Hospital Effluent as a New Source of Anthropogenic Lanthanum in the Environment

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Abstract

Excess gadolinium (Gd) in the environment, originating from Gd-chelating contrast agents present in hospital wastewater, has been extensively studied as a micropollutant. However, the source of excessive lanthanum (La) levels in the environment remains unclear. In this study, we analyzed rare earth elements (REEs) in treated water from nine wastewater treatment plants (WWTPs) and sewage sludge/incinerated ash from two sludge treatment centers in Sapporo, Japan, during 2019–2020. We found that the annual discharge of excess Gd and La in a treatment area positively correlated with the number of hospitals in that area. The excess Gd concentration in the treated water increased by an order of magnitude late at night Monday, whereas the excess La concentration remained constant. Sequential extraction experiments on sewage sludge revealed that excess La is predominantly incorporated in phosphate, not silicate, as in zeolite catalysts. We identified lanthanum carbonate tablets (e.g., Fosrenol®), prescribed daily to kidney patients to prevent hyperphosphatemia, as the source of excess La. Due to its low solubility, most of the anthropogenic lanthanum settles as sewage sludge in WWTPs, and only a small percentage is released into treated water. This raises concerns about the potential degradation of natural REE patterns in the environment.

KEYWORDS: *Lanthanum anomaly, Gadolinium anomaly, Sewage sludge, Wastewater treatment, Sapporo, Rare-earth-element pattern, Fosrenol, Lanthanum carbonate*

Synopsis: Analysis of sewage sludge and treated water in Sapporo revealed that kidney disease medications are sources of significant environmental lanthanum contamination.

Introduction

All rare earth elements (REEs) possess stable trivalent cations with slightly decreasing ionic radii and minor changes in chemical properties as the atomic number increases, showing interconnected behavior.[1] We divided the REE content of a sample by the REE literature values in the Post-Archean Australian shale[2] (PAAS) and plotted the results on a logarithmic scale according to the atomic number from La to Lu. The plot showed smooth variations, known as the shale-normalized (SN) REE pattern.[2,3] Depending on their redox states, Ce and Eu may appear as tetravalent and divalent ions, respectively, causing anomalies in their abundance in environmental materials. The anomaly degree is widely known to reflect the history and fingerprint of material in earth sciences.[1] The importance of quantifying REE abundance in environmental and ecological risk and toxicity studies has recently received considerable attention.[3,4]

Gadolinium Anomaly. Even if the valences of La, Gd, and Lu ions remain unchanged, their electronic configurations (with no, half-filled, and full-filled 4f-electron subshells) facilitate complex formation with organic substances in water, resulting in higher solubility than that of their neighboring elements.[5,6] For Gd, interpolated normalized values of Sm and Tb (Sm_{SN} and Tb_{SN}) yield the hypothetical normalized value of Gd concentration in the absence of anomalies (Gd_{SN}*): $Gd_{SN}^* = (Sm_{SN})^{(1/3)} \times (Tb_{SN})^{(2/3)}$. The ratio of observed normalized Gd concentrations to Gd_{SN}* in natural water environments typically increases to around 1.3.[7] However, some reports show $(Gd/Gd^*)_{SN}$ values significantly exceeding 1.3 in river water.[7,8] This Gd contamination is attributed to Gd-based contrast agents used in magnetic resonance imaging (MRI) procedures in hospitals. The agents show excellent water solubility, stability, and rapid excretion from the human body, thereby reaching wastewater treatment facilities via sewage flow and being released

into the environment through treated water. [7]

Lanthanum Anomaly. Much remains unknown about La anomalies, including how the La/La* ratio changes naturally. Lanthanum is essential for aerobic methane-oxidizing bacteria,[9] and microbial enzymic activity may lead to La anomalies.[10] Since 2011, severe La contamination has been reported in river water and shell samples in the Lower Rhine River due to a spill from a petroleum-refining-catalyst (La-containing zeolite) production plant.[11-15] Further, La enrichment was reported in sewage sludge collected in Switzerland in 2016.[16] In 2019, filtered treated-water samples from Tokyo's wastewater treatment plants (WWTPs) showed significant positive La and Gd anomalies.[17] In both cases, the source of La enrichment has not yet been identified. Incidentally, La anomalies were not observed in sewage sludge and river water samples collected in Tokyo in 1996.[18,19]

We hypothesize that the recent La enrichment observed in sewage sludge[16,20] and treated sewage water[17] is due to lanthanum carbonate tablets administered daily to hospitalized renal patients to prevent hyperphosphatemia. If this hypothesis is correct, lanthanum phosphate excreted by patients should always be present in the particulate phase of hospital wastewater and accumulate in sewage sludge and other sources. This paper confirmed that the lanthanum anomaly[21] is concentrated in the phosphate by the sequential extraction analysis of sewage sludge. We analyzed the geographical distribution and temporal variation of La enrichment in treated water samples of Sapporo city.[22] Bulk analysis of incinerated sludge ash was also examined.

Methods and Materials

Geographic Information Sapporo city, the capital of Hokkaido—Japan's northernmost island—has nearly 2 million residents (Figure 1). The upstream Toyohira

River serves as the primary water source. Excluding the southern mountainous region, Sapporo has nine areas that are covered by 12 WWTPs (marked with stars A–I in Figure 1).[22] The sludge that settles in the settling tanks of the WWTPs is transferred separately via sewage pipes to two sludge treatment centers ('West' and 'East' in Figure 1),[22] located across the Toyohira River, where it is dewatered and incinerated. We obtained dewatered sludge and incinerator ash samples from these two centers in May 2020.

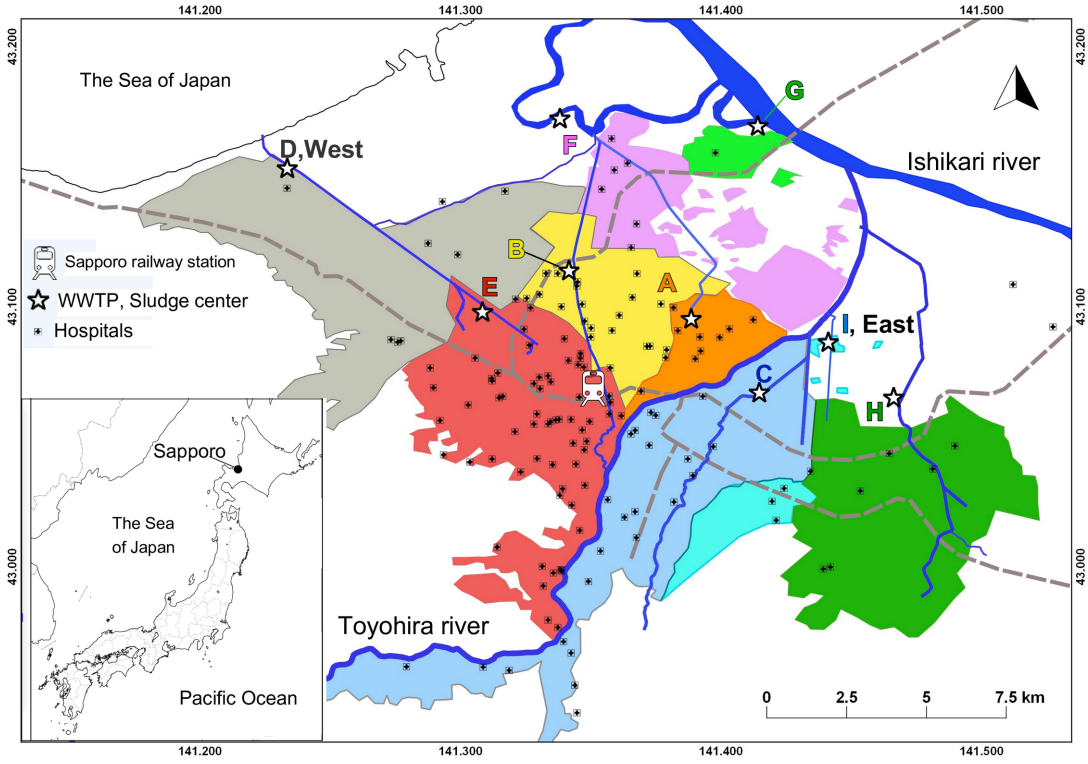


Figure 1. Sapporo city map showing the locations of wastewater treatment plants (WWTPs: A–I), sludge (treatment) centers (West (Seibu) and East (Tobu)), and distribution of hospitals (denoted by small crosses in squares). The area covered by each WWTP is color-coded as follows.[22] A: Fushikogawa (orange), B: Soseigawa (yellow), C: Toyohira (light blue), D: Teine (grey), E: Shinkawa (red), F: Barato (pink), G: Takuhoku (light green), H: Atsubestu (green), I: Tobu (cyan). The names of each WWTP are listed in Table 1. Hospital locations are available at:

https://gisdata.mapog.com/japan/hospitals_point.

Treated-water sampling. We directly collected treated water in acid-washed PET (polyethylene terephthalate) bottles from the discharge outlets of the nine WWTP sites and kept it in a refrigerator until the chemical analysis. The treated water was sampled in three modes (Tables S1 and S2): i) weekly sampling (sampling on Thursdays for 2–3 months) at plants C and E, ii) intraday sampling (sampling every 4 hours over a period of 36 hours) at plant C, and iii) WWTP-dependent sampling (sampling at different WWTPs).

