

SUPPLEMENTARY MATERIAL

Distribution of REE and Yttrium among particulate, colloidal and dissolved fractions in peri-urban river systems under low and high flow conditions.

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SI-1 Sampling area

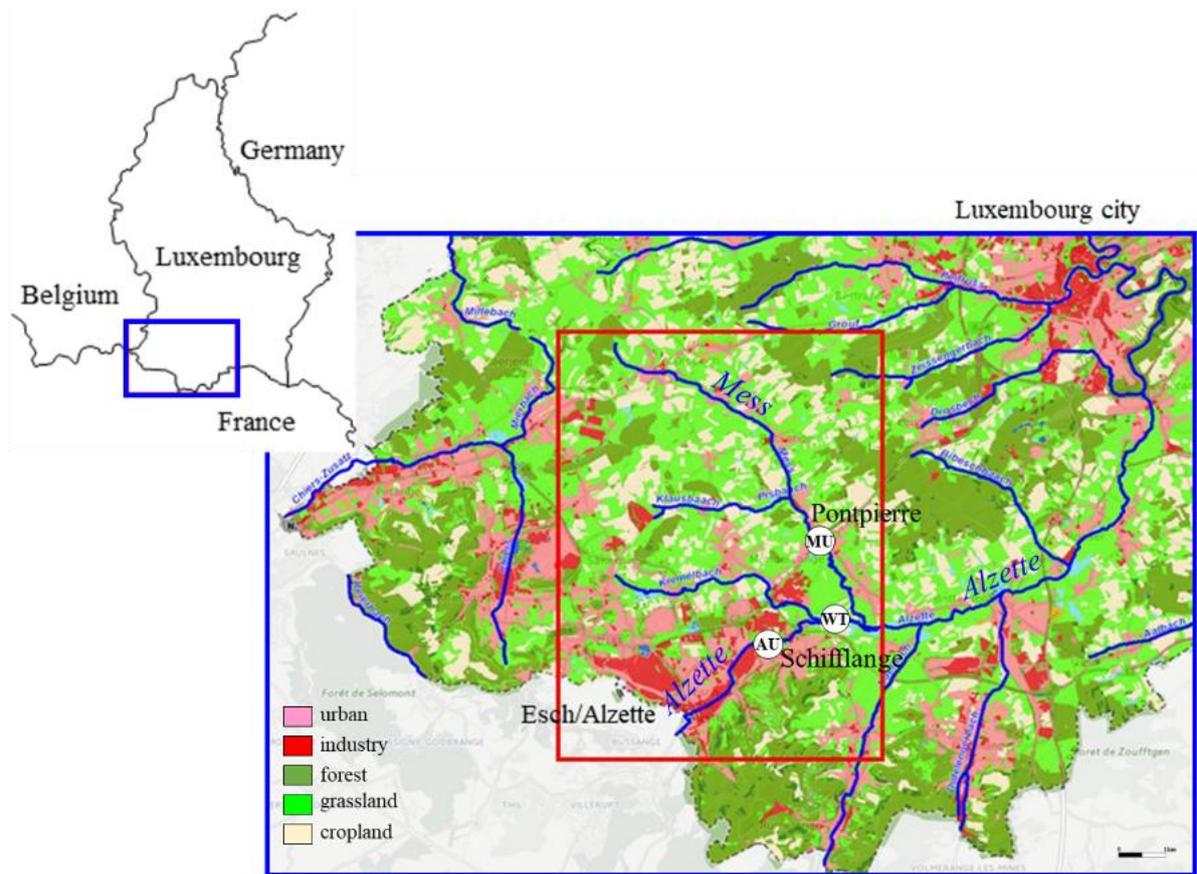


Figure S1: Localization of the different sampling sites and land use in the Alzette River basin south of Luxembourg City: the upper Alzette River sub-basin (AU) of 51 km²; the wetland area (WT); the Mess River basin (MU) of 33 km².

