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Titanium Dioxide Nanoparticles in Food and Personal Care Products

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Abstract

Titanium dioxide is a common additive in many food, personal care, and other consumer products used by people, which after use can enter the sewage system, and subsequently enter the environment as treated effluent discharged to surface waters or biosolids applied to agricultural land, incinerated wastes, or landfill solids. This study quantifies the amount of titanium in common food products, derives estimates of human exposure to dietary (nano-) TiO_2, and discusses the impact of the nanoscale fraction of TiO_2 entering the environment. The foods with the highest content of TiO_2 included candies, sweets and chewing gums. Among personal care products, toothpastes and select sunscreens contained 1% to >10% titanium by weight. While some other crèmes contained titanium, despite being colored white, most shampoos, deodorants, and shaving creams contained the lowest levels of titanium (<0.01 μg/mg). For several high-consumption pharmaceuticals, the titanium content ranged from below the instrument detection limit (0.0001 μg Ti/mg) to a high of 0.014 μg Ti/mg. Electron microscopy and stability testing of food-grade TiO_2 (E171) suggests that approximately 36% of the particles are less than 100 nm in at least one dimension and that it readily disperses in water as fairly stable colloids. However, filtration of water solubilized consumer products and personal care products indicated that less than 5% of the titanium was able to pass through 0.45 or 0.7 μm pores. Two white paints contained 110 μg Ti/mg while three sealants (i.e., prime coat paint) contained less titanium (25 to 40 μg Ti/mg). This research showed that while many white-colored products contained titanium, it was not a prerequisite. Although several of these product classes contained low amounts of titanium, their widespread use and disposal down the drain and eventually to WWTPs deserves attention. A Monte Carlo human exposure analysis to TiO_2 through foods identified children as having the highest exposures because TiO_2 content of sweets is higher than other food products, and that a typical exposure for a US adult may be on the order of 1 mg Ti per kilogram body weight per day. Thus, because of the millions of tons of titanium based white pigment used annually, testing should focus on food-grade TiO_2 (E171) rather than that adopted in many environmental health and safety tests (i.e., P25), which is used in much lower amounts in products less likely to enter the environment (e.g., catalyst supports, photocatalytic coatings).

Keywords

nanotechnology; nanomaterial; TiO_2; exposure; fate; transport; wastewater; P25; E171

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Introduction

As a bulk material, titanium dioxide (TiO_2) is primarily used as a pigment because of its brightness, high refractive index, and resistance to discoloration. The global production of TiO_2 for all uses is in the millions of tons per year. Nearly 70% of all TiO_2 produced is used as a pigment in paints, but it is also used as a pigment in glazes, enamels, plastics, paper, fibers, foods, pharmaceuticals, cosmetics, and toothpastes [1]. Other TiO_2 uses include antimicrobial applications, catalysts for air and water purification, medical applications, and energy storage. Recently more attention has been given to the use of TiO_2 as a nanomaterial. In 2005 the global production of nanoscale TiO_2 was estimated to be 2000 metric tons worth $70 million [2]; approximately 1300 metric tons were used in personal care products (PCPs) such as topical sunscreens and cosmetics. By 2010 the production had increased to 5000 metric tons, and it is expected to continue to increase until at least 2025 with greater reliance upon nano-size TiO_2 [3]. Consequentially, many sources of nanoscale TiO_2 could result in human exposure and entrance of this material into the environment (air, water, or soil compartments).

TiO_2-containing materials are produced in a range of primary particle sizes. Many applications of TiO_2 would benefit from smaller primary particle sizes, and the percentage of TiO_2 that is produced in or near the nano range is expected to increase exponentially [4, 5]. TiO_2 nanoparticles are generally synthesized with a crystalline structure (anatase, rutile, or brookite, each of which has unique properties) [6]. The most common procedure for synthesis of TiO_2 nanoparticles utilizes the hydrolysis of titanium (Ti) salts in an acidic solution [7]. Use of chemical vapor condensation or nucleation from sol-gel can control the structure, size, and shape of the TiO_2 nanoparticles [8, 9]. To increase photostability and prevent aggregation, TiO_2 nanomaterials (particles, tubes, wires, etc.) are commonly coated with aluminum, silicon, or polymers [10, 11].

TiO_2 nanomaterials in foods, consumer products, and household products are discharged as feces/urine, washed off of surfaces, or disposed of to sewage that enters wastewater treatment plants (WWTPs). Although WWTPs are capable of removing the majority of nano-scale and larger-sized TiO_2 from influent sewage, TiO_2 particles measuring between 4 and 30 nm were still found in the treated effluent [2, 12, 13]. These nanomaterials are then released to surface waters, where they can interact with living organisms. One study monitoring TiO_2 nanomaterials found the highest concentrations in river water to be directly downstream of a WWTP [14]. TiO_2 nanomaterials removed from sewage through association with bacteria may still end up in the environment if the biomass is land applied.

Although the release of TiO_2 nanomaterials to the environment has been shown qualitatively, quantification of how much is released is difficult. The same is true for the human exposure, as estimated uptake rates of different types of nanoparticles range from 0 to 8.5% depending on type, size, and shape of the nanoparticles [15, 16]. Because it is impossible to determine all sources or measure the amount of TiO_2 nanomaterials, emissions are often modeled to better predict the impact of TiO_2 nanomaterials on the environment [17].

