. This peak concentration was approximately ten times higher than the average. The data showed significantly lower levels of Gd when samples were collected on holidays, supporting the hypothesis that Gd concentrations are linked to hospital activities. The consistent presence of excess La in treated water, may be attributed to the continuous use of lanthanum carbonate tablets by kidney patients.

To confirm the source, we analyzed sludge samples collected from the treatment center. In the sludge samples, the study observed a La enrichment relative to other REEs, with no Gd anomaly detected. This aligns with previous studies, as Gd remains dissolved in treated water and does not accumulate in sludge. La concentrations in the sludge were found to be significantly higher than those reported in Japan 22 years ago, likely due to the use of lanthanum carbonate medication. Sequential extraction of sludge samples revealed that La was primarily associated with the extraction using citric acid and hydrochloric acid, indicating that phosphate-bound La in hospital wastewater contributes to the observed positive La anomalies. The study also estimated the annual La consumption in Sapporo and compared it to the amount of La discharged into WWTPs, showing a partial overlap between the two. This work identified and characterized anthropogenic sources of REEs, particularly La, in the treated water and sludge from WWTPs in Sapporo. Significant positive La and Gd anomalies were observed in treated water, linked to the use of lanthanum carbonate medication and Gd-based MRI contrast agents in hospitals. La anomalies remained constant regardless of the day, while Gd anomalies peaked during weekdays. Most anthropogenic La settled in sewage sludge, with only a small fraction released into treated water, highlighting the need for further investigation into the environmental impacts of these REEs.

Finally, a preliminary analysis of trace elements beyond the REEs was performed on treated water samples collected from twelve WWTPs. Conventional WWTPs often struggle to remove micropollutants, particularly trace elements like iodine and Gd, which are stable and resistant to treatment processes. Despite previous studies on iodine concentrations in various water bodies in Japan, no analysis has focused on iodine levels in wastewater, particularly in Sapporo. This gap is significant, as iodine, along with other trace elements like La and Gd, is increasingly recognized as a marker of medical activity, especially from hospital effluents. The COVID-19 pandemic further underscored the importance of monitoring these elements in wastewater, as changes in public behavior and hospital activities could influence their concentrations.

The study found varying iodine concentrations across different area of WWTPs in Sapporo. These levels were significantly higher in treated wastewater compared to river water. The strong correlation between Gd_{anth} and iodine in treated wastewater suggests that hospitals and medical facilities are significant sources of these elements, likely due to their use in MRI and CT scan applications, respectively. Iodine levels in treated wastewater showed significant variations between working days and holidays. The Kruskal–Wallis test confirmed that iodine concentrations were higher on weekdays, reflecting increased hospital activities. A detailed temporal study revealed a sharp increase in iodine levels at 10 pm on Monday, coinciding with the resumption of hospital activities after the weekend. This pattern is consistent with the use of iodinated contrast media (ICM) in CT scans, similar to the behavior observed for Gd. The study estimated iodine annually from WWTPs in Sapporo, which is nearly three times higher than estimated based on the number of CT machines in the city. This discrepancy suggests that other sources, such as households, restaurants, and industrial activities, also contribute significantly to iodine levels in wastewater. Unlike Gd and La, iodine levels did not strongly correlate with the number of hospitals in Sapporo ($R = 0.54$), indicating that hospital effluents are not the sole source of iodine. Excess Gd and iodine showed similar patterns, with higher concentrations on working days. No significant correlation was found between these concentrations and the number of COVID-19 patients, suggesting that medical diagnostics and treatments continued unaffected during the pandemic.

Trace elements such as V, Cr, Co, Ni, Cu, Ga, Ge, As, Se, Rb, Ag, Cd, In, Sn, Cs, Re, Pt, Au, Pb, Th, and U were measured. Among them Indium (In) which could be linked to medical applications, was highest in two areas, likely due to the use of indium-containing compounds in medical diagnostics. Silver (Ag) was notably higher in one area, and Platinum (Pt) and Gold (Au) were elevated in three areas, indicating industrial or medical sources. The study found that hospitals were a significant source of Cu, correlating with Gd, used in MRI procedures to enhance image quality. However, other elements, such as Cd, Pb, and As, are likely originate from urban runoff, industrial activities, and natural sources. These findings underline the heterogeneity of pollution sources across different areas, with certain elements like Re and Cs linked to high-tech industries.

The study revealed significant anthropogenic impacts on the distribution of REEs, particularly La and Gd, in Sapporo's water systems, primarily stemming from WWTPs. In treated water, the persistent presence of La points to its primary source: the use of lanthanum carbonate daily in medications for treating kidney patients. A strong correlation between iodine and Gd concentrations suggests that both elements share common sources, primarily from medical facilities. Temporal variations also showed similar behavior among iodine and Gd, reflecting hospital activity. Both elements took about half a day for sewage discharged from the hospital to be released into the river as treated water. A significant gap between annual iodine emissions from WWTPs and number of CT scan usage, indicating additional sources such as households and industries. The discharge of treated water containing anthropogenic REEs, such as La and Gd, poses a potential risk to aquatic ecosystems. Furthermore, the application of sewage sludge, rich in phosphorous, as fertilizer could further spread REEs into the environment, emphasizing the need for careful management of such practices. The study highlighted how these anthropogenic REEs disrupt the natural balance of REEs in aquatic ecosystems.