Chemical Analysis. See the Supporting Information (SI) for more details of this section. Sludge incinerated ash samples were acid-digested into a solution using a Teflon-lined stainless steel autoclave, leaving no residue. Dewatered sludge was subjected to sequential extraction[24] using the following solutions: 25% acetic acid, 0.3 M citric acid, and 0.2 M HCl. The residue was then digested using an acid digestion method.[23]

REE, Ba, and Sb contents in the treated water, digested solution, and extracts (refer to Tables S1–S3) were determined at Hokkaido University using an Agilent 8800 triple quadrupole ICP-MS (Inductively coupled plasma mass spectrometry) equipment operating in the helium collision mode.[25] Where necessary, isobaric interference corrections were performed.[26] The CeO^+/Ce^+ ratio (156/140) was approximately 0.2%, and the Ce^{2+}/Ce^+ ratio (70/140) was within 1%–1.5%. 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 (Table S4).[23,25] No systematic error was observed. All blank sample concentrations were below the determination limits. ICP-OES (optical emission spectrometry) using a Shimazu ICPE-9000 was employed to determine the phosphorus content in the sludge extracts and residues.[23]

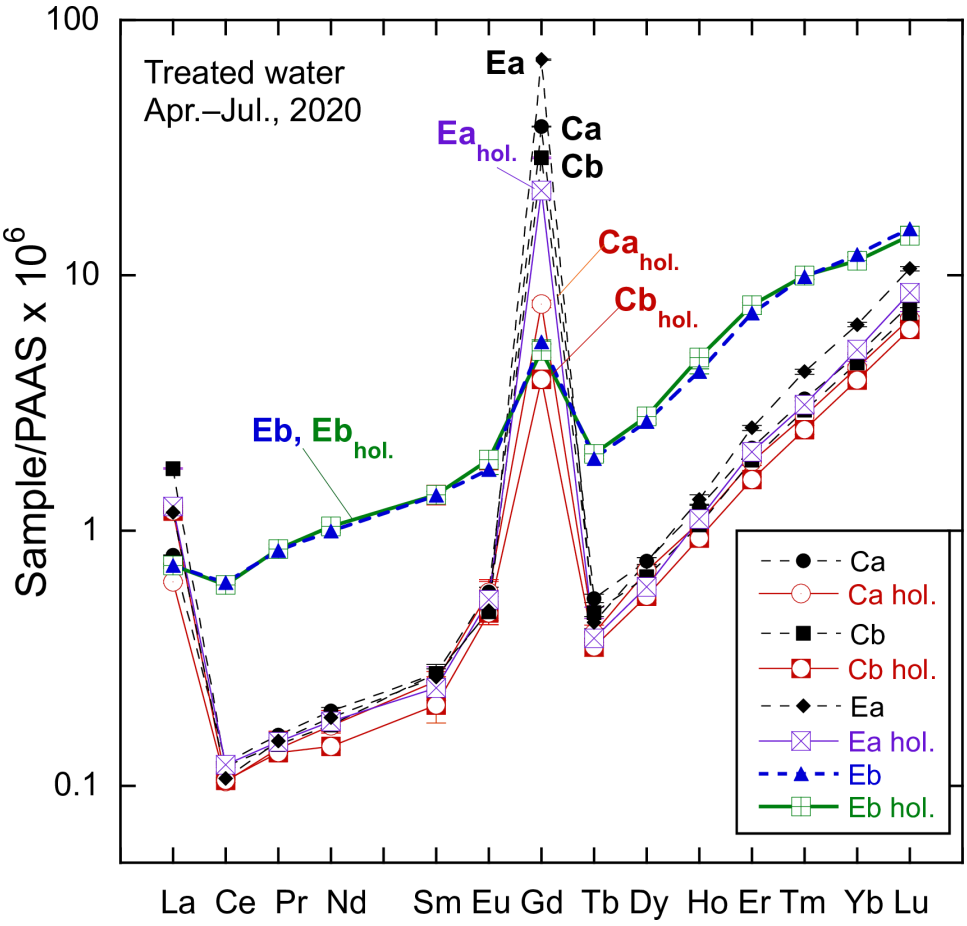


Figure 2. Post-Archean Australian shale (PAAS)-normalized REE patterns in treated water samples collected at the C (Ca and Cb) and E (Ea and Eb) wastewater treatment plants (WWTPs) on Thursdays from April to July 2020 (Table S1). The graph compares REE patterns on days following a holiday (labeled with 'hol.') to those following a weekday (no label). The 'hol.' label denotes averages for three weeks when the preceding day (Wednesday) was a holiday. Labels without 'hol.' represent the average measurements (n = 8) taken on weekdays. The Ca and Cb WWTPs manage sewage from the north and south C areas, respectively, while the Ea plant processes urban sewage, and the Eb plant primarily handles suburban sewage.

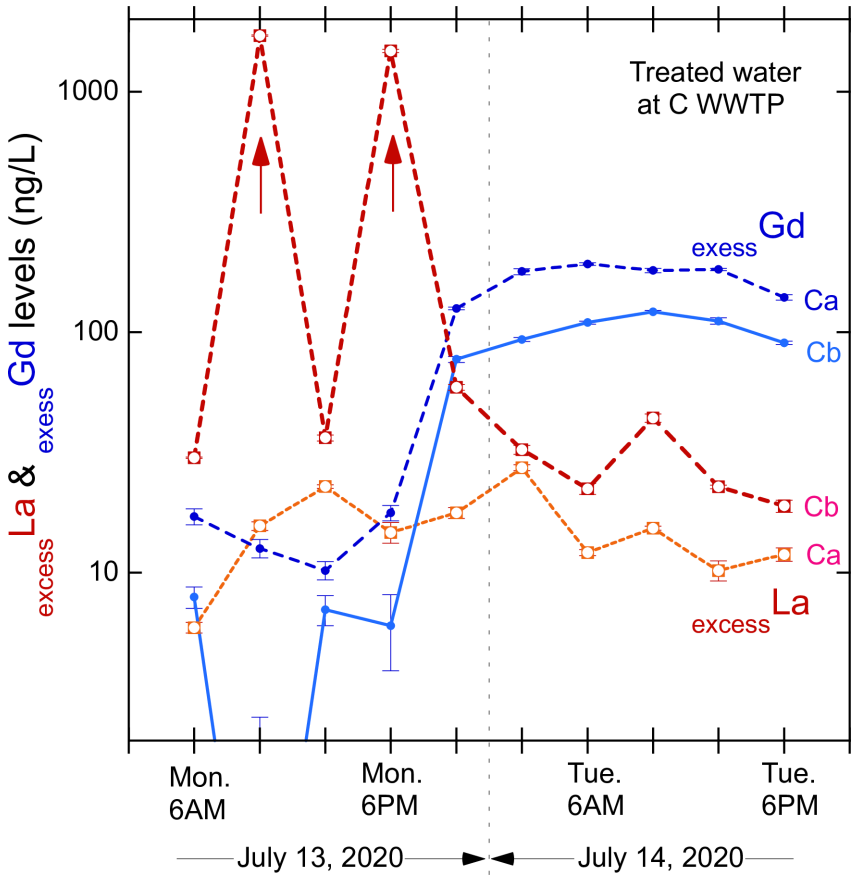
Results

147 Refer to the SI of Sapporo Sewerage for study data.[27] There was little change in the
148 data between 2019 and 2020.

149 **Treated water.** Figure 2 shows the average REE concentrations of treated water
150 discharged from the four WWTPs (Table S1). The upward-trend patterns are attributed to
151 heavier REEs with smaller ionic radii forming more soluble complexes with organic
152 components[6]. The samples from urban areas (Ca, Cb, Ea) showed significant positive La
153 and Gd anomalies. In contrast, the suburban sewage sample (Eb) did not show any
154 positive La anomaly and had a weak positive Gd anomaly. The positive Gd anomalies
155 were notably smaller in samples collected after a holiday ($Ca_{hol.}$, $Cb_{hol.}$, $Ea_{hol.}$) than those
156 collected after a weekday (Ca, Cb, Ea). In contrast, the large positive La anomalies
157 showed minor differences regardless of whether the preceding day was a holiday or a
158 weekday.

159 The temporal variation in the excess La and Gd concentrations at the Ca and Cb plants
160 from Monday morning to Tuesday evening (Figure 3; Table S1) shows that the Gd
161 concentration increases by a single-digit factor at 10 pm on Monday. Meanwhile, the La
162 concentration remains nearly constant, except for the La levels at Cb at 10 am and 6 pm,
163 when the simplified treated water[27] was discharged. The excess La concentration in the
164 simplified treated water is approximately 30 times greater than that in normal (high-level)
165 treated water.

166 In Figure 4, the quantity of excess La inflow per year was calculated for each facility
167 by multiplying the excess concentration by the annual treatment volume.[27] Similarly, the
168 excess Gd inflow quantity per year was calculated and correlated with the number of
169 hospitals in the treatment area; a strong positive correlation was found for both La and
170 Gd (R = 0.88, 0.82).



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172 **Figure 3.** Temporal variations every 4 hours in excess (anthropogenic) La (in red) and
173 Gd (in blue) discharges from Ca and Cb WWTPs from Monday at 6 am to Tuesday at 6
174 pm in July 2020 (Table S1). The error bars indicate the propagated error from the standard
175 deviation of the concentration measurements. The two arrows indicate samples in which
176 the removal of suspended solids was incomplete, resulting in simplified treated water
177 discharge[27]. The hypothetical concentration of La (La*) in the absence of anomalies was
178 estimated from the shale-normalized Pr and Nd values[21]: $La_{SN}^{*} = (Pr_{SN})^3/(Nd_{SN})^2$. [Excess
179 La] = measured [La] − [La*]. [Excess Gd] = measured [Gd] − [Gd*] × 1.3.

