Is there evidence for man-made nanoparticles in the Dutch environment?

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HIGHLIGHTS

- Different types of water were screened for nAg, nAu, nTiO$_2$ and fullerenes.
- Air samples were analysed for the presence of inorganic nanoparticles.
- C$_{60}$ was detected in air, STP influents, effluents and sludge, but in no other aqueous samples.
- In STP sludge and influent evidence for nAg and nAu was found.
- 1 to 5% of the total mass in the air samples were from particles smaller than 100 nm.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Only very limited information is available on measured environmental concentrations of nanoparticles. In this study, several environmental compartments in The Netherlands were probed for the presence of nanoparticles. Different types of water were screened for the presence of inorganic (Ag, Au, TiO$_2$) and organic nanoparticles (C$_{60}$, C$_{70}$, [6,6]-phenyl-C$_{61}$-butyric acid octyl ester, [6,6]-phenyl-C$_{61}$-butyric acid butyl ester, [6,6]-phenyl-C$_{61}$-butyric acid methyl ester, [6,6]-bis-phenyl-C$_{61}$-butyric acid methyl ester, [6,6]-phenyl-C$_{71}$-butyric acid methyl ester, [6,6]-thienyl-C$_{61}$-butyric acid methyl ester). Air samples were analysed for the presence of nanoparticulate Mo, Ag, Ce, W, Pd, Pt, Rh, Zn, Ti, Si, B as well as Fe and Cu. ICP-MS, Orbitrap-HRMS, SEM and EDX were used for this survey. Water samples included dune and bank filtrates, surface waters and ground waters as well as influents, effluents and sludge of sewage treatment plants (STPs), and surface waters collected near airports and harbours. Air samples included both urban and rural samples.

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C_{60} was detected in air, sewage treatment plants, influents, effluents and sludge, but in no other aqueous samples despite the low detection limit of 0.1 ng/L. C_{70} and functionalised fullerenes were not detected at all. In STP sludge and influent the occurrence of Ag and Au nanoparticles was verified by SEM/EDX and ICP-MS. In air up to about 25 m% of certain metals was found in the nanosize fraction. Overall, between 1 and 6% of the total mass from metals in the air samples was found in the size fraction <100 nm.

1. Introduction

Engineered nanomaterials (ENMs) can be found in many different consumer products, and are used for industrial and agricultural processes (Baalousha et al., 2016). The production of ENMs is rising substantially (Keller et al., 2013; Foss Hansen et al., 2016; Virji and Stefaniak, 2014), due to their unique properties. C_{60} and C_{70} are constituents in cosmetics (Benn et al., 2011), while functionalised fullerenes are good semiconductors in organic solar cells (Kolkman et al., 2013). Also, C_{60} is a product of combustion of common fuels (Tiwari et al., 2016). Nanosized silver (nAg) is applied in healthcare products and textiles (Foss Hansen et al., 2016; Benn and Westerhoff, 2008). nAu is an integral part of electronic equipment and is employed as catalyst (Toro et al., 2007). nTiO$_2$ is used in consumer products such as sunscreens, cosmetics, tooth paste, paintings and certain food products (chewing gum) (Peters et al., 2014; Helsper et al., 2016). In the automotive industry nanomaterials of metals such as Mo, Ag, Ce, W, Pd, Pt, Rh, Zn, Ti, Si, B as well as Fe and Cu are common constituents in brake pads and discs, and due to abrasion nanoparticles can be formed. PGE (platinum group elements) are used in catalytic converters and coated diesel particulate filters (Jarvis et al., 2001; Wiseman and Zereini, 2009). In most car tyres besides black carbon also nSiO$_2$ is used as reinforcing filler and nZnO is always used as an vulcanisation activator (Semaan et al., 2002). In addition, more nano-additives, such as W$_2$S, Mo$_2$S, BN, CeO$_2$ and possibly C_{60} are being used in engine oils and fuels to improve performance (Lahouij et al., 2012; Jung et al., 2005).

Concerns have risen that ENMs may be toxic or harmful to the environment (Peralta-Videa et al., 2011; Pettitt and Lead, 2013; Klaine et al., 2008; Noël et al., 2016; León-Silva et al., 2016). Some ENMs are applied because of their antimicrobial properties (e.g. nAg) (Marambio-Jones and Hoek, 2010) and it can therefore be expected that they have adverse environmental effects. Due to their high surface to volume ratio, many ENMs are highly active catalysts (Bäuerlein et al., 2009) which can – for example in combination with UV-light – cause reactive oxygen species (ROS) to be formed that have the potential to cause cell damage (Lin et al., 2014; Kamat et al., 2000; Miller et al., 2012; Bennett and Keller, 2011; Pulskamp et al., 2007; Alkahtane, 2015). It has also been shown that nanoparticles have the potential to damage DNA (Auffan et al., 2009). Apart from the toxicological problems caused by nanoparticles, they also can physically disturb vital functions of a cell, for example by blocking cell pores (Elsaesser and Howard, 2012). A more detailed review of the toxicological effects can be found elsewhere (Sajid et al., 2015).

Owing to their increasing production, application and their potentially adverse effects, it is important that qualitative and quantitative analysis of nanoparticles in various environmental compartments is possible. Relatively little is known about actual environmental exposure to ENM. This type of information is, however, crucial for sound environmental risk assessments (Foss Hansen et al., 2016; Meesters et al., 2014). Still, there are knowledge gaps regarding the actual use of nanoparticles (Tiede et al., 2016).There are no official inventories on production and use of ENMs. However, Foss Hansen et al. have launched a webpage that keeps track of products claiming to contain nanoparticles (Foss Hansen et al., 2016). Additionally, some papers have been published that give estimated numbers on production volumes (Tiede et al., 2016; Piccinno et al., 2012; Markus et al., 2013). Emissions of

ENMs to air, water and soil during their life cycle are largely unclear, quantitative data are currently lacking (Hischier and Walser, 2012). Based on emission estimates and market research information, coupled to fate and transport models, both emissions (Keller et al., 2013, 2014) and environmental concentrations (Gottschalk and Nowack, 2011; Gottschalk et al., 2009, 2013a, b; Sun et al., 2014) have been estimated (Markus et al., 2016). Not only the pristine form of the ENM, but also transformation products formed during treatment and in the environment are of relevance (Nowack et al., 2012). By using probabilistic techniques and comparing modelled environmental concentrations to species sensitivity distributions, the environmental risk of nAg, nTiO$_2$, nZnO, carbon nanotubes and fullerenes are expected to be generally low with the exception of nAg and nTiO$_2$ levels in sewage effluents (Gottschalk et al., 2009, 2013b).

Measured field data are essential in order to validate the expected concentrations and allow sound risk assessment (Paterson et al., 2011; Isaacson et al., 2009; Hasellöv and Kaegi, 2009).

