Release of TiO2 Nanoparticles from Sunscreens into Surface Waters: A One-Year Survey at the Old Danube Recreational Lake

6 AUTHORS, INCLUDING:

Robert B. Reed
Colorado School of Mines
8 PUBLICATIONS **223** CITATIONS

Stephan Wagner
Helmholtz-Zentrum für Umweltforschung
15 PUBLICATIONS **163** CITATIONS

James F Ranville
Colorado School of Mines
145 PUBLICATIONS **2,883** CITATIONS

Thilo Hofmann
University of Vienna
167 PUBLICATIONS **3,328** CITATIONS

Release of TiO₂ Nanoparticles from Sunscreens into Surface Waters: A One-Year Survey at the Old Danube Recreational Lake

Andreas P. Gondikas,[†] Frank von der Kammer,*[,†,‡] Robert B. Reed,[§] Stephan Wagner,[†] James F. Ranville,[§] and Thilo Hofmann*[,†,‡]

[†]Department of Environmental Geosciences, University of Vienna, Vienna, Austria
[‡]Research Network Environmental Sciences, University of Vienna, Vienna, Austria
[§]Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401, United States

Ⓢ *Supporting Information*
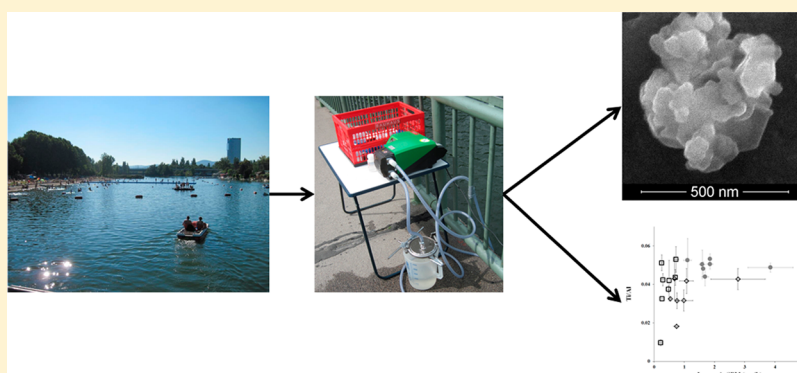
ABSTRACT: Monitoring data are necessary for the future production of engineered nanomaterials and the development of regulations for nanomaterials. Therefore, it is necessary to develop methods that reliably detect and quantify nanomaterials in real-world systems at expectedly low concentrations. In this work we tested several methodological approaches to detect titanium dioxide nanomaterials released from sunscreen products into the Old Danube Lake (Vienna, Austria), which is heavily used for recreational activities like bathing and water sports during the summer season. During a 12-month period suspended particulate matter (SPM) was collected from the lake and analyzed using a combination of complementary techniques. By sampling at a location approximately 50 m from the nearest bathing area and at one meter depth from the water surface, we focused on the potentially mobile fraction of the released nanoparticles. We were able to identify titanium dioxide nanoparticles stemming from sunscreens in the suspended matter of the lake using electron microscopy. Bulk analysis of SPM clearly shows an increase of Ti-containing particles during the summer season. These analyses, however, are not able to distinguish sunscreen nanoparticles from natural Ti-bearing nanoparticles. Therefore, Elemental ratios of Ti with Al, V, Ga, Y, Nb, Eu, Ho, Er, Tm, Yb, and Ta as determined by ICPMS and ICPOES, in combination with single particle ICPMS analysis were applied to establish local background values. The observed mild increase of Ti elemental ratios, compared to spring background values indicates that the residence time of released nanomaterials in the water column is rather short. Overall, the advantages and disadvantages of the methods used to detect and characterize the nanomaterials are discussed.

INTRODUCTION

The cycle of information flow between risk assessment studies (RAS) and industrial research and development (R&D), which is vital for the production of engineered nanomaterials (ENMs) is currently lacking appropriate momentum.[1] One of the major reasons is the lack of information regarding exposure levels of organisms to nanomaterials in real world systems, which is limiting RAS to theoretical estimations that are based on laboratory studies and consumer usage data.[2] However, the gap between controlled lab-scale studies and realistic environmental conditions (e.g., complex media, transformations of ENMs, realistic concentrations, time-dependent exposure, and relation to background materials) introduces major uncertainties in

RAS.[1] In order to reduce these uncertainties, it is necessary to develop methods that are able to detect and quantify ENMs in real world environments.[3] This task would require taking advantage of the physicochemical properties of both the ENMs and their surrounding environment.[1,4] To date, there have been relatively few studies on the detection and quantification of ENMs in natural systems. In addition to the low concentrations expected in the environment, detection and quantification are
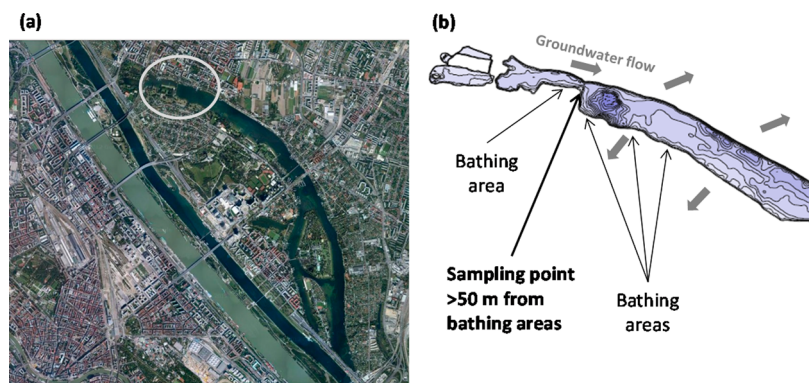
Figure 1. (a) aerial photograph of the Old Danube Lake in Vienna; the sampling site area is marked with a circle. (b) the sampling point and nearby bathing areas at the northwest part of the lake; approximate groundwater flows (not exceeding 30 L/s) are shown with gray arrows.

hampered by the relatively high abundance of natural colloids with similar characteristics and the possibility of modifications of the ENMs.[5]

One of the most-used ENMs is TiO_2, with applications ranging from photocatalysis,[6,7] environmental remediation,[8] to consumer products for food whitening[9] and blocking of ultraviolet radiation.[10] The latter application means that TiO_2 ENMs have found use in a variety of commercially available coatings and sunscreens, normal use of which provides a direct route for release into the environment during bathing activities.[11] In addition, TiO_2 is incorporated into textiles for ultraviolet protection[12] and antimicrobial purposes.[13] Although TiO_2 is widely used as an ingredient in food and sunscreen, knowledge of its potential risk to humans at sizes less than 100 nm is generally lacking.[14] Nowack, Mueller,[15] and Gottschalk[16] have used probabilistic material flow modeling to predict environmental concentrations of TiO_2 ENMs. They concluded that surface water concentrations would range in the part-per-trillion (ppt) to low part-per-billion (ppb) range. TiO_2 ENMs have not been demonstrated to be toxic in this concentration range and in fact are not typically toxic to bacteria or *Daphnia magna* until reaching the mg/L range.[17,18] In addition, TiO_2 particles in sunscreens are coated with materials which suppress their photocatalytic properties. They tend to aggregate and settle in most environmentally relevant water chemistry conditions, a process which is significantly influenced by the properties of local natural organic matter and microorganism communities.[19,20] These complex interdependencies and the general assumptions in the current models make it difficult to predict the concentration range of manufactured TiO_2 nanoparticles in surface waters. Therefore, the aim of this study was to quantify the concentrations of TiO_2 nanoparticles in surface waters with clearly identified sources to understand better the real-world release from sunscreens and gain a better understanding of nanomaterial fate in real-world settings.

