Titanium distribution in swimming pool water is dominated by dissolved species

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ABSTRACT

The increased use of titanium dioxide nanoparticles (nano-TiO_2) in consumer products such as sunscreen has raised concerns about their possible risk to human and environmental health. In this work, we report the occurrence, size fractionation and behavior of titanium (Ti) in a children's swimming pool. Size-fractionated samples were analyzed for Ti using ICP-MS. Total titanium concentrations ([Ti]) in the pool water ranged between 21 μg/L and 60 μg/L and increased throughout the 101-day sampling period while [Ti] in tap water remained relatively constant. The majority of [Ti] was found in the dissolved phase (<1 kDa), with only a minor fraction of total [Ti] being considered either particulate or microparticulate. Simple models suggest that evaporation may account for the observed variation in [Ti], while sunscreen may be a relevant source of particulate and microparticule Ti. Compared to diet, incidental ingestion of nano-Ti from swimming pool water is minimal.

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1. Introduction

Swimming pools are a source of great enjoyment for bathers, and the annual opening of outdoor pools is always a welcomed event for people living in colder climates. Yet swimming pools may receive a significant amount of waste products, including urine, faeces, sweat, skin, and cosmetic, soap, and sunscreen lotion residuals (De Laat et al., 2011). Collectively, these substances cause water quality to deteriorate, thereby requiring constant physical and chemical treatment. Typical treatment processes include of sand filtration and chlorination; water is constantly recirculated between the swimming pool and sand filter to remove particulate material and chlorine is either continuously or periodically dosed to eliminate microbiological activity and to manage the distribution of free chlorine and chloramine species (World Health Organization, 2006). Yet contaminants not efficiently removed by this treatment scheme can accumulate in the swimming pool water (Zwiener et al., 2007), especially if used swimming pool water is not periodically removed and replaced with clean water. While much attention has been given to the behavior of organic compounds (Zwiener et al., 2007), bathers

may also be an inadvertent source of inorganic contamination (Erdinger et al., 1997). For example, titanium (Ti) may be contaminating heavily-used aquatic environments since this element is widely used as a pigment in food (Ti content ranges from 2×10^{-4} μg Ti/mg to 3.5 μg Ti/mg), sunscreens (<0.01 μg Ti/mg to 90 μg Ti/mg), cosmetics and soaps (Weir et al., 2012) and in UV-protected textiles (Windler et al., 2012).

Although Ti (as TiO_2) has a long history of use by the food and cosmetics industry, the nanoparticulate form is becoming increasingly favored (Nohynek et al., 2007). A reduction in TiO_2 size for sunscreens, for example, translates to a less visible and hence more desirable product. This increased use means a higher probability of nano-TiO_2 environmental contamination (Kaegi et al., 2008). Indeed, nano-TiO_2 is expected to have the highest environmental concentrations among common engineered nanomaterials (Gottschalk et al., 2009). Yet swimming pool environments may have other Ti sources and, with a high density of bathers and recirculated water, could be considered as an overly-simplified mesocosm for heavily impacted natural environments. For example, Ti can also be found in atmospheric dust (Amato et al., 2011), rainwater (Poissant et al., 1994), and substances unintentionally released by bathers, such as urine and faeces (Davis and Mirick, 2006) and sweat (Sera et al., 2005). Different Ti sources may contribute to unique Ti size fractions, rendering total Ti

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quantification unable to provide a complete understand of Ti behavior in aquatic systems. The projected increased use of nano-TiO$_2$ suggests the importance of establishing benchmark concentrations in different environments to more accurately gauge the level of environmental contamination.

The objective of this study was to quantify the particulate, microparticulate and dissolved fractions of Ti in a children's recreational swimming pool. Preliminary analysis revealed that pool use (density of bathers) and pool volume are important factors in monitoring Ti behavior, and therefore a children's pool (with a high user density, relatively small volume, and typically high sunscreen use) was chosen as the sample location. Samples were obtained over the entire swimming season (101 days), size fractionated, and quantified for Ti using inductively coupled plasma mass spectrometry (ICP-MS). The experiment was also designed to observe the impact of sand filtration on Ti behavior. UV−vis and fluorescence spectroscopy of the size fractionated water samples was also obtained.

