Environmental impact of nano-functionalized construction materials: leaching of titanium and nitrates from photocatalytic pavements under outdoor conditions

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HIGHLIGHTS

- Evaluation of side effects of photocatalytic pavements to aquatic ecosystems
- TiO_2 nanoparticles leached from photocatalytic pavements
- Nitrates due to photocatalytic processes collected in rainwater
- Monitoring in real outdoor conditions 7 different materials for more than 800 days

GRAPHICAL ABSTRACT

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ABSTRACT

There is a growing use of nano-functionalized construction materials, which contain nanoparticles embedded in their bulk or deposited on their surfaces. In the case of photocatalytic materials, nano- TiO_2 is usually added to provide its functionality. One concern about these materials, in addition to release of nanoparticles as airborne, is that they can be leached into the aquatic environment. Moreover, water eutrophication could be caused due to the increase in NO_3^- as a product of the photocatalytic oxidation of NO_x in runoff. In this paper, a systematic long term campaign assessing these potential side effects in the real outdoor environment has been carried out. Rainwater leachates from 4 m^2 slabs of 7 different photocatalytic materials exposed outdoors in two different locations (platforms) were collected and analysed over more than 800 days. Ti , NO_3^- , pH and conductivity were analysed. Ti was found in the leachates of almost every material, without a clear relation with the type of application (percolated cementitious slurry, suspension/emulsion or TiO_2 built-in). The highest concentration found was of $60 \mu\text{g/L}$, which seems to be rather small when comparing with some threshold values for drinking water. In all the cases, the detected TiO_2 nanoparticles from water leachates were embedded in large microparticle agglomerates coming from the construction material matrix, which are less dangerous than nanoparticles. Nitrates were leached in clear relation with the NO_x oxidation photocatalytic performance, and the observed concentrations were not higher than those in the recycled water used by the Madrid City Council to clean the streets.

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1. Introduction

The incorporation of nanoparticles into construction materials is an increasing tendency. Among the different functionalities introduced

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by nanoparticles, photocatalysis (Fujishima and Honda, 1972), by incorporation of nanosemiconductors, mainly TiO_2 , in the materials, has developed over the last few decades as a promising technology to remediate air quality (Bengtsson and Castellote, 2014; Cassar, 2004; Chen and Poon, 2009; Hüsken, 2009; Bengtsson and Castellote, 2010; Dillert et al., 2013; Jimenez-Relinque and Castellote, 2014; Sánchez et al., n.d.; Jiménez-Relinque et al., 2019), self-sterilize (Goswami et al., 1997; Sikora et al., 2017), self-clean (Bengtsson and Castellote, 2014; Folli et al., 2009; Peruchon et al., 2009; Folli et al., 2012; Diamanti et al., 2013), impart anti-fog capabilities (Cannavale et al., 2010), degrade pollen and allergens (Sapiña et al., 2013; Jimenez-Relinque et al., 2016; Sapiña et al., 2017) and remove soot (Smits et al., 2013).

However, the benefits of adding nanoparticles to construction materials are starting to be offset by concerns about possible unwanted effects (Chapman, 2006; Bystrzejewska-Piotrowska et al., 2009; Dwivedi et al., 2015; Buzea et al., 2007; Pacheco-Blandino et al., 2012). It is becoming clear that in addition to the advantages, there are some drawbacks of using nanotechnology mainly related to the nanoparticles potential to behave as harmful environmental contaminants after their release; although not conclusive in humans, there are experimental evidences that ultrafine particles are causally involved in adverse responses seen in sensitive humans (Zhu et al., 2004; Pacheco-Torgal and Jalali, 2011; Jayapalan et al., 2013). Even though they are not aerosolized, nanoparticles may be released in other media, such as in water runoff, affecting aquatic ecosystems (Lovern et al., 2007; Federici et al., 2007), which are especially vulnerable due to the potential of pollutant mixing and dispersal. Another possible unwanted effect of the use of photocatalysts in construction is the potential for water eutrophication due to the increase in NO_3^- in the water runoff (Devahastin et al., 2003; Herrmann, 1999; Ansari et al., 2010), which is the product of the photocatalytic oxidation of NO_x .