The detection of ENMs in the environment after release through real or simulated processes has been the focus of recent studies. Silver ENMs have been detected in washing machine effluent after washing of textiles with incorporated TiO_2 and Ag ENM,[21,22] in washing-water after release from Ag ENM containing socks.[23] The release of TiO_2 ENMs has been reported from paints in facade runoff[24,25] and from wastewater treatment plants[26,27] to receiving waters. Carbon nanotubes (CNTs) have been detected after release from CNT-containing polymers by single particle inductively coupled plasma mass spectrometry (SP-ICPMS).[28] It has also been demonstrated that single wall CNTs can be detected in spiked estuarine sediments by near-infrared fluorescence spectroscopy at environmentally relevant concentrations.[29] In soils and sediments titanium is one of the main constituting elements with an average concentration in the earth's crust of 5 g/kg.[30] In surface waters, naturally occurring particles that contain titanium make quantifying the input from manufactured nanomaterials especially challenging.

We attempted to address the issues of detecting the release of ENMs (TiO_2 from sunscreens) in a complex matrix (lake water), at environmentally relevant concentrations, while taking into account the time-dependent nature of the release and the presence of natural background (natural Ti-containing colloids). Suspended particulate matter (SPM) samples were taken from the Old Danube Lake (Vienna, Austria) periodically (seven times every three months in the spring and summer and eight times total during the fall and winter). By sampling at one meter depth from the water level and at a distance of more than 50 m from a bathing area, we focused on the potentially mobile fraction of the released ENMs. We collected suspended matter samples over a period of 12 months and quantified its elemental composition. In an attempt to determine whether there is a significant release of TiO_2 from sunscreens in the lake, the temporal variation of the elemental ratio of titanium to aluminum and several other elements was established.

In order to distinguish natural and manufactured nanomaterials, the natural mix of elements present in most naturally occurring colloids can be used to distinguish them from the relatively pure composition of ENMs. Specifically the use of isotopic or elemental ratios such as Ce:La, has been proposed for the detection of CeO_2 ENMs.[1] In the framework of this study elemental ratios of Ti were used to separate natural TiO_2 bearing particles from industrial TiO_2 ENMs released from sunscreens into a surface water body. In natural soils these ratios are prone to change due to the weathering resistant nature of TiO_2 compared to other minerals; however, weathering processes take place over the time span of years, while we chose to study elemental ratios of Ti in the SPM of the Old Danube Lake, which remain suspended for the course of several hours. Elemental ratios of titanium to aluminum and other elements were used, which showed comparably good correlations across European soils.[31] Although sunscreen products may contain TiO_2 particles that are coated with a thin layer of aluminum oxide, which serves to protect against reactive oxygen species generation on human skin when exposed to sunlight, in natural particles the abundance of

aluminum is much higher than that of titanium (Ti/Al ratios are approximately 20−50 for manufactured UV-filter particles and 0.1 for natural soils). Hence the elemental ratio between titanium and aluminum could be a promising property for distinguishing manufactured from natural particles, under the condition that the rise of the Ti concentration caused from ENMs is sufficiently high to increase the Ti/Al ratio in the SPM significantly above the variation of the natural background. Additional elements were used to further test the applicability of elemental ratios for detecting ENMs release. This method was complemented with electron microscopy and SP-ICP-MS for particle specific analysis.

MATERIALS AND METHODS

Sampling Site. The Old Danube Lake (Vienna, Austria) was cut off from the main Danube River in 1875. It contains a water volume of approximately 3.5×10^6 m^3 and is predominantly groundwater-fed. Exchange with the Danube River is nonexistent, the water quality is excellent in terms of eutrophication prevention, SPM levels are low (1−5 mg/L), and visibility is in the range of 1−6 m, with seasonal dependence; the water depth in the majority of the lake is less than 2.5 m, and the maximum depth is 7 m, so thermal stratification is not expected.[32]

Sample Collection and Analysis. SPM samples were collected from the Old Danube Lake at one meter depth, in the vicinity of a public bathing area (Figure 1). Three replicate samples were collected during each of 22 campaigns that took place from May 5, 2012 through June 4, 2013, except for samples collected on November 8, 2012 (one sample) and December 14, 2012 (two samples).

Before filtering, five liters of lake water were pumped directly into a bucket where pH, conductivity, and water temperature were measured. During filtration, lake water was pumped into a pressure-filtration membrane case (Schleicher & Schuell, Germany, now Whatman, stainless steel, max. pressure 180 psi) using a high pressure peristaltic pump (Watson Marlow, Wilmington, MA; max. pressure 100 psi). Samples were collected by filtration through 142 mm diameter cellulose acetate membranes with 0.2 μm pore size (Sartorius AG, Göttingen, Germany). Although the monomer TiO$_2$ particle size in sunscreen is expected to be in the range of 60 nm, membranes with 0.2 μm pore size were selected because (i) particles in the sunscreen product are aggregated to sizes larger than 100 nm[33] and (ii) calcium levels in the lake water (Supporting Information (SI) Table S1) are likely to induce aggregation of the TiO$_2$ particles, even in the presence of NOM.[19] Additional controls showed no detectable traces of Ti in the filtrate and the number of particles per volume of filtrate decreased with filtration time (SI Figure S1). ICP-MS trace analysis in the filtrate was performed for every one or five liters of filtrate (depending on how fast filters were clogged). Al, Fe, and Mn in the filtrate were monitored to detect possible membrane failure, whereas Ti levels remained below detection limits (0.2 ppb) throughout the filtration process. Additionally, pressure on the feed-side was continuously monitored to follow the cake formation process and detect possible membrane disintegration. After sample collection, the membranes were dried at 105 °C overnight and then ashed by heating to 550 °C for 3 h. The inorganic part of SPM in mg/L was determined by weighing the solid residue on a microbalance (AT201, Mettler-Toledo Intl., Inc., Switzerland) and dividing by the amount of lake water filtered through the membrane. The residue (3−19

mg) was digested in a solution consisting of 29.5% nitric acid, 7.3% hydrofluoric acid, 5.5% hydrogen peroxide, and 5.5% hydrochloric acid. All acids used were suprapure grade purchased from Merck KGaA (Darmstadt, Germany). The digestion process was performed in a microwave oven (Multiwave 3000, Anton Paar GmbH, Graz, Austria) and a two-step microwave program was used for the dissolution of TiO$_2$ and complexation of HF residues with boric acid (SI Table S1). The digested samples were analyzed with an inductively coupled plasma mass spectrometer (ICP-MS) (7700 series ICP-MS, Agilent Technologies, Santa Clara, CA).

