Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting information for

Urban runoff drives titanium dioxide engineered particle concentrations in urban watersheds: field measurements

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1. Detailed description of the sampling locations

Saluda River: Water samples were collected from the lower Saluda River, Hope ferry landing, Columbia, SC 29072 (34°02'45.7"N 81°11'27.3"W) which is approximately 2.7 kms downstream from the Lake Murray dam **(Figure 1)**. The Lower Saluda River flows out of the Lake Murray dam and merges downstream with the Broad River. Therefore, lower Saluda River is an engineered river controlled from the Lake Murray dam. Lake Murray serves as a retention reservoir for the suspended particulate matters, those come with the stream of upstream Saluda River. The Saluda River is approximately 291 km long, originates in the Blue Ridge Mountains of northwest of Greenville County, South Carolina, and flows generally southeastwardly in South Carolina [1]. The Saluda River basin covers approximately 6535 square kilometers and contains twenty-one (21) watershed [2]. The dominant land use throughout the Saluda River basin is forested (53.7%); agricultural (26.1%); urban (12.9%); water (4.2%) and others (0.1-3.3%): swampland, barren land and marshland. There are permitted 9 major wastewater treatment plants (WWTP); 15 minor WWTPs; 92 industrial, mining and quarrying facilities, 35 municipal separate stormwater facilities in the Saluda River basin [3]. The Saluda River is crossed 26 times by many highways, and three of those highway's bridges cross the Saluda River near the sampling location. The lake Murray dam (34°03'14.4"N 81°13'9.8"W) on highway 6 between the lake Murray and lower Saluda River is situated 2.75km upstream from the sampling location, and had an estimated AADT of 26,700 in 2019 [4]. The I20 bridge over Saluda River (34°01'31.7"N 81°07'42.9"W) is situated 6.2kms downstream from the sampling location, and had an estimated AADT of 84,000 in 2019 [4]. The interstate I26 bridge (34°01'25.7"N 81°06'12.6"W) over Saluda River is situated 8.4km downstream from the sampling location, and had an estimated AADT of 95,400 in 2019 [5].

Water samples were collected from the Saluda River during a range of hydrologic conditions (**Table S5**). There had been 20.5 mm rainfall (in total) during the entire sampling campaign with a major rainfall event of 15.7 mm occurred on 30/4/2020 near the sampling location. Major rainfall events of 54.5 mm and 3.1 mm occurred on 29/4/2020 and 30/4/2020 in the upstream region of the Saluda River at Rock reservoir, Cleveland, SC [6]. The rainfall and discharge data were collected from the USGS station number 02168504 (34°03'03"N 81°12'35"W), nearly 1.8 km upstream from the sampling location.

Broad River: Water samples were collected from the Broad River, Columbia rowing club, Columbia, SC 29201 (34°02'36.9"N 81°04'23.7"W) **(Figure 1)**. The Broad River is approximately 240 km long, originates in the Blue Ridge Mountains of eastern Buncombe County, North Carolina, and flows generally south-southeastwardly in South Carolina. The total catchment area of the Broad River is approximately 14,000 square kilometers. Apart from the forested land (66%) in the headwaters of the Broad River basin; the dominant land use throughout the Broad River basin is agricultural (23%); urban (9%): commercial and residential; others (2-4%): mining operations, and logging operations. There are permitted 14 major wastewater treatment plants (WWTP), 30 minor WWTPs, 20 animal operation facilities, 92 general and individual stormwater facilities in the Broad River basin [7]. The Broad River is crossed 22 times by many highways. There are three bridges crossing the Broad River near the sampling location. The interstate I20 bridge (34°02'52.5"N 81°04'23.6"W) over Broad River is situated 481m upstream from the sampling location, and had an estimated AADT of 119,100 in 2019 [5]. The Broad River bridge on highway 176 (34°01'33.3"N 81°04'9.9"W) is situated 2 kms downstream from the sampling location, and had an estimated AADT of 24,400 in 2019 [5]. The interstate I126 bridge (34°00'33.7"N 81°03'36.1"W) over Broad River is situated 4km downstream from the sampling location, and had an estimated AADT of 71,800 in 2019 [5].

Water samples were collected from the Broad River during a range of hydrologic conditions (**Table S4**). There had been 18.8 mm rainfall (in total) during the entire sampling campaign with a major rainfall event of 16.8 mm occurred on 30/4/2020 near the sampling location. Moreover, there were major rainfall events of 40.2 mm and 9.7 mm occurred on 29/4/2020 in the upstream region of the Broad River at Ashville, NC and Knoxville, TN respectively [8,9]. The rainfall data was collected from the USGS station number 021695045 (34°00'24"N 81°01'18"W), nearly 3.1 km from the sampling location. The **discharge** data was

collected from the USGS station number 02162035 (34°02'54"N 81°04'24"W), nearly 5.3 km upstream of the sampling location.

Congaree River: Water samples had been collected from the Congaree River at West Columbia Riverwalk, West Columbia, SC 29169 (33°59'35.4"N 81°03'1.8"W) and Thomas Newman public boat landing, Cayce, SC 29033 (33°56'57.3"N 81°01'44.1"W) **(Figure 1)**. Thomas Newman public boat landing sampling location is 5.3 km downstream of West Columbia Riverwalk sampling location. The Congaree River basin is formed by the confluence of the Saluda and Broad River basins in central South Carolina near Columbia. Therefore, the Broad River and Saluda River merge to form the Congaree River, which flows southeasterly for 50 miles and merges with the Wateree River to form the Santee River Basin which finally discharges into the Atlantic Ocean. The Congaree River basin area is 1785 square kilometers and contains four (04) watersheds. In the Congaree River basin, 34.6% is forested land, 26.6% is agricultural land, 19.0% is forested wetland (swamp), 17.9% is urban land, 0.3% is barren land, 1.3% is water, and 0.3% is non-forested wetland (marsh). There are permitted 2 major wastewater treatment plants (WWTP); 4 minor WWTPs; 35 industrial, mining and quarrying facilities; 20 municipal separate stormwater facilities in the Congaree River basin [3]. The Congaree River is crossed 7 times by many highways. There are three bridges crossing the Congaree River near the sampling locations. The Jarvis Klapman Blvd bridge (33°59'57.2"N 81°03'12.3"W) on highway 12 and The Gervais street bridge on highway 1 (33°59'43.8"N 81°03'6.9"W) are situated 729 m and 288 m respectively upstream from the Congaree River, Columbia sampling location, and had an estimated AADT of 22,700 and 28,000 respectively in 2019 [4]. The Blossom street bridge (33°59'17"N 81°02'48"W) on highway 176 over Congaree River is situated 674 m downstream from the Congaree River, Columbia sampling location and 4.6 km upstream from the Congaree River, Cayce sampling location, and had an estimated AADT of 27,500 in 2019 [5].

Congaree River is downstream from the confluence of the Saluda and Broad River, therefore, the prevailed diverse climatic or hydrologic conditions on the upstream of the Saluda and Broad River during the sampling campaign also affected the Congaree River. Moreover, the Congaree River basin's hydrologic conditions had also been diverse during the water samples collection (**Table S4**). There had been 18.8 mm rainfall (in total) during the entire sampling campaign with a major rainfall event of 16.8 mm occurred on 30/4/2020 near the sampling location. The rainfall data was collected from the USGS station number 021695045 (34°00'24"N 81°01'18"W), nearly 3.1 km from the West Columbia Riverwalk sampling location and 6.4 km from the Thomas Newman public boat landing sampling location. The discharge data were collected from the USGS station number 02169500 (33°59'35"N 81°03'00"W), nearly 0.05 km from the West Columbia Riverwalk sampling location and 5.3 km from the Thomas Newman public boat landing sampling location.

2. Sample digestion

The bulk river water samples were digested in 15 mL Teflon vessels (Savillex, Eden Prairie, MN, United States) on custom-made Teflon covered hotplates placed in a box equipped with double-HEPA filtered forced air in a metal-free HEPA filtered air clean lab. 10 mL water aliquots or 5 mL extracted particle suspensions were placed in the vessel and weighed (Mettler Toledo, Excellence Plus, Columbus, OH, United States). Samples were dried at 110°C and treated with 1 mL of 30% H_2O_2 (Fisher Chemical, Fair Lawn, NJ, United States) for 2 h at 70°C to remove organic matters. H_2O_2 was then evaporated, and the sample was digested with 2 mL of HF:HNO_3 (3:1) mixture (ACS grade acids distilled in the laboratory, Sigma Aldrich, St. Louis, MO, United States) for 48 h at 110°C. After evaporation of the acid mixture at 110°C, the residue was reacted with 1 mL of distilled HNO_3 to break up insoluble fluoride salt that may have formed during the sample digestion and HNO_3 was left to evaporate at 110°C. This step was repeated twice before weighing the sample and adding 5 mL of 1% HNO_3. The sample was sonicated for 10 min in a sonication bath (Branson, 2800, 40kHz, Danbury, CT, United States) and warmed for 2 h at 50°C for full dissolution. The solution was transferred to 15 mL polypropylene centrifuge tubes (Fisher Scientific, San Nicolás de los Garza, Nuevo León, Mexico) and stored at 4°C. Samples were centrifuged (Eppendorf, 5810 R, Hamburg, Germany) for 5 min at 3100 g prior to ICP-MS analysis as prophylactic measure to remove

any undigested minerals in order to prevent clogging of the ICP-TOF-MS introduction system. This step does not impact the recovery (approximately 100%), precision (2-3%), or the accuracy (better than 5%) of metal analysis as demonstrated in our previous studies [10,11].

