



Spatial and temporal distribution of rare earth elements in the Neuse River, North Carolina

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ABSTRACT

Rare earth elements (REEs) signatures in the dissolved loads of rivers serve as excellent monitors of weathering processes within a basin. However, quantifying REE behavior spatially (along a river's profile) and temporally (seasonal variations) is rare. This investigation reports REE concentrations of dissolved river loads collected during four sampling seasons at five monitoring stations along the Neuse River, North Carolina. The areal percentage of the Neuse River's catchment lithology composition, Post Archean Australian Shale (PAAS) normalized REE patterns, inter-REE ratios, and calculated anomalous REE values (i.e. cerium anomaly, gadolinium anomaly) were determined at each site in four seasons over a year. Our results show slight differences among inter-REE relationships and anomalous REE values in the dissolved loads along the length of the river. PAAS normalized REE patterns of dissolved water loads vary slightly spatially and temporally among the five sampling stations, and experience varying values of anomalous REE values. Collected data indicates that both variations in localized REE patterns and local bedrock occur along the river profile. Significant gadolinium (Gd) anomalies varied seasonally and spatially at select sites, suggesting changes in REE behavior along a river result from both natural and anthropogenic processes.

1. Introduction

Continental weathering is an important process that modulates global climates and transport nutrients into the ocean. During weathering, REEs mobilize partially as dissolved loads in rivers, during which physicochemical properties such as pH, salinity, flow conditions (Braun et al., 1990; Cidu and Biddau, 2007; Leleyter et al., 1999; Sholkovitz et al., 1994), and bedrock are important controls in localized REE content (Aubert et al., 2001; Cidu and Biddau, 2007; Elderfield et al., 1990; Goldstein and Jacobsen, 1988; Leybourne and Johannesson, 2008; Tricca et al., 1999). Within a river, REE patterns are thought to be good tracers of overall basin processes due to the relative consistency of physicochemical properties and bedrock types within a river; except in rare cases where atmospheric variations can significantly alter the dissolved load REE distribution (Meybeck, 1987; Stallard and Edmond, 1983; Tosiani et al., 2004).

Due to this invariable behavior, REE patterns are a prevalent geochemical tools in describing the dissolved loads of natural waters (Cidu and Biddau, 2007; Dia et al., 2000; Elderfield et al., 1990; Fisher and Kara, 2016; Goldstein and Jacobsen, 1988; Haley et al., 2014; Hatje et al., 2016; Kulaksiz and Bau, 2013; Lawrence and Kamber, 2006; Leybourne and Johannesson, 2008; Möller et al., 2014; Tosiani et al.,

2004; Tricca et al., 1999; Wood, 1990).

In addition to normalized REE patterns, relationships among the REEs are also useful as geochemical tracer of natural waters because all REEs primarily exist in the 3+ (III) state with the exception of Cerium (Ce) and Europium (Eu). These two elements can experience a 4+ (IV) and a 2+ (II) state respectively, thus allowing for the possibility to discriminate dissolved load samples with differing Ce and Eu anomalies (Leleyter et al., 1999; Wood, 1990). REEs in dissolved loads can be classified as either enriched in the light rare earth elements (LREEs, Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd)) or heavy rare earth elements (HREEs, terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Th), ytterbium (Yb) and lutetium (Lu) (Goldstein and Jacobsen, 1987). For some river catchments, the preferential incorporation of LREEs occur during formation of carbonates, ferromanganese nodules, and organic matter can significantly influence the overall distribution of REEs (Kulaksiz and Bau, 2013). However, the full impact of these processes on REE concentrations in the dissolved loads of rivers is not well quantified (Leleyter et al., 1999).

Recent anomalous REE patterns of rivers studied in both Europe and North America are linked to the growing usage of REEs in modern industries (Bau and Dulski, 1996; Hatje et al., 2016; Kulaksiz and Bau,

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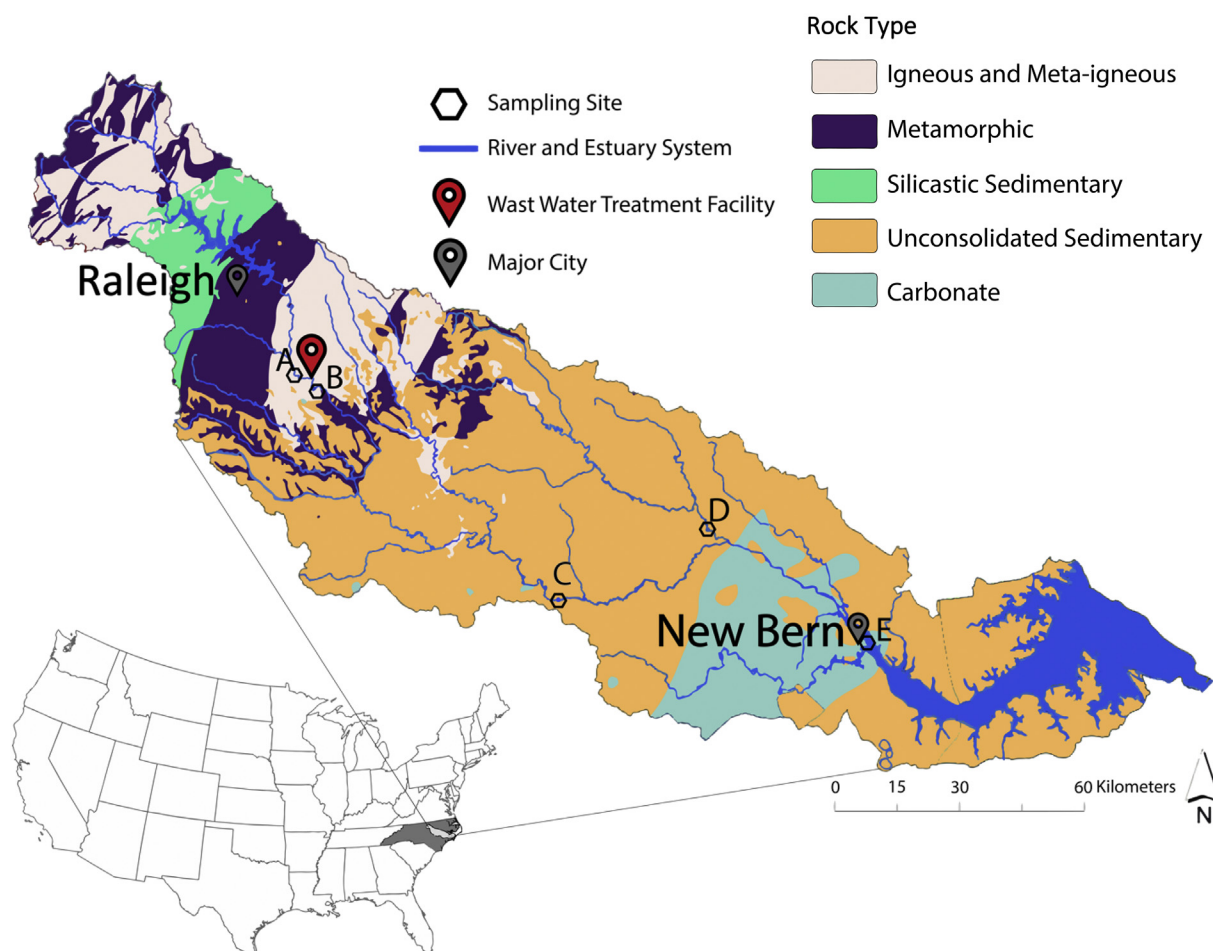