Several methods have been developed to analyse inorganic and organic nanoparticles. These methods should comply with the definition of the European Commission on 'nanomaterial', i.e. they should be able to determine the particle size distribution in the 1–100 nm size range of single particles and aggregates (Calzolai et al., 2012) as well as the mass or the number of particles per unit of volume or mass. The most common analytical methods for the determination of nanoparticles are single particle inductively coupled plasma (SP-ICP-MS) (Pace et al., 2012; Mitrano, 2012; Borovinskaya et al., 2014; Lee et al., 2014), field flow fractionation (FFF) with and without ICP (Hagendorfer et al., 2012; Krystek et al., 2015; Astefanei et al., 2015), transmission electron microscopy (Kaegi et al., 2010), HPLC - high resolution mass spectrometry (HRMS) (Kolkman et al., 2013; Emke et al., 2015), UHPLC-HRMS (Carboni et al., 2016), LC-UV (Xiao and Wiesner, 2013; Carboni et al., 2014), and FFF coupled to HRMS (Herrero et al., 2015, 2014), multi angle light scattering and dynamic light scattering (Astefanei et al., 2015; Brar and Verma, 2011).

So far, most work has been focused on the development of analytical techniques, but the actual application of these methods has not been reported frequently. Relatively few groups collected environmental samples in order to determine the presence of nanoparticles, whether inorganic or organic. Fullerenes and functionalised fullerenes (C_{60}, C_{70} and N-methylfulleropyrrolidine C_{60}) were measured in suspended material of wastewater effluents in Spain in concentrations up to the microgram per litre range (Farré et al., 2010). These high concentrations are, however, disputed (Wang et al., 2010).

Applying an UPLC-MS method around Barcelona, C_{60} was detected up to 1.1 ng/kg and 25 pg/L levels in sediments and surface waters, respectively. C_{70} was detected up to 330 pg/L in surface water and up to 7.2 ng/kg in sediments. Higher fullerenes, C_{76}, C_{78} and C_{84} were not detected (Astefanei et al., 2014).

Using LC-MS, concentrations of aqueous nC_{60} aggregates were found up to 130 ng/L in an industrial effluent and 98 ng/L in surface waters in Taiwan, nC_{70} was found in industrial and municipal effluents in concentrations up to 37 ng/L (Chen and Ding, 2012). Emke et al. reported on C_{60} concentrations between 2 and 19 ng/L in sewage treatment plants (STP) influents. The effluents did not contain any fullerenes (LOD < 0.1–0.2 ng/L) (Emke et al., 2015). Concentrations of functionalised fullerenes in influents and effluents were below the LOD (<0.1 ng/L).

C_{60} and C_{70} were detected in aerosols above the Mediterranean Sea. Median concentrations were 0.06 ng/m^3 for C_{60} and 0.48 ng/m^3 for C_{70}, ranging up to 233.8 ng/m^3 for C_{70} (Sanchís et al., 2012).

Studies on the occurrence of inorganic nanoparticles are also still scarce. In two papers the application of SP-ICP-MS is reported on the presence of nAg in waste water treatment plants (Tuoriniemi et al., 2012; Li et al., 2013) and copper in soil (Navratilova et al., 2015). In another study the release of nTiO$_2$ from sunscreens is monitored (Gondikas et al., 2014). Two other papers report on the emission of nanosized TiO$_2$ and Ag from outdoor facades into the aquatic environment. Kaegi et al. found that these particles are released into the environment at concentrations as high as 600 µg TiO$_2$/L (20–300 nm) and 145 µg Ag/L (<15 nm) (Kaegi et al., 2010, 2008). However, these are the concentrations directly at the source, further dilution is hence to be expected.

In this paper an inventory is made on the presence of nanomaterials in the Dutch environment. We analysed environmental samples from various environmental compartments in order to assess the presence of 8 different fullerenes (C_{60}, C_{70}, [6,6]-phenyl-C_{61}-butyric acid octyl ester, [6,6]-phenyl-C_{61}-butyric acid butyl ester, [6,6]-phenyl-C_{61}-butyric acid methyl ester, [6,6]-bis-phenyl-C_{61}-butyric acid methyl ester, [6,6]-phenyl-C_{71}-butyric acid methyl ester, [6,6]-thienyl-C_{61}-butyric acid methyl ester) as well as Au, Ag, and TiO$_2$ nanoparticles. Air samples are analysed for the presence of Mo, Ag, Ce, W, Pd, Pt, Rh, Zn, Ti, Si, B, Fe, and Cu nanoparticles and (functionalised) fullerenes. The objective of this paper is to report for the first time on the presence or absence of these nanoparticles in the Dutch environment. In addition, where nanoparticles were found, we compare the concentrations found with model estimation of environmental concentrations from the literature. When referring to nanosized particles, an italic "n" is placed before the metal in question.

2. Materials and methods

2.1. Chemicals and materials

C_{60} fullerene (purity >99.9%) was obtained from MER Corporation (Tucson, AZ, U.S.A.). C_{70} fullerene (purity >99%), [6,6]-phenyl-C_{61}-butyric acid butyl ester ([60]PCBB) (purity >97%), and [6,6]-phenyl-C_{61}-butyric acid octyl ester ([60]PCBO) (purity >99%) were purchased from Sigma-Aldrich (Steinheim, Germany). [6,6]-Phenyl-C_{61}-butyric acid methyl ester ([60]PCBM) (purity >99%), [6,6]-(bis)phenyl-C_{61}-butyric acid methyl ester [60]-bisPCBM (purity >99.5%), [6,6]-thienyl-C_{61}-butyric acid methyl ester [60]ThCBM (purity >99%), and [6,6]-phenyl-C_{71}-butyric acid methyl ester [60]PCBM (purity >99%) were purchased from Solenne B.V. (Groningen, The Netherlands). Silver nanoparticles (40 and 80 nm, polyvinylpyrrolidone) as well as Au nanoparticles (40 and 90 nm, citrate) were purchased from Nanocomposix Europe (Prague, Czech Republic). Toluene, methanol, acetonitrile, and acetone (all analytical grade or higher), NaCl, and sea sand (100 µm) were purchased from Mallinckrodt Baker B.V. (Deventer, The Netherlands). Cellulose nitrate filters of 47 mm diameter with a pore size of 8 µm (ref 11301-50-AHN) and 0.45 µm (ref. 11306-50-ACN) were purchased from Sartorius Stedim Biotech (Göttingen, Germany). PES (polyethersulfone) syringe filters (0.22 µm) were purchased from Millex (Cork, Ireland). Glass fibre filters of 0.7 µm pore size were obtained from Whatman (Maidstone, Kent, UK). Solid phase extraction (SPE) cartridges with reversed phase end-capped octadecylsilane (C18) material, bonded to silica gel (40 µm, 60 Å), were supplied by Mallinckrodt Baker B.V.