Despite the several studies on different aspects of photocatalytic construction materials, only a few papers address the leaching of Ti and the production of NO_3^- . To the best of the authors' knowledge, the first data of leached Ti from photocatalytic construction materials under natural wear were reported by Kägi et al. (2008), who described

concentrations of Ti in the runoff of a new facade as high as $600 \mu\text{g/L}$ over the period of one complete rain event. No other paper addressing leached Ti from photocatalytic construction materials under natural exposure has been found. There are some reports of laboratory trials on the leaching of photocatalytic construction materials. In Olabarrieta et al. (2012), in accelerated ageing under a water flow of two different photocatalytic coatings, TiO_2 concentrations of up to $150.5 \mu\text{g/L}$ were found. Al-Kattan, 2013 investigated the release of Ti from panels covered in paint with and without nano TiO_2 that were exposed to simulated weathering by sunlight and rain in climate chambers and observed a very low release that was close to background values. Zuin et al. (2014) performed leaching tests of TiO_2 , Ag and SiO_2 nanoparticles contained in experimental water-borne paints by using a permanent immersion procedure and reported "a very low release of Ti ($4\text{--}8 \mu\text{g/L}$)". Shandilya et al. (2015), after conducting experiments in a weathering chamber, also concluded that despite deterioration by weathering, the nanocoated sample surfaces were still strong enough to resist leaching of the constituent nanoparticles into the runoff water. Bossa et al. (2017) performed leaching of photocatalytic cement pastes simulating "a worst case scenario", and after 168 h of leaching, the total Ti released was $33.3 \pm 5.1 \text{ mg Ti/m}^2$ of cement for pastes with a water/cement ratio of 0.5.

From these results, it can be observed that there is relatively high variation in previous data, which can be attributed to the differences between the samples and the experimental procedures used. In most of these studies, samples were analysed by inductively couple plasma (ICP) techniques. As stated in Kägi et al. (2008) and demonstrated in Gibson et al. (2006), Goodall et al. (1993), Halicz et al. (1993), Wang (2005) and Wu et al. (2007) for Al_2O_3 , SiO_2 and TiO_2 , particles $<1.5 \mu\text{m}$ behave similarly in aqueous solutions and in an ICP source under standard hot plasma conditions. This implies that the recovery rates of the samples might have been artificially low due to incomplete ionization of particles $>1.5 \mu\text{m}$ in the plasma. However, the recovery of Ti nanoparticles could be considered complete when analysed with ICP techniques. Concerning the leaching of nitrates, in (Dylla and Hassan, 2014), TiO_2 nanoparticles and nitrates were measured after 4.5 h of photocatalytic oxidation of NO_x using environmentally relevant conditions, and 49%

Fig. 1. Details of the water collection system on the leaching workbenches (a–c) AR-P and (d) M-P.

Fig. 2. Application of photocatalytic materials on slabs: (a) cement slurries (A and B) (b) emulsions (C, D and E), and (c) built-in photocatalytic tiles (F and G).

of the theoretical amount of produced nitrates in water was recovered, while Ti was not detected in any of the samples. In (Hassan et al., 2012), the presence of nitrates was correlated with the activity of permeable pavement under different environmental conditions.

Experiments reflecting the authentic outdoor exposure of photocatalytic construction materials as exposed to different factors taking place during natural weathering, such as time, rain, freeze-thaw cycling, drying and saturation, wind, natural irradiation or other damaging agents, have not been found in the literature.

Within this context, as pioneering research, the aim of this paper is to assess the potential side effects of nanoparticles leaching, as well as possible release of nitrates generated by the photocatalytic oxidation of air nitrogen oxide, associated to the use of photocatalytic construction technologies in the real outdoor environment. Monitoring of the leachates in rainwater after coming into contact with 4 m² slabs of 7 different photocatalytic materials exposed outdoors in two different locations was carried out for 800 days pH, conductivity and the amount of Ti and NO₃⁻ for each material were analysed.