Scanning Electron Microscopy. Particles of a few SPM samples were imaged using a scanning electron microscope (SEM, FEI Quanta 3D FEG, Hillsborough, OR) equipped with an energy dispersive X-ray spectroscopy (EDS on the FEI Quanta 3D FEG). Secondary electron images and backscatter electrons were acquired at 10 and 15 kV acceleration voltages. One sunscreen product bought from the local market and a standard material, cosmetic grade TiO$_2$ powder with hydrophilic coating (NM104, obtained from Joint Research Centre, IHCP, Ispra, Italy) were processed in a similar way (ashed at 550 °C for 3 h) as the SPM samples and as well imaged with SEM and analyzed with EDS.

Single Particle Inductively Coupled Plasma Mass Spectrometry (SP-ICP-MS). Unfiltered water samples collected at the Old Danube Lake during the 12 month sampling period were diluted in Milli-Q water and measured in Time Resolved Analysis mode with ICP-MS (7700x ICP-MS, Agilent Technologies, Santa Clara, CA). The dwell time used was 10 ms, and total sample collection time was 3.4 min. This method can be used for obtaining both the number concentration and size distribution of ENMs. When a sufficiently large particle is atomized in the ICP-MS plasma, a "pulse" above background is detected for the analyte of interest (here Ti). The number of pulse events for a given sample can then be related to the particle number concentration of the analyte (e.g., ref 34). However, we found that high concentrations of calcium in the lake water (on the order of 50 mg/L), produced strong interferences on mass 48, which is the most abundant isotope of Ti (73.8% abundance). We therefore used ^{47}Ti for our measurements with only 7.3% abundance, which increased the smallest TiO$_2$ particle size measurable with SP-ICP-MS to 130 nm. We therefore did not include size characterization results in this work and only report number concentrations.

RESULTS

In total, 22 sampling campaigns took place from May 5, 2012 to June 4, 2013 and the volume of lake water that was filtered before membrane clogging varied between 3.4 and 25.1 L, depending on the season (SI Table S2); larger volumes were filtered during the winter, when the lake water contained only small amounts of SPM and the turbidity (only visually observed) was accordingly very low. The relation between the volume filtered and weather conditions reflects the intensity of biological activity in the lake. Algae and other micro-organisms proliferate during the spring and summer seasons and combined with possible resuspension of sediments by recreational activities effectively form a cake on the membrane material, which leads to clogging of the membrane relatively fast. The pH and conductivity of the lake water were 8.4 ± 0.2 and 451 ± 27 μS/cm, respectively (SI Table S2).
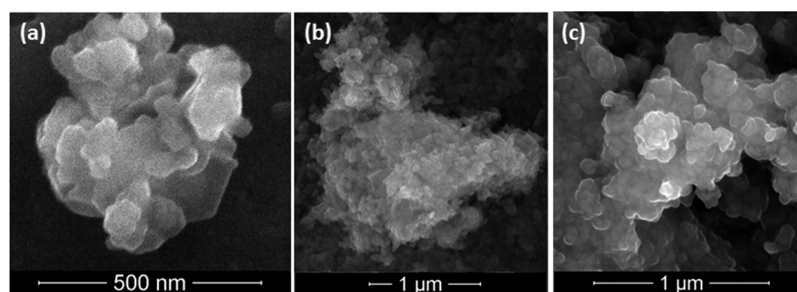
Figure 2. SEM images of TiO_2 particles from (a) suspended minerals collected from the Old Danube Lake on September 9, 2012, (b) a popular sunscreen product, and (c) cosmetic grade reference material NM104.
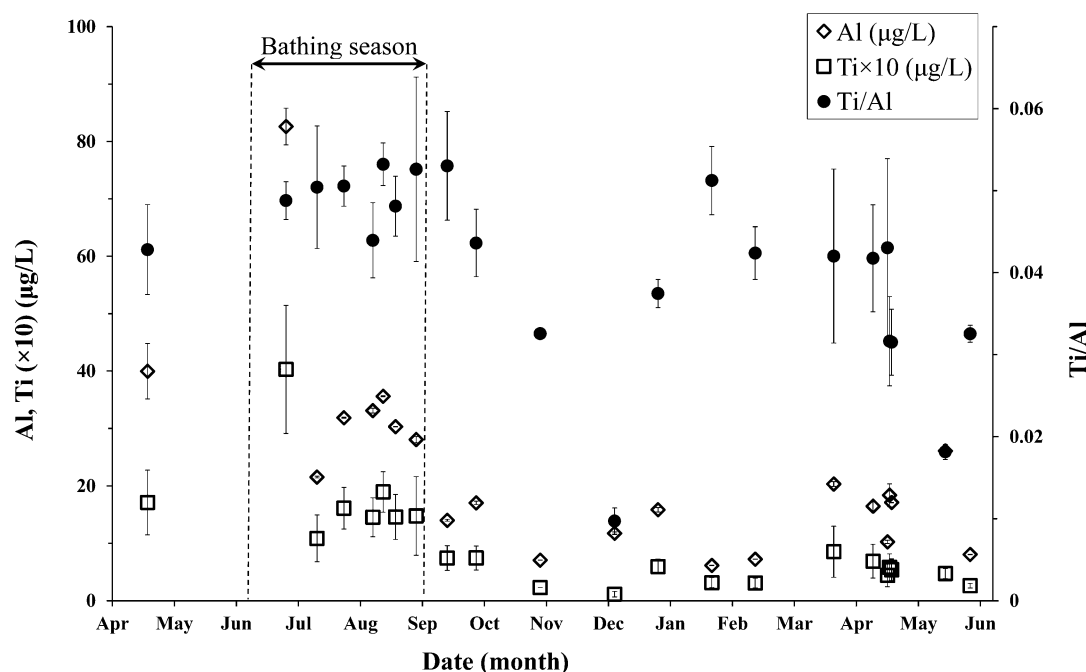

Figure 3. Variations of Ti concentration (μg/L, multiplied by 10, empty squares, left-hand side axis), Al concentration (μg/L, empty diamonds, left-hand side axis), and Ti/Al elemental ratio (solid circles, right-hand side axis) in the Old Danube Lake. Standard deviation of three replicate samples is shown for all measurements, except for samples collected on November 8, 2012 (one sample) and December 14, 2012 (two replicates). The bathing season is marked with dashed lines.