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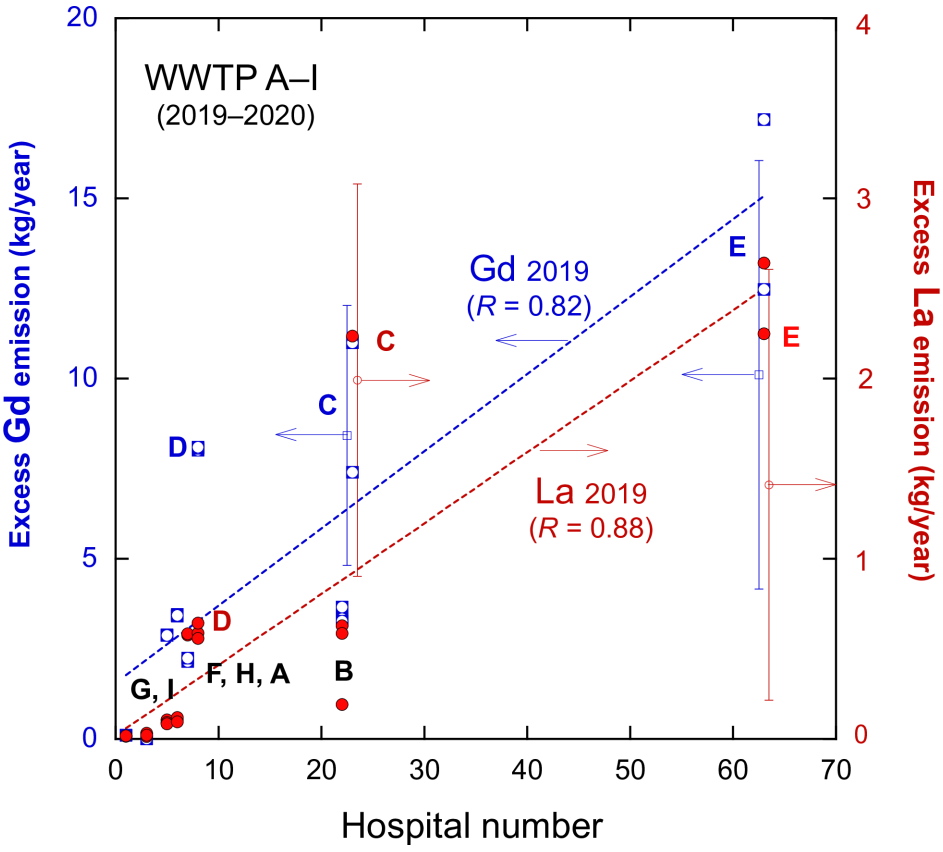

Figure 4. Correlation between annual inflows of excess La (red symbols) and Gd (blue symbols) and the number of hospitals within each wastewater treatment plant (WWTP) area A–I for 2019. The average relative standard deviations (RSDs) for La and Gd measurements were 4% and 2%, respectively (Table S2). The error bars on data for areas C and E represent the standard deviation across 8–14 measurements taken in 2020, also documented in Table S2.

Sewage Sludge. Figure 5 displays the REE patterns in three sequentially extracted components of dewatered sludge using a) 25% acetic acid, b) 0.3 M citric acid, c) 0.2 M hydrochloric acid, and d) the residues, along with incineration ash, averaged per sludge center plant (Table S2). The d) residue showed a slight La anomaly ($La/La^* = 2.1 \pm 0.5$). In contrast, the other four components (a–c, ash) exhibited significant positive La

anomalies, with values of 21.4, 14.7, 33.0, and 9.4, respectively. None of the patterns showed Gd anomalies (1.08−1.34). The REE concentrations in incinerated sludge ash were one order of magnitude higher than those in the total sewage sludge. The REE concentrations in the a) acetic acid extract were nearly one order of magnitude lower than those in the b) citric acid or c) HCl extracts.

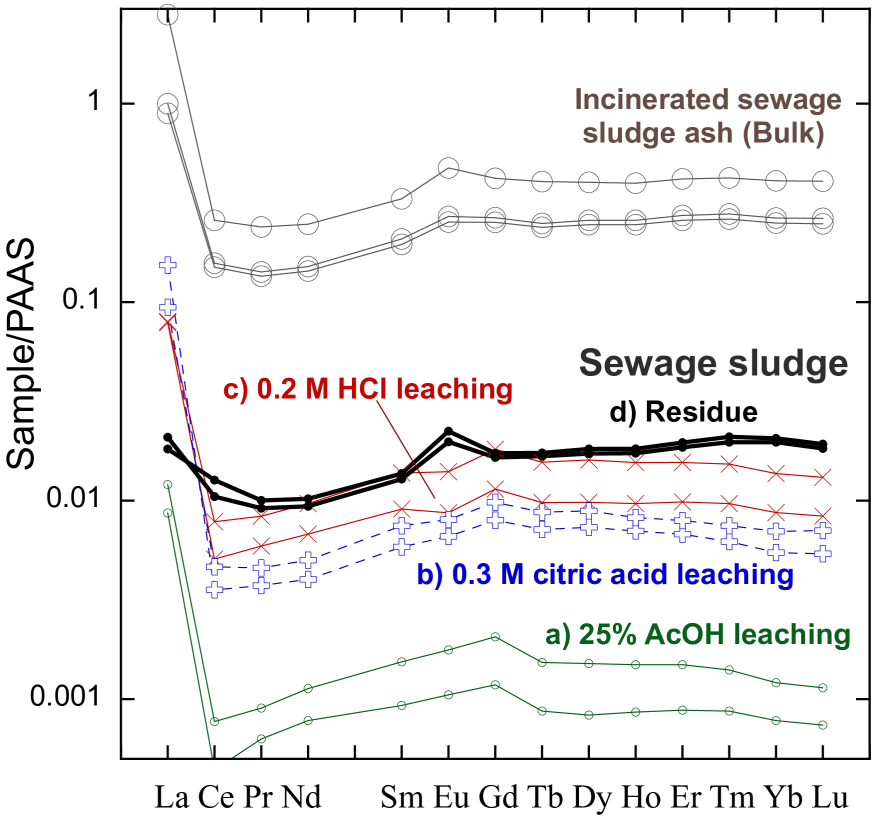

Figure 5. Post-Archean Australian Shale (PAAS)-normalized REE pattern of incinerated sludge ash (gray open circles) and sequential extracts: (a) 25% acetic acid (small green circles), (b) 0.3 M citric acid (blue crosses), (c) 0.2 M HCl (red X marks) solution, and (d) the residue (black closed circles). Average concentrations in ash samples (n = 3) are shown for each sludge incinerator (East, West 1, and West 5) (Table S3). The average and standard deviation (SD) of La/La* are as follows: a) 21.4 ± 4.7, b) 14.7 ± 3.5, c) 33.0 ± 15.6, d) 2.1 ± 0.5, East) 12.7 ± 0.9, West 1) 7.3 ±1.0, and West 5) 8.1 ± 0.9.

Discussion

Gd Anomaly Tracer. Injections of gadolinium contrast agents and MRI measurements on patients are mainly performed during standard weekday work hours at a hospital.[17] A single-digit increase in the Gd level of treated water was noted at 10 pm on Monday (Figure 3). Substantially lower levels were observed when samples were collected on the day following a holiday (Figure 2), which suggests that it takes about half a day for sewage discharged from the hospital to be released into the river as treated water. The sewage that reaches C-WWPT is normally disinfected after being decanted for 9 hours in three settling tanks[27], which aligns with our findings. Given that the WWTP in District C is at an altitude of 7m above sea level and the upstream area 10km south is around 140m, it is reasonable for sewage to travel 10km in 2-3 hours. Due to the high solubility and stability of the Gd agent,[8] no detected Gd anomaly is expected for the sludge (Figure 5).

Origin of the La Anomaly. The hypothesis of this study explains the consistency in the excess La level in treated water between weekdays and holidays (Figures 2 and 3) and the correlation between excess La emission and the number of hospitals in each WWTP area (Figure 4). Because the strength of acids is ranked as follows: acetic acid < phosphoric acid < citric acid < hydrochloric acid, the principle that strong acid displaces a weak acid from its salt led us to anticipate that a lanthanum anomaly in sludge phosphate would be weakly leached by acetic acid but efficiently extracted by citric and dilute hydrochloric acids, leaving minimal residue. Our results (Figure 5) confirmed this hypothesis. The involvement of La-zeolite aluminosilicate[14] and the activity of aerobic methane-oxidizing bacteria[10] can be ruled out. Therefore, we attribute the positive La anomalies observed in this study to the consumption of lanthanum carbonate tablets (e.g.,

231 Fosrenol®)[28] in Sapporo. The reported La enrichment in Swiss sewage sludge[16] and in
232 Tokyo's treated water[17] likely followed the same trend.

Table 1. Calculation of Annual Inflow of La into Sapporo Sewers (2020).

Sludge Center	Incinerated ash[#]		Excess-La (mg/kg)	Ash La (kg/y)
East (Tobu)	1827	ton/y	98.7 ± 23	180 ± 42
West (Seibu)	13976	ton/y	31.4 ± 6.5	439 ± 91
			Total:	**619** ± 133

WWTP	Treated water ($10^3 m^3$/y)		Excess-La (ng/kg)[&]	La weight (kg)[$]
weekday only	Simplified[¥]	normal #	Mean ± SD	Mean ± SD
A: Fushikogawa	664	14487	39.5 ± 1.58	1.36 ± 0.05
B: Soseigawa 1,2	741	36346	11.7 ± 0.47	0.69 ± 0.03
Ca: Toyohira 2	2693	28637	21.9 ± 9.7	2.40 ± 1.06
Cb: Toyohira 1	1971	23899	50.2 ± 16.0	4.17 ± 1.33
D: Teine	6467	65809	8.2 ± 0.33	2.13 ± 0.09
Ea: Shinkawa 1	607	29697	41.4 ± 21	1.98 ± 1.03
Eb: Shinkawa 2	1504	28015	5.3 ± 3.6	0.39 ± 0.26
F: Barato	1971	32250	3.0 ± 0.12	0.27 ± 0.01
G: Takuhoku	0	2905	5.5 ± 0.22	0.02 ± 0.00
H: Atsubestu	249	36517	2.8 ± 0.11	0.12 ± 0.00
I: Tobu	0	11482	1.9 ± 0.08	0.02 ± 0.00
			Total excess-La in treated water from WWTPs:	**13.5** ± 3.9
			Annual Inflow of La into Sapporo Sewers:	**633** ± 137

¥: Simplified treatment: 2-hour decantation in the first tank only.
&: Levels in normal treated water: 2019 data except for C and E.
$: Assuming simplified treated water contains 30 times excess-La of normal.
#: Including filtration process by sand bed and its disposal (incineration).