Toxicity studies mainly report a risk from nanoparticular TiO_2 due to inhalation (inflammation and possible link to asthma), but titania has also been linked to Crohn's disease from gastrointestinal intake and it has been classified as possibly carcinogen [18-21]. However, a risk assessment has not been published yet and care has to be taken when comparing exposure to effect. Not only modifications have been reported to have diverging toxicological properties (anatase is 100 times more toxic than rutile in the nanoparticular form), but also coatings, size and shape modify the toxicity of nanoparticles and only a small number of them have been tested [20, 22]. Once in the environment, even less is known about how TiO_2 nanomaterials affect organisms, although nanosized TiO_2 has been shown to inhibit growth of algae and bioaccumulate in *Daphnia magna* [23, 24]. However, several studies have indicated that TiO_2 tends to be less hazardous to organisms than other nanomaterials such as multi-wall carbon nanotubes, nano-cerium oxide, and nano-zinc oxide [3, 23]. Previously, primary particle size was generally accepted as a large factor in toxicity, with smaller particles tending to be more toxic. However, recent studies have shown that particle size is only a single (and perhaps minor) factor influencing the toxicity of nanoparticles [24]. Risk assessment of certain nanomaterials is still quite difficult because nanotoxicology studies rarely have enough reliable information on the physicochemical characteristics of the nanoparticles tested [25, 26].

Many fate and transport as well as toxicity studies have used a readily available TiO_2 nanomaterial (Evonik Degusa P25) because the primary crystals are <50 nm in size and uncoated. P25 is advertised as “titanium dioxide without pigment properties”. Based upon information on the manufacturers website P25 is used primarily as a photocatalyst, catalyst carrier, and heat stabilizer for silicon rubber. This material is agglomerated in the dry powder state and readily aggregates to several hundred nanometers in water [27, 28]. However, usage of TiO_2 in the food, beverage, and paint markets dwarfs the usage of P25. For example, food-grade TiO_2 (referred to as E171) is purchased by the ton and is available as synthetic forms of anatase, rutile, and others. Only one study reports the titanium content of a few commercial products [29]; we know very little about size or surface properties E171 forms of these TiO_2 in comparison with the vast amount of data on P25 even though E171 and other commercially used whiteners represent the majority of TiO_2-containing materials that enter the ecosystem today.

This paper aims to begin filling the large knowledge gaps that exist regarding commonly used sources of TiO_2 materials. We obtained a broad spectrum of commercial products that either listed titanium dioxide on the label or had a “white” color and quantified the titanium content. Selected products were further characterized by electron microscopy. Using this new and already existing TiO_2 data, a human exposure analysis was conducted that indicates children may be disproportionately exposed to higher levels of all sizes of TiO_2. Finally, characteristics of E171 were compared against those of the titanium observed in food products and against those of P25 in an attempt to argue that greater efforts to elucidate fate and transport are needed for materials containing E171.

Methods

Consumer products (food, PCPs, paints, adhesives) were purchased in March 2011 from stores in Arizona (USA). Attempts were made to purchase at least two brands of each product, usually a name brand and a separate generic brand. Samples were transported to the laboratory, stored in a clean and dry location, and analyzed prior to the expiration dates listed on the product labels. Information about the products, including whether or not titanium-bearing materials were mentioned on the label, is provided in supplemental information.

Samples of synthetic TiO_2 were also obtained from commercial suppliers. P25 that consists of a 81%/19% anatase/rutile TiO_2 crystal structure mixture with an average primary particle size of 24 nm was obtained from Evonik Degussa Corporation [30]. A stock solution was prepared by adding the desired weight of P25 to nanopure water and sonicating for 30 minutes in a Bronson 2510 bath sonicator at a 40 kHz frequency. A serial dilution of the stock was carried out to create various concentrations for the digestion evaluation.

E171 is a European Union designation for a white food color additive that is known elsewhere by other designations (CI 77891, Pigment White 6). For this research, an E171 sample was obtained from a large commercial supplier in Italy (Fiorio Colori Spa).

Digestion of Samples

Anatase and rutile are essentially insoluble at ambient pH levels. Therefore, we focus on solid phases only and concentrations were determined after chemical digestion. Previous reports on titanium content in food used nitric and sulfuric acid digestion followed by ICP-OES [29]. Although this digestion method may provide a good recovery of Ti, it was not optimal for ICP-MS analysis because the sulfur oxide species (S-O) has a mass to charge ratio (m/z) of 48 that interferes with the primary Ti isotope, which also has m/z = 48. Thus, using sulfuric acid as a digestion reagent would have made quantification of trace concentrations of Ti impossible by ICP-MS. Packer et al. found that a combination of nitric acid, hydrogen peroxide, and hydrofluoric acid was able to digest Ti in ceramic materials [31]. Nitric acid (70%), hydrogen peroxide (30%), and hydrofluoric acid (50%), all ultrapure acids purchased from JT Baker, were evaluated as reagents for TiO_2 digestion using both hotplate and microwave methods. Because microwave digestion had higher reproducibility, only this data is presented. As-received products were weighed and added to a 55-mL microwave digestion vessel along with 8 mL of nitric acid and 2 mL of hydrofluoric acid. The vessels were digested using a Microwave Accelerated Reaction System (MARS) Express instrument (1200 W, ramp up to 150°C over 15 minutes, ramp up to 180°C over 15 minutes, hold at 180°C for 20 minutes). After cooling, the vessel was rinsed into a Teflon beaker >3 times using approximately 20 mL of a 2% nitric acid solution. Then, 2 mL of hydrogen peroxide was added to each beaker to digest any remaining organics. The beaker was heated on a hot plate at 180°C until between 0.1 and 0.5 mL of solution remained. The solution was evaporated and then diluted to ensure that the maximum concentration of HF in the final sample was 2% to prevent damage to the ICP-MS. The beakers were removed from the hot plate and allowed to cool before being rinsed >3 times with a 2% nitric acid solution into a 25 mL volumetric flask before prior to storage for analysis. In blank samples digested 12 times on different days, a minimum detection limit of 1 μg titanium from TiO_2 (P25) was determined. Spike recovery tests using 50 mg each of P25 and E171 in separate samples of a low titanium-containing food product (500 mg chocolate) were digested and analyzed in triplicate. Spike recoveries were 81 ± 2.7% and 87 ± 2.3% for P25 and E171, respectively, based upon the weighed mass of the TiO_2 and the ratio of titanium to oxygen.

