Environmental release of engineered nanomaterials from commercial tiles under standardized abrasion conditions

Christophe Bressot, Nicolas Manier, Cécile Pagnoux, Olivier Aguerre-Chariol,
Martin Morgeneyer

Release to the environment of engineered nanomaterials from commercial tiles under standardized abrasion conditions.

Authors

Bressot, Christophe

Direction de risques chroniques

Institut National de l'Environnement Industriel et des Risques (INERIS)

Verneuil en Halatte, France

christophe.bressot@ineris.fr

Manier, Nicolas

Direction de risques chroniques

Unité EXES

Institut National de l'Environnement Industriel et des Risques (INERIS)

Verneuil en Halatte, France

nicolas.manier@ineris.fr

Pagnoux, Cécile

CEC - 12 rue Atlantis

87068 Limoges Cedex

cecile.pagnoux@unilim.fr

Aguerre-Chariol, Olivier

Direction des Risques Chroniques

Institut National de l'Environnement Industriel et des Risques (INERIS)

Verneuil en Halatte, France

olivier.aguerre-chariol@ineris.fr

Morgeneyer, Martin

Génie de Procédés Industriels

Sorbonne Universités, Université de Technologie de Compiègne (UTC)

Compiègne, France

martin.morgeneyer@utc.fr

CORRESPONDING AUTHOR

Morgeneyer, Martin martin.morgeneyer@utc.fr

Abstract

The study presented here focuses on commercial antibacterial tiles whose emissivity of (nano) particles due to abrasion has yet barely been investigated. The tiles have been characterized regarding their surface properties and composition throughout their chain-of-use, *i.e.* from their state of commercialization until the experimental end-of-service life. In contrast to plane standard tiles, their surfaces form hilly surfaces. In the depressions, titanium dioxide is found at the surface, thus theoretically protected by the hilly areas against abrasion on the tile's surface.

Furthermore, a deposition technique has been put in place by producers allowing for coating the before mentioned commercial tiles with titanium dioxide, thus being similar to those commercially available. It consists in depositing titanium dioxide on the surface, latter one allowing fixing the first. This development allows for better understanding the future options for product formulation and thus improvement with respect to particle release.

The tests reveal the aerosolization from commercial antibacterial tiles of micronic and submicronic particles in the inhalable region or particles that can subjected to be released in the environment (< 10 μm). The aersolization of the particles from the coated tiles was found to be significantly higher compared to the non coated tiles.

1   Introduction

Nanoparticles are nowadays often found embedded in commercial consumer products, endowing the latter with new and innovative properties [1, 2]. So called self-cleaning or antibacterial coatings for instance, selectively bind and remove bacteria, *e.g.* when using silver or titanium dioxide nanoparticles [3].

Sole the soaring presence of nanoparticles in consumer goods increases the risks along their life cycle, *i.e.* to workers, consumers and the environment. Nanoparticles incorporated into products can indeed be released over the whole product life cycle, particularly during use and disposal, both into the gas and/or the aqueous phase (i.e *via* mechanical solicitation and/or leaching processes). Looking at the possible routes for nanoparticles or nanomaterials to enter the environment, both the aquatic and terrestrial compartment can be substantially exposed [4]. As an example, many studies have confirmed the potential release of nanoparticles from antibacterial textiles or antibacterial wound dressing as well as from coatings [5]. There is also evidence that nanoparticles can affect the terrestrial compartment, *e.g.* through the use of sewage sludge as fertilizer in agricultural process [6]. From a toxicological point of view, out of the dermal, ingestion or inhalation penetration routes to the human body, the inhalation route is considered to be critical [7].

The assessment of the ecotoxicological and toxicological effects of nanoparticles and nanomaterials has, consequently, become a major issue worldwide, and in the last five to ten years an increasing number of studies concerning the nanoparticles or nanomaterials hazard assessment were published [8-12]. For example, the "pristine" forms of titanium dioxide nanoparticles are reported to cause acute and sub-lethal effects to several freshwater or marine species including bacteria, micro-algae, micro-invertebrates, mollusk, insect larvae and fishes [10, 13, 14]. Nano titanium dioxide is also identified for its toxicological damage [15], such as reproduction troubles [16, 17] or splenic [18], kidney [19] injury or hippocampal apoptosis [20], which is supposed to be a consequence of its large surface area [21]. For given nanometric particle sizes, titanium dioxide was however shown to have lesser effects on the respiratory ducts than zinc oxide or silver [22].

However, most of the works published on nanoparticles or nanomaterials is considering their so-called "pristine" forms, as produced, whatsoever regardless of ecotoxicity studies, toxicity studies or environmental fate studies. Although providing useful (eco)toxicological informations, the quantity of available data for the "pristine" form contrasts with the very few studies that have investigated the environmental exposure and the ecotoxicity or toxicity of nanoparticles released from consumer products according to relevant scenarios. In addition, some authors have shown that modifications of the nanoparticles can happen when they are included in consumer products and/or released during their life cycle [23, 24]. Therefore the physico-chemical properties of the nanoparticles released from consumer product could markedly differ from the pristine form and, as a consequence, the potential ecotoxicological or toxicological effect could change in equal measure.

Currently, both with nanoaerosol formation as well as with nanoleachate formation, two fundamental paths of nanoparticle transport away from the source are investigated, *i.e.* either in gas or liquid phase [25].

The formation of aerosols and suspensions prior to this transport is the result of mechanical solicitation, *i.e.* the exertion of mechanical stresses going along with deformations and cracking fissuration of asperities on the surface [26]. Here, abrasion is one of the most prominent processes allowing for experimentally simulating these stresses [27-32].

Further to the (eco)toxicological studies on pristine nanoparticles, a realistic risk assessment with respect to the exposure to engineered nanomaterials should thus lead to a holistic approach. Processes that lead to the particle release must be taken into account, since the environmental behavior supposedly strongly depends on the respective *release scenario*. Yet, very few is known about this and further research is needed here [4].

In this context, the agglomeration behavior of nanoparticles should also be brought into focus, which is – in the wet phase- known to happen rapidly for TiO_2 [33]. For the dry phase, some researchers argue that agglomeration might reduce the risk of inhalation [34]. On the contrary, no exposure alleviation has up to now been demonstrated for the so called nanoobjects, agglomerates and aggregates (NOAAs), endorsing the imperative of experimental strategies based on holistic release scenarios [35, 36].

Conscious of the concerns related to the nanorisks, tile producers might try to modify their production process in order to avoid any possible nanoparticle release. As a result a new generation of photocatalytic tiles were for example prepared by the manufacturer GranitiFiandre deploying a commercial micron-sized TiO_2 suspension [37].

A second prominent *release scenario* is the washing out of nanoparticles from their matrix. It is known that this happens easily to nanosilver [5] or to nanometric titanium dioxide, which has been traced from exterior façade paints via its detachment from new and aged façade paints by natural weather conditions to its release into surface waters [38]. Titanium dioxide can deteriorate its surrounding paint matrix by its in principle desired photocatalytic action, whereby plane the question raises whether there is a point in embedding nanoparticles into paints [39].