Imaging of Suspended Particulate Matter. Electron microscopy, commonly used for the detection of nanomaterials in real-world systems[24,35,36] for its high lateral resolution and elemental selectivity, was initially applied to trace TiO_2 ENMs among an overwhelming majority of natural particles. Particles consisting of mainly TiO_2 were identified in a sample of suspended minerals taken from the lake during the bathing season, on September 9, 2012 (Figure 2). These particles were similar in shape and size with particles from a commercial sunscreen that is popular in Vienna and with particles from cosmetic grade TiO_2 (reference material NM104). EDS analysis showed that the elemental composition of those TiO_2 particles found in the suspended minerals of the Old Danube Lake was almost identical to the composition of particles from the sunscreen product (SI Table S3).

These results verify the presence of TiO_2 ENMs in the bulk water body of the lake. The location of sample collection (50 m distance from two bathing areas, 1 m depth from the surface) in combination to the resemblance in size, shape, and composition of the particles in the SEM images indicate that TiO_2 particles of high elemental purity that are likely to originate from

sunscreens may remain suspended in the lake. However, the extent to which these particles are released and distributed throughout the lake is not revealed by the imaging analysis used. Therefore, we complemented our SEM findings with calculations on the potential for release of TiO_2 particles from sunscreens in the lake based on the number of bathers and then used bulk elemental analysis of the suspended minerals to verify the extent of this release.

Ti/Al Elemental Ratio in Inorganic Suspended Particulate Matter. The input of TiO_2 in the lake is influenced by (i) the number of bathers, (ii) the amount of sunscreen used per bather, (iii) the concentration of TiO_2 in the sunscreen, (iv) the amount of sunscreen that is washed off in the lake water during bathing activities,[37] and specifically for ENMs (v) the stability of TiO_2 ENMs in the lake water and their ability to distribute throughout the lake water. A "worst case scenario" was developed on estimations of the maximum amount of TiO_2 possibly released from sunscreens in the lake, using information about the lake's use for bathing activities and the local sunscreen market (SI). Under this scenario, particles would remain suspended and accumulate in the water column

during the bathing season, to a final concentration of 27.1 μg/L TiO$_2$. We found that the average total TiO$_2$ concentration in the lake water during the spring, fall, and winter seasons was less than 1.7 μg/L. The calculated release would then translate to an increase of titanium concentration during the bathing season by more than 1 order of magnitude. In parallel to release of these particles from sunscreen, limited wash off, aggregation, deposition, and spatial variations are expected to significantly limit their presence in the water column.

Elemental analysis of the inorganic SPM showed temporal variations for the concentrations of Ti and Al, as expected for a natural system (Figure 3, SI Table S4). Concentrations of both Ti and Al increased during the summer. However, when expressed in mass per volume units these values may be influenced by highly variable factors, such as biological activity, resuspension of lake sediments and weather conditions. Elemental ratios of the inorganic fraction of the SPM are less likely to be influenced by such factors and may provide clues about the origin of this material. The Ti/Al ratio was 0.043 ± 0.006 in May, 2012 (1 day sampled), then increased to 0.050 ± 0.003 during the bathing season of 2012 (7 days sampled), followed by a decrease to 0.039 ± 0.014 in the fall and winter of 2012−2013 (8 days sampled). During the fall and winter relatively large variations were observed. Initially, the ratio remained close to summer season levels (0.053 ± 0.007, $N = 3$, on September 24, 2012) and gradually decreased in the fall. Relatively large variations were observed during the winter, especially at two sampling days, when the top layer of the lake was frozen (0.010 ± 0.002, $N = 2$ and 0.051 ± 0.004, $N = 3$ on December 14, 2012 and January 30, 2013, respectively). These measurements are likely influenced by the lack of mixing in the lake, due to ice coverage. In the spring of 2013 the average Ti/Al ratio was 0.033 ± 0.009 (6 days sampled).

Our data suggest a dependency of the Ti/Al ratio on seasonal conditions which are influenced by local weather, biogeochemical, and anthropogenic factors. Student's t tests were performed between seasonal values. The Ti/Al ratio was significantly different between the summer and spring ($p < 0.001$), but not between summer and fall/winter. The relatively high standard deviation observed during the fall/winter measurements resulted in the test failure between summer and fall/winter values. The variability in these measurements was influenced by the high Ti/Al ratio measured close to the end of the bathing season (September 24, 2012) and two measurements collected at times when the top layer of the lake was frozen and was therefore not mixed (December 14, 2012 and January 30, 2013). However, a comparison between summer and spring values might be more relevant in the context of the lake's biogeochemistry. During the fall and winter biological activity, such as algal growth is suppressed, as indicated by the rapid decrease of the concentration of inorganic SPM (Figure 4). In order to test the effect of rainwater runoff on the Ti/Al ratios, we used meteorological data from a weather station in the vicinity of the Old Danube Lake (SI Figure S3). The sum of precipitation 3 days before sampling was plotted against Ti/Al ratios measured during our sampling campaigns (SI Figure S4) and no correlation was found. Therefore, the quantification of elemental ratios such as Ti/Al in inorganic SPM, could potentially serve as an indicator of anthropogenic input of titanium to surface waters, under the condition that local values are well established.

