Natural and Anthropogenic Gadolinium in Natural Water Systems in the Columbus, OH and Rochester, NY Areas

Undergraduate Research Thesis

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Abstract

Gadolinium (Gd) chelates used to enhance contrast in Magnetic Resonant Imaging (MRI) are the most common source of anthropogenic Gd in water systems and humans. Most of the ~1 g of Gd injected is excreted in urine and likely enters water systems through wastewater treatment plants (WWTPs). Anthropogenic Gd concentrations in water samples from the Scioto Valley Watershed in the Columbus, OH area ranged from 8 parts per trillion (ppt (ng/L)) upstream of WWTPs to 78 ppt directly downstream of WWTPs consistent with anthropogenic Gd being added to the rivers from WWTPs.

Although most of the Gd injected for a contrast enhanced MRI is excreted in urine, a small fraction of the Gd can be retained in the body for years. Furthermore, there is some evidence that a small percentage of humans that have no medical history of a Gd chelate-enhanced contrast MRI have slightly elevated Gd in body tissues (e.g. placentas, bones). A possible source this anthropogenic Gd could be anthropogenic Gd in drinking water. Municipal drinking water for the Rochester, NY, area comes from Hemlock Lake, Lake Ontario, or a mixture of the two. WWTP effluent flows into Lake Ontario but not into Hemlock Lake. Municipal drinking water samples from locations served by the different sources were collected. Anthropogenic Gd concentrations in the drinking water ranged from 0.5 to 2.7 ppt.

Water samples were also collected from Hemlock Lake (2 locations) and from Lake Ontario (4 locations). The natural concentrations of rare earth elements (REEs) in these samples were much larger (5.2 to 17 ppt) than the natural concentrations of REEs in the drinking water samples (0.9 to 3.5 ppt) or the river system samples from the Columbus, OH area (4 to 14 ppt).

Introduction

Due to its paramagnetic properties, water-soluble Gadolinium (Gd) chelate compounds (Blomqvist et al., 2022) are commonly used to enhance Magnetic Resonance Imaging (MRI) contrast. Gadolinium-based contrast agents (GBCAs) are injected intravenously in relatively high doses, ranging from approximately 1.1 to 3.3 g Gd in the average adult (Kulaksiz & Bau, 2011). Approximately 10 million doses of GBCAs (a total of more than 10 tons of Gd) are administered annually across the globe (Blomqvist et al., 2022). Following a contrast MRI procedure, patients naturally clear most Gd from the body via processing through the kidneys; the intact GBCAs are excreted in urine (Blomqvist et al., 2022). This waste is then processed by wastewater treatment facilities before entering waterways (Kulaksiz & Bau, 2007). However, gadolinium is not removed by current wastewater treatment methods, and as such is introduced and flows through waterways downstream of treatment plants (Kulaksiz & Bau, 2007).

GBCAs are likely the most prominent source of anthropogenic Gd, but other potential sources include REE use in technology such as electronics, airplane and shipbuilding, and metallurgy (Alkan et al., 2020). Anthropogenic Gd can be distinguished from natural sources of Gd because the fifteen naturally occurring Lanthanide Rare Earth Elements (REEs) (including Gd) exist in nature together rather than separately and occur in consistent REE concentration ratio patterns (Henderson & Humphris, 1984). These patterns can be represented by average concentrations of the REEs in the Upper Continental Crust (UCC) and allow us to identify the expected natural

concentration patterns of REEs (Rudnick & Gao, 2003). The ratio of each REE concentration in a sample (e.g. river water, drinking water, biological tissues, biological fluids) to the natural REE concentrations in the appropriate standard will be similar if the source of REEs is natural. As a result, the concentration of Gd from natural sources can be estimated from the measured concentrations of other REEs. The concentration of Gd in each sample from anthropogenic sources can then be estimated by subtracting the estimated concentration of Gd from natural sources from the measured total Gd concentration in the sample.

Anthropogenic Gd concentrations in some rivers, lakes, reservoirs, and drinking water have been reported previously. A study conducted in Berlin, Germany reported concentrations of anthropogenic Gd in drinking water up to 18 ppt (parts per trillion, ng/L) in some locations (Kulaksiz & Bau, 2011). In the northeastern United States, measured samples from the Great Lakes and surrounding rivers reported concentrations anthropogenic gadolinium up to 31 ppt within the urban and densely populated areas of Pennsylvania (Bau et al., 2006). A recent study within the Scioto River valley found anthropogenic Gd concentrations up to 32 ppt (Bradley, 2019). We measured REEs and determined anthropogenic Gd concentrations at twelve locations in rivers upstream and downstream of and reservoirs upstream of Columbus, OH, including upstream and downstream of waste treatment plants to identify sources of anthropogenic Gd.

While most Gd is not retained in the human body, some is. Darrah et al. (2009) showed some Gd used as MRI GBCAs was retained in the body, specifically in bones. Retained Gd has been found in the brain, kidneys, and bones (Blomqvist et al., 2022; Darrah et al., 2009). While chelated gadolinium is non-toxic in most humans, free gadolinium ions are highly toxic and have been known to be retained within the body, especially in cases involving patients with renal dysfunction, and can lead to renal failure (Blomqvist et al., 2022). Gadolinium ions can precipitate in tissues and disrupt calcium chemistry and other cellular processes (Kulaksiz & Bau, 2011).

It is now not surprising to find that some anthropogenic Gd (even a very small fraction of 1 to 3 g can be detected) is retained in the body of people who have had an MRI with GBCAs. However, there is some evidence that some people with no history of an MRI with GBCAs have anthropogenic Gd concentrations in bone that are above typical background levels, ranging from 1 to 15 nmol/g higher than the control (Darrah et al., 2006). There are few potential sources to explain this. One possible source for this anthropogenic Gd could be uptake from drinking water with elevated anthropogenic Gd levels.

In order to explore the possibility of Gd from drinking water being a potential source of somewhat elevated Gd concentrations in people who did not have a history of a Gd-enhanced MRI we planned to compare Gd concentrations previously measured in human placentae to Gd concentrations in the drinking water for their area of residence. Depending on the area of residence, the source of Rochester municipal drinking water was Lake Ontario, Hemlock Lake, or mixture of water from Lake Ontario and Hemlock Lake. Effluent from WWTPs flows into Lake Ontario but not Hemlock Lake so higher Gd concentrations were expected in tap water from Lake Ontario. Drinking water samples from each of the three areas were acquired and the total, natural and anthropogenic Gd concentrations were measured. Water samples directly from Lake Ontario and Hemlock Lake were also collected and measured. Unfortunately, the data set that included Gd concentrations measured in placentae from residents in the Rochester area did not include the

history of the number of Gd-enhanced MRIs each study subject had so we could not identify those who had no history of having a Gd-enhanced MRI.
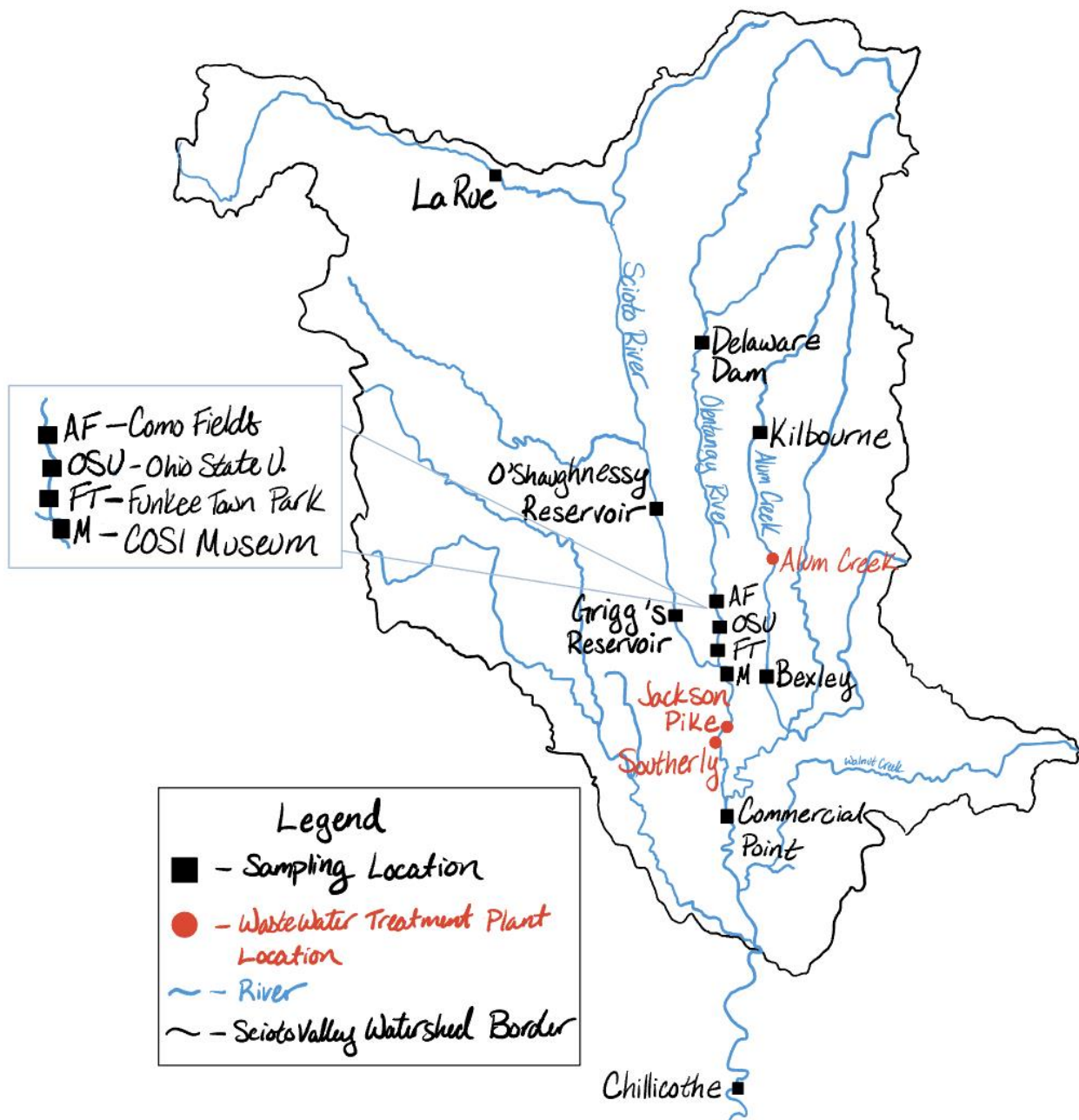
Experimental

Sampling Locations

Figure 1. Map of Upper Scioto River Basin with labeled sample locations. (LR) La Rue, (DD) Delaware Dam, (K) Kilbourne, (SH) O'Shaughnessy Reservoir, (G) Griggs Reservoir, (AF) Como Athletic Fields, (OSU) Ohio State University, (FT) Funkee Town Park, (M) COSI Museum, (B) Bexley, (CP) Commercial Point, (C) Chillicothe (adapted from Bradley, 2019)

