



UvA-DARE (Digital Academic Repository)

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

Markus, A.A.; Krystek, P.; Tromp, P.C.; Parsons, J.R.; Roex, E.W.M.; de Voogt, P.; Laane, R.W.P.M.

DOI

[10.1016/j.scitotenv.2018.03.007](https://doi.org/10.1016/j.scitotenv.2018.03.007)

Publication date

2018

Document Version

Final published version

Published in

Science of the Total Environment

License

Article 25fa Dutch Copyright Act (<https://www.openaccess.nl/en/in-the-netherlands/you-share-we-take-care>)

[Link to publication](#)

Citation for published version (APA):

Markus, A. A., Krystek, P., Tromp, P. C., Parsons, J. R., Roex, E. W. M., de Voogt, P., & Laane, R. W. P. M. (2018). Determination of metal-based nanoparticles in the river Dommel in the Netherlands via ultrafiltration, HR-ICP-MS and SEM. *Science of the Total Environment*, 631–632, 485–495. Advance online publication. <https://doi.org/10.1016/j.scitotenv.2018.03.007>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (<https://dare.uva.nl>)



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



A.A. Markus^{a,b,*}, P. Krystek^d, P.C. Tromp^e, J.R. Parsons^b, E.W.M. Roex^a, P. de Voogt^{b,c}, R.W.P.M. Laane^{b,1}

^a Deltares, P.O.Box 177, Delft 2600 MH, The Netherlands

^b Earth Surface Science, IBED, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

^c KWR Watercycle Research Institute, Nieuwegein, The Netherlands

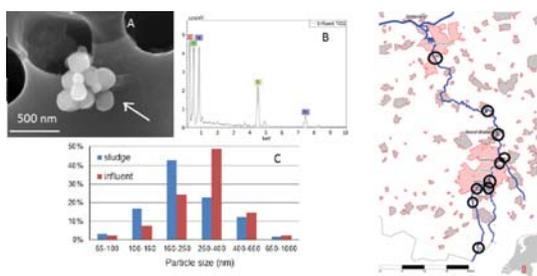
^d Dep. Environment & Health, VU University, De Boelelaan 1085, Amsterdam 1081 HV, The Netherlands

^e TNO Earth, Life and Social Sciences, Princetonlaan 6, Utrecht 3584 CB, The Netherlands

HIGHLIGHTS

- Ultrafiltration shows that most metal is adsorbed to particles larger than 0.5 μm .
- Nanoparticles found in influent and sewage sludge are mainly aggregated.
- Estimated concentration of nanoparticles is at most 10% of total metal concentration.
- Titanium concentrations may be enhanced due to urban runoff.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 9 January 2018

Received in revised form 28 February 2018

Accepted 1 March 2018

Available online xxxx

Editor: D. Barcelo

Keywords:

Nanoparticles

Metals

HR-ICP-MS

Ultrafiltration

Electron microscopy

ABSTRACT

We investigated the occurrence of metal-based nanoparticles in a natural system, the river Dommel in the Netherlands. The river itself is well-studied as far as hydrology and water quality is concerned, easily accessible and contains one major wastewater treatment plant discharging onto this river. We sampled water from various locations along the river and collected samples of influent, effluent and sewage sludge from the wastewater treatment plant. The sampling campaign was carried out in June 2015 and these samples were analysed for seven elements using high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS), ultrafiltration with a sequence of mesh sizes and scanning electron microscopy (SEM).

From the results we conclude that there are indeed nanoparticles present in the treatment plant we studied, as we found titanium and gold particles in the influent and effluent. In the river water only 10 to 20% of the mass concentration of titanium, cerium and other elements we examined is made up of free, i.e. unattached, particles with a size smaller than 20 nm or of dissolved material. The rest is attached to natural colloids or is present as individual particles or clusters of smaller particles, as it could be filtered out with 450 nm ultrafilters.

We found evidence that there is no appreciable anthropogenic emission of cerium into the river, based on the geochemical relationship between cerium and lanthanum. Besides, the effluent of the treatment plant has lower concentrations of some examined elements than the surface water upstream. The treatment plant discharges much less of these elements than estimated using previous publications. However, a potential diffuse source of titanium dioxide in the form of nanoparticles or of larger particles is their use in paints and coatings, as the concentration of titanium increased considerably in the urbanised area of the river Dommel.

© 2018 Elsevier B.V. All rights reserved.

* Corresponding author at: Deltares, P.O.Box 177, Delft 2600 MH, The Netherlands.

E-mail address: arjen.markus@deltares.nl (A. Markus).

¹ Deceased May 31 2016.

1. Introduction

With the increasing use of nanoparticles in consumer products and industrial processes it becomes more and more important to know in what concentrations they occur in the environment in order to perform proper risk assessment (Keller and Lazareva, 2014). Pathways for the release of nanoparticles into surface waters are among others wastewater from households and atmospheric deposition (Petersen et al., 2011). For the most common types of nanoparticles, titanium dioxide, zinc oxide and silver, it is likely that the main pathway is via wastewater from households and industry, as their main application is in personal care products, paints and coatings and textiles, as a UV filter or for their antimicrobial properties. In particular paints and coatings may be an important diffuse source (Kaegi et al., 2008). A fourth type, cerium dioxide is also used as an abrasive and, in some European countries, as an additive in fuel for automobiles, so that atmospheric deposition is a possible pathway (Gómez-Rivera et al., 2012; Erkados et al., 2014).

One of the problems encountered with research into the occurrence of engineered nanoparticles in the environment is the difficulty in actually detecting and measuring them in complex environmental matrices. It is also difficult to distinguish engineered nanoparticles from particles in that size range that have a natural origin (Wagner et al., 2014). One advantage of investigating metal-based nanoparticles is that the elemental composition makes it somewhat easier to distinguish them from background (organic) material, even though it is still difficult to determine if they are engineered or natural.

This article reports on the use of a combination of separation and detection techniques in order to determine the presence of nanoparticles in a river in the south of the Netherlands. This river, the Dommel, was chosen because it is easily accessible and there is one large city, Eindhoven, with one of the largest wastewater treatment plants in the Netherlands that discharges into it. Thus a relatively large potential source of nanoparticles is present in the study area.

In 2013 a first sampling campaign was held along the Dommel and the concentrations of several elements, aluminum, cerium, titanium and zirconium, were measured using asymmetric flow field flow fractionation, to separate the particles, and HR-ICP-MS for measuring the elemental concentrations. These measurements have been reported by Klein et al. (2016), as part of a study into the modelling of the transport and fate of nanoparticles in the river Dommel. A second sampling campaign was performed in 2015, using largely the same sampling points. As noted by Bäuerlein et al. (2017) there are up to date few studies reporting measured environmental concentrations of nanoparticles. This study contributes to this collection by using a variety of techniques.

2. Materials and methods

2.1. Selection of elements of interest

The following elements were measured: zinc, titanium, gold, silver, cerium, lanthanum and zirconium. Several of these elements were chosen as they are among the materials most commonly used as nanomaterials or discussed in the recent literature (Hansen et al., 2016; Gottschalk et al., 2013). Lanthanum was chosen because of its known relationship with cerium. In undisturbed, “natural”, circumstances the various rare earth elements occur in a rather constant ratio (Klaver et al., 2014; Kulaksız and Bau, 2011). If there is an anthropogenic influence, such as the use of cerium dioxide nanoparticles, then a discrepancy in this ratio would occur (Peters et al., 2018; Praetorius et al., 2016). This may manifest itself as non-constant ratio or as a different ratio from the published ones. While it is somewhat arbitrary to set a limit, we used the standard error found by regression analysis to determine bounds for such a discrepancy.

2.2. Sampling locations

The river Dommel is a small river located in the south of the Netherlands. It originates in Belgium, runs northwards and passes the city of Eindhoven including the wastewater treatment plant (WWTP) with a capacity of about 750,000 inhabitant equivalents and joins the river Meuse after about 80 km near the city of 's Hertogenbosch. It is joined by several tributaries, of which the Tongelreep and the Kleine Dommel are the main ones. Of these the river Tongelreep is one of the largest in terms of flow rate. Water samples were collected at 11 locations along the river Dommel on 4 June 2015, and samples of the influent, effluent and sewage sludge of the treatment plant, were collected the day before (see Fig. 1). The latter were obtained as instantaneous samples by the operators of the plant.