2. Materials and methods

2.1. Testing site

This research was framed within the LIFE-PHOTOSCALING project (LIFE 13/ENV/ES/001221), where duplicate demonstration platforms were constructed on a pilot scale (www.lifephotoscaling.eu). Both platforms were located at the premises of the IETcc-CSIC, one of them in the north of the city of Madrid (M-P) and the other in the city of Arganda del Rey (AR-P) in the region of Madrid. Each platform consisted of 3 workbenches (*leaching, abrasion and natural exposure*), each of which contained sets of slabs of photocatalytically active materials exposed outdoors. The results reported in this paper were carried out on the *leaching workbenches*.

The *leaching workbenches* were composed up of 4 m² slabs of different photocatalytic materials. The *leaching workbenches* were constructed with a slight slope to drive the leachates through a mesh strainer to a pipe that channelled them into an individual collector for each material. The different materials were limited by curbs so that runoff coming from different tests and rainwater were not mixed between the different materials (see Fig. 1).

7 photocatalytic materials were installed between October and November 2016 in both platforms, and leaching samples were taken immediately after installation until February 2019.

The types of material tested were the following:

- I. Photocatalytic slurries percolated on asphalt substrates (slabs A and B)
- II. Photocatalytic suspensions/emulsions sprayed on asphalt and cementitious tiles (slabs C, D and E)
- III. Factory-supplied photocatalytic tiles with TiO₂ built-in (slabs F and G)

A reference slab from plain, non-photocatalytic concrete (Ref) was also incorporated in both leaching workbenches.

In Fig. 2, examples of the application of the photocatalytic materials are given. The materials were labelled from A to G without identifying them specifically for confidentiality reasons.

2.2. Procedure

2.2.1. Leachate collection and analysis

Rain runoff from each of the slabs on the *leaching workbenches* was collected separately in plastic containers (see Fig. 1d) and analysed to evaluate the Ti and NO₃⁻ contents, pH and conductivity for 800 days. Samples were also collected from plain, non-photocatalytic concrete (Ref) for the last 300 days of the study.

In addition to the rainwater, on three different occasions, high-pressure water cleaning in the streets of Madrid was recreated at the M-P site (Fig. 3). Madrid City Council (MCC) staff conducted the high-pressure water cleaning using a real pressurized water tank truck. The water pressure was obtained with a pump (Zeda pump zh 40, 40–45 m³/h, 8 bar).

Ti was analysed using a Varian 725 ICP-optical emission spectrometry (OES) instrument at a 1.25 kW power and a 15 L/min flux of plasma. Nitrates were analysed colorimetrically using a UV/VIS spectrophotometer. To perform this measurement, a VISOCOLOR® nitrate kit was used. The VISOCOLOR® nitrate kit made measurement of the nitrate concentration in water solutions through a colorimetric chemical reaction. The nitrates were reduced to nitrite with an inorganic reducing agent. Nitrite was then diazotized with an aromatic amine and simultaneously coupled to form an azo dye (yellow colour). Therefore, the resulting intensity of the yellow colour was directly related to the concentration of the nitrates. To perform a calibration curve for quantitative measurement of nitrates, the CIELAB b* coordinate (yellow) was used with solutions of AgNO₃ at different concentrations. In addition, leachate samples were investigated using field emission scanning electron microscopy (FE-SEM) images with

Fig. 3. High-pressure water cleaning at the Madrid platform by a staff member of the Madrid City Council.

Fig. 4. Evolution of a) pH and b) conductivity of the runoff water collected at M-P.

energy-dispersive X-ray spectrometry (EDX) measurements to detect TiO_2 micro- and nanoparticles and to determine the features of release.

2.2.2. Measurement of NO_x removal

The photocatalytic efficiency for NO_x removal (R_{NO_x} , %) was assessed on-site at different times by means of the PhotonSite device (Jiménez-Relinque et al., 2019). The operational conditions of the tests were 450 ± 50 ppb of NO gas in air at a flow rate of 3 L/min with a relative humidity RH_{int} inside the chamber of approximately 25%. The irradiance inside the chamber was 10 W/m^2 (LEDs 365 nm) for 15 min. Prior to and after irradiation, the gas flow passed through the PhotonSite chamber until stabilization of the conditions. The NO_x concentration of the gas was monitored using a chemiluminescence analyser (AC-32 M, Environment S.A.). The pavement was not preconditioned prior to the measurements. Additionally, R_{NO_x} (%) was measured at the time of application of photocatalytic materials at the laboratory according to the standard ISO 22197-1:2007.