Water flows from north to south in the Upper Scioto River Basin. The Scioto River, Olentangy River, and Alum Creek were chosen as sample locations because of the wastewater treatment plants which deposit effluent into these rivers. The Scioto River has two WWTPs, Jackson Pike

and Southerly, located between sampling locations COSI Museum and Commercial Point. Alum Creek has one WWTP located between sampling locations Kilbourne and Bexley. The Olentangy River flows into the Scioto just upstream of location COSI Museum, and Alum Creek flows into the Scioto just upstream of Commercial Point. Most sampling locations were adapted from Bradley (2019), who had measured REEs within the Upper Scioto River Basin waters approximately four years prior.
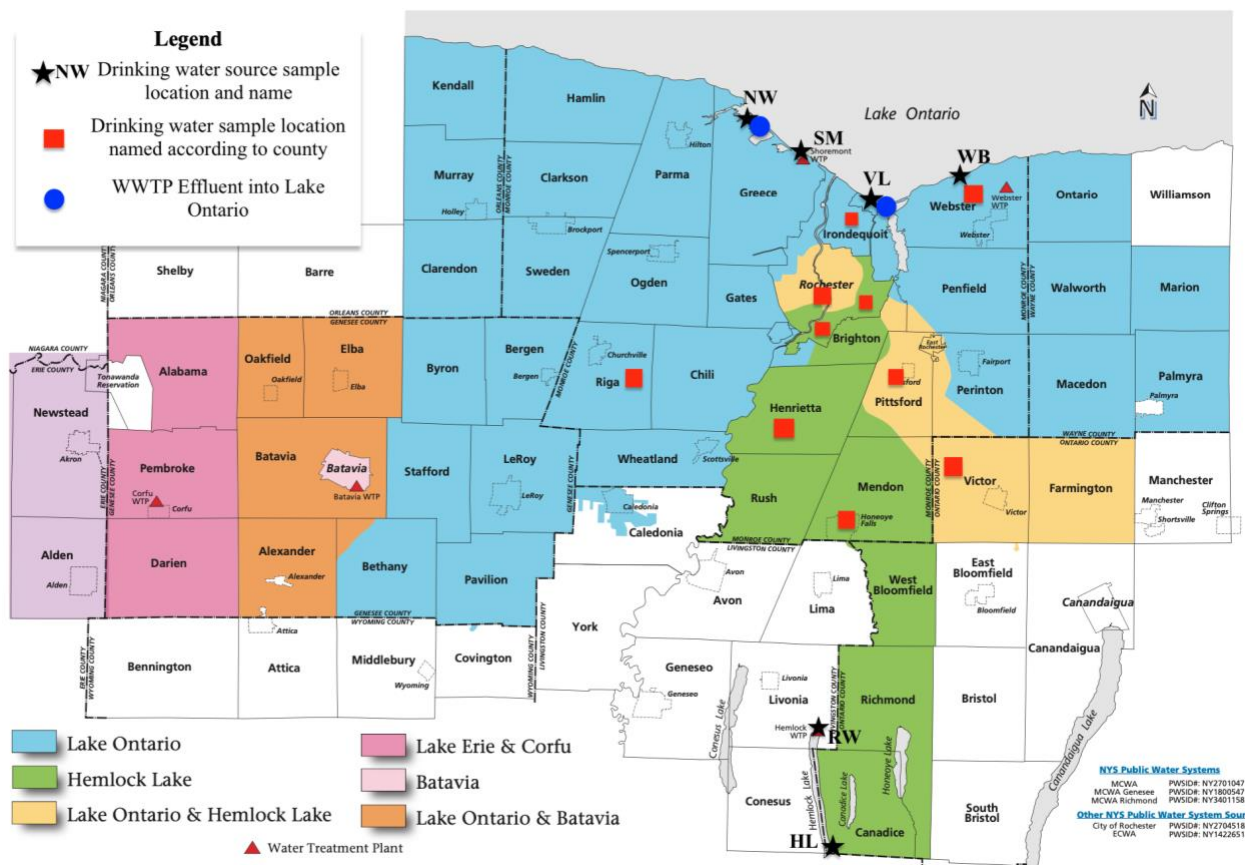

Figure 2. Map of Monroe County (Rochester, NY area) by water source with labeled sample locations. (NW) Northwest Quadrant WWTP, (SM) Shoremont Drinking Water Treatment Plant, (VL) Van Lare WWTP, (WB) Webster Drinking Water Treatment Plant.

Sampling locations along Lake Ontario were chosen due to their proximity to either a WWTP or a drinking water treatment plant to measure influent and effluent into Lake Ontario. Sampling locations along Hemlock Lake were chosen due to their proximity to a drinking water treatment plant, and another location on the opposite end of the lake.

Pre-Sampling Preparations

250 mL low density polyethylene (LDPE) bottles were cleaned in baths of 10% trace metal grade nitric acid for one week, then two separate baths of 2% ultrapure nitric acid for one week each bath to remove any possible trace metal or rare earth element contaminants. LDPE bottles were chosen because of their low trace metal concentrations and overall compatibility with most reagents. Once washed, the bottles were completely filled with deionized water and were double bagged to further

prevent contamination. The bottles were stored in sealed plastic containers until they were removed for sampling.

Columbus Sample Collection

On November 2, 2022, following the pre-sampling preparations, two 250 mL samples of water were collected at five locations upstream of the Columbus urban area. Weather conditions the week prior to collection were sunny with some cloud coverage and no rain for five days prior (National Weather Service, 2022). On the date of sampling, the weather was mostly clear with some cloud coverage. Dr. Rachel Coyte and I collected the samples using the Clean Hands/Dirty Hands procedure outlined in Fitzgerald & Davidson (1999). The person designated "Clean Hands" interacted only with the sample collection bottles and the water sample to be collected, while the person designated as "Dirty Hands" interacted with the other instruments. Samples were collected approximately 2 to 3 m from the riverbank. The samples were filtered in the field using 1.5 µm pore size, 30 mm diameter, nylon filter attached to a 12 mL polypropylene and polyethylene syringe. The syringes were acid washed using the same procedure as the 250 mL LDPE bottles. The first 5 mL of filtered sample were discarded to clean the filter.

The remaining Columbus locations were sampled on November 14, 2022. Two 250 mL samples were each collected from nine locations south of and within the urban area of Columbus. Weather conditions prior to November 14 consisted of heavy rains the three days prior to sampling (total precipitation 1.21 inches (National Weather Service, 2022)). On the date of sampling, the weather was sunny with some cloud coverage and no rain. Samples were collected using the Clean Hands/Dirty Hands procedure as on the first day but were not field filtered in the interest of time.

Rochester Sample Collection

Throughout the week of March 27th to 31st, 2023, drinking water samples were collected from the surrounding Rochester, New York area. Drinking water was sourced from Hemlock Lake, Lake Ontario, or a combination of both sources. After running the tap for 3 minutes, acid-washed LDPE bottles were uncapped and held under the tap water stream to collect the sample. Samples were collected using a modified Clean Hands/Dirty Hands procedure to account for one collector rather than a pair.

On April 1, 2023, following pre-sampling preparations, two samples were collected from Hemlock Lake, and four samples were collected from Lake Ontario in the Rochester, New York area. Weather conditions during the Hemlock Lake collections were sunny with no cloud cover. However, weather conditions immediately before and during Lake Ontario collections were cloudy with a significant amount of rain. Samples were collected following the same procedure as the Columbus locations and were not filtered in the field.

Sample Pre-Analysis Preparations

To prepare for ICP-MS analysis, all samples were filtered through a 1.5 µm pore size, 30 mm diameter, nylon filter attached to an acid washed polypropylene and polyethylene syringe. To clean out the filter, one 10 mL aliquot of 2% vol/vol ultrapure nitric acid, then one 10 mL aliquot of distilled water were filtered through the syringe. 250 mL of each sample was filtered into a new acid-washed 250 mL LDPE bottle and acidified to 2% vol/vol HNO_3. The acidified samples were transferred, in 15 mL aliquots, to triple rinsed 15 mL centrifuge tubes. This process was repeated for all field blanks.

Measurement of REE concentrations by Inductively Coupled Plasma-Mass Spectrometry

The unknown concentrations of the rare earth elements in the samples were measured on December 8, 2022, using a PerkinElmer ELAN DRC II Inductively Coupled Plasma-Mass Spectrometer. The nebulizer gas flow was optimized for a CeO^+/Ce^+ ratio of less than 0.3. Corrections were made for monoxides of measured isotopes (see Appendix A16 for correction equations), so it is assumed the oxide overlap is insignificant and is not considered. A 2% vol/vol HNO_3 blank standard solution was made and measured, and its signal intensity was subtracted from the signals of the standards and sample solutions. Six standard solutions—at concentrations of 1 ppt (ng, 5 ppt, 10 ppt, 20 ppt, 50 ppt, and 100 ppt—diluted from a 100 ppb Plasma-CAL multi-element REE standard were measured to create a weighted linear regression calibration. The calibration was then used to determine the concentrations of REEs within the sample solutions. REE isotopes were chosen based on natural abundance with the intent to measure the most abundant isotopes and isotopes with the least spectral overlap. Three replicates were measured and averaged for each isotope.

Table 1. Elements (isotopes) measured.

^{141}Pr	^{144}Nd	^{145}Nd	^{146}Nd	^{147}Sm	^{149}Sm
^{157}Gd	^{158}Gd	^{160}Gd	^{161}Dy	^{163}Dy	^{165}Ho
^{166}Er	^{167}Er	^{169}Tm	^{173}Yb	^{174}Yb	^{175}Lu

Normalization of measured REE concentrations to average concentrations in the Upper Continental Crust to estimate natural and anthropogenic Gd concentrations

REEs existing in nature have a characteristic concentration pattern. There is some variance in exact concentrations but, overall, this pattern remains consistent across the Earth. Solid measurements are used to establish a basis in the lab of this expected natural REE concentration pattern. Four sets of averaged REE concentrations in different geological material—Upper Continental Crust (UCC), Post-Archean Australian Shale (PAAS), North American Shale Composite (NASC), and European Shale (ES)—are commonly used to predict the REE concentrations within the Earth's crust, while one set of REEs in chondrite is used to represent primitive Earth REE compositions.

Normalization to the average REE concentrations in the Upper Continental Crust allows us to easily identify concentrations that do not follow the known composition of REEs, and we are thus

able to determine whether these values may be due to anthropogenic sourcing. Normalizing the ICP-MS measured concentrations to one of the above averaged REE concentrations allows us to determine the overall relationship between the expected REE concentration patterns (Piper & Bau, 2013). For this study, the collected samples will be normalized to the UCC, as these averaged REE concentrations gave the flattest ratios of the four references (see Appendix A2), indicating the composition of the UCC matches the REE distribution of the Columbus area surface water. Ce, La, and Eu have been shown to exhibit anomalous behaviors in comparison to other REEs (Hatje et al., 2016; Kulaksiz & Bau, 2011) and therefore were not included in the analysis.