For a better understanding of the geography and the interpretation of the results the context for the various locations is given:

- The locations D11 down to D08 represent the stretch from the Belgian border through the sediment trap Klotputten. The purpose of this sediment trap is to reduce the load of suspended particulate matter (SPM), as the river Dommel carries SPM that is contaminated by a former zinc smelter (Petelet-Griaud et al., 2009). Location D08 is just downstream of the sediment trap and one would expect the lowest element concentrations in this location, at least if the elements are attached to SPM or are present as particles that are large enough to settle.
- Locations D07 and D05 are upstream of the WWTP, whereas D06 is the location in the tributary Tongelreep.
- Location D04 is just downstream of the WWTP and one would expect the highest concentrations there, if indeed there are noticeable emissions of the elements from the WWTP considered in this study. The river Kleine Dommel joins the Dommel between locations D04 and D03.
- The locations D03 to D01 are downstream of Eindhoven. Before location D03 the tributary Kleine Dommel enters and between D02 and D01 the Essche Stroom enters, so that the water becomes mixed with the contributions from these tributaries as well.

2.3. Sample collection and preservation

The water samples were collected using a plastic bucket, which was first rinsed with the river water at the site. All samples were taken half a meter below the surface. The samples were then transferred to 60 mL polystyrene bottles that had not been used before. For each location two such bottles were filled:

- One bottle was filled with surface water filtered in situ, using a mesh size of 0.45 µm (MDI syringe filters, 0.45 µm, type SY25NN).
- A second bottle was filled with unfiltered water but in the field 0.6 mL of nitric acid (68%) was added to preserve the sample.

These bottles were stored at 5 °C until the analysis.

2.4. Measurement techniques

Several techniques were employed to determine if nanoparticles are present in the river and if so in what concentrations and in what sizes (see Fig. 2):

- The samples that were acidified in the field, were used to measure the total concentration of the seven selected elements

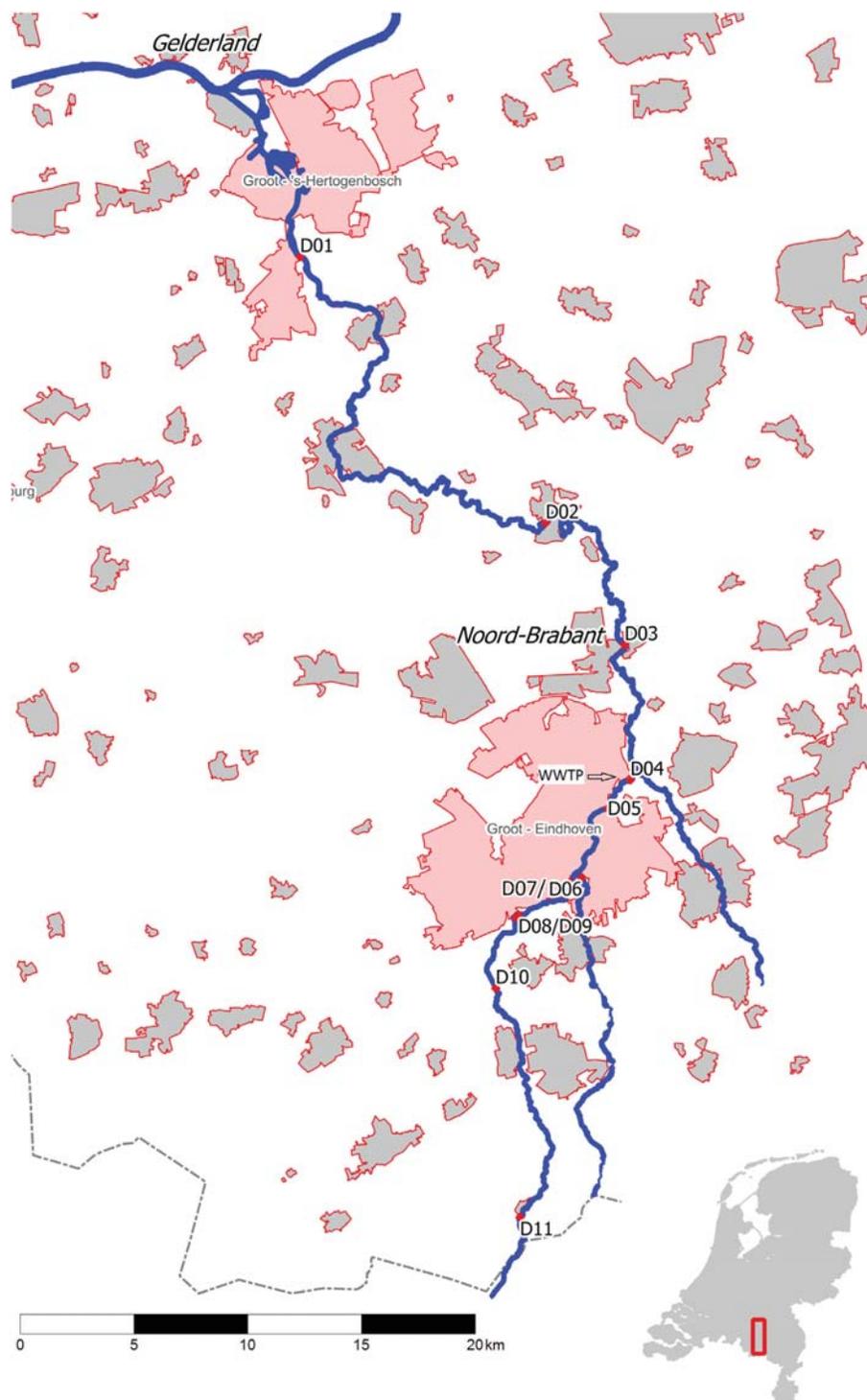


Fig. 1. Map of the sampling locations along the river Dommel. At the top it joins the river Meuse. The two tributaries are the river Tongelreep (near location D06) and the river Kleine Dommel (just north of D04). Other tributaries are not shown. In the inset: the location of the study area within the Netherlands. Location D07 is close to D06 and location D09 is close to D08.

via HR-ICP-MS. The samples from all locations including the samples from the WWTP were used. These results were subsequently used to determine which samples and elements were to be used for further identification by ultrafiltration and SEM analysis.

- Ultrafiltration was applied to separate the particles in size fractions. The subsamples came from both the filtered samples and the acidified samples. The concentration of three elements

in these filtered samples was measured with HR-ICP-MS, to determine how much is present in each size fraction.

- Several samples were examined using SEM to identify individual nanoparticles and clusters of nanoparticles.

The mass spectrometer was a high-resolution instrument, HR-ICP-MS type ELEMENT XR, Thermo Fisher Scientific, Breda, the Netherlands.

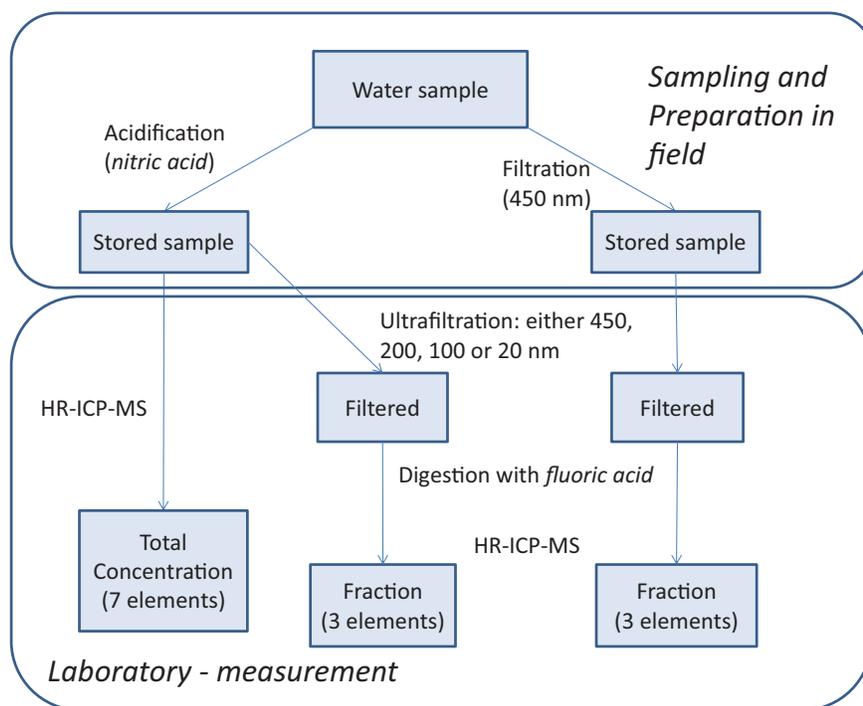


Fig. 2. Schematic overview of the sampling and analysis by HR-ICP-MS.