Size Discrimination of TiO_2 in Products—To determine how much TiO_2 is in the nanosize range, a separation method had to be created to separate smaller TiO_2 particles from larger TiO_2 particles and organic materials. In this method, 500 mg of a food sample was added to a beaker. The organic material from the food was broken down by adding 10 mL of hydrogen peroxide and 0.5 mL of HNO_3 and then heating on a hot plate at 110°C. Peroxide and HNO_3 did not change the size of P25 or E171, but they largely digested the organic matrices within which the TiO_2 was embedded. The exceptions were paint samples, which could not be completely digested by this approach. When the volume of liquid remaining in the sample was less than 1 mL, the beakers were removed from the hot plate and allowed to cool. The beaker sides and bottom were then rinsed with approximately 20 mL of nanopure water. The sample was filtered with a 0.45-μm nylon filter and added to a microwave vessel. To determine the total TiO_2 that was able to pass the 0.45-μm filter, the sample was then digested using the microwave digestion with HF and HNO_3. A 0.45-μm filter was chosen because preliminary tests evaluating 0.45-μm filters and GF/F filters (data not shown) found that a measurable amount of Ti was able to pass both filters. The pH of the samples was determined before filtration to ensure that the nylon filter would not be damaged during filtration.

Other Analytical Methods—Samples for scanning electron microscopy (SEM; Nova NanoSEM 230 FEI) were prepared by crushing samples of P25 or E171 with a mortar and pestle before adding acetone, placing a drop of the mixture on a metallic stub, and evaporating the acetone under a heat lamp. Dynamic light scattering (DLS) measurements were made using a Malvern Zetasizer NanoSeries Instrument (Nano S90).

Human exposure modeling—To demonstrate one potential use of the analytical data generated in this study, two realistic human dietary exposure scenarios were created using statistical consumer intake data from the National Diet and Nutrition Survey (NDNS) in the UK for different food categories together with point values for measured TiO_2 concentrations in food for the UK (Lomer et al., 2000) and the US (this paper). The aggregate exposure distribution was calculated probabilistically by combining the single exposures via Monte Carlo simulations (100,000 steps). This procedure mimics 100,000 individuals of a specified age that eat several foods (with fixed TiO_2-concentrations) based on the odds ratio indicated by the intake distribution from the nutrition survey. Detailed modeling assumptions are summarized in Supplemental Information.

Results

Composition and Properties of Food-Grade Titanium Dioxide

Figure 1 contrasts a sample of the food-grade TiO_2 identified as E171 against the TiO_2 material more commonly used in studies of environmental fate and transport or human and ecosystem toxicity (namely P25). The E171 sample has a mean particle size of 110 nm based upon electron microscopy analysis but a very broad size distribution (30 to 400 nm based upon SEM with at least 36% of the particles less than 100 nm in at least one dimension based upon TEM analysis; see Figure SI.1), whereas the P25 particles are primarily on the order of 30 to 40 nm. E171 products can be purchased as rutile or anatase, whereas P25 is a 15/85 mixture of rutile/anatase. It should be noted that we examine a single source of E171, and because many suppliers exist a more extensive study should be undertaken into differences in physical and chemical properties of E171.

To further characterize E171 and P25, they were analyzed by DLS in DI water in the presence of salts or bovine serum albumin (BSA) because BSA has been used as a dispersant for P25. After mild sonication (water bath for 10 minutes) in the presence of 0.75% BSA, E171 had a mean diameter of 150 nm (PDI = 0.39) with a primary peak at 255 nm but a shoulder at 37 nm. Under the same conditions P25 exhibited a mean diameter of 2.5 μm; a smaller mean diameter was obtained after prolonged ultrasonication (30 minutes in a Bronson 2510 bath sonicator at a 40 kHz frequency). Many others have reported that the mean aggregated particle diameter of P25 is approximately an order of magnitude greater in size than the primary particles [32, 33].

A matrix of experiments using E171 (12.5 mg/L) was conducted in 2 mM $NaHCO_3$ with and without dissolved organic carbon (4 mg/L Suwannee River fulvic acid) and variable NaCl concentrations (0, 50, 500, 5000 mg/L). Samples were bath sonicated for 5 minutes in 50-mL centrifuge vials and then set vertically in a holder for 2 hours with aliquots periodically removed for DLS analysis. For E171 little variation in mean diameter occurred for any of the solution chemistries; the mean size remained between 360 and 390 nm (PDI ~ 0.2). Likewise, over time (0, 5, 10, 15, 30, 45, 75, 120 minutes) the mean diameter in solution did not change, indicating that E171 was quite stable in these solutions. In contrast with E171, parallel experiments with P25 showed rapid and extensive aggregation in the presence of salts. Thus, food-grade TiO_2 (E171) appears to readily form moderately stable suspensions, somewhat as expected because during food preparation E171 is regularly used in liquid formulations.

