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Determination of metal-based nanoparticles in the river Dommel in the Netherlands via ultrafiltration, ICP-MS and SEM – Supporting information

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1 Detailed of the sampling locations

For the sampling eleven locations (labelled D01 to D11) over the entire river were selected. In addition three samples (labelled W01 to W03) were taken from the wastewater treatment plant (WWTP). The details are shown below:

ID	*Address*
D01	Paardensteeg, Vught
D02	Hoge Vonderstraat, St. Oedenrode
D03	Dommelpas, Son en Breugel
D04	Van Oldenbarneveltlaan (park), downstream of the WWTP Eindhoven
D05	Onze Lievevrouwestraat, Eindhoven
D06	Busken Huetstraat, Eindhoven (near tank station). Tributary: Tongelreep
D07	Tongelreeppad, Eindhoven
D08	Klotputten (sediment trap) downstream
D09	Klotputten (sediment trap) upstream
D10	Volmolen, Waalre
D11	Peedijk, Borkel
W01	Influent WWTP Eindhoven
W02	Effluent WWTP Eindhoven
W03	Sewage sludge WWTP Eindhoven

2 Precipitation and flow rates in the sampling period

Table S1 shows the daily precipitation and the flow rate of the river Dommel upstream of the WWTP and the outflow rate of the WWTP in the period of sampling. The flow rate of the river is hardly affected by the rainfall. There may be some influence on the outflow rate of the WWTP. The daily sum of precipitation is the average of four stations in the region of the river.

Table S1: Hydrological data for the sampling period.

Date	Precipitation mm/day	Flow rate river m^3/s	Outflow WWTP m^3/s
2015-5-30	2.3	–	–
2015-5-31	2.1	–	–
2015-6-1	7.2	1.74	2.84
2015-6-2	0.8	1.64	1.54
2015-6-3	1.8	1.65	1.38
2015-6-4	0.0	1.59	1.27
2015-6-5	0.0	1.63	1.20
2015-6-6	6.0	1.63	3.23

3 Measured concentrations

Table S2 shows the limits of quantification for the metals. Table S3 shows the measured total concentrations of the seven metals considered. For the analysis the samples were used directly.

The results for the ultrafiltration are shown in tables S4 and S5.

Table S2: Limits of quantification for the seven metals in μg/l.

Ag	Ce	Au	Ti	Zn	La	Zr
0.02	0.1	0.02	0.5	4	0.06	0.04

Table S3: Measured total concentrations for seven metals. The samples were acidified in the field using nitric acid. The concentrations are given in μg/l.

Location	Ag	Ce	Au	Ti	Zn	La	Zr
D01	0.027	0.50	0.34	1.7	26	0.20	0.29
D02	0.02	0.53	0.23	1.6	43	0.23	0.28
D03	0.016	0.54	0.17	1.3	41	0.22	0.26
D04	0.008	0.59	0.14	1.7	56	0.26	0.22
D05	0.006	0.92	0.11	1.8	47	0.39	0.23
D06	0.006	0.53	0.10	1.5	18	0.21	0.24
D07	0.006	1.4	0.09	1.7	67	0.57	0.25
D08	0.005	0.82	0.07	1.4	66	0.35	0.21
D09	0.003	0.66	0.073	0.62	77	0.29	0.19
D10	0.004	0.63	0.078	0.66	86	0.29	0.24
D11	0.005	0.64	0.10	0.69	112	0.29	0.19
W01	0.019	0.64	0.11	4.1	164	0.42	0.39
W02	0.007	0.052	0.15	0.41	52	0.019	0.21
W03	0.013	1.8	0.10	8.3	$1.16{\cdot}10^3$	0.87	1.4

4 Additional figures

Fig. S1 shows the concentration of zirconium along the river. As the concentration is more or less constant, it is likely that the river and its tributaries carry a background level only.

Fig. S3 shows a picture and the EDX spectrum of a gold nanoparticle that was found in the sewage sludge. Fig. S4 shows in a similar way an agglomerate of cerium and lanthanum particles. The size distribution of these particles is shown in Fig. S5.