2.4.1. Calibration and limits of quantification

The mass spectrometer was calibrated for the various elements using a rhodium internal standard and standard solutions with concentrations in ranges selected for the expected concentrations:

- For gold and lanthanum the following series was used, 0, 0.1, 0.5, 1 µg/L, as the concentrations were expected to be in this range.
- For zirconium, the dedicated series was: 0, 0.5, 1, 5 µg/L.
- For titanium, the series 0, 1, 5, 10 µg/L was used.
- As zinc was expected to have a fairly high concentration, the series 0, 10, 50, 100 µg/L was used.

The limits of quantification were determined from the calibration curves (see the Supporting Information for actual values).

2.4.2. Ultrafiltration and preparation

Four locations were selected that seemed of particular interest, on the basis of the analysis of the total concentration. Both the samples that were filtered in the field and the unfiltered samples that were acidified with nitric acid were analysed, as a quality check that the preparation of the samples did not influence the results (see, however, Section 3.2). The mesh sizes for the syringe filters were: 450 nm, 200 nm, 100 nm and 20 nm (type Whatman© Anotop, from GE Healthcare Life Sciences, Eindhoven, The Netherlands). For each mesh size a new water sample was taken. The samples were analysed for titanium, gold and cerium, as the longitudinal profiles found in the first round showed the most interesting features for these three elements.

In total 32 samples were measured according to the following procedure (Dekkers et al., 2011):

- 10 mL of the original acidified surface water sample was filtered using an ultrafilter with one particular mesh size.

- The filtered water was stored in a 15 mL polyethylene tube and then nitric acid (60%) was added, 0.45 mL for the samples that were not acidified on site and 0.35 mL for the ones that were acidified on site. To all tubes 0.1 mL of hydrofluoric acid (40%) was added.
- Overnight the sample was heated to a temperature of 70 °C for further dissolution of the particulate matter.
- The final volume was registered for correction of the measured concentration.
- Via the same HR-ICP-MS instrument the concentration of cerium, gold and titanium was measured.

As demonstrated by Krystek and Ritsema (2009), measurements of comparably low concentration levels in groundwater via HR-ICP-MS have a total measurement uncertainty in the order of 15% for most elements. The uncertainty is caused by measurement errors but also by deviations in the treatment of the sample, sample stability and inhomogeneities. This value of 15% has been used as the uncertainty in the current measurements.

2.5. Electron microscopy (FEG-SEM/EDX)

Because size distributions can be influenced by aggregation of particles during sample treatment (Hassellöv et al., 2008), the particle load of the filters was minimized (less than 10%). In (Peters et al., 2014) it was shown that under these conditions the number-based size distributions of titanium dioxide determined with SEM and AF4-ICP-MS were comparable. The particle load (i.e. the particle occupancy) of the filter was determined by dividing the particle-occupied filter area (mm²) by the total filter area (mm²).

To confirm the presence of titanium dioxide and gold nanoparticles in influent and sludge from the WWTP, subsamples were studied using scanning electron microscopy (SEM).

2.5.1. Sample preparation

Droplets of 50 µL of the influent and sludge samples were transferred to nickel-coated polycarbonate filters (mounted on aluminum

specimen holders) and were evaporated into dryness. Subsequently the filters were plasma-ashed for 1 h at 15 W in order to remove organic material.

2.5.2. Analysis procedure

The filters were analysed using a high-resolution field emission gun scanning electron microscopy in combination with energy dispersive X-ray analysis (FEG-SEM/EDX). The instrument used in this study was a Tescan MIRA-LMH FEG-SEM (Tescan Benelux, Brussels, Belgium) equipped with a Bruker AXS spectrometer and a 10 mm² XFlash 4010 Silicon Drift Detector (Bruker Nano GmbH, Berlin, Germany).

The filter surface area (314 mm²) was inspected on a field-by-field basis at a magnification of 20,000× (field of view 13.9 × 10.4 μm) for titanium dioxide particles and 50,000× (field of view 5.5 × 4.2 μm) for gold particles. In approximately 200 randomly selected fields of view, covering the complete filter surface, particles were manually recognized and X-ray spectra from the detected particle and surrounding matrix were acquired to determine the identity. Of each particle, shape and size was determined with Scandium SIS software package (Olympus Soft Imaging Solutions GmbH, Germany).

The surface of the filters were systematically searched for titanium dioxide and gold nanoparticles using the backscattered electron imaging mode. After detection of particles in a field of view, X-ray spectra from the detected particle and surrounding matrix were acquired to determine the identity. The SEM was equipped with Scandium SIS software package (Olympus Soft Imaging Solutions GmbH, Germany) for automated particle analysis.

2.5.3. Determination of size distribution

The size distribution of titanium dioxide was determined in accordance with Peters et al. (2014). From each particle or cluster of particles the projected area equivalent diameter (dpa) was measured. A magnification of 10,000× (field of view 27.7 × 20.8 μm) – 50,000× (field of view 5.5 × 4.2 μm) was chosen to measure the size range of 25–2500 nm. Per size bin a minimum of 5 particles were measured. Per size bin the standard deviation (95% confidence interval) was calculated on the basis of the Poisson distribution. The numerical concentration was converted into mass concentration, using the particle density, dpa and volumetric shape factor, in accordance with Wagner and Leith (2001). For titanium dioxide an average density of 4.0 g/cm³ and a shape factor of 1.35 was used (Whitehead and Leith, 2008).

2.6. Estimated emissions of nanoparticles

The WWTP is expected to contribute to the concentration of several of the elements considered in the river Dommel. Whether such a contribution can be identified on just the concentration pattern, depends on the size of the contribution in comparison to the background concentration. Since the WWTP was identified as a potential source of nanoparticles, the estimates from Markus et al. on emissions via nano-enabled products by consumers were used (Markus et al., 2013). Furthermore, WWTPs are likely to retain at least 95% of the nanomaterial in the sewage sludge (Barton et al., 2015; Kaegi et al., 2011). This is further discussed in Section 3. For more details, see the Supporting Information.

By comparing the results of this study with the results from the above publications an independent check is obtained whether or not nanoparticles may have a noticeable effect on the concentration in the river. Table 1 summarises the estimates.

Table 1

Estimates of the amount of nanoparticles in wastewater, the net yearly emission and concentrations in the influent and effluent of the WWTP in Eindhoven. The total estimated amounts were obtained using the per-capita contributions reported in (Markus et al., 2013). It was further assumed that 95% of the elements is retained in the sludge. The discharge of the WWTP and the representative flow rate of the river are taken as 1.3 and 1.6 m³/s, so downstream of the WWTP the flow rate is 2.9 m³/s.

Element	Total amount	Net emission	Influent	Effluent	River
Zinc	2.5 t/y	0.13 t/y	61 μg/L	3.0 μg/L	1.4 μg/L
Titanium	1.9 t/y	0.09 t/y	46 μg/L	2.3 μg/L	1.0 μg/L
Silver	23 kg/y	1.2 kg/y	0.56 μg/L	28 ng/L	13 ng/L

3. Results and discussion

Of the seven elements that were analysed in the surface water samples during the first step, silver showed the lowest concentrations with a maximum of 0.03 μg/L, which is in the range of the limit of quantification of 0.02 μg/L (see the supporting information). This is in accordance with Klein et al. (2016). The concentration of silver that was found in the effluent of the WWTP, 0.013 μg/L was even below this limit. Therefore the measurements for silver will not be considered further.

