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

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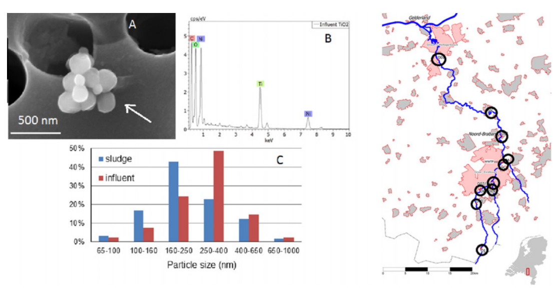
HIGHLIGHTS

- 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



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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.

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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