Sludge Center	Dehydrated sludge		Excess-La (mg/kg)	Sewage La (kg/y)
East (Tobu)	19801	ton/y	9.36 ± 5	185 ± 100
West (Seibu)	32782	ton/y	6.80 ± 1.09	223 ± 36
			Total:	408 ± 136

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234 **Consumption Estimates.** The annual shipment volume of lanthanum carbonate tablets
235 (29,893,509,000 yen including tax) in 2019[29] and the drug prices ranging from 458 to 616
236 yen per gram of La (excluding tax on 1st October 2019),[30] suggest that 44.1 to 59.3 metric
237 tons of La in the tablets were purchased annually in Japan. Considering Japan's
238 population of 126 million and Sapporo's population of 1.97 million, the annual

consumption of the tablet is estimated to be 689 to 927 kg of La in Sapporo. In comparison, the total amount of La flowing into the nine WWPTs, estimated from collected samples, is 633 ± 137 kg annually (Table 1), which partially overlaps with the estimated purchased tablet weight. It also revealed that 13.5 kg —or 2.1% of the inflow—was discharged into rivers in 2020.

Environmental Implications. Most of the excess La in hospital wastewater that enters a WWTP is precipitated, and the resulting incinerated ash (Table 1) serves as cement and backfill in Japan[22,27]. In Sapporo, approximately 2% of excess La processed by WWTPs is released into the river as treated water. Anthropogenic La, due to its low water solubility, may be unevenly distributed in the soil downstream of WWTPs. This study explores a new possibility of disrupting natural REE patterns.[12] For example, incinerated sludge ash, rich in phosphorus, could potentially be used as a fertilizer.[31] Since the late 2000s, lanthanum carbonate has been widely prescribed worldwide[28]; thus, the impact of anthropogenic lanthanum from hospital wastewater warrants further investigation across various countries.

Supporting information

■ Supporting information 1

1. The details of chemical analysis
2. Table S1. Rare-earth-element levels in treated waters discharged from Ca, Cb, Ea, and Eb wastewater treatment plants (WWTPs).
3. Table S2. Calculation of weights of excess La and Gd in treated water discharged from outlets at A–I wastewater treatment plants (WWTPs).
4. Table S3. Rare-earth-element concentrations in incinerated sludge ash and sequential

extracts of dewatered sewage sludge from plants at east and west in Sapporo in 2020.

5. Table S4. Comparison between analytical results and certified values for five igneous rock standard materials.

■ Supporting information 2: Only for review

Summary of 2019: Sapporo Sewerage Maintenance and Management Annual Report (in Japanese)

■ Supporting information 3: Only for review

Summary of 2020: Sapporo Sewerage Maintenance and Management Annual Report (in Japanese)

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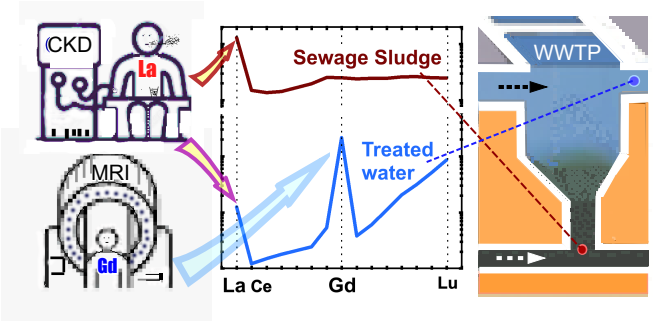

Supporting Information 1

Hospital Effluent as a New Source of Anthropogenic Lanthanum in the Environment

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The details of Chemical Analysis – Supporting information

Preparation and Handling of Reagents and Equipment in Chemical Analysis:

All sample manipulations were performed within a HEPA-filtered and temperature-controlled Class-1000 clean room in our school at Hokkaido University. In this study, all acid reagents employed for digestion, extraction, and measurement purposes were of ultrapure grade (Kanto Chemicals, Japan), with the exception of citric acid, which was of analytical grade. Containers were washed using special reagent grade nitric acid and hydrochloric acid. Water with a resistivity of 18.2 MΩ·cm, produced by a Milli-Q system (Milli-Q, Simplicity UV, and Gradient with Elix10, Millipore), was utilized for all procedures, including container washing and solution dilution.

Instrumentation and containers were handled with particular care to prevent contamination. New PET bottles and polypropylene containers were soaked overnight in 2M dilute nitric acid and for several days in the case of polypropylene to ensure thorough cleaning. Post-soaking, these containers were rinsed with Milli-Q water to eliminate any acid residues, dried on a clean bench within the same class-1000 room, and then stored with closed lids to maintain cleanliness.

Teflon containers used for decomposition were subjected to a rigorous cleaning process. After initial use, they were soaked overnight in a 2M nitric acid solution of reagent grade. This was followed by an overnight soak in 6M hydrochloric acid on a hot plate in a fume hood within the class-1000 environment. Subsequently, these containers were boiled overnight in 7M nitric acid and then in Milli-Q water. After a final rinse in Milli-Q water, the containers were dried on a clean bench and stored in a clean box, all within the class-1000 room. It is important to note that Teflon containers previously used for rock analysis were cleaned with a 6M hydrochloric acid and 5% hydrogen fluoride solution instead of the standard 6M hydrochloric acid to ensure the removal of any potential mineral residues.

Acid Decomposition Method for Incinerated Ash:

1. Approximately 0.5 g of incinerator ash is weighed into a 50 mL Teflon container (Model HU-50, San Ai Chemical). Add 5 mL of 46–51% (v/v) hydrofluoric acid and heat the mixture overnight on a hot plate set to 80°C within an open system in a clean evaporator.

2. Once the sample has dried and solidified, add 2.5 mL of 69% (v/v) nitric acid and 0.5 mL of 31% (v/v) hydrochloric acid. Seal the container in a Teflon-lined stainless-steel autoclave (Model HU-50, San-Ai Chemical) and heat in a constant temperature chamber at 200°C overnight.

3. After heating, stop the autoclave and immediately dilute the decomposed material in the Teflon container with Milli-Q water while the autoclave is still warm, keeping the volume constant at 50 mL and delaying dilution until the solution has cooled often results in precipitation.

4. If a precipitate forms in the solution after dilution, transfer all solutions containing the precipitate to a 50 mL Teflon beaker. Allow the mixture to dry on a 100°C hot plate within a clean evaporator.

5. Then, transfer the dried material to a hot plate in a clean fume hood in the clean room, add 5 mL of concentrated nitric acid and 2 mL of perchloric acid, and cover with a Teflon beaker. Heat the beaker to 230°C overnight, making the sample a syrupy wet mass. Before it dries and solidifies, spray 2.5 mL of concentrated nitric acid on the syrupy mass while it is heating and immediately add approximately 20 mL of MilliQ water.

6. Afterward, heat the Teflon beaker containing the sample solution on a hot plate at 80°C for about 1 hour and allow it to cool.

7. Finally, the solution should be brought up to a constant volume of 50 mL with Milli-Q water and transferred to a 50 mL polypropylene container for storage.

8. A blank solution is prepared identically to the sample solution but without adding the sample to the initial 50 mL volume Teflon container. This blank solution is then stored in the same manner as the sample solution.
9. These sample solutions were filtered at the time of ICP measurement using polytetrafluoroethylene microsyringe filters with a pore size of 0.22 μm.

Separate Extraction Method for Sewage Sludge:

1. Approximately 0.5 g of dewatered sewage sludge is weighed into a 15 mL polypropylene centrifuge tube. Next, 10 mL of a 25% acetic acid solution is added. The sludge is dispersed into the solution using a vortex mixer before being heated and extracted in an aluminum block bath at 85°C for 30 minutes.

2. Following the heating, the mixture is thoroughly shaken and stirred. The residue is then centrifuged at 3500 rpm for 30 minutes, and the extract (a) is completely transferred from the 15 mL polypropylene tube to a 50 mL Teflon beaker.

3. Subsequently, 10 mL of a 0.3 M citric acid solution is added to the tube containing the residue, and extract (b) is obtained using the same procedure as above. After processing extract (b), 10 mL of a 0.2 M hydrochloric acid solution is added to the residual material and repeated.

4. This process yields three 50-mL Teflon beakers, each containing approximately 10 mL of extracts (a), (b), and (c).

5. The extract (c) residue in the 15-mL tube is then thoroughly washed with approximately 20 mL of Milli-Q water and transferred to a new 50-mL Teflon beaker. The four Teflon beakers containing extracts (a), (b), (c), and residue (d) are dried on a 100°C hot plate in a clean evaporator.

6. After drying, 5 mL of hydrofluoric acid is added to the Teflon beaker containing residue (d), and the mixture is heated on an 80°C hot plate in an open system until dry. The hot plate is then transferred to a draft-protected area, and 5 mL of concentrated nitric acid along with 2 mL of perchloric acid are added. The contents are completely dissolved, similar to the acid decomposition method for incinerator ash described previously. No residue remains.