We can estimate the concentration of natural Gd by normalizing the sample REE concentration data to the average concentration of REEs in the UCC. An expected normalized concentration pattern should be a nearly straight, horizontal line. Deviations from the expected pattern can thus be visually determined by the presence of a peak, indicating that element corresponding to the peaked normalization curve does not follow the expected concentration pattern of REEs. The natural Gd concentration can be estimated using the normalized REE concentrations, and these can then be used with the measured concentration to determine the anthropogenic Gd concentration.
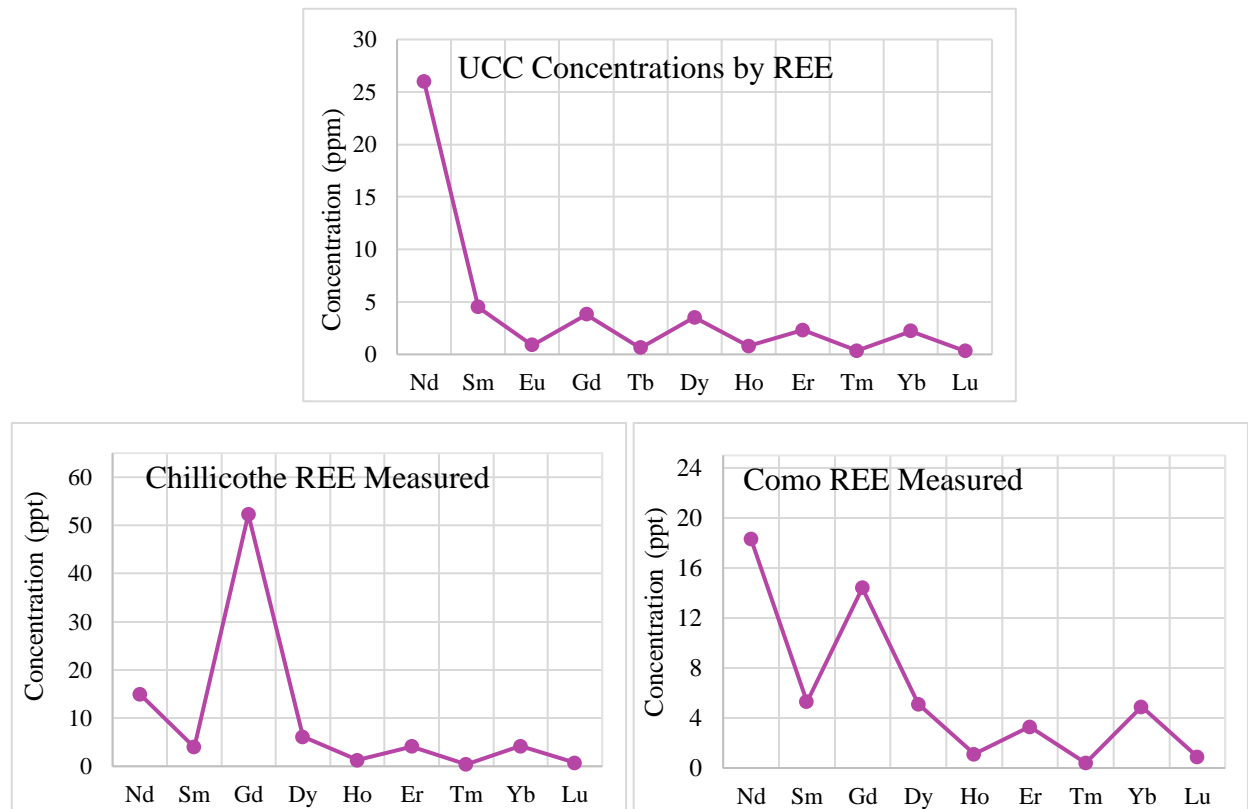

Figure 3. Average concentrations of REEs in the UCC *(upper)*; Raw ICP-MS measured concentrations of sample Chillicothe *(lower left)*; Raw ICP-MS measured concentrations of sample Como Athletic Fields *(lower right)*.
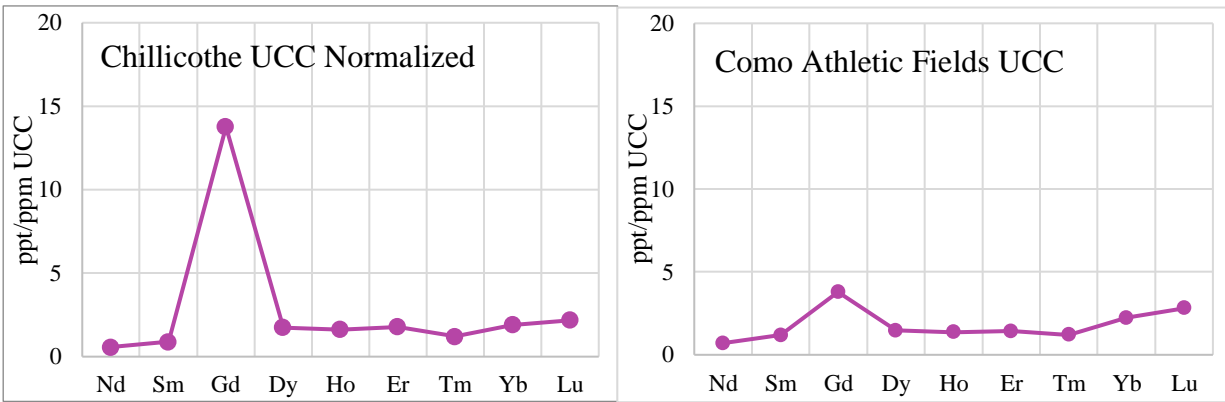
Figure 4. UCC normalized plots of sample Chillicothe *(left)* and Como Athletic Fields *(right).*

Once the gadolinium concentrations have been measured in the samples the estimated anthropogenic Gd concentration at each sampling location can be estimated using the measured sample concentrations that have been UCC normalized. Normalization to PAAS was first attempted, however this yielded negative estimated anthropogenic Gd concentrations that were inconsistent with the normalized diagrams that showed a positive Gd anomaly when normalized to the average concentration of each REE in the UCC.

The calculation procedure was adapted from Ogata & Terakado (2006), interpolating the expected natural Gd concentration (Gd_n^*) using the normalized concentrations of neighboring REEs, Sm (Sm_n) and Dy (Dy_n).

$$\ln{(Gd_n^*)} = 1/2(\ln(Sm_n) + \ln(Dy_n))$$

Once the expected natural concentration had been calculated, we were able to determine the anthropogenic Gd concentration (Gd_A) by subtracting the expected natural concentration (Gd^*) from the total measured concentration (Gd).

$$Gd_A = Gd - Gd^*$$

Results and Discussion

Scioto Valley Watershed (Columbus, OH)

Table 2. Total, and estimated natural, and anthropogenic Gd concentrations at each of the sampling sites.

	Sam-pling date (Nov)	Location	River	Total Gd (ppt)	Natural Gd (ppt)	Anthro-pogenic Gd (ppt)	% Anthro-pogenic Gd	Std Dev of total Gd* (ppt)
LR	2	La Rue	Scioto	28.2	13.8	14.4	51%	4.3
SH	14	O'Shaughnessy Reservoir	Scioto	27.8	5.8	22.0	79%	1.7
G	14	Grigg's Reservoir	Scioto	21.9	3.9	18.0	82%	1.4
K	2	Kilbourne	Alum Creek	21.3	8.1	13.2	62%	5.0
B	**14**	**Bexley**	**Alum Creek**	**81.8**	**3.1**	**78.6**	**96%**	**3.7**
DD	2	Delaware Dam	Olentangy	12.6	5.1	7.5	60%	1.8
AF	14	Como Athletic Fields	Olentangy	14.4	5.0	9.4	65%	0.76
OSU1	*2*	*Ohio State University*	*Olentangy*	*85.7*	*9.7*	*76.0*	*89%*	*5.5*
OSU2	14	Ohio State University	Olentangy	18.9	4.7	14.2	75%	1.1
FT	14	Funkee Town Park	Olentangy	14.4	4.5	9.9	69%	2.5
M	14	COSI Museum	Scioto	18.0	4.7	13.3	73%	1.7
CP	**14**	**Commercial Point**	**Scioto**	**62.5**	**4.0**	**58.5**	**94%**	**2.2**
C	**14**	**Chillicothe**	**Scioto**	**52.3**	**4.7**	**47.6**	**91%**	**2.1**

Locations in **bold** are downstream of a wastewater treatment plant. Italics indicates surprising [Gd]
*based on 5 replicates
See Appendix A11 for detection limits
Weather conditions the week prior to sampling on Nov 2, 2022 were cloudy with no rain
Weather conditions the week prior to sampling on Nov 14, 2022 were rainy, total precipitation 1.21 inches (National Weather Service, 2022).
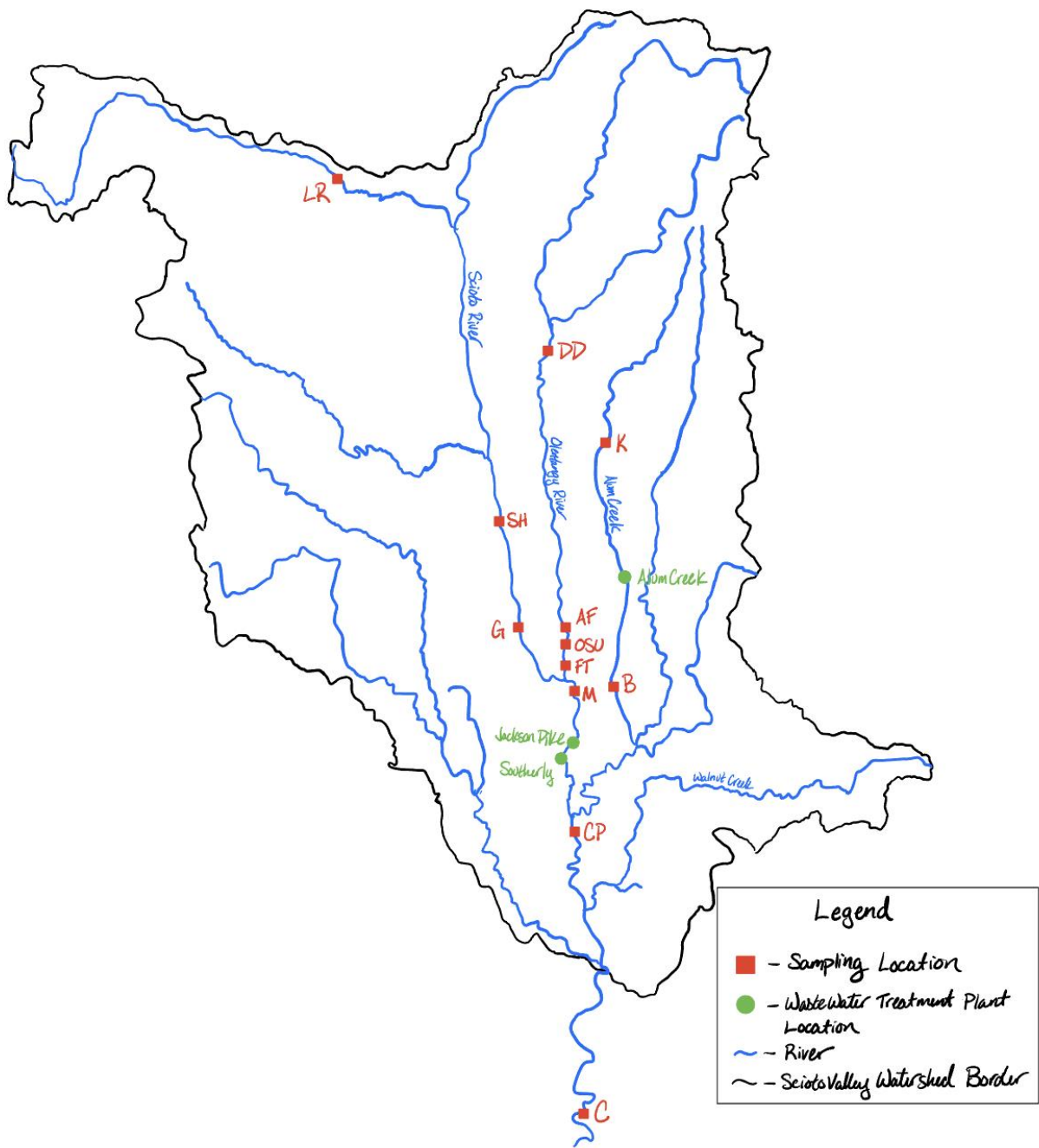
Figure 5. Map of Scioto River Valley water bodies with labeled sampling locations and wastewater treatment plants.

