



Rapid communication

Synthetic TiO₂ nanoparticle emission from exterior facades into the aquatic environment

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The release of synthetic TiO₂ particles from exterior applications into the aquatic environment is demonstrated.

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ABSTRACT

We present direct evidence of the release of synthetic nanoparticles from urban applications into the aquatic environment. We investigated TiO₂ particles as these particles are used in large quantities in exterior paints as whitening pigments and are to some extent also present in the nano-size range.

TiO₂ particles were traced from exterior facade paints to the discharge into surface waters. We used a centrifugation based sample preparation which recovers TiO₂ particles between roughly 20 and 300 nm. Analytical electron microscopy revealed that TiO₂ particles are detached from new and aged facade paints by natural weather conditions and are then transported by facade runoff and are discharged into natural, receiving waters. Microscopic investigations are confirmed by bulk chemical analysis. By combining results from microscopic investigations with bulk chemical analysis we calculated the number densities of synthetic TiO₂ particles in the runoff.

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1. Introduction

Due to the increasing use of nanoparticles (NPs) in different consumer products, it is generally assumed that NPs will enter the aquatic environment (Colvin, 2003; Guzman et al., 2006; Lecoanet and Wiesner, 2004; Nowack and Bucheli, 2007). An exposure modeling study revealed that nano-TiO₂ particles will most likely be found in significant concentration in natural surface waters (Mueller and Nowack, 2008). These authors therefore ask for more detailed studies on the release and fate of nano-TiO₂ in natural surface waters. Yet, the term 'nanoparticle' is not strictly defined. Many authors refer to NPs when at least one dimension of the particle is less than 100 nm. The TiO₂ particles investigated within this study range from a few tens up to a few hundreds of nm and therefore well extend into the nano-scale. In order to include also the larger TiO₂ particles we use the more general term 'particle' instead of nanoparticle within this study.

Natural (geological) sources of TiO₂ are dominated by the minerals Rutile (TiO₂) and Ilmenite (FeTiO₃). Both are commonly found as accessory minerals in plutonic and metamorphic rocks but occur also as detrital minerals in beach sands (Deer et al., 1992).

Wigginton et al. (2007) found natural nanoscale TiO₂ in river water, but to date, there is no direct evidence for a transport of synthetic NPs from their original application to aquatic systems. Whether NPs released to the environment will immediately agglomerate, form larger particles (>1 μm) which will then settle to the sediment or form stable colloidal suspensions which might be transported over distances is not yet clear. The behavior of NPs in the environment follow the same laws as natural colloids, and thus their stability will depend on physical properties such as particle size, concentration and surface charge as well as pH, composition and ionic strength of the solution (Gregory, 2006; Omelia, 1980). In urban surface runoff it is very difficult to predict the behavior of NPs due to the inhomogeneous flow patterns and the complex matrix (particles of varying size and chemistry suspended in a water of different pH-values, conductivity and temperature).

Recent studies have highlighted the need for a detailed chemical and physical characterization of NPs when performing experimental studies (Limbach et al., 2005). Adams et al. (2006) showed that the nominal size of NPs and the actual measured size of the NPs used for experimental studies can significantly deviate, which either is caused by an agglomeration of the particles during the experiments or by the use of different measurement methods. Manufacturers of NPs refer to the size of the primary crystallites, which is often determined either by XRD (X-ray diffraction, peak broadening) or BET (Brunauer–Emmett–Teller, surface area)

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measurement. In the latter technique, a 'pseudo-particle' size is derived from the specific surface area (available for N₂ adsorption) assuming spherical particles. In experimental studies DLS (dynamic light scattering) is usually used to determine the particles size. The DLS technique provides information about the aggregate size which is different from the crystallite size if aggregation occurred. In addition, the different techniques require different sample preparations (DLS: suspension, XRD: dry powders or pastes, BET: dried powder) which may introduce artifacts. However, when dealing with natural systems, sizing techniques used for the characterization of the raw and pure particles (such as DLS and X-ray disc centrifugation) are not applicable due to the low particle concentration and or the polydispersity of natural systems (Filella et al., 1997; Schurtenberger and Newman, 1992), which makes the detection of NPs in the environment extremely challenging. Although the analytical tools which are available to characterize NPs (both synthetic and environmental) have been described in recent reviews (Handy et al., 2008; Lead and Wilkinson, 2006; Wilkinson and Lead, 2007), they have not been applied to detect synthetic NPs in the environment thus far.