Nitric acid (65%, suprapur) and hydrochloric acid (37%) were purchased from Merck (Darmstadt, Germany). Calibration standard solutions for ICP-MS including Rh were purchased from Inorganic Ventures (Christiansburg, USA). For the online addition of the internal standard a dilution of 10 µg/L Rh in 2% HNO$_3$ was used. Teflon filters (47 mm, 2.0 µm) were purchased from PALL (USA) and Fluoropore filters (Millipore FGL P02500, 25 mm, 0.2 µm) from Sigma-Aldrich (Zwijndrecht, The Netherlands).

2.2. Instrumental detection

2.2.1. Inorganic nanoparticles

2.2.1.1. Total metal concentration.
An ICP-MS type XSeries II (Thermo Fisher Scientific, Breda, The Netherlands) was used for the detection of Au, Ag and Ti in water by two laboratories (Vitens and KWR). The digestion of samples was achieved by adding nitric acid to the sample and subsequently either heated to 100 °C (method Vitens), or using a Multiwave ECO microwave (Anton Paar, The Netherlands) to dissolve the sample (method KWR).

2.2.1.2. Particle size detection.
An Element XR High Resolution ICP-MS (HR-ICP-MS; Thermo, Bremen, Germany) was used for the analysis of metals in air samples. The digestion of the Teflon filter samples was performed in a Microwave Digestion System (CEM Corporation, USA).

A high resolution field emission gun scanning electron microscope in combination with energy dispersive X-ray analysis (FEG-SEM/EDX) was used to confirm the presence of nano-sized Au, Ag and TiO$_2$ ENM in influent and sludge, The instrument used was a Tescan MIRA-LMH FEG-SEM (Tescan Benelux, Brussels, Belgium) equipped with a Bruker AXS spectrometer and a 10 mm^2 XFlash 4010 Silicon Drift Detector (Bruker Nano GmbH, Berlin, Germany). The surface of the samples were systematically searched for 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 microscope was equipped with Scandium SIS software package (Olympus Soft Imaging Solutions GmbH, Germany) for automated particle analysis. From each particle/cluster of particles the projected area equivalent diameter (dpa) was measured. A magnification of 10.000×–50.000× was chosen to measure the size range of 25 nm–1600 nm divided into 9 size bins: 25–40, 40–65, 65–100, 100–160, 160–250, 250–400, 400–650, 650–1000, 1000–1600 and 1600–2500 nm. For more information on the method the reader is referred to this paper (Peters et al., 2014).

The ICP-MS was used in single particle mode for the detection of nAu and nAg particles in STP's. The dwell time for this measurement was set to 10 ms. A rhodium solution (10 µg/L) was used as an internal standard. nAg 40 nm and 80 nm as well as nAu 40 nm and 90 nm were used as standards to get an indication of the size of particles in the samples. MilliQ water samples were measured to define the minimum signal intensity that will be considered to represent a particle.

2.2.2. Organic nanoparticles

Fullerenes were determined using a hybrid LTQ Orbitrap mass spectrometer (Thermo Electron, Bremen, Germany) provided with an atmospheric pressure photo ionisation (APPI) interface that was hyphenated to a Surveyor HPLC system (Thermo Electron, Bremen, Germany) for the chromatographic separation.

2.3. Sampling

Water and STP samples were taken in Autumn 2013. All samples were 2 L grab samples, except for STP samples which were 24 h flow dependent composite samples. Influent (collected after the sand-trap) and effluent samples were obtained from six different locations. All samples were stored in high density polyethylene containers and immediately after collection kept at 4 °C until analysis. In total 44 locations were selected as sampling locations. The exact locations, except the STP, are shown in Table S1 and their locations within The Netherlands is shown in Fig. 1. All STPs serve cities in The Netherlands.

- 6 STPs (influent, effluent, sludge). Data for (functionalised) fullerenes in influent were reported earlier (Emke et al., 2015) but are again reported here for comparison.
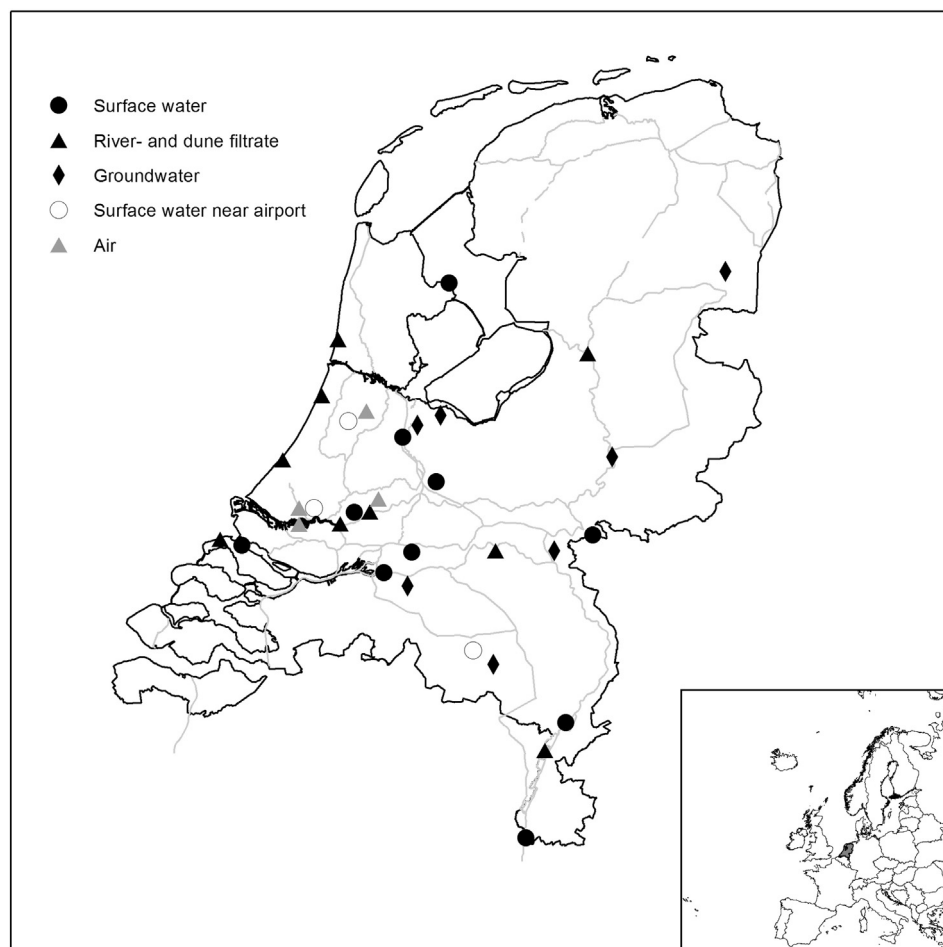
Fig. 1. Sampling locations in The Netherlands (STP are not shown).