5 Estimated emissions of nanoparticles

With a capacity of 750,000 inhabitant equivalents and an assumed retention efficiency of 95% [**?**], the concentration of nanoparticles in the influent and the net emission can be estimated. According to Markus et al. [**?**] the annual per-capita contributions to nanoparticles of titanium dioxide, zinc oxide and silver are:

Titanium dioxde:	3.7 g
Zinc oxide:	5.0 g
Zinc oxide:	46 mg

As the Dommel had a flow rate of 1.6 m^3/s upstream of the discharge of

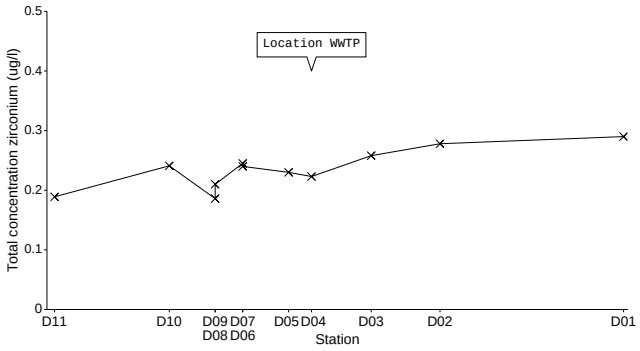

Figure S1: Measured concentration of zirconium along the river, dd. 4 June 2015.

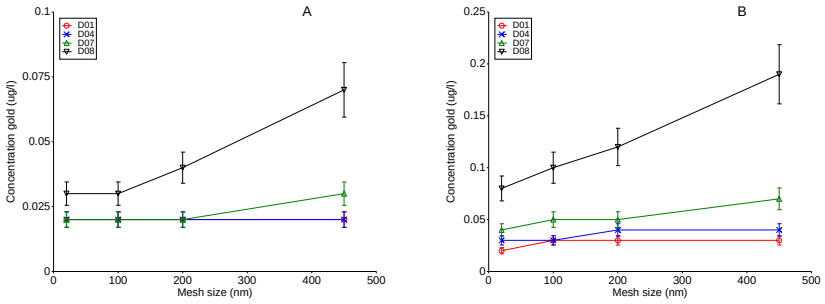

Figure S2: Concentration of gold as measured after ultrafiltration. (A) The original sample was acidified, but not filtered, immediately after collection. (B) The original sample was filtered, immediately after collection, with a 450 nm filter. The concentration is in μg/l, the mesh size in nm.

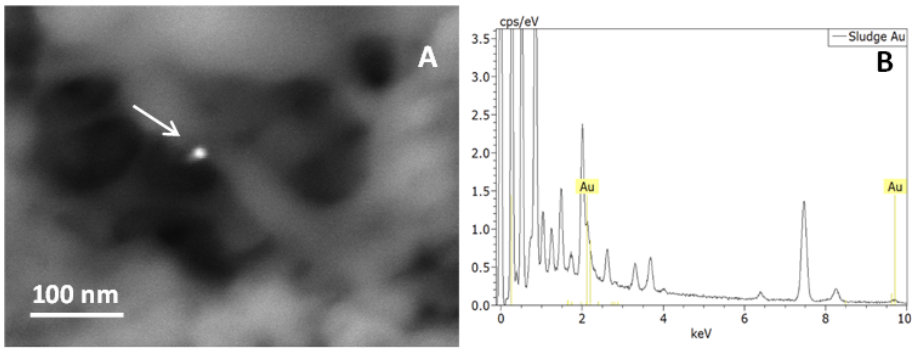

Figure S3: Representative SEM image of a gold nanoparticle, as indicated by the arrow, in a sludge sample (W03) from the WWTP (A) and the corresponding EDX-spectrum of the nanoparticle (B).