Table S1: Land use of the two studied catchments from Pfister *et al.* (2017).

	forest	grassland	cropland	urban/industry
Mess	9%	58%	23%	10%
Upper Alzette	27%	27%	27%	19%

SI-2 Procedure of the Cross-Flow Ultrafiltration (CFF) used in this study

Pellicon® XL Cassettes Ultracel® (Millipore) were used in this study. Membrane were made from composite regenerated cellulose with a surface area of 50 cm² and a manufacturer specified cut-off of 10 kDa. This system was the same as the one tested by Larsson *et al.* (2002), which is suitable for natural water colloid isolation (Larsson *et al.*, 2002). The CFF cassettes were operated with a peristaltic MCP-Process IP65 pump (ISMATEC®) connected to the different compartments (PP Nalgene® bottles) with TYGON LMT-55 (ISMATEC®) tubing. Two separate compartments were used, one called “permeate” (to collect what went through the membrane) and the other called “retentate” (where colloids were concentrated). Flow rates were optimized to have a retentate flow that was at least 15 times higher than the permeate flow (Larsson *et al.*, 2002). Each bottle was weighed at the beginning and at the end of each experiment and the retentate concentration factor (cf) was calculated as:

$$cf = \frac{V_{\text{Perm}} + V_{\text{Ret}}}{V_{\text{Ret}}} \quad (\text{A1})$$

where V refers to the volume (in L) of the permeate and retentate fractions. Approximately 0.5L of prefiltered (0.22 μm) sample was ultrafiltered.

Colloidal concentration [X]_{col} was calculated using equation A2 where [X]_{Ret} was the concentration measured in the retentate, [X]_{perm} was the concentration measured in the permeate and cf was the concentration factor defined using equation A1:

$$[X]_{\text{col}} = \frac{[X]_{\text{Ret}} - [X]_{\text{perm}}}{cf} \quad (\text{A2})$$

Finally, a budget B and a mass balance R were calculated for the fractionation process with equations A3 and A4, respectively:

$$B = [X]_{\text{col}} + [X]_{\text{perm}} \quad (\text{A3})$$

$$R = \frac{B}{[X]_{\text{meas}}} \quad (\text{A4})$$

where [X]_{meas} was the concentration measured in the prefiltered water at 1000 or 220 nm, according to the step of the “cascade” filtration.

Ultrafiltration blanks were run before each sample. Prior to each experiment (and to the blank run), ultrafiltration membranes were cleaned by recirculating first 1L of ultrapure water (milliQ, Millipore), then 0.5M of HCl for 20 minutes, followed by rinsing them with ultrapure water until a neutral pH and 0.1M of NaOH for another 20 minutes and finally rinsing again with ultrapure water until a neutral pH. Cartridges were stored filled with a solution of 0.05M NaOH between runs.

SI-3 REY blank values for the mineralized filters

All values are summarized in the SI-3 sheet of the SI Excel files.

SI-4 REY concentration and recovery average values for the NRC-CNRC/SLRS-6

Table S2: Average SLRS-6 values (n=5) for REY concentrations measured by ICP-MS (Agilent 7900) in the present study. Five measurements were taken randomly during multiple analysis runs. C_{av} is the arithmetic mean of the measured concentrations in $ng\ L^{-1}$ and σ_C is one standard deviation in $ng\ L^{-1}$; R_{av} is the average recovery and σ_R is one standard deviation in % (n=5). For recoveries, the average concentrations were normalized to concentration from Yeghicheyan *et al.* (2019; C_{SLRS-6} in the table) as no certified values exist for REY in SLRS-6.