- 28 drinking water abstraction sites (3 dune filtrates, 14 surface waters, 7 ground waters, 4 bank filtrates)
- 3 surface waters near airports
- 3 surface waters from harbours
- 4 air samples

Air sampling campaigns were held in summer 2012 (Bentinckplein), winter 2013 (Cabauw), spring 2014 (Maastunnel) and summer 2014 (Schiphol). Bentinckplein is a square at a major junction (Bentincklaan/Statenweg) in Rotterdam. The Maastunnel is a tunnel with four lanes in Rotterdam. Cabauw is small village in the province of Utrecht and can be considered as a regional background site. Schiphol is one of five major airports within Europe and the largest airport in The Netherlands. At each sampling site two-weekly samples were collected with a PM_{10} Harvard impactor, using Teflon filters and an air flow of approximately 10 L/min, and a Dekati Low Pressure Impactor (DLPI, Dekati Ltd., Finland). The DLPI Dekati low pressure impactor consists of 13 stages to generate 14 different size fractions of particulate matter. Flow rate was set at 30 L/min. The 50% cut-off diameters for the 13 stages were 0.028, 0.055, 0.093, 0.16, 0.26, 0.38, 0.61, 0.95, 1.6, 2.4, 4.0, 6.5 and 9.9 μm. Teflon filters were used as collection substrates.

PM_{10} filter samples and size selective impactor samples from three locations (Maastunnel, Bentinckplein and Cabauw) were analysed for the presence of traffic related metal containing nanomaterials. In addition, PM_{10} filter samples from two locations (Bentinckplein and Schiphol airport) were screened for fullerenes.

2.4. Sample preparation and analytical method

2.4.1. Inorganic nanoparticles

For measurement of the total concentration of inorganic particles in sewage water the samples were digested in nitric acid in combination with a microwave and subsequently analysed using ICP-MS. Concentrations in sludge are given in mg/kg (dry weight). Surface water and groundwater samples were homogenised without additional treatment and subsequently analysed with ICP-MS.

Total concentrations of Ag, Au and Ti were measured to probe if applying techniques to detect nanoparticles will be useful. SP-ICP-MS was used to detect Ag and Au nanoparticulate matter in the influent samples of the STP. The influent samples were chosen because the total concentrations of Ag, Au and Ti were the highest here. Samples were placed in an ultra sound bath for 10 min and subsequently filtered through 0.22 μm PES filters.

SEM/EDX was used to verify the presence of nanoparticles (nAg, nAu, nTiO$_2$) in STP 1 and 4. Other samples were not subjected to SEM/EDX due to the time-consuming nature of this method and the slim chance of success.

To confirm the presence of nAu, nAg and nTiO$_2$ in influent and sludge, droplets of 25 μL of the influent and sludge samples were transferred to nickel-coated polycarbonate filters, which were mounted on aluminium specimen holders. First the filters were dried to evaporate the water, after that the filters were plasma-ashed for 1 h at 15 W in order to remove organic material. The filters were analysed using FEG-SEM/EDX.

Teflon filters from the air monitoring campaigns were digested with aqua regia (mixture of concentrated hydrochloric acid and nitric acid 3:1) in a microwave oven and subsequently analysed using HR-ICP-MS.

Total metal concentrations were measured at two laboratories, *i.e.* KWR and Vitens. The detection limit for silver in effluent was lower at Vitens laboratory (<0.1 μg/L), so only this data was used. For Au the averaged values of both laboratories was used. The detection limit for the three metals in all other types of water was also 0.1 μg/L, with the sole exception of STP influent (2 μg/L). For sludge the detection limit was 0.1 μg/kg (dry weight).

2.4.2. Organic nanomaterials

This analytical method is based on the methods described in earlier papers (Kolkman et al., 2013; van Wezel et al., 2011).

Sample preparation for all aqueous samples except influent was carried out on a 6 mL polypropylene column filled with 1000 mg of reversed phase end-capped octadecylsilane. For surface water samples, the solid phase extraction (SPE) column was preceded by a 6 mL polypropylene column with a 20 μm frit filled with 4 g of sea sand in order to prevent the C18 material from clogging. The extraction column and the filtration column were preconditioned by rinsing with 6 mL of toluene, followed by 12 mL of methanol, and finally with 6 mL of ultrapure water. An amount of 3 g of NaCl was added to the water sample (1 L) (0.05 M). After passing the water sample (1 L) through the sand filter column and SPE column, both columns were dried under vacuum overnight and subsequently eluted with 3×6 mL of toluene and combined to one extract. The Teflon filters, used for air sampling, were extracted *via* an accelerated solvent extraction method (ASE) with toluene. Both the extracts and the eluate were evaporated to <1 mL by using an automated blow-down apparatus (Barkey, Germany) and transferred to an amber glass vial. The volume of the extract was adjusted to 1 mL with toluene by weight.

The sludge samples were analysed according to a method described earlier by Carboni et al. (2014). Previous works into soil matrices
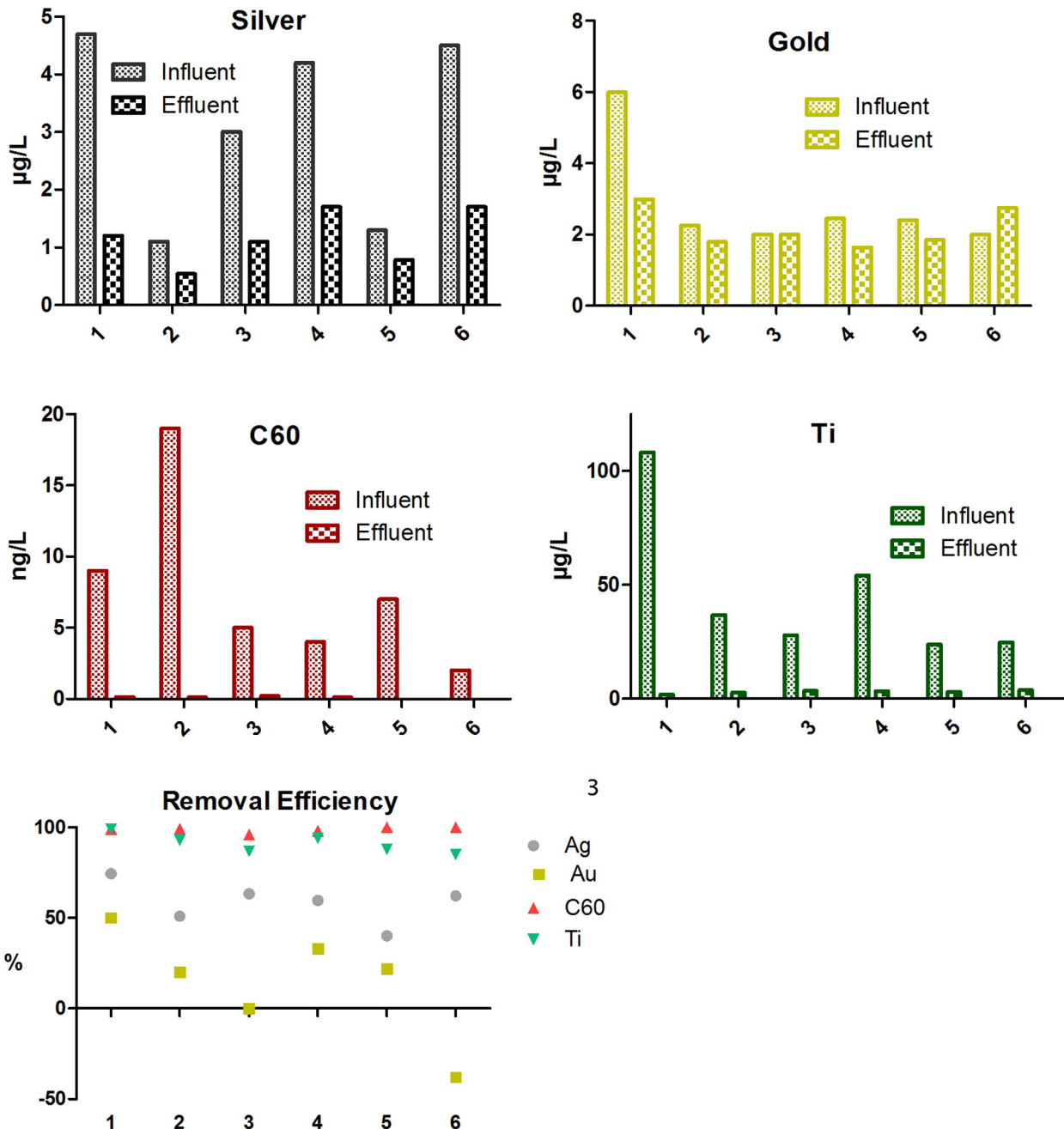