7. Finally, the decomposed solutions of extracts (a), (b), (c), and residue (d) are brought up to a constant volume of 50 mL and transferred to a 50 mL polypropylene container for storage.

8. A blank solution is prepared identically to the sample solution but without the addition of the sample in the initial 50 mL volume Teflon container. This blank solution is then stored in the same manner as the sample solution.

9. These sample solutions were filtered at the time of ICP measurement using

polytetrafluoroethylene microsyringe filters with a pore size of 0.22 μm.

Preparation for the treated water samples:

After the sample water stored in the refrigerator is thoroughly stirred, it is divided into 50 ml polyethylene containers. At least one day before analysis, ultrapure-grade nitric acid was added to the sample in the container to acidify the treated water sample to a 0.6 M nitric acid solution. The nitric acid solution was then filtered at the time of ICP measurement using polytetrafluoroethylene microsyringe filters with a pore size of 0.22 μm.

Incidentally, when using polytetrafluoroethylene microsyringe filters with a pore size of 0.45 μm before adding nitric acid to treated sewage water, the positive anomaly for Gd was not affected at all. However, the positive anomaly for La decreased from 20% to 40%. No measurements were taken with a filter of 0.22 μm.

ICP-MS measurements:

REE, Ba, and Sb contents in the treated water, digested solution, and extracts were determined at Hokkaido University using an Agilent 8800 triple quadrupole ICP-MS (Inductively coupled plasma mass spectrometry) equipment operating in the helium collision mode. Measured were three repeats of 100 sweeps at three points per peak with dwell times of 3 seconds for each of the following analytical isotopes: ^{123}Sb, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu.

All working and running standard solutions (0, 2, 5, 10, and 50 μg/L) were prepared by serial diluting ICP multi-element standard solutions (SPEX Certi Prep Co.; Kanto Chemical Co.). with ultrapure water. Internal standard solutions were not added to the materials in this study. The intensity drift was monitored and corrected through the analytical sequence by the analysis of a standard solution for every 10 samples, followed

by an acid-blank solution.

Interferences from oxide and hydroxides of ^{135}BaO on ^{151}Eu, ^{137}BaO on ^{153}Eu, ^{123}SbO on ^{139}La, and light REE on heavy REE were quantified and subtracted when necessary. Interference corrections were calculated from the oxide and hydroxide production rates of Ba and Sb 1 ppm solutions measured at the completion of the analytical run. The degree of interference from light REEs to heavy REEs was measured beforehand, and no interference from lanthanum to heavy REEs in particular was observed. The CeO^+/Ce^+ ratio (156/140) was approximately 0.2%, and the Ce^{2+}/Ce^+ ratio (70/140) was within 1%–1.5%.

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 (Table S4). No systematic error was observed. All blank sample REE concentrations were below the determination limits.

Table S1. Rare earth elemental levels in treatment waters from Ca Cb, Ea, and Eb WWTPs (wastewater treatment plants).

Sapporo city, Japan in 2020				PAAS normalized		Concentrations / ng/L (ppt)															
WWTP	day	note	Time	La/La*	Gd/Gd*	excess-**La**	excess-**Gd**	Y	**La**	Ce	Pr	Nd	Sm	Eu	**Gd**	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ca	13-Jul	*	6:00	2.31	9.59	**5.9**	**17.1**	28.4	**10.5**	5.53	1.19	4.85	0.69	0.48	**19.7**	1.33	3.11	1.21	6.02	1.33	13.66	3.36
Cb	13-Jul	*	6:00	7.97	4.20	**30.0**	**7.8**	27.4	**34.3**	8.97	1.34	6.00	1.75	0.58	**11.3**	1.10	2.95	0.99	5.16	1.10	10.91	2.82
Ca	13-Jul	*	10:00	7.74	6.19	**15.6**	**12.6**	30.2	**17.9**	6.94	0.97	5.04	1.28	0.76	**15.9**	1.35	3.21	1.20	6.44	1.35	13.45	3.72
Cb	13-Jul	*#	10:00	16.60	1.25	**1712**	**-2.1**	254	**1821**	263	34.7	156	36.3	8.37	**47.3**	3.83	35.6	7.84	25.3	3.83	31.29	5.55
Ca	13-Jul	*	14:00	12.85	4.66	**22.8**	**10.2**	30.8	**24.7**	7.17	0.90	4.93	1.63	0.66	**14.1**	1.33	3.64	1.15	6.15	1.33	14.20	3.69
Cb	13-Jul	*	14:00	7.88	4.39	**36.3**	**7.0**	24.6	**41.6**	9.10	1.49	6.35	1.12	0.51	**9.9**	1.05	2.81	1.00	4.59	1.05	11.25	2.74
Ca	13-Jul	*	18:00	7.13	8.17	**14.7**	**17.7**	26.2	**17.1**	6.98	1.00	5.14	1.45	0.57	**21.0**	1.21	3.02	0.92	4.88	1.21	12.49	3.10
Cb	13-Jul	*#	18:00	15.99	1.46	**1475**	**5.2**	219	**1573**	231	29.4	129	30.0	7.73	**47.7**	3.49	31.15	6.74	22.26	3.49	26.08	5.04
Ca	13-Jul	*	22:00	6.37	55.09	**17.7**	**125.4**	27.5	**21.0**	7.35	1.10	5.10	1.09	0.63	**128.5**	1.16	3.00	1.01	5.17	1.16	12.09	2.91
Cb	13-Jul	*	22:00	19.51	31.93	**58.9**	**77.0**	26.3	**62.1**	10.47	1.35	7.06	1.75	0.61	**80.2**	0.93	2.65	0.94	4.28	0.93	9.68	2.45
Ca	14-Jul		2:00	7.54	69.43	**27.3**	**178.4**	27.0	**31.5**	7.87	1.22	5.29	1.28	0.72	**181.9**	1.24	3.30	0.98	5.50	1.24	12.42	2.99
Cb	14-Jul		2:00	10.20	46.20	**32.4**	**93.1**	23.0	**35.9**	7.30	1.15	5.24	1.14	0.50	**95.8**	0.94	2.46	0.90	3.97	0.94	9.51	2.41
Ca	14-Jul		6:00	6.38	82.94	**12.1**	**191.9**	26.8	**14.4**	6.76	0.87	4.31	1.26	0.55	**195.0**	1.25	2.82	0.97	5.54	1.25	12.07	3.14
Cb	14-Jul		6:00	9.42	62.43	**22.3**	**109.4**	20.7	**24.9**	5.36	0.77	3.35	0.95	0.46	**111.8**	0.85	2.16	0.73	4.10	0.85	9.27	2.37
Ca	14-Jul		10:00	7.67	75.99	**15.3**	**180.5**	27.2	**17.5**	5.82	0.97	5.03	1.01	0.59	**183.6**	1.14	3.29	1.06	5.20	1.14	12.27	2.95
Cb	14-Jul		10:00	13.71	50.17	**43.9**	**121.5**	25.3	**47.4**	9.17	1.24	5.93	1.59	0.64	**124.7**	0.94	2.73	0.88	4.40	0.94	9.70	2.47
Ca	14-Jul		14:00	7.25	75.02	**10.2**	**181.8**	28.0	**11.9**	5.25	0.80	4.45	1.06	0.56	**185.1**	1.31	3.32	1.22	5.83	1.31	14.06	3.35
Cb	14-Jul		14:00	8.10	45.46	**22.7**	**111.1**	26.5	**25.9**	7.03	1.11	5.21	1.44	0.50	**114.4**	1.20	2.93	0.97	5.11	1.20	13.35	3.07
Ca	14-Jul		18:00	5.13	60.12	**11.9**	**139.5**	29.4	**14.8**	6.29	0.92	4.13	1.06	0.55	**142.6**	1.32	3.12	1.12	5.63	1.32	14.08	3.43
Cb	14-Jul		18:00	6.01	38.74	**18.9**	**90.0**	26.1	**22.6**	7.25	1.12	4.85	1.26	0.46	**93.1**	1.17	2.92	0.97	5.20	1.17	12.53	2.84
Ca	24-Jul	*	10:30	5.10	31.54	**12.2**	**70.0**	26.2	**15.1**	5.53	1.02	4.75	1.06	0.76	**73.1**	1.20	3.02	1.12	5.33	1.20	12.53	3.24
Cb	24-Jul	*	10:35	4.64	17.97	**29.5**	**35.7**	22.2	**37.6**	8.35	1.36	4.46	1.10	0.59	**38.5**	1.05	2.62	0.96	4.28	1.05	11.28	2.57
Ea	24-Jul	*	12:05	10.45	48.36	**44.9**	**146.2**	32.5	**49.7**	11.32	1.47	6.50	1.77	0.75	**150.3**	1.57	3.64	1.37	7.24	1.57	17.75	4.77
Ea	16-Apr		13:00	9.08	133.9	**34.5**	**396.2**	32.8	**38.8**	8.92	1.42	6.54	1.29	0.65	**400.1**	1.77	4.01	1.47	7.37	1.77	18.56	4.73
Ea	23-Apr		12:05	15.87	88.3	**90.5**	**314.8**	36.9	**96.5**	15.51	2.05	9.53	2.16	0.67	**319.5**	1.77	4.15	1.43	7.60	1.77	17.49	4.75
Ea	30-Apr	*	12:05	14.58	52.3	**53.9**	**136.7**	30.1	**57.9**	11.99	1.62	8.24	1.42	0.59	**140.2**	1.50	3.25	1.21	6.55	1.50	16.31	4.04
Ea	7-May	*	12:50	9.94	6.7	**31.3**	**7.5**	18.1	**34.8**	5.70	0.87	3.49	0.84	0.39	**9.3**	0.72	1.56	0.72	3.59	0.72	9.20	2.31
Ea	14-May		12:05	16.20	132.4	**50.9**	**328.4**	29.0	**54.3**	8.30	1.19	5.64	1.12	0.50	**331.6**	1.58	3.30	1.32	6.48	1.58	17.11	4.29
Ea	21-May		11:30	14.38	161.5	**40.9**	**403.5**	28.7	**44.0**	7.08	0.99	4.49	1.42	0.42	**406.8**	1.57	2.95	1.09	6.43	1.57	17.67	4.45
Ea	28-May		15:35	6.97	94.9	**31.9**	**243.4**	28.2	**37.2**	9.68	1.51	6.45	1.58	0.50	**246.8**	1.48	2.94	1.10	6.67	1.48	15.54	3.72
Ea	6-Jun		12:40	10.99	118.0	**27.5**	**341.1**	32.8	**30.2**	6.07	1.17	6.09	1.25	0.55	**344.9**	2.01	3.95	1.43	8.59	2.01	21.60	5.36
Ea	11-Jun		12:50	11.42	103.5	**28.1**	**349.6**	35.5	**30.8**	7.02	1.18	6.27	1.70	0.52	**354.1**	1.99	4.29	1.53	8.54	1.99	22.34	5.76
Ea	18-Jun		11:40	10.15	89.2	**27.0**	**203.1**	25.4	**29.9**	5.50	1.06	5.07	1.31	0.39	**206.1**	1.43	2.70	1.10	5.97	1.43	14.46	3.75
Eb	16-Apr		12:30	1.18	2.9	**1.85**	**16.7**	132.4	**11.9**	16.30	3.40	15.84	4.06	1.63	**30.4**	6.28	15.27	6.31	32.24	6.28	49.36	9.10
Eb	23-Apr		12:30	1.38	2.7	**3.05**	**14.1**	117.9	**11.0**	15.11	3.22	16.34	4.09	1.62	**27.0**	5.46	13.93	6.01	29.61	5.46	44.52	8.19
Eb	30-Apr	*	12:30	1.24	2.4	**3.37**	**12.1**	125.9	**17.4**	27.88	5.04	24.17	5.24	1.59	**26.3**	5.28	14.28	5.93	28.47	5.28	41.78	7.97
Eb	7-May	*	13:10	1.32	1.7	**9.30**	**5.3**	90.1	**38.4**	69.72	9.92	46.28	10.09	2.50	**21.0**	2.80	11.90	3.53	15.08	2.80	22.52	4.43
Eb	14-May		12:35	1.38	2.6	**10.12**	**19.0**	124.1	**36.4**	71.39	9.87	48.29	10.28	2.22	**38.8**	6.28	16.70	5.61	29.95	6.28	55.56	10.70