3.1. Total concentrations of five elements in surface water samples

The total concentrations of the elements were measured using the unfiltered samples that had been acidified with nitric acid in the field. The results are discussed for each element separately, except for cerium and lanthanum as for these a specific relationship is expected. Section 5 in the SI contains a further analysis of the concentration using a mass balance approach.

The measured concentration of zirconium was approximately constant along the river, 0.25 μg/L, with no discernible pattern (see Fig. S1 in the SI). The other elements show variable patterns discussed below (the SI presents the measured values).

3.1.1. Gold

The concentration profile for gold is shown in Fig. 3A. It can be seen that the concentration amounts to 0.1 μg/L near the border with Belgium (location D11), well above the limit of quantification of 0.02 μg/L, and remains more or less constant, until the Dommel reaches the sediment trap the Klotputten (locations D08 and D09), from where it steadily increases to a value of 0.35 μg/L at the most downstream location D01. There is no known source of gold anywhere in the basin of the Dommel or its tributaries. As the increase in downstream direction is rather steady, a possible explanation is that gold is leaching from the soil in the urbanised areas or in the more rural environment inbetween the towns along the river. Similar concentrations of gold for surface waters in the Netherlands are reported by Bäuerlein et al. (2017) in their report on evidence for nanoparticles in the Netherlands as a whole. Klein et al. (2016) found concentrations of gold in the Dommel in this same range.

3.1.2. Zinc

The zinc concentration in the river Dommel upstream of Eindhoven is rather high, between 40 and 110 μg/L, as a consequence of the former presence of a zinc smelter, just over the Belgian border. In the river Meuse, for example, a typical concentration of 25 μg/L is observed (Markus et al., 2013), quite comparable to the concentration in the Tongelreep (location D06). According to the current measurements (see Fig. 3B), the concentration of zinc is by far the highest upstream, 110 μg/L, and decreases steadily. The lowest concentration is found at location D06, which is in the tributary Tongelreep. The WWTP in Eindhoven does not appear to contribute significantly – the concentration in the effluent collected on that day

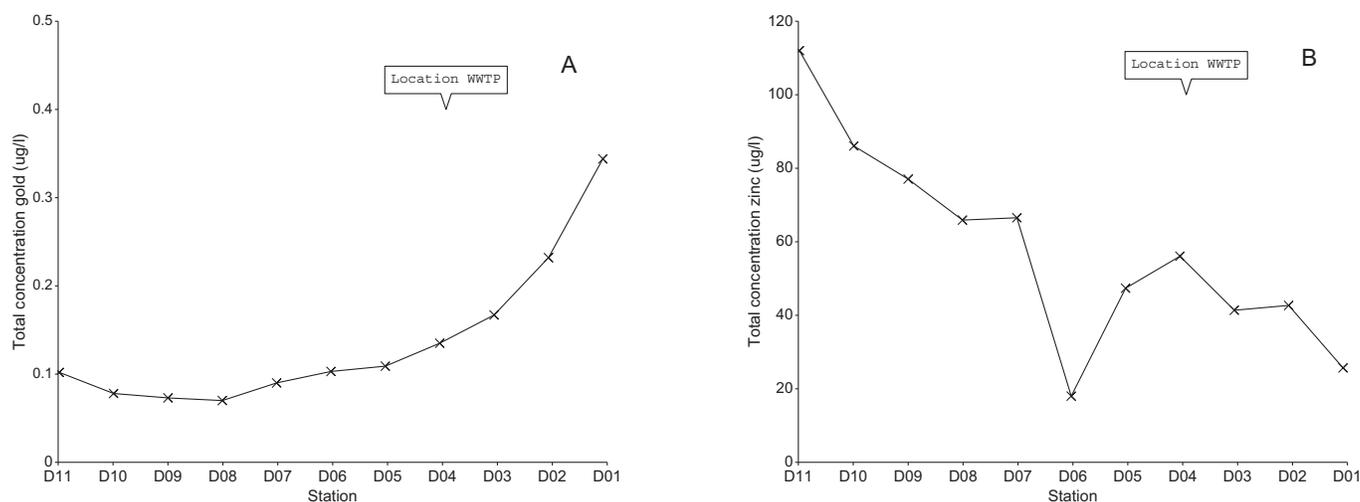


Fig. 3. Measured concentration ($\mu\text{g/L}$) of gold (A) and zinc (B) along the Dommel. Notice the difference in scale for the vertical axis. The distance along the horizontal axis represents the distance of the stations along the river. Station D06 does not lie in the Dommel itself.

was $52 \mu\text{g/L}$, whereas the concentration in location D04, just downstream of the WWTP was $56 \mu\text{g/L}$. At the upstream location D05 a concentration of $47 \mu\text{g/L}$ was measured.

The decrease in the concentration in the upstream part around the sediment trap Klotputten (locations D08 and D09) indicates that at least part of the zinc is present as free particles or adsorbed to particles that get trapped there. The decrease between locations D02 and D01, in the downstream part, is probably due to yet another tributary, the Essche Stroom, joining the river Dommel. This tributary has been reported by the waterboard De Dommel to have a mean zinc concentration of $28 \mu\text{g/L}$ (data from 2005; Lüers et al., 2006).

3.1.3. Titanium

The concentration profile for titanium is quite different from that of gold and zinc, in that the concentration increases significantly around the sediment trap (location D08; see Fig. 4A): from $0.6 \mu\text{g/L}$ at location D09 (upstream) to $1.6 \mu\text{g/L}$ at location D08 (downstream) and remains at that level for the whole downstream section. It should be noted that the acidification with nitric acid, as applied for these measurements, leads to an underestimation of the total concentration of titanium by a factor 2 (see also Section 3.2).

The factor is roughly constant over the four locations that were examined in detail.

The increase in the measured concentration of titanium in the river between locations D08 and D09 and the continued higher concentration downstream may be due to urban runoff (see Fig. 4A). This part of the river passes through the communities south of Eindhoven and the city itself. In the several days before the samples were collected on 4 June 2015 a total amount of 10 mm of rain had fallen, however this is not apparent from the flow rates of the Dommel river in this period (see Section 2 in the SI). Kaegi et al. (2008) found a concentration of 10 to $15 \mu\text{g/L}$ of titanium in the stormwater in their study regarding emissions from exterior facades. It is difficult to translate their observations to the current situation, since it strongly depends on the local circumstances. Nonetheless, the increase in concentration that was observed in the river Dommel is in a similar range, taking dilution into account.

The WWTP was expected to be a source of titanium in view of the use of titanium dioxide as a food additive (EU code E171) and as a component of various personal care products. The influent had a concentration of $4.1 \mu\text{g/L}$, however, due to the effective retention in the WWTP, the effluent had a titanium concentration significantly

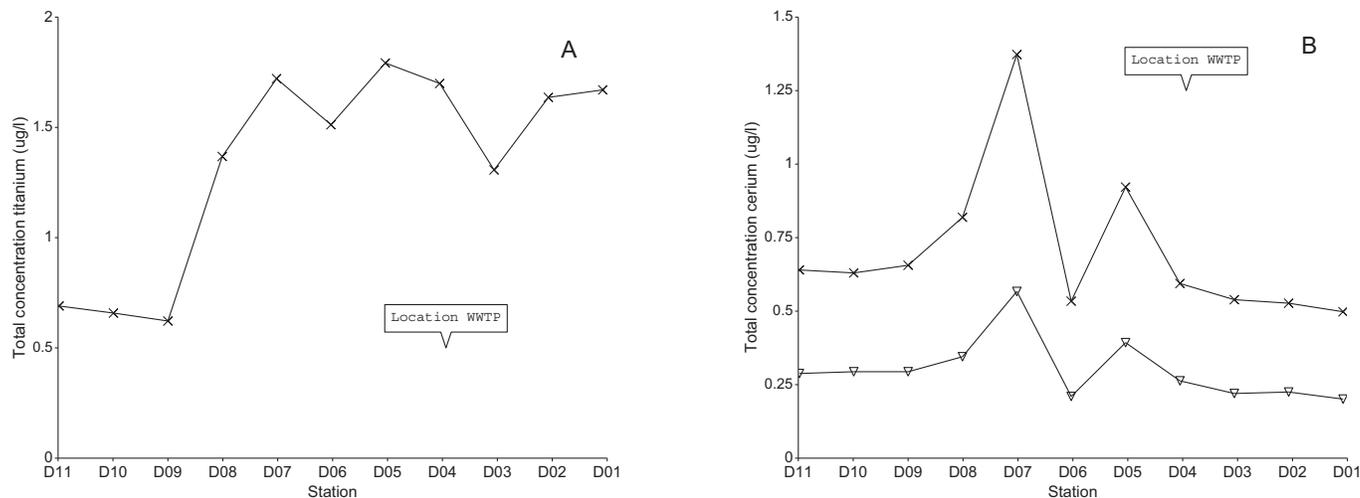


Fig. 4. Measured concentration ($\mu\text{g/L}$) of titanium (A) and of cerium (x) and lanthanum (∇ ; B) along the Dommel.

lower than that of the receiving Dommel water: 0.41 $\mu\text{g/L}$ compared to a concentration of 1.7 $\mu\text{g/L}$ at location D04 (SI, Table S2). 90% of the titanium is retained in the sewage sludge.