Fig. 2. Total concentrations and removal efficiencies of C_{60}, Au, Ag, and Ti in 6 different STPs. Note different scales used for Y-axes. Concentrations of C_{60} are given in ng/L, others in μg/L.

showed acceptable recoveries (around 70%) for the extraction technique used for the present study (Carboni et al., 2014). The samples were placed in a freezer at −20 °C overnight and lyophilised with a Scanvac Coolsafe freeze-dryer (Labogene, Lynge, Denmark). The dried sludge from each STP were weighed and placed into a glass centrifuge tubes, 10 mL of toluene were added and the samples were placed open into a Bransonic 12 ultrasonic bath (Branson, Danbury CT, United states) operating at 50 kHz for 30 min. Then, the tubes were closed with a glass stopper and shaking extraction was performed with an orbital shaker at 160 rpm for 90 min. Subsequently, the samples were centrifuged at 2000 rpm and the toluene supernatant was filtered through a 4–7 μm pore size prepleated paper filter (Whatman, Maidstone, United Kingdom) into 60 mL amber glass vials. The filter was rinsed with 3 mL of toluene and the extraction was repeated a second time by adding 8 mL of toluene. In this latter procedure, the samples were not centrifuged and the soil samples were transferred directly to the paper filters. After elution of the solvent, each sample was rinsed with 5 mL of toluene and the extracts were evaporated in a water bath at 60 °C under a gentle nitrogen flow until approximately 3 mL Finally, the extracts were filtered with 0.45 μm regenerated cellulose filters and concentrated to a final volume of ~0.5–1 mL. All experiments were performed in triplicate and non-spiked soils were extracted with the same protocol as reference.

3. Results and discussion

3.1. Water and sludge

3.1.1. Inorganic nanomaterials

3.1.1.1. Sewage treatment plant: influent, effluent and sludge. For the STP samples total concentrations of Ag, Au, and Ti are shown in Fig. 2. Ag was found in all influents and effluents. Total concentrations of Ag observed in the present study are in the same range (1–5 μg/L) as those found in 9 German STPs (0.3–3 μg/L) (Li et al., 2013). The presence of Ag is not surprising given the fact that nAg nanoparticles are employed

in many products (Foss Hansen et al., 2016; Technologies, P. o. e., n.d.), especially textiles and health care products (von Götz et al., 2013; Kaegi et al., 2013; Mitrano et al., 2015). Due to release during washing, silver will migrate into the sewer system (von Götz et al., 2013; Geranio et al., 2009). The influent samples were also analysed using SP-ICP-MS. However, the number of particles was insignificantly higher than the number particles (false positives) in pure water. Therefore, an extrapolation to the real number of particles in the sample is not appropriate. Anyway, the number of particles could not nearly make up for the total mass of silver found in the sample. This can mean that the rest of the silver is (I) dissolved, (II) part of particles that are smaller than 20 nm (approximate lower size limit for SP-ICP-MS (Lee et al., 2014)) or (III) the silver was attached to larger particles that were removed in the filtration step. Latter explanation is supported by the fact that nAg particles are surrounded by organic matter as seen by SEM. Also, (IV) it is possible that the silver particles are larger than 220 nm (pore size of the filters used). This explanation would agree with findings that e.g. Ag particles released from textiles are mostly larger than 450 nm (Gottschalk and Nowack, 2011). It was abstained from using field flow fractionation to determine the size of the particles due to the low concentration (Krystek et al., 2015).