Eb	21-May		11:50	1.26	3.4	**2.23**	**14.7**	77.8	**10.9**	15.18	2.92	13.48	3.77	1.08	**24.0**	3.66	8.80	3.35	17.02	3.66	33.66	7.05
Eb	28-May		16:00	1.25	1.9	**6.05**	**5.9**	67.4	**30.0**	54.89	7.83	35.75	7.25	1.70	**18.2**	1.96	9.73	2.53	11.02	1.96	15.93	3.05
Eb	6-Jun		13:15	1.20	1.8	**10.90**	**9.3**	133.2	**65.5**	122.71	16.92	75.18	17.32	3.67	**34.7**	4.38	18.89	5.03	22.01	4.38	38.89	8.00
Eb	11-Jun		13:30	1.18	2.0	**5.38**	**8.1**	86.2	**36.0**	66.26	9.47	42.04	9.09	2.06	**23.2**	3.38	11.83	3.39	16.59	3.38	30.21	6.04
Eb	18-Jun		12:05	1.15	1.5	**2.73**	**1.0**	35.2	**21.0**	36.16	5.41	23.51	5.30	1.01	**8.1**	0.58	4.95	1.12	3.66	0.58	4.18	0.66
Ca	16-Apr		10:30	7.52	74.7	**18.49**	**206.7**	36.1	**21.3**	6.72	1.20	6.27	1.15	0.64	**210.4**	1.61	3.89	1.46	7.41	1.61	16.41	4.02
Ca	23-Apr		10:05	2.28	15.8	**11.25**	**46.8**	35.6	**20.0**	11.83	2.24	9.07	1.64	0.60	**51.0**	1.58	4.01	1.41	7.58	1.58	17.24	4.11
Ca	30-Apr	*	9:55	5.12	9.2	**19.32**	**27.3**	28.7	**24.0**	9.02	1.45	6.45	2.02	0.57	**31.8**	1.37	4.01	1.21	6.48	1.37	15.17	3.38
Ca	7-May	*	10:30	10.30	1.4	**29.70**	**0.2**	17.9	**32.9**	10.27	1.25	6.27	1.20	0.52	**3.1**	0.85	2.73	0.87	4.10	0.85	9.07	2.13
Ca	14-May		10:30	12.99	79.8	**28.73**	**227.4**	24.8	**31.1**	7.80	1.01	5.27	1.63	0.62	**231.2**	1.39	3.41	1.26	6.44	1.39	13.88	3.56
Ca	21-May		9:50	10.51	79.3	**36.20**	**242.5**	30.3	**40.0**	9.65	1.37	6.54	1.64	0.56	**246.5**	1.31	3.78	1.26	5.77	1.31	13.88	3.36
Ca	28-May		13:40	4.42	46.7	**19.74**	**127.4**	23.7	**25.5**	11.96	1.48	5.96	1.40	0.59	**131.1**	1.26	3.50	1.21	5.57	1.26	12.48	2.84
Ca	6-Jun		10:35	10.71	88.4	**27.24**	**236.9**	26.0	**30.0**	10.50	1.36	7.60	1.66	0.75	**240.4**	1.30	3.07	1.18	5.60	1.30	13.35	3.35
Ca	11-Jun		11:00	9.39	62.7	**29.48**	**184.1**	25.7	**33.0**	10.10	1.32	6.43	1.52	0.60	**188.0**	1.21	3.73	1.18	5.52	1.21	12.77	3.12
Ca	18-Jun		9:30	17.62	47.5	**40.36**	**124.2**	21.1	**42.8**	9.78	1.14	6.27	1.61	0.60	**127.7**	0.96	3.06	0.82	4.16	0.96	9.27	2.15
Cb	16-Apr		10:40	14.46	52.3	**41.63**	**139.1**	25.8	**44.7**	6.38	1.12	5.35	1.28	0.45	**142.7**	1.36	3.52	1.24	6.42	1.36	15.24	3.71
Cb	23-Apr		10:10	14.81	28.7	**41.00**	**71.0**	25.8	**44.0**	6.60	1.11	5.40	1.26	0.55	**74.4**	1.41	3.27	1.18	6.35	1.41	14.58	3.57
Cb	30-Apr	*	10:00	12.93	5.5	**43.25**	**10.6**	24.1	**46.9**	9.74	1.29	6.17	1.29	0.60	**13.8**	1.23	3.04	1.09	5.49	1.23	12.89	3.38
Cb	7-May	*	10:35	16.70	1.4	**48.36**	**0.2**	15.7	**51.4**	7.07	0.91	3.95	1.04	0.35	**2.6**	0.75	2.12	0.74	3.77	0.75	8.70	2.03
Cb	14-May		10:35	14.79	71.3	**46.94**	**161.1**	19.9	**50.3**	8.27	1.12	5.10	1.14	0.37	**164.1**	1.23	2.88	0.97	5.03	1.23	12.70	2.91
Cb	21-May		9:55	23.68	47.5	**41.26**	**99.4**	19.9	**43.1**	6.35	0.78	4.06	1.31	0.38	**102.2**	1.06	2.42	0.93	4.75	1.06	11.74	3.09
Cb	28-May		13:45	10.19	39.3	**35.07**	**97.3**	23.7	**38.9**	7.96	1.04	4.36	1.37	0.47	**100.7**	1.32	3.08	0.99	5.84	1.32	14.13	3.41
Cb	6-Jun		10:40	16.48	64.7	**76.99**	**174.2**	24.4	**82.0**	11.65	1.51	6.64	1.56	0.54	**177.7**	1.21	3.21	1.02	5.46	1.21	12.06	2.92
Cb	11-Jun		11:05	12.43	77.6	**52.45**	**177.7**	19.5	**57.0**	9.26	1.23	5.08	1.52	0.58	**180.7**	1.09	2.54	0.96	4.54	1.09	11.83	2.73
Cb	18-Jun		9:35	25.89	36.6	**169.01**	**130.2**	29.1	**175.8**	19.39	2.33	10.91	2.83	0.81	**135.0**	0.92	3.73	1.07	4.71	0.92	10.04	2.21

*: The day before is a holiday
#: When abnormal discharge
$: Mean value without # data

$La_{SN}^* = (Pr_{SN})^3/(Nd_{SN})^2$

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

[Excess-La] = measured [La]−[La*]