Table S1. Power plants on the Broad River.

Power plant	GPS Coordinates	Type	Distance from the sampling site	Type of dam/water control
Duke Energy -- Cliffside Plant	35°12'47.9"N, 81°45'39.2"W	Thermo	145 km	
Broad River energy, Cherokee	35°4'53.4"N, 81°34'18.9"W	Thermo	124 km	
Power plant 1, Cherokee	35°3'52.2"N, 81°32'41.6"W	Hydro	120 km	Gravity-type concrete spillway
Magna Energy Systems	34°59'57.5"N, 81°56'11.6"W	Hydro	132 km	Low head
Lower Pacolet Hydro	34°55'11.9"N, 81°44'16.2"W	Hydro	115 km	Low head
Lockhart Power Company	34°46'46.3"N, 81°27'24.9"W	Hydro	89 km	Diversion and Low head
Neal Shoals Hydro, Union Hydroelectric project	34°39'51.8"N, 81°26'54.8"W	Hydro	77 km	Low head
SCE&G - Fairfield Pumped Storage, Jenkinsville, SC 29065	34°18'19.7"N, 81°19'54.8"W	Hydro	38 km	Diversion
Virgil C. Summer Nuclear Station	34°17'52.5"N, 81°18'55.9"W	Thermo	36 km	
Parr hydro	34°15'35.2"N, 81°19'50.4"W	Hydro	34 km	low head
Columbia Hydroelectric Project	34°0'8.5"N, 81°3'14.8"W	Hydro	4 km	low head

Table S2. The annual average daily traffic (AADT) on the bridges crossing the Broad, Saluda and Congaree Rivers near the sampling locations in 2019.

Name of the River	Highways	GPS coordinates	Distance from respective sampling location	AADT	Ref
Saluda River	The interstate I26 bridge	34°01'25.7"N 81°06'12.6"W	8.4 km downstream	95,400	5
	The I20 bridge	34°01'31.7"N 81°07'42.9"W	6.2 km downstream	84,000	4
	The lake Murray dam	34°03'14.4"N 81°13'9.8"W	2.75 km upstream	26,700	4
Broad river	The interstate I126 bridge	34°00'33.7"N 81°03'36.1"W	4 km downstream	71,800	5
	The Broad River bridge on highway 176	34°01'33.3"N 81°04'9.9"W	2 km upstream	24,400	5
	The interstate I20 bridge	34°02'52.5"N 81°04'23.6"W	481 m upstream	119,000	5
Congaree River	The Jarvis Klapman Blvd bridge	33°59'57.2"N 81°03'12.3"W	729 m upstream Columbia sampling location	22,700	4
	The Gervais Street bridge on highway 1	33°59'43.8"N 81°03'6.9"W	288 m upstream Columbia sampling location	28,000	4
	The Blossom Street bridge	33°59'17"N 81°02'48"W	4.6 km upstream the Cayce sampling location	27,500	5

3. Operating conditions of TOFWERK ICP-TOF-MS.

Table S3. TOFWERK ICP-TOF-MS operating conditions.

Instrument parameter	**Value**				
Plasma Power	1550 V				
Nebulizer Gas Flow	1.1 L/min				
Auxiliary Gas Flow	0.8 L/min				
Cooling Gas Flow	14 L/min				
Injector Diameter	2.5 mm				
Collision Cell Gas	5 mL/min He with 4.5% H_2				
CCT Bias	-4.15 V				
Notch	Mass	29	32	36.3	41
	Amplitude (V)	1.6	2.0	2.0	1.2
TOF Repetition Rate	33 kHz				
Detected Mass Range	14-275 m/Z				
(CeO/Ce)	< 3.0%				
Data Acquisition	Continuous Mode				
TOF Time Resolution	300 ms for elemental concentration, 2 ms for particle analysis				
Sample Flow Rate	0.4 mL/min				

4. Elemental analysis of standard materials

Table S4. Elemental analysis of the USGS reference materials BHVO-2 Hawaiian basalts.

Concentration (µg/kg)	Mean	Standard Deviation	Recommended values [12]	Precision (%)	Error (%)	Accuracy (%)
^{27}Al	7.55×10^7	3.13×10^6	7.11×10^7	4.15	6.1	93.9
^{49}Ti	1.52×10^7	5.73×10^5	1.64×10^7	3.78	4.1	95.9
^{57}Fe	9.43×10^7	3.44×10^6	8.67×10^7	3.65	8.8	91.2
^{90}Zr	1.51×10^5	4.45×10^3	1.71×10^5	2.94	11.7	91.9
^{93}Nb	1.57×10^4	1.24×10^2	1.81×10^4	0.79	11.0	89.0
^{139}La	1.38×10^4	3.98×10^2	1.52×10^4	2.89	2.9	97.1
^{140}Ce	3.39×10^4	9.29×10^2	3.75×10^4	2.74	4.3	95.7
^{141}Pr	4.77×10^3	1.20×10^2	5.34×10^3	2.52	4.8	95.2
^{142}Nd	2.23×10^4	4.01×10^2	2.43×10^4	1.80	2.0	98.0
^{152}Sm	5.70×10^3	1.24×10^1	6.02×10^3	0.22	5.3	94.7
^{153}Eu	1.91×10^3	1.77×10^0	2.04×10^3	0.09	6.3	93.7
^{158}Gd	6.33×10^3	1.96×10^2	6.21×10^3	3.10	1.9	98.1
^{159}Tb	9.06×10^2	4.12×10^0	9.39×10^2	0.45	3.5	96.5
^{164}Dy	5.01×10^3	3.66×10^1	5.28×10^3	0.73	5.1	94.9
^{165}Ho	9.42×10^2	3.15×10^1	9.89×10^2	3.34	4.7	95.3
^{166}Er	2.44×10^3	4.12×10^0	2.51×10^3	0.17	3	97.0
^{169}Tm	3.36×10^2	2.38×10^1	3.35×10^2	7.09	0.3	99.7
^{174}Yb	1.92×10^3	3.20×10^1	1.99×10^3	1.67	3.7	96.3
^{175}Lu	3.24×10^2	2.61×10^1	2.75×10^2	8.07	14.2	85.8

Precision (%) = standard deviation/mean * 100

Error (%) = |(Measured concentration – recommended value)| / recommended value * 100

Accuracy = 100 –Error (%)

5. Precipitation, discharge, base flow and runoff

Table S5. Total daily precipitation (mm) in the sampling locations, Columbia, SC during the sampling campaign. S: Lower Saluda River, B: Broad River, Co: Congaree River at Columbia, and C: Congaree River at Cayce, ADP: Antecedent dry period

Date	Precipitation (B)	Precipitation (Co and C)	Precipitation (S)	ADP (Days) (C and B)	ADP (Days) (S)
27/4/2020	0	0	0		
28/4/2020	0	0	0		
29/4/2020	0.5	0.5	2.5	5	4
30/4/20020	16.8	16.8	15.7	0	0
1/5/2020	0	0	0		
2/5/2020	0	0	0		
3/5/2020	0	0	0		
4/5/2020	0	0	0		
5/5/2020	0.5	0.5	0	4	
6/5/2020	0	0	1.5		5
7/5/2020	0	0	0		
8/5/2020	1.0	1.0	0.8	2	1
9/5/2020	0	0	0		
10/5/2020	0	0	0		
11/5/2020	0	0	0		
12/5/2020	0	0	0		

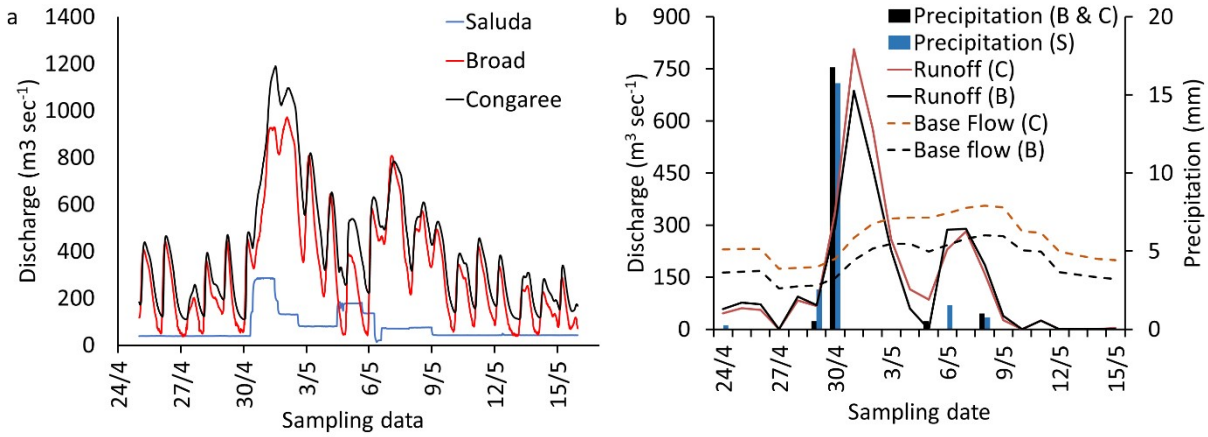


Figure S1. (a) 15-minutes time resolution discharge in the Saluda, Broad, and Congaree Rivers and (b) the separated runoff and baseflow in the Broad and Congaree Rivers based on daily discharge data together with the precipitation in Columbia, South Carolina near the Lower Saluda River (S), Broad and Congaree River (B & Co).