Elemental Ratios of Ti with Various Elements in Suspended Minerals. In addition to aluminum, several other
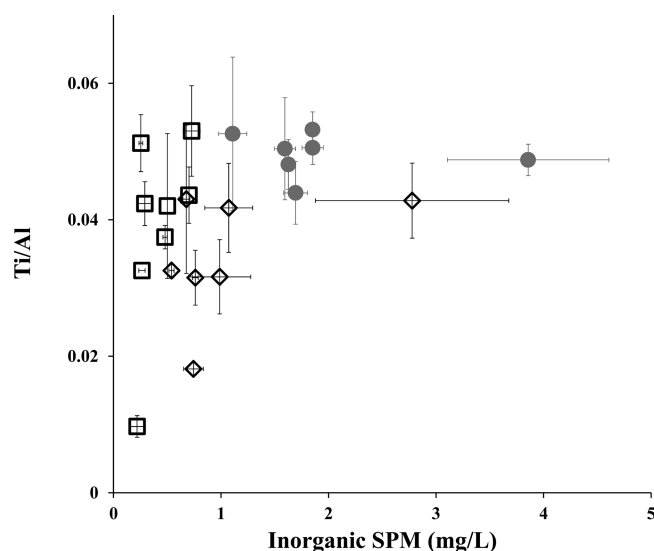

Figure 4. Variations of Ti/Al elemental ratio and concentration of inorganic SPM in the Old Danube Lake during the summer (solid gray circles), fall and winter (open squares), and spring (open diamonds). Standard deviations of three replicate samples are shown for all measurements, except for two samples collected in the fall/winter seasons, on November 8, 2012 (one sample) and December 14, 2012 (two replicates).

elements were measured and their elemental ratio with titanium was calculated. We limited this analysis to a small group of elements that are likely to coexist with titanium in nature. We studied the composition of floodplain and stream sediments in Europe, using data from the Forum of European Geological Surveys (FOREGS)[31] and searched for correlations between titanium and other elements. Overall, we found poor correlations, with R^2 values ranging from <0.01 up to 0.66 (SI Table S5). We arbitrarily selected a minimum R^2 value of 0.2 for both floodplain and stream sediments and identified a small group of elements that exhibit higher likelihood to coexist with titanium in nature ($R^2 > 0.2$): Nb, V, Eu, Ga, Er, Al, Y, Ta, Ho, Yb, Tm. The average values of these elements during the summer, fall/winter, and spring are reported in Table 1 and SI Table S6.

Similar to the Ti/Al ratio, the elemental ratios of Ti with V, Ga, Y, Nb, Eu, Ho, Er, Tm, Yb, and Ta are significantly different between summer and spring. However, the test failed when comparing summer and fall/winter values, possibly due to the large variations that were observed during the fall and winter, which also influenced the results for the Ti/Al ratio.

Number Concentrations of Ti-Containing Particles. In an attempt to quantify TiO$_2$ ENMs in Old Danube Lake, water samples from the lake were diluted in Milli-Q water and analyzed with SP-ICP-MS. The dilution factor varied by sample and was chosen to keep the fraction of particle detection events in the 5−10% range.[38] Results of particle number concentration analysis are shown in Figure 5. This technique does not discriminate between engineered and natural Ti-containing particles, but it is clear from the data that the number concentration of Ti-containing particles in the summer is higher than the fall, winter, and spring.

Severe ^{48}Ca interferences (the water in the Old Danube has calcium concentrations of about 34−50 mg/L) on the most abundant isotope ^{48}Ti (73.8% abundant) require the use of ^{47}Ti (7.3% abundance) as the monitored isotope. The use of a low

Table 1. Average Concentrations of Elements (X) in Inorganic SPM of the Old Danube Lake during the Summer of 2012 (SMR), Fall and Winter 2012−2013 (FW), and Spring of 2013 (SPR) in mg/L Units[a]

X	summer	fall/winter	spring	(Ti/X)$_{summer}$	(Ti/X)$_{fall/winter}$	SD$_{fall/winter-summer}$	(Ti/X)$_{spring}$	SD$_{spring-summer}$
V	74.7 ± 32.5	106 ± 26	61.4 ± 11.2	14.0 ± 4.8	11.5 ± 5.4	no	10.4 ± 2.5	no
Ga	194 ± 56	304 ± 66	273 ± 72	5.16 ± 1.47	3.89 ± 1.57	no	2.49 ± 1.03	yes ($P = 0.002$)
Y	5.27 ± 0.97	7.22 ± 1.37	5.09 ± 1.02	182 ± 20	159 ± 46	no	125 ± 24	yes ($P = 0.001$)
Nb	2.78 ± 0.54	3.39 ± 0.62	2.64 ± 0.38	345 ± 47	331 ± 81	no	224 ± 85	yes ($P = 0.002$)
Eu	0.262 ± 0.041	0.330 ± 0.058	0.249 ± 0.040	3640 ± 380	3380 ± 870	no	2530 ± 500	yes ($P ≤ 0.001$)
Ho	0.176 ± 0.045	0.265 ± 0.047	0.182 ± 0.037	5510 ± 630	4260 ± 1110	yes ($P = 0.023$)	3500 ± 770	yes ($P ≤ 0.001$)
Er	0.549 ± 0.107	0.754 ± 0.154	0.533 ± 0.086	1750 ± 240	1500 ± 410	no	1180 ± 220	yes ($P ≤ 0.001$)
Tm	0.070 ± 0.018	0.101 ± 0.023	0.066 ± 0.018	13900 ± 2100	11300 ± 3100	no	9880 ± 2760	yes ($P = 0.010$)
Yb	0.444 ± 0.114	0.750 ± 0.155	0.541 ± 0.143	2190 ± 270	1550 ± 490	yes ($P = 0.010$)	1210 ± 340	yes ($P ≤ 0.001$)
Ta	0.784 ± 0.208	1.17 ± 0.58	0.905 ± 0.184	1260 ± 270	1160 ± 490	no	701 ± 131	yes ($P ≤ 0.001$)

[a]Errors represent the standard deviation for seven measurements from each season. Also shown are elemental ratios of titanium to each element (Ti/X) for the three seasons and whether there was statistical difference (SD) between fall/winter or spring values with summer values (using Students t-test).
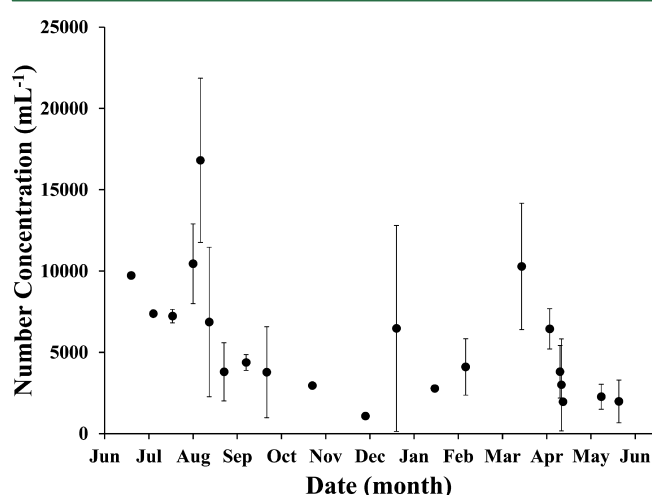

Figure 5. Number concentration of Ti-containing particles as measured with SP-ICP-MS in unfiltered surface water samples collected from the Old Danube Lake between July 8, 2012 and June 4, 2013. The mass detection limit was approximately 3 fg Ti, which corresponds to ~130 nm diameter TiO$_2$ particle. Error bars represent the standard deviation of three replicate samples.

abundance isotope, however, results in a lower Ti pulse intensity for a given particle, which translates into a larger minimum particle size which can be detected. After applying a particle cutoff of the average background signal plus three times the standard deviation, only particles containing ~3 fg of Ti, equivalent to a spherical TiO$_2$ particle with a diameter of ~130 nm, could be discriminated from the background signal. As such, we are not detecting what is typically defined as the "nano" size range of particles from 1 to 100 nm. However, based on SEM analysis of TiO$_2$ ENMs found in sunscreens (Figure 2), detecting TiO$_2$ ENMs above 130 nm should be valid for determining relative amounts of release from sunscreens.