Titanium Content of Foods

A wide range of white foods was selected from grocery stores; some of the foods were labeled as containing TiO_2, and others were not but the primary product or surface coatings (e.g., icings) had a white color. All 89 foods were digested and their Ti concentration determined. Sixteen of the foods were digested in triplicate. The agreement among the triplicates was less than 30%. The blank average was 0.579 μg of Ti. Dickinson's Coconut Curd had the highest concentration of Ti in any food at 3.59 μg/mg. The rest of the Ti concentrations spanned five orders of magnitude, from 0.00077 to 210 μg Ti/mg product (Table SI.1). Some foods had levels below the ICP-MS detection limit. The 20 highest titanium concentrations in the foods are shown in Figure 2 (others are shown in Figure SI.2).

To compare the titanium content of different foods, the data were normalized to the titanium content per serving (Table SI.1). The titanium content of the products was as high as 100 mg Ti per serving for powdered donuts, and many products with the highest titanium contents could be characterized as sweets or candies, including chewing gums, chocolate, and products with white icing or powdered sugar toppings. Many products contained 0.01 to 1 mg Ti per serving. Only a limited number of the products listed titanium materials on the packaging. This type of content data therefore is useful for human exposure analysis and demonstrates the widespread use of titanium-bearing materials in foods.

The chewing gum products tested consistently had some of the highest concentrations of Ti of any products, and all listed TiO_2 as an ingredient. All five gum products analyzed are in the top 20 products in terms of Ti concentration and had greater than 0.12 μg Ti/mg. Of those five gum products, the cinnamon gum that had a red coating had the lowest and the gum products with white coatings the highest Ti content. Importantly, all of the gum products had a hard shell coating the gum-based center. For two of the gum products, the titanium content of the outer shell versus the inner gum was determined by first dissolving the outer shell and then removing the residual gum base. Most of the titanium (>90%) was associated with the outer shell (Figure SI.3). The candy products with hard outer shells (M&Ms, M&Ms with peanuts, and Good and Plenty) all are in the top 10 products in terms of Ti concentration. If the gums and candies are combined into a more general hard shell candy category, 8 of the 20 products with the highest Ti concentrations are in this category. A random gum product sample was further investigated to visualize the form of titanium present. A sample was placed in DI water and mixed on a vortex mixer; the outer white shell rapidly dissolved from the inner gum portion. The latter was removed and the whitish-colored supernatant diluted and then filtered for SEM analysis (Figure 1; Figure SI.4). Small aggregates of titanium oxide solids were present with size distributions of primary particles similar to that in the E171 sample (Figure 1). The mean size of the aggregates was 100 to 300 nm.

Another group of products that is well represented in the top 20 foods with the highest Ti concentrations is powder products mixed into foods. For example, two drink mixes were in the top 20 products with the highest Ti concentration. Two pudding samples in the top 20 too. However, other powdered milk-based products (Carnation Instant Breakfast and Nestle Coffee Mate) had much lower concentrations (33rd and 61st highest, respectively) with less than 0.015 μg Ti/mg for each product. Titanium-based materials may have been added to these powders as anti-caking ingredients.

Chocolate products that did not have a hard outer shell had much lower Ti concentrations compared to those with a shell. Hershey's Special Dark chocolate bar had the highest Ti concentration for shell-less chocolate products at 0.0050 μg Ti/mg. In comparison, M&Ms had a Ti concentration of 1.25 μg Ti/mg.

Generally, a large difference between generic and name brand products was not observed. The largest was between a generic marshmallow (Albertsons Mini Marshmallows) at 0.307 μg Ti/mg and a name-brand one (Kraft Jet Puffed Marshmallow) at 0.00255 μg Ti/mg. However, other comparison products were ranked nearly identically based upon their titanium content. For instance, Hershey's Chocolate Syrup and Albertsons Chocolate Syrup were measured at 0.0026 and 0.0025 μg Ti/mg, respectively. Likewise, Nestle Coffee Mate and Albertsons Coffee Creamer measured 0.040 and 0.036 μg Ti/mg, respectively.

Several dairy products (e.g., milk, cheese, yogurt) were studied. Because of their white color and based upon internet readings it was conceivable that TiO_2 may be added to some low-fat dairy products to enhance color and texture. Low-fat milk contained 0.26 μg Ti/mL, which was comparable with non-dairy substitutes including soy- and rice-based drinks (0.10 to 0.15 μg Ti/mL). This equates to 0.02 to 0.06 mg Ti per serving (240 mL), compared with 0.06 to 0.08 mg Ti per serving for white-colored non-dairy creamers. Although not a dairy product, mayonnaise also represents a white-colored emulsion, so it was tested and ranked with the dairy products. White dairy products such as cheeses, mayonnaise, and whipped cream routinely had low concentrations of Ti; 10 of the 12 products with the lowest Ti concentrations were dairy products. The yogurts tested also had low Ti content. The highest ranked of any dairy product was a cheese (Albertsons American Single) at 37th with 0.0069 μg Ti/mg.

The 12 food products with the highest concentrations of Ti were filtered to determine what percentage of the total Ti was small enough to pass a 0.45-μm filter (Figure SI.5). A gum product had the highest percentage at 3.9%. For four of the samples, less than 0.5% passed through the filter. More Ti passed through a GF/F filter (0.7 μm), which indicated that our sample preparation method probably did not completely degrade the food products. Additional research better simulating stomach digestion fluids may shed additional light on the ultimate size fractions of Ti in digested food. However, these results clearly show the potential for release of small-scale titanium from these foods.