2. Materials and methods

2.1. Sample location and collection description

Water samples from a public children's swimming pool, filter backwash, and the tap water used to fill the pool were collected from a local swimming club between May 21, 2009 and August 30, 2009. The children's pool is a concrete, circular structure with a 3.7 m diameter and a gently sloping bottom that reaches a maximum depth of 0.4 m in the middle. The pool water was continuously pumped through a standard swimming pool sand filter that was periodically (and manually) backwashed. The children's pool had separate plumbing, pumping and filtration systems and therefore water was not mixed with the main pool. Water samples were collected either prior to the pool being opened (morning or "AM" samples) or after the pool was closed (afternoon or "PM" samples) from approximately 5 cm below the water surface. Sample volumes and number of samples collected: AM, whole water: 12 L, $n = 14$; PM, whole water: 12 L, $n = 12$; filter backwash: 300 mL, $n = 11$; tap water: 500 mL, $n = 6$. Eleven of the PM/AM samples were paired, meaning the AM sample was taken the morning following the previous PM sample. In this manner, the impact of the sand filter on Ti behavior could be assessed. Whenever samples could not be processed immediately (within 30 min of collection), they were placed in a refrigerator and processed the following day (within 24 h). pH measurements were made on all samples with an accumet Excel pH/mV meter (Fisher Scientific, Pittsburg, PA). The pH during the sampling period ranged between 7.6 and 8.1.

2.2. Sample preparation − filtration, microparticulate isolation, and preservation

Whole water samples were collected via grab sample and preserved immediately. Filtered samples were produced on-site by pumping the whole water through a 2.0 μm spiral wound filter to remove any particulate material; filter backwash samples were filtered through a 2.0 μm membrane filter (Millipore) at the lab. Filtered samples were then measured for pH, dechlorinated with sodium thiosulfate, and the pH measured again. Sodium thiosulfate addition was necessary to protect long-term membrane integrity but did not appreciably change the pH or the Ti phase fractions (data not shown). A Prep/Scale tangential flow filtration (TFF) system (Millipore) equipped with a 1000 Da (1 kD) nominal weight molecular cutoff membrane cartridge (regenerated nitrocellulose with a filter area of 0.23 m^2) was used to fractionate the filtered pool water into a dissolved phase (<1 kD) and a concentrated microparticulate phase (1 kD−2.0 μm). The cross-flow ratio and concentration factor were kept above 15 and 10, respectively (Dammshauser and Croot, 2012). The membrane system was cleaned and preconditioned before each isolation experiment as described by Gueguen et al. (2002). It is understood that the as-produced concentrated microparticulate fraction includes nanoparticles (1 nm−100 nm, National Science and Technology Council Committee on Technology and Subcommitte on Nanoscale Science, 2011), colloids (Gustafsson and Gschwend, 1997) and microparticles (Inoue et al., 2004); the use of microparticulate is for comprehensive purposes within this work. All whole, size fractionated, field blanks and control samples were preserved (pH < 2) with ultra-pure 14 N HNO$_3$ (Sigma−Aldrich) and stored in PTFE bottles. Leaching experiments to quantify contamination from laboratory materials yielded insignificant increases in [Ti] (<0.2 μg/L), and all field blank samples were <1 μg/L.