The concentrations measured in the influent and the effluent are about 8 times and 3 times lower, respectively, than the estimated contribution of titanium dioxide nanoparticles to the total emission of titanium from the effluent of the WWTP Eindhoven (see Table 1). Therefore the estimates regarding titanium dioxide nanoparticles are likely to be too high. Nevertheless, the estimates given in Table 1 are in the same range as the values found by Johnson et al. (2011). They measured concentrations of titanium (size < 0.45 μm) in a sewage treatment plant in Southern England ranging from 17 to 40 $\mu\text{g/L}$ in the influent and on average 3 $\mu\text{g/L}$ in the effluent.

Klein et al. (2016) report total concentrations in the order of 0.7 $\mu\text{g/L}$ for titanium for most of the reach of the Dommel. Only for the three locations further down stream were higher concentrations observed, in the order of 1 $\mu\text{g/L}$. As shown in Section 3.2 on the ultrafiltration results, applying a 0.45 μm filter has a significant effect on the observed concentrations, indicating that a large fraction is present as particles of at least that size or attached to such particles.

3.1.4. Cerium and lanthanum

The concentrations of cerium and lanthanum along the river Dommel are shown in Fig. 4B. The concentrations for both elements is fairly constant, except at locations D05 and D07 where the values are considerably higher than at the other locations. At location D06, situated in the river Tongelreep, the concentration is somewhat lower than in the Dommel itself. Why there is a higher concentration at location D07 is unclear.

Klein et al. (2016) report concentrations for cerium that decrease from 0.27 $\mu\text{g/L}$ at the most upstream point (near the Belgian border, location D11) to 0.08 $\mu\text{g/L}$ north of Eindhoven (location D02). of the Dommel. These are two to four times lower than the concentrations observed in the present study. They filtered their samples and then added nitric acid to dissolve the samples. This treatment is comparable to the ultrafiltration steps used in this study – the corresponding concentrations we found were significantly lower (see Section 3.2).

As mentioned above, cerium and lanthanum are expected to occur in a fairly constant ratio, unless there is an anthropogenic influence (Klaver et al., 2014; Kulaksız and Bau, 2011). As shown in Fig. 5 there is in fact a strong correlation between the concentrations of these two elements. The only exception is the concentration in the influent of the WWTP, where the ratio lanthanum/cerium is almost 1.5 times higher than at the other locations, which may indicate anthropogenic influence. The ratio in the present study is 0.46, whereas the data published by Petelet-Griaud et al. (2009) show a ratio of 0.49 for a single location in this river (“Dommel downstream”, time series data from July 2005 to July 2007).

The regression analysis shows a standard error of 0.025 $\mu\text{g/L}$ in the interception of the correlation and a standard error of 0.03 in the slope. This means that the slope reported by Petelet-Griaud et al. of 0.49 is within the limits of the present observations. It also means that the interval for the intercept contains 0 and thus the relationship can be assumed to be linear. As described in the supporting information, given these standard errors, a change in the cerium concentration of 0.05 $\mu\text{g/L}$ would give a noticeable discrepancy from the linear relationship. A concentration change of that order would mean a change in the total load of the river by 4 to 5 kg/y.

Therefore we conclude there is no indication of a significant anthropogenic source of either cerium or lanthanum in this region. Such a source might have been the use of cerium as a catalyst in fuel (Boxall et al., 2007) or as an abrasive in the electronics industry (Cheng et al., 2011).

In this study the concentrations observed in the influent for cerium and lanthanum are 0.64 and 0.42 $\mu\text{g/L}$ respectively, while the concentrations in the effluent are 0.05 and 0.02 $\mu\text{g/L}$ respectively,

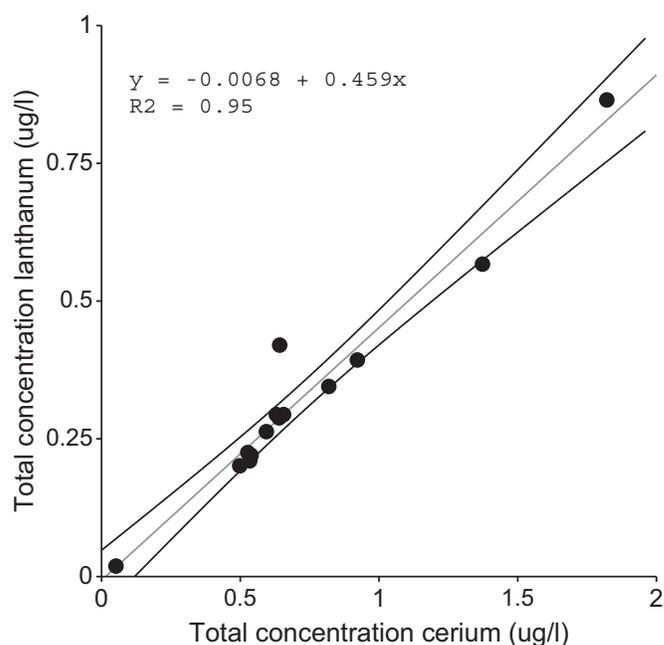


Fig. 5. Correlation between the cerium and lanthanum concentrations in the Dommel. The solid lines represent the best linear fit and the 95% confidence limits.

indicating a retention efficiency of 90 to 95% (see SI). For both elements the concentrations in the receiving Dommel are 10 times as high. This shows that the WWTP does not contribute any significant amount for these elements.

3.2. Results of ultrafiltration

As described in Section 2.4.2, four locations were selected for a closer examination into the presence of nanoparticles. Both series of samples were analysed, that is, the samples that were filtered in the field and the samples that were acidified instead. The selection of locations was based on the concentration patterns reported above:

- D01, near the inflow into the Meuse, in 's Hertogenbosch, where relatively high concentrations of gold were found.
- D04, as it is just downstream from the WWTP, potentially a large source of nanoparticles.
- D07, which is upstream of the WWTP but showed an unexpectedly high concentration of cerium.
- D08, which is downstream of the sediment trap but nonetheless shows an increased concentration of titanium.

The results for cerium are shown in Fig. 6 and for titanium in Fig. 7. The data are summarised in the SI.