[Eexcess-Gd] = measured [Gd]−[Gd*]x1.3

PAAS: Post-Archean Australian shale				Y	**La**	Ce	Pr	Nd	Sm	Eu	**Gd**	Tb	Dy	Ho	Er	Tm	Yb	Lu
PAAS (ppm)				27.0	**38.2**	79.6	8.83	33.9	5.55	1.08	**4.66**	0.774	4.68	0.991	2.85	0.405	2.82	0.433
Above average		excess-**La**	excess-**Gd**	Y	**La**	Ce	Pr	Nd	Sm	Eu	**Gd**	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ca hol*	(n = 7)	**17.2**	**22.1**	26.9	**20.3**	7.35	1.11	5.35	1.33	0.62	**25.5**	1.24	3.25	1.10	5.63	1.24	12.94	3.23
Ca	(n = 14)	**21.9**	**171.0**	27.8	**25.3**	8.40	1.21	5.84	1.36	0.61	**174.5**	1.29	3.38	1.15	5.78	1.29	13.31	3.23
Cb hol*$	(n = 5)	**37.5**	**12.2**	22.8	**42.4**	8.65	1.28	5.38	1.26	0.53	**15.2**	1.03	2.71	0.95	4.66	1.03	11.01	2.71
Cb	(n = 12)	**50.2**	**118.0**	24.0	**53.9**	8.75	1.21	5.61	1.46	0.52	**121.2**	1.12	2.89	0.98	5.01	1.12	11.88	2.87
Ea hol*	(n = 3)	**43.4**	**96.8**	26.9	**47.5**	9.67	1.32	6.08	1.34	0.58	**99.9**	1.26	2.82	1.10	5.79	1.26	14.42	3.71
Ea	(n = 8)	**41.4**	**322.5**	31.2	**45.2**	8.51	1.32	6.26	1.48	0.52	**326.2**	1.70	3.54	1.31	7.20	1.70	18.10	4.60
Eb hol*	(n = 2)	**6.3**	**8.7**	108.0	**27.9**	48.80	7.48	35.23	7.66	2.04	**23.6**	4.04	13.09	4.73	21.78	4.04	32.15	6.20
Eb	(n = 8)	**5.3**	**11.1**	96.8	**27.9**	49.75	7.38	33.80	7.64	1.87	**25.6**	4.00	12.51	4.17	20.26	4.00	34.04	6.60

Table S2. Calculation of excess La and Gd weights in treatment waters from outlets at A–I WWTPs (wastewater treatment plants).

WWTP (hospital number)	Total treated water volume 2019 (km^3/y)	Outlet #	Longitude	Latitude	Sampling date/time 2019	La/La*	Excess-La ng/kg	ICPMS La RSD (%)	Excess-La weight (kg/y)!	Gd/Gd*	Excess-Gd ng/kg	Gd RSD (%)	Excess-Gd weight (kg/y)
A (7) Fushiko-gawa	14688	A1	43°05'57.50"N	141°23'17.99"E	2-Jul Thu 11:05 AM	7.12	39.29	1.3	**0.577**	49.6	146.5	0.9	**2.15**
		A2	43°05'59.04"N	141°23'18.91"E	2-Jul Thu 11:20 AM	6.81	39.74	1.9	**0.584**	46.6	152.2	1.4	**2.24**
B (22) Soseo-gawa	39941 (20929 +19012)	B1	43°06'52.54"N	141°20'37.75"E	2-Jul Thu 4:48 PM	1.17	4.74	3.4	**0.189**	8.7	83.5	1.9	**3.33**
		B2	43°06'56.70"N	141°20'36.82"E	12-Dec Thu 12:05 PM	3.02	15.69	1.1	**0.627**	19.3	91.7	3.0	**3.66**
		B1	43°06'52.54"N	141°20'37.71"E	12-Dec Thu 12:15 PM	2.53	14.68	2.9	**0.586**	15.7	81.8	3.3	**3.27**
C (23) Toyohira	32682	Ca 1	43°04'00.62"N	141°24'57.03"E	6-Aug Thu 10:30 AM	12.46	48.90	1.7	**(1.598)**	85.2	154.5	1.2	**5.05**
		Ca 1	43°04'00.78"N	141°24'56.70"E	13-Dec Fri 12:40 PM	2.63	14.83	3.6	**0.485**	50.3	136.1	1.9	**4.45**
	25761	Cb 1	43°04'02.39"N	141°24'59.28"E	6-Aug Thu 10:40 AM	29.14	89.00	1.3	**(2.293)**	78.4	230.7	2.0	**5.94**
		Cb 1	43°04'02.75"N	141°24'59.14"E	13-Dec Fri 12:50 PM	14.52	67.93	3.5	**1.750**	45.0	114.3	1.9	**2.94**
D (8) Teine	72620	D1	43°09'15"N	141°14'02"E	14-Sep Sat 10:40 AM	3.64	8.09	4.7	**0.588**	51.0	110.2	0.9	**8.01**
		D2			14-Sep Sat 10:42 AM	4.51	8.86	7.4	**0.644**	48.0	111.0	1.5	**8.06**
		D3			14-Sep Sat 10:44 AM	3.61	7.66	3.7	**0.557**	54.2	111.5	1.0	**8.10**
E (63) Shin-kawa	29389	Eb 1	43°05'35.45"N	141°19'07.17"E	23-Dec Mon 12:00 PM	0.95	0.00	3.9	**0.000**	84.6	129.5	1.5	**3.81**
	33119	Ea 1	43°05'54.05"N	141°18'41.09"E	3-Nov Sun 2:36 PM	11.03	79.71	2.0	**2.640**	114.2	455.1	2.8	**13.37**
		Ea 1	43°05'54.24"N	141°18'41.52"E	23-Dec Mon 1:00 PM	11.37	67.86	0.5	**2.248**	83.3	294.9	1.5	**8.67**
F (5) Barato	31392	F1	43°10'22"N	141°20'16"E	14-Sep Sat 12:00 PM	2.90	3.37	2.9	**0.106**	34.8	91.4	2.0	**2.87**
		F2			14-Sep Sat 12:01 PM	2.17	2.90	6.0	**0.091**	34.7	92.1	2.1	**2.89**
		F3			14-Sep Sat 12:02 PM	2.12	2.63	4.3	**0.083**	33.6	91.5	1.8	**2.87**
G (1) Takuhoku	2801	G1	43°10'12"N	141°24'60"E	14-Sep Sat 12:50 PM	5.34	5.60	2.5	**0.016**	18.9	38.0	1.8	**0.11**
		G2			14-Sep Sat 12:55 PM	5.18	5.24	4.3	**0.015**	19.5	37.8	2.6	**0.11**
		G3			14-Sep Sat 12:56 PM	4.84	5.61	8.7	**0.016**	19.5	36.6	4.9	**0.10**
H (6) Atsu-bestu	37614	H1	43°03'56"N	141°28'09"E	14-Sep Sat 4:30 PM	2.62	2.85	5.9	**0.107**	30.9	90.4	2.1	**3.40**
		H2			14-Sep Sat 4:35 PM	3.04	3.14	2.7	**0.118**	35.9	91.8	1.4	**3.45**
		H3			14-Sep Sat 4:37 PM	1.90	2.54	5.1	**0.095**	32.9	91.0	2.3	**3.42**

I (3) Tobu	11443	I 1	43°05'22.37"N	141°26'32.88"E	14-Sep	Sat	2:50 PM	1.13	1.02	3.1	**0.012**	1.1	0.0		**0.00**
		I 2	43°05'12.48"N	141°26'32.23"E	14-Sep	Sat	2:55 PM	1.52	2.75	2.8	**0.032**	1.0	0.0		**0.00**
		I 3	43°05'09.75"N	141°26'31.83"E	14-Sep	Sat	3:05 PM	1.30	1.85	3.6	**0.021**	1.2	0.0		**0.00**

For Table 1

!: Values in parentheses are unusually high, excluded from the calibration curve.

(km^3/y) in 2020		Only weekday and normal			Excess-La ng/kg	±sd ng/kg	Excess-La (kg/y)	Excess-Gd ng/kg	±sd ng/kg	Excess-Gd (kg/y)
31330	Ca	(n = 14)	April 16–June 18, July 13,14, 2020		21.9	9.7	0.685	171.0	53.6	5.36
25970	Cb	(n = 12)	April 16–June 18, July 13,14, 2020		50.2	16.0	1.305	118.0	34.4	3.06
				Ca+Cb			**1.990**			**8.42**
30304	Ea	(n = 8)	April 16–June 18, 2020		41.4	21.4	1.255	322.5	69.4	9.77
29519	Eb	(n = 8)	April 16–June 18, 2020		5.3	3.6	0.156	11.1	6.1	0.33
				Ea+Eb			**1.411**			**10.10**

Table S3. Rare earth element concentrations in incinerated sludge ash and sequential extraction of dewatered sewage sludge from East and West sewage sludge plants in Sapporo in 2020.