The expectation was to see little to no evidence of anthropogenic Gd upstream of wastewater treatment plants within the Scioto River Valley, while locations downstream of the WWTPs would have evidence of anthropogenic Gd, shown by an increase in Gd concentration relative to the distribution of the other REEs. Bradley (2019), after measuring locations upstream and downstream of wastewater treatment plants in the Columbus metro area, found the anthropogenic Gd concentrations increased significantly at locations downstream of WWTPs.

The sample collected from Ohio State University on November 2, 2022 (OSU 1) exhibits a surprisingly high anthropogenic Gd concentration (76 ppt) despite being upstream from the city's wastewater treatment plants. The anthropogenic Gd concentration was considerably lower (14 ppt) for the sample collected November 14, 2022 (OSU 2). The discrepancy between the two samples is not due to contamination during collection or pre-analysis preparations, as the field blanks do not exhibit any evidence of contamination (see Appendix A6). The data are consistent with another source of wastewater although the source is unknown. Our initial thought was that this discrepancy was due to dilution, as weather conditions prior to the two sampling days differed significantly in terms of rainfall. There was no rain prior to sampling on November 2 (OSU 1), and there was a considerable amount of rainfall (1.21 inches (National Weather Service, 2022) three days prior to sampling on November 14 (OSU 2). However, OSU 2's total Gd concentration is comparable to that of locations sampled upstream of WWTPs on November 2 (La Rue and Kilbourne). If dilution was responsible for the lower Gd concentration in OSU 2 compared to OSU 1, it would be expected that the other measured REEs would be diluted as well, which is not what is observed (see Appendix A12 and A13).

Looking solely at the concentration of anthropogenic Gd within the samples, we see a similar distribution trend to that of Bradley (2019): locations upstream of WWTPs area have much lower anthropogenic Gd concentrations than downstream. Verplanck et al. (2010) also saw evidence of increased anthropogenic Gd within the WWTP effluent compared to the influent.

In the northernmost samples along the Scioto River (LR, SH, and G) had similar anthropogenic Gd concentrations, ranging from 14 to 22 ppt. Locations of WWTPs along the Olentangy River (DD, AF) and Alum Creek (K) have anthropogenic Gd concentrations under 30 ppt at these locations.

Bexley, considered to be within the Columbus city limits, exhibits a high anthropogenic Gd concentration (79 ppt). This location was sampled along Alum Creek, with its northern location corresponding to Kilbourne. The sample collected at Kilbourne was collected on a different day than the sample collected at Bexley, however Kilbourne's total Gd concentration (21 ppt) is comparable to that of samples upstream of WWTPs sampled the same day as Bexley (e.g Grigg's Reservoir total Gd concentration was 22 ppt). Because these upstream locations are comparable, we can compare the two locations sampled along Alum Creek. Between Kilbourne and Bexley lies the Alum Creek Water Reclamation Plant, a water treatment facility, which likely explains Bexley's high anthropogenic (and total) Gd content.

In our data, we see a significant jump in anthropogenic Gd from 13 ppt measured at the COSI Museum directly upstream of both WWTPs along the Scioto River, to 59 ppt measured at Commercial Point, a location just downstream of the Jackson Pike Wastewater Treatment Plant. From the anthropogenic Gd concentrations, we can determine an effluent enters the Scioto river downstream of the WWTPs.
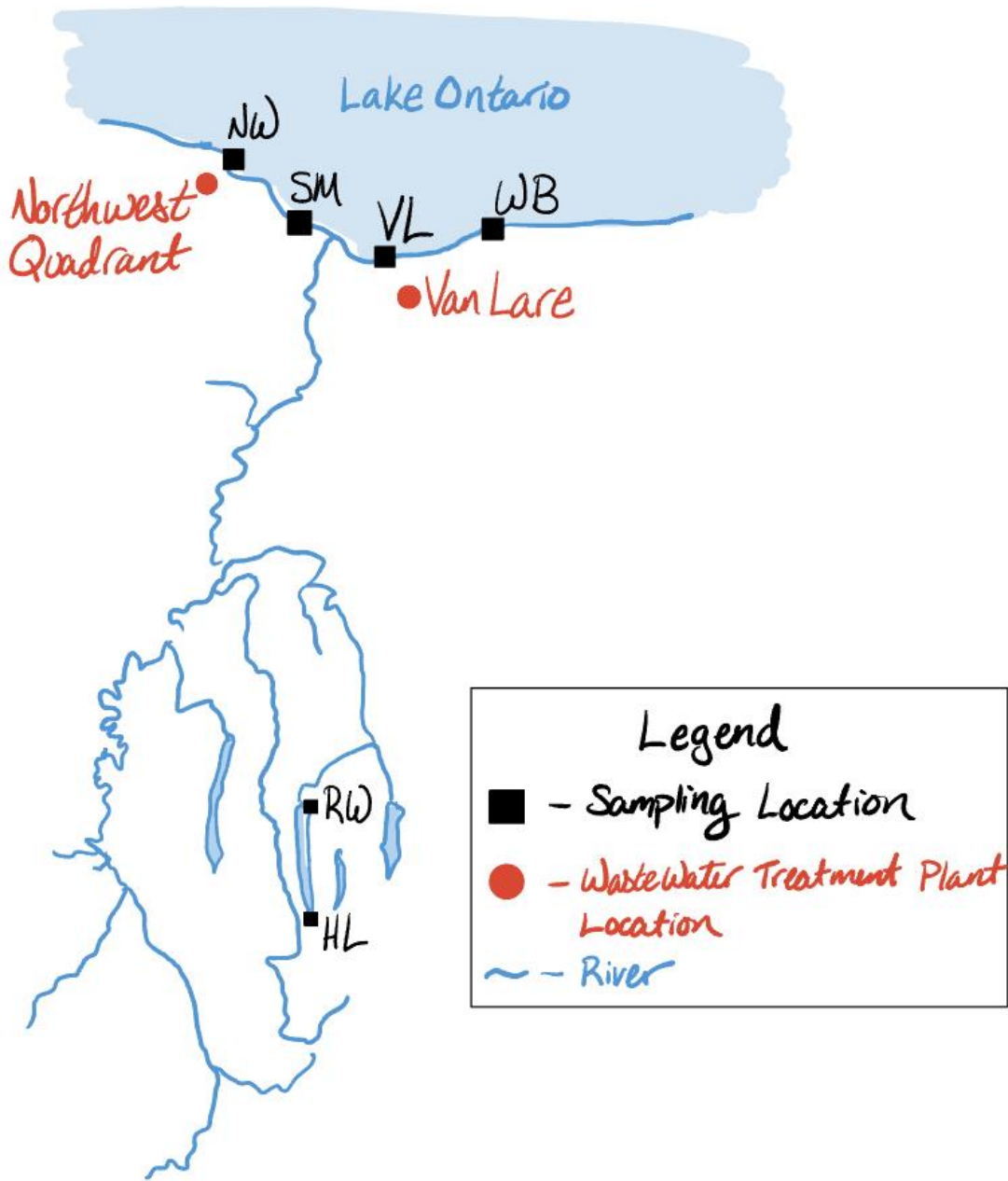
Figure 6. Map of Lake Ontario and Hemlock Lake sampling locations with labeled wastewater treatment plants. (NW) Northwest Quadrant WWTP, (SM) Shoremont Drinking Water Treatment Plant, (VL) Van Lare WWTP, (WB) Webster Drinking Water Treatment Plant, (RW) Rochester drinking Water Treatment Plant, (HL) Hemlock Lake.

Table 3. Total and estimated natural, and anthropogenic Gd concentrations according to Rochester water source sampling location.

	Location		Water Source	Total Gd (ppt)	Natural Gd (ppt)	Anthro-pogenic Gd (ppt)	% Anthro-pogenic Gd	Std Dev of Total Gd (ppt)
HL	Hemlock Lake	-	Hemlock Lake	8.1	5.2	2.9	35%	2.1
RW	Rochester Drinking Water Treatment Plant	Inlet	Hemlock Lake	23.7	18.8	4.9	21%	1.6
NW	**Northwest Quadrant Wastewater Treatment Plant**	**Outlet**	**Lake Ontario**	**22.0**	**16.8**	**5.2**	**24%**	**2.0**
WB	Webster Drinking Water Treatment Plant	Inlet	Lake Ontario	14.1	9.6	4.5	32%	1.5
SM	Shoremont Drinking Water Treatment Plant	Inlet	Lake Ontario	15.8	11.0	4.8	28%	2.4
VL	**Van Lare Wastewater Treatment Plant**	**Outlet**	**Lake Ontario**	**15.4**	**11.7**	**3.8**	**24%**	**6.7**

*See Appendix A11 for detection limits

There are two main sources of wastewater effluent into Lake Ontario from the Rochester Metro Area—Northwest Quadrant and Van Lare wastewater treatment plants—both of which are included in this sample set. Both sample sites have evidence of anthropogenic Gd within the sample, 5 ppt was calculated at Northwest Quadrant (NW) and 4 ppt was calculated at Van Lare (VL). There is also evidence of anthropogenic Gd at sampling sites located near an influent to a drinking water treatment plant. The anthropogenic Gd concentration was calculated to be 5 ppt at Webster (WB) and Shoremont (SM) drinking water treatment plants. It was expected that the anthropogenic Gd concentrations would be higher near the WWTP effluent sites, however the samples from the WWTP and the drinking water treatment plants are of similar Gd concentrations. This could be due to the size of Lake Ontario. Because it is a large body of water, there is a significant dilution factor associated with it. The exact location of the WWTP effluent was not known, and so it is possible the concentration was diluted very quickly after entering Lake Ontario.

Hemlock Lake also has evidence of anthropogenic Gd within its two samples. Water sampled near the Rochester Water Treatment Plant (RW) location on Hemlock Lake has the second highest level of anthropogenic Gd, comparable to that of Northwest Quadrant. This was unexpected, as there are no WWTPs with effluent into Hemlock Lake. It is unlikely that this is due to a contamination error, as the field blank from RW has a similar intensity to the calibration blank made in lab (see Appendix A8). It is likely due to a high natural Gd concentration in Lake Ontario when compared to that of Columbus. This suggests that all REE concentrations in Lake Ontario are higher, leading to a lower calculated anthropogenic Gd concentration.

All locations sampled in the Rochester Metro area have a high estimated natural Gd concentration when compared to the estimated natural Gd concentration in Columbus, OH. As such, the percent anthropogenic Gd concentration relative to the total is much lower in the Rochester samples than

in the Columbus Samples (see Table 3). This trend of a high natural concentration is seen throughout all REEs measured in the Rochester Metro Area water sources (see Appendix A14). This is consistent with measurements from Bau et al. (2006), recording that approximately 75-80% of the measured Gd was natural.

Rochester's treated wastewater flows into Lake Ontario, and, as such, it was expected that anthropogenic Gd levels would be higher in samples collected from Lake Ontario compared to Hemlock Lake. However, there is no significant difference (p-value: 0.45; > 0.05 confidence level) (details in Appendix A14) between the anthropogenic Gd concentrations measured in the two sources. Due to the high p-value, it cannot be stated that Lake Ontario has a higher anthropogenic Gd content than Hemlock Lake.

Comparison of natural and anthropogenic Gd concentrations in Columbus and Rochester water systems

When compared to the samples from Columbus, the Rochester sample set has a much higher concentration of neighboring REEs. This is comparable to the data from Bau et al. (2006), who also found higher concentrations (75-80% natural Gd) of natural REEs within Lake Ontario, compared to the other locations samples, Lake Erie (27% natural Gd) and various Pennsylvania rivers (40% natural Gd).