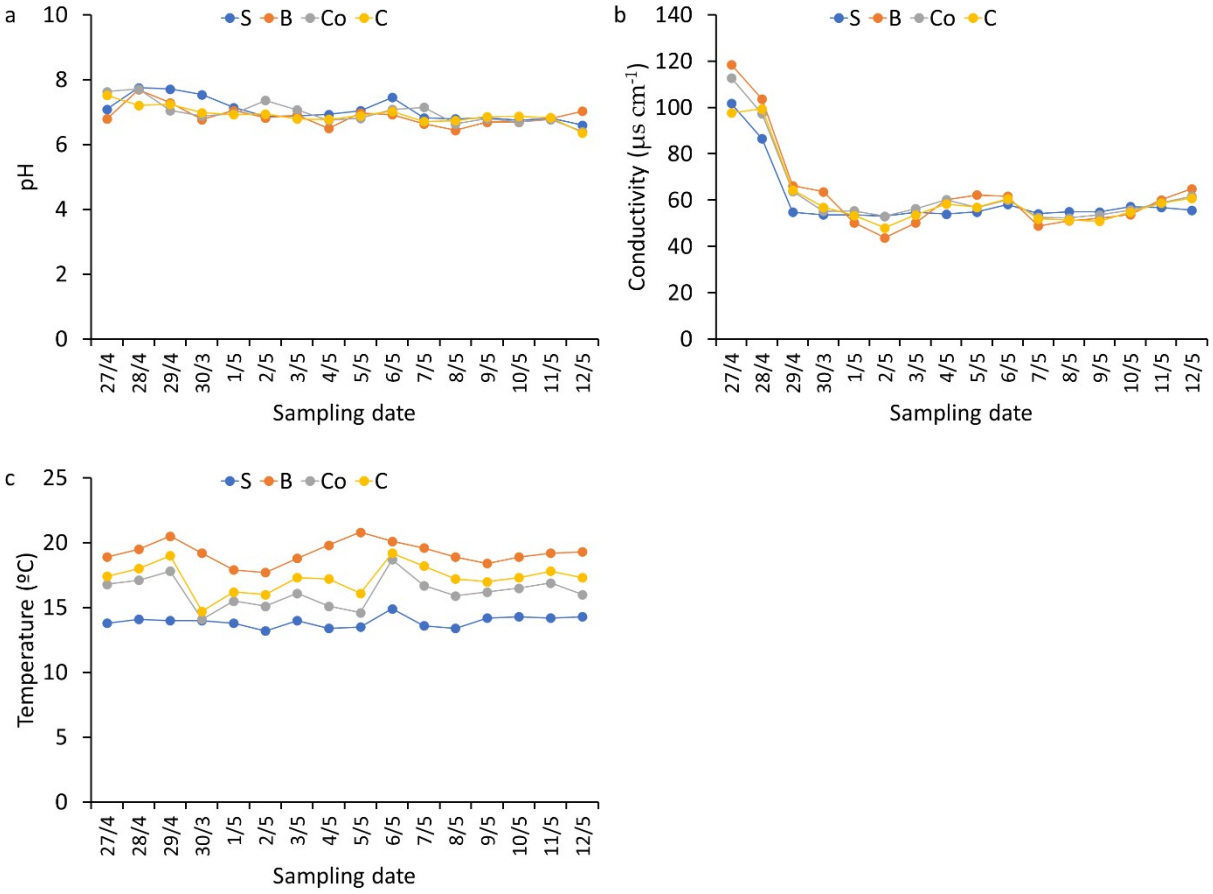
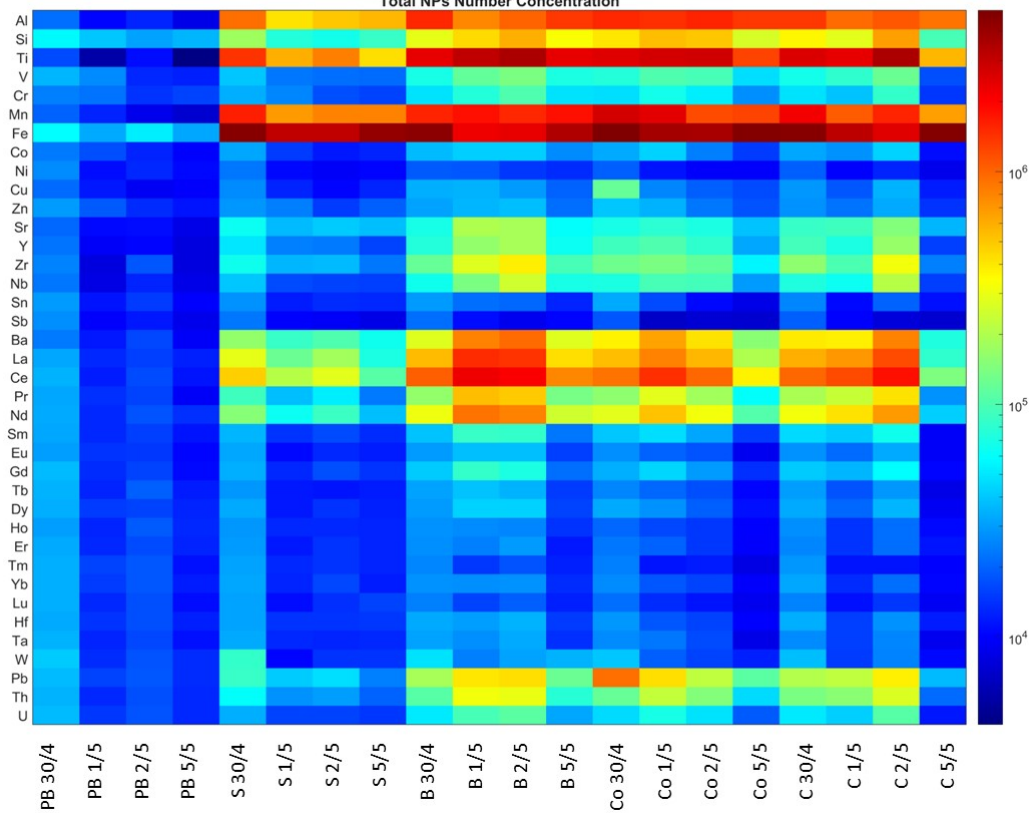


Figure S2. Water physicochemical properties at the sampling sites during the sampling period (a) pH, (b) conductivity, and (c) temperature. S: Lower Saluda River, B: Broad River, Co: Congaree River at Columbia, and C: Congaree River at Cayce.

a


Total NPs Number Concentration
Al
Si
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Sr
Y
Zr
Nb
Sn
Sb
Ba
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Hf
Ta
W
Pb
Th
U
10^6
10^5
10^4
PB 30/4
PB 1/5
PB 2/5
PB 5/5
S 30/4
S 1/5
S 2/5
S 5/5
B 30/4
B 1/5
B 2/5
B 5/5
Co 30/4
Co 1/5
Co 2/5
Co 5/5
C 30/4
C 1/5
C 2/5
C 5/5