3. Results and discussion

3.1. pH and conductivity

The evolution of pH and conductivity of the leachates collected in the catch basins for each of the materials for M-P and AR-P are depicted in Figs. 4 and 5, respectively. In Fig. 4, the events of high-pressure water cleaning by the MCC are highlighted in yellow. The temporal point of

these episodes was not the same for all materials, as they were implemented over several months. Water used by the MCC to clean the slabs was, as is usual for cleaning the city, recycled water. This can be observed in Fig. 4-b, where an increase in the conductivity of the leachates was observed at approximately 270, 600 and 700 days, corresponding to the three campaigns of high-pressure water cleaning.

Concerning pH, the overall behaviour was quite similar on both platforms. The different materials started to leach at different pH values depending on their composition (B and G: above 10; A and C: approximately 8–9; and D, E and F: approximately 7.5). Then, the pH gradually and smoothly decreased at approximately 300 days, and then it increased more or less abruptly, depending on the material, stabilizing with an increasing tendency at approximately 600 days. At M-P, there were more differences in pH between materials than at AR-P. Only a small influence of high-pressure water cleaning was detected.

Concerning conductivity (corrected at 25°C), the evolution over time was similar at both platforms if the high values of conductivity observed for the water used by the MCC during high-pressure water cleaning was not taken into account. The conductivity increased initially and reached a kind of maximum at approximately 150–200 days and then decreased, exhibiting a period of low conductivity for approximately 100 days for every material; the conductivity increased during the subsequent approximately 100 days and then decreased again. At both platforms, the conductivity was higher for materials C, E and G than for the other materials, and the values corresponding to the reference slab were relatively low and followed the same tendency for both pH and conductivity.

Fig. 5. Evolution of a) pH and b) conductivity of the runoff water collected at AR-P.

Fig. 6. Leaching of Ti from the samples at a) M-P and b) AR-P.

3.2. Leaching of Ti

The results corresponding to the amount of Ti leached per unit area (mg/m^2) in each of the liquid samples collected are given in Fig. 6a and b for M-P and AR-P, respectively. As stated in the introductory section, the analytical method used was expected to recover particles $<1.5 \mu\text{m}$ in size. Thus, even though the amount of Ti could be underestimated, the leached nanoparticles were included in these results. Values found for the reference slab were always below the limit of detection of the analytical technique ($2 \mu\text{g/L}$).

For both platforms, from the 50th day, no Ti was found in the leachates, with the results always being below the detection limit of the instrument used. After 100 days, no Ti was detected with the exception of the samples taken after the high-pressure water cleaning carried out by the MCC at M-P (circled points in Fig. 6).

The accumulated Ti contents measured during the whole period are given in Fig. 7, where it can be seen that the trend for different materials was the same at both platforms, with smaller values observed for the materials at AR-P because the volume of the containers to collect the leachates was smaller. During episodes of heavy rain, the containers overflowed, so the volume considered to make the calculations was that of the full container. This caused the values in Fig. 6 to be underestimated and should therefore only be used for comparative purposes of the behaviour of the different materials, which was quite consistent between the two platforms.

To obtain real reference values, the concentration of Ti in the leachate was considered. The highest concentrations found for the different materials at M-P and AR-P are listed in Table 1, where the accordance between the platforms can be again observed for the different materials.

These results are in accordance with the wide variety of data reported in the literature, as under the same conditions independent of the level of efficiency, some products leached Ti while others did not. Beside this, there is no clear behaviour on the basis of the type of application (slurry, suspension or TiO_2 built-in). This finding suggests that before a real implementation of photocatalytic materials, it is necessary to ensure that the material does not leach Ti nanoparticles into aqueous media. The significance of the levels of exposure has to be determined through toxicological studies, as will be discussed below.