Fig. 1. Geologic map of the Neuse River basin, North Carolina. Rock units have been simplified to 5 distinctive regions, igneous/meta-igneous (includes volcanic), metamorphic, siliclastic sedimentary, unconsolidated sedimentary, and carbonate rich rock. Flow data gathered from USGS HydrSHEDS and rock types determined via USGS. Hollow hexagons indicate approximate sampling locations (see text and Table 1 for exact locations). (Map Projection: WGS 1984 UTM: 17N)

2013). Applications of REEs continue to grow in a variety of industries, such as the use of Gd as a chelating agent in medical imagery (Hatje et al., 2016; Kulaksiz and Bau, 2013) or the use of REEs in tagging hatchery fish (Pérez de Nancrales et al., 2016). Thus, describing riverine REE behavior from a single sample may yield incorrect interpretations derived from REEs, especially in rivers experiencing REE inputs from anthropogenic sources. Instead, determining if variability exist among normalized REE patterns and inter-REE relationships at different locations along a river is critical for reducing inconsistent knowledge that could be derived from single point sampling, and will become increasingly important for future studies of REEs as their use continues to grow in modern industries.

Here we investigated REE geochemistry in dissolved river water samples collected at multiple spots along the Neuse River of North Carolina, (Fig. 1) and during all four seasons to characterize the distribution of the REEs as they mobilize in a river basin with diverse bedrock lithology.

2. Geologic setting

The overall geological setting of the Neuse River basin is composed of two parts: Piedmont and the coastal plain. The detailed geological map is shown in Fig. 1 (GPS coordinates listed in Supplementary Table S1).

2.1. Piedmont

The western portion of the Neuse River basin, referred to as the Piedmont, is composed of a series of terranes, which accreted to Laurentia during the formation of the Pangea supercontinent. The Neuse River originates in the Piedmont region where overlying soils are rich in feldspar-derived clay, mica, and loams derived from the underlying bedrock (Phillips, 1992). Crystalline bedrock of the Piedmont is primarily composed of Proterozoic to late Cambrian granite, gneiss, mica gneiss, felsic and mafic meta-volcanics, amphibolite, and metamorphosed epiclastic and volcanoclastic rock (Phillips, 1992; Stuckey, 1965). Neoproterozoic to Cambrian rocks of the Piedmont are intruded by dike swarms of Jurassic aged olivine and quartz-normative diabase (Hibbard et al., 2002).

Northeast-southwest trending rift basins formed during the Triassic period when North America and Africa split apart during the rifting of the supercontinent Pangea (Stuckey, 1965). Within the Neuse watershed the Deep River Triassic Basin contains sandstone, mudstone, shale, and conglomerate deposited by rivers carrying material eroded from the ancestral Blue Ridge Mountains (Stuckey, 1965).

2.2. The Coastal Plain

The units of the Carolina Coastal Plain are primarily composed of Cretaceous to Quaternary age deposits of unconsolidated sediments and carbonate rocks (Stuckey, 1965). Surficial gravel, sand, and clay deposits of Pliocene age overlay the western portion of the Neuse River

Table 1

REE concentrations (pg/g) for river water and station data.

	B1 ^a	C1	D1	E1	A2 ^b	B2	C2	D2	E2	A3 ^c	B3	C3	D3	E3	A4 ^d	B4	C4	D4	E4
La	32.3	192	215	130	88.6	77.6	295	231	139	59.9	47.1	107	155	45.8	78.5	73.5	182	75.6	32.4
Ce	38.7	349	480	168	126	101	491	469	262	62.0	46.5	130	339	70.4	97.1	81.8	291	177	55.1
Pr	8.46	50.4	64.5	39.5	22.5	20.0	74.6	65	39.3	15.8	11.9	27.2	43.3	12.9	20.2	18.3	46.4	21.1	9.06
Nd	38.5	220	292	179	101	90.2	311	279	168	71.6	58.5	124	188	58.1	88.9	78.8	201	94.8	40.5
Sm	8.20	43.3	60.4	38.1	21.6	19.1	62.4	56.9	34.2	15.8	12.0	34.7	37.3	12.3	17.8	16.0	41.7	19.2	9.71
Eu	3.49	13.3	16.9	11.6	7.17	6.15	16.7	15.7	10.1	5.23	4.25	9.13	10.6	4.67	5.26	4.59	11.8	5.81	3.98
Gd	50.6	97.4	67.8	43.9	31.8	61.2	342	62.9	131	19.8	25.4	57.4	41.5	73.8	23.9	97.4	131	25.6	21.0
Tb	1.30	6.56	9.02	5.53	3.15	2.83	8.74	8.19	4.98	2.19	1.80	3.80	5.52	1.96	2.78	2.28	6.03	2.94	1.60
Dy	9.12	39.8	53.8	34.6	20.9	18.2	54.1	48.8	29.8	15.5	12.5	23.7	32.3	12.9	16.7	14.2	37.6	17.8	9.85
Ho	2.21	8.81	11.8	7.38	4.93	4.29	11.3	10.3	6.49	3.71	3.19	5.37	6.93	2.86	3.80	3.30	8.20	3.93	2.11
Er	7.62	27.0	36.7	22.9	15.6	13.9	34	31.3	19.1	13.0	10.9	17.2	20.5	9.08	12.2	10.7	25.6	12.0	7.39
Tm	1.32	3.91	5.34	3.53	2.31	2.23	4.77	4.60	2.86	1.95	1.70	2.44	3.11	1.37	1.81	1.60	3.57	1.77	1.14
Yb	9.35	26.0	34.7	23.8	16.2	15.4	32.5	29.4	19.4	12.2	12.1	16.4	19.3	9.62	12.5	11.8	23.1	11.8	8.48
Lu	2.01	4.42	5.87	3.86	3.02	2.91	5.2	4.90	3.54	2.2	1.93	2.55	3.09	1.53	2.19	1.76	3.48	1.90	1.40
ΣREE	213	1080	1350	712	465	435	1740	1320	870	300	250	561	906	317	384	416	1010	471	204
La/Yb	0.17	0.36	0.31	0.27	0.27	0.25	0.45	0.39	0.35	0.24	0.19	0.32	0.40	0.23	0.31	0.31	0.39	0.31	0.19
Ce/Ce*	0.50	0.77	0.88	0.51	0.60	0.55	0.73	0.84	0.78	0.44	0.41	0.51	0.91	0.62	0.53	0.48	0.69	0.95	0.70
Gd*	21.4	70.8	88.8	63.4	40.4	34.2	85.7	82	53.7	29.7	24.1	52.1	55.6	27.5	27.9	24.2	62.7	31.2	25.0
Gd _{ANTH}	29.2	26.6	< 0.0	< 0.0	< 0.0	27.0	256	< 0.0	77.6	< 0.0	1.28	5.30	< 0.0	46.3	< 0.0	73.2	68.4	< 0.0	< 0.0
Turbidity	13.5	27.4	5.2	3.5	– ^e	13.6	31.7	9.6	4.1	31.4	3.3	30.4	7.7	4.9	14.0	31.2	–	113.0	–
pH	7.46	6.85	6.11	6.85	–	8.89	6.84	6.67	7.38	7.25	7.04	6.84	6.74	7.48	6.99	5.43	–	6.42	–
Salinity (ppt)	–	–	–	0.42	–	–	–	–	0.34	–	–	–	–	0.08	–	–	–	–	–