b

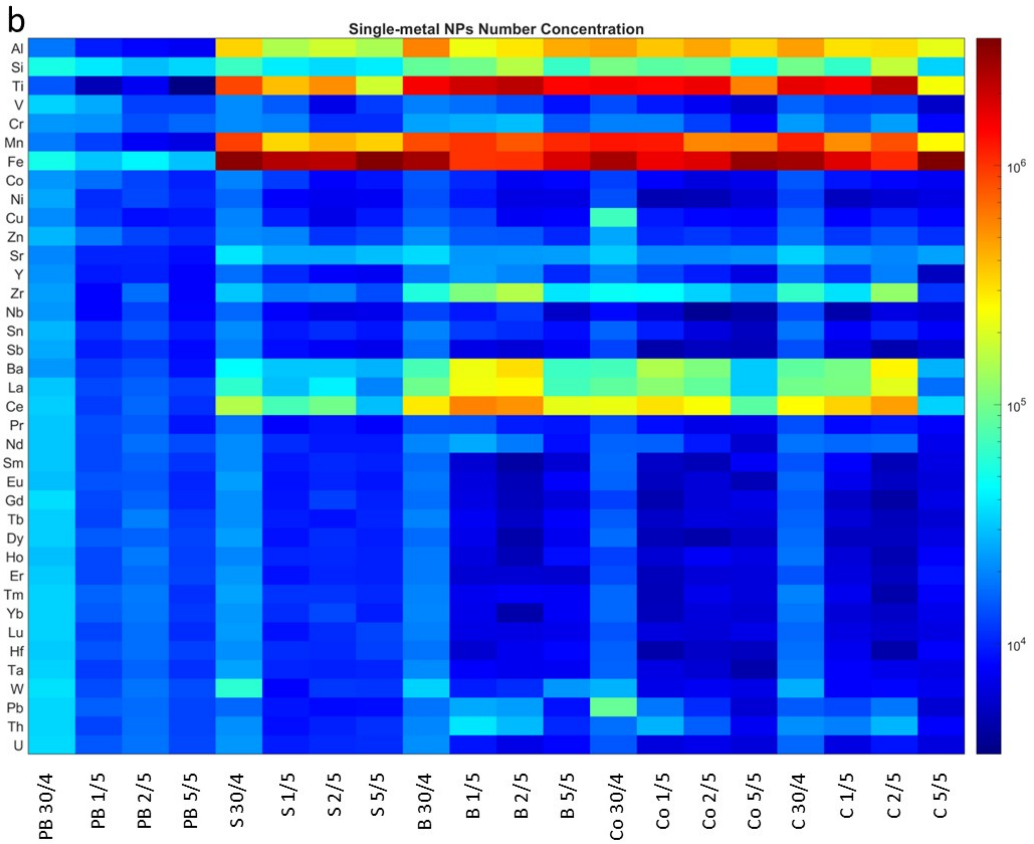
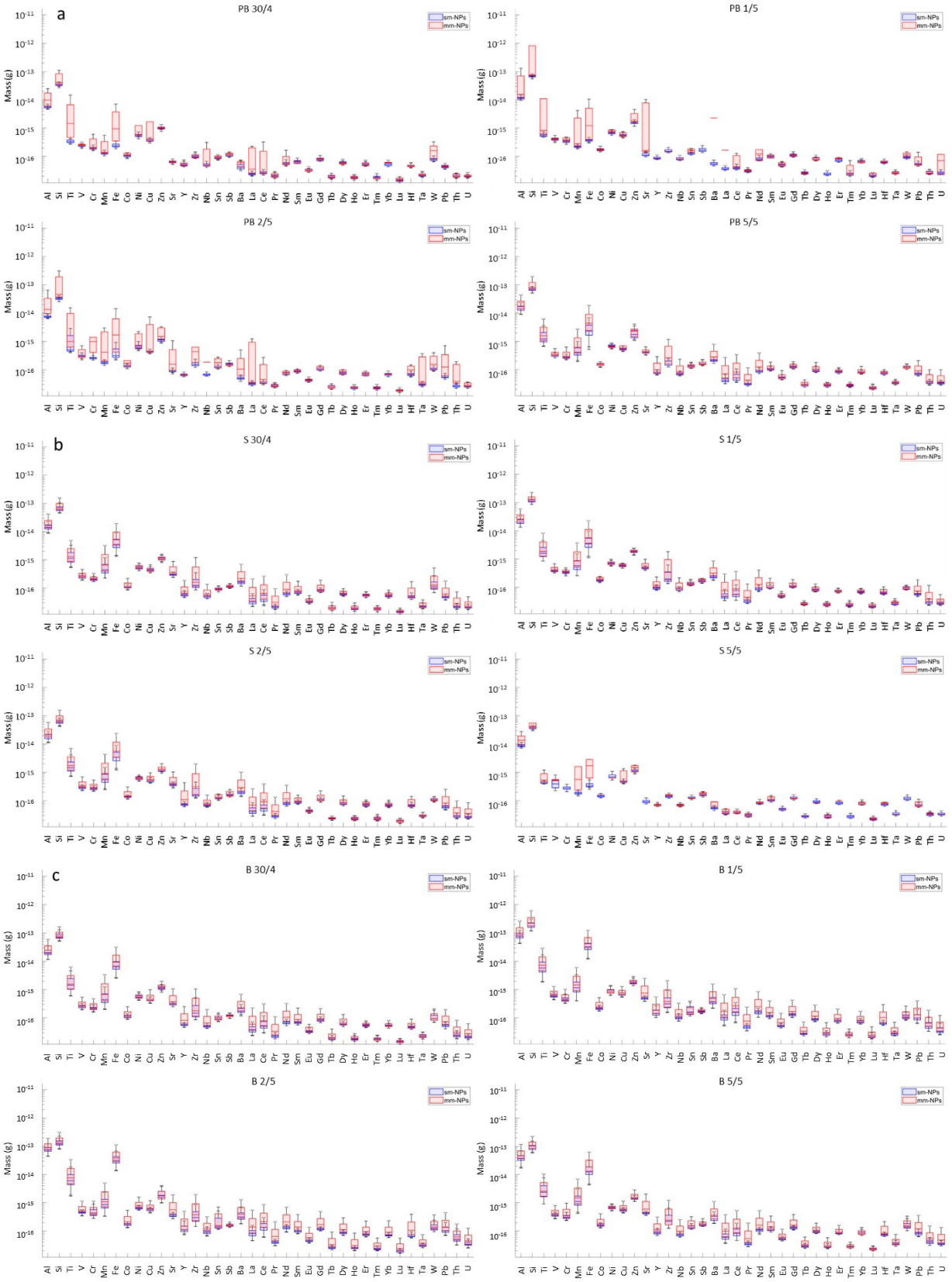

Single-metal NPs Number Concentration
Al
Si
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Sr
Y
Zr
Nb
Sn
Sb
Ba
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Hf
Ta
W
Pb
Th
U
10^6
10^5
10^4
PB 30/4
PB 1/5
PB 2/5
PB 5/5
S 30/4
S 1/5
S 2/5
S 5/5
B 30/4
B 1/5
B 2/5
B 5/5
Co 30/4
Co 1/5
Co 2/5
Co 5/5
C 30/4
C 1/5
C 2/5
C 5/5

Figure S3. Uncorrected number concentrations of (a) NPs, (b) smNPs and (c) mmNPs in procedural blanks and the selected River samples. PB: procedural blanks, S: Lower Saluda River, B: Broad River, Co: Congaree River at Columbia, and C: Congaree River at Cayce.


a
PB 30/4
PB 1/5
PB 2/5
PB 5/5
b
S 30/4
S 1/5
S 2/5
S 5/5
c
B 30/4
B 1/5
B 2/5
B 5/5
sm-NPs
mm-NPs
Mass (g)