	C_{SLRS-6}	σ_{SLRS-6}	C_{av}	σ_C	R_{av}	σ_R
⁸⁹ Y	128	6	124.5	1.3	97.3	1.0
¹³⁹ La	248.3	12.1	241.4	1.5	97.2	0.6
¹⁴⁰ Ce	292.7	15.1	282.7	3.0	96.6	1.0
¹⁴¹ Pr	59.1	1.9	58.2	0.9	98.5	1.5
¹⁴⁶ Nd	227.8	9.4	221.4	2.7	97.2	1.2
¹⁴⁷ Sm	39.5	1.7	37.3	1.1	94.5	2.8
¹⁵³ Eu	7.26	0.35	6.9	0.2	94.6	2.1
¹⁵⁷ Gd	31.6	2.5	31.2	1.0	98.8	3.0
¹⁵⁹ Tb	4.07	0.27	3.8	0.1	98.9	2.7
¹⁶¹ Dy	21.9	1.1	21.1	0.4	96.4	1.9
¹⁶⁵ Ho	4.3	0.3	4.3	0.1	99.3	1.0
¹⁶⁶ Er	12.4	0.7	11.3	0.2	91.1	1.6
¹⁶⁹ Tm	1.79	0.18	1.7	0.1	95.7	4.7
¹⁷² Yb	11.2	0.7	11.3	0.3	100.6	2.3
¹⁷⁵ Lu	1.91	0.23	1.7	0.1	89.5	2.7

SI-5 REY Pre-concentration by matrix evaporation: Tm recoveries and pre-concentration factors

All data are gathered in the SI-5 sheet in the SI Excel file.

SI-6 Quantification of the coarse colloidal fraction between 1000 and 220 nm (CC)