^a October 14, 2015.^b December 21, 2015.^c April 26, 2016.^d August 4, 2016.^e Monitor malfunction

basin, referred to as the Coastal Plain (Stuckey, 1965). Cretaceous age sands, clays, which underlie younger Coastal Plain sediments, and argillaceous clays are derived from erosion of the Piedmont with some dark-to black coloring, suggesting carbonaceous matter (Spangler, 1950; Stuckey, 1965). Further east into the Neuse River basin, limestone, clay, and sand units of upper Cretaceous to Cenozoic age make up the last portion of the Neuse River basin before reaching the Pamlico Albemarle Sound (Stuckey, 1965).

3. Methods

3.1. Field methods

River water samples were collected along the length of the Neuse River at five locations, Auburn Knightdale Bridge (A), Seven Springs (B), Grifton (C), Clayton (D), and New Bern (E) (Fig. 1). These sites were selected based on their readably accessible chemical parameters (pH, salinity, turbidity, etc.) through Rivernet (<http://rivernet.ncsu.edu/>) and MODMON (<http://www.unc.edu/ims/neuse/modmon/>) network (Table 1). Rivernet is managed by the North Carolina State University while MODMON is overlooked by a collaborative effort between the University of North Carolina and the North Carolina Department of Environmental Quality (NCDEQ). Collectively the two programs monitor gauge height, turbidity, and pH along 290.0 km of the river and estuary system. As shown in Table 1, pH and turbidity data were gathered by MODMON and Rivernet stations.

To capture variability of precipitation and temperature influenced parameters and their effects on REEs, samples were collected a total of 4 times at each station on October 14, 2015; December 21, 2015; April 26, 2016; and August 4, 2016. These sampling times will be referred to as sampling times 1, 2, 3, and 4, respectively. Water samples were filtered off site with use of Sterlitech™ polyethersulfone membrane 0.45 μm filters and a reusable filter holder (Thermo Scientific™ Nalgene™) within the same day of the sample collection. Before collecting water samples, sampling bottles were rinse three time using local river water and 100 mL of local river water was run through a new membrane filter and filter device and then discarded to avoid cross

contamination from previous sampling. At minimum, a total of 250 mL of river water was filtered per sample and membrane filters never experienced significant blockage or accumulation of particulate during the filtering. Between each filtering session, the filtering device was rinsed with ~750 mL of milliQ™ water (18.2 mΩ·cm). The collection bottles were wrapped with parafilm to minimize evaporation and stored in a Fisher Scientific™ Isotemp refrigerator under temperature control until later REE analysis.

3.2. Analytical procedures

All Thermo Scientific™ Nalgene™ collection bottles were filled with double distilled ultrapure nitric acid 5% (v/v), which is used as the cleaning acid. Each bottle filled with the cleaning acid was heated on a hotplate at 45 °C overnight. Afterwards, collection bottles were emptied of cleaning acid, rinsed once with milliQ™ water, and left under a fume hood to dry. The reusable filter holder used in this study was rinsed first with the cleaning acid and then with milliQ™ water between each usage. Additional cleaning acid was run through the filter holder in order to clean the inner workings of the device. All loose parts of filter were also acid cleaned each time.

All water samples were analyzed by an Agilent™ 7900 Quadrupole-Inductively Coupled Plasma Mass-Spectrometer (Q-ICP-MS) at the Department of Geological Sciences of the University of North Carolina at Chapel Hill. Double distilled, highly concentrated nitric acid was made into 2% (v/v) with milliQ™ water to carry samples into the Q-ICP-MS during analysis. An internal standard of 10 ppb Indium was utilized to monitor the instrumental drift. Calibration standards of 1000, 100, 10, and 5 ppt of the lanthanide group elements were made from a 1000 ppm REE standard to accurately measure the REE concentrations of dissolved loads in river waters. To minimized interferences oxides were controlled to be < 1% in no gas mode and < 0.3% in collision cell (He gas) mode. The instrument blank for individual elements during analysis was shown in Table S2.

Different sample preparation methods have been shown to reduce the sensitivity of REE analysis (Fisher and Kara, 2016). Thus, the SLRS-5 standard, which is a river water standard produced by the National

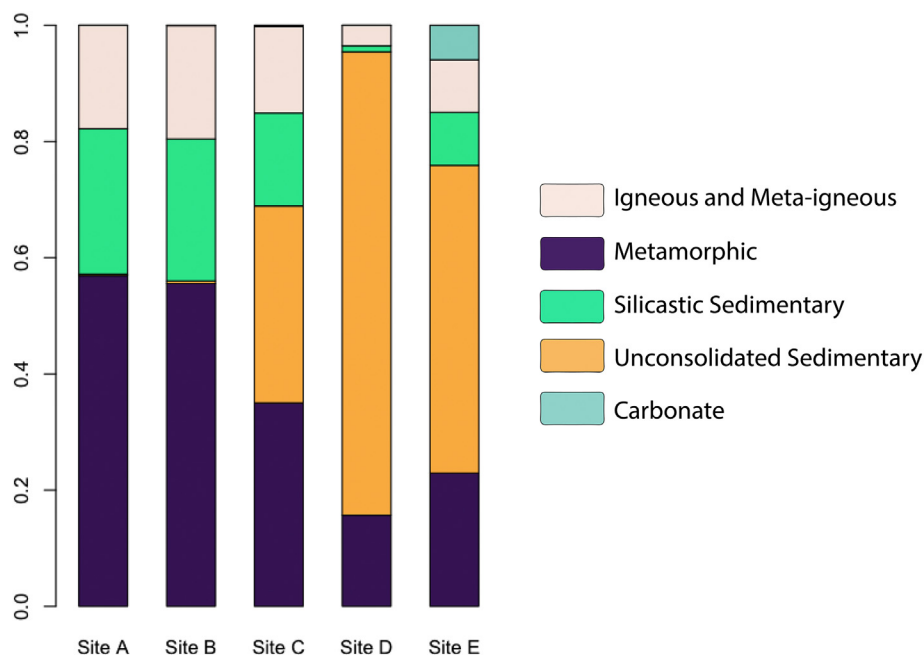


Fig. 2. Composite lithology percentage of each drainage basin feeding into respective sampling sites. Vertical length represents the lithological fraction a certain underlying rock type constitutes for its corresponding watershed.