Further to the basic functionalities of tiles, such as excellent mechanical and chemical resistance which make them ideal for professional and hygienic environments, targeted functionalities are reached today, owing to the embedding of nanoparticles. The temperature resistance of tiles, unlike plastics, makes them an ideal substrate for directly attaching photocatalytic layers by sintering [40]. By reason of their self-cleaning properties, the so produced tiles are becoming widely spread used, which still limited to a worthwhile outdoor use [41]. Thousands of tall buildings are reported to have been covered with self-cleaning tiles in Japan [42]. Tiles, together with other products, have already been the topic of release studies about a decade ago [43], which, due to the absence of references in sample preparations, exposure scenarios and measurement equipment unfortunately make clear conclusions impossible [44]. Moreover, the manufacturing processes of these nanocoated tiles still requires much research progress [45], which also leads to the different scenarios which need to be investigated.

Consequently, the investigation of the release of engineered nanomaterials from commercial tiles under mechanical solicitation is of vital importance for this growing, at this stage established market of consumer goods. The connection of both manufacturing considerations as well as release scenarios, to the worker, to the consumer or to the environment, to the experimental work contributes to a realistic study of the hazardousness of the tiles.

2   Materials and Methods

2.1   Antibacterial tiles

2.1.1   Specificities of the ceramic materials and characterization of the commercial products

The majority of commercial tiles are obtained by molding and pressing a suspension containing the ceramic material. The obtained raw tile is then heated in a roller kiln, allowing for stoving the tiles during short cycles, to temperatures ranging from 1200°C to 1250°C [46, 47]. At this temperature, its future mechanical resistance is conferred to the tile. The so-produced tile which did not yet receive any antibacterial treatment, is denominated 'TNT' in this paper.

The antibacterial properties are obtained by adding titanium dioxide in a further process step. This mineral can exhibit different crystal structures varieties: The anatase phase forms at temperatures below 800°C, while as the rutile phase formed above 800°C does not exhibit the targeted antibacterial properties and is for this used as pigment only. Further to the crystal structure, their presence with or without a matrix and the granulometry govern their activity [48]. The annealing of the TiO_2 to the tile must thus take place below 800°C, *i.e.* much

below the stoving temperature, and is often done at about 500°C, whilst an optimum temperature has been reported for a lower temperature of 300°C [40]. The so-treated tile is denominated 'TT' in this paper.

2.1.2   Antibacterial surface coating of the hilly tiles

The flow chart of the figure 1 describes the steps of the process used to deposit anatase particles. The raw tile (TNT) is firstly coated with a melting phase in which titanium particles are added and the layer is heated to stick to the tile surface.
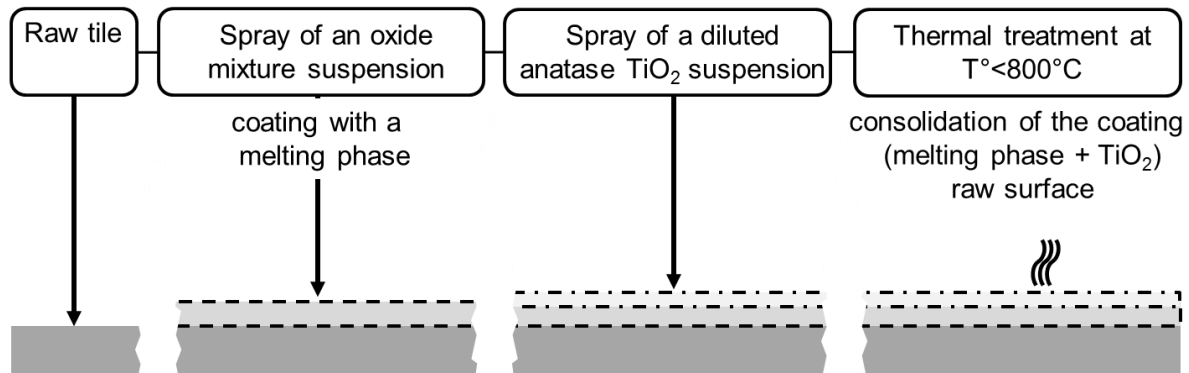

Figure 1 : Surface treatment of a raw tile (TNT) to give antibacterial properties

The titanium dioxide is attached to the surface in a two-step process. The role of the vitreous phase, brought onto the substrate tile, is to melt at low temperature in order to serve as a matrix on which the titanium dioxide is dispersed. This interphase leads to an increase in terms of surface roughness. During stoving, the titanium dioxide accumulates in the surface's depressions.

In the study presented here, the commercially available products have been characterized in order to understand the specificities of TT with respect to standard ones. The surface of products have been observed by means of scanning electron microscopy (S260 Cambridge instruments), and a chemical analysis was performed by EDS (energy dispersive X-ray spectroscopy) by using the emitted X-rays in the S260 equipped with a tungsten filament electron gun and a PGT Synergie4 spectrometer with a germanium diode. The spectral resolution is 112 eV at 15 kV on the line of manganese.

The specificity of the antibacterial tiles is their surface topography, which is hilly (figure 2) and titanium particles are detected with back scattered electrons (figure 3). Due to the deposition method, the nanoTiO_2 presence is intermittent on the tile surface and mainly located in the surface's depressions, where most particles have sizes between 100 and 300 nm, few also have sizes below 100 nm (figure 4). Although the quantities of the applied titanium dioxide should be small, the EDS analysis shows that both tiles have the same raw composition but the antibacterial product exhibits a large peak of titanium (figure 5). The figure 6 illustrates the surface modifications to deposit the coating on the tiles properly.
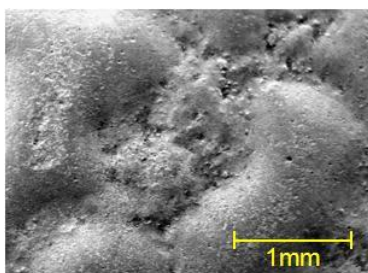

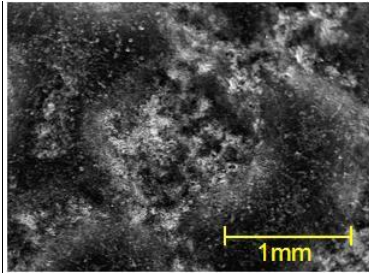Figure 2 : Topographic surface view of TT (x20)

Figure 3 : Titanium dioxide on the surface of TT (x20)(back scattered electrons)
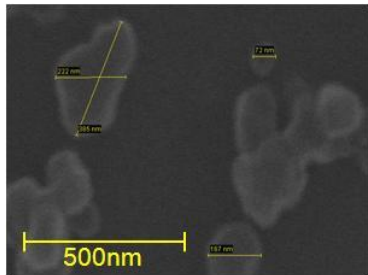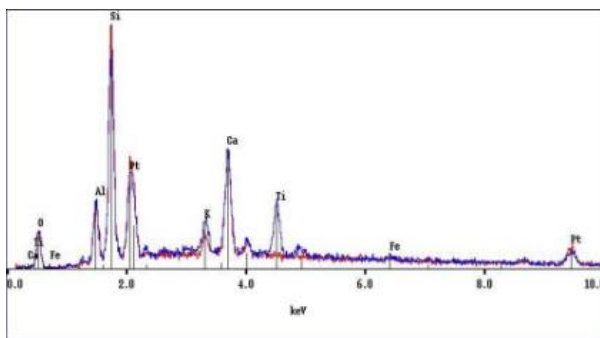

Figure 4: Size of the titanium dioxide on TT surface

Figure 5: EDS analysis of tile surface (red: TNT, blue: TT)

Figure 6: Surface treatment of classic commercial and antibacterial tiles.