■ DISCUSSION

Our data show that time-resolved elemental ratios of Ti with Al and other elements is a useful tool for quantifying the relative input of TiO$_2$ ENMs into the study area from an external source. TiO$_2$ ENMs contain low or zero concentration of elements such as Al, V, Ga, Y, Nb, Eu, Ho, Er, Tm, Yb, and Ta that are likely to coexist with Ti in naturally occurring particles.

Release of TiO$_2$ ENMs from sunscreens would result in an increased population of "pure" Ti-containing particles. However, at this point, we are not able to directly link the relative increase of Ti ratios with the release from sunscreen products. The measured increase of Ti/Al from 0.033 ± 0.009 in the spring to 0.050 ± 0.003 is too low compared to the "worst case scenario" value of 0.35 and the influence of other possible sources of higher Ti/Al ratios cannot be excluded. The measured 0.051 ± 0.004 Ti/Al ratio measured on January 30, 2012 when the top layer of the lake was frozen indicates that there may be a natural source of Ti-rich SPM. Assuming that sunscreen TiO$_2$ ENMs are solely responsible for the Ti/Al ratio increase, we calculate a mass concentration of 1.38 μg/L of TiO$_2$ ENMs (corresponding to a number concentration of approximately $3 \cdot 10^9$ particles per liter, assuming 60 nm diameter). This concentration is at the lower end of the range predicted by exposure models,[15] is in the range of the most conservative scenario we considered (Table 1), and equals only 5% of the maximum possible input of TiO$_2$ ENMs from sunscreens. Other anthropogenic sources, such as façade-paint runoff or resuspension of Ti-rich sediment due to bathing activities, as well as natural sources such as atmospheric depositionand biological activity, may add to the changes we observed during the summer season.[24,39,40] The impact of these sources, however, was not determined in this study. Advanced particle analysis techniques are necessary to distinguish between natural and anthropogenic sources and these techniques are currently missing.

Measuring elemental ratios on a single particle basis is critical for distinguishing between natural and anthropogenic sources and also between the various man-made materials. On one hand, electron microscopy images show that the release from sunscreen products is highly likely, but do not provide a quantitative measure of the emission. On the other hand, elemental composition measurements give a quantitative measure of Ti/Al increase, but are not source specific. Ti-containing particle number concentrations calculated using SP-ICP-MS proved to be a very promising tool for bridging this gap. However, this method is currently limited by analytical challenges related to the TiO$_2$ size detection limit, which need to be resolved before this method is used for quantitative analysis and determination of particle size distributions. Also, SP-ICP-MS currently cannot measure more than one isotope simultaneously, hence the use of element ratios or isotopic ratios on individual particles for a differentiation of

manufactured and natural particles is not possible with existing instruments. Other approaches, such as the use of crystal structural differences between manufactured and natural TiO_2 materials are not particularly promising. Rutile is the predominant phase in sunscreen products and although other phases such as brookite and anatase or Ti substitutions in mineral structures may be present in natural materials,[41] rutile is the most thermodynamically stable phase of TiO_2 and it would be impossible to link its presence with manufactured products. In addition, crystal structure of our samples would be affected by ashing at 550 °C for 3 h, enhancing the formation of rutile (e.g., ref 42). Isotopic ratios that have been successfully used with other elements such as mercury to trace their source to manufacturing processes[43] are also not likely to be useful in the case of TiO_2 due to the quantitative conversion of the source material to ENMs.[1] Given these limitations, our method to use locally established background elemental ratios seems to be the most promising solution for detecting the release of TiO_2 ENMs in surface waters.

Overall, our data show that TiO_2 ENMs from sunscreen are very likely released into the main water body of the lake, but do not remain suspended for a long time. The most likely fate for released ENMs is aggregation and settling onto the sediments[11,44] due to water chemistry conditions and the presence of natural colloids, although this process is strongly affected by NOM and living organisms.[19,45] The organic material that is part of sunscreen products is readily removed from the particles' surface,[46,47] leaving the ENMs exposed to the surrounding environment. Lab scale tests showed that the hydrochemistry of the Old Danube Lake favors fast aggregation of cosmetic grade TiO_2 ENMs (SI Figure S2). It should also be noted that the organic part of sunscreens contains several hydrophobic compounds that are likely to accumulate on the air–water interface. The potential accumulation of TiO_2 ENMs in the air/water interface, with hydrophobic organic compounds in sunscreen matrixes would also be of interest due to the possible reactions that may take place under the influence of sun radiation.[48−50] Further work on the sediments, air–water interface, and the lake surrounding soils is necessary to determine the short-term and long-term presence of sunscreen TiO_2 ENMs in the lake.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org/.

AUTHOR INFORMATION

Corresponding Authors
*Phone: 0043 1 4277 53380; fax: 0043 1 4277 9533; e-mail: frank.kammer@univie.ac.at.
*Phone: +43 1 4277 53320; fax: +43 1 4277 53371; e-mail: thilo.hofmann@univie.ac.at.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Klaine, S. J.; Koelmans, A. A.; Horne, N.; Carley, S.; Handy, R. D.; Kapustka, L.; Nowack, B.; von der Kammer, F. Paradigms to assess the environmental impact of manufactured nanomaterials. *Environ. Toxicol. Chem.* **2012**, *31* (1), 3−14.

(2) Robichaud, C. O.; Uyar, A. E.; Darby, M. R.; Zucker, L. G.; Wiesner, M. R. Estimates of upper bounds and trends in nano-TiO_2 production as a basis for exposure assessment. *Environ. Sci. Technol.* **2009**, *43* (12), 4227−4233.

(3) Money, E. S.; Reckhow, K. H.; Wiesner, M. R. The use of Bayesian networks for nanoparticle risk forecasting: Model formulation and baseline evaluation. *Sci. Total Environ.* **2012**, *426*, 436−445.

(4) von der Kammer, F.; Legros, S.; Larsen, E. H.; Loeschner, K.; Hofmann, T. Separation and characterization of nanoparticles in complex food and environmental samples by field-flow fractionation. *TrAC, Trends Anal. Chem.* **2011**, *30* (3), 425−436.