Research Council of Canada (NRC), was repeatedly analyzed to evaluate the reproducibility and accuracy of the data. Replicate analysis ($n = 18$) of our SLRS-5 standard measured in both 'no gas' and 'helium gas' mode had relative standard deviation (RSD) ranging from 0.9–15.3% with a mean RSD of 5.0%. Repeated measurement ($n = 6$) of SLRS-5 compared with the compiled values of Yeghicheyan et al. (2013) produced accuracy data ranging from 0.8–13.9% with mean accuracy of 3.9% (see Supplementary Tables S3–S8).

4. Results

4.1. Catchment summary

Each site along the Neuse River has a different drainage area with its own unique lithological composition and localized water chemistry. Station lithology percent areas for each site are shown in Fig. 2. As moving downstream along the Neuse River, the lithological percent composition changes (see Supplementary Table S9 for exact values). Station D does not share any tributaries with stations A, B, and C. Stations A, B, C, and D drain through Site E.

Dissolved load REE concentrations collected from the Neuse River are reported in Table 1 (regard Table S3–S6 for duplicate measurements in Supplementary data). All reported REE concentrations fall in the range of ~1–500 parts per trillion (ppt). Surface water samples include both the dissolved load and the colloidal portions due to the pore-size (0.45 μm) of the filter (Leybourne and Johannesson, 2008; Pokrovsky and Schott, 2002). Due to the natural abundance of LREEs relative to HREEs in the upper crust and the naturally occurring Oddo-Harkins effect in the lanthanide sequence, shale-normalization of REE concentrations allows for better data comparison of REEs in dissolved loads of river water. Therefore, normalized REE pattern in the dissolved loads of river water tend to be relatively flat because they share a similar REE pattern with upper continental crust (Rudnick and Gao, 2013). However, most Gd values in the studied river water significantly differ from those reported in other natural river studies (Goldstein and Jacobsen, 1988) as shown by large Gd anomalies present in sites B, C, and E (Figs. 3 and 4). Possible causes of observed Gd anomalies will be discussed in details later in this paper.

A normalized ratio between lanthanum (La) and ytterbium (Yb) is

utilized to quantify the relative enrichment or depletion a specific group of the lanthanides (LREE or HREE) to others. Values that show enrichment are denoted as $[\text{La}/\text{Yb}]_p$ (Table 1) and expressed as:

$$[\text{La}/\text{Yb}]_p = [\text{La}/\text{Yb}]_{\text{SAMPLE}} / [\text{La}/\text{Yb}]_{\text{PAAS}} \quad (1)$$

where PAAS stands for Post Archean Australian Shale (Yeghicheyan et al., 2013). Although each station experiences varying levels of absolute concentrations (Fig. 5), overall shale normalized-patterns display various degrees of enrichment of HREEs over LREEs ($[\text{La}/\text{Yb}]_p < 1$) at all sites.

4.2. Station-station patterns

Stations A and B experience more confined REE concentration ranges and have noticeably lower total REE concentrations ($\Sigma\text{REE} = 213.2$ to 465.3 ppt) relative to the total REE concentrations in sites C and D ($\Sigma\text{REE} = 470.9$ to 1744.2 ppt) as seen in Fig. 5 and Table 1. Sites C and D experience higher total REE concentrations (max $\Sigma\text{REE} = 1744.2$ ppt) compared to all other sampling sites, including site E which is stationed slightly into the estuary system, at the end of the river's profile. Unlike the preceding 4 sites, station E, which is located within the estuary and experiences varying degrees of salinity levels ranging from 0.0 to 5.0 parts per thousand annually in 2015 and 2016 (MODMON). Due to the known effect of salinity, a net drop in total REE concentrations is expected at site E relative to preceding stations C and D (Elderfield et al., 1990). Other than HREE enrichment, Ce anomalies, and Gd anomalies, station-station shale-normalized data do not significantly differ along the Neuse River.

4.3. Cerium anomaly

Cerium experiences a naturally occurring oxidation state (Ce^{4+}) and therefore can be used to calculate cerium anomalies (Ce/Ce^*) values to indicate local redox conditions. Ce/Ce^* are quantified in Table 1 and expressed by the following:

$$\text{Ce}/\text{Ce}^* = 3\text{Ce}_p / (2\text{La}_p + \text{Nd}_p) \quad (2)$$

where subscript P refers to PAAS normalized concentrations (Bayon et al., 2015; Goldstein and Jacobsen, 1988; Yeghicheyan et al., 2013).