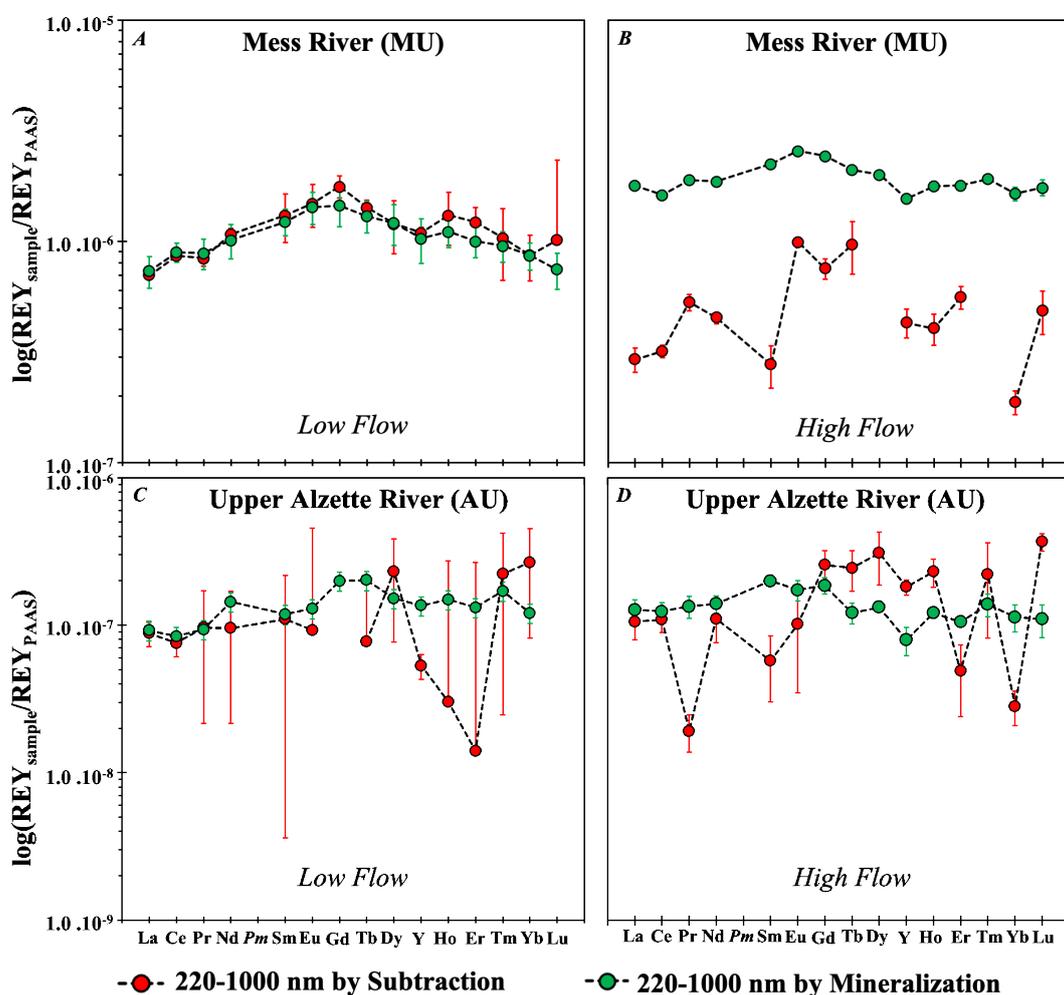


Figure S2: PAAS-normalized REY patterns of the coarse colloidal fraction (CC) according to the calculation procedure and the hydrological conditions in the Mess River and the upper Alzette River. Subtraction refers to eq. 3 and mineralization to eq. 4 and the error bars are 2Δ (see equations 11 and 12 in Table 2 of the main text).

SI-7 Calculation of $\text{Eu}_{\text{PAAS}}^*$ and $\text{Gd}_{\text{PAAS}}^*$

Table S3: Parameters used in the least square method for a linear regression (eq. 8 and 9 in the main text); b_1 is the slope; b_0 the intercept; r^2 the correlation coefficient; $t_{(n-2)}$ ($n=3$) and σ_{XREY} are calculated according to Miller and Miller (2010) and are used to estimate the error on $\log \text{Eu}_{\text{PAAS}}^*$ and $\log \text{Gd}_{\text{PAAS}}^*$ (eq. 14 in table 2 of the main text).

	<u>MU (HF)</u>		<u>AU (HF)</u>		<u>MU (LF)</u>		<u>AU (LF)</u>	
	$\text{Eu}_{\text{PAAS}}^*$	$\text{Gd}_{\text{PAAS}}^*$	$\text{Eu}_{\text{PAAS}}^*$	$\text{Gd}_{\text{PAAS}}^*$	$\text{Eu}_{\text{PAAS}}^*$	$\text{Gd}_{\text{PAAS}}^*$	$\text{Eu}_{\text{PAAS}}^*$	$\text{Gd}_{\text{PAAS}}^*$
b_1	16.09	16.09	17.16	17.16	5.58	5.58	6.02	6.02
b_0	104.18	104.18	119.21	119.21	45.48	45.48	49.03	49.03
r^2	1.00	1.00	0.93	0.93	1.00	1.00	0.96	0.96

$t_{(n-2)}$	64.67	64.67	3.74	3.74	14.69	14.69	5.09	5.09
$\sigma_{x_{REY}}$	0.004	0.004	0.06	0.07	0.04	0.05	0.12	0.14

SI-8 Error analysis

SI-8.1. Measured REY concentrations

The 288 data shown in Table S4 and Figure S3 are all REY concentrations measured in this study, including values for the filter blanks, the mineralized filters for the particulate and coarse colloid (CC) fractions and the concentrations measured for the small colloids (SC) and the dissolved fractions, using both CU and CFF separation techniques. The matrix of the water samples was always acidified using HNO₃ 1%. The measured atomic mass of all REY was considered in this calculation. The samples that presented REY concentrations lower than 1 ng L⁻¹ were preconcentrated using evaporation and the ICP-MS analysis done on the preconcentrated samples were used. For this reason, those samples always present concentrations higher than the detection and quantification limits of the ICP-MS instrument.