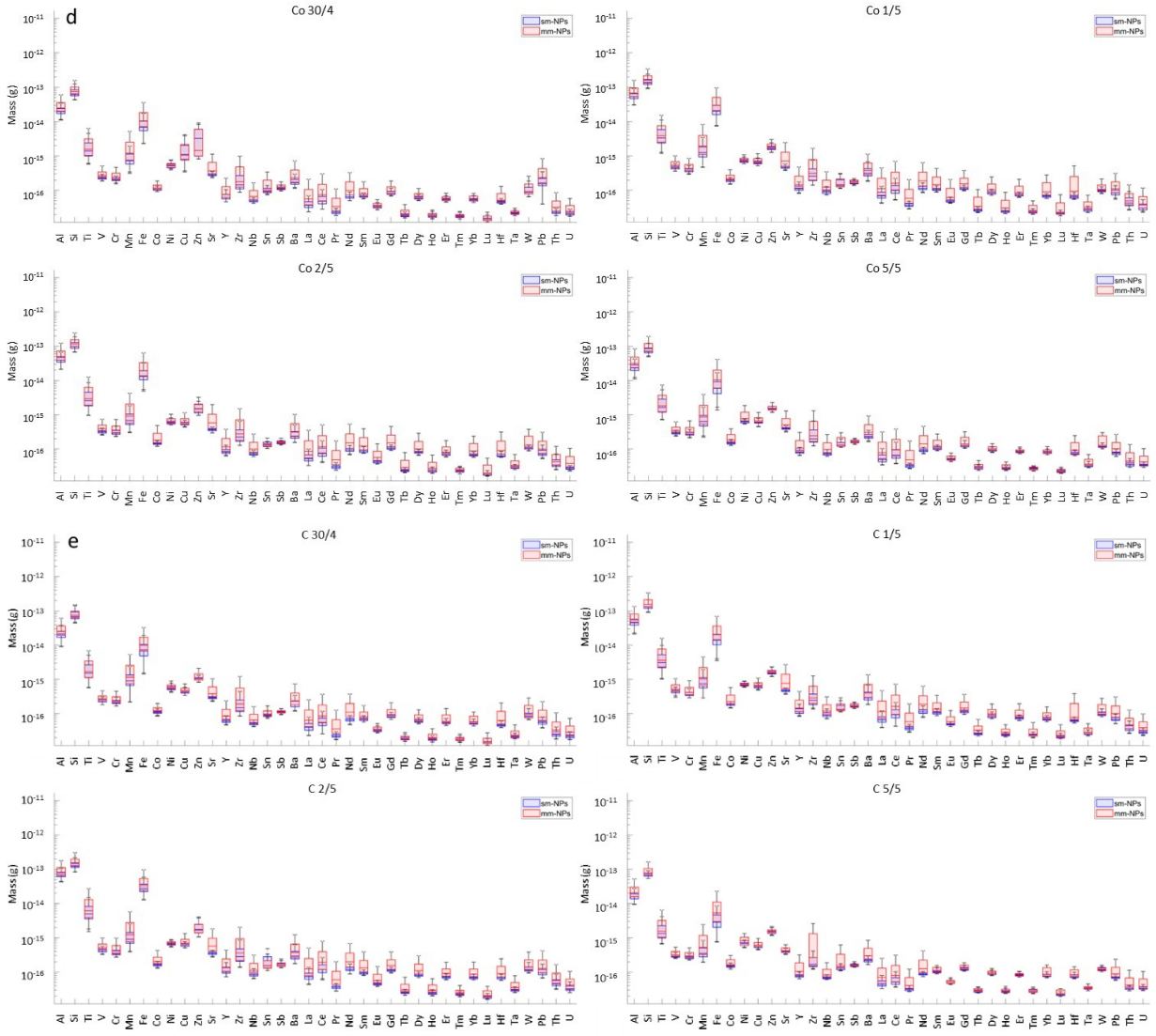


Figure S4. Mass distribution of smNPs (blue) and mmNPs (red) within individual particles in (a) procedural blanks (PB), (b) Lower Saluda River (S), (c) Broad River (B), (d) Congaree River at Columbia (Co), and (e) Congaree River at Cayce (C).

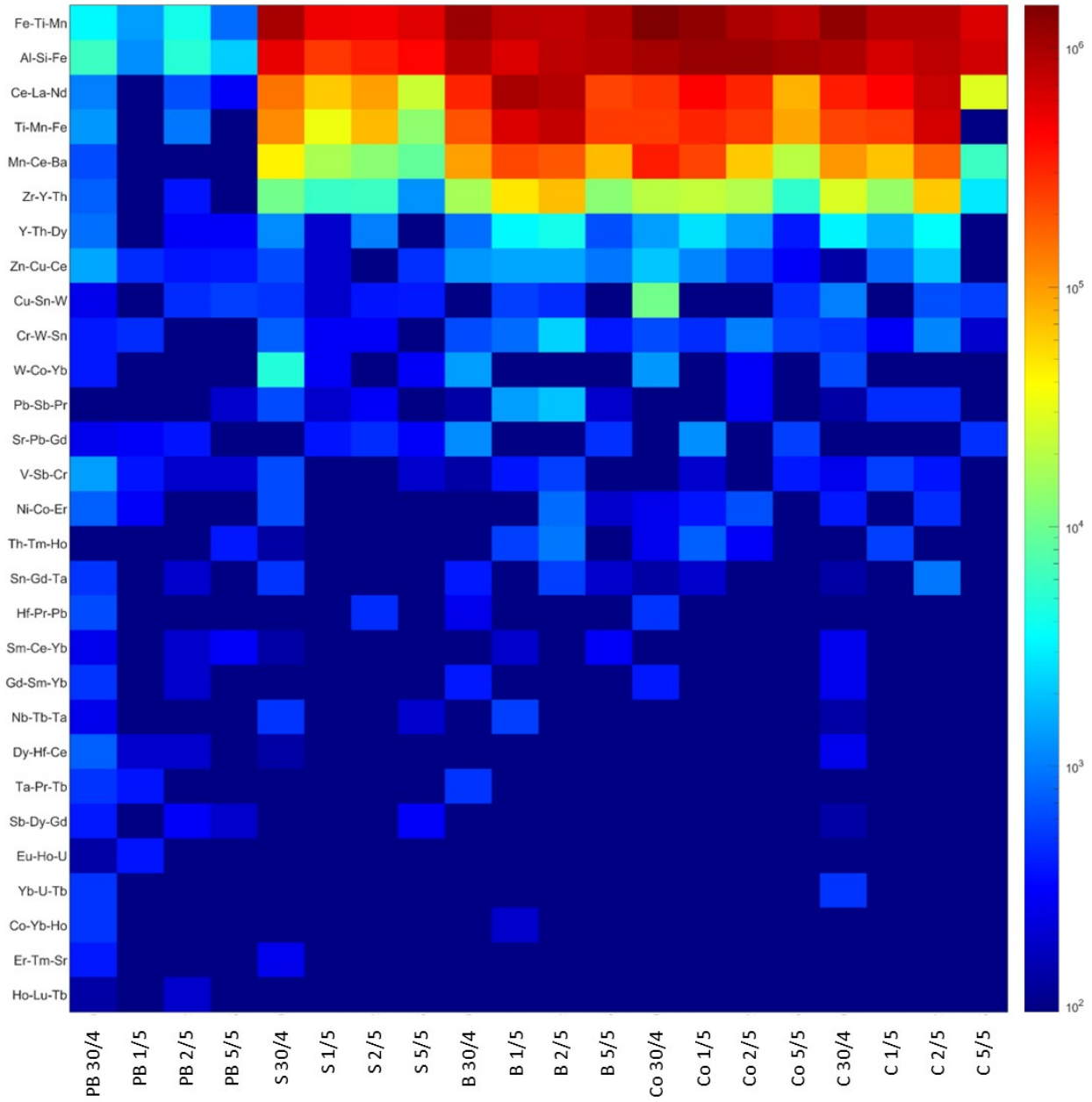


Figure S5. Number concentrations of the members of mmNP clusters. Clustering parameters were: maximum number of first stage clusters = 30, first and second stage cutoffs were 0.65 and 0.2. PB: procedural blank, S: Lower Saluda River, B: Broad River, Co: Congaree River at Columbia, and C: Congaree River at Cayce.

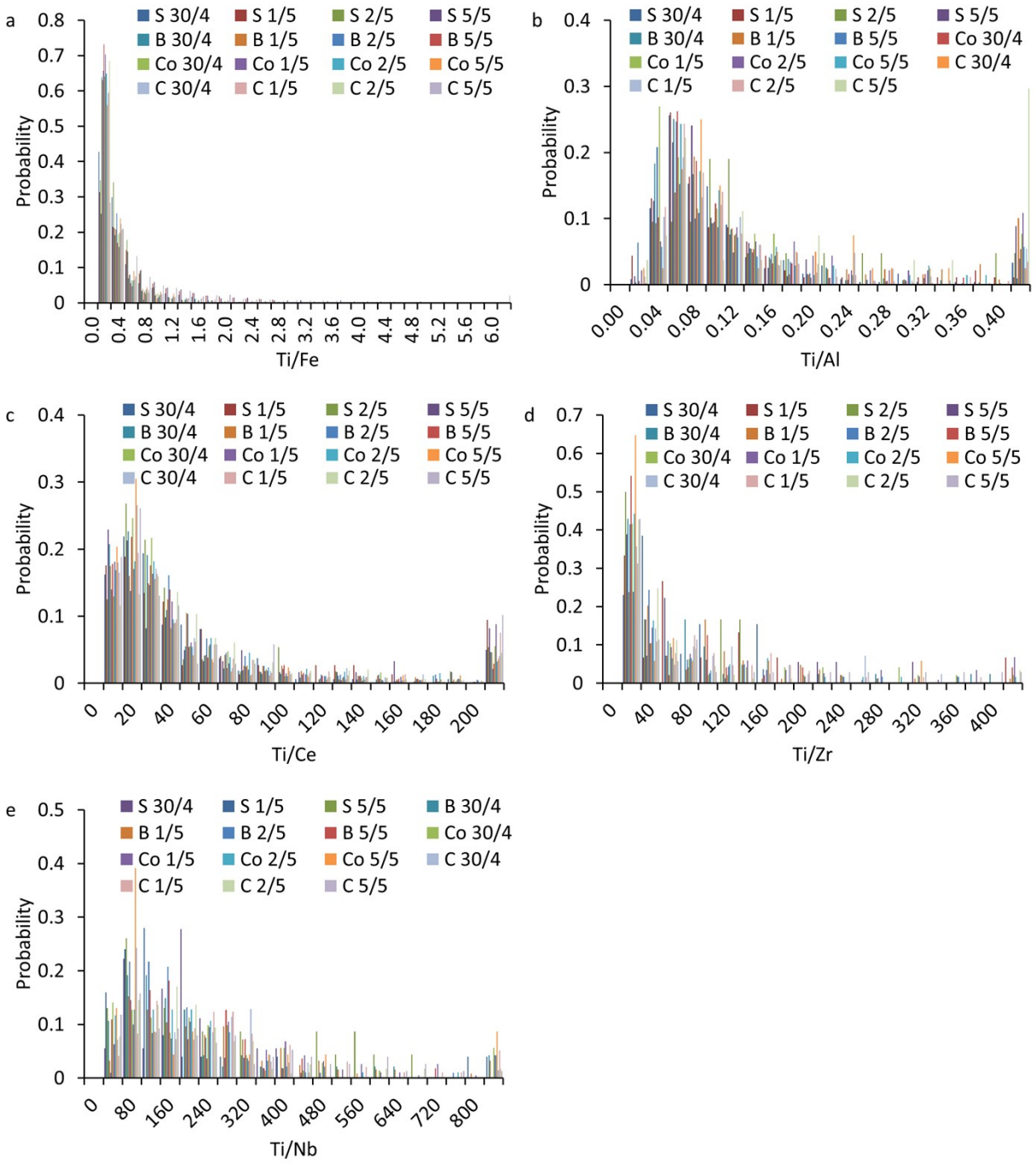


Figure S6. Elemental ratios of (a) Ti/Fe and (b) Ti/Al, and (c) Ti/Ce, (d) Ti/Zr, and (e) Ti/Nb in Fe-rich clusters. S: Lower Saluda River, B: Broad River, Co: Congaree River at Columbia, and C: Congaree River at Cayce.