2.2   Study of release under mechanical solicitation

2.2.1   Abrasion of the tiles

The abrasion test of floor coverings and similar products is delineated in several international standards [49-51], where also the Taber linear abrasion apparatus (Model 5750; Taber Inc. USA) is indicated. This test was used in the study presented here. The abrasion stress being applied through a Taber apparatus corresponds to the typical ones applied to surface coatings in a domestic setting, for example, walking with shoes and displacement of different objects [27, 52]. The abrasion is generated by an abrader of given composition. Here, a commercial H38 abrader, Taber Inc. USA, has been used. The contact of tile and abrader is constantly loaded in the vertical,

i.e. normal-to-the-sample-surface direction by a weight. A motor unit allows for back-and-forth moving the abrader on the fixed sample, yielding a tangential abrasion stress in the contact. Representativeness of the stress levels, reproducibility of those compared to professional tribometers and reproducibility of the measurements has been ensured in a preliminary study [53].

2.2.2 Aerosol measurement

The abrading device is mounted inside a self-designed emission chamber [54] (0.5 m × 0.3 m × 0.6 m) which is located in a larger nanosecured work post (HPPE10, Erma Flux SA, France), in which the abrader's motor unit is fixed and through which cleaned air (high efficiency particulate air filter, efficiency 99.99%) is passed. Part of the cleaned air is passed through the emission chamber already before starting the abrasion in order to reduce the presence of background particles. The chamber is then sealed and air can only enter the emission chamber via the slot through which the arm, which is connecting motor unit and abrading device, passes. The vicinity of the abrasion contact is covered by a cylindrical sampling hood of 713 cm³, which follows the back-and-forth movement, to which the pipes leading to the particle detectors are connected. Sampling hoods have been used in other studies in order to minimize particle losses to the emission chamber [27]. The antistatic conducts of 6 mm diameter suck the air at 6.8 L/mm from the sampling hood to a condensation particle counter (CPC), a scanning mobility particle sizer (SMPS), a aerodynamic particle sizer (APS), and a Mini Particle Sampler (MPS; Ecomesure Inc.). The particles collected by MPS on a porous copper grid (Model S143-3; Quantifoil Micro Tools GmbH Germany) are characterized with a Transmission Electron Microcopy (TEM, Model CM12; Philips, Netherlands). Aerosols of particles from 4 nm to 20 μm can be characterized with respect to their concentration and sizes (see figure 7). Test runs prior to the abrasion tests show low background noises of less than 0.7 particles per cm³. Particle losses on walls and conducts have been estimated to range between 17% for particles smaller than 10 nm and below 1% for particles bigger than 100 nm [55].
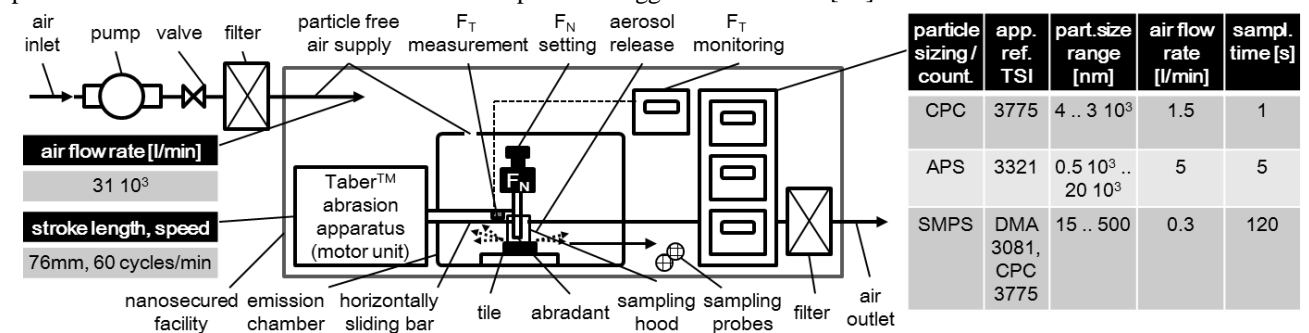

particle sizing / count	app. ref. TSI	part.size range [nm]	air flow rate [l/min]	sampl. time [s]
CPC	3775	4 .. 3 10³	1.5	1
APS	3321	0.5 10³ .. 20 10³	5	5
SMPS	DMA 3081, CPC 3775	15 .. 500	0.3	120

Figure 7: The measurement set-up used in this study

2.2.3 Experimental parameter

A Taber H22 nonresilient vitrified clay-carborundum abradant was used during the whole study. The abrasion stroke length, abrasion speed, abrasion duration, and the number of abrasion cycles were kept constant at 76.2 mm, 60 cycles per minute (cpm), 10 min, and 600, respectively.

3   Experimental results

The third part of the work presented here consists of a comparative study of the release from two series of commercial tiles, which are in the following referenced as non-treated tiles (TNT), *i.e.* the original, plane, commercial ones, and as treated tiles (TT), *i.e.* the hilly and titanium dioxide coated ones.

3.1   Comparative cumulative study of particle release from nanocoated and non-coated tiles

In general, the results show a significantly higher particle number concentration for treated tiles (TT), compared to the non-treated (TNT) ones: The average concentration for particle sizes ranging from 15 nm to 20 µm (cumulated data of SMPS and APS) is with 56,480 particles/cm^3 175 times higher for TT samples than for TNT ones, releasing 321 particles.cm^{-3}. However, the detected nanosized objects (sizes 15 nm to 103 nm) represent only 1.7 % of the total measured number of particles released from TT (940 out of 56,480 objects per cm^3), which is relatively much less than the 10% nanosized particles released from TNT (32 out of 321 objects per cm^3).