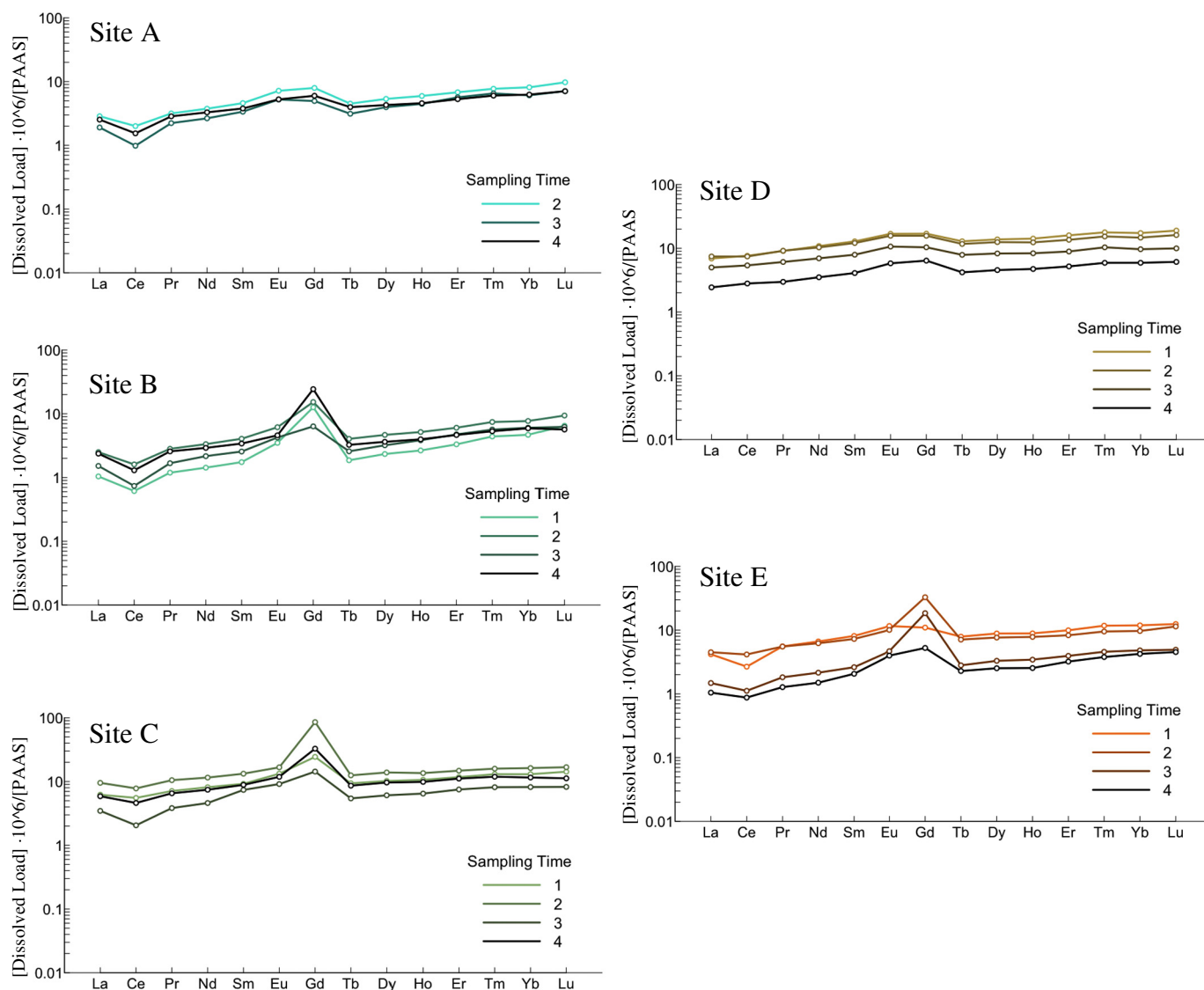


Fig. 3. PAAS shale-normalized REE patterns for each site (A–E). Each individual line represents a shale-normalized pattern for a specific sampling time, while each plot contains all shale-normalized pattern collected during the 4 different sampling times. Sampling times are as follows, 1, fall 2015; 2, winter 2015; 3, spring 2016; and 4, summer 2016.

As seen in Table 1, all Ce/Ce^* are smaller than 1, ranging from the lowest value occurring at site B ($Ce/Ce^* = 0.41$) to the highest occurring at site D ($Ce/Ce^* = 0.95$). Sites A and B experience the lowest Ce/Ce^* values during all sampling periods (0.41–0.60) while site D displays distinctively high negative Ce/Ce^* during each sampling period ($Ce/Ce^* = 0.88$ –0.95). Despite variability, station-to station Ce/Ce^* maintain similar values across seasons, which can be seen in Fig. 3. Interestingly, Site D experiences the least temporal variability (0.88–0.95) in Ce/Ce^* values while neighboring site E experiences the greatest range (0.51–0.78) of Ce/Ce^* variability.

5. Discussion

5.1. Control of REE patterns

The REE patterns of the Neuse River basin (Figs. 3 and 4) are characteristically flat with negative Ce anomalies, similar to those found in other dissolved load REE studies (Aubert et al., 2001; Cidu and Biddau, 2007; Elderfield et al., 1990; Goldstein and Jacobsen, 1988; Leybourne and Johannesson, 2008; Tricca et al., 1999). Similarities in the REE patterns of dissolved loads are attributed to the major factor pH

plays in controlling REEs in solution and interactions with solid phases (Goldstein and Jacobsen, 1988) due to the fact that natural waters tend to have pH values ranging from 6 to 8 (Sholkovitz et al., 1994). In contrast, differences in REE patterns observed in the Neuse River may reflect difference in local river chemistry and weathered material due to the localized ranges of pH being restricted at the five sampling sites with the exception of site B during its summer 2016 sampling period, which experiences an uncharacteristically low pH of 5.43. In this study, all dissolved load samples show $[La/Yb]_p$ values < 1 , indicating HREE enrichment relative to LREE. The greatest disparity of $[La/Yb]_p$ values occurs between site B and C during all sampling periods with its peak differentiation occurring during the fall 2015 collection period (from 0.17 to 0.36).

River $[La/Yb]_p$ trends (Fig. 6) vary in a consistent manner throughout different sampling times. An exception is noted between stations C and D during winter 2015, when $[La/Yb]_p$ values increase from station C to D. The consistency of the $[La/Yb]_p$ trend may indicate that local river chemistry remains relatively constant throughout the Neuse River despite seasonal differences. Less preferential adsorption of LREE onto secondary minerals, lower preferential HREE complexation, variability in DOC (which were not determined in this report), or