Some observations from these results:

- For both titanium and cerium a higher concentration was found in these samples that were all treated with hydrofluoric acid than in the corresponding samples that were only treated with nitric acid (compare Fig. 4A with Fig. 7A for instance). The explanation for this is that nitric acid alone cannot dissolve all of the titanium and cerium, so that these measurements resulted in an underestimation of the actual total concentrations (Weir et al., 2012).
- The concentrations of cerium and titanium found in the samples that were filtered in the field are much lower than the concentrations in the samples to which nitric acid had been

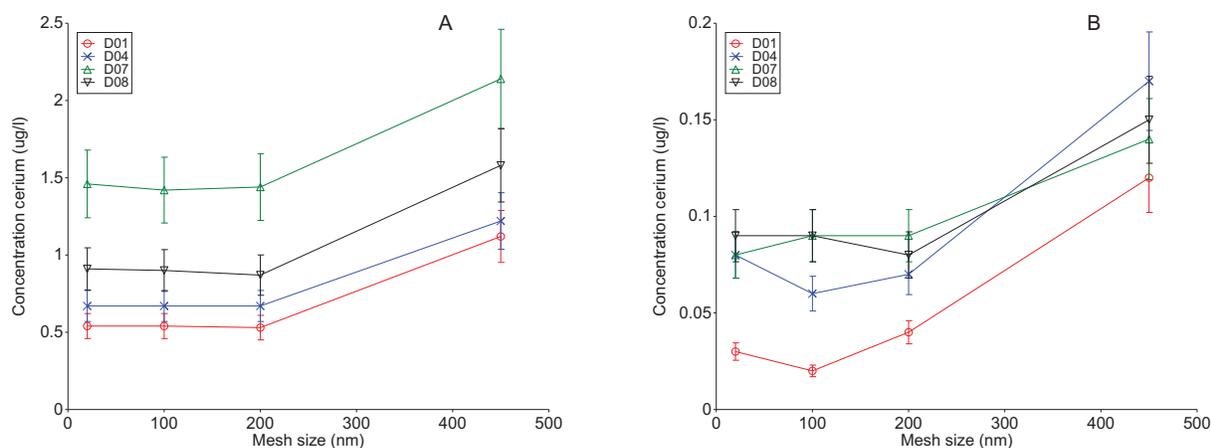


Fig. 6. Concentration of cerium as function of the ultrafilter mesh size. (A) The original sample was acidified immediately after collection, but not filtered. (B) The original sample was filtered, immediately after collection, with a 450 nm filter. The concentration is in $\mu\text{g/L}$, the mesh size in nm.

added. The difference is a factor of 10 for cerium (Fig. 6) and a factor 6 for titanium (Fig. 7). For gold higher concentrations were found in the samples that were filtered in the field, but the concentrations are quite low (in the order of $0.1 \mu\text{g/L}$, though well above the limit of quantification; results shown in the SI).

A possible explanation for this large difference in concentration levels is that the very first filtration, on site, already removed a significant amount of these elements, since they are present as particles or clusters of particles with sizes in the order of $0.45 \mu\text{m}$ or larger. In the acidified samples these larger particles were not filtered out on site. Instead they have probably dissolved under the influence of the acid.

- For cerium the trend in the concentrations after ultrafiltration is quite clear: the 200 nm filter removes one third to one half of the total amount present, with a particle size range of 200 to 500 nm, and the finer filters have little impact (see Fig. 6). This is visible in both sets of samples. It can be concluded that no significant particulate fraction of a size between 20 and 200 nm is present.
- For titanium the effect of the various filtrations is much less pronounced (see Fig. 7A). The increase in measured concentration is somewhat puzzling, though the margins in the measurements are large enough to attribute it to experimental error. It

seems reasonable to assume that titanium is mostly present as very small nanoparticles, though Peters et al. (2014) conclude that titanium dioxide nanoparticles in food and personal care products are almost always larger than 20 nm.

As discussed by Hassellöv et al. (2008), filtration methods to separate particles by size are prone to a number of complications. The overall effect is that not all particles will pass the filters and that the effective mesh size is smaller than the nominal size. All in all this leads to an underestimation of the actual concentrations. While that may have occurred in this study, the difference in the measured concentration between the filtered and the acidified samples indicates that a significant fraction of the cerium and titanium must have been attached to the micrometer-sized particles in the water samples. If the effective mesh size of the filters was significantly diminished, one would expect a rapid decrease in concentrations with smaller mesh size. There is a more or less consistent decrease, but it is not very rapid. The complications mentioned by Hassellöv et al. (2008) appear to have had at most a limited effect. An advantage of ultrafiltration as a separation method is that it is easy to apply (Schaumann et al., 2015).

The tentative conclusion that can be drawn from these measurements is that the nanoparticles that may be present in the

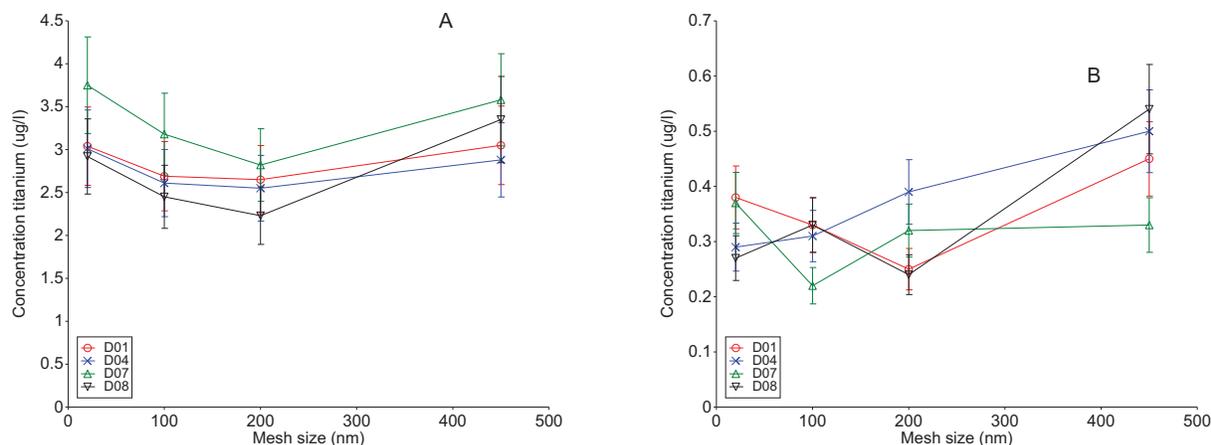


Fig. 7. Concentration of titanium as function of the ultrafilter mesh size. (A) The original sample was acidified immediately after collection, but not filtered. (B) The original sample was filtered, immediately after collection, with a 450 nm filter. The concentration is in $\mu\text{g/L}$, the mesh size in nm.

river Dommel (that is, particles smaller than 100 nm) are mostly attached to coarser particles, such as organic matter or clay, or aggregated into clusters of nanoparticles. Only a very small fraction is likely to be present in an unattached, free floating form.

This can be understood from a mechanistic point of view: natural waters contain a large amount of natural colloidal particles of micrometer size, rather than nanometer size. This is even more true for wastewater from households, in the sewerage system and in the wastewater treatment plant. For instance, Kaegi et al. (2013) report a very high retention of silver nanoparticles in an urban wastewater system.

These relatively large particles will trap nanoparticles and these will remain attached. The rate at which this attachment occurs depends on the concentration of SPM, but given enough time all nanoparticles will become entrapped.

Gondikas et al. (2014) have investigated the occurrence of titanium dioxide nanoparticles in an old reach of the Danube river near Vienna, which is used for recreational purposes. While they found some evidence for such nanoparticles from sunscreens, the seasonal variation was much more limited than they expected. Their explanation is that the nanoparticles remain suspended only for a short while and aggregate with organic matter to then settle on the water bottom. Neal et al. (2011) conclude that aggregation of titanium dioxide nanoparticles and subsequent sedimentation play an important role in the spreading of this material in the British rivers they examined.

3.3. Independent confirmation of the presence of titanium dioxide and gold nanoparticles using FEG-SEM/EDX

As already discussed in Section 3.2, the sample conservation and ultrafiltration methods applied in this study both have their shortcomings in determining the presence of nanomaterials. Therefore FEG-SEM/EDX was used as an independent technique for the

confirmation of nano-sized titanium dioxide and gold particles in influent and sludge samples from the wastewater treatment plant in the river Dommel. The titanium dioxide nanoparticles that were found were both spherically shaped and elongated and present as agglomerates as well as primary particles, the latter with diameters in the range of 50 to 300 nm. In general the agglomerates have diameters in the range of 50 to 1000 nm with an average size of 250–300 nm (Fig. 8). The majority of gold nanoparticles were present as primary particles with diameters in the range of 10 to 20 nm (see SI). On the filter, both titanium dioxide and gold particles appeared attached to and surrounded by organic matter and nutrients. However, it is not clear whether this is also the case in the original influent and sludge samples, because it could have been caused by the sample preparation technique (Hassellöv et al., 2008).

