Exposure Evaluation of Airborne Titanium Dioxide from Use in Spray Sunscreens

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ABSTRACT

In this study, we simulated consumer application of a spray sunscreen containing nanoscale TiO_2 to determine the nature of consumer TiO_2 exposure from the product's use (e.g. form of TiO_2 [primary particle, aggregate/agglomerate], size of TiO_2 and air concentration). Air samples were collected within the breathing zone of a mannequin using a Dekati Low Pressure Impactor (DLPI), which allows for size fractionation of the particles across 13 stages to facilitate size-specific exposure assessment. Samples from all stages were analyzed for the presence of titanium (as a marker for TiO_2) and resulting air concentrations were calculated by size fraction. Upon determination of stages where TiO_2 was detected, subsequent analysis by field emission scanning electron microscopy was used to determine the form and morphology of the TiO_2 particles. This paper presents the results of this study along with interpretation with respect to the potential for health risk from this consumer product.

1 INTRODUCTION

Nanomaterials, including titanium dioxide (TiO_2), are currently used in a wide variety of consumer products and applications, including spray sunscreens. A review by RIVM has identified sunscreens as the consumer product with the highest probability of exposure and associated health risk for consumers [1]. Nano-TiO_2 is utilized as a UV light attenuator in cosmetics and personal care products, and although production volume in the U.S. is unknown, it but is believed to increase over time [2, 3].

Titanium dioxide has been listed as a carcinogen by the International Agency for Research on Cancer (IARC; class 2B carcinogen, possible human carcinogen), and the National Institute for Occupational Safety and Health (NIOSH; possible carcinogen in ultrafine form) based on specific studies that found increased cancer rates in rats exposed to fine and ultrafine TiO_2 particles [4, 5]. As a result of these classifications, the State of California listed airborne unbound respirable particles of TiO_2 on the Proposition 65 list on September 2, 2011, with cancer as the endpoint. In addition to studies on carcinogenicity, some studies utilizing large doses in animal models indicate the potential for airway inflammation with fine and ultrafine TiO_2 [4, 6]. NIOSH has established recommended exposure limits (RELs) for both fine and ultrafine TiO_2. The REL for nanoscale TiO_2 is approximately 10-fold lower than for "bulk" TiO_2 (0.3 mg/m3 vs. 2.4 mg/m3).

In this study, we aim to evaluate the potential for exposure to TiO_2 from the use of a spray sunscreen thought to contain nanoscale TiO_2. We simulated sunscreen use scenarios, collected air samples using a cascade impactor (Dekati Low Pressure Impactor [DLPI], and analyzed samples for the presence of TiO_2 to determine magnitude of exposure to TiO_2. In addition, the air samples were analyzed via microscopy to understand morphology and structure of the TiO_2 particles found in the aerosol.

2 METHODS

2.1 Product Identification

According to the U.S. EPA, only nanoscale TiO_2 provides the UV protection necessary for use in sunscreens (macroscale TiO_2 does not). However, as of 2010, the U.S. EPA was unable to identify spray sunscreens that contained TiO2 [2]. Therefore, in order to identify a candidate sunscreen for testing, we searched existing databases of nanoenabled products for spray sunscreens containing TiO_2, and identified a sunscreen containing titanium dioxide (3.8%), identified for its UVA and UVB protection. Therefore, we assumed that the TiO_2 used in this product was nanoscale TiO_2. This assumption would be evaluated during microscopic evaluation of the air samples collected during product use.

2.2 Simulation of Exposure and Sample Collection

In order to simulate exposure, we sprayed a mannequin with sunscreen under two scenarios: 1) use of the entire bottle of sunscreen [Scenario 1] and 2) spraying of five persons at 1 minute per person (simulating application on a family of five) [Scenario 2]. For both scenarios, we recorded duration of spraying, duration of air sampling, and mass of sunscreen applied (Table 1). This documentation would allow for subsequent adjustment of exposure based on volume of anticipated usage and/or duration of application, as different scenarios would warrant different application rates (e.g. family vs. individual). During the spraying and for five minutes post-completion of sunscreen application, air samples were collected within the breathing zone of the mannequin using a Dekati Low Pressure Impactor (DLPI). The DLPI is a cascade impactor with 13 stages, ranging from 10 µm to 30 nm; each stage is mounted with a polycarbonate substrate onto which the particles consistent with the stage's size are deposited and used for subsequent analysis. Air sampling was conducted at a flow rate of 10 L/min.

	Duration of Spraying (min)	Total Duration of Sampling (min)	Mass of Sunscreen Used (g)
Scenario 1	16	21	198.5
Scenario 2	5	10	79.4

Table 1: Sample Collection Conditions

2.3 Sample Analysis

All of the samples collected with the DLPI (e.g. substrates from each stage) were analyzed for elemental composition using Particle Induced X-Ray Emission Spectroscopy (PIXE; Elemental Analysis Inc., Lexington, KY). Air concentrations of TiO_2 were calculated based on the detection of titanium from this analysis. In addition, one selected sample representing the smallest stage upon which detectable titanium was found (1.6 µm; Scenario 1) underwent preliminary analysis via microscopy for morphology and structural information. Sections of the polycarbonate substrate were prepped for Field Emission Scanning Electron Microscopy (FESEM) equipped with Energy Dispersive Spectroscopy (EDS) and images were collected of titanium-containing particles for morphological analysis. Automated analysis that gathers information on size, shape, and elemental composition on a particle-by-particle basis were conducted using a computer-controlled SEM (CCSEM) for 995 particles (RJ Lee Group, Monroeville, PA).