Sample Extract.	Sludge Center	Sampling time	P (mg/kg)	Sb (μg/kg)	Ba (mg/kg)	(μg/kg) Y	**La**	Ce	Pr	Nd	Sm	Eu	**Gd**	Tb	Dy	Ho	Er	Tm	Yb	Lu
a) 25% acetic acid extract from dewatered sewage sludge	East	May26 8am	659	6	8.8	46.7	**452.3**	49.5	7.7	36.4	7.20	1.62	**7.99**	0.98	5.71	1.28	3.69	0.52	3.19	0.46
	East	May26 13am	731	17	7.2	26.0	**252.6**	30.6	5.0	23.0	4.33	0.91	**4.19**	0.50	2.74	0.59	1.83	0.26	1.63	0.24
	East	May28 8am	526	14	4.9	25.9	**287.1**	24.5	4.0	19.8	3.97	0.86	**4.30**	0.52	3.19	0.67	2.01	0.28	1.77	0.26
	West 2	May27 10am	438	16	5.5	48.0	**382.5**	40.6	6.1	30.7	6.82	1.51	**7.71**	0.94	5.75	1.21	3.44	0.47	2.90	0.43
	West 2	May28 9am	459	22	7.7	71.8	**468.5**	69.6	10.1	48.7	10.95	2.46	**12.10**	1.52	8.97	1.89	5.49	0.73	4.24	0.61
	West 6	May28 9am	381	36	7.2	65.7	**714.3**	65.1	9.4	44.6	9.77	2.23	**11.26**	1.38	8.22	1.67	4.74	0.63	3.84	0.56
	West 7	May27 10am	472	30	5.7	45.1	**277.0**	68.6	6.1	29.6	6.71	1.45	**7.34**	0.89	5.35	1.13	3.27	0.43	2.67	0.39
b) 0.3 M citric acid extract from dewatered sewage sludge	East	May26 8am	666	222	34.3	407	**4496**	487	62.2	275.6	60.8	11.43	**64.4**	9.35	56.0	11.73	34.16	4.71	29.41	4.25
	East	May26 13am	719	129	28.0	215	**1609**	255	32.4	140.4	29.2	5.79	**31.6**	4.38	26.9	5.67	16.94	2.45	15.87	2.41
	East	May28 8am	740	221	35.6	376	**2924**	472	61.6	274.8	60.9	10.91	**63.6**	8.97	54.8	11.36	33.01	4.59	28.35	4.19
	West 2	May27 10am	1644	283	50.8	492	**3454**	617	74.4	334.1	77.1	16.03	**86.4**	12.39	77.3	16.09	46.48	6.54	40.70	6.01
	West 2	May28 9am	1004	305	35.1	530	**3377**	739	88.5	394.4	92.8	17.62	**100.0**	14.35	89.4	18.21	52.25	7.17	44.66	6.46
	West 6	May28 9am	764	378	32.5	448	**3116**	633	75.4	333.8	78.4	14.80	**85.7**	12.27	75.6	15.40	43.89	6.10	38.17	5.62
	West 7	May27 10am	1287	250	37.8	364	**2247**	500	56.3	249.0	57.5	11.92	**65.7**	9.28	57.6	11.91	34.96	4.89	30.62	4.57
c) 0.2 M HCl soln. extract from dewatered sewage sludge	East	May26 8am	308	25	104.1	276	**8478**	326	38	159	38.43	8.41	**43.81**	6.53	40.25	8.11	22.24	2.88	17.84	2.71
	East	May26 13am	287	51	43.2	167	**1893**	191	21	84	19.08	4.53	**23.42**	3.52	22.51	4.71	13.46	1.76	10.93	1.71
	East	May28 8am	289	127	53.9	271	**7212**	331	39	164	39.76	8.42	**44.25**	6.55	40.22	8.09	22.21	2.90	17.52	2.59
	West 2	May27 10am	429	130	61.3	295	**3337**	403	42	179	43.76	9.22	**48.87**	7.21	44.42	8.83	24.79	3.30	21.49	3.36
	West 2	May28 9am	242	53	63.9	293	**3809**	418	47	195	47.79	9.86	**51.99**	7.72	46.96	9.14	25.12	3.39	22.22	3.46
	West 6	May28 9am	197	41	43.5	207	**3632**	286	32	136	32.67	6.91	**36.10**	5.41	32.98	6.48	17.88	2.38	15.39	2.34
	West 7	May27 10am	314	35	47.2	217	**2619**	307	30	126	31.60	6.81	**36.09**	5.35	33.19	6.69	18.41	2.51	16.14	2.52
d) Residue of sewage sludge after the above three extractions	East	May26 8am	755	134	23.5	628	**891**	1128	108.5	423.4	95.1	28.64	**102.7**	17.7	108.7	23.0	70.8	10.7	74.3	10.5
	East	May26 13am	902	159	7.4	233	**369**	435	39.7	154.7	34.7	10.16	**37.2**	6.1	38.3	8.3	25.6	3.8	27.0	3.9
	East	May28 8am	780	162	19.4	549	**1129**	939	93.9	372.7	83.6	25.31	**90.6**	15.0	95.3	20.3	62.4	9.4	65.1	9.4
	West 2	May27 10am	1128	155	14.8	427	**722**	911	74.6	294.9	64.7	19.95	**70.1**	11.7	73.7	15.7	48.1	7.3	49.5	7.1
	West 2	May28 9am	710	255	21.0	642	**762**	1322	119.4	468.0	102.4	32.70	**108.5**	18.0	114.8	24.4	75.7	11.6	78.5	11.3
	West 6	May28 9am	575	144	17.4	513	**691**	1025	95.7	373.0	82.0	27.02	**86.3**	14.3	91.3	19.5	60.0	9.1	62.5	9.0
	West 7	May27 10am	832	106	10.3	348	**606**	785	64.1	248.4	54.5	16.82	**58.1**	9.8	60.5	12.7	39.5	6.0	41.4	5.9

Dewatered sewage sludge (Bulk: Sum of a–d fractions)	East	May26 8am	2389	386	171	1357	**14318**	1990	217	894	202	50.1	**219**	34.6	210.6	44.1	130.9	18.8	124.7	18.0
	East	May26 13am	2638	356	86	641	**4124**	911	98	402	87	21.4	**96**	14.5	90.5	19.3	57.8	8.3	55.5	8.2
	East	May28 8am	2335	525	114	1222	**11552**	1767	199	831	188	45.5	**203**	31.1	193.5	40.4	119.6	17.2	112.8	16.4
	West 2	May27 10am	3639	584	132	1263	**7895**	1971	197	838	192	46.7	**213**	32.2	201.3	41.8	122.8	17.6	114.6	16.9
	West 2	May28 9am	2415	636	128	1536	**8416**	2548	265	1106	254	62.6	**273**	41.6	260.1	53.7	158.5	22.9	149.6	21.8
	West 6	May28 9am	1917	599	101	1234	**8154**	2010	213	887	203	51.0	**219**	33.3	208.1	43.0	126.5	18.2	119.9	17.5
	West 7	May27 10am	2905	421	101	974	**5748**	1660	157	653	150	37.0	**167**	25.3	156.7	32.4	96.2	13.8	90.9	13.4

Sample Extract.	Sludge Center	Sampling time	Sb (mg/kg)	Ba (μg/kg)	(mg/kg) Y	**La**	Ce	Pr	Nd	Sm	Eu	**Gd**	Tb	Dy	Ho	Er	Tm	Yb	Lu
incinerated sewage sludge ash (Bulk)	East	26-May	3.67	2018	10.52	**95.3**	17.63	1.74	6.96	1.52	0.445	**1.70**	0.275	1.61	0.344	1.06	0.151	1.03	0.157
	East	27-May	1.95	2056	14.62	**136.4**	25.98	2.77	11.03	2.43	0.645	**2.52**	0.404	2.45	0.506	1.52	0.220	1.47	0.225
	East	28-May	1.41	1633	10.06	**89.8**	18.01	1.81	7.16	1.57	0.446	**1.65**	0.261	1.56	0.330	0.99	0.142	0.95	0.146
	West 1	27-May	2.63	671	7.16	**38.4**	12.90	1.25	5.02	1.12	0.283	**1.20**	0.186	1.15	0.243	0.73	0.105	0.71	0.106
	West 1	28-May	2.68	646	7.42	**37.2**	11.99	1.19	4.86	1.09	0.272	**1.21**	0.189	1.17	0.251	0.76	0.110	0.71	0.110
	West 1	29-May	1.32	492	6.77	**26.7**	10.82	1.13	4.62	1.04	0.265	**1.12**	0.178	1.12	0.234	0.72	0.104	0.69	0.106
	West 5	28-May	3.35	764	10.33	**47.2**	16.45	1.71	6.96	1.58	0.401	**1.69**	0.265	1.64	0.349	1.06	0.153	1.02	0.157
	West 5	28-May	1.93	468	5.74	**29.3**	10.16	0.93	3.81	0.85	0.215	**0.92**	0.144	0.90	0.190	0.57	0.084	0.55	0.085
	West 5	29-May	2.17	616	7.07	**37.8**	10.78	1.11	4.55	1.03	0.258	**1.10**	0.170	1.09	0.228	0.70	0.101	0.67	0.101

Table S4. The comparison between analytical results and certified values for five ignious rock standard materials.

	JA-1 (n = 5)		JA-2 (n = 5)		JB-1a (n = 5)		JB-2 (n = 5)		JB-3 (n = 5)	
(mg/kg)	Result	Lit.(1)	Result	Lit.(1)	Result	Lit.(1)	Result	Lit.(1)	Result	Lit.(2)
Y	26.81	28.0	16.07	16.89	20.95	22.91	22.24	23.56	24.12	26.9
La	4.78	4.880	15.43	15.46	37.13	37.74	2.18	2.281	8.31	8.81
Ce	12.55	13.15	31.95	32.86	65.2	65.93	6.26	6.552	20.8	21.5
Pr	2.057	2.082	3.67	3.691	7.02	7.10	1.123	1.129	3.17	3.11
Nd	10.63	10.69	14.07	14.04	26.3	26.15	6.19	6.392	15.7	15.6
Sm	3.28	3.396	2.96	3.032	5.00	5.099	2.20	2.266	4.23	4.27
Eu	1.075	1.112	0.879	0.893	1.470	1.484	0.814	0.836	1.28	1.32
Gd	4.16	4.15	2.99	3.013	4.75	4.70	3.20	3.123	4.63	4.46
Tb	0.704	0.727	0.465	0.4786	0.684	0.699	0.572	0.5863	0.71	0.73
Dy	4.80	4.75	2.96	2.851	4.20	4.07	4.01	3.868	4.65	4.54
Ho	0.987	1.032	0.581	0.591	0.810	0.805	0.844	0.863	0.94	0.80
Er	3.02	2.959	1.720	1.676	2.30	2.232	2.58	2.537	2.68	2.49
Tm	0.431	0.455	0.249	0.2546	0.313	0.3197	0.381	0.393	0.39	0.41
Yb	2.90	2.949	1.630	1.645	2.07	2.100	2.55	2.529	2.53	2.55
Lu	0.420	0.454	0.241	0.2549	0.295	0.3147	0.391	0.3894	0.369	0.39

Lit.(1): Jochum, K. P. et al. (2016) Stand. Geoanal. Res. 40, 333-350 (2016).

Lit.(2): https://gbank.gsj.jp/geostandards/welcome.html GSJ: Geochemical Reference samples DataBase