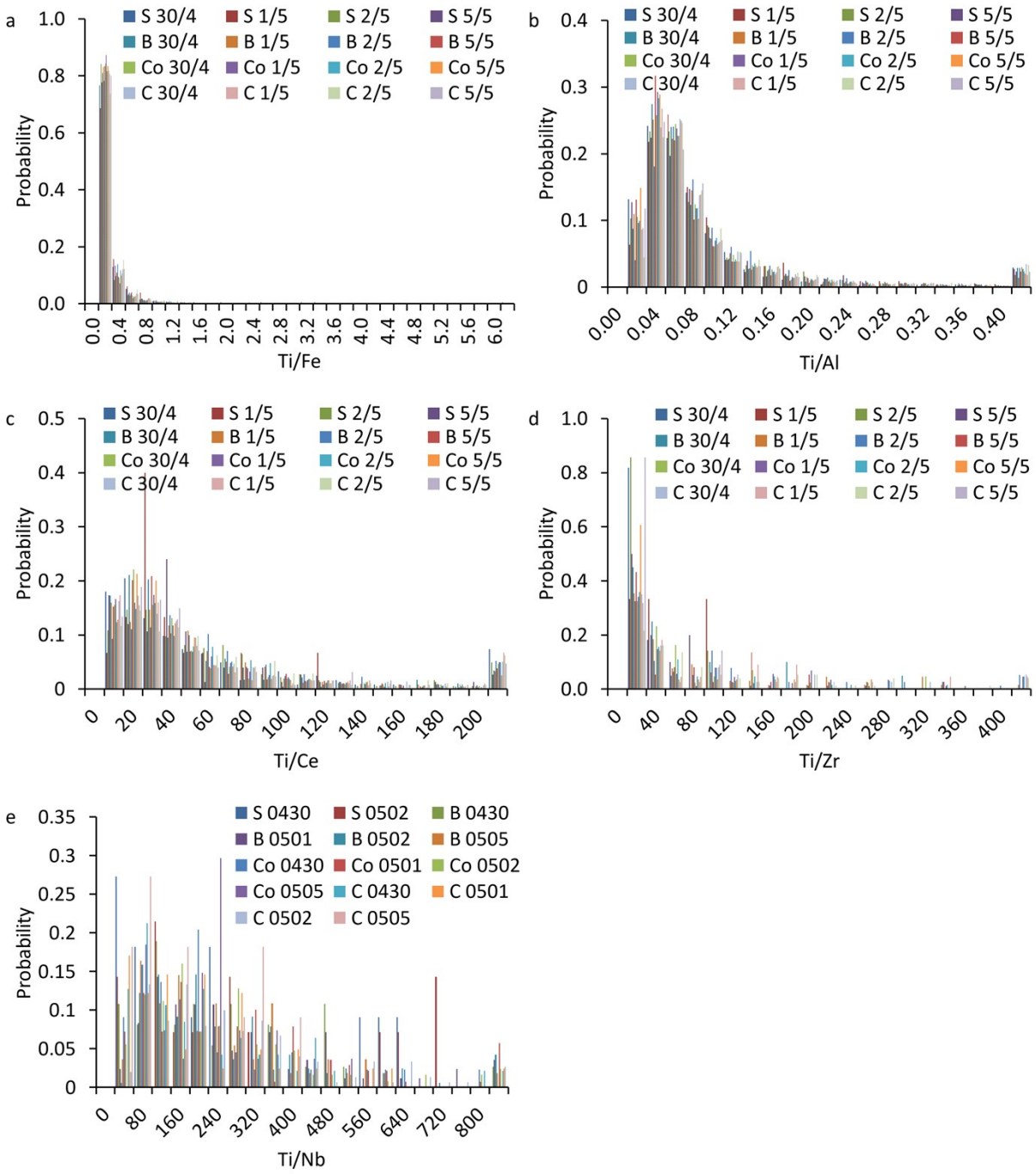


Figure S7. Elemental ratios of (a) Ti/Fe, (b) Ti/Al, (c) Ti/Ce, (d) Ti/Zr, and (e) Ti/Nb in Al-rich clusters. S: Lower Saluda River, B: Broad River, Co: Congaree River at Columbia, and C: Congaree River at Cayce.

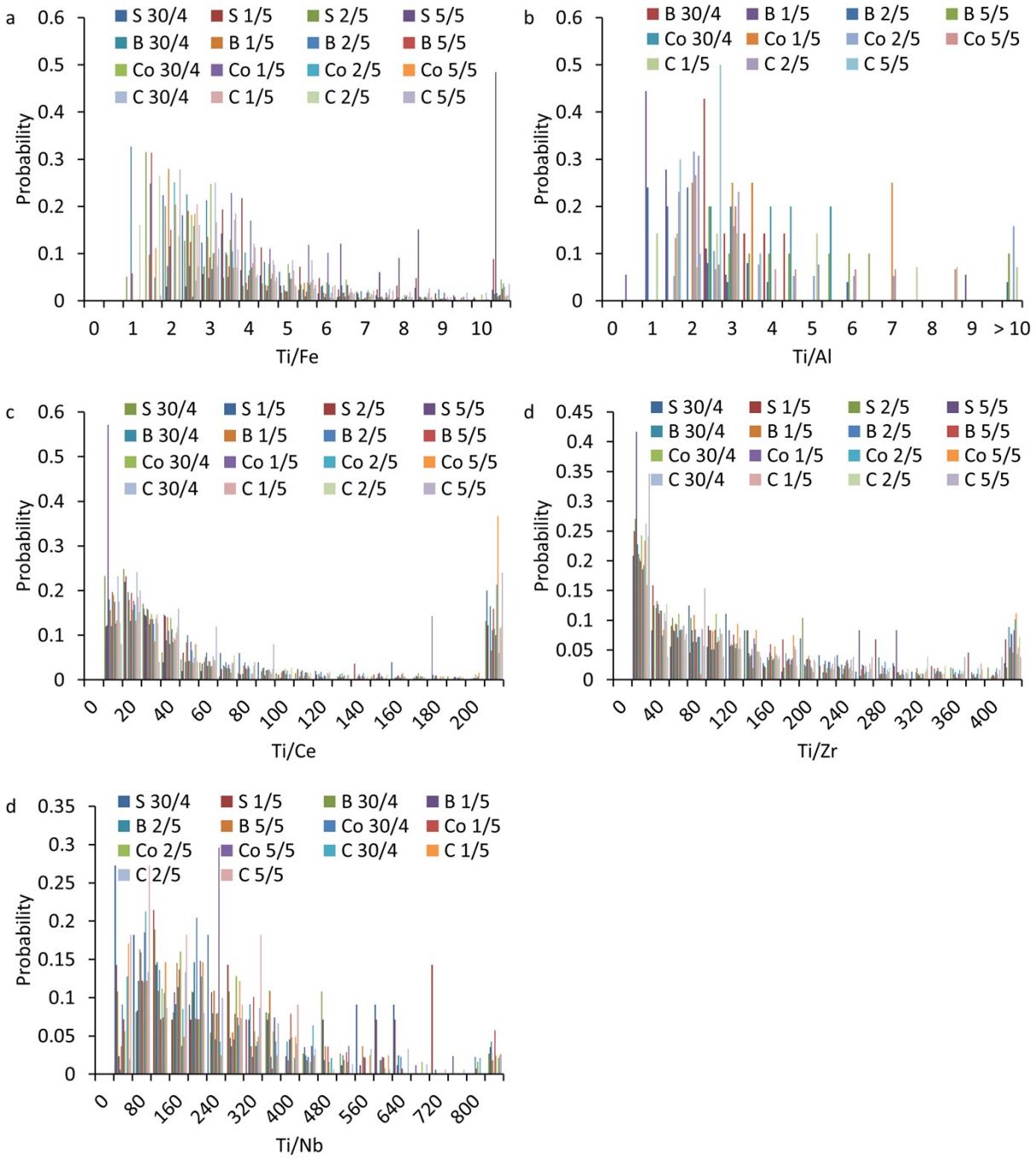


Figure S8. Elemental ratios of (a) Ti/Fe and (b) Ti/Al, and (c) Ti/Ce, (d) Ti/Zr, and (e) Ti/Nb in Ti-rich clusters. S: Lower Saluda River, B: Broad River, Co: Congaree River at Columbia, and C: Congaree River at Cayce.