Manufactured TiO₂ particles are used in most differing applications ranging from sunscreens to construction materials, mainly as a whitening pigment. The durability of the TiO₂ containing paints has been investigated by several authors (Allen et al., 1998; Allen et al., 2004; Blakey, 1985; Braun, 1990). During the weathering of the paint containing white pigments in the form of TiO₂ particles, oxidation occurs at the surface layer of the material which eventually erodes away leaving the TiO₂ particles exposed at the surface. This so-called 'chalking' effect has been investigated using microscopic methods such as SEM (Kaempfer et al., 1974) and AFM (atomic force microscopy) (Biggs et al., 2001). Nanoscale TiO₂ is manufactured and applied in the greatest quantities amongst NP (Aitken et al., 2006). Several studies have been published on the ecotoxicological effects of nanoscale TiO₂ (Adams et al., 2006; Block et al., 1997; Federici et al., 2007; Hund-Rinke and Simon, 2006; Kwak et al., 2001; Wei et al., 1994). Lovren and Klaper (2006) reported toxic effects of nanoscale TiO₂ to *Daphnia magna* and concluded that TiO₂ toxicity may need to be re-evaluated. On the other hand, Warheit et al. (2007) concluded that ultrafine TiO₂ particles (<100 nm) pose only a low hazard potential to mammals and aquatic species following short-term exposures. However, Brunner et al. (2006) suggest that due to the TiO₂ persistence, insoluble materials should be assessed in terms of long-term toxic effects. Baun et al., 2008a observed an adhesion of engineered NPs (TiO₂ and C60) to the exoskeleton of organisms which potentially causes physical effects and loss of mobility and Sun et al. (2007) reported a higher uptake of As(V) in carp in the presence of nano-TiO₂. Baun et al. (2008b) thus suggested that the role of NPs as transport vehicles for contaminants needs to be included in risk assessment. The enhanced transport of classical contaminants by co-transport with colloids is a well known phenomena and in the literature referred to as colloid facilitated transport (Kretzschmar et al., 1999; McCarthy and Zachara, 1989). Compared to the surface provided by naturally occurring colloids (1–1000 nm), the synthetic NPs in the environment still provide a minuscule fraction (Wigginton et al., 2007) limiting the importance of NPs regarding colloid facilitated transport. Exceptions may occur in areas, where high concentrations of synthetic NPs can be expected such as close to the source of an unintended release of NPs.

For an environmental risk assessment of NPs, both the exposure in the environment and the hazard, such as toxicity, needs to be taken into account. But, as highlighted in latest reviews (Moore, 2006; Nowack and Bucheli, 2007; Wiesner et al., 2006), the release of synthetic NPs into the aquatic environment is largely unknown. Handy et al. (2008) pointed out the analytical challenges arising when measuring synthetic NPs in environmental samples but also

concluded that a risk assessment requires quantifying the real concentrations of NPs in the environment.

In this study we investigated whether TiO₂ particles used in common exterior paints and plasters of facade can reach the surface waters via the urban transport pathways. We analyzed solid coatings of facades and water samples with a combination of electron microscopy (transmission electron microscopy (TEM), scanning electron microscopy (SEM)) and inductive coupled plasma optical emission spectrometry (ICP-OES) and mass spectrometry (ICP-MS). Microscopy enables a clear identification of the TiO₂ particles. In addition to the particle size, morphology and the aggregation state, also the chemical composition can be determined using energy dispersive X-ray analysis (EDX). These properties can then be used to distinguish synthetic from natural TiO₂ particles. The ICP-MS measurements provide quantitative information about the mass concentration of Ti and other elements.

2. Materials and methods

The experimental setup including the collection and preparation procedures is schematically given in Fig. 1 and described in more detail in the following sections. All samples for TEM and ICP-MS analysis were derived from the same, well-mixed batch water sample collected over the period of one complete rain event.

2.1. Sampling sites

Facade runoff from a building painted in May 2006 (referred to as aged facade), was collected with an aluminum gutter (1.0 m length) mounted at the bottom of the facades' drain rail. The runoff drained into a plastic bottle. The spacing between the facade and the aluminum gutter was kept as minimal as possible at a distance of approximately 2–3 mm in order to avoid dilution with additional rain water. After each runoff event, samples were directly taken to the laboratory and processed within a few hours. In addition to that building, runoff from a new facade (an experimental building area, 1.3 m²) painted with the same product was studied. The sampling procedure was identical to the one described for the previous building.