(5) Gottschalk, F.; Sun, T. Y.; Nowack, B. Environmental concentrations of engineered nanomaterials: Review of modeling and analytical studies. *Environ. Pollut.* **2013**, *181*, 287−300.

(6) Allen, N. S.; Edge, M.; Sandoval, G.; Verran, J.; Stratton, J.; Maltby, J. Photocatalytic coatings for environmental applications. *Photochem. Photobiol.* **2005**, *81*, 279−290.

(7) Puddu, V.; Choi, H.; Dionysiou, D. D.; Puma, G. L. TiO_2 photocatalyst for indoor air remediation: Influence of crystallinity, crystal phase, and UV radiation intensity on trichloroethylene degradation. *Appl. Catal., B* **2010**, *94* (3−4), 211−218.

(8) Balasubramanian, G.; Dionysiou, D. D.; Suidan, M. T.; Baudin, I.; Laine, J.-M. Evaluating the activities of immobilized TiO_2 powder films for the photocatalytic degradation of organic contaminants in water. *Appl. Catal., B* **2004**, *47*, 73−84.

(9) Weir, A.; Westerhoff, P.; Fabricius, L.; Hristovski, K.; von Goetz, N. Titanium dioxide nanoparticles in food and personal care products. *Environ. Sci. Technol.* **2012**, *46* (4), 2242−2250.

(10) Popov, A. P.; Kirillin, M. Y.; Priezzhev, A. V.; Lademann, J.; Hast, J.; Myllyla, R. Optical sensing of titanium dioxide nanoparticles within horny layer of human skin and their protecting effect against solar UV radiation. *Proc. Soc. Photo-Opt. Instrum. Eng.* **2005**, *5702*, 113−122.

(11) Botta, C.; Labille, J.; Auffan, M.; Borschneck, D.; Miche, H.; Cabie, M.; Masion, A.; Rose, J.; Bottero, J. Y. TiO2-based nanoparticles released in water from commercialized sunscreens in a life-cycle perspective: Structures and quantities. *Environ. Pollut.* **2011**, *159* (6), 1543−1548.

(12) Paul, R.; Bautista, L.; De la Varga, M.; Botet, J. M.; Casals, E.; Puntes, V.; Marsal, F. Nano-cotton fabrics with high ultraviolet protection. *Text. Res. J.* **2010**, *80* (5), 454−462.

(13) Dastjerdi, R.; Montazer, M. A review on the application of inorganic nano-structured materials in the modification of textiles: Focus on anti-microbial properties. *Colloid Surf., B* **2010**, *79* (1), 5−18.

(14) Colvin, V. L. The potential environmental impact of engineered nanomaterials. *Nat. Biotechnol.* **2003**, *21* (10), 1166−1170.

(15) Mueller, N. C.; Nowack, B. Exposure modeling of engineered nanoparticles in the environment. *Environ. Sci. Technol.* **2008**, *42* (12), 4447−4453.

(16) Gottschalk, F.; Sonderer, T.; Scholz, R. W.; Nowack, B. Modeled environmental concentrations of engineered nanomaterials (TiO$_2$, ZnO, Ag, CNT, fullerenes) for different regions. *Environ. Sci. Technol.* **2009**, *43* (24), 9216−9222.

(17) Adams, L. K.; Lyon, D. Y.; Alvarez, P. J. J. Comparative eco-toxicity of nanoscale TiO$_2$, SiO$_2$, and ZnO water suspensions. *Water Res.* **2006**, *40* (19), 3527−3532.

(18) Heinlaan, M.; Ivask, A.; Blinova, I.; Dubourguier, H. C.; Kahru, A. Toxicity of nanosized and bulk ZnO, CuO and TiO$_2$ to bacteria *Vibrio fischeri* and crustaceans *Daphnia magna* and *Thamnocephalus platyurus*. *Chemosphere* **2008**, *71* (7), 1308−1316.

(19) Ottofuelling, S.; Von der Kammer, F.; Hofmann, T. Commercial titanium dioxide nanoparticles in both natural and synthetic water: Comprehensive multidimensional testing and prediction of aggregation behavior. *Environ. Sci. Technol.* **2011**, *45* (23), 10045−10052.

(20) Battin, T. J.; Kammer, F. V. D.; Weilhartner, A.; Ottofuelling, S.; Hofmann, T. Nanostructured TiO$_2$: Transport behavior and effects on aquatic microbial communities under environmental conditions. *Environ. Sci. Technol.* **2009**, *43* (21), 8098−8104.

(21) Geranio, L.; Heuberger, M.; Nowack, B. The behavior of silver nanotextiles during washing. *Environ. Sci. Technol.* **2009**, *43* (21), 8113−8118.

(22) Windler, L.; Lorenz, C.; von Goetz, N.; Hungerbuhler, K.; Amberg, M.; Heuberger, M.; Nowack, B. Release of titanium dioxide from textiles during washing. *Environ. Sci. Technol.* **2012**, *46* (15), 8181−8188.

(23) Benn, T. M.; Westerhoff, P. Nanoparticle silver released into water from commercially available sock fabrics. *Environ. Sci. Technol.* **2008**, *42* (11), 4133−4139.

(24) Kaegi, R.; Ulrich, A.; Sinnet, B.; Vonbank, R.; Wichser, A.; Zuleeg, S.; Simmler, H.; Brunner, S.; Vonmont, H.; Burkhardt, M.; Boller, M. Synthetic TiO$_2$ nanoparticle emission from exterior facades into the aquatic environment. *Environ. Pollut.* **2008**, *156* (2), 233−239.

(25) Kaegi, R.; Sinnet, B.; Zuleeg, S.; Hagendorfer, H.; Mueller, E.; Vonbank, R.; Boller, M.; Burkhardt, M. Release of silver nanoparticles from outdoor facades. *Environ. Pollut.* **2010**, *158* (9), 2900−2905.

(26) Kiser, M. A.; Westerhoff, P.; Benn, T.; Wang, Y.; Perez-Rivera, J.; Hristovski, K. Titanium nanomaterial removal and release from wastewater treatment plants. *Environ. Sci. Technol.* **2009**, *43* (17), 6757−6763.

(27) Westerhoff, P.; Song, G. X.; Hristovski, K.; Kiser, M. A. Occurrence and removal of titanium at full scale wastewater treatment plants: Implications for TiO$_2$ nanomaterials. *J. Environ. Monit.* **2011**, *13* (5), 1195−1203.

(28) Reed, R. B.; Goodwin, D. G.; Marsh, K. L.; Capracotta, S. S.; Higgins, C. P.; Fairbrother, D. H.; Ranville, J. F. Detection of single walled carbon nanotubes by monitoring embedded metals. *Environ. Sci.: Processes Impacts* **2013**, *15* (1), 204−213.