The total measured Gd concentrations from Lake Ontario and Hemlock Lake are comparable to that of the Columbus reservoirs, O'Shaughnessy and Grigg's, which are the most similar bodies of water measured in Columbus to those measured in Rochester (See Appendix A13 and A14). The anthropogenic Gd concentrations of the Rochester locations are significantly lower than in Columbus locations upstream of WWTPs (p-value: 0.03; < the 0.05 confidence level). This could be due to a difference in the geology of the two areas. The elemental composition of rocks and sediment in waterways in Rochester may have higher concentrations of REEs than the composition of rocks and sediments in waterways in Columbus. Another explanation could be due to the difference in body of water type. Because the water in the Scioto River flows at a faster rate than the water into and out of Lake Ontario, there may be more of an opportunity for the water in Lake Ontario to erode rocks, allowing for greater accumulation of REEs in the lake.

Table 4. Total and estimated natural and anthropogenic Gd concentrations in Rochester tap water depending on the source of the water.

	Location	Water Source	Total Gd (ppt)	Natural Gd (ppt)	Anthro-pogenic Gd (ppt)	% Anthro-pogenic Gd	Std Deviation of Total Gd (ppt)
14472	Mendon	Hemlock Lake	0.9	0.3	0.6	68%	0.3
14618	Brighton 1	Hemlock Lake	1.4	0.4	1.0	73%	0.4
14620	Brighton 2	Hemlock Lake	1.2	0.3	0.9	76%	0.3
14623	Henrietta	Hemlock Lake	1.0	0.2	0.8	75%	0.4
14580	Webster	Lake Ontario	2.4	0.2	2.1	90%	0.2
14617	Irondequoit	Lake Ontario	2.9	0.5	2.4	82%	0.6
14428	Riga	Lake Ontario	3.4	0.7	2.7	80%	0.7
14564	Victor	Mix	3.0	0.4	2.6	86%	0.2
14534	Pittsford	Mix	1.88	0.31	1.57	84%	0.5
14608	Rochester	Mix	1.45	0.24	1.21	83%	0.4

*See Appendix A11 for detection limits

Almost all natural Gd concentrations from the Rochester drinking water samples, apart from Riga (Natural Gd: 0.7 ppt) are less than the detection limit (0.6 ppt). Because these calculated concentrations are below, or very near, the detection limit, and the total Gd concentration is fairly close to the detection limit, it is nearly impossible to say that these are the true measured REE concentrations within the drinking water of Rochester, NY. As such, as such the further discussions surrounding this set of data is uncertain due to the high uncertainty of the values measured.

Comparison of natural and anthropogenic Gd concentrations in municipal drinking water from Hemlock Lake and Lake Ontario

Drinking water samples were sampled from taps which sourced water from Hemlock Lake, Lake Ontario, or a mix of both. Overall, the total concentration of REEs in the drinking water are much lower (p-value < 0.0001) than in the lakes. The normalization curve of the drinking water samples lies closer to the y-axis, indicating the REE concentrations are lower in the drinking water than in the drinking water sources. In almost all samples, the calculated natural Gd is lower than the detection limit and so the uncertainty of the natural Gd concentrations in the Rochester drinking water samples is high.

The anthropogenic Gd concentrations in the drinking water of Rochester, NY (Table 4) are much lower than that of the water sources, Lake Ontario and Hemlock Lake (Table 3). Anthropogenic Gd from Hemlock Lake sourced drinking water range from 0.6 to 1.0 ppt, while water sampled from Hemlock Lake ranges from 2.9 to 4.9 ppt. The anthropogenic Gd concentration in Lake Ontario sourced drinking water ranges from 2.1 to 2.7 ppt, while the anthropogenic Gd concentrations within Lake Ontario range from 4.5 to 5.2 ppt. This suggests that the drinking water treatment process removes much of the Gd. Rochester's methods of drinking water treatment

include flocculation, filtration, pH adjustment, and fluoridation (City of Rochester, NY, 2021). Rochester's treated wastewater flows into Lake Ontario, and as such, the anthropogenic Gd levels in the drinking water sourced from Lake Ontario should be comparable to that sourced from the lake itself. However, the measured concentrations show that the levels within the drinking water are much lower than the levels measured within the lake water. This is also true for the drinking water sourced from Hemlock Lake and the water from Hemlock Lake, itself. It is possible that the GBCAs are removed during drinking water treatment. When compared to the samples sourced directly from Hemlock Lake and Lake Ontario, the fraction of anthropogenic Gd is significantly higher in the drinking water samples.

Conclusion

After final analysis, the dissolved REE concentrations of the Scioto and Olentangy river systems were determined, and from that, the anthropogenic Gd concentrations were then calculated. From this, a significant increase in anthropogenic Gd concentration was detected between locations upstream and locations downstream of the city's wastewater treatment plants. This suggests that the WWTPs within the Columbus metro area are a probable source of anthropogenic Gd into the Columbus Metro Area, with anthropogenic Gd concentrations measured up to 79 ppt (see Table 2).

The presence of anthropogenic Gd upstream of the Columbus, OH wastewater treatment plants, while not to the degree of the samples downstream of wastewater treatment plants, indicate that there are sources of anthropogenic Gd upstream of the Scioto River Basin. There are additional WWTPs north of the Scioto River Basin which have effluent that will eventually drain into the Scioto River, contributing to the presence of anthropogenic Gd upstream of the Columbus WWTPs. The field blanks do not give any indication that there was an issue with contamination, as the field blanks have similar measured ICP-MS intensities to the blank standard (see Appendix A8).

While there is evidence suggesting anthropogenic Gd is added to the Columbus area water systems from WWTPs, the same cannot be said for the drinking water sources of the Rochester Metro area, Lake Ontario and Hemlock Lake. There was no significant increase in the anthropogenic Gd concentrations between the locations sampled near WWTP effluent and locations sampled near drinking water treatment plant influent. Because there is no significant increase of Gd concentration near WWTPs, we cannot say that WWTPs are a possible source of anthropogenic Gd into the Rochester Metro area drinking water sources (City of Rochester, NY, 2021).

The anthropogenic Gd concentration in the drinking water of the Rochester, NY metro area is significantly lower than the anthropogenic Gd concentration of the water sources, Lake Ontario and Hemlock Lake. From these results, it is possible that REEs are removed during the drinking water treatment process in the Rochester, NY area. Investigation into methods of REE removal in drinking water treatment plants did not yield any specific step in the Rochester drinking water treatment process that may remove dissolved REEs.

Due to insufficient data with elevated anthropogenic Gd concentration and no prior contrast MRI,

we cannot say that the drinking water of Rochester, NY is a possible source of Gd retention in people with no history of a Gd contrast MRI.

Suggestions for Future Work

Future studies could measure samples of drinking water in the Columbus metropolitan area, as Columbus drinking water sources (SH: 22 ppt, G: 18ppt) have higher levels of anthropogenic Gd than Rochester drinking water sources, to determine whether there are comparable concentrations of anthropogenic Gd between Columbus drinking water and wastewater effluent. Because Rochester's drinking water had significantly lower anthropogenic Gd concentrations (RW: 4.9 ppt, WB, 4.5 ppt) it would be interesting to determine whether the same phenomenon occurs within the Columbus drinking water treatment process. It would also be beneficial to identify additional sources of anthropogenic Gd introduction to determine whether Gd uptake is possible via methods other than intravenous injection of GBCAs.

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Appendix

A1- REE Concentrations in Post-Archean Australian Shale (PAAS), North American Shale Composite (NASC), European Shale (ES), and Upper Continental Crust (UCC)

Analyte	PAAS	NASC	ES	UCC
Nd	32	33	40.1	26
Sm	5.6	5.7	7.3	4.5
Gd	4.7	5.2	6.03	3.8
Dy	4.4	5.8	-	3.5
Ho	1	1.04	1.2	0.8
Er	2.9	3.4	3.55	2.3
Tm	0.4	0.5	0.56	0.33
Yb	2.8	3.1	3.29	2.2
Lu	0.43	0.48	0.58	0.32

A2- PAAS, NASC, ES, and UCC normalized plot of sample C (Chillicothe)
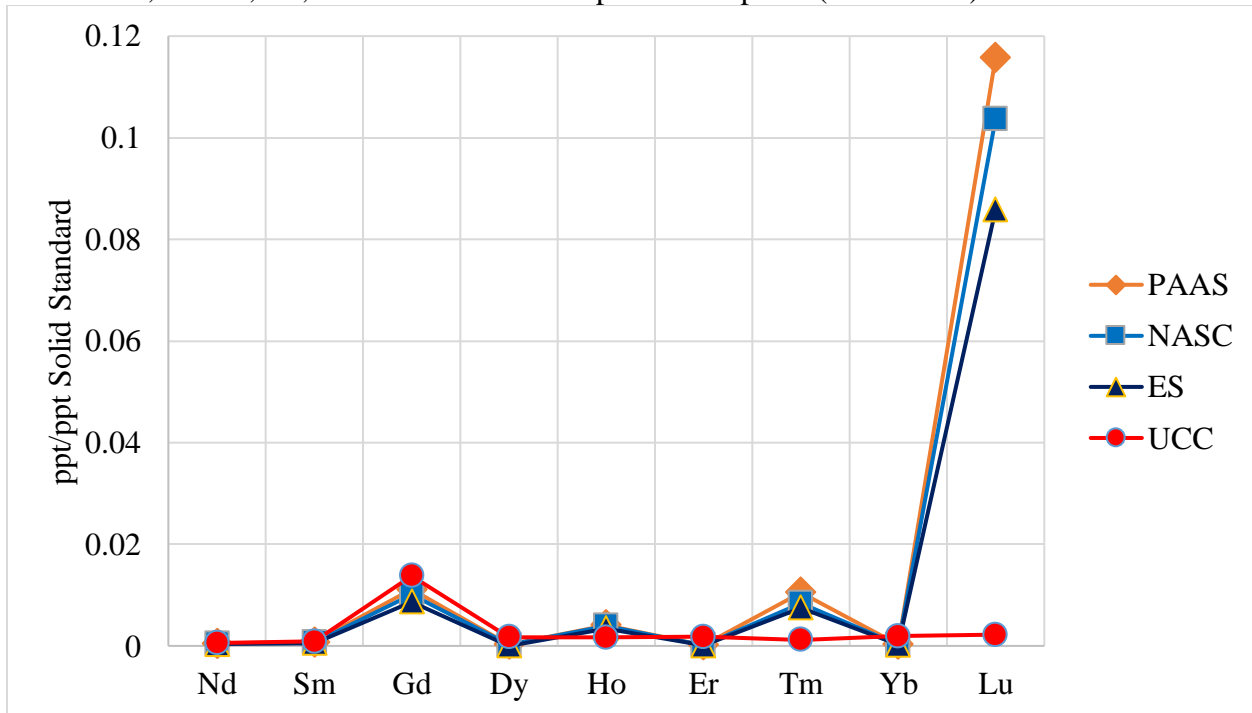
A3- ICP-MS Experimental Parameters

Uptake Rate	400 uL/min
Sweeps per Reading	10
Readings per Replicate	3
Replicates	5
Nebulizer	PFA-ST
Dwell Time per AMU (ms)	50

A4- pH and water temperature measurements from samples collected November 2, 2022

	Location	pH	Temp (C)
OSU1	Ohio State University	7.03	12.4
LR	La Rue	7.16	15.6
DD	Delaware Dam	8.17	12.8
K	Kilbourne	7.75	13.1

A5- pH and water temperature measurements from samples collected November 14, 2022

	Location	pH	Temp (C)
OSU2	Ohio State University	7.6	8.9
C*	Chillicothe	7.87	25
CP	Commercial Point	7.86	10.6
B	Bexley	7.91	8.9
M	COSI Museum	8.22	9.4
FT	Funkee Town Park	8.18	9.83
AF	Como Athletic Fields	8.43	9.9
G	Grigg's Reservoir	6.88	12
SH	O'Shaughnessy Reservoir	8.24	11.5

A6- pH and Temperature measurements from samples collected April 1, 2023

	Location	pH	Temp (C)
HL	Hemlock Lake	6.69	11.5
RW	Rochester Water Treatment	6.23	9.1
NW	Northwest Quadrant Water Treatment	7.03	9.0
WB	Webster Water Treatment	6.31	5.0
SM	Shoremont Water Treatment	6.85	6.8
VL	Van Lare Water Treatment	6.50	8.9

A7- pH and Temperature measured in lab from tap water samples collected March 27-29 from towns/cities with different drinking water sources.