3.2   Release - time response of the tiles under abrasion

The particle release response of the tiles under abrasion confirms the observations made before. After two minutes with the abrasion apparatus at rest - correspondingly only a very low background noise is detected-, the abrasion is started. This leads to an immediate response, the maximum of which is reached within 20 seconds (figure 8). Under continuous abrasion during about 10 minutes, the samples continuously release particles, although with a decline in quantity. For any given instant of time, the number of particles released from nanocoated tiles (TT) is significantly higher than the corresponding one of non-coated ones (TNT). Once the abrasion stopped, the particle concentration decays within two minutes to values below 200 particles per cubic centimeter.
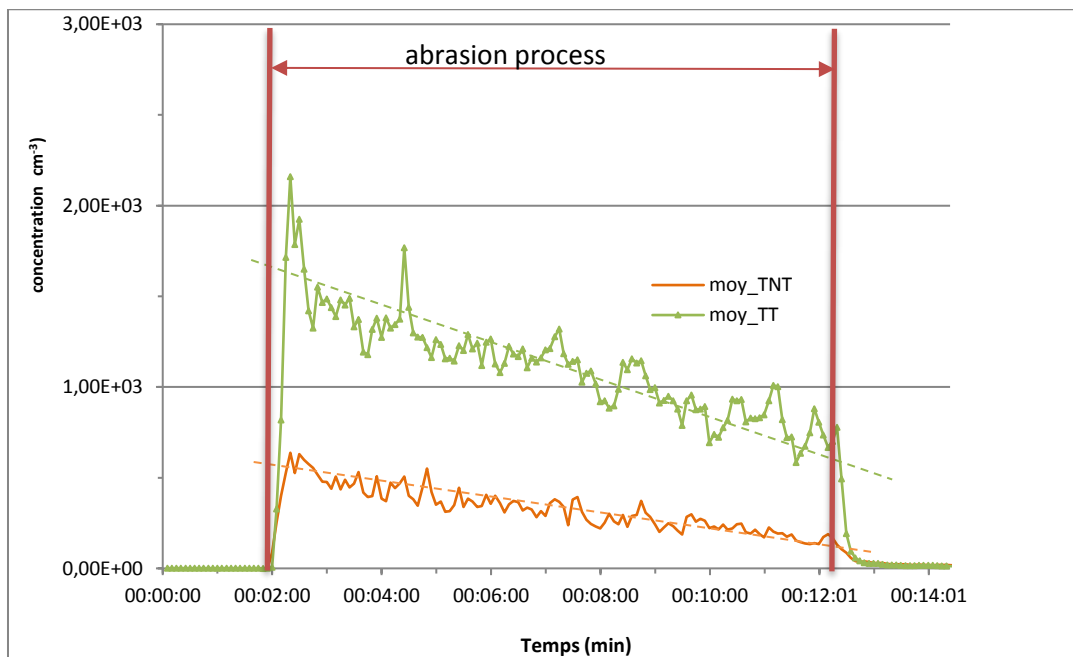

Figure 8: Linear representation of the emitted particle number concentration (4 nm to 3 µm) of treated (TT) and non-treated (TNT) commercial tiles under abrasion, plotted with time. Dashed lines guide the eyes.

3.3   Comparative study of the size distributions of particles released from treated and non-treated tiles

The particle sizes of the treated and non-treated tiles show qualitatively similar distributions, when measured with APS and SMPS. The measured size distributions reveal considerable submicron sized fractions for both sample types. The observed modes (SMPS) correspond to 407 nm (TNT) and 470 nm 470 (TT), respectively. A secondary micronic mode is also detected by APS at 898 nm (TNT) and 965 nm (TT) respectively (see figure 9 and figure 10). As a result the nanomaterial tile shifts in both cases the main modes to bigger particles. However, as already shown in the previous sections, the quantitative picture is different with about one order of magnitude higher levels for the treated tiles, compared to the non-treated ones.
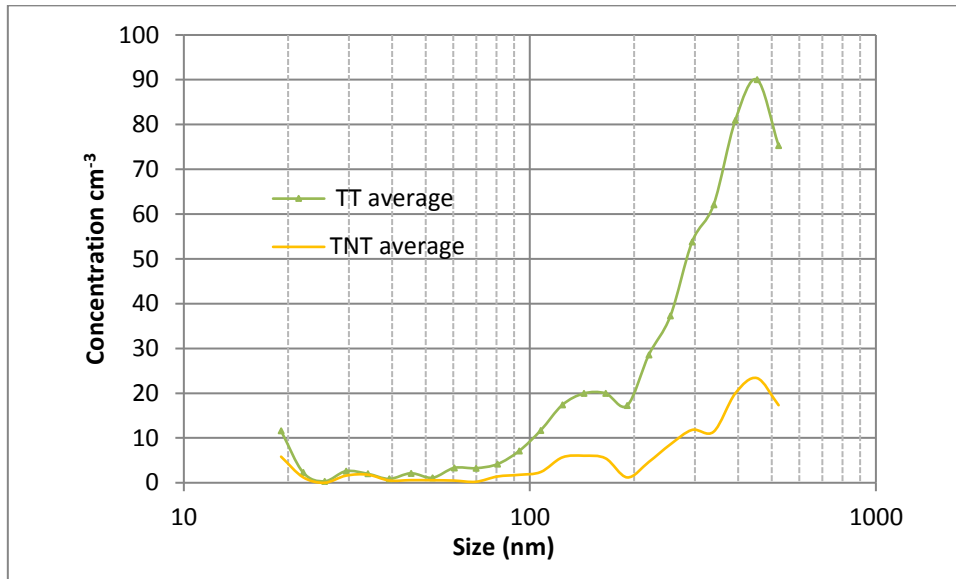
Figure 9: Size distributions (10 nm – 500 nm) of particles released from treated (TT) and non-treated (TNT) tiles under abrasion, measured with SMPS. Each curve corresponds to an average of two tests.

Figure 10: Size distributions (0.5 µm – 20 µm) of particles released from treated (TT) and non-treated (TNT) tiles under abrasion, measured with APS. Each curve corresponds to an average of two tests.
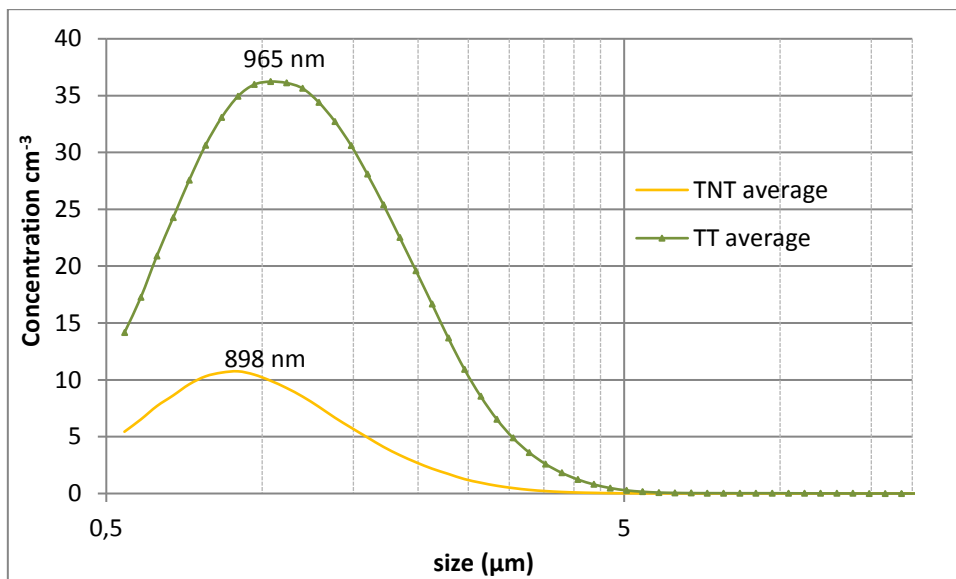
3.4 TEM analysis of the aerosol released from commercial tiles

The following section summarizes the observations made regarding the debris collected on grids by MPS sampling, a recent method described elsewhere [25, 53, 56]. The sampling duration covers only the first minute of the abrasion test in order to avoid a high overlapping of the collected particle on the TEM grid. In the case of treated tiles (TT), the number of objects collected on the grid is bigger than for the non-treated references. However, the morphology of the collected debris particles does not visibly change: Both varieties release objects of mainly submicronic size and of irregular shapes. A small part of the observed particles have nanoscale.