Modeling of human exposure to TiO_2 in food

Figure 3 shows the simulated exposure to TiO_2 for the US population, with an average of 1-2 mg TiO_2/kg_{bw}/day for children under the age of 10 years and approximately 0.2–0.7 mg TiO_2/kg_{bw}/day for the other consumer age groups. Figure SI.6 shows the realistic exposure to TiO_2 for the UK population, with an average of 2-3 mg TiO_2/kg_{bw}/day for children under the age of 10 years and approximately 1 mg TiO_2/kg_{bw}/day for the other consumer age groups. Exposure to TiO_2 depends largely on dietary habits. In special cases the exposure is several hundreds of milligrams per day. Because our measurements showed that roughly 36% of the particles in E171 may be in the nano range (less than 100 nm in at least one dimension), a large exposure to nano-TiO_2 can be presumed.

Titanium Content in Personal Care Products

Previous SEM analysis of titanium in toothpaste indicated the presence of TiO_2 aggregates, which were similar to the aggregates present in biosolids at WWTPs [12]. Others have characterized the size distribution of titanium in a few sunscreens and face creams [34] [35, 36]. Here we quantify the amount of titanium in several toothpastes and 24 additional PCPs (3 deodorants, 1 lip balm, 6 shampoos, 1 shaving cream, 13 sunscreens) that were believed to have a probability of entering sewage (Figure 4). For eight samples of toothpaste, the titanium content varied from 0.7 to 5.6 μg/mg, or from <0.1% to nearly 0.5% by weight of the product, which is within the ranges reported on the products. Analysis of several sunscreens indicated that some contained very high amounts of titanium (14 to 90 μg/mg). The three sunscreens with TiO_2 listed as an ingredient had the highest concentrations of any

PCPs, whereas others that were not labeled as containing titanium dioxide contained less than 0.01 μg/mg, and contained instead an organic sunscreen agent (e.g., benzonates).

A recent survey showed that one-third of people questioned observe the advice of health experts, saying they use sunscreen regularly. It is estimated that 33 million Americans use sunscreen every day and another 177 million use it occasionally [37]. The FDA regulates sunscreens and cosmetics as over-the-counter drugs. TiO_2 nanomaterials are not considered to be a new additive, but rather a variation in the particle size of an existing drug additive [38]. The only FDA-stipulated limitation for sunscreens is that the TiO_2 concentration be less than 25%. Most have a lower concentration, between 2% and 15% [37]. With the wide prevalence of sunscreen use and the lack of a distinction between TiO_2 nanomaterials and larger-sized particles, the general public is being exposed to nanomaterials of which they are largely ignorant.

Two face creams contained titanium dioxide at intermediate product concentration levels. White-colored shampoos, deodorants, and shaving creams contained the lowest levels of titanium (<0.01 μg/mg). Additionally, two low-dose aspirin products (81-mg aspirin dose) were analyzed; both were advertised as being "safety coated." The generic brand contained 10.0 ± 0.63 μg Ti/mg, compared to only 0.017 ± 0.005 μg Ti/mg in the name-brand aspirin product. For several high-consumption pharmaceuticals, the titanium content ranged from below the instrument detection limit (0.0001 μg Ti/mg) to a high of 0.014 μg Ti/mg [39]. Issues with TiO_2 pharmaceutical coatings have moved many manufacturers toward the use of polymeric coatings instead [40].

Although several of these product classes contained low amounts of titanium, their widespread use and disposal down the drain and eventually to WWTPs deserves attention. For example, one study showed that the aging of sunscreen in natural waters caused 30% of the total TiO_2 nanomaterials to be released. Once released, they created a stable dispersion of sub-micron aggregates [41]. For the PCPs with the highest concentration of Ti, we approximated size distributions using H_2O_2/nitric acid degradation of organics followed by filtration (Figure SI.7). For the Neutrogena Pure and Free Baby sunscreen, 6.3% of the total Ti passed through the filter, the highest of any sample. Less than 1% of the total Ti in the toothpastes passed through the filter.

Titanium Content of Paints and Adhesives

Paints contain white pigments, and application on exterior facades can result in titanium dioxide in rainfall runoff [42]. In addition, a small fraction of paint products will enter the sewage system as users wash brushes and dispose of leftover paint. Rather than conduct a comprehensive analysis of many paint products, we selected two primary white paints, three primers, and two base paints to which pigments are added. Colored paints were also analyzed for contrast (Figure SI.8). The two white paints (name brand and generic) contained the highest titanium content (~110 μg Ti/mg). The three sealants (i.e., prime coat paint) contained less titanium (25 to 40 μg Ti/mg). The two base paints, to which tinting is added to yield colors, were white colored but had significantly lower titanium levels (0.03 to 0.22 μgTi/mg) Only one common all-purpose white glue was tested, which contained 0.03 ± 0.007 μgTi/mg. Other non-white adhesives were tested but did not contain detectable amounts of titanium. Thus, while many paints contain white titanium dioxide based pigments, color alone does not indicate the presence of titanium dioxide based pigments (e.g., white adhesives) and other white coloring agents can be used (e.g., calcium carbonate, barium sulfate, antimony white, zinc white, talc, chalk).