Zip code	Town/City	Water Source	pH	Temperature (C)	Date collected
14617	Irondequoit	**Ontario**	7.72	21.1	3/28/23
14580	Webster	**Ontario**	7.27	20.9	3/27/23
14534	Pittsford	**Mix**	7.70	21.0	3/27/23
14618	Brighton 1	**Hemlock**	7.83	20.5	3/27/23
14472	Mendon	**Hemlock**	7.80	20.9	3/26/23
14428	Riga	**Ontario**	7.50	20.8	3/29/23
14623	Henrietta	**Hemlock**	7.67	21.0	3/28/23
14608	Rochester	**Mix**	7.52	21.3	3/28/23
14564	Victor	**Mix**	7.77	21.0	3/28/23
14620	Brighton 2	**Hemlock**	7.72	21.2	3/29/23

A8- Field Blank Raw Intensities November 2, 2022 (cps)

Analyte	Blank	K field blank	OSU1 field blank	DD field blank
^{140}Ce	7	12	10	38
^{141}Pr	8	10	9	12
^{144}Nd	7	6	10	14
^{145}Nd	8	6	9	12
^{146}Nd	7	7	9	10
^{147}Sm	8	8	10	8
^{149}Sm	9	8	8	8
^{153}Eu	8	7	8	7
^{157}Gd	6	8	8	9
^{158}Gd	7	7	7	8
^{160}Gd	5	4	3	3
^{161}Dy	8	5	6	8
^{163}Dy	7	6	7	9
^{165}Ho	6	8	5	7
^{166}Er	7	8	8	8
^{167}Er	8	7	6	5
^{169}Tm	10	10	12	10
^{173}Yb	8	6	5	6
^{174}Yb	5	5	8	10
^{175}Lu	7	6	9	6

A9- Field Blank Raw Intensities November 14, 2022 (cps)

Analyte	Blank	Field Blank 1	Field Blank 2	Field Blank 3
^{140}Ce	13	24	7	30
^{141}Pr	7	11	9	13
^{144}Nd	7	11	6	9
^{145}Nd	8	8	6	9
^{146}Nd	8	8	6	9
^{147}Sm	7	9	7	8
^{149}Sm	5	7	7	7
^{153}Eu	7	6	7	7
^{157}Gd	6	5	7	7
^{158}Gd	7	8	8	7
^{160}Gd	4	2	4	1
^{161}Dy	5	6	7	6
^{163}Dy	7	8	7	7
^{165}Ho	6	9	7	8
^{166}Er	7	5	6	7
^{167}Er	6	7	9	7
^{169}Tm	10	8	9	10
^{173}Yb	8	8	9	7
^{174}Yb	5	6	5	6
^{175}Lu	7	6	5	7

A10- Field Blank Raw Intensities Rochester Samples (cps)

Analyte	Blank	Field Blank NW	Field Blank RW	Field Blank A	Field Blank B	Field Blank C
^{140}Ce	5	5	5	3	3	2
^{141}Pr	4	3	4	1	3	2
^{144}Nd	2	3	3	1	2	2
^{145}Nd	6	4	5	4	2	4
^{146}Nd	3	3	3	2	2	2
^{147}Sm	5	3	2	4	3	2
^{149}Sm	3	3	4	3	3	3
^{153}Eu	4	2	2	3	3	2
^{157}Gd	3	2	3	4	3	3
^{158}Gd	3	2	3	2	3	3
^{160}Gd	1	1	2	1	3	1
^{161}Dy	4	2	3	2	2	3
^{163}Dy	4	2	3	3	3	3
^{165}Ho	3	3	2	3	3	2
^{166}Er	3	3	2	2	3	2
^{167}Er	5	3	2	4	2	2
^{169}Tm	8	7	7	7	5	4
^{173}Yb	3	3	3	1	2	2
^{174}Yb	3	2	3	2	4	2
^{175}Lu	3	2	3	2	3	2

A11- Detection Limits for analytes used to calculate anthropogenic Gd concentration. Based on 20 replicate measurements of the blank. Calculated by 3x the Standard Deviation of 0.2 ppt in each case.