2.3. Elemental quantification

Upon receipt at analytical facility, 50 μL of concentrated hydrofluoric (HF) acid was added to each sample and thoroughly mixed. Samples were allowed to condition at least overnight before analysis. Microwave assisted digestion was carried out on select samples, but there was no difference in total [Ti] between the two conditioning methods. An Agilent Technologies (Santa Clara, CA) model 7500c ICP-MS

system in collision mode was used for analysis of Ti. Instrument parameters are detailed in Table 1. A 250 μg/L scandium solution in reagent water was added online via peripump for use as internal standard (ISTD) and to dilute sample matrix. Sc^{45} was used for signal correction of Ti$^{48/49}$. Ti^{48} in samples were quantified against a calibration curve constructed from standards in reagent water (pH < 2, HNO$_3$) with trace HF. Ti^{49} was measured for confirmation as allowed. A calibration curve from 1.0 μg/L to 500 μg/L was used for quantification with a minimum R^2 of 0.995. The method reporting limit (MRL) was set conservatively at 1.0 μg/L.

Instrument stability was confirmed by limiting measured Sc^{45} counts in each sample to ±30% when compared to calibrator counts. Calibration curves were verified against a second-source standard fortified at mid-calibration, with RPD limits at 10%. A sample duplicate, a 1:5 dilution, and a sample fortified with Ti at 50 μg/L−100 μg/L were analyzed at a minimum frequency of every ten samples, and at least once for each sample matrix in a batch. A blank and a continuing calibration verification (CCV) standard were also analyzed at the same frequency. Acceptable recovery for fortified samples and CCVs was set at ±15%. Blank counts were limited to 1/3 of MRL counts. For duplicates, dilutions, and quantification-confirmation results, RPD was set at 15%.

Isobaric interferences from Ca^{48} were anticipated and carefully monitored. When necessary, samples were diluted to meet quality control criteria and MRLs adjusted accordingly. Potential polyatomic interferences from the HNO$_3$ matrix, sulfur and carbon species were eliminated in the collision cell of the ICP-MS using He gas. Ti recoveries (based on mass balance calculations from the separate size fractions) ranged between 88% and 115%.

2.4. Organic matter characterization

Both the fluorescence and absorbance properties were measured for each sample, typically within 72 h of processing, to provide bulk water characterization. Fluorescence excitation-emission matrix (EEM) spectroscopy was modeled with parallel factor analysis (PARAFAC). Further details can be found in the Supporting Information (SI).

2.5. Electron microscopy imaging and microanalysis

Selected filters were imaged and analyzed in an environmental scanning electron microscope (ESEM, Quanta 200, FEI, Inc., Hillsboro, OR). Energy dispersive spectroscopy (EDS, Quantax 200, Bruker, Ewing, NJ) was used to investigate the elemental distribution of specific particles. Imaging was conducted at either 15 or 20 keV while all EDS analysis was conducted at 20 keV.

2.6. Chemicals and standards

Nitric acid (Suprapur, 65%) was purchased from EMD (Gibbstown, NJ). Metals grade hydrofluoric acid (48%) was obtained from Sigma Chemical (St. Louis, MO). Titanium (3%HNO$_3$/trace HF) and zinc (3%HNO$_3$) standards were purchased from AbsoluteGrade (Hamden, CT) and also from Ricca Chemical Company (Arlington, TX). Scandium standard at 1000 mg/L (3% HNO$_3$) was purchased from Ricca Chemical Company (Arlington, TX).

3. Results

3.1. Ti quantification in whole water samples

Titanium concentrations ([Ti]) in the swimming pool samples ranged between 21 μg/L and 60 μg/L (Fig. 1). The whole pool water

Table 1
Analytical parameters for Ti determination.

ICP-MS parameters			
RF power			1430w
Carrier gas			1.12 mL/min
Collision mode			He, 0.5 mL/min
Tuning masses (m/z):			7, 45, 89, 205

Acquisition			
Mass	Dwell time (ms)	Points/mass	Repetitions
Ti^{48}	150	3	5
Ti^{49}	300	3	5
Sc^{45} (ISTD)	150	3	5

Sample introduction			
Nebulizer pump speed			1.0 rps
Sample flow			~0.4 mL/min
ISTD flow			~0.4 mL/min