DISCUSSION

Exposure Assessments

More than a decade ago, the titanium content in several UK food products was determined [29]. Many of the same food classes identified there (candies, salad dressing, creamers, icing, and marshmallows) were shown to contain higher levels of TiO_2 in our larger survey of products, which also had a lower defined detection limit. Lomer et al. reported 0.045 to 225 mg TiO_2 per serving for products with detectable amounts of titanium [29]. For our food products, concentrations were likewise converted to mass Ti per serving (Figure SI.9) and to mass TiO_2 per serving assuming that all the titanium is present as titanium dioxide (Figure SI.10). For our food products, the samples ranged from 0.0013 to 340 mg TiO_2 per serving. Our analysis for the USA and UK exposures (Figure 3 and SI.6) showed difference of approximately a factor of two, but ranged between 0.2 and 3 μg TiO_2/kg_{bw}/day. The large standard deviations of the UK and US exposure confirm that habits are important for the exposure of different consumer groups and that a small variation in habits can change the exposure noticeably. The variation between males and females in the US is fairly small, but the variation between children and adults is significant. A child potentially consumes 2-4 times as much TiO_2 per kg_{bw} as an adult. For children, compared to adults, the consumption of sweet products is relatively large, both for the amount consumed and the number of consumers. As consumption of sweets falls with age, products such as dairy-based desserts and salad dressing become more important. As differences exist in concentrations found in UK products and US products (this study), the model output for the different consumers varies. Consequently, the intake of TiO_2 in foods will impact part of the nano-scale TiO_2 loading to WWTPs. Assuming an average adult weight of 80 kg, intake of 1 mg TiO_2/kg_{bw}/day and per capita US contribution towards sewage of 280 L/day, then ~0.3 mg TiO_2/person/day could represent the daily loading rate to sewage systems. Assuming 36% of the food grade TiO_2 is below 100 nm in at least one dimension, then this decreases to roughly 0.1 mg TiO_2/person/day of nano-scale TiO_2.

Clearly, routes of exposure other than ingestion of food-grade TiO_2 but were beyond the scope of this current research. However, our findings provide titanium content of sunscreens (Figure 4) which could be used to assess dermal exposures. Workplace inhalation exposures to E171 or P25 would probably require field measurements. We focused on ingestion and exposure of food grade TiO_2 not only as a potential human hazard, but because such values become informative in predicting one important flux of nanomaterials into sewage systems.

Selection of Titanium Dioxide Models for Environmental Studies

This research highlights and quantifies the importance of food and product color additives that are widely used in society today. Many of these products do not carry the “nano” label, but based upon product information from suppliers and microscopy analysis, they contain titanium dioxide nanoparticles. Not every product in our study was verified to contain titanium dioxide by microscopy techniques. Titanium can also be present in clays that are widely used in plastics and even in fillers in some foods and paints. Therefore, the titanium data reported here represent an “upper bound” for the titanium present as TiO_2. Furthermore, since the white pigments should absorb light at wavelengths longer than 350 nm only a fraction of the primary particle sizes may be < 100 nm. Again, we observed in one food-grade TiO_2 sample that roughly 36% of the TiO_2 particles in E171 were less than 100 nm in at least one dimension. Therefore, our data would also represent an upper limit on the nano-scale TiO_2 materials with potential to be released into sewage or other wastestreams.

A huge market exists for TiO_2 as a food and other color additive. Many of the companies selling TiO_2 as a white food additive (e.g., E171) and for other coloring applications are located in China and can be accessed through supplier websites. For example, a search on one such website (www.alibaba.com) yields more than 25 suppliers of E171 for which the smallest purchase volumes are on the order of 500 kg to 20 metric tons. P25 is used primarily as a photocatalyst, catalyst carrier, and heat stabilizer for silicon rubber, and P25 is less likely to enter sewage treatment systems, and subsequently the environment, when compared with E171. P25 has been used in more than 100 reports on titanium dioxide environmental fate, toxicity, and human inhalation, likely because it contains primary particles <100 nm, possesses a unique property (photocatalysis), and has been readily available. We were unable to ascertain the annual production of P25, but it is likely far less than the one to two million tons of pigment TiO_2. If only 0.1% of the TiO_2 in these pigments (e.g., E171) is in the nanoscale range of <100 nm, that would be of the same magnitude as all the nano-TiO_2 produced in 2005. The actual percentage of the pigment TiO_2 that is actually <100 nm may be much more than 0.1%, and therefore pigment TiO_2 represents an enormous source of nanoscale TiO_2 entering sewage systems, rivers, landfills, and other sensitive environmental compartments. It also appears that through surface modifications E171 is more readily dispersed into water than P25, which potentially influences TiO_2 fate, transport, and toxicity. Therefore, more environmental ecotoxicology and fate studies should use the fraction of smaller sized TiO_2 in pigments because exposure to these materials is likely to be much higher and more representative than exposure to P25.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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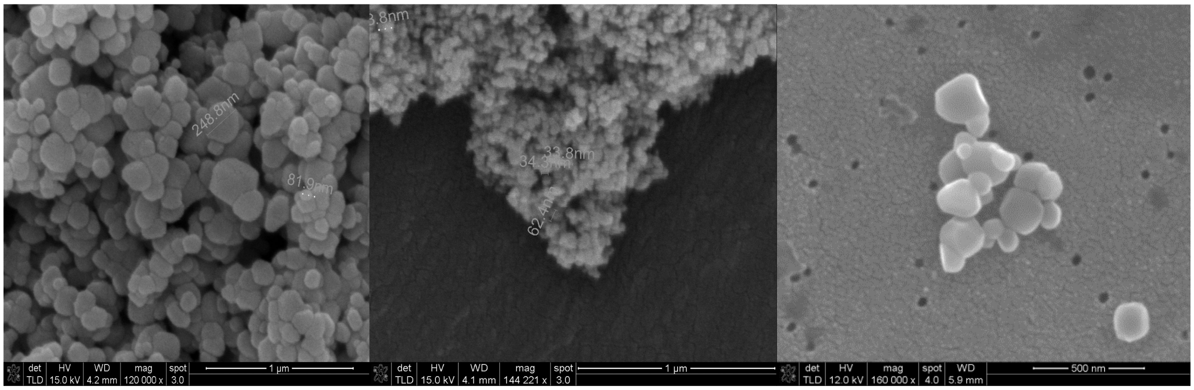

Figure 1.