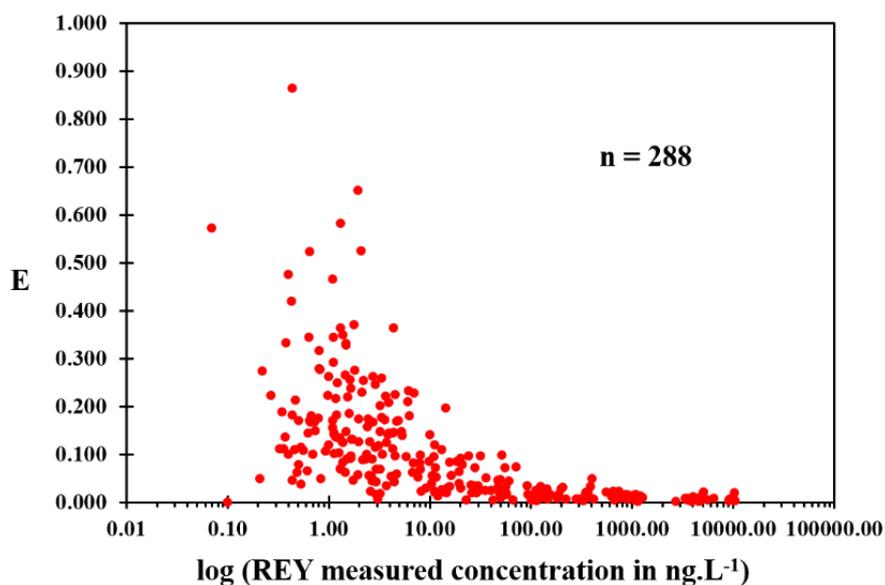


Figure S3: Evolution of E (eq. 15 main manuscript) according to the REY concentrations measured.

Table S4: Median, mean, standard deviation (stdev), maximum (max) and minimum (min) value for E (in %) depending of concentration classes. p_x corresponds to the probability of observing an error E (x corresponds to the threshold of error).

[REY] (ng.L ⁻¹)	[0-1]	[1-2]	[2-5]	[5-10]	[10-20]	[20-100]	[100-1000]	>1000	total
n	42	45	48	17	21	35	50	30	288
median (E)	16.8	14.7	12.4	9.4	5.2	3.0	1.1	0.7	6.1
average (E)	20.6	20.2	13.8	11.4	5.9	3.9	1.4	0.7	10.4
stdev (E)	16.6	13.4	9.6	6.5	4.3	2.7	0.9	0.5	12.3
E min	0.1	4.5	0.6	2.2	1.3	0.4	0.2	0.1	0.1
E max	86.4	65.0	52.4	23.3	19.6	9.7	4.8	2.0	86.4
$p_{<0.10}$	0.17	0.222	0.396	0.588	0.857	1.000	1.000	1.000	0.622
$p_{<0.05}$	0.095	0.022	0.167	0.118	0.476	0.743	1.000	1.000	0.455

$P_{0.10-0.20}$	0.476	0.422	0.417	0.235	0.143	0.000	0.000	0.000	0.198
$P_{>0.20}$	0.357	0.356	0.188	0.176	0.000	0.000	0.000	0.000	0.181

Table S5: Median, average, standard deviation (σ), maximum (max) and minimum (min) values for the E error (in %), depending on the concentration classes for all data used for the small colloid (SC) and the dissolved fractions (n=60).

[REY] (ng.L ⁻¹)	[0-1]	[1-2]	[2-5]	[5-10]	[10-20]	>20	Total
n	26	10	12	4	3	5	60
median (E)	17.0	15.6	15.1	7.3	2.0	5.0	14.0
average (E)	21.5	17.4	13.3	10.0	3.2	4.7	16.1
stdev (E)	17.6	10.8	5.5	7.6	1.7	3.2	14.2
E min	0.1	4.5	2.3	2.8	2.0	0.4	0.1
E max	86.4	36.4	20.7	22.8	5.6	9.1	86.4

Table S6: Median, average, standard deviation (σ), maximum (max) and minimum (min) values for the REY concentrations (ng L⁻¹) according to the E classes for all data used for the small colloid (SC) and the dissolved fractions (n=60). Table S6 was used for Figure 1 in the manuscript.