Analyte	Detection Limit (ppt)
Sm	0.6
Gd	0.6
Dy	0.6

A12- UCC Normalized Plots for Columbus Samples November 2, 2022
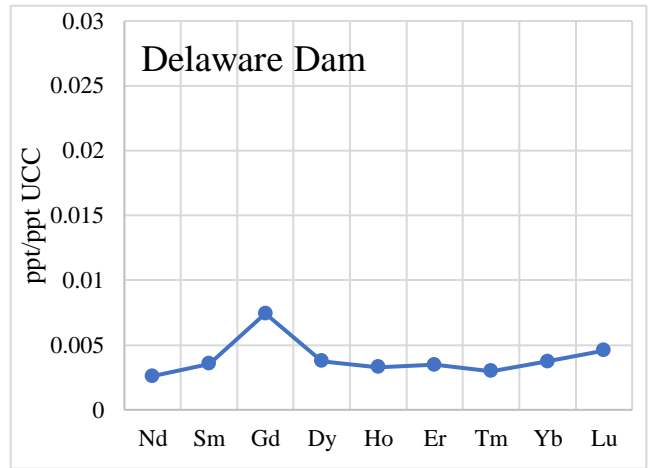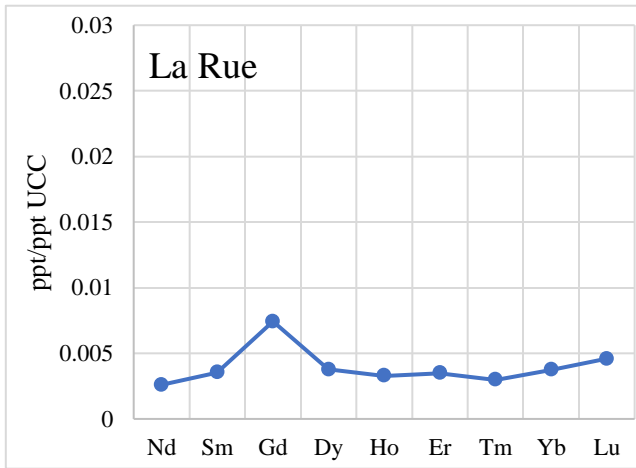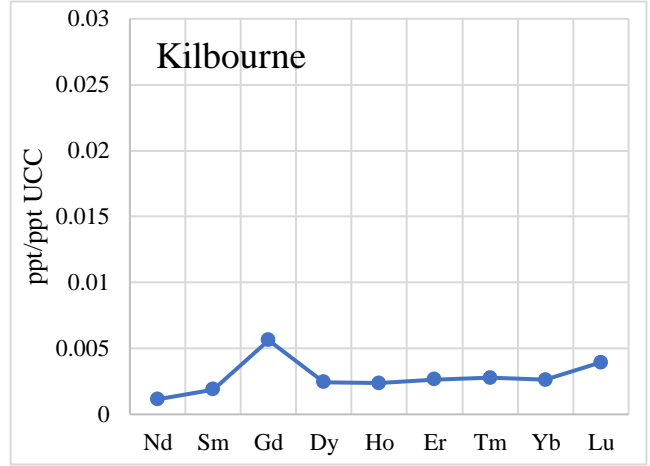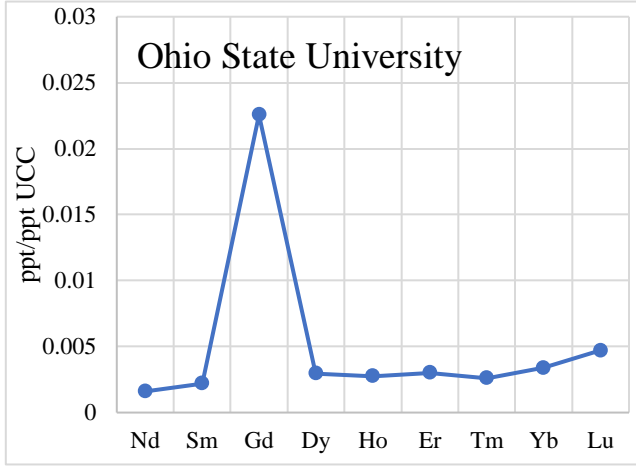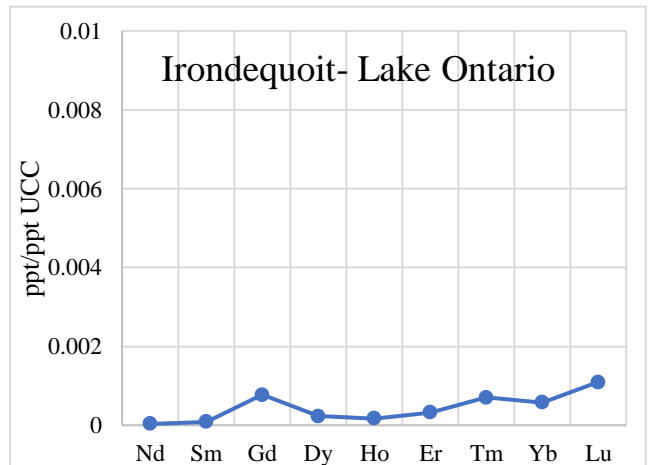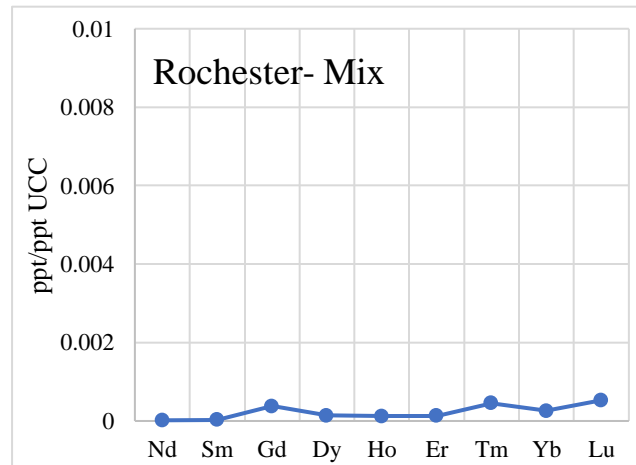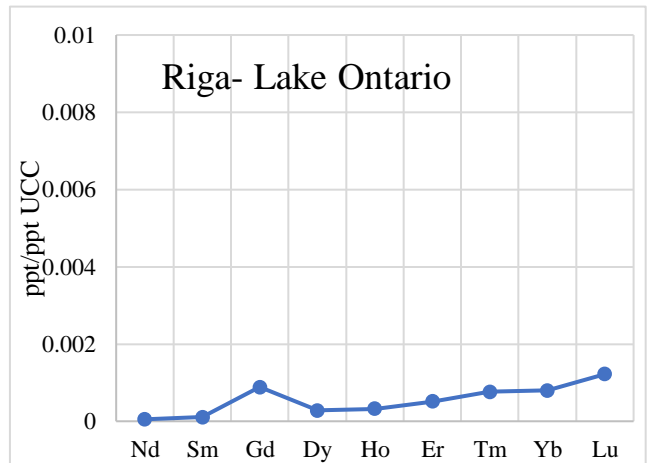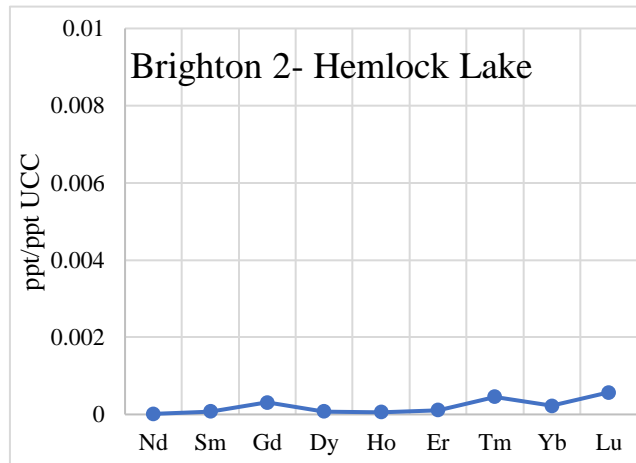
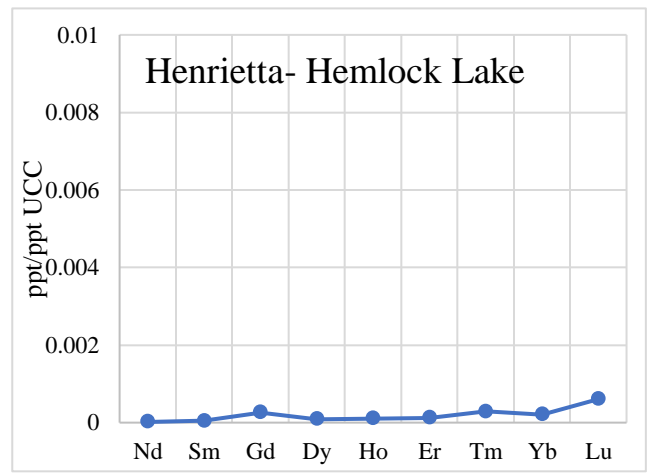**A13-** UCC Normalized Plots for Columbus Samples November 14, 2022
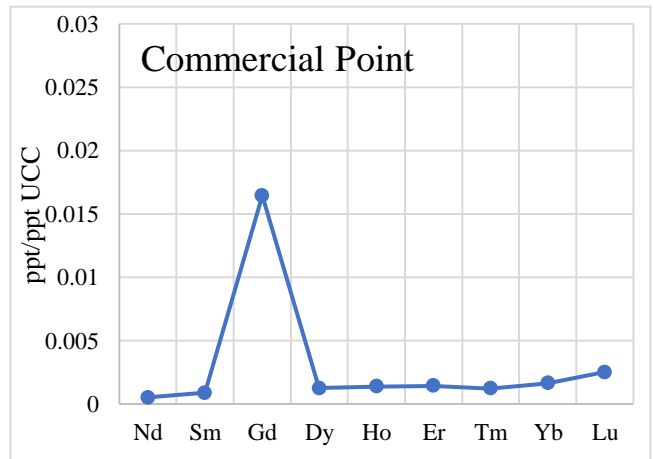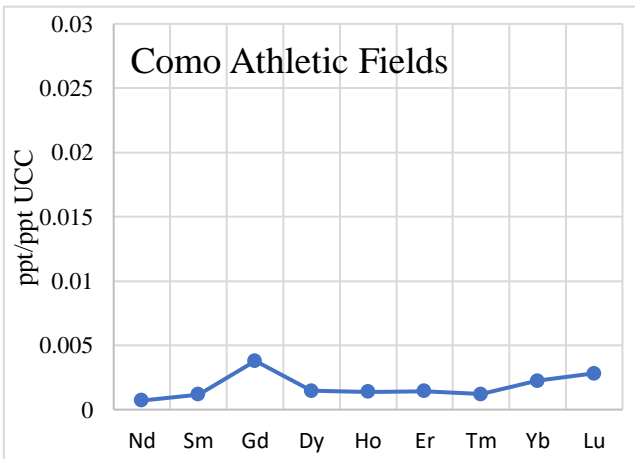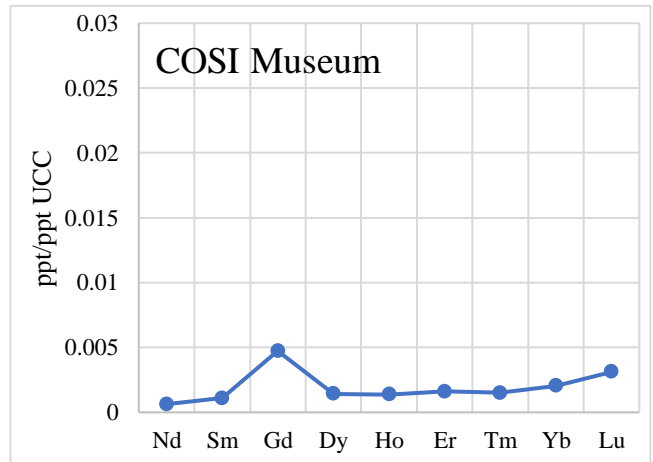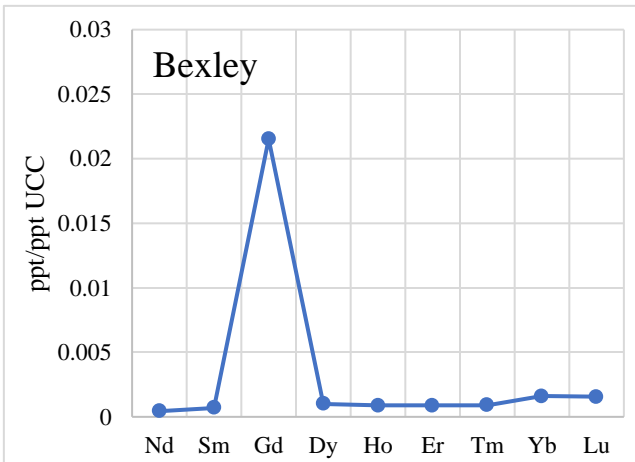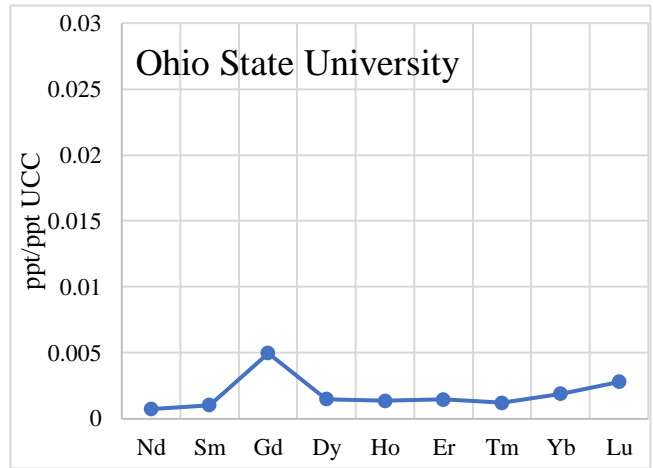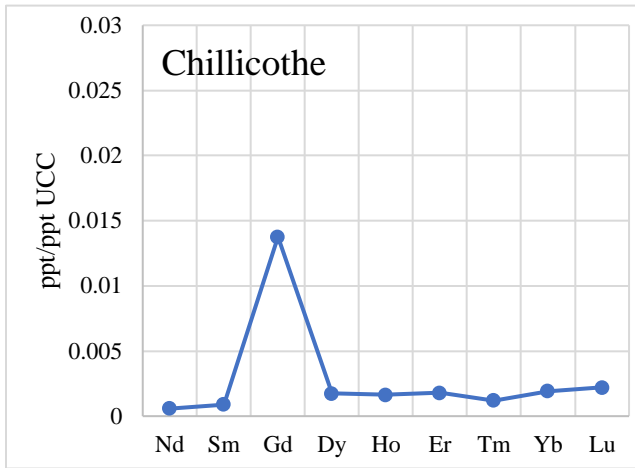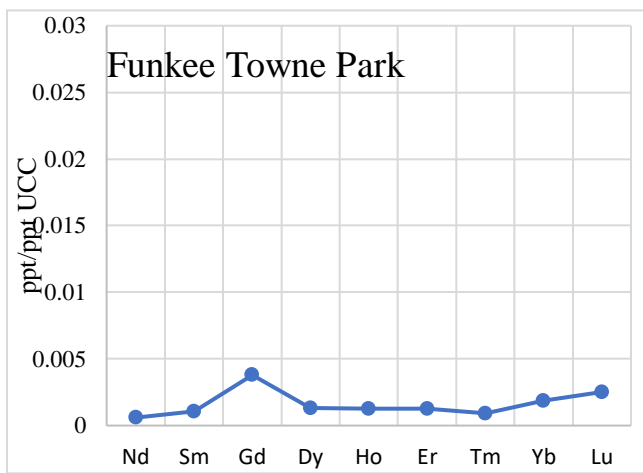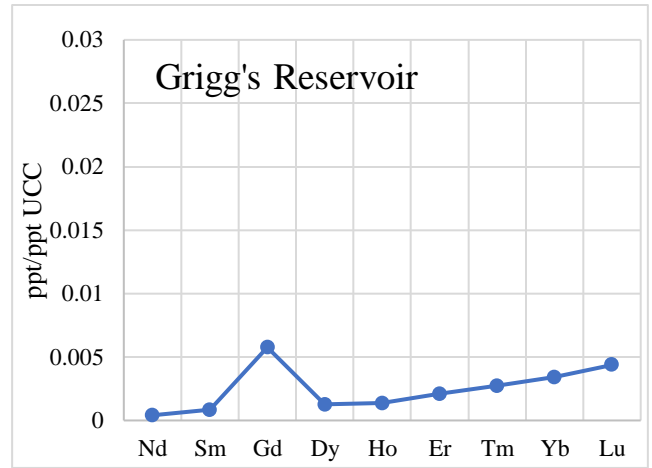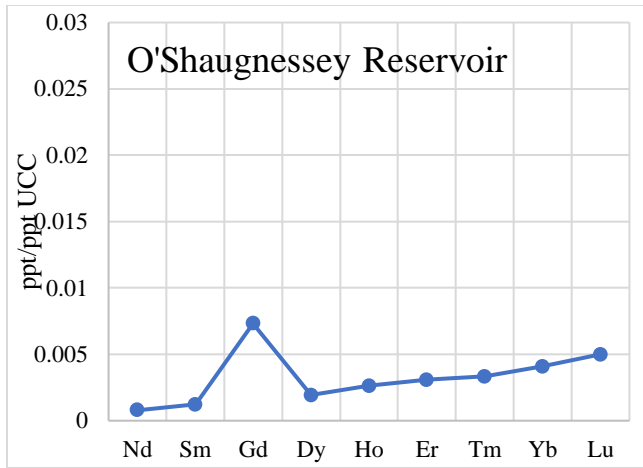
A14- UCC Normalized Plots for Rochester Water Source Samples