Table 1 gives a summary of the observations via TEM analysis.

Table 1: Summary of the TEM analyses and the EDS microanalysis of commercial tiles

Sample reference	Number of coatings	Objects on the grid	Deposition level	Presence of nano-objects	Presence of sub-micron sized objects	Presence of micron sized objects	Presence of TiO$_2$ in the objects	Presence of free TiO$_2$ particles
TNT	0	✓	✗	+/-	+/-	-	✗	Inv.
TT	1	✓	✓	+/-	+	-	✓	✗

✓ = yes ; ✗ = no ; - = very low ; +/- = low ; + =strong ; ++ very strong ; inv. = invalid

Figure 11 shows the variety of debris shapes which can be observed when abrading the non-treated tiles. Few objects have nanometric sizes, see figure 12.
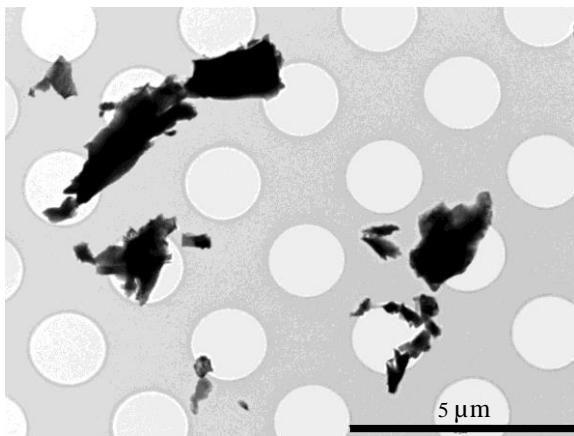

Figure 11: Particles observed after abrasion of a TNT sample. The particles are mainly submicron sized. Few particles are micron sized.
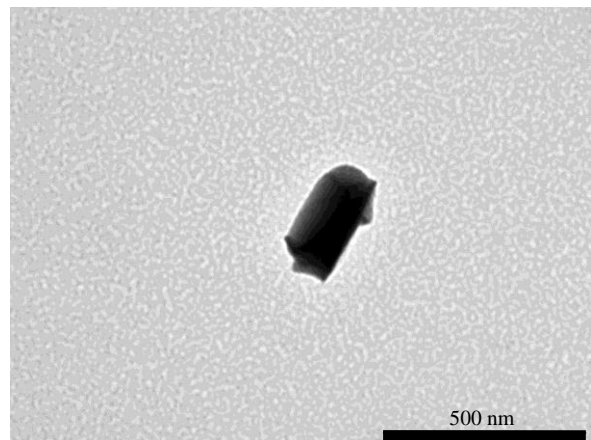

Figure 12: Example of a nanoparticle observed after abrading a TNT sample.

The TEM analysis of debris originated from treated tiles (TT) shown in figure 13, reveals objects which are similar to the ones observed for non-treated tiles.
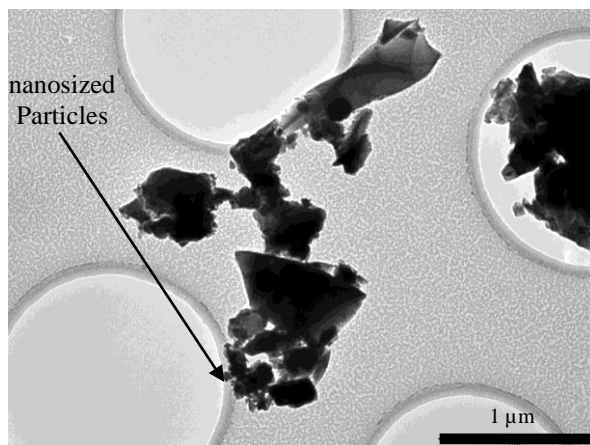

Figure 13: Cluster of particles observed after abrasion of the TT sample. Particle sizes are below one micron. Some nanosized particles can be observed.

The chemical analysis of the objects collected after the abrasion of the non-treated sample (TNT) correspond to elements generally observed in ceramics, such as zinc, iron, silicon and oxygen (see figure 14).
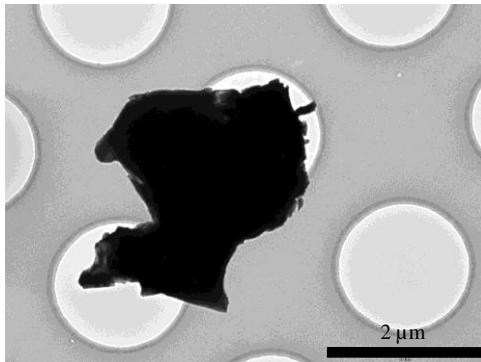

Figure 14: Particle from the abrasion of TNT. Strong presence of zinc (80%), iron (4 %), oxygen (57 %) and silicon (5 %) detected by EDS microanalysis of the particle.

In the case of the abrasion of treated tiles (TT), the expected titanium is found as component of the ceramic matrix. (figure 15 and figure 16).
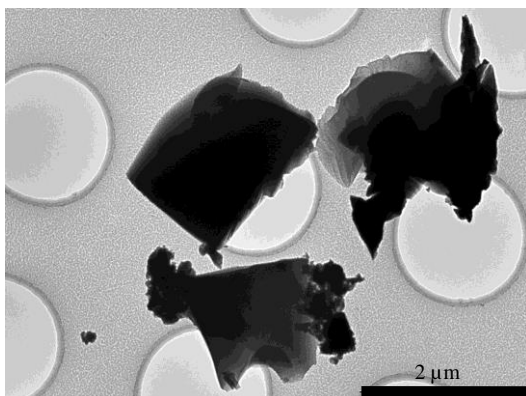

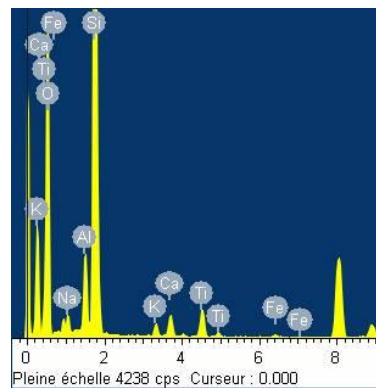Figure 15: Particles from the abrasion of TT. Scale bar 2 µm.