Samples in which Ti was detected by ICP were deposited dropwise on amorphous carbon filters supported on copper transmission electron

microscopy (TEM) grids or on aluminium TEM grids and were allowed to dry. Then, the morphology and chemical composition of the particles in the substrate were analysed using FE-SEM and EDX. Ti was only detected in two samples, which corresponded to materials C and E at AR-P (see Fig. 8). Fig. 8-a and d give a general view of the particles on the grid. The general image shows sparse micrometre-sized particles. Most of the observed particles had high contents of Ca, Al, Si, O, Mg, Na, K and other elements, which suggests that these particles mostly originated from the substrates of the materials. At higher magnification, fine and ultrafine particles could be distinguished. In some of them, seem as brighter points in Fig. 8-b and c, Ti nanoparticles could be detected attached to larger micrometre-sized particles (Fig. 8-c and f). No isolated Ti nanoparticles were detected. The release of TiO_2 nanoparticles embedded into micro size particles of construction material matrix may prevent the potential harmful environmental and health effect of the isolated TiO_2 nanoparticles.

Fig. 7. Accumulated values of Ti leached (mg/m^2) for the different materials on both localizations.

Table 1
Highest leachate Ti concentrations ($\mu\text{g/L}$) observed for the different materials on platforms M-P and AR-P.

Platform	A	B	C	D	E	F	G	Ref
M-P	42	9	48	28	2	11	<2	<2
AR-P	46	8	60	36	7	<2	<2	<2

3.3. Leaching of nitrates

The concentration of NO_3^- (ppm) in the leachates from the materials on both platforms are given in Fig. 9(a–b), where the events of high-pressure water cleaning at M-P have been highlighted in yellow, and the upper value of the highlighted area represents the concentration of NO_3^- in the recycled water used during cleaning. The mean value for rainwater is also given in the figure. It can be seen that the pattern of Fig. 9-a was clearly influenced by the amount of nitrates in the leaching agent; thus, further analysis on the leaching of nitrates will be carried out on the AR-P data (Fig. 9-b). From Fig. 9-b, it can be seen that the maxima concentration is at approximately the beginning of monitoring, between 200 and 350 days and at 600 days and no noticeable NO_3^- leaching occurring between these time points. To discriminate the amount of NO_3^- that originated from the photocatalytic oxidation of NO_x , the accumulated value of NO_3^- collected from the reference slab was subtracted from the values of the leachate samples collected during the same period from the photocatalytic slabs, which were higher than the reference value for all materials. This result indicated that the excess nitrates might be assigned to the photocatalytic oxidation of atmospheric NO_x . As the absolute NO_3^- values were underestimated, as for Ti, the results were normalized with respect to the material that leached the most NO_3^- and are presented in Fig. 10-a.

Fig. 10-a shows that the largest amount of nitrates during the accumulated period (last 300 days) corresponded to the leachate from material E. The leached nitrate ranking of the samples was $E > G > D > A > C > F > B$. During this final period, the increase in leached nitrates for the photocatalytic platforms in relation to the reference material ranged from 14% for material B to 77% for material E.

The initial percentage of nitrogen oxide removal, R_{NO_x} (%), for each material was determined according to the standard ISO 22197-1:2007. In addition, on-site measurements were performed at the platforms at different times using the PhotonSite prototype (Jiménez-Relinque et al., 2019). The normalized values of accumulated NO_3^- versus R_{NO_x} for the initial values determined at the laboratory and for the values obtained in July 2018 (likely pre-activated by sunlight), within the period of the last 300 days for AR-P are presented in Fig. 10-b, illustrating that a

positive relationship exists between the photocatalytic activity and the production of nitrates. The correlation coefficient is much better for that corresponding to on-site values.

3.4. Overall behaviour

First, it should be mentioned that the slabs on both platforms were subjected to semi-controlled conditions, and even though all water was driven to the sampling containers through a light slope, they were located in the open air and subject to uncontrolled and unforeseen events. At M-P, samples were taken for almost every rain event; even though the authors tried to collect the leachates as soon as possible, on several occasions (as heavy rain during weekends), the containers were full, and water had overflowed. It could have also been the case that some samples underwent partial evaporation, especially during the hotter months, as the sampling containers were not airtight. As the slabs were cleaned only by rain (and also by high-pressure water in the case of M-P), dirt, leaves and mud were occasionally present in the containers, which could have interfered with the measurements. Additionally, there are stray cats on the premises of the IETcc in Madrid, which were seen several times near the slabs. Therefore, attention must be paid to the tendencies and comparative values within each platform more than to specific values. On the other hand, it should be noted that effects on leaching, such as the abrasion of tires, aggressive detergents or other factors, were not considered.