Nothwest Quadrant

Rochester Water Treatment

Webster

Hemlock Lake

Van Lare

Shoremont
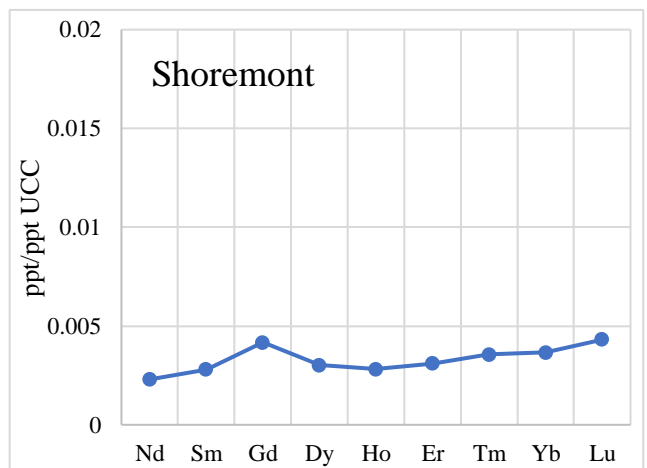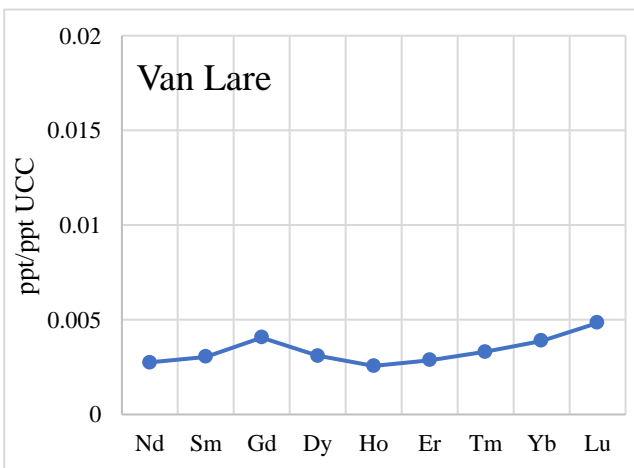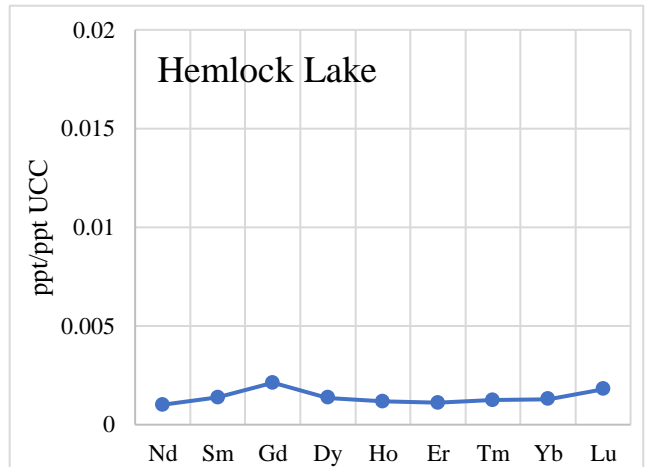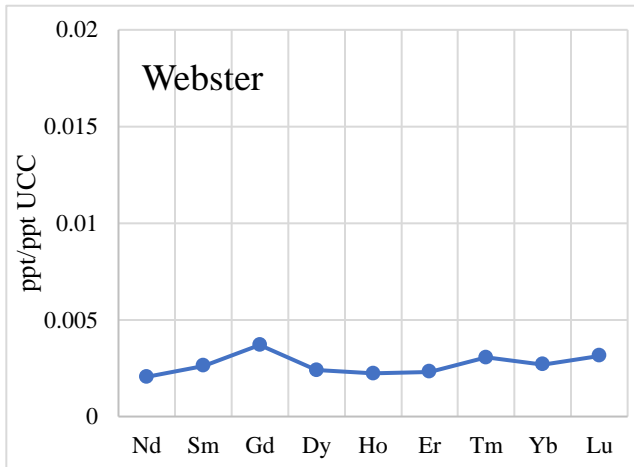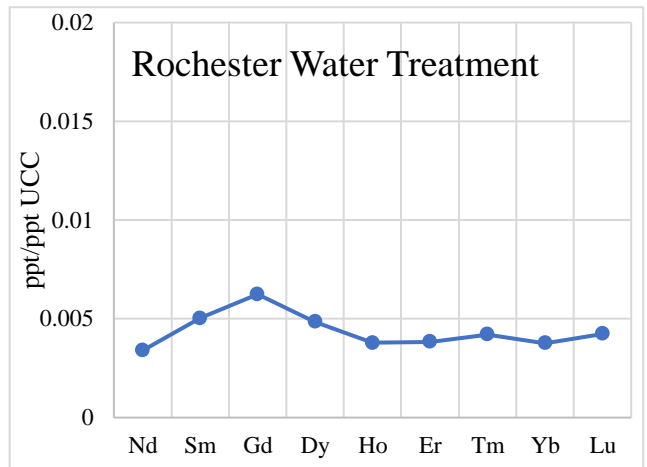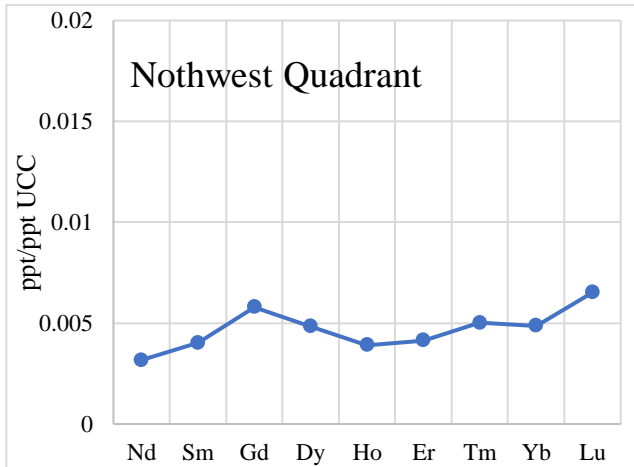
A15- UCC Normalized Plots for Rochester Drinking Water Samples

Victor- Lake Ontario

Pittsford- Mix

Webster- Lake Ontario

Henrietta- Hemlock Lake
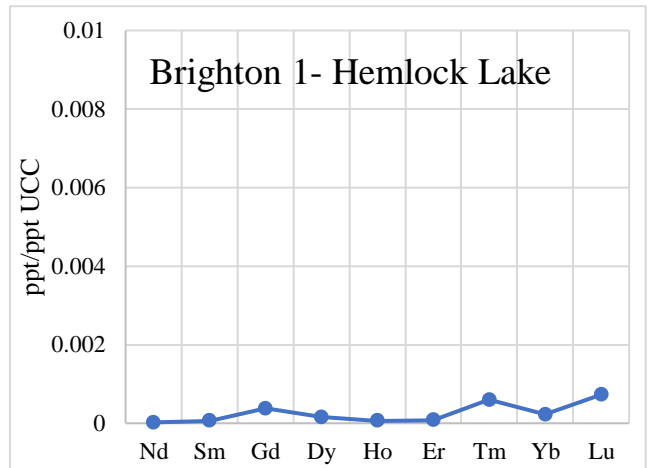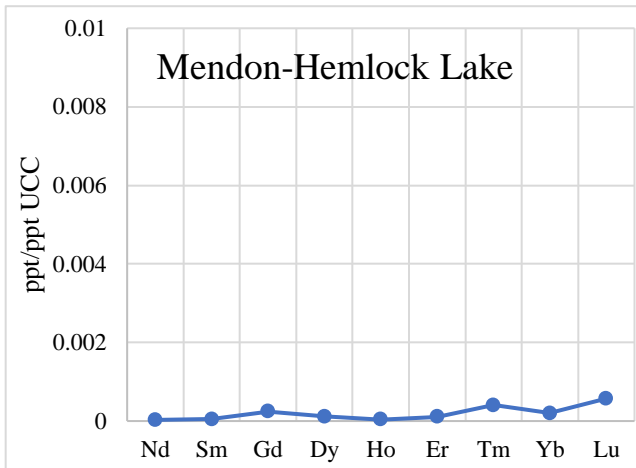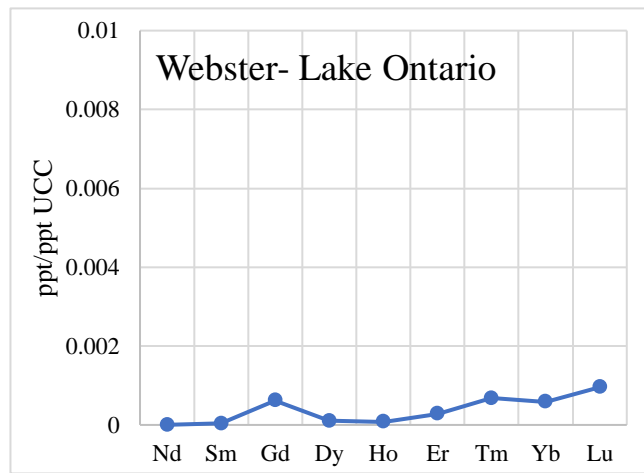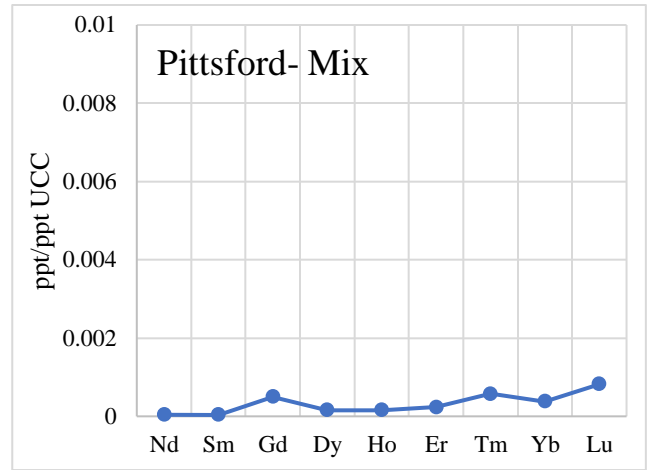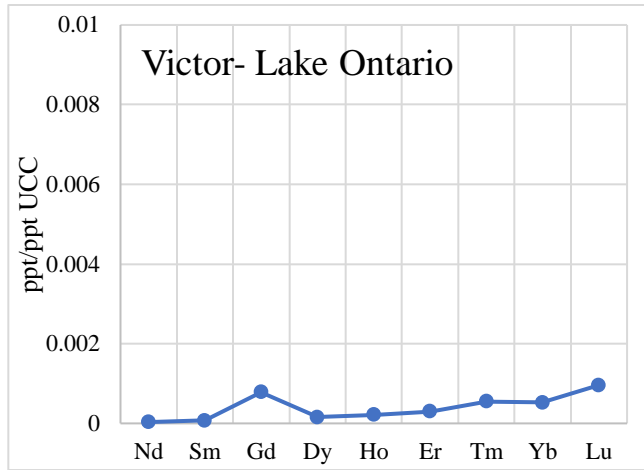
A16- Correction Equations for ICP-MS REE analytes.

Analyte	Equations
^{144}Nd	$-0.204 * {}^{147}$Sm
^{153}Eu	$-0.00092 * {}^{137}$Ba
^{157}Gd	$-0.0171 * {}^{141}$Pr
^{158}Gd	$-0.004016 * {}^{163}$Dy
^{160}Gd	$-0.0939 * {}^{163}$Dy - 0.324 * {}^{142}$Ce
^{161}Dy	$-0.01496 * {}^{145}$Nd
^{163}Dy	$-0.00235 * {}^{147}$Sm
^{169}Tm	$-0.000394 * {}^{153}$Eu