Figure 16: EDS microanalysis of the left particle (figure 15, TT). Presence of oxygen (46 %), silicon (45 %), aluminum (3 %) and titanium (2 %). Traces of iron (0.3 %)

4   Discussion

The study presented here allows for making several fundamental observations with respect to the differences and similarities of nanotreated and non-treated commercial tiles under standardized abrasion conditions. On the contrary to prior studies on nanocoatings which prevented particle release [25, 53] the tiles' surface treatment with nanoscale titanium dioxide investigated in the present study leads to a significantly higher emission level with slightly bigger particles, when compared to the behavior of non-treated specimen.

The system coupling nanoTiO$_2$ depositions and the modified tiles used as substrate of the coating seems to enhance the emission rather than protecting the coating in its depressions. A first possible cause can be the intermittent deposition on the tile surface which prevents an efficient protection. Instead of protecting the support by a continuous protective coating, the intermittent deposition can increase the emission because of facilitating tangential forces actions. This tangential forces are indeed the mean process involved in aersolization of the material asperities during an abrasion [57]. Furthermore, the mechanical resistance of the nanocoating appears to be mechanically less resistant than the one of the substrate tile, since its chemical composition is not the same (no alumina) and the process fusion temperature is lower involving a less performing sintering process. This vitreous phase is removed more easily than its substrate and does not serve as protection of the TiO$_2$ in the

long run. The coating systematically requires a change of the surface morphology. A higher rugosity on the coated tile surfaces is clearly observed with respect to the smooth surfaces of the uncoated tiles. TiO_2 deposition necessitates a change of the surface morphology which facilitates wrench of protruding nano-TiO_2 NOAAs attached to ceramic debris while the abrasive moved on the irregular surfaces of coated tiles. This last observation is certainly the main reason of the major releases noticed during the abrasion tests of the nanotreated tiles.

However, the shapes of the released particles do not change visibly. In both cases the released particles are mainly of sub-micron and micron size, but not free nanoTiO_2 are detected by TEM. Observed nanoparticles, released from the nanocoating, are mostly attached to bigger objects, *i.e.* these form composite aggregates (NOAAs) adding nano-TiO_2 and ceramic matrix.

Emission of NOAAs from marketed product was already pointed out by some authors and only few works have shown the release of free ENM. Al-Kattan et al. [23] reported that some free nano-TiO_2 particles were emitted from aged paint containing nano-TiO_2, but the majority were enclosed by the organic paint binder forming small piece of paint matrix containing nanoTiO_2. Shandilya et al. [55] also showed that free TiO_2 can be release into air by abrasion of a commercial photocatalytic nanocoating put on building materials, especially after they were exposed to weathering for seven month. Beside these few examples, most of the studies have indicated that nanomaterials are likely to be emitted embedded in the debris or aerosol produced by weathering, usage, maintenance activities and during end of life [27, 38, 58]. Given the sizes of the so-formed particles, although NOAAs, they are potentially inhalable and can be transfer to the environment [59]. Various transport pathways may bring NOAAs to the different environmental compartments. Nowack et al.,[4] highlight that the particles can be release directly into the soil or the surface water through weathering and leaching for example, or indirectly *via* emission to the atmosphere and aerial deposition process. Whether directly or indirectly, the emitted NOAAs from consumer products all end up in the terrestrial or aquatic compartment. They can thus contribute to the exposure of the biota and can impact the living organisms (*i.e* by uptake, bioaccumulation, interaction or inducing deleterious effect). The fact that in our work we showed a more important emission during the abrasion tests of the nanotreated tiles by comparison with the non-treated ones suggest that the potential environmental impact of NOAAs should be studied. Moreover, a special consideration to the smaller NOAAs emitted in the form of aerosol during voluntary or involuntary abrasion process should be made.

At the best of our knowledge, no work has studied the potential ecotoxicological effect of NOAAs released from consumer products, as most of the works published on nanoparticles was considering their "pristine" forms. Few studies give information concerning the alteration of "pristine" nanoparticles in suspension. Manier et al. [60] showed that after 3 days and one month in water (under artificial alteration process), cerium dioxide nanoparticles form large agglomerates, while their ecotoxicity toward freshwater microalgae do not change. However this study was still considering the pristine form of the nanoparticles, before to be embedded in the final product. Our results demonstrate that the key point is not only the release of pristine nanoparticles under abrasion but the release of NOAAs, which could, with a particle size below 10 µm, be inhaled and easily be disseminated to the environment [59]. In addition, the knowledge of speciation of particles is also vital for assessment of the environmental implications of these materials [15]. Studying both physico-chemical parameters and the effect of such particles, according to realistic scenario involving life cycle studies, logically appears as the next step to fully understand the potential impact of the nanoparticles to health and to the environment. These studies are still seldom published and lacking [44].

. This means that the recent development of micron-sized titanium dioxide coatings [37] might not substantially change the risk scenario.

5   Conclusion

Standardized abrasion tests were carried out on commercial tiles, which were either nanotreated (containing nanotitanium dioxide) or not (reference). A 175 times higher emission level has been detected in the case of nanotreated tiles when compared to the non-treated references samples. The generated aerosol is mainly dominated by NOAAs where titanium is widely detected but at low concentrations, which is in accordance with the relatively low nanotitanium dioxide presence on the tile surface. This high emission level can be attributed (i) to the intermittent deposition on the tile surface, (ii) to the low mechanical resistance of the nanocoating and (iii) to the change of the surface morphology which facilitates the deposition of nanoTiO_2 suspension at the respective production step.

Ecotoxicological studies are today mostly limited to the use of pristine nanoparticles. This approach is helpful to understand the fundamental mechanisms in ecotoxicology but it is too unrealistic to assess the real effects of

emissions occurring during the product life cycle. Ecotoxicological cross-effects of embedded particles together with the ceramic matrix are for example impossible to estimate using alone pristine nanotitanium dioxide.

The method to characterize aerosol generation by abrasion presented in this paper could also feed in a near future the *in-vivo/in vitro* ecotoxicology tests.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

References

[1] D.M. Mitrano, S. Motellier, S. Clavaguera, B. Nowack, Review of nanomaterial aging and transformations through the life cycle of nano-enhanced products, Environment International, 77 (2015) 132-147.

[2] F. Piccinno, F. Gottschalk, S. Seeger, B. Nowack, Industrial production quantities and uses of ten engineered nanomaterials in Europe and the world, Journal of Nanoparticle Research, 14 (2012) 1-11.

[3] J. Chapman, T. Sullivan, F. Regan, Nanoparticles in Anti-microbial Materials : Use and Characterisation, Royal Society of Chemistry, Cambridge, U.K., 2012.

[4] B. Nowack, J.F. Ranville, S. Diamond, J.A. Gallego-Urrea, C. Metcalfe, J. Rose, N. Horne, A.A. Koelmans, S.J. Klaine, Potential scenarios for nanomaterial release and subsequent alteration in the environment, Environmental toxicology and chemistry / SETAC, 31 (2012) 50-59.

[5] R. Kaegi, B. Sinnet, S. Zuleeg, H. Hagendorfer, E. Mueller, R. Vonbank, M. Boller, M. Burkhardt, Release of silver nanoparticles from outdoor facades, Environ Pollut, 158 (2010) 2900-2905.