Near the existing building, surface runoff from a greater urban catchment was sampled right before its discharge into the receiving creek. The catchment is characterized by residential and business buildings, paved surfaces around these buildings and pavements on sidewalks and roads. Therefore, all particulate

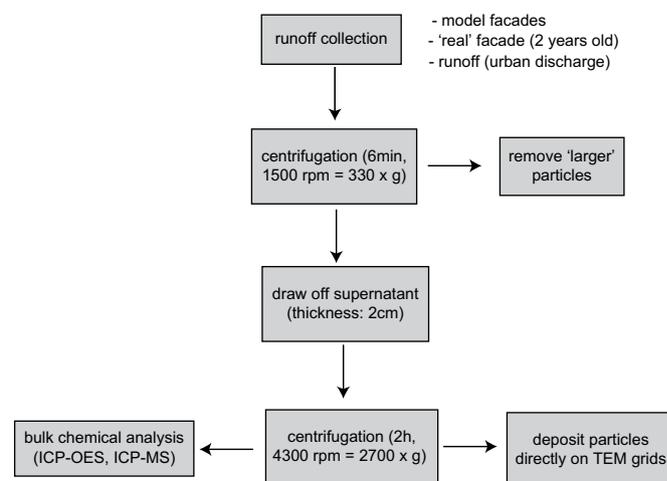


Fig. 1. Schematic layout of the sampling protocol. The cut-off for particles of different densities and sizes, respectively, is given in Table 1.

Table 1
Experimental conditions for the particle size fractionation procedure

Centrifugation	Time	g applied	Cut-off (1.1 g/cm ³)	Cut-off (2.7 g/cm ³)	Cut-off (4.2 g/cm ³)
Step 1	6 min	330 × g	1.8 μm	410 nm	300 nm
Step 2	2 h	2700 × g	130 nm	30 nm	20 nm

and dissolved substances in storm water runoff enter inevitably into the surface water. Water samples were collected of complete runoff events.

The bulk materials from the facades were additionally investigated using scanning electron microscopes (SEM). For that purpose undisturbed samples (1 cm²) were removed from both painted facades.

2.2. Sample preparation

The focus of this study was on synthetic NPs of TiO₂ with a size of up to a few 100 nm. We therefore optimized our preparation procedure to selectively deposit these particles on TEM grids and to remove larger particles which could negatively interfere (large particles deposited on the smaller ones) with the particles of interest. Our setup consisted of a two stage centrifugation procedure (Megafuge, Heraeus, equipped with a swinging bucket rotor). During the first step, larger particles are removed. Just after the centrifugation the uppermost supernatant (2 cm, 40 mL) of the centrifuge tubes is removed using a peristaltic pump. This supernatant containing TiO₂ particles <300 nm, was centrifuged again for 2 h at 2700 × g which resulted in a total deposition of TiO₂ particles larger than about 20 nm. A schematic layout of the sample preparation protocol is given in Fig. 1. The minimal particle diameters removed during the first and the second centrifugation step calculated for different densities are given in Table 1. Thereby, the density of 1.1 g/cm³ is used as a proxy value for organic material, the density of 2.7 g/cm³ is used as a proxy for silicates (quartz and clay minerals) and the density of 4.0 g/cm³ corresponds to the TiO₂ particles.

Based on Table 1 it can be seen that the preparation procedure allows recovering TiO₂ particles with a diameter between roughly 20 and 300 nm. The size of the TiO₂ particles (20–300 nm) is within the dynamic range of the TEM of roughly one logarithmic unit, meaning that the TiO₂ particles can be detected without changing the resolution of the microscope. However, the method of stepwise centrifugation does not provide a sharp cut-off and the particle size distributions remain rather polydisperse which precludes the use of DLS for size determination.

2.3. ICP-MS and ICP-OES

Samples for ICP-MS and ICP-OES measurements were taken in polypropylene sampling tubes. Raw samples and samples after the first centrifugation step were analyzed. Blanks, referring to ultrapure water samples which underwent the same centrifugation procedure, were treated identically. The sample after the first centrifugation step can be directly compared to the respective TEM analysis. The difference between raw sample and centrifuged sample can be attributed to larger particles or aggregates (>300 nm for TiO₂).

ICP-OES measurements were carried out on a simultaneous radial Varian Vista Pro. ICP-MS measurements were performed on a high resolution magnetic sector field ICP-MS Thermofinnigan Element II.