The removal efficiencies in STPs vary between 50 and 98% for silver (Fig. 2), which is in accordance with earlier findings (Li et al., 2013; Kaegi et al., 2013, 2011; Wang et al., 2012). The total concentrations of Ag in the effluents are approximately 1 μg/L and slightly higher than the predicted concentrations by Gottschalk et al., that are between 33 and 111 ng/L in STP effluents (Gottschalk et al., 2009). Sun et al. expected lower concentrations (0.06–16 ng/L) (Sun et al., 2014). The literature values only concern nAg and the higher concentrations measured in the present study can be explained as also non-nanoparticulate Ag is included in the results. In three STP sludge samples Ag was found in concentrations of 0.19 mg/kg, 0.33 mg/kg and 0.19 mg/kg. At the other locations the Ag concentration was below the limit of detection. The concentrations for Ag are between predicted concentrations of 1.3–4.4 mg/kg (Gottschalk et al., 2009) and 0.01–0.08 mg/kg (Sun et al.,
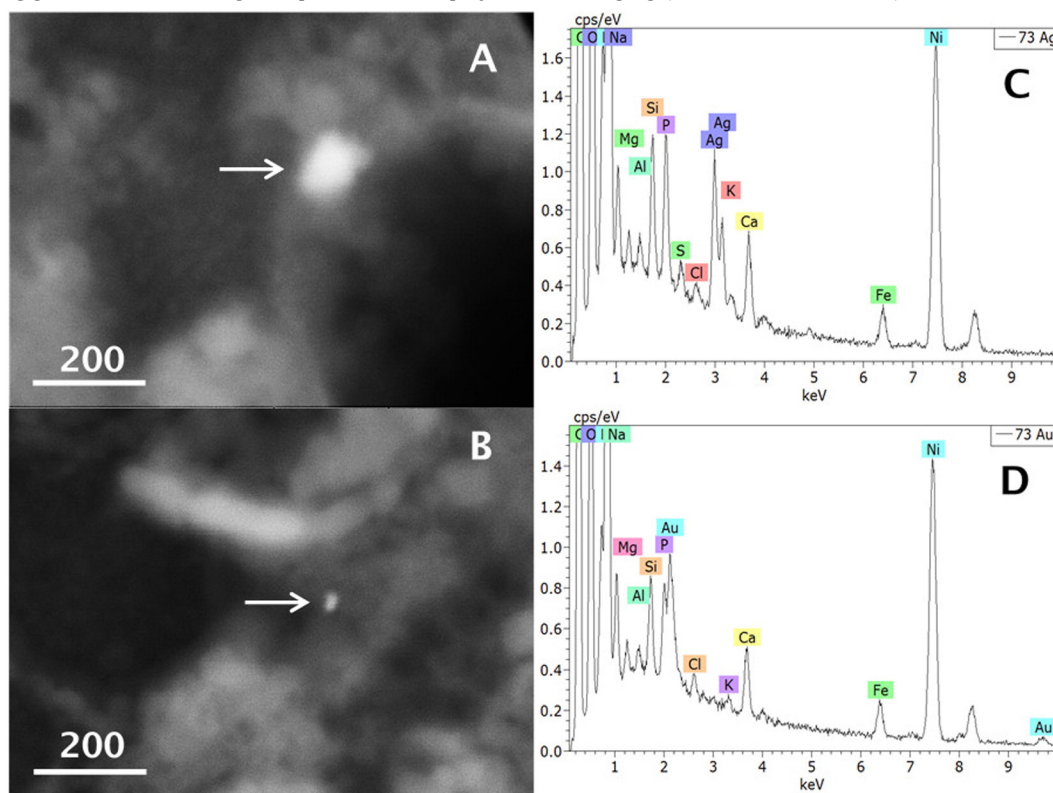

Fig. 3. Representative SEM images of Ag (A) and Au (B) ENPs indicated by the arrows in sludge samples from STP 4 and corresponding EDX-spectra of the ENPs (C,D).

2014). However, it was not possible to determine the exact contribution of nAg. SEM and EDX analysis could only show that silver nanoparticles are present in sludge (Fig. 3). The diameters of these particles are in the range of 50–150 nm. It can be seen that all particles are attached to- and surrounded by organic matter and nutrients. In the elemental composition, besides Ag, traces of sulfur and chlorine were detected, suggesting that part of the nAg (surface) has been 'changed' to silver sulfide/chloride. This is in accordance with findings by other groups (Kaegi et al., 2013, 2011; Levard et al., 2012; Baalousha et al., 2013).

Au was present in all STP waters sampled, both in the influent and effluent (see Fig. 2). In one case the Au concentration found in the effluent was higher than in the influent (STP 6). This could have been caused by a short-during peak emission. For STPs in Apeldoorn and Amsterdam it has been shown in an earlier study that its hydraulic retention time or lag time spans between 13 and 24 h, respectively. In case of peak concentrations this can lead to incorrect estimations of removal efficiencies (Bijlsma et al., 2012) because in the present study influent and effluent samples were collected at the same moment. The average removal efficiency of water treatment for Au observed in the present study is <50%. This was unexpected, as literature reported a tendency to adsorb to solid matter in the sewer system for Au that is comparable to Ag (Kaegi et al., 2013). For Au in sludge samples, only in one STP a concentration above the limit of detection (0.1 mg/kg) was found (0.12 mg/kg). Despite the low concentration, SEM/EDX confirmed the presence of Au nanoparticles in the sludge of STP 4 (Fig. 3). However, it was impossible to find nAu particles in the other sludge samples. It is – as was already stated by other authors - fortuitous that any particle could be found (Westerhoff et al., 2015). With SP-ICP-MS analysis only in three of the six influent samples particles were found. However, also here the numbers were too low to venture to estimate the total particle number concentration in these samples. In any case, as with silver the number of particles cannot make up for the total mass of gold that was observed. The same explanations do apply. Only influent but not effluent was measured as the number of particles was already very low.

The presence of Au and other metals in STPs has recently also been shown by Westerhoff et al. sparking the discussion of whether or not it is worthwhile to recover the metals from STP sludge (Westerhoff et al., 2015; Peccia and Westerhoff, 2015). They estimated an economic value of about $280/ton sludge. For STP 5 we estimated the quantity of Au that will enter the STP per year based on the flow rate. About 200 kg of Au will enter the STP per year, which translates into a value of €7 million. Unfortunately, as the removal efficiency of Au is rather low, the Au would have to be removed from the water stream.

Ti was detected in all STP influents (24–108 μg/L) and effluents (1–4 μg/L). The total concentrations of Ti observed in effluents were a factor 5 lower than those predicted in the literature (Sun et al., 2014). All STPs remove about 90% of the titanium. SEM/EDX analysis from sludge (Fig. 4) showed that $nTiO_2$ nanoparticles are spherical and present both as agglomerates as well as primary particles, the latter with diameters in the range of 60 to 300 nm. In general the agglomerates have diameters in the range of 100 to 1000 nm with an average size of 300 nm (Fig. 4). For STP 1 and 4 the estimated concentrations of $nTiO_2$ are calculated based on SEM/EDX particle counting. This resulted in concentrations of 1.8 (0.8–3.8) and 1.5 (0.4–4.7) μg/L. These concentrations are far lower than the measured concentrations in influent for the six STPs (24–108 μg/L) and <0.1% of the total mass of Ti is <100 nm. The size distribution of the TiO_2 particles in the sludge samples are in the range of the particles sizes found in food and personal care products (Helsper et al., 2016; Weir et al., 2012). Given this similarity it's likely that the TiO_2 particles found in STPs originate from these types of products.
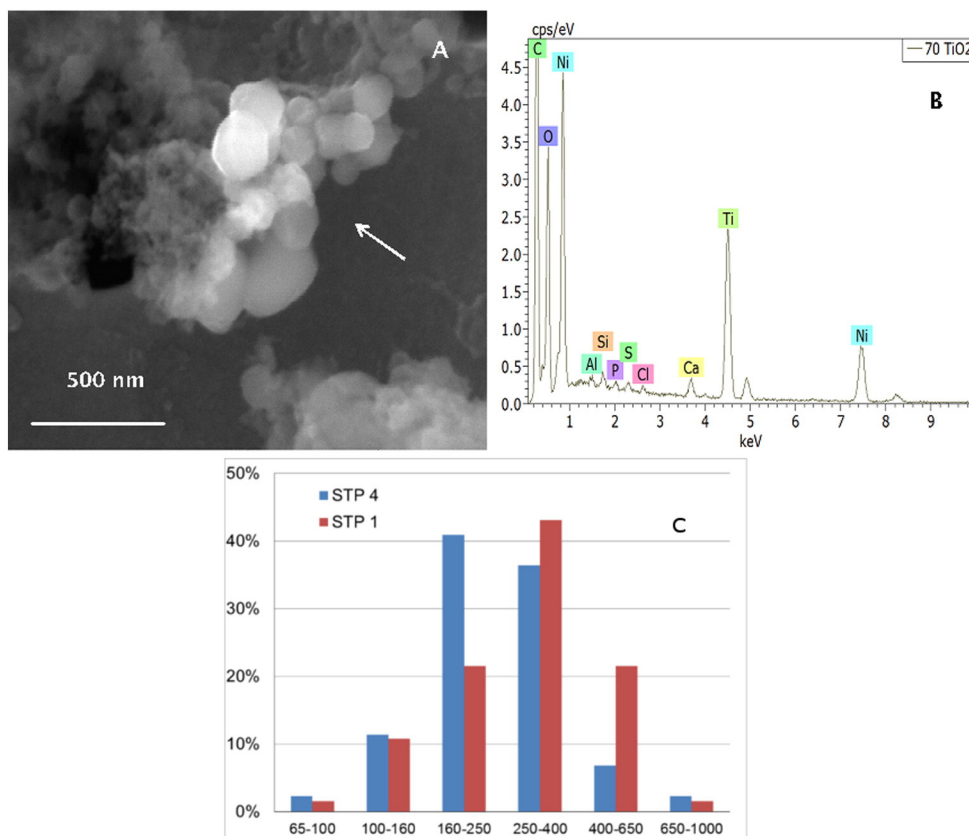