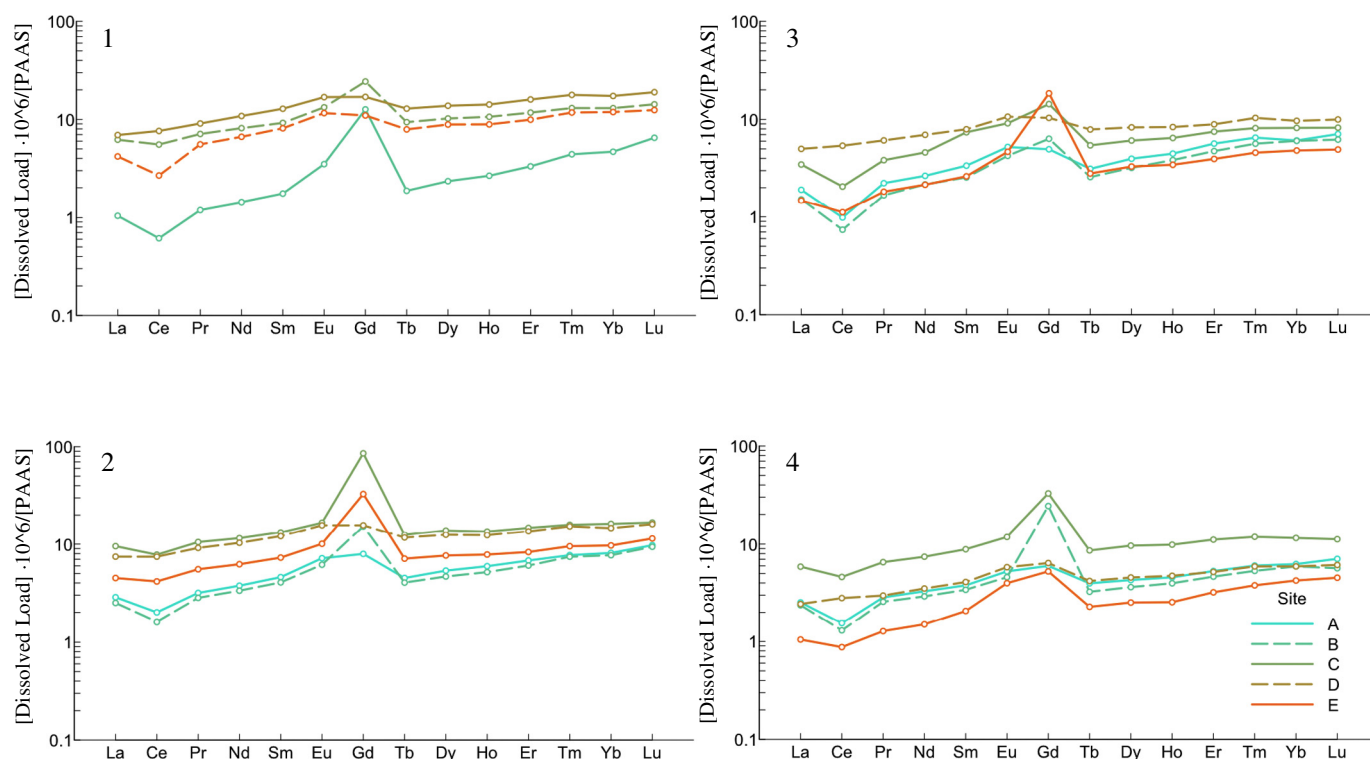


Fig. 4. PAAS Shale-normalized REE patterns of entire Neuse River from sampling locations A–E, with the exception of sampling time 1 which does not have a REE pattern for site A. Each plot includes the samples collected on the same day along the length of the river. Headwater represented by teal colors (site A) while mouth of the river is orange (site E), and the gradient colors are sites that fall between sites A and E. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

combination of the three could explain the systematic shift upwards in $[La/Yb]_p$ values between stations B and C (Kulaksiz and Bau, 2013; Shiller, 2010). Flux of HREE to the dissolved pool could also originate from dissolution and precipitation of oxides in river sediments and catchment soils (Liu et al., 2017; Shiller, 2010). This transition is also marked by a higher areal percentage of unconsolidated sedimentary rocks (Fig. 2), which could possibly modify secondary mineral formation processes and disrupt the sourcing of dissolved REE, at least to some small extent (Aubert et al., 2001; Goldstein and Jacobsen, 1988).

After station C, $[La/Yb]_p$ values slightly decrease at stations D and E except during sampling time 3 (spring 2016) at which $[La/Yb]_p$ values increase from station C to station D (Fig. 6). This decreasing trend does not support the assumption that an increasing areal percentage of unconsolidated sedimentary material increases $[La/Yb]_p$ values. Instead, HREE enrichment at station D and E could be explained by preferential incorporation of LREEs during the formation of secondary minerals and organic complexes (Kulaksiz and Bau, 2013). The addition of underlying carbonate lithology at station E could provide another explanation for the consistent HREE enrichment seen from station D to E (Figs. 1 and 2). More data regarding the REE composition of the carbonate influencing station E's dissolved load pattern is yet to be determined.

Stations A, B, and C all experience pronounced negative Ce/Ce^* values that vary at different sampling times. In contrast, station D lacks any strong negative Ce/Ce^* value and little seasonal variability (Ce/Ce^* from 0.84 to 0.95). Station D originates outside the tributaries of stations A, B, and C (Fig. 1). As opposed to stations A, B, and C, site D characterizes a sub drainage basin within the larger Neuse River basin that mainly drains atop unconsolidated sedimentary rock (Fig. 2). Station E, which is located at the mouth of the river, exhibits the largest Ce/Ce^* seasonal variability with values ranging from 0.51–0.78. The mixing of river waters between stations A, B, and C and waters draining through station D may be the process that increases the variability of

Ce/Ce^* values. The perpetual increase in Ce/Ce^* values and HREE enrichment between station D and E (Figs. 1 and 2) are consistent with the findings of other rivers draining over carbonate rock (Johannesson et al., 2000; Xu and Han, 2009).

5.2. Temporal variation of REE patterns

To determine the extent of seasonal variability, samples were collected during the fall (1), winter (2), spring (3), and summer (4). Excessive REEs (e.g. La, Sm, and Gd) have been shown to be a product of waste treatment (Hatje et al., 2016; Kulaksiz and Bau, 2013). Anomalous Gd was observed in this study and the degree varied throughout different sampling periods. Throughout the sampling periods total REE vary at each station (Table 1). REE concentrations in the Neuse River maintain similar ratios to each other under temporal chemical conditions throughout our study. However, stations B, C and D experience wider ranges of REE concentrations during each sampling period (Fig. 5). Ecological factors such as microbes, plants, and time weathering surfaces studied in a controlled setting have shown to influence overall REE mobility (Zaharescu et al., 2017). Thus, the decrease of REE mobilizing in the dissolved pool from winter to spring samplings may suggest that developing vascular plants in the Neuse River basin decrease total REE as suggested by Zaharescu et al. (2017). pH and turbidity were recorded at each sampling site during each sampling period, but no relationships between the REE and these parameters were found (Table 1). Seasonal redox, hydrological processes, and suspended loads may also influence to total dissolved REE load in the Neuse River, as well as inter-REE relationships (Shiller, 2010).

Station E experiences a wide range of total REE concentration, but unlike the other sites, station E is positioned near the estuary. The effects of estuarine salinity deplete total dissolved REE concentrations, but maintain the REE patterns (Bayon et al., 2015; Elderfield et al.,