The samples were acidified to 1% using concentrated nitric acid (HNO₃) Merck suprapur[®]. This treatment will not dissolve TiO₂

particles. Metal oxides such as TiO₂, or SiO₂ are highly resistant even against strongly oxidizing acids (e.g. nitric acid or Aqua Regina). The centrifugation procedure we applied to all of our samples removed all TiO₂ particles >300 nm. In addition, the samples were diluted before analysis to an appropriate degree. Systematic analytical investigations on slurry introduction for plasmaspectrometry demonstrated that particles <1.5 μm behave like aqueous solutions in ICP under standard hot plasma conditions (Gibson et al., 2006; Goodall et al., 1993; Halicz et al., 1993; Wang et al., 2005; Wu et al., 2007). This was shown for ceramics particles (Al₂O₃), geological samples (SiO₂) and metal oxides (e.g. TiO₂). Hence, recovery rates close to 100% can be achieved performing calibration with aqueous standards for particles <1.5 μm. The calibration standards were prepared from single and multi-element standards in ICP-quality (Merck and Alfa Aesar) and acidified as described for water samples. All analyses were performed under standard hot plasma conditions. Rhodium was used as internal standard for ICP-MS analysis.

The recovery rates of the raw samples might be lower due to an incomplete ionization of particles >1.5 μm in the plasma. In the following, we use the results from measurements performed on the bulk samples only qualitatively. The quantification of the number concentrations is based exclusively on centrifuged samples.

2.4. Electron microscopy

For the investigation of the runoff particles a TEM (CM30, source LaB6, FEI) was used. The TEM was operated in bright field mode with an acceleration voltage of 300 kV. Elemental analysis was performed with an EDX system (System SIX, Noran) coupled to the TEM. For that purpose the electron beam was focused to a spot and directed over the selected particles.

For the analysis of the solid facade samples (new and aged) an ESEM (environmental scanning electron microscope, XL-30, FEG, FEI) and a HR-SEM (high resolution scanning electron microscope, S-4800, Hitachi) were used. Both devices allow the analysis of uncoated materials by using either low vacuum (ESEM) or low voltage (HR-SEM). The HR-SEM provides a higher spatial resolution but does not permit elemental analysis due to the low acceleration voltage. For elemental analysis, an EDX (energy dispersive X-ray system, EDAX), coupled to the ESEM was used.

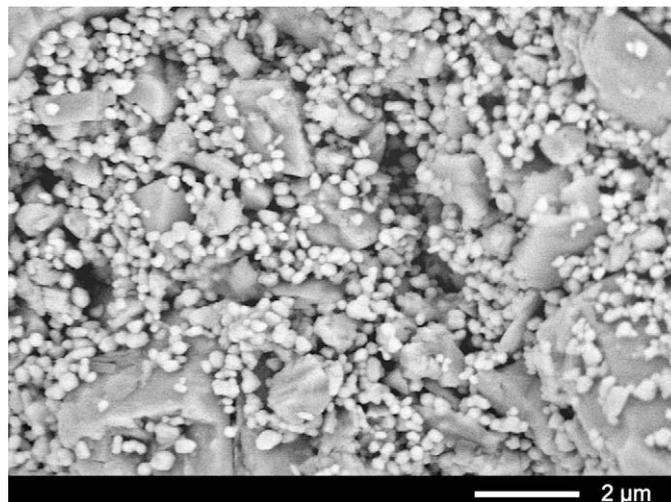


Fig. 2. SEM-BSE image (scanning electron microscope-backscattered electrons) of the new painted facade. The bright spots are TiO₂ particles.

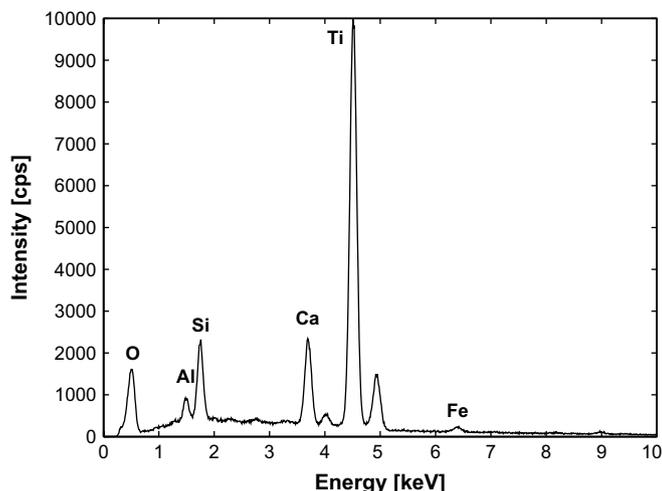


Fig. 3. SEM-EDX (energy dispersive X-ray) spectrum of the surface of the new facade paint. Besides TiO₂ also Al, Si and Ca are detected.