To confirm the identity as titanium dioxide, an EDX scan was carried out of the conglomerate and the surrounding matrix. The resulting EDX graph shows an increase in the response of titanium and oxygen at the position of the particle, a clear indication that the detected particle cluster indeed consists of titanium dioxide (Fig. 8B; see the SI for the EDX spectrum of the gold particle).

For titanium dioxide size distributions and numerical and mass concentrations are derived from the particle counting results. The size distributions of the titanium dioxide particles in the sludge and influent samples are in the range of the particles sizes found in food and personal care products (Peters et al., 2014; Weir et al., 2012). Given this similarity it is likely that the titanium dioxide particles found in the WWTP originate from these food and personal care products. By contrast Gondikas et al. (2014) found aggregated particles of 500 nm and larger in the Old Danube reach – presumably originating from sunscreens.

The uncertainty of the numerical concentration determined with SEM depends on the number of counted particles in a certain size range (Hassellöv et al., 2008). For the influent and sludge samples respectively 82 and 130 titanium dioxide particles were counted

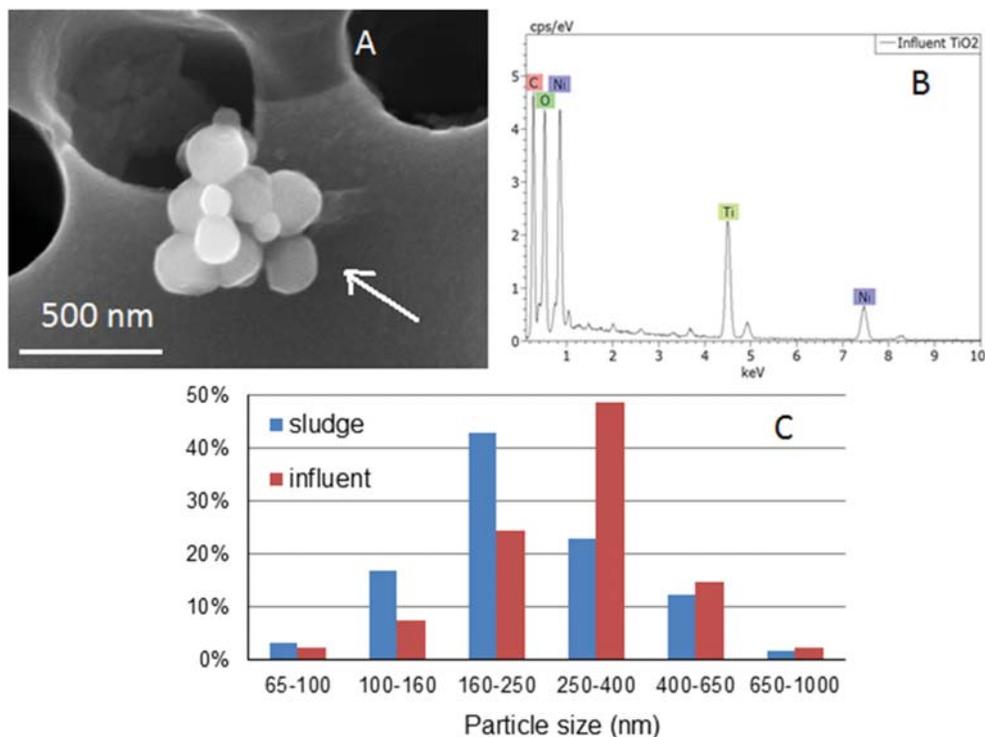


Fig. 8. Representative SEM image of an agglomerate of titanium dioxide nanoparticles (A), the corresponding EDX-spectrum (B) and the number size distribution of titanium dioxide particles (C) in the sludge and influent samples from the WWTP. The method for obtaining the size distribution is that reported in (Peters et al., 2014).

which translates to a numerical concentration of $3.7 (1.8 - 7.4) \times 10^9$ and $2.1 (1.2 - 3.7) \times 10^{10}$ particles/L. The uncertainty of the counting method is determined based on a 95% confidence interval (Poisson distribution). The estimated mass concentration of titanium dioxide nanoparticles is $0.6 (0.3 - 1.5) \mu\text{g/L}$ for the sludge and $0.13 (0.05 - 0.34) \mu\text{g/L}$ for the influent. In comparison with the concentration of total titanium measured with HR-ICP-MS (as titanium dioxide) this corresponds to 8 (4–20)% for the sludge and 3 (1–8)% for the influent. These concentration estimates are about two orders of magnitude lower than those shown in Table 1. Only 2–3% of the titanium dioxide particles is nano-sized (<100 nm). After conversion to mass this corresponds to 0.1%. Most of these particles are present as aggregates, which hampers identification via ultrafiltration.

4. Conclusions

The analyses of the surface water samples that were collected in the river Dommel have shown some remarkable features. First of all, the wastewater treatment plant does not cause an increase in the concentration of the considered elements. In fact, the concentrations in the effluent for the examined elements are lower than the concentrations in the river. Secondly, runoff of coated external surfaces may be responsible for a large fraction of the titanium concentration in the river in the period after rainfall. This effect should be considered when setting up new measurement campaigns for this region or similar regions.

While nanoparticles have indeed been detected in both the influent and the sewage sludge, the concentrations estimated from the SEM images are two or three orders lower than the concentrations in the river water itself. Besides, it should be noted that the samples were only $50 \mu\text{L}$ in size and no attempt was made to examine the heterogeneity in these samples. However, the concentrations in the surface water were determined via ultrafiltration combined with HR-ICP-MS, and no identification of nanoparticles has been done by these samples.

Furthermore, there is no evidence of the emission of cerium in the region, as the ratio of lanthanum and cerium concentrations clearly indicates that all cerium is of a natural origin.

The systematic difference in observed concentrations between the samples that were filtered in the field and the samples that were instead acidified indicates that a significant fraction (80 to 90%) of titanium and cerium is present either as large particles, clusters of particles or adsorbed to natural colloids. When applying filtration techniques, nanoparticles sorbed to natural colloids or present as agglomerates will be missed.

Acknowledgments

This work is supported by NanoNextNL, a micro and nanotechnology programme of the Dutch Government with 130 partners.

We thank the Water Authorities “De Dommel”, especially Oscar van Zanten, for providing the samples from the wastewater treatment plant as well as detailed information on the flow rates in the Dommel system in the sampling period.

Furthermore we thank Joris Quik (National Institute for Public Health and the Environment, RIVM) and Jeroen de Klein (Wageningen University) for discussions during the preparation phase and regarding the interpretation of the data. Gerrit Hendriksen (Deltares) kindly prepared Fig. 1.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.03.007>.