Table S6. Descriptive statistics of the elemental ratios in mmNMs in Fe-rich particle cluster

		S 0430	S 0501	S 0502	S 0505	B0430	B0501	B0502	B0505	Co0430	Co0501	Co0502	Co0505	C0430	C0501	C0502	C0505
Ti/Al	**Median**	0.08	0.07	0.11	0.07	0.06	0.10		0.06	0.07	0.07	0.11	0.08	0.09	0.09	0.08	0.12
	Mean	0.11	0.10	0.14	0.15	0.10	0.18		0.10	0.14	0.19	0.17	0.17	0.13	0.16	0.12	0.61
	STD	0.14	0.09	0.11	0.25	0.25	0.20		0.14	0.31	0.54	0.18	0.32	0.12	0.41	0.17	0.90
	Count	242	92	21	79	311	129		409	187	26	46	70	40	166	349	27
Ti/Fe	**Median**	0.24	0.37	0.28	0.45	0.15	0.15	0.15	0.12	0.14	0.13	0.14	0.17	0.16	0.16	0.14	0.41
	Mean	0.34	0.58	0.32	0.78	0.25	0.24	0.19	0.17	0.25	0.25	0.23	0.27	0.29	0.29	0.19	0.96
	STD	0.33	0.60	0.22	0.92	0.31	0.23	0.13	0.17	0.32	0.39	0.25	0.26	0.38	0.36	0.15	1.73
	Count	2516	1594	1555	1779	3841	3588	3725	4741	3958	5876	5485	3325	3375	4578	4547	2217
Ti/Ce	**Median**	25	29	23	26	24	31	35	25	24	29	28	20	22	29	37	23
	Mean	48	69	45	88	50	56	50	46	56	82	54	50	53	70	62	70
	STD	83	118	58	218	109	100	55	79	111	188	90	109	104	185	106	140
	Count	160	74	56	61	366	543	465	444	378	740	462	167	222	515	640	69
T/Zr	**Median**	33	46	23	37	37	53	28	15	34	67	30	11	40	61	23	27
	Mean	55	82	50	74	67	81	44	63	94	134	74	43	74	77	53	103
	STD	52	119	53	94	91	95	46	103	140	178	119	78	83	77	104	174
	Count	13	15	6	18	42	84	82	48	48	117	61	17	42	64	89	35
T/Nb	**Median**	160	90	172	141	123	184	128	132	173	230	160	79	168	215	152	181
	Mean	156	183	172	245	239	240	154	170	230	280	204	228	189	273	187	237
	STD	98	300	1	217	455	194	104	131	258	221	198	333	142	253	150	202
	Count	18	25	2	23	47	125	106	55	71	190	94	23	70	97	117	76

Table S7. Descriptive statistics of the elemental ratios in mmNMs in Al-rich particle cluster

		S 0430	S 0501	S 0502	S 0505	B 0430	B 0501	B 0502	B 0505	Co0430	Co0501	Co0502	Co0505	C 0430	C 0501	C 0502	C 0505
Ti/Al	**Median**	0.05	0.06	0.05	0.06	0.05	0.05	0.06	0.04	0.05	0.05	0.05	0.04	0.05	0.05	0.06	0.05
	Mean	0.08	0.09	0.09	0.08	0.09	0.08	0.10	0.08	0.09	0.09	0.08	0.07	0.10	0.08	0.10	0.09
	STD	0.14	0.11	0.15	0.09	0.16	0.09	0.12	0.12	0.16	0.18	0.11	0.11	0.19	0.11	0.13	0.16
	Count	720	220	766	558	1575	1964	2379	2634	2021	4086	4204	2553	1670	1844	2268	1008
Ti/Fe	**Median**	0.09	0.13	0.07	0.09	0.09	0.08	0.10	0.08	0.07	0.07	0.09	0.07	0.08	0.09	0.13	0.08
	Mean	0.20	0.30	0.17	0.20	0.18	0.14	0.18	0.15	0.15	0.14	0.17	0.15	0.17	0.15	0.22	0.20
	STD	0.43	0.74	0.41	0.50	0.31	0.23	0.36	0.32	0.30	0.29	0.32	0.31	0.34	0.21	0.34	0.97
	Count	634	179	704	531	1239	1633	1726	2123	1680	3805	3545	2402	1380	1590	1571	966
Ti/Ce	**Median**	27	28	40	34	24	36	43	25	28	30	37	27	32	31	41	31
	Mean	60	37	60	50	44	54	68	52	57	63	65	47	65	68	82	55
	STD	97	28	68	69	60	71	83	97	105	137	111	68	132	180	170	75
	Count	122	15	184	75	232	613	580	388	366	1220	811	428	295	387	386	127
Ti/Zr	**Median**	13	30	15	17	28	32	61	49	37	47	36	11	38	43	57	5
	Mean	17	40	25	27	55	78	108	74	65	108	93	41	102	123	108	18
	STD	10	39	29	25	75	99	144	82	79	151	170	62	132	236	133	30
	Count	11	3	7	10	20	65	77	37	43	88	64	28	37	22	74	7
Ti/Nb	**Median**	189		203		176	208	198	187	162	214	194	203	149	162	225	137
	Mean	236		293		243	275	264	227	200	294	237	202	198	242	266	162
	STD	233		253		284	220	225	182	174	321	205	109	202	406	204	134
	Count	11		14		37	84	164	55	44	139	125	27	47	41	150	11

Table S8. Descriptive statistics of the elemental ratios in mmNMs in Ti-rich particle cluster

		S 0430	S 0501	S 0502	S 0505	B 0430	B 0501	B 0502	B 0505	Co0430	Co0501	Co0502	Co0505	C 0430	C 0501	C 0502	C 0505
T/Al	**Median**	2.1			5.2	3.0	1.0	1.6	3.8	3.9	3.0	2.5	2.5		2.3	1.7	2.1
	Mean	2.3			6.4	2.9	1.5	2.2	5.7	3.7	3.6	5.0	3.3		3.6	2.2	2.0
	STD	0.8			5.6	0.8	1.9	2.1	5.7	1.3	2.1	5.3	2.1		3.0	1.1	0.7
	Count	3			4	7	18	25	10	5	4	19	15		14	13	10
T/Fe	**Median**	2.9	4.2	1.8	8.5	3.0	2.4	1.3	1.9	3.3	4.1	2.7	2.5	3.6	3.3	1.7	2.8
	Mean	3.5	7.7	2.5	20.3	3.7	2.9	2.0	2.6	4.3	4.7	3.7	3.6	4.2	3.9	2.5	3.7
	STD	2.1	22.9	2.3	41.1	2.1	1.8	2.0	2.4	2.9	2.1	3.3	4.4	1.8	1.8	2.1	3.2
	Count	259	124	409	33	244	236	648	465	154	118	410	402	116	264	509	360
Ti/Ce	**Median**	21.0	30.8	29.7	6.9	26.6	30.4	41.0	27.8	30.8	30.4	39.0	56.4	21.4	29.5	37.7	44.9
	Mean	94.7	888.0	130.8	36.7	160.1	72.5	115.2	161.1	115.1	104.5	237.3	399.4	73.6	103.0	110.7	141.3
	STD	249.6	3809.0	338.6	64.3	480.9	210.5	293.3	458.3	288.0	315.4	652.7	697.4	264.5	302.7	255.7	212.0
	Count	129	50	82	7	371	2178	2361	508	332	880	671	128	380	906	1960	25
Ti/Zr	**Median**	90	65	60	62	82	71	77	90	69	94	103	111	69	97	82	73
	Mean	112	353	109	86	144	126	141	162	111	152	191	154	107	151	142	134
	STD	108	1254	187	96	167	181	201	288	137	180	447	202	131	196	184	193
	Count	72	44	48	12	158	732	1055	251	198	301	364	107	232	295	879	26
Ti/Nb	**Median**	167	219	160	262	207	195	235	214	158	193	256	265	164	206	237	217
	Mean	226	272	233	263	259	275	294	280	235	264	317	314	231	299	297	255
	STD	202	236	273	183	215	334	244	241	247	243	296	295	214	333	268	204
	Count	125	59	69	37	312	1103	2177	535	333	611	723	180	318	477	1796	69

6. Gadolinium anomaly

The major anthropogenic source of anthropogenic Gd is domestic sewage effluent, widely recognized as the major source of Gd in polluted streams. Anomalies in REE patterns are commonly quantified by the ratio of the normalized measured concentration of the normalized theoretical concentration (determined by interpolation between neighboring elements) for the anomalous element. Here, we use neodymium (Nd) and samarium (Sm) to extrapolate the background Gd values in the samples, and to quantify Gd anomalies according to Eq. 1 [13].

$$Gd_N/Gd_N^* = Gd_N/10^{(2logSm - logNd)} \quad \text{(Eq. 1)}$$

A size of $Gd_N/Gd_N^* =$ 1.5 is commonly used as the benchmark to distinguish between the natural and anthropogenic Gd anomaly. The size of the Gd anomalies varied in the range from $Gd_N/Gd_N^* =$ 1.1 ± 0.0 and 2.1 ± 0.1 **(Figure S9b)**, suggesting that there is minimal or absence of Gd anomaly during the sampling event in the Saluda, Broad and Congaree River surface water which might be attributed to insignificant (mean: 5.2%) contribution of WWTP effluent discharge into the river stream in comparison to the direct runoff.