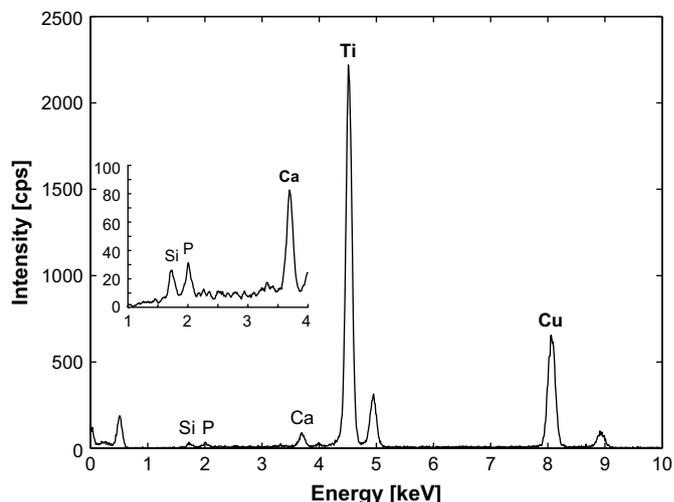


Fig. 6. TEM-EDX of TiO₂ particles detected in the runoff of the new facade. Minor amounts of Si, P and Ca were also detected which most likely result from the organic binder (inset with enlarged scale).

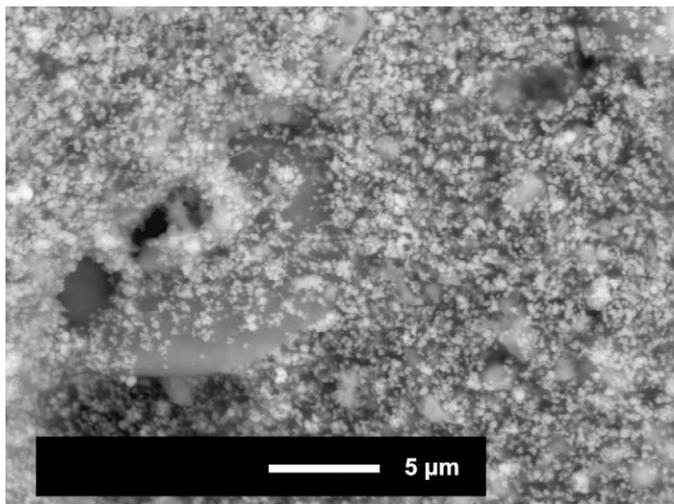


Fig. 4. SEM-BSE (scanning electron microscope-backscattered electrons) image of the aged facade. The white spots on the surface represent TiO₂ particles.

3. Results and discussion

3.1. Solid facade paints

The presence and spatial distribution of synthetic TiO₂ particles were investigated by SEM. A representative image of a new facade surface is given in Fig. 2. TiO₂ particles are homogeneously spread all over the facade and, most importantly, they seem to be only loosely attached to the facade's surface. This makes these particles susceptible to leaching during rain events. The chemical composition recorded with the EDX system is given in Fig. 3. The dominant element is Ti resulting from the TiO₂ particles used as white pigments in the exterior facade paint. The diameter of the TiO₂ particles ranges from about 50 to more than 200 nm. Besides Ti the elements Ca, Al, and Si were also observed in the EDX spectrum (Fig. 3). Larger particles (>1 μm) consist of those elements and are essentially carbonates and silicates typically used as mineral admixtures in exterior paints.

A representative SEM image of the aged facade, where the same paint was used, after nearly 2 years of exposure to natural weather conditions is given in Fig. 4. Also on this image small (50–200 nm) particles can readily be observed. Based on the elemental analysis