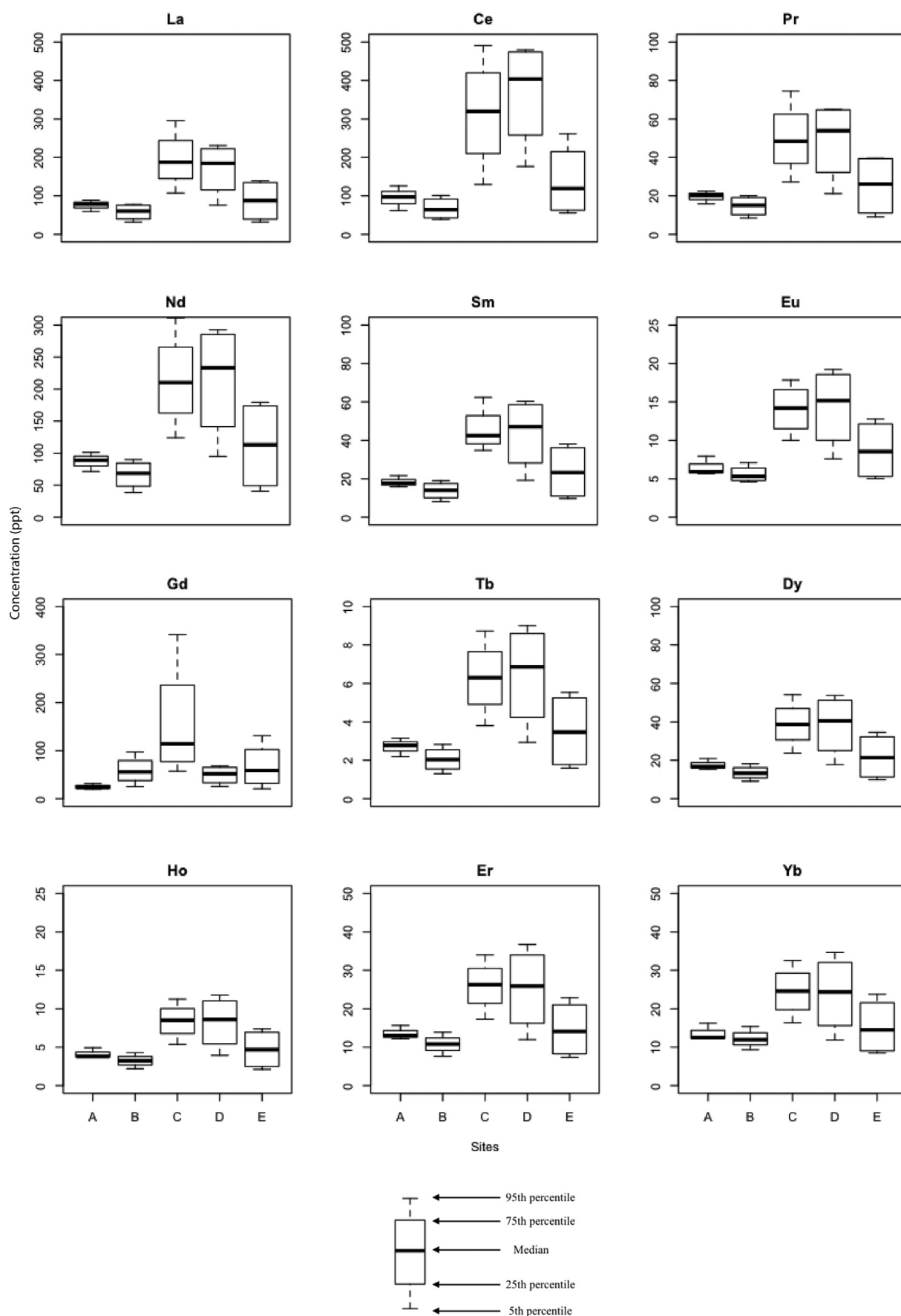


Fig. 5. Selected REEs are shown as box and whiskers plots indicating varied distribution of selected REE concentrations (Y-axis) at each site (X-axis). Each boxplot represents the specified REE concentration (ppt) of all sampling times. Values for each specific REE concentration can be found in [Table 1](#).

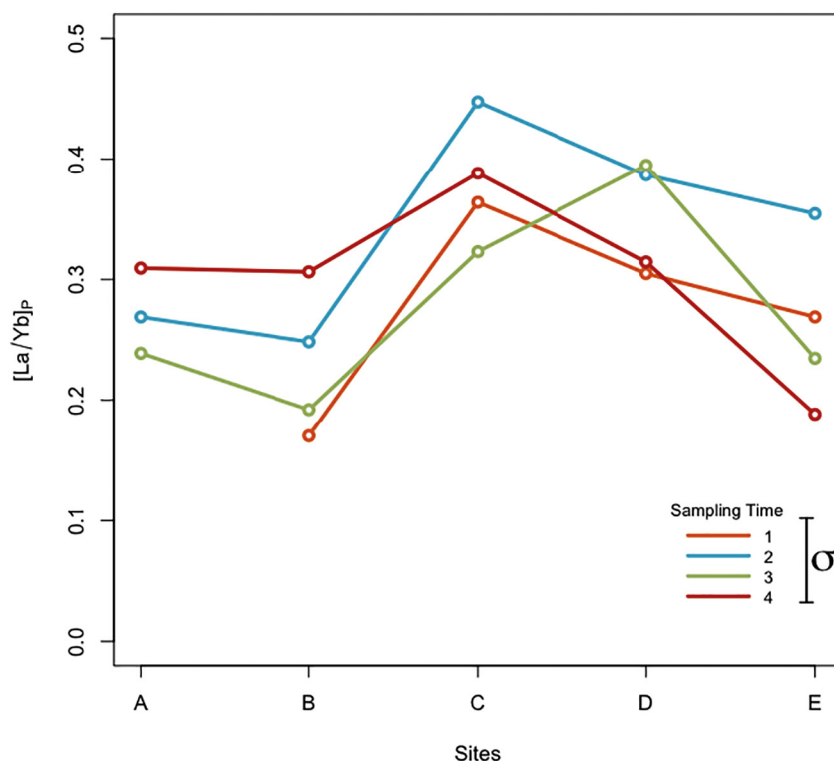


Fig. 6. PAAS shale-normalized $[La/Yb]_P$ values for each site (A–E). Subscript _P denotes PAAS normalization. Max standard deviation (σ) value of all samples = 0.7. Mean 2σ of all samples = 0.07. Sampling listed times are as follows, 1, fall 2015; 2, winter 2015; 3, spring 2016; and 4, summer 2016.

1990). Thus, salinity data at Site E were collected by MODMON around the time of sampling. Salinity values during these times were lower than 0.5 parts per thousand (ppt) except for the sampling time 1 (fall 2015) when salinity was 0.99 ppt. Thus, it may be the case that salinity depletes the total REEs of sample E1 by some amount, however, REE patterns should be unaffected.

Cidu and Biddau, (2007) have indicated that rivers exhibit HREE enrichment relative to LREE during periods of low energy, suggesting that the fractionation of REEs occurs via adsorption during the formation of secondary mineral phases. Since higher total REE concentrations in the river system may partially be responsible for the observed increasing $[La/Yb]_P$ values indicating high LREEs (e.g., La) compared to HREEs (e.g., Yb) (Fig. 7), REE adsorption by secondary minerals may partially explain why there is a consistent decrease in $[La/Yb]_P$ between stations D and E during each sampling period.

5.3. Gadolinium anomaly

Positive Gd Anomalies are observed in stations B, C, and E, (Fig. 3) and quantified in Table 1 with the following equations:

$$\log Gd^*_P = (4 \log Eu_P - \log Nd_P)/3 \quad (4)$$

$$Gd_{ANTH} = Gd_{MEASURED} - Gd^* \quad (5)$$

where subscript P denotes PAAS normalization, superscript * denotes a geogenic Gd source interpolated from Eu and Nd, Gd_{ANTH} denotes the calculated non-geogenic Gd by subtracting Gd^* from measured Gd ($Gd_{MEASURED}$) at each station (Kulaksiz and Bau, 2013). A distinctive feature of the shale-normalized patterns for station E is the lack of a positive Gd anomaly during the fall collection. Stations B and C exhibit pronounced positive Gd anomalies during each sampling period while station A and D experiences little to no positive Gd anomaly during the sampling periods. The spatial relationship of the sites indicates that either 1) high amounts of Gd enter the river at some location after site A and remains in dissolved phase throughout the system, or 2) Gd enters

the river at several locations along the length of the river after site A.