A comparison of the data from the meteorological stations of M-P and AR-P indicated that even though there were small differences (data not shown), the locations were same geographical region, and the general trends were very similar. However, the concentration of NO_2 was different between the two locations and was higher at M-P in Madrid than at AR-P in Arganda del Rey. The monthly average concentrations of NO_2 in both locations (data taken from the air quality stations closest to both platforms) are presented in Fig. 11, where the relative humidity, total radiation and precipitation for Madrid are also given. Values of nitrates for both platforms (mg/m^2) are depicted as isolated points. It should be noted that the meteorological station in the specific location of the platforms started to run in April 2017, so data corresponding to precipitation from 01/10/2016 to 31/03/2017 were taken from the nearest meteorological station in Madrid.

In addition to the data in Fig. 10-b, Fig. 11 shows that nitrate leaching is clearly related to the factors affecting the photocatalytic activity. During the periods corresponding to a high relative humidity and low solar irradiation on the platforms, almost no nitrates were leached (November to January), and the level of leached nitrates increased with increasing radiation and decreasing relative humidity (around March) with higher amounts of NO_2 . On the other hand, the total amount of nitrates

Fig. 8. SEM images of leachate samples from material C at AR-P (a–c) and of material E at AR-P (d–f). a and d) General view of the grid with the sample particles at 350 $\times$ magnification; b and e) particles that contained titanium; (c and f) EDX spectra of the areas marked in figures (b) and (e).

Fig. 9. Concentration of nitrates (ppm) in the leachates. a) M-P; b) AR-P. The events of high-pressure water cleaning in M-P are highlighted in yellow, the upper value of which is the concentration of NO_3^- of the recycled water used during cleaning. The mean values obtained for rainwater are also shown.

decreased overall as the photocatalytic activity decreased over time (Al-Kattan, 2013). Additionally, in correspondence with the smaller amount of leached nitrates, the pH of the leachates increased during the periods of no photocatalytic activity, which might be attributed to the non-occurrence of decomposition of water at the holes (h^+) of photocatalyst, which led to the formation of H^+ ($\text{H}_2\text{O} + \text{h}^+ \rightarrow \bullet\text{OH} + \text{H}^+$).

Leaching of Ti did not seem to be related to ageing factors, as Ti was only detected in the leachates during the first few days of monitoring. During the weathering and degradation of the materials, Ti was only detected when the materials were high-pressure water cleaned (11 $\mu\text{g/L}$ for material C after the first cleaning and 2 $\mu\text{g/L}$ for materials A and E after the third cleaning). Concerning the effects of nano- TiO_2 on humans and the environment, most references are found for airborne (D.-G.f.E. European Commission, 2020). Recently, the Committee for Risk Assessment in its Opinion of 14 September 2017 proposed to classify respirable TiO_2 as carcinogen category 2 by inhalation to mixtures in powder