SEM images of E171 (left) and P25 (middle) TiO_2. The sample on the right is from the dissolved hard coating on a chewing gum (Trident White) after it was placed in water and the supernatant filtered onto a 20-nm filter; samples were confirmed by EDX to be titanium and oxygen.

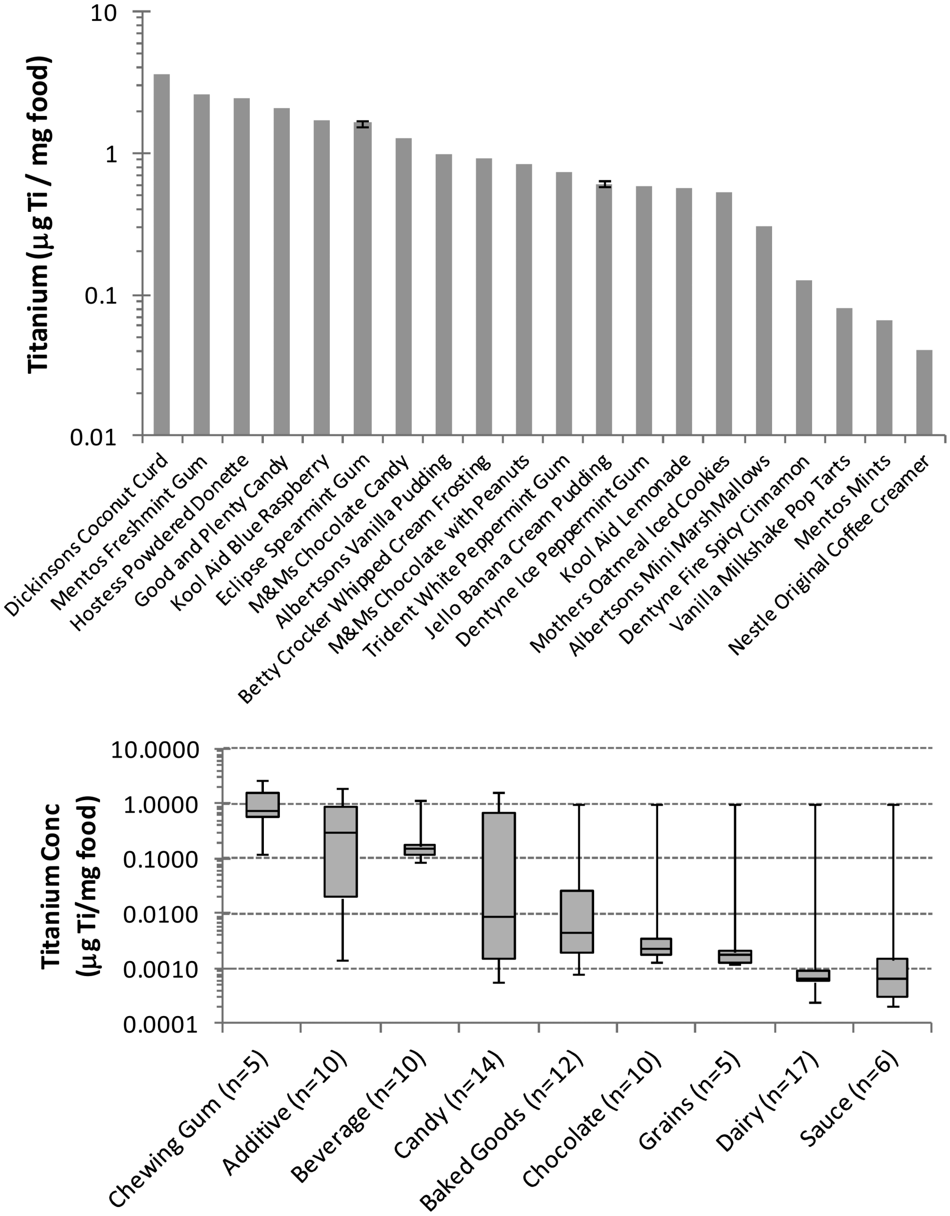

Figure 2.

Normalized Ti concentration in food products. For the top 20 products (upper), error bars represent the standard deviation from samples digested in triplicate. The bar-and-whisker diagram (lower) for all products shows the minimum and maximum values as whiskers and the lower-quartile, median, and upper-quartile as the box.