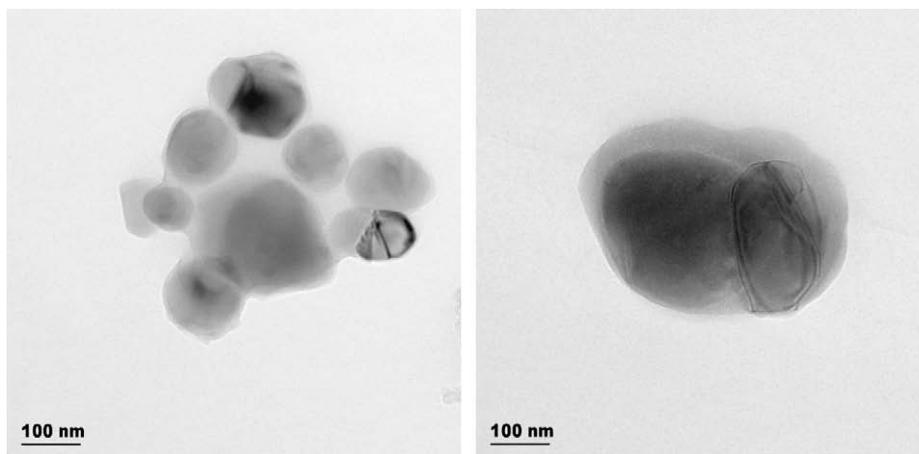


Fig. 5. TEM bright field image of TiO₂ particles from the runoff of the new facade. The TiO₂ particles mostly occur as aggregates consisting of a few particles embedded in the organic binder of the paint (light gray) and individual particles.

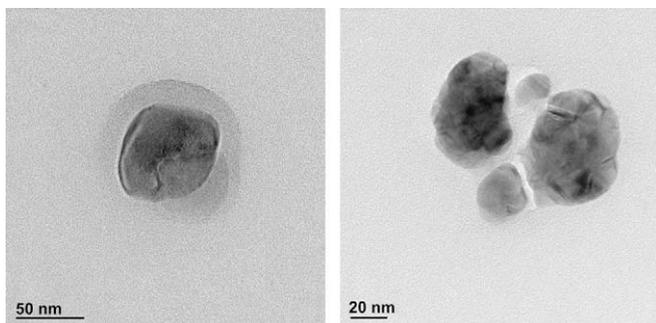


Fig. 7. TEM bright field image of TiO_2 particles found in the runoff of the aged facade. As in the runoff from the model facade, the TiO_2 particles are often embedded in an organic binder (light gray).

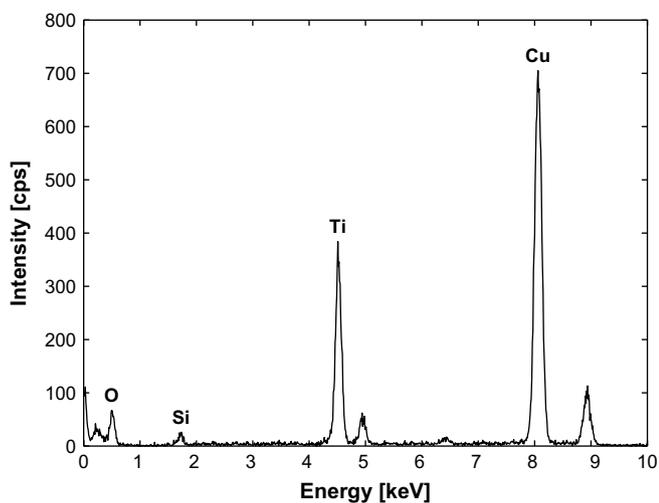


Fig. 8. TEM-EDX of TiO_2 particles detected in the runoff of the aged facade.

of the small particles performed in the ESEM they were identified as TiO_2 particles. Although the number of the TiO_2 particles is much lower (qualitative) than the number on the new facade, nano-sized TiO_2 particles are still loosely distributed on the paint surface.

3.2. Facade runoff

The particles observed in the runoff of the new facade span over a size range of a few tens to several hundreds of nm. This rather narrow size distribution is the result of applied sample preparation procedure. TEM analysis of the collected runoff revealed particles of roughly 150 nm diameter, either isolated or in groups of a few particles (Fig. 5). The chemical analysis using EDX confirmed that the particles are TiO_2 (Fig. 6). The particles are often embedded in a low-contrast matrix. Using EDX analysis the elements Si, P, and Ca were identified in the respective material. Further, the matrix was not stable under the electron beam and started to form bubbles. Taking the information together, it is very likely that the light gray matrix represents the organic binder used in paints.

An example of TiO_2 particles detected in the runoff of the aged facade is given in Fig. 7. The corresponding chemical composition determined with EDX (Fig. 8) confirms that the particles are made of TiO_2 . Also these particles were partly embedded in the organic binder matrix. However, qualitatively the number of TiO_2 particles was significantly lower than in the runoff of the new facade.