Fig. 4. Representative SEM image of a TiO_2 ENP agglomerate (A). Corresponding EDX-spectrum (B) and the number size distribution of TiO_2 particles (C) in sludge samples from STP 1 and 4.

3.2. Surface waters, dune and bank filtrates and groundwater

Silver was merely found in one groundwater sample: from Waalwijk (0.88 μg/L). However there is no indication that this is nanoparticulate matter. These concentrations are in accordance with predicted concentrations (Gottschalk et al., 2009; Sun et al., 2009) and the estimated use of nAg in Europe of roughly 10 t/y in paints, coating, textiles, cosmetics and electronica (Piccinno et al., 2012). If 10 t of Ag were evenly distributed over European surface waters, this would result in a concentration below the pg/L level under the assumption that waterbodies are 1 m deep.

Low concentrations of Au were found in three drinking water winning sites, i.e. surface waters in Ouddorp (0.25 μg/L) and Brakel (0.21 μg/L) and a river bank filtrate in Macharen (0.13 μg/L). FFF was not used as the concentrations were too close to the detection limit (Krystek et al., 2015). At the remaining drinking abstraction sites no Au was detected above the detection limit of 0.1 μg/L.

Titanium was found in 12 of the 14 surface waters that are used for drinking water production and in three other surface waters. In one case near the airport of Eindhoven a significantly higher concentration (33 μg/L) was found compared to the other concentrations (1.3–5.7 μg/L). In general the concentrations were higher than the predicted concentrations for $nTiO_2$. This can be explained as the concentrations observed also include non-nanoparticulate matter.

3.1.2. Organic nanomaterials

C_{60} was detected in the influents of all 6 STPs, as reported earlier (Emke et al., 2015). Concentrations varied between 2 and 19 ng/L. STPs remove C_{60} almost completely from the waste water stream. In four cases a level of 0.1–0.2 ng/L was detected in the effluent (not reported earlier), corresponding to a removal efficiency of >95%. This is in accordance with the literature where the precipitation of C_{60} in the presence of organic matter and Ca^{2+} is described (Haftka et al., 2015). Despite the high removal efficiency only in STP 6 a detectable level of C_{60} was found in sludge (32 ng/kg). The effluent concentrations of C_{60} were significantly lower than the concentrations reported earlier (up to the mg/L) in Spain. C_{70} was not encountered in the present study while the concentrations of C_{70} observed in the Spanish study were a factor 10 higher than those of C_{60} which is quite remarkable since soot formation in general favours C_{60} (Tohji et al., 1995). The effluent concentrations of C_{60} observed in the present study are lower than concentrations predicted by Gottschalk et al. (2009) (4.23–26.4 ng/L) and Sun et al. (2014) (1.3–7 ng/L).

None of the fullerenes were detected in any of the other aqueous samples (detection limit <0.5 ng/L). Based on our data neither STPs nor deposition from air are at present likely significant sources for fullerenes in the environment. Once present, fullerenes in surface water are subjected to UV-degradation (Lee et al., 2009) and can form larger clusters that can be retained by sediments (Pakarinen et al., 2014). These factors could also explain the absence of fullerenes in aqueous samples. The absence of fullerenes in surface waters in The Netherlands also matches the findings in Spanish surface waters where concentrations in the pg/L-range were observed (Astefanei et al., 2014). In Taiwan, however, concentrations up to around 100 ng/L were detected (Chen and Ding, 2012).

3.2. Air samples

3.2.1. Inorganic nanomaterials

Fig. S1 and Table 1 show the data of metals that are known to be used as nanomaterials in automotive parts (tyres, coatings and catalytic converters), engine oils and fuels. For comparison also Fe and Cu are shown, which are common "non-nano" constituents in brake pads and discs. Comparing data of the city centre of Rotterdam with the reference area of Cabauw it can be seen that as expected total concentrations (PM_{10}) and concentrations of nano-sized metals ($PM_{0.1}$) increase with traffic density. The highest PM_{10} and $PM_{0.1}$ concentrations were be observed in the Maastunnel and can be explained by the relatively closed system of a tunnel compared to an open road.

The majority of metals is found in the size fraction larger than 100 nm. The total mass of metals in the nanosize fraction sums up to 16 ng/m³ (Maastunnel), 4.5 ng/m³ (Bentinckplein) and 0.3 ng/m³ (Cabauw). This is 4.7, 5.6 and 1.5 m% of the total metal content, respectively. The method applied does not discriminate between engineered and natural nanoparticulate matter. However, because naturally occurring levels of Pt, Pd, Rh and Ag are negligible, only anthropogenic sources are relevant for these elements. Furthermore the majority of the platinum group elements (PGE) have been used only as ENMs in products like electronics and catalytic converters automotive parts (Wiseman and Zereini, 2009). Measured concentrations of PGEs in Rotterdam (4–25 ng/m³) were comparable to concentrations measured in other European cities (0.1–57 pg/m³) (Wiseman and Zereini, 2009). Measured nAg concentrations in outdoor air (0.04–0.14 ng/m³) were in general 5–10 times higher than expected from predicted concentrations in literature (0.003–0.02 ng/m³ (León-Silva et al., 2016; Lin et al., 2014)). As Pd, Pt and Rh to the best of our knowledge have only one source, namely catalytic converters and as in these catalytic converters the PGE are nanosized, there is strong evidence that the reported $PM_{0.1}$ concentrations of Pt, Pd and Rh (a few pg/m³) stem indeed from nanoparticles.