3 RESULTS

3.1 Concentration by Size Fraction

Titanium dioxide[1] was only detected on stages where median particle size is greater than or equal to 1.6 µm (Table 2). In general, air concentrations of titanium dioxide for any given particle size (calculated from mass-based measurements of titanium found on each stage) tended to increase with particle size, but were low ($\leq$ 12 µg/m^3) in terms of magnitude for both scenarios. Though the amount of sunscreen used during Scenario 1 was more than twice that of Scenario 2, the air concentration of TiO_2 was lower, possibly the result of agglomeration of aerosolized sunscreen droplets (resulting in deposition, rather than suspension in air).

1 Based on detection of titanium

3.2 Microscopy

Images collected with the FESEM indicate that the primary particles of TiO_2 were likely in the nanoscale, confirming the presence of nanoscale TiO_2 in this sunscreen. These particles were typically agglomerated, and were always found to be associated with hexagonal carbonaceous particles of unknown source (Figure 1). No unbound TiO_2 particles were identified, albeit the analysis was limited to a single stage. Data from the CCSEM confirmed that TiO_2 particles were typically bound to carbon, as only 2 Ti-rich particles were identified in the automated scan of 995 particles; all other titanium-containing particles were associated with carbon (Table 3).

	Air Concentration of TiO_2 (µg)[a]	
Median Particle Size of Stage (nm)	**Scenario 1**	**Scenario 2**
<30	< 0.070[b]	< 0.067[b]
30	< 0.062[b]	< 0.083[b]
60	< 0.022[b]	< 0.090[b]
108	< 0.031[b]	< 0.060[b]
170	< 0.031[b]	< 0.083[b]
260	< 0.044[b]	< 0.117[b]
400	< 0.062[b]	< 0.167[b]
650	< 0.094[b]	< 1.33[b]
1000	< 0.277	< 0.117[b]
1600	0.571	< 0.488[b]
2500	1.88	1.60
4400	1.62	2.16
6800	1.23	12.0
10000	2.48	3.77
Total	**8.40**	**22.1**

[a] Based on sample times of 21 minutes for Scenario 1 and 10 minutes for Scenario 2, both at 10 L/min
[b] Based on detection limit

Table 2: Summary of Air Sampling Data

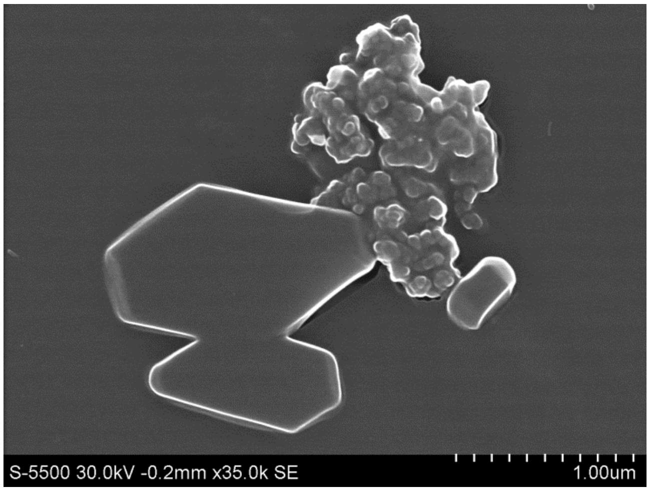

Figure 1: Representative Image of TiO_2 agglomerates (right, top) and unidentified carbonaceous particle (left, bottom). EDS spectra (data not presented) were used to identify chemical composition of particles.

Classes	#	Number %	Weight %
C-Ti	249	25.03	5.45
C-Si	176	17.69	27.53
Si/Al	174	17.49	19.54
C-rich	118	11.86	11.57
Si-rich	76	7.64	19.27
Ca/Si	67	6.73	5.03
Ca-rich	63	6.33	2.64
Misc.	34	3.42	2.05
Si/Mg	15	1.51	6.46
Ca/Mg	13	1.31	0.25
Zn-rich	8	0.80	0.17
Ti-rich	2	0.20	0.04

Table 3: Summary of CCSEM Results for 1.6 µm Stage of DLPI

4 CONCLUSIONS

Collectively, these results indicate that while consumers may be exposed to nanoscale TiO_2 from the use of commercially available sunscreens, the magnitude of exposure is low. Total concentration of TiO_2 over all stages is well below the recommended exposure limits for both pigmentary or ultrafine TiO_2 established by NIOSH of 2.4 and 0.3 mg/m^3 (8-hour time-weighted average) respectively, even with repeated application, indicating that the likelihood of risk to consumers from exposure to TiO_2 in spray sunscreens is negligible. Additional research, particularly microscopy evaluation of other stages, including those with non-detect titanium dioxide, may be warranted to better understand the nature of the titanium dioxide forms over the entire size distribution. However, this preliminary study demonstrates the usefulness of this methodology in evaluating the potential for exposure to nanomaterials from the use of consumer products.

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6 REFERENCES

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