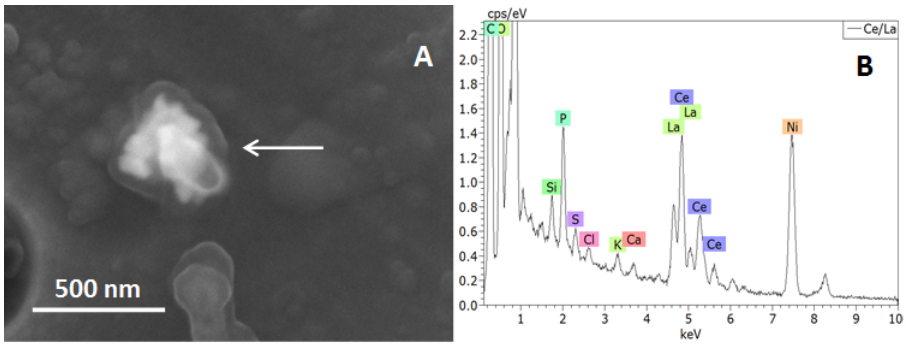

Figure S4: Representative SEM image of a cerium and lanthanum agglomerate, as indicated by the arrow, in a sludge sample (W03) from the WWTP (A) and the corresponding EDX-spectrum of the nanoparticle (B).

Table S4: Measured concentrations of titanium, gold and cerium after ultrafiltration. This set of samples used had been filtered on site with a 450 nm ultrafilter. The concentrations are given in μg/l and the mesh size in nm.

Location	*Mesh*	Ce	Au	Ti
D01	450	0.11	0.03	0.43
D01	200	0.04	0.03	0.24
D01	100	0.02	0.03	0.32
D01	20	0.03	0.02	0.36
D04	450	0.16	0.04	0.47
D04	200	0.06	0.04	0.37
D04	100	0.05	0.03	0.30
D04	20	0.07	0.03	0.28
D07	450	0.13	0.07	0.31
D07	200	0.08	0.05	0.31
D07	100	0.08	0.05	0.21
D07	20	0.07	0.04	0.35
D08	450	0.14	0.19	0.51
D08	200	0.08	0.12	0.23
D08	100	0.09	0.10	0.32
D08	20	0.09	0.08	0.26

Table S5: Measured concentrations of titanium, gold and cerium after ultrafiltration. This set of samples used had not been filtered on site, but was instead acidified with nitric acid. The concentrations are given in μg/l and the mesh size in nm.

Location	*Mesh*	Ce	Au	Ti
D01	450	1.1	0.02	2.9
D01	200	0.51	0.02	2.5
D01	100	0.52	0.02	2.6
D01	20	0.52	0.02	2.9
D04	450	1.2	0.02	2.7
D04	200	0.64	0.02	2.4
D04	100	0.64	0.02	2.5
D04	20	0.64	0.02	2.9
D07	450	2.0	0.03	3.4
D07	200	1.4	0.02	2.7
D07	100	1.4	0.02	3.1
D07	20	1.4	0.02	3.5
D08	450	1.5	0.07	3.2
D08	200	0.83	0.04	2.1
D08	100	0.86	0.03	2.3
D08	20	0.87	0.03	2.8

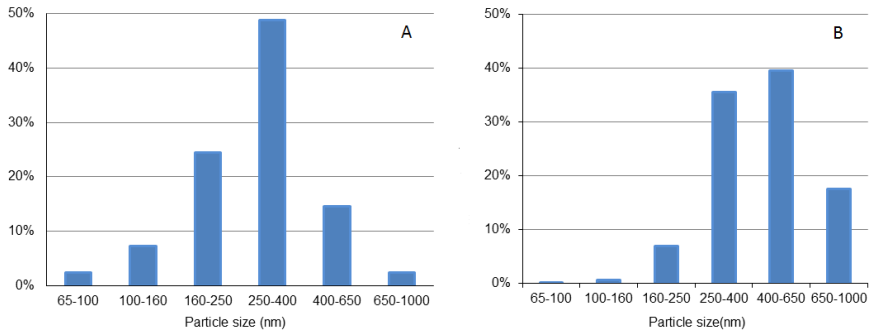

Figure S5: Size distribution of the nanoparticles found in the sludge (W03), distribution by numbers (A) and distribution by mass (B).

the WWTP effluent in the period of sampling, the expected contribution to the concentration for these three elements can also be estimated. Since the water of the Dommel is mixed with the effluent from the WWTP, for which the flow rate was 1.3 m^3/s in this period, the resulting concentration depends on the concentration upstream as well as the concentration in the effluent:

$$C_{result} = \frac{Q_{eff}C_{eff} + Q_{up}C_{up}}{Q_{eff} + Q_{up}} \tag{1}$$

where Q_{eff} and C_{eff} are the flow and the concentration of the effluent and Q_{up} and C_{up} are the flow and the concentration upstream of the WWTP. The WWTP therefore has a twofold influence: dilution because of the volume of the effluent and an increase in the mass flux, due to the presence of the various elements, in dissolved or nano form.