E	[0.00-0.05]	[0.05-0.10]	[0.10-0.20]	>0.20	Total
n	10	12	22	16	60
median ([REY] in ng.L⁻¹)	10.16	4.65	0.70	0.91	1.31
average ([REY] in ng.L⁻¹)	20.50	7.61	1.48	1.51	5.88
stdev ([REY] in ng.L⁻¹)	29.00	8.27	1.45	1.75	14.28
[REY] min (in ng.L⁻¹)	0.10	0.40	0.33	0.10	0.10
[REY] max (in ng.L⁻¹)	100.13	28.20	4.74	6.98	100.13

SI-8.2. Parameters used to calculate mineralized fractions

Table S7: Repartition by class of measured [REY], dispersion of V_{filt} and dispersion of V_{digest} .

<i>measured [REY]</i>						
[REY] (ng.L ⁻¹)	<5	[5-10]	[10-100]	[100-1000]	>1000	Total
n	2	4	42	114	136	298
<i>dispersion V_{filt}</i>						
σ (%)	<5	[5-10]	[10-20]	>20	Total	
n	4	5	9	8	26	
<i>dispersion V_{digest}</i>						
σ (%)	<5	[5-10]	[10-20]	>20	Total	
n	25	0	0	0	25	

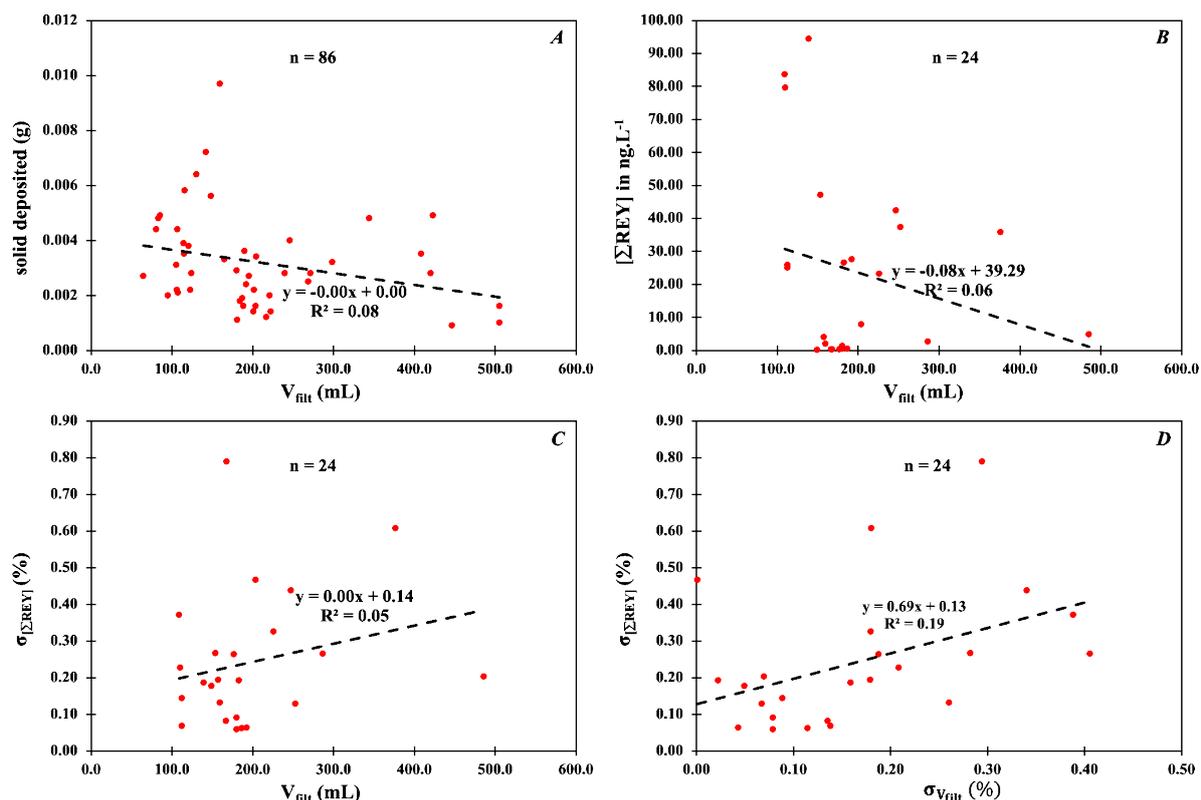


Figure S4: A) correlation between V_{filt} and the mass of solid deposited on the filter. B) correlation between the ΣREY (La to Lu) concentration and V_{filt} . C) correlation between the standard deviation of the measured ΣREY concentrations and V_{filt} . D) correlation between the standard deviation of the measured ΣREY concentrations and the V_{filt} standard deviation. The red dots on the scatterplots represent the ΣREY concentrations and V_{filt} average values of the triplicate measurements taken for each sample and the standard deviations are calculated based on this triplicate analysis.

Table S8: Average and standard deviation (σ) of V_{filt} (mL) and of the measured ΣREY concentration (ng L^{-1}) for AU and MU sampling sites in the particulate and the coarse colloidal fractions for each sample ($n = 3$). LF and HF correspond to low and high flow conditions, respectively.

		MU (HF)		MU (LF)		AU (HF)		AU (LF)	
		average	σ	average	σ	average	σ	average	σ
V_{filtered} (mL)	Part.	112.51	0.138	138.90	0.159	192.34	0.043	203.90	0.001
		$[\Sigma\text{REY}]$ (ng.L^{-1})	25.88	0.068	94.45	0.186	27.58	0.064	7.87
V_{filtered} (mL)	CC	157.29	0.179	-	-	180.17	0.079	-	-
		$[\Sigma\text{REY}]$ (ng.L^{-1})	3.94	0.194	-	-	0.37	0.059	-

SI-9 REY Concentration data

All data are summarized in the SI-7 sheets of the SI Excel file. The different water fractions are presented in independent sheets. They were used for all calculations (e.g. PAAS normalization for REY).