[6] K. Schlich, T. Klawonn, K. Terytze, K. Hund-Rinke, Hazard assessment of a silver nanoparticle in soil applied via sewage sludge, Environmental Sciences Europe, (2013) 1.

[7] C.C. Daigle, D.C. Chalupa, F.R. Gibb, P.E. Morrow, G. Oberdorster, M.J. Utell, M.W. Frampton, Ultrafine particle deposition in humans during rest and exercise, 2003.

[8] R.D. Handy, B.J. Shaw, Toxic effects of nanoparticles and nanomaterials: Implications for public health, risk assessment and the public perception of nanotechnology, Health, Risk & Society, 9 (2007) 125.

[9] A. Lapresta-Fernandez, A. Fernandez, J. Blasco, Nanoecotoxicity effects of engineered silver and gold nanoparticles in aquatic organisms, Trac-Trend Anal Chem, 32 (2012) 40-59.

[10] A. Menard, D. Drobne, A. Jemec, Ecotoxicity of nanosized TiO2. Review of in vivo data, Environ Pollut, 159 (2011) 677-684.

[11] A. Kahru, H.C. Dubourguier, From ecotoxicology to nanoecotoxicology, Toxicology, 269 (2010) 105-119.

[12] A.D. Maynard, R.J. Aitken, T. Butz, V. Colvin, K. Donaldson, G. Oberdorster, M.A. Philbert, J. Ryan, A. Seaton, V. Stone, S.S. Tinkle, L. Tran, N.J. Walker, D.B. Warheit, Safe handling of nanotechnology, Nature, 444 (2006) 267-269.

[13] Z. Clemente, V.L. Castro, M.A. Moura, C.M. Jonsson, L.F. Fraceto, Toxicity assessment of TiO(2) nanoparticles in zebrafish embryos under different exposure conditions, Aquat Toxicol, 147 (2014) 129-139.

[14] Z. Clemente, V.L. Castro, L.O. Feitosa, R. Lima, C.M. Jonsson, A.H.N. Maia, L.F. Fraceto, Fish exposure to nano-TiO2 under different experimental conditions: Methodological aspects for nanoecotoxicology investigations, Science of The Total Environment, 463–464 (2013) 647-656.

[15] C. Gunawan, A. Sirimanoonphan, W.Y. Teoh, C.P. Marquis, R. Amal, Submicron and nano formulations of titanium dioxide and zinc oxide stimulate unique cellular toxicological responses in the green microalga Chlamydomonas reinhardtii, J Hazard Mater, 260 (2013) 984-992.

[16] F. Hong, X. Zhao, W. Si, Y. Ze, L. Wang, Y. Zhou, J. Hong, X. Yu, L. Sheng, D. Liu, B. Xu, J. Zhang, Decreased spermatogenesis led to alterations of testis-specific gene expression in male mice following nano-TiO exposure, J Hazard Mater, 300 (2015) 718-728.

[17] G. Gao, Y. Ze, X. Zhao, X. Sang, L. Zheng, X. Ze, S. Gui, L. Sheng, Q. Sun, J. Hong, X. Yu, L. Wang, F. Hong, X. Zhang, Titanium dioxide nanoparticle-induced testicular damage, spermatogenesis suppression, and gene expression alterations in male mice, J Hazard Mater, 258-259 (2013) 133-143.

[18] L. Sheng, L. Wang, X. Sang, X. Zhao, J. Hong, S. Cheng, X. Yu, D. Liu, B. Xu, R. Hu, Q. Sun, J. Cheng, Z. Cheng, S. Gui, F. Hong, Nano-sized titanium dioxide-induced splenic toxicity: a biological pathway explored using microarray technology, J Hazard Mater, 278 (2014) 180-188.

[19] S. Gui, Z. Zhang, L. Zheng, Y. Cui, X. Liu, N. Li, X. Sang, Q. Sun, G. Gao, Z. Cheng, J. Cheng, L. Wang, M. Tang, F. Hong, Molecular mechanism of kidney injury of mice caused by exposure to titanium dioxide nanoparticles, J Hazard Mater, 195 (2011) 365-370.

[20] R. Hu, L. Zheng, T. Zhang, G. Gao, Y. Cui, Z. Cheng, J. Cheng, M. Hong, M. Tang, F. Hong, Molecular mechanism of hippocampal apoptosis of mice following exposure to titanium dioxide nanoparticles, J Hazard Mater, 191 (2011) 32-40.

[21] Z. Luo, Z. Wang, Q. Wei, C. Yan, F. Liu, Effects of engineered nano-titanium dioxide on pore surface properties and phosphorus adsorption of sediment: its environmental implications, J Hazard Mater, 192 (2011) 1364-1369.

[22] H. Liu, D. Yang, H. Yang, H. Zhang, W. Zhang, Y. Fang, Z. Lin, L. Tian, B. Lin, J. Yan, Z. Xi, Comparative study of respiratory tract immune toxicity induced by three sterilisation nanoparticles: Silver, zinc oxide and titanium dioxide, Journal of Hazardous Materials, 248-249 (2013) 478-486.

[23] A. Al-Kattan, A. Wichser, R. Vonbank, S. Brunner, A. Ulrich, S. Zuin, Y. Arroyo, L. Golanski, B. Nowack, Characterization of materials released into water from paint containing nano-SiO2, Chemosphere, 119 (2015) 1314-1321.

[24] J. Labille, J. Feng, C. Botta, D. Borschneck, M. Sammut, M. Cabie, M. Auffan, J. Rose, J.Y. Bottero, Aging of TiO(2) nanocomposites used in sunscreen. Dispersion and fate of the degradation products in aqueous environment, Environ Pollut, 158 (2010) 3482-3489.

[25] N. Shandilya, O. Le Bihan, C. Bressot, M. Morgeneyer, Emission of titanium dioxide nanoparticles from building materials to the environment by wear and weather, Environ Sci Technol, 49 (2015) 2163-2170.

[26] U. Olofsson, L. Olander, A. Jansson, Towards a model for the number of airborne particles generated from a sliding contact, Wear, 267 (2009) 2252-2256.

[27] M. Vorbau, L. Hillemann, M. Stintz, Method for the characterization of the abrasion induced nanoparticle release into air from surface coatings, Journal of Aerosol Science, 40 (2009) 209-217.

[28] S. Stewart, R. Ahmed, Rolling contact fatigue of surface coatings—a review, Wear, 253 (2002) 1132-1144.

[29] N. Govindarajan, R. Gnanamoorthy, Study of damage mechanisms and failure analysis of sintered and hardened steels under rolling-sliding contact conditions, Mat Sci Eng a-Struct, 445 (2007) 259-268.

[30] Y. Ding, N.F. Rieger, Spalling formation mechanism for gears, Wear, 254 (2003) 1307-1317.

[31] W. Wohlleben, S. Brill, M.W. Meier, M. Mertler, G. Cox, S. Hirth, B. von Vacano, V. Strauss, S. Treumann, K. Wiench, L. Ma-Hock, R. Landsiedel, On the Lifecycle of Nanocomposites: Comparing Released Fragments and their In-Vivo Hazards from Three Release Mechanisms and Four Nanocomposites, Small, 7 (2011) 2384-2395.