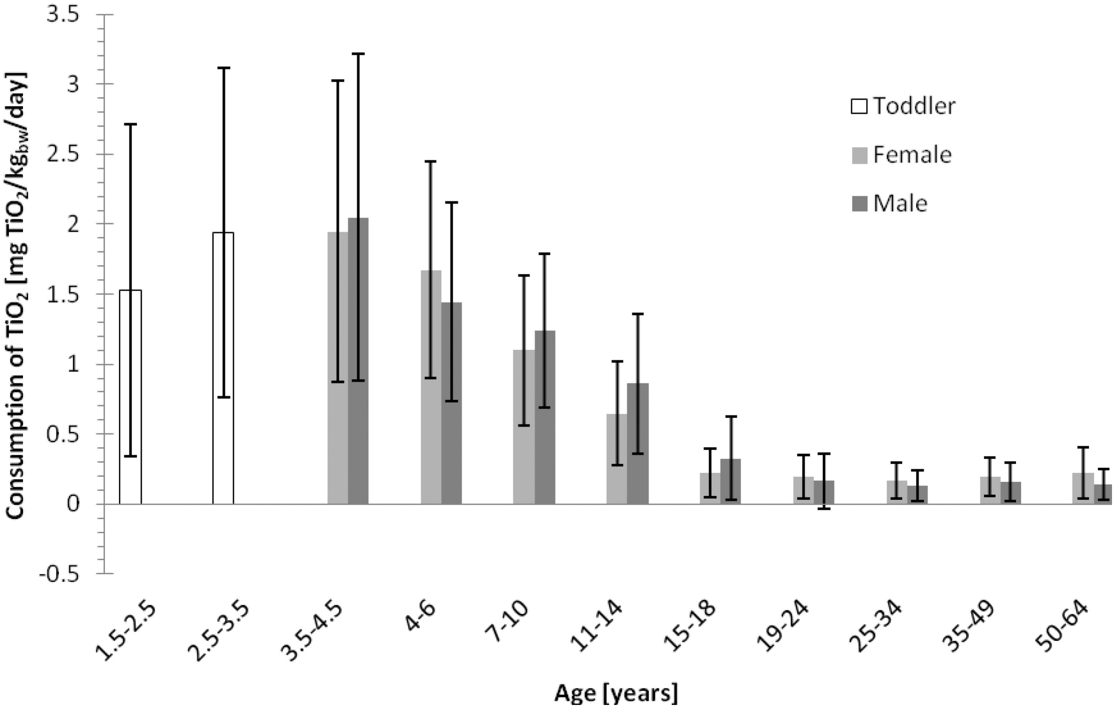

Figure 3.

Histogram of the average daily exposure to TiO_2 for the US population (Monte Carlo simulation). Error bars represent the upper and lower boundary scenarios.

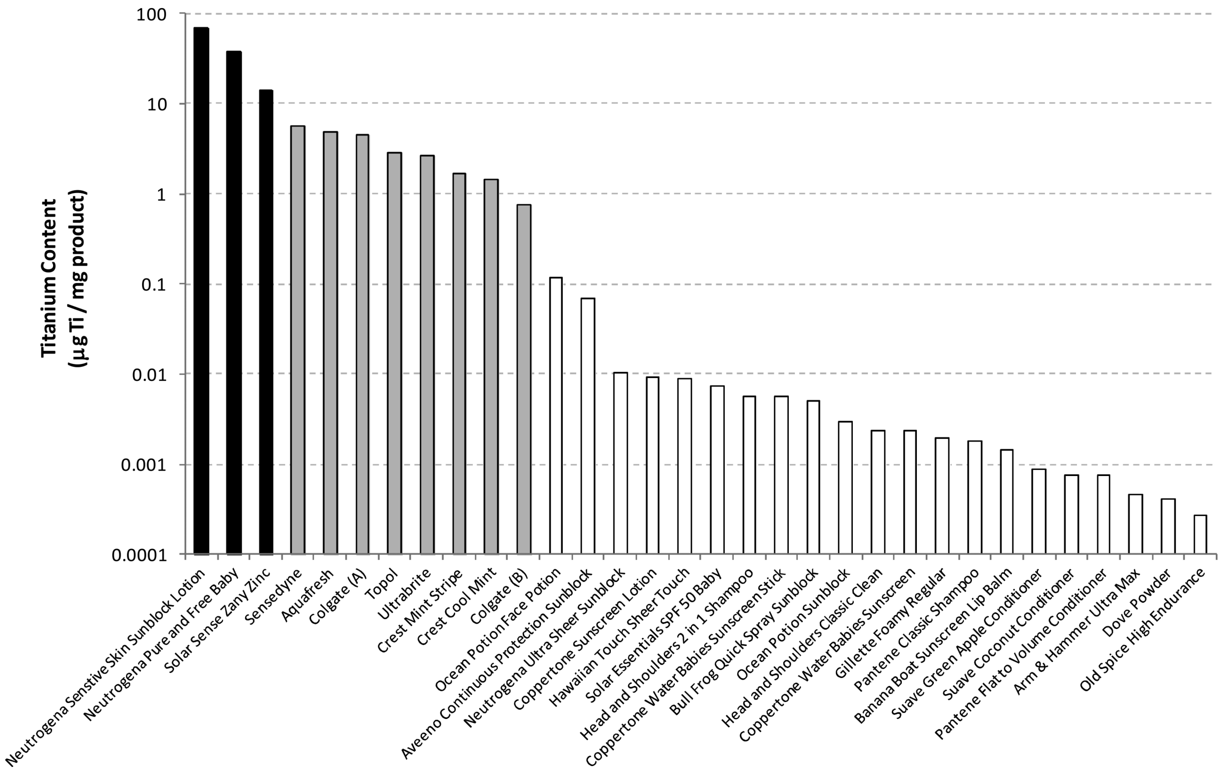

Figure 4.

Total titanium concentration for PCPs. Black bars are sunscreens with TiO_2 listed on the label. Grey bars are toothpastes with TiO_2 listed on label. Open bars are for products whose labels did not reference TiO_2.