(29) Schierz, A.; Parks, A. N.; Washburn, K. M.; Chandler, G. T.; Ferguson, P. L. Characterization and quantitative analysis of single-walled carbon nanotubes in the aquatic environment using near-infrared fluorescence spectroscopy. *Environ. Sci. Technol.* **2012**, *46* (22), 12262−12271.

(30) Anke, M.; Seifert, M. *Elements and Their Compounds in the Environment*; Wiley-VCH Verlag GmbH & Co KGaA: Weinheim, 2003; Vol. 2.

(31) Salminen, R. The Geochemical Atlas of Europe Continent-wide distribution patterns of elements. *Geochim Cosmochim Acta* **2007**, *71* (15), A869−A869.

(32) Nagel, G.; Pekarek, W.; Loew, G. *Sanierung Alte Donau*; Magistrat der Stadt Wien: Vienna, 2011; pp 1−114.

(33) Samontha, A.; Shiowatana, J.; Siripinyanond, A. Particle size characterization of titanium dioxide in sunscreen products using sedimentation field-flow fractionation-inductively coupled plasma-mass spectrometry. *Anal Bioanal Chem.* **2011**, *399* (2), 973−978.

(34) Pace, H. E.; Rogers, N. J.; Jarolimek, C.; Coleman, V. A.; Higgins, C. P.; Ranville, J. F. Determining transport efficiency for the purpose of counting and sizing nanoparticles via single particle inductively coupled plasma mass spectrometry. *Anal. Chem.* **2011**, *83* (24), 9361−9369.

(35) Hennebert, P.; Avellan, A.; Yan, J.; Aguerre-Chariol, O. Experimental evidence of colloids and nanoparticles presence from 25 waste leachates. *Waste Manage* **2013**, *33* (9), 1870−81.

(36) Kim, B.; Murayama, M.; Colman, B. P.; Hochella, M. F. Characterization and environmental implications of nano- and larger TiO2 particles in sewage sludge, and soils amended with sewage sludge. *J. Environ. Monit.* **2012**, *14* (4), 1129−1137.

(37) Poiger, T.; Buser, H. R.; Balmer, M. E.; Bergqvist, P. A.; Muller, M. D. Occurrence of UV filter compounds from sunscreens in surface waters: Regional mass balance in two Swiss lakes. *Chemosphere* **2004**, *55* (7), 951−963.

(38) Reed, R. B.; Higgins, C. P.; Westerhoff, P.; Tadjiki, S.; Ranville, J. F. Overcoming challenges in analysis of polydisperse metal-containing nanoparticles by single particle inductively coupled plasma mass spectrometry. *J. Anal Atom Spectrom* **2012**, *27* (7), 1093−1100.

(39) Holbrook, D.; Motabar, D.; Quinones, O.; Stanford, B.; Vanderford, B.; Moss, D. Titanium distribution in swimming pool water is dominated by dissolved species. *Environ. Pollut.* **2013**, *181*, 68−74.

(40) Boncagni, N. T.; Otaegui, J. M.; Warner, E.; Curran, T.; Ren, J. H.; De Cortalezzi, M. M. F. Exchange of TiO$_2$ nanoparticles between streams and streambeds. *Environ. Sci. Technol.* **2009**, *43* (20), 7699−7705.

(41) Plathe, K. L.; von der Kammer, F.; Hassellov, M.; Moore, J.; Murayama, M.; Hofmann, T.; Hochella, M. F. Using FlFFF and aTEM to determine trace metal-nanoparticle associations in riverbed sediment. *Environ. Chem.* **2010**, *7* (1), 82−93.

(42) Fu, X. Z.; Clark, L. A.; Yang, Q.; Anderson, M. A. Enhanced photocatalytic performance of titania-based binary metal oxides: TiO$_2$/SiO$_2$ and TiO$_2$/ZrO$_2$. *Environ. Sci. Technol.* **1996**, *30* (2), 647−653.

(43) Bartov, G.; Deonarine, A.; Johnson, T. M.; Ruhl, L.; Vengosh, A.; Hsu-Kim, H. Environmental impacts of the Tennessee Valley Authority Kingston Coal Ash Spill. 1. Source apportionment using mercury stable isotopes. *Environ. Sci. Technol.* **2013**, *47* (4), 2092−2099.

(44) Von Der Kammer, F.; Ottofuelling, S.; Hofmann, T. Assessment of the physico-chemical behavior of titanium dioxide nanoparticles in aquatic environments using multi-dimensional parameter testing. *Environ. Pollut.* **2010**, *158* (12), 3472−3481.

(45) Chowdhury, I.; Cwiertny, D. M.; Walker, S. L. Combined factors influencing the aggregation and deposition of nano-TiO$_2$ in the presence of humic acid and bacteria. *Environ. Sci. Technol.* **2012**, *46* (13), 6968−6976.

(46) Labille, J.; Feng, J. H.; Botta, C.; Borschneck, D.; Sammut, M.; Cabie, M.; Auffan, M.; Rose, J.; Bottero, J. Y. Aging of TiO$_2$ nanocomposites used in sunscreen. Dispersion and fate of the degradation products in aqueous environment. *Environ. Pollut.* **2010**, *158* (12), 3482−3489.

(47) Auffan, M.; Pedeutour, M.; Rose, J.; Masion, A.; Ziarelli, F.; Borschneck, D.; Chaneac, C.; Botta, C.; Chaurand, P.; Labille, J.; Bottero, J. Y. Structural degradation at the surface of a TiO$_2$-based nanomaterial used in cosmetics. *Environ. Sci. Technol.* **2010**, *44* (7), 2689−2694.

(48) Ma, H. B.; Brennan, A.; Diamond, S. A. Photocatalytic reactive oxygen species production and phototoxicity of titanium dioxide nanoparticles are dependent on the solar ultraviolet radiation spectrum. *Environ. Toxicol. Chem.* **2012**, *31* (9), 2099−2107.

(49) Jassby, D.; Budarz, J. F.; Wiesner, M. Impact of aggregate size and structure on the photocatalytic properties of TiO$_2$ and ZnO Nanoparticles. *Environ. Sci. Technol.* **2012**, *46* (13), 6934−6941.

(50) Bennett, S. W.; Zhou, D. X.; Mielke, R.; Keller, A. A. Photoinduced disaggregation of TiO$_2$ nanoparticles enables trans-dermal penetration. *PLoS One* **2012**, *7*, 11.

5422

dx.doi.org/10.1021/es405596y | *Environ. Sci. Technol.* 2014, 48, 5415−5422