3.3. Urban runoff

The sampling site covers urban surface runoff before it discharges into surface waters. Storm water runoff drains part of a residential and business district area. Thus, particles from different diffuse sources are expected in the runoff sample. The high particle load observed in the urban runoff samples made it necessary to dilute the samples (1:10, diluted after centrifugation). Different particle morphologies can readily be observed on the TEM image. The rather 'narrow' size distribution of the particles on the TEM grid with the individual particles well separated from each other, confirm that the sample preparation protocol combined with a dilution of 1:10 is appropriate for optimal particle coverage. An example of a nano-sized TiO_2 particle in urban runoff together with

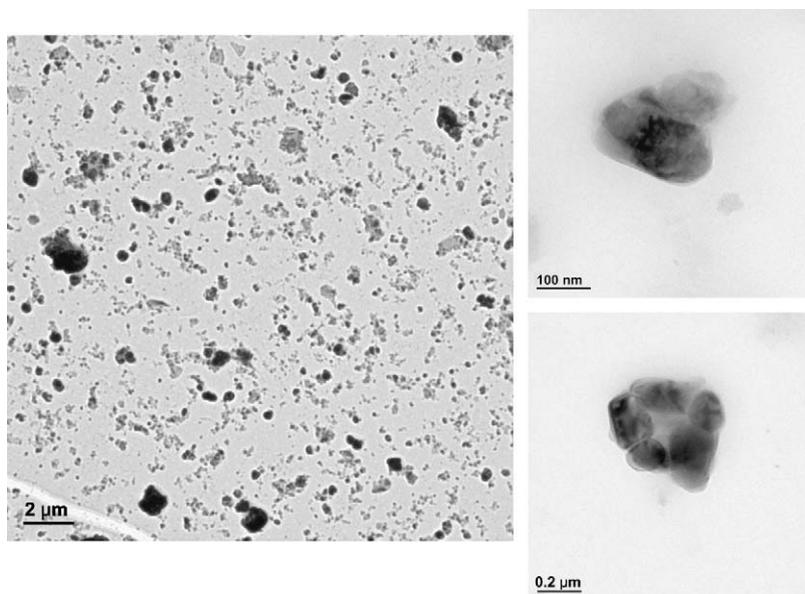


Fig. 9. Overview of the urban runoff sample (left) two TiO_2 particles recorded at a higher magnification on the right hand side. The size distribution of the particles is rather narrow indicating a proper working of our sampling protocol.

the respective EDX spectrum is given in Figs. 9 and 10. TiO₂ particles occurred either as single particles or in agglomerates of a few individual particles. The agglomerates appear to be stuck together by an organic material. Although different sources could account for these particles, the strong similarities between these particles/agglomerates and the particles/agglomerates found in the runoff of the new and aged facades suggest that the particles originate from the same source; in this case, paints from exterior applications. However, agglomerates in the urban runoff were less frequently observed than in the samples from the direct facade runoff. It seems plausible that the organic matrix either has been dissolved or degraded during the transport pathway to the surface water.

3.4. Bulk chemical analysis

The elements Ca, Al, and Si were measured with ICP-OES and found in significant amounts (Ca: 20–40 mg/l, Al: 1–5 mg/l, Si: 1–10 mg/l), which is consistent with the results from the microscopic investigation.

Results of the ICP-MS measurements of Ti concentrations are given in Fig. 11. The concentrations of Ti in the runoff of the new facade were as high as 600 µg/L.

The Ti concentrations in the samples directly collected from either the new or the aged facade, were between 10 and 15% higher in the raw samples compared to centrifuged samples. This shows that 85–90% of all TiO₂ particles occur in the range of 20–300 nm diameter which agrees well with the results from the microscopic analysis. The difference of 10–15% (mass based) can be explained by the rather blurred cut-off of the centrifugation and the larger agglomerates TiO₂ particles embedded in organic binder. In runoff from the urban area, the Ti concentration between raw and centrifuged samples is more pronounced with a difference of about 50% (mass based). This means that half of the particulate load consisted of larger TiO₂ particles or agglomerates with >300 nm diameter, which might originate from other sources such as road paints or other surface coatings.