[32] D. Gohler, M. Stintz, L. Hillemann, M. Vorbau, Characterization of nanoparticle release from surface coatings by the simulation of a sanding process, Ann Occup Hyg, 54 (2010) 615-624.

[33] B.J. Thio, D. Zhou, A.A. Keller, Influence of natural organic matter on the aggregation and deposition of titanium dioxide nanoparticles, J Hazard Mater, 189 (2011) 556-563.

[34] H. Godwin, C. Nameth, D. Avery, L.L. Bergeson, D. Bernard, E. Beryt, W. Boyes, S. Brown, A.J. Clippinger, Y. Cohen, M. Doa, C.O. Hendren, P. Holden, K. Houck, A.B. Kane, F. Klaessig, T. Kodas, R. Landsiedel, I. Lynch, T. Malloy, M.B. Miller, J. Muller, G. Oberdorster, E.J. Petersen, R.C. Pleus, P. Sayre, V. Stone, K.M. Sullivan, J. Tentschert, P. Wallis, A.E. Nel, Nanomaterial categorization for assessing risk potential to facilitate regulatory decision-making, ACS Nano, (2015) 3409-3417.

[35] D.H. Brouwer, G. Lidén, C. Asbach, M.G.M. Berges, M. van Tongeren, Chapter 5 - Monitoring and Sampling Strategy for (Manufactured) Nano Objects, Agglomerates and Aggregates (NOAA): Potential Added Value of the NANODEVICE Project, in: U.V.S.W.v.T.B. Berges (Ed.) Handbook of Nanosafety, Academic Press, San Diego, 2014, pp. 173-206.

[36] ISO, XP ISO/TS 12901-1 Nanotechnologies — Occupational risk management applied to engineered nanomaterials — Part 1: Principles and approaches, in, 2012, pp. 37

[37] C.L. Bianchi, S. Gatto, C. Pirola, M. Scavini, S. Vitali, V. Capucci, Micro-TiO2 as a starting material for new photocatalytic tiles, Cement and Concrete Composites, 36 (2013) 116-120.

[38] R. Kaegi, A. Ulrich, B. Sinnet, R. Vonbank, A. Wichser, S. Zuleeg, H. Simmler, S. Brunner, H. Vonmont, M. Burkhardt, M. Boller, Synthetic TiO2 nanoparticle emission from exterior facades into the aquatic environment, Environ Pollut, 156 (2008) 233-239.

[39] J.P. Kaiser, S. Zuin, P. Wick, Is nanotechnology revolutionizing the paint and lacquer industry? A critical opinion, Sci Total Environ, 442 (2013) 282-289.

[40] M.J. Hanus, A.T. Harris, Nanotechnology innovations for the construction industry, Progress in Materials Science, 58 (2013) 1056-1102.

[41] D. Synnott, N. Nolan, D. Ryan, J. Colreavy, S.C. Pillai, 14 - Self-cleaning tiles and glasses for eco-efficient buildings, in: F. Pacheco-Torgal, M.V. Diamanti, A. Nazari, C.G. Granqvist (Eds.) Nanotechnology in Eco-Efficient Construction, Woodhead Publishing, 2013, pp. 327-342.

[42] A. Fujishima, X.T. Zhang, D.A. Tryk, TiO2 photocatalysis and related surface phenomena, Surface Science Reports, 63 (2008) 515-582.

[43] L.Y. Hsu, H.M. Chein, Evaluation of nanoparticle emission for TiO2 nanopowder coating materials, Journal of Nanoparticle Research, 9 (2007) 157-163.

[44] S.J. Froggett, S.F. Clancy, D.R. Boverhof, R.A. Canady, A review and perspective of existing research on the release of nanomaterials from solid nanocomposites, Particle & Fibre Toxicology, 11 (2014) 1-28.

[45] E. Sánchez, J. García-Ten, V. Sanz, A. Moreno, Review: Porcelain tile: Almost 30 years of steady scientific-technological evolution, Ceramics International, 36 (2010) 831-845.

[46] M. Dondi, G. Ercolani, C. Melandri, C. Mingazzini, M. Marsigli, The chemical composition of porcelain stoneware tiles and its influence on microstructural and mechanical properties, in, Germany, VERLAG SCHMID GMBH, 1999, pp. 75-83

[47] J. Martin-Marquez, J.M. Rincon, M. Romero, Effect of firing temperature on sintering of porcelain stoneware tiles, Ceramics International, 34 (2008) 1867-1873.

[48] D.B. Warheit, How to measure hazards/risks following exposures to nanoscale or pigment-grade titanium dioxide particles, Toxicology Letters, 220 (2013) 193-204.

[49] ASTM International, Standard test methods for dry abrasion mar resistance of high gloss coatings ASTM D6037. , 1996.

[50] ASTM International Standard test method for the abrasion of organic coatings by the Taber abradant ASTM D4060, 2007[

51] ASTM International Standard test method for resistance of transparent plastics to surface abrasion, ASTM D1044., (2008).

[52] M.M. Hassan, H. Dylla, L.N. Mohammad, T. Rupnow, Evaluation of the durability of titanium dioxide photocatalyst coating for concrete pavement," Construction and Building Materials, 2010

[53] N. Shandilya, O. Le Bihan, C. Bressot, M. Morgeneyer, Evaluation of the particle aerosolization from n-tio2 photocatalytic nanocoatings under abrasion, Journal of Nanomaterials, Article ID 185080 (2014) 11 pages.

[54] Le Bihan O., Morgeneyer M., Shandilya N., Aguerre-Chariol O., B. C, Handbook on Safe Use of Nanomaterials: Chapter 9.2 – Emission chambers, a method for nanosafety,, in: A.P. Elsevier Inc., San Diego, California, USA, 2014 (Ed.), 2014.[55] N. Shandilya, O. Le Bihan, M. Morgeneyer, Effect of the Normal Load on the Release of Aerosol Wear Particles During Abrasion, Tribology Letters, 55 (2014) 227-234.

[56] B. R'mili, O.L.C. Le bihan, C. Dutouquet, O. Aguerre-charriol, E. Frejafon, Particle Sampling by TEM Grid Filtration, Aerosol Science and Technology, 47 (2013) 767-775.

[57] N. Shandilya, O. Le Bihan, M. Morgeneyer, Effect of the Normal Load on the Release of Aerosol Wear Particles During Abrasion, Tribol Lett 55 (2014) 227–234.

[58] I.K. Koponen, K.A. Jensen, T. Schneider, Sanding dust from nanoparticle-containing paints: Physical characterisation, Journal of Physics: Conference Series, 151 (2009) 012048.

[59] F. Gottschalk, B. Nowack, The release of engineered nanomaterials to the environment, J Environ Monit, 13 (2011) 1145-1155.[60] N. Manier, A. Bado-Nilles, P. Delalain, O. Aguerre-Chariol, P. Pandard, Ecotoxity of non-aged and aged CeO2 nanomaterials towards freshwater microalgae, Environ Pollut, 180 (2013) 63-70.