SI-10 Comparison between CU and CFF

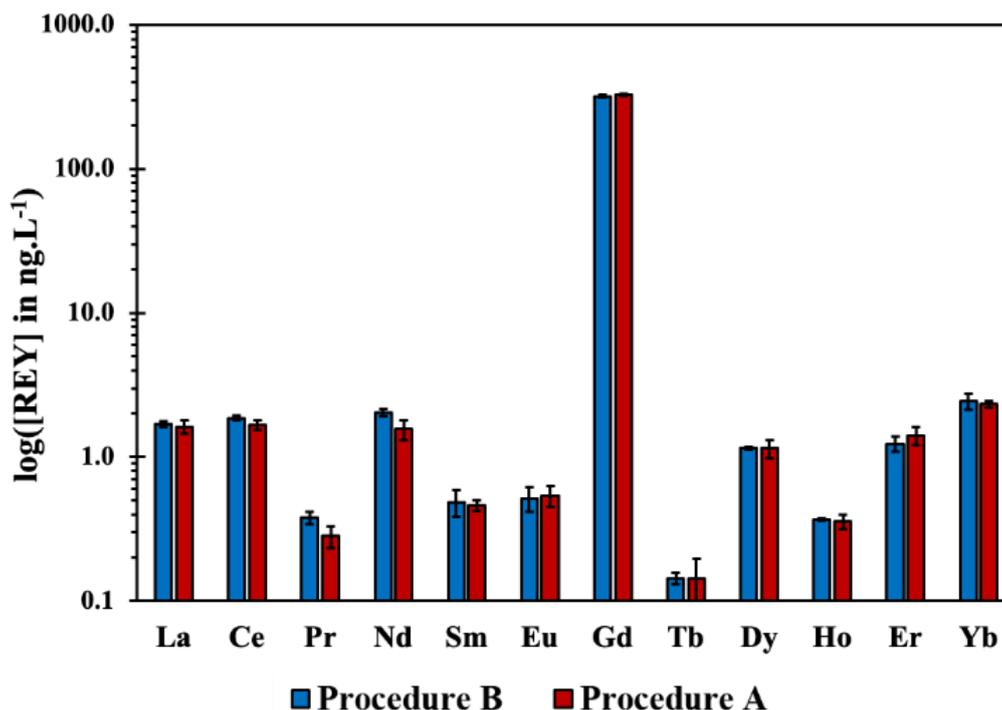


Figure S5: Comparison between Procedure A and Procedure B during the small colloid and the dissolved fraction separation using the CU technique for two sites of the Alzette River basin (A and B). Procedure A = 2x15 mL successive centrifugations with the same Amicon[®] Ultra 15 10 kDa tube for one sample. Procedure B = 1X15 mL centrifugation with 2 different Amicon[®] Ultra 15 10 kDa tubes for one sample. In both procedures, the total recovered volume was 30 mL. The indicated errors are 2Δ (Table 2 in the main text).

SI-11 Data for the Waste Water Treatment Plant sampled in the Alzette River basin

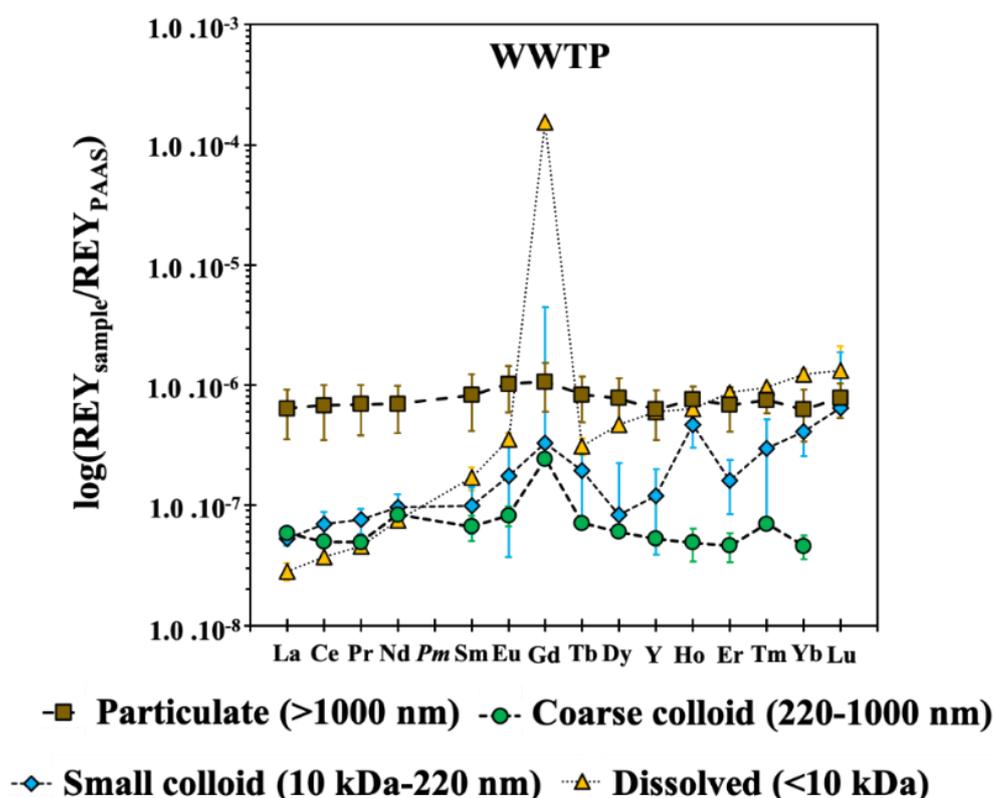


Figure S6: PAAS- normalized REY patterns for the different water fractions collected in the effluent of the wastewater treatment plant in the Alzette River basin. The error bars are 2Δ (table 2 in the manuscript).

SI-12 References

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