We used a log-normal distribution (mean = 150 (number based), standard deviation = 1.6) to describe the particle size distribution of the TiO₂ particles, which is consistent with our microscopic observation of the TiO₂ particles. Taking the TiO₂ concentration from the ICP-MS measurements (13.4 µg/L) and assuming a density of 4.0 g/cm³ for TiO₂ particles, the number of TiO₂ particles in the runoff can be calculated. The concentration of the particles <300 nm in diameter is about 3.5 × 10⁸ particles/L, whereby about 10% or 3.5 × 10⁷ particles/L are smaller than 100 nm

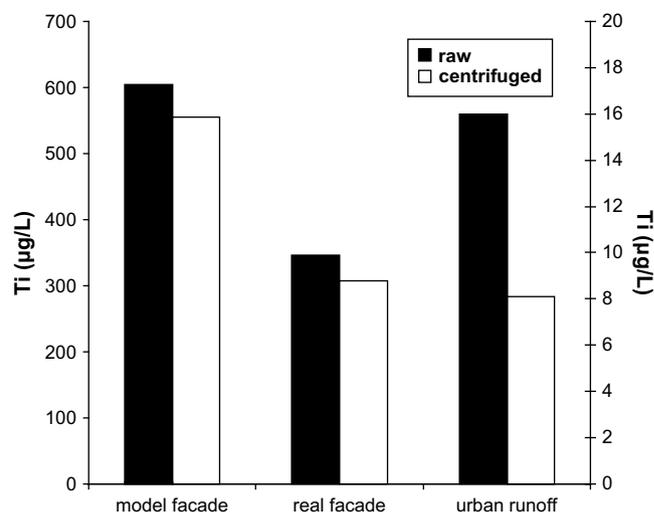


Fig. 11. Mass concentrations (ICP-MS measurements) of Ti in the surface runoff measured directly and after the first centrifugation step. Left axis: runoff from the model facade. Right axis: runoff from the real facade and from the urban runoff.

in diameter. The largest uncertainties are related to the assumptions of the mode and the standard deviation of the particle size distribution. We therefore calculated particle concentrations resulting from two (extreme) modes and standard deviations. Varying the mode from 120 to 180 nm results in an increase/decrease of the particle number concentrations of roughly a factor of 2 relative to the number concentration obtained for a mode of 150 nm. The same increase/reduction of the particle number concentration was obtained when the standard deviation was reduced from 1.6 to 1.4 (increased particle number concentration) or increased to 1.8 (decreased particle number concentration).

4. Conclusions

Synthetic TiO₂ particles within a size range of a few tens to a few hundreds of nm in diameter were successfully detected and identified in the environment using a combination of analytical electron microscopy (TEM-EDX) and bulk chemical (ICP-MS) methods. Based on this information, we were able to give a rough estimate of the number of synthetic TiO₂ NPs in runoff samples. This is the first step towards an assessment of released NPs in environmental samples. An evaluation of the number or mass flux of synthetic NPs in urban runoff further requires data on dynamics of individual runoff events as well as on other urban transport pathways to the aquatic environment.

Based on a modeling study, Mueller and Nowack, 2008 concluded that the nano-TiO₂ particles in water may pose a risk to aquatic life. In this study we show for the first time that TiO₂ particles are released in significant amounts to the aquatic environment. Other exterior applications, such as nano-silver in paints, exposed to natural weather conditions may release NPs in a similar way. The rather fast surface runoff under heavy rainfall conditions may transport NPs without significant retention mechanisms, which inevitably leads to a discharge of synthetic NPs into surface waters.

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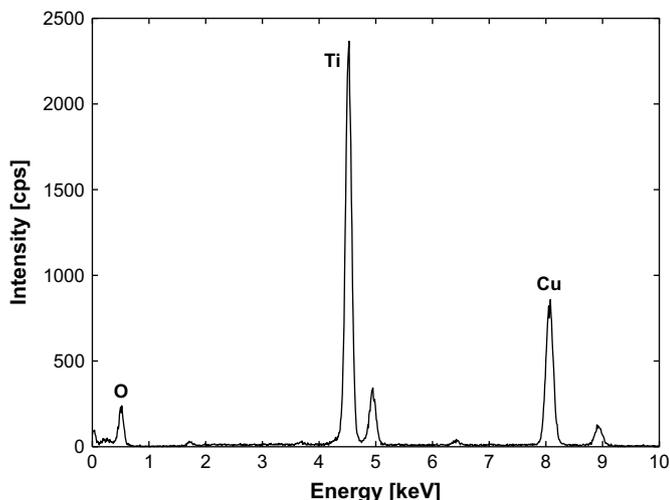


Fig. 10. TEM-EDX of TiO₂ particles detected in the urban runoff sample.

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