form containing 1% or more of TiO_2 which is in the form of or incorporated in particles with aerodynamic diameter $\leq 10 \mu\text{m}$ (Nevshupa et al., 2020). In our best knowledge no normative references have been found on admissible limits for the concentration of Ti in water. According a compilation by ECHA (European Chemicals Agency) in July 2020 (ECHA, 2020), concerning aquatic toxicity, micro- and nano- TiO_2 is not acutely and chronically toxic to aquatic organisms. Concerning sediments micro- and nano- TiO_2 appear to have a low potential for acute and chronic freshwater and marine sediment toxicity based on data available for insect, crustacean and annelid species (ECHA, 2020). Concerning terrestrial toxicity, data from standard toxicity tests indicate that micro- and nano- TiO_2 materials are not toxic to soil organisms including microbes, plants and invertebrates up to at least 1000 mg/kg soil (ECHA, 2020). Other authors found different results. Simonin et al. (2017) using soil microcosms, with nano- TiO_2 concentrations ranging from 0.05 to 500 mg/kg dry-soil found that after 90 days of exposure, non-classical dose-response relationships were observed for nitrifier abundance or activity, making threshold concentrations impossible to compute even though significant reduction in the different colonies were found. Adams et al. (2006) found bacterial growth inhibition, in presence of nano- TiO_2 even under dark conditions, highlighting the need for caution during the use and disposal of such manufactured nanomaterials to prevent unintended environmental impacts. Thus, as a normative reference, the Drinking Water Parameter Cooperation Project, in support of the revision of Annex I Council Directive 98/83/EC on the Quality of Water Intended for Human Consumption (Drinking Water Directive) published by the WHO (2017), can be used. This document stated that several emerging contaminants and groups of contaminants were considered but not given any parametric value because the data show that concern for health was highly unlikely. Among the contaminants considered, nanoparticles were included under the paragraph “While there are very few data to show that they reach drinking-water, there is some evidence that they would be removed in treatment (FERA, 2011). However, there are no appropriate means of measuring them or setting drinking-water standards at this time, but it would be appropriate to ensure that any proposals to include them in materials for use in contact with drinking-water should be assessed under a European approval scheme”. As a matter of comparisons, according to WHO (2017) the parametric values for arsenic and chromium are 10 and 50 $\mu\text{g/L}$, respectively. For copper, the parametric value is 2000 $\mu\text{g/L}$. These values can be compared with those obtained for Ti in this research, which had a maximum concentration of 60 $\mu\text{g/L}$.

Fig. 10. Normalized values of accumulated nitrates leached from materials at AR-P during the last 300 days of exposure a) for individual materials and b) as a function of photocatalytic efficiency.

Fig. 11. Values of nitrate concentrations collected at both platforms (mg/m^2) (circles: M-P; squares: AR-P). Meteorological parameters and mean concentration of NO_2 at the station of Madrid (continuous lines).

Concerning NO_3^- , the relationship between the photocatalytic activity of the materials and an increase in nitrates in the runoff waters was clearly observed. In any case, the observed values were lower than that in the recycled water used to clean the streets of Madrid in the high-pressure water process. According to the Directive 2006/118/EC on the protection of groundwater against pollution and deterioration, one of the criteria for groundwater quality standards is related to nitrates and is set to 50 mg/L . This is also the threshold chemical reviewed by WHO in 2011. This threshold was never reached as a consequence of the photocatalytic activity of the materials tested (AR-P).

4. Conclusions

This paper presents a systematic and long-term study assessing the potential side effects associated with the use of photocatalytic construction technologies in outdoor environment. Leaching of Ti as well as nitrates generated by the photocatalytic oxidation of nitrogen oxides have been evaluated by analyzing the leachates coming from rainwater after lapping slabs of $2 \text{ m} \times 2 \text{ m}$ of 7 different materials exposed in two locations during more than 800 days. The following main conclusions have been derived:

- Almost every material released TiO_2 , not having found a clear behaviour with the type of photocatalytic material/application (slurry, suspension or TiO_2 built-in). The higher concentration found was of 60 $\mu\text{g}/\text{L}$ corresponding to a suspension coating while the highest accumulated amount corresponds to a cementitious slurry percolated on asphalt. One of the built-in TiO_2 photocatalytic tile, presented always Ti values under the limit of detection of the analytic equipment used ($<2 \mu\text{g}/\text{L}$). Comparison of the concentration values found for Ti with the threshold limits for some metals for drinking water, the amount of Ti leached seems to be rather small.
- All the observed TiO_2 nanoparticles in the leachates were embedded in large microparticle agglomerates of the construction matrix, which is less dangerous than release of nanoparticles.
- Leaching of Ti did not seem to be related to ageing factors, as Ti was only detected in the leachates during the first few days of monitoring.
- Nitrates were leached in clear relation with the nitrogen oxide photocatalytic oxidation performance. Even though, the concentration of nitrates found in the samples leached was mostly lower than what it is

normally found in recycled waters, used for street cleaning by the Madrid City Council and other applications.

CRediT authorship contribution statement

Eva Jimenez-Relinque: Investigation, Writing - review & editing, Visualization. **Maria Grande:** Investigation. **Teresa Duran:** Investigation. **Ángel Castillo:** Methodology, Investigation. **Marta Castellote:** Conceptualization, Methodology, Writing - original draft, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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