6 Interpretation of the concentrations

To further interpret the measured concentrations one can combine the concentrations at various points with the flow rates of the river and its tributaries or the WWTP to predict the concentrations after the point of confluence. This is done for locations D05 and D04:

- Using the measured concentrations at locations D07 (downstream of the sediment trap) and D06 (the sampling point in the Tongelreep tributary), it should be possible to predict the concentration at D05 (downstream of the confluence).
- Using sampling point D05 and the effluent of the WWTP (W02), it should be possible to predict the concentration at D04 (the sampling point downstream of the WWTP).

- The predicted concentration is based on a mass balance for the river Dommel and its tributary or the WWTP.

Deviations of the actually measured concentrations from the predictions may indicate that the underlying assumptions are false: it is assumed that the river is well-mixed at these sampling points, so that the measurements are representative and it is assumed that the concentration measured in the effluent is representative for the WWTP, that is, the composition of the effluent is fairly constant.

For these calculations the measured concentrations in Table S3 and the flow rates in Table S6 have been used.

Table S6: Flow rates as used in the mass balance calculations.

Dommel, upstream of location D07	1.8 m^3/s
Tongelreep	1.0 m^3/s
WWTP	1.3 m^3/s

For zinc and cerium the results are shown in Table S7 and for titanium the results are shown in Table S8.

Table S7: Predicted and observed concentrations for zinc and cerium (values in μg/l).

Location	Predicted Zn	Observed Zn	Predicted Ce	Observed Ce
D05	47.1	47	1.04	0.9
D04	49.7	56	0.52	0.6

The deviations are in the order of 13%, so comparable to the (estimated) measurement uncertainty.

Table S8: Predicted and observed concentrations for titanium (values in μg/l).

Location	Predicted Ti	Observed Ti
D05	1.64	1.8
D04	1.15	1.7

The deviation between the measured and the predicted concentration for location D04, 47%, is much larger than for the other location and also than for the other substances.

If one assumes a contribution of runoff from painted surfaces to explain this difference, the emission per year would be in the order of 40 kg. With

some further assumptions about the amount of paint that is typically used for an exterior surface (0.2 L/m^2) and the content of titanium pigment (5% by weight), the surface area needed for such an emission can be estimated: 4000 m^2 would have to lose its titanium content. This does not seem excessive, given a population of half a million people in the region of Eindhoven.

7 Interpretation of the correlation for cerium and lanthanum

To further interpret the results, it has to be considered by what amount the measured concentrations of cerium should be raised to make the intercept clearly non-zero:

$$[La] = a_{new} + b([Ce] + \Delta[Ce]) = a + b[Ce] \tag{2}$$

The coefficient b remains the same, as all measured concentrations are raised by the same amount. Originally the intercept a takes values in the interval [-0.0068-0.025,-0.0068+0.025] μg/l. To make sure the interval for the new intercept a_{new} does not contain 0 anymore:

$$a_{new} = a - b\Delta Ce < 0 \tag{3}$$

Therefore:

$$-0.0068 + 0.025 - b\Delta Ce < 0 \tag{4}$$

An overall increase in the cerium concentration of 0.05 μg/l would guarantee this.

Alternatively, one can consider an increase in the cerium concentration by a certain factor. Using the standard error in the slope such a factor could be (0.46+0.03)/0.46 = 1.07 to change the slope of the correlation well away from the reported value. As the typical concentration measured in the Dommel river is 0.6 μg/l, this would mean an increase by 0.042 μg/l, almost the same as the other considered change.

A change in concentration of 0.05 μg/l corresponds to a change in the annual transport in the river by 4.5 kg/y.

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