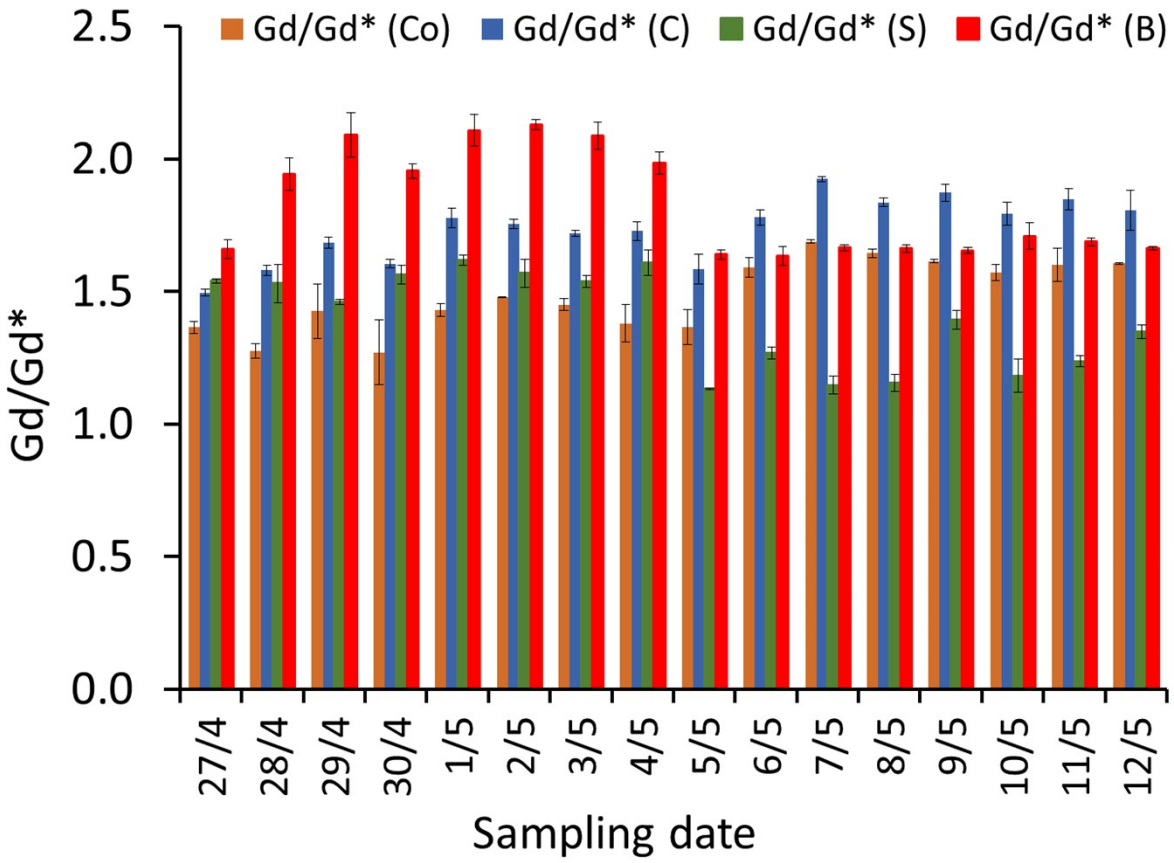


Figure S9. Gadolinium anomaly in Saluda River (S), Broad River (B), Congaree River, Columbia (Co), Congaree River, Cayce (C) based on the equation 1.

29 **Table S9.** Gd anomalies across the world.

SI	Country	Location	Gd_N/Gd_N^* size	Reference
1	USA	River waters in Pennsylvania	1.58 to 4.94	[14]
2	Germany	Rhine River	4.4 to 21	[15]
3	Germany	Wupper River, Leverkussen; Others: Sieg, Rhein, Elbe, and Mosel River	9.1 to 30; other rivers: 1.5 to 3	[16]
4	Germany	Spree, Dahme, Upper Havel River	1.6 to 1.8	[17]
5	France	Vene River	2.1 to 5.25	[18]
6	Czech Republic	Berounka, Vltava, Jizera River	1.1 to 11.3	[19]
7	Japan	Ara, Tama, and Tone River	1.0 to 7.0	[20]
8	Luxembourg	Alzette River	20 to 30	[21]

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References:

1. U.S. Army Corps of Engineers & Stanley Consultants. *Saluda River Basin, Charleston district navigability study*. (1977).

2. Congaree River Keeper. Lower Saluda River. Available at: https://www.congareeriverkeeper.org/lower-saluda-river. (Accessed: 8th January 2021)

3. SCDHEC. *Watershed Water Quality Assessment Saluda River Basin*. (2011).

4. SCDOT. Annual average daily traffic. (2019). Available at: https://www.scdot.org/travel/pdf/trafficcounts/2019/Lexington.pdf. (Accessed: 2nd April 2021)

5. SCDOT. Annual average daily traffic. (2019). Available at: https://www.scdot.org/travel/pdf/trafficcounts/2019/Richland.pdf. (Accessed: 1st April 2021)

6. U.S. Geological Survey (USGS). USGS Current Conditions for USGS 02162285 TABLE ROCK RESERVOIR NR CLEVELAND, SC. Available at: https://waterdata.usgs.gov/nwis/dv?cb_00045=on&format=html&site_no=02162285&referred_module=sw&period=&begin_date=2020-04-27&end_date=2020-05-12. (Accessed: 10th January 2021)

7. NC DEQ. *Broad river Basin restoration priorities*. (2009).

8. U.S. Geological Survey (USGS). USGS Current Conditions for USGS 03451500 FRENCH BROAD RIVER AT ASHEVILLE, NC. Available at: https://waterdata.usgs.gov/nwis/dv?cb_00045=on&format=html&site_no=03451500&referred_module=sw&period=&begin_date=2020-04-20&end_date=2020-05-10. (Accessed: 8th January 2021)

9. City of Knoxville. Rainfall Data - City of Knoxville. Available at:

https://knoxvilletn.gov/government/city_departments_offices/engineering/stormwater_engineering_division/rainfall_data. (Accessed: 8th January 2021)

10. Loosli, F. *et al.* Sewage spills are a major source of titanium dioxide engineered (nano)-particle release into the environment. *Environ. Sci. Nano* **6**, 763–777 (2019).

11. Nabi, M. M., Wang, J. & Baalousha, M. Episodic surges in titanium dioxide engineered particle concentrations in surface waters following rainfall events. *Chemosphere* **263**, 128261 (2021).

12. Jochum, K. P. *et al.* Reference Values Following ISO Guidelines for Frequently Requested Rock Reference Materials. *Geostand. Geoanalytical Res.* **40**, 333–350 (2016).

13. Kulaksiz, S. & Bau, M. Contrasting behaviour of anthropogenic gadolinium and natural rare earth elements in estuaries and the gadolinium input into the North Sea. *Earth Planet. Sci. Lett.* **260**, 361–371 (2007).

14. Bau, M., Knappe, A. & Dulski, P. Anthropogenic gadolinium as a micropollutant in river waters in Pennsylvania and in Lake Erie, northeastern United States. *Chemie der Erde* **66**, 143–152 (2006).

15. Kulaksiz, S. & Bau, M. Rare earth elements in the Rhine River, Germany: First case of anthropogenic lanthanum as a dissolved microcontaminant in the hydrosphere. *Environ. Int.* **37**, 973–979 (2011).

16. Bau, M. & Dulski, P. Anthropogenic origin of positive gadolinium anomalies in river waters. *Earth Planet. Sci. Lett.* **143**, 245–255 (1996).

17. Knappe, A., Möller, P., Dulski, P. & Pekdeger, A. Positive gadolinium anomaly in surface water and ground water of the urban area Berlin, Germany. *Geochemistry* **65**, 167–189 (2005).

18. Elbaz-Poulichet, F., Seidel, J. L. & Othoniel, C. Occurrence of an anthropogenic gadolinium anomaly in river and coastal waters of Southern France. *Water Res.* **36**, 1102–1105 (2002).

19. Möller, P., Paces, T., Dulski, P. & Morteani, G. Anthropogenic Gd in surface water, drainage system, and the water supply of the City of Prague, Czech Republic. *Environ. Sci. Technol.* **36**, 2387–2394 (2002).

20. Nozaki, Y., Lerche, D., Alibo, D. S. & Tsutsumi, M. Dissolved indium and rare earth elements in three Japanese rivers and Tokyo Bay: Evidence for anthropogenic Gd and In. *Geochim. Cosmochim. Acta* **64**, 3975–3982 (2000).

21. Hissler, C., Stille, P., Guignard, C., François Iffly, J. & Pfister, L. Rare Earth Elements as hydrological tracers of anthropogenic and critical zone contributions: a case study at the Alzette River basin scale. *Procedia Earth Planet. Sci.* **10**, 349–352 (2014).