Since the early reports of anthropogenic Gd anomalies in rivers by Bau and Dulski (1996) similar positive Gd anomalies in dissolved loads have been reported in many urban rivers and coastal environments worldwide (e.g., Hatje et al., 2016; Kulaksiz and Bau, 2011; Möller et al., 2014). The observed positive Gd anomalies have been attributed to sewage and waste water treatment plants (Kulaksiz and Bau, 2013). Between sampling stations A and B along the Neuse lies the Neuse River Resource Recovery Facility, a waste water treatment plant, which may be the source of the positive Gd anomalies seen in Fig. 3. Determining if the Gd anomalies result from underlying rock-water interaction or human-activity is a difficult task given that background levels of Gd in the dissolved load have not previously been documented in the Neuse River. Comparing the shale-normalized patterns of dissolved loads of other rivers (salinity ~0 psu) in Fig. 8, we argue that the observed Gd anomalies in the Neuse River are not entirely a result of natural rock-water interaction (Aubert et al., 2001; Haley et al., 2014; Tricca et al., 1999). Therefore, we suggest that human activity produces positive Gd anomalies in the Neuse River by elevating Gd concentrations above naturally occurring background levels.

6. Conclusion

Shale-normalized REE patterns (ie. $[La/Yb]_P$ values, Ce anomaly, Gd anomaly, and total REE) of the dissolved load vary both spatially and temporally in the Neuse River, North Carolina. Shale normalized REE patterns are useful indicators of chemical weathering and transportation processes, but these insights may be obscured by the rise of anthropogenic REEs. Anthropogenic REEs, particularly Gd, have altered shale normalized patterns of dissolved loads by orders of magnitude both spatially and temporally.

The spatial and temporal variations of $[La/Yb]_P$ values and Ce anomalies are believed to be naturally occurring, suggesting that dissolved LREE and HREE complexation within the Neuse River cannot be completely captured by single point sampling. Collectively, $[La/Yb]_P$

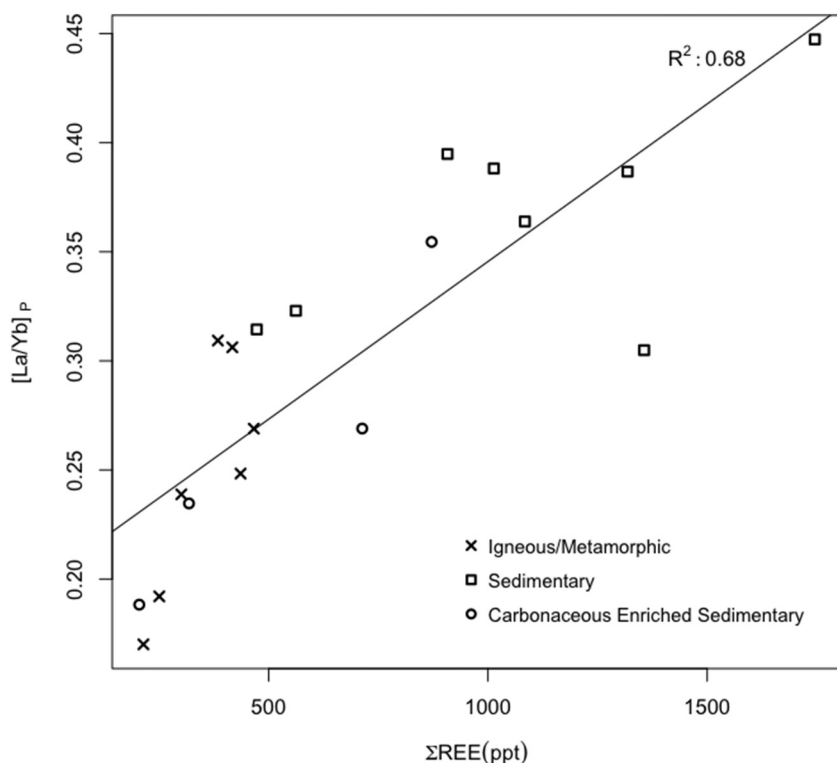


Fig. 7. PAAS shale-normalized $[La/Yb]_P$ values for each sampling site during all sampling periods. Total REE concentrations were calculated by summing La–Lu (ppt) values from Table 1. Positive linear correlation was determined via R function *lm()* and an ANOVA goodness of fit test was applied at a 0.99 confidence interval to conclude that the correlation was significant.

values increase with total REE concentrations in the dissolved load. This trend in complexation is likely controlled by 1) preferential weathering of LREEs during higher flow conditions, 2) uptake of LREE into secondary mineral phases during periods of low flow or a combination of the two. A more detailed investigation of local carbonate ions, organic ligand content, and other localized aquatic parameters could likely identify the critical factor that systematically controls $[La/Yb]_P$ in the Neuse River.

While most of the REE behavior in this study is controlled by hydrogeological processes, the observed Gd anomalies are not believed to be naturally occurring and are attributed to anthropogenic sources. Significant spatial and temporal variation in both Gd anomalies and total REEs in the dissolved load, which may have partially developed as a result of anthropogenic inputs of REEs in natural waters. Variability of inter-REE patterns identified in this study suggest that single point sampling may yield incorrect estimates of larger geologic processes due to natural REE complexation during weathering, and also because of rising anthropogenic REEs introduced into natural waters.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemgeo.2018.04.003>.

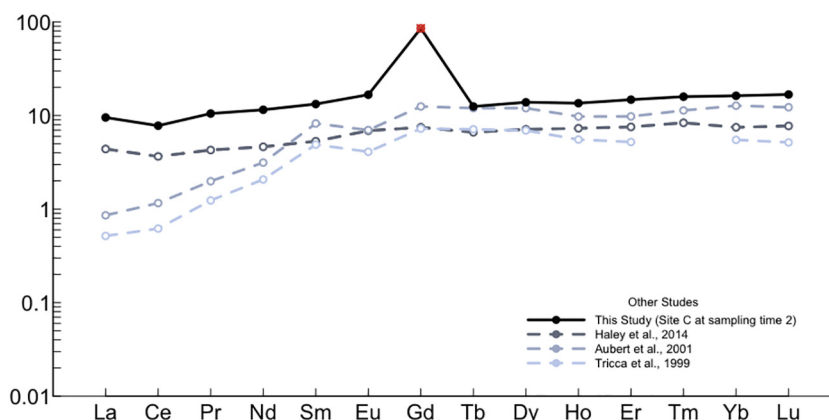


Fig. 8. PAAS shale-normalized values of dissolved river load samples from the Neuse River of this study, compared with the Strengbach Catchment, France (Aubert et al., 2001), river sample 4109;32 of the Vosges Rivers (Tricca et al., 1999), and the Copper River of Alaska (Haley et al., 2014).

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