Table 1

PM_{10} and $PM_{0.1}$ airborne concentrations of metals (ng/m³) that are known to be used (as nanomaterials) in automotive parts, engine oils and fuels, including the mass percentage (%m/m) in the size fraction smaller than 100 nm.

	Maastunnel Rotterdam			Bentinckplein Rotterdam			Cabauw		
	PM_{10} ng/m³	$PM_{0.1}$ ng/m³	<100 nm %(m/m)	PM_{10} ng/m³	$PM_{0.1}$ ng/m³	<100 nm %(m/m)	PM_{10} ng/m³	$PM_{0.1}$ ng/m³	<100 nm %(m/m)
	n = 2	n = 1		n = 4	n = 3		n = 2	n = 2	
Mo	4.6 (0.6)	0.039	0.8%	1.7 (0.4)	0.096 (0.043)	5.6%	1.7 (0.6)	0.1 (0.1)	4.9%
Ti	19.1 (7.6)	0.200	1.0%	4.7 (1.7)	0.020 (0.031)	0.4%	1.3 (0.9)	<0.001	<0.2%
Fe	7300 (1700)	7.5	0.1%	520 (120)	3.6 (2.4)	0.7%	190 (95)	0.2 (0.3)	0.1%
Cu	230 (33)	0.27	0.1%	24.2 (5.2)	0.10 (0.05)	0.4%	4.2 (2.8)	<0.001	<0.05%
Ag	0.27 (0.06)	0.003	1.1%	0.14 (0.09)	0.012 (0.008)	8.6%	0.044	<0.001	<2%
Ce	0.92 (0.32)	0.059	6.4%	0.27 (0.07)	0.003 (0.003)	1.1%	0.042 (0.003)	0.0001 (0.0001)	0.2%
W	6.5 (3.7)	1.2	18%	1.0	0.23	23%	0.18	<0.001	<0.6%
Pd	0.10 (0.02)	0.009	9.0%	0.025 (0.013)	0.002 (0.001)	8.0%	0.001 (0.001)	0.0001 (0.0001)	7.0%
Pt	0.015 (0.002)	0.002	13%	0.004 (0.002)	0.0001 (0.0001)	2.5%	0.0004 (0.0004)	<0.0001	3.7%
Rh	0.009 (0.004)	0.0002	2.2%	0.004	<0.0001	<2.3%	0.0002 (0.0002)	<0.0001	<6%
Zn	105 (31)	0.94	0.9%	21.6 (3.0)	0.087 (0.064)	0.4%	11.1 (8.1)	<0.001	<0.01%
Si	560 (220)	5.80	1.0%	810 (190)	<0.001	<0.01%	72	<0.001	<0.01%
B	2.8 (0.3)	0.20	7.0%	1.6 (0.3)	0.3 (0.10)	18%	1.4 (0.7)	0.012 (0.012)	1.2%
Sum	8250	16.0	4.7%	1380	4.5	5.6%	280	0.3	1.5%

The measured concentrations of Ti and Zn in the size fraction < 100 nm are comparable to predicted concentrations of $nTiO_2$ (<0.5–1 ng/m^3) and $nZnO$ (<1 ng/m^3) (Gottschalk et al., 2009; Sun et al., 2014).

3.2.2. Organic nanomaterials

C_{60} was the only fullerene that was found and it was detected at Bentinckplein (5 pg/m^3). Its presence might be attributed to nearby industrial activities. The results agree with predicted concentrations mentioned in the literature (1 pg/m^3) (Sun et al., 2014) and also measured concentrations in exhaust from various fuels (Tiwari et al., 2016). These prediction are based on production volumes and their allocation. However, Sanchis et al. found 60 pg C_{60}/m^3 in the atmosphere above the Mediterranean Sea (Sanchis et al., 2012).

4. Conclusion

To revert to the title of this article: Yes, there is evidence for manmade nanoparticles in the Dutch environment, but it is not always possible to make the distinction between natural and man-made.

In air, concentrations of metals in the nano-sized fraction (PM$_{0.1}$) are higher in the city than in the village. About 5 m% was present in the ultra-fine fraction (particles <100 nm) in the city compared to about 1 m% in the village. Observed Ag concentrations in the size fraction < 100 nm in outdoor air (0.04–0.14 ng/m^3) were 5–10 times higher than predicted in literature. PGE's were found in the size fraction < 100 nm (pg/m^3). As these metals to the best of our knowledge are only used in nanoparticulate form in car catalysts, it can be assumed that nanosized particles of PGE's are present in the air. Measured concentrations of Ti and Zn in the size fraction <100 nm are comparable to predicted concentrations. C_{60} was found at one location (5 pg/m^3).

In STPs, concentrations of Ag in the effluents amount to 1 μg/L. This is slightly higher than predicted (50–98%). In sludge Ag was found in concentrations up to 0.3 mg/kg as predicted in the literature. SEM/EDX analysis shows that nAg nanoparticles are present. However, the data does not allow for an estimation of the total amount in that sample. In the remaining water samples, Ag was only found in one groundwater sample but not in any of the other dune and bank filtrates, surface waters and groundwaters, which is in accordance with model predictions.

Au is found in both influents and effluents, and the Au removal efficiency of sewage treatment was lower than expected (<50%). SEM/EDX results confirmed the presence of nAu nanoparticles in the STP, but also here no exact numbers can be given for nAu. Detectable concentrations of Au were observed in three drinking water abstraction sites (up to 0.25 μg/L).

Ti was detected in all STP influents and effluents at levels between 24 and 108 μg/L. The total concentration of Ti in effluents is a factor 5 lower than those predicted in the literature by model calculations. For Ti only a small percentage of the total Ti concentration could be identified as $nTiO_2$ nanomaterial (<0.1% of the total Ti concentration). All STPs remove on average about 90% of the Ti. Ti was found in most surface waters that are used for drinking water production.

C_{60} was the only fullerene found in STP samples. Concentrations in influents varied between 2 and 19 ng/L. In effluents invariably concentrations below the level of 0.2 ng/L were measured. This means that STPs remove C_{60} almost completely. None of the 8 fullerenes were detected in any of the other aqueous samples. Given that at the moment neither STPs nor deposition from air are likely sources for C_{60}, its absence in surface waters is understandable.

Non-functionalised C_{60} fullerene was only detected in STPs and in one air sample. Other fullerenes were not detected at all, although the detection limit for these compounds is as low is 0.1 ng/L.

The two main conclusions of this survey are that (I) the total concentrations of Ag, Au and fullerenes are very low (μg/L and ng/L) if detected at all. (II) It is therefore often not possible to verify if the metals exist as nanoparticles or get information on the size of fullerene clusters.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.09.206.

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