References

- Barton, L.E., Auffan, M., Durenkamp, M., McGrath, S., Bottero, J.Y., Wiesner, M.R., 2015. Monte Carlo simulations of the transformation and removal of Ag, TiO₂ and ZnO nanoparticles in wastewater treatment and land application of biosolids. *Sci. Total. Environ.* 511, 535–543.
- Bäuerlein, P., Emke, E., Tromp, P., Hofman, J.A., Carboni, A., Schooneman, F., de Voogt, P., van Wezel, A.P., 2017. Is there evidence for man-made nanoparticles in the Dutch environment? *Sci. Total. Environ.* 576, 273–283.
- Boxall, A.B.A., Chaudhry, Q., Sinclair, C., Jones, A., Aitken, R., Jefferson, B., Watts, C., 2007. Current and Future Predicted Environmental Exposure to Engineered Nanoparticles. Tech. rep., University of York. http://randd.defra.gov.uk/Document.aspx?Document=CB01098_6270_FRP.pdf.
- Cheng, Y.C., Lu, J., Chen, Z., 2011. Preparation, characterization and oxide CMP performance of composite polystyrene-core ceria-shell abrasives. *Microelectron. Eng.* 88 (2), 200–205.
- Dekkers, S., Krystek, P., Peters, R.J., Lankveld, D.P., Bokkers, B.G.H., van Hoven-Arentzen, P.H., Bouwmeester, H., Oomen, A.G., 2011. Presence and risks of nanosilica in food products. *Nanotechnology* 5, 393–405.
- Erkados, G.B., Bhavne, P.V., Pouliot, G.A., Simon, H., Mathur, R., 2014. Predicting the effects of nanoscale cerium additives in diesel fuel on regional-scale air quality. *Environ. Sci. Tech.* 48, 12775–12782.
- Gómez-Rivera, F., Field, J.A., Brown, D., Sierra-Alvarez, R., Gómez-Rivera, F., Field, J.A., Brown, D., Sierra-Alvarez, R., 2012. Fate of cerium dioxide (CeO₂) nanoparticles in municipal wastewater during activated sludge treatment. *Bioresour. Technol.* 108, 300–304.
- Gondikas, A.P., Von der Kammer, F., Reed, R.B., Wagner, S., Ranville, J.F., Hofmann, T., 2014. Release of TiO₂ nanoparticles from sunscreens into surface waters: a one-year survey at the Old Danube recreational lake. *Environ. Sci. Tech.* 48, 5415–5422.
- Gottschalk, F., Sun, T., Nowack, B., 2013. Environmental concentrations of engineered nanomaterials: review of modeling and analytical studies. *Environ. Pollut.* 181, 287–300.
- Hansen, S.F., Heggelund, L.R., Besora, P.R., Mackevica, A., Boldrin, A., Baun, A., 2016. Nanoparticles - what is actually available to European consumers? *Environ. Sci. Nano* 3, 169–180.
- Hassellöv, M., Readman, J.W., Ranville, J.F., Tiede, K., 2008. Nanoparticle analysis and characterization methodologies in environmental risk assessment of engineered nanoparticles. *Ecotoxicology* 17, 344–361.
- Johnson, A.C., Bowes, M.J., Crossley, A., Jarvie, H.P., Jurkschat, K., Jürgens, M.D., Lawlor, A.J., Park, B., Rowland, P., Spurgeon, D., Svendsen, C., Thompson, I.P., Barnes, R.J., Williams, R.J., Xu, N., 2011. An assessment of the fate, behaviour and environmental risk associated with sunscreen TiO₂ nanoparticles in UK field scenarios. *Sci. Total Environ.* 409, 2503–2510.
- Kaegi, R., Ulrich, A., Sinnet, B., Vonbank, R., Wichser, A., Zuleeg, S., Simmler, H., Brunner, S., Vonmont, H., Burkhardt, M., Boller, M., 2008. Synthetic TiO₂ nanoparticle emission from exterior facades into the aquatic environment. *Environ. Pollut.* 156, 233–239.
- Kaegi, R., Voegelin, A., Ort, C., Sinnet, B., Thalmann, B., Krümer, J., Hagendorfer, H., Elumelu, M., Mueller, E., 2013. Fate and transformation of silver nanoparticles in urban wastewater systems. *Water Res.* 47, 3866–3877.
- Kaegi, R., Voegelin, A., Sinnet, B., Zuleeg, S., Hagendorfer, H., Burkhardt, M., Siegrist, H., 2011. Behavior of metallic silver nanoparticles in a pilot wastewater treatment plant. *Environ. Sci. Tech.* 45, 3902–3908.
- Keller, A.A., Lazareva, A., 2014. Predicted release of engineered nanomaterials: from global to regional to local. *Environ. Sci. Technol. Lett.* 1, 65–70.
- Klaver, G., Verheul, M., Bakker, I., Petelet-Giraud, E., Négrel, P., 2014. Anthropogenic rare earth elements in rivers: gadolinium and lanthanum. Partitioning between the dissolved and particulate phase in the Rhine River and spatial propagation through the Rhine-Meuse Delta (The Netherlands). *Appl. Geochem.* 47, 186–197.
- Klein, J.D., Quik, J.T., Bäuerlein, P.S., Koelmans, A.A., 2016. Towards validation of the NanoDUFLOW nanoparticle fate model for the river Dommel, The Netherlands. *Environ. Sci. Nano* 3, 434–441.
- Krystek, P., Ritsema, R., 2009. Validation assessment about the determination of selected elements in groundwater by high-resolution inductively coupled plasma mass spectrometry (HR-ICPMS). *Int. J. Environ. Anal. Chem.* 89 (5), 331–345.
- Kulaksız, S., Bau, M., 2011. 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.
- Lüers, F., Peters, R., Scheepens, M., 2006. Feiten en cijfers 2005 - waterkwantiteit en waterkwaliteit. Tech. Rep. U-06-04820, Waterboard De Dommel. http://library.wur.nl/ebooks/1879175_2005.pdf.
- Markus, A., Parsons, J., Roex, E., Kenter, G., Laane, R., 2013. Predicting the contributions of nanoparticles (Zn, Ti, Ag) to the annual metal load in the Dutch reaches of the Rhine and Meuse. *Sci. Total Environ.* 456–457, 154–160.
- Neal, C., Jarvie, H., Rowland, P., Lawler, A., Sleep, D., Scholefield, P., 2011. Titanium in UK rural, agricultural and urban/industrial rivers: geogenic and anthropogenic colloidal/sub-colloidal sources and the significance of within-river retention. *Sci. Total Environ.* 409, 1843–1853.
- Petelet-Giraud, E., Klaver, G., Négrel, P., 2009. Natural versus anthropogenic sources in the surface- and groundwater dissolved load of the Dommel river (Meuse Basin): constraints by boron and strontium isotopes and gadolinium anomaly. *J. Hydrol.* 369 (3–4), 336–349. May.
- Peters, R.J., Bommel, G.v., Milani, N.B., Hertog, G.c.d., Undas, A.K., Lee, M.V.d., Bouwmeester, H., 2018. Detection of nanoparticles in Dutch surface waters. *Sci. Total Environ.* 621, 210–218.

- Peters, R.J., Bommel van, G.v., Herrera-Rivera, Z., Helsper, H.P., Marvin, H.J., Weigel, S., Tromp, P.C., Oomen, A.G., Rietveld, A.G., Bouwmeester, H., 2014. Characterization of titanium dioxide nanoparticles in food products: analytical methods to define nanoparticles. *Environ. Sci. Tech.* 48, 6285–6293.
- Petersen, E.J., Zhang, L., Mattison, N.T., O'Carroll, D.M., Whelton, A.J., Uddin, N., Nguyen, T., Huang, Q., Henry, T.B., Holbrook, R.D., Chen, K.L., 2011. Potential release pathways, environmental fate, and ecological risks of carbon nanotubes. *Environ. Sci. Tech.* 45, 9837–9856.
- Praetorius, A., Gundlach-Graham, A., Goldberg, E., Fabienke, W., Navratilova, J., Gondikas, A., Kaegi, R., Gunther, D., Hoffmann, T., von der Kammer, F., 2016. Single-particle multi-element fingerprinting (spnef) using inductively-coupled plasma time-of-flight mass spectrometry (icp-tofms) to identify engineered nanoparticles against the elevated natural background in soils. *Environ. Sci. Nano* 4, 307–314.
- Schaumann, G.E., Philippe, A., Bundschuh, M., Metrevli, G., Klitzke, S., Rakcheev, D., Grün, A., Kumahor, S.K., Kühn, M., Baumann, T., Lang, F., Manz, W., Schulz, R., Vogel, H.-J., 2015. Understanding the fate and biological effects of Ag- and TiO₂-nanoparticles in the environment: the quest for advanced analytics and interdisciplinary concepts. *Sci. Total. Environ.* 535, 3–19.
- Wagner, J., Leith, D., 2001. Passive aerosol sampler. Part 1: principle of operation. *Aerosol Sci. Tech.* 34, 186–192.
- Wagner, S., Gondikas, A., Neubauer, E., Hofmann, T., von der Kammer, F., 2014. Spot the difference: engineered and natural nanoparticles in the environment - release, behavior and fate. *Angew. Chem. Int. Ed.* 53, 12398–12419.
- Weir, A., Westerhoff, P., Fabricius, L., Hristovski, K., von Goetz, N., 2012. Titanium dioxide nanoparticles in food and personal care products. *Environ. Sci. Tech.* 46, 2242–2250.
- Whitehead, T., Leith, D., 2008. Passive aerosol sampler for particle concentrations and size distributions. *J. Environ. Monit.* 10, 331–335.