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Detection and quantification of engineered particles in urban runoff

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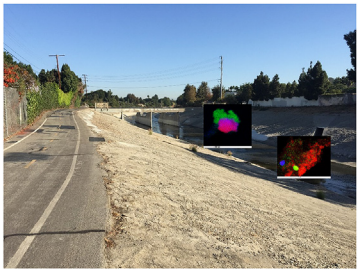
HIGHLIGHTS

- Analysis of engineered and anthropogenic nanoparticles in urban runoff.
- Wet- and dry-runoff convey engineered nanoparticles and pigments to the urban environment.
- Urban runoff is a source of TiO_2 engineered nanoparticle release to the environment.
- Elemental ratios of Ti to Nb are used to estimate the concentrations of TiO_2 engineered in urban runoff.
- The occurrence of TiO2 nanoparticles and pigments was confirmed by TEM-EDS analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

Urban runoff conveys contaminants including titanium dioxide (TiO_2), widely used as engineered nanoparticles (*e.g.*, 1–100 nm) and pigments (*e.g.*, 100–300 nm) in the urban environment, to receiving surface waters. Yet, the concentrations of TiO_2 engineered particles (*e.g.*, engineered nanoparticles and pigments) in urban runoff has not been determined due to difficulties in distinguishing natural from engineered TiO_2 particles in environmental matrices. The present study examines the occurrence and estimates the concentrations of TiO_2 engineered particles in urban runoff under wet- and dry-weather conditions. Urban runoff was collected from two bridges in Columbia, South Carolina, USA under wet-weather conditions and from the Ballona Creek and Los Angeles (LA) River in Los Angeles, California, USA under dry-weather conditions. The concentrations of TiO_2 engineered particles were determined by mass balance calculations based on shifts in elemental concentration ratios in urban runoff relative to natural background elemental ratios. Elemental ratios of Ti to Nb in urban runoff were higher than the natural background ratios, indicating Ti contamination. The occurrence of TiO_2 engineered particles was further confirmed by transmission electron microscopy coupled with energy dispersive spectroscopy. The concentration of TiO_2 engineered particles in urban runoff was estimated to be in the range of 5–150 μg L^{-1}. Therefore, this study identifies urban runoff as a previously unaccounted source of TiO_2

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engineered particle release to the environment, which should be included in engineered nanoparticle fate modeling studies and in estimating environmental release of engineered nanoparticles.

1. Introduction

Quantifying the concentrations of engineered particles, including TiO_2, in environmental systems is challenging because of the similarity of the physicochemical properties of engineered and natural particles; the high background concentration of natural particles (*ca.* 1–1000 mg L^{-1} in fresh waters) (Buffle and Van Leeuwen, 1992); and the low environmental concentrations of engineered particles (Gottschalk et al., 2009; Gottschalk et al., 2013). Nonetheless, engineered particles are typically produced with strict control on their properties to maximize their desired function for engineered applications. Consequently, engineered particles often possess well-defined properties such as elemental composition, purity, surface coating, narrow size distribution, and morphology (Christian et al., 2008). This in turn results in subtle differences in the physicochemical properties of natural and engineered particles such as elemental composition (Tong et al., 2015), elemental ratios (von der Kammer et al., 2012; Gondikas et al., 2014), and morphology (Luo et al., 2011), which can be exploited to differentiate natural from engineered particles. For instance, Nb has been suggested as a tracer for titanium containing natural particles because naturally occurring TiO_2 particles have been shown to be the major carrier phases for Nb in the rocks (Loosli et al., 2019a; Loosli et al., 2019b; Yi et al., 2019; Loosli et al., 2019c). On the other hand, TiO_2 engineered particles are relatively pure. In fact, All TiO_2 engineered particles, except TiO_2 used as a food additive, contain 1%–15% of artificial coatings by weight, most commonly oxyhydrates and oxides of silicon and aluminum (Working Group on the, 2010). Therefore, the increase in the elemental ratio of Ti to Nb, due to discharge of pure TiO_2 engineered particles, has been implemented to quantify the concentration of titanium oxide particles in surface waters impacted by sewage spills (Loosli et al., 2019a).

Although wastewater treatment plants, and thus sewage spills and combined sewer flows have received significant attention as major sources of engineered particles into the environment (Loosli et al., 2019a; Saharia et al., 2019; Kiser et al., 2009); other sources, such as urban runoff, have received much less attention (Baalousha et al., 2016). Engineered particles are widely used in the urban settings, which is expected to result in high concentrations of engineered particles in urban runoff (Baalousha et al., 2016). For instance, TiO_2 is widely used in paint as a pigment and in self-cleaning surfaces as a photocatalyst in urban settings. TiO_2 is used as pigment in white road marking, which contains at least 10% by weight TiO_2 pigments (ASTM. ASTM D7942 - 15, 2015). The volume of road marking material applied in the US is estimated at 350,000 metric tons in 2018 and is predicted to be 450,000 tons in 2025, including new infrastructure and repainting degraded paint (Grand View Research. http, 2018). Thus, the TiO_2 pigment used in road marking is estimated at 35,000 tons in 2018 and is predicted to be at 45,000 tons 2025, which may result in a significant release of TiO_2 pigment to urban runoff. Additionally, the US paint demand is estimated at 1.4 billion gallons in 2019, a third of which (*e.g.,* 470 million gallons) is used for exterior paint, which can also contribute to the release of TiO_2 into the urban environment (Coatingsworld, 2019).

Several studies identified the occurrence of titanium oxide particles in the urban environment. High concentrations of Ti were reported in different road-environment samples (*e.g.,* road dust, sludge from storm drains, and roadside soils), which were suspected to be of anthropogenic origin (Adamiec, 2017). Additionally, fine and ultrafine atmospheric particulate matter in Kraków, Poland have been reported to contain TiO_2 smaller than 100 nm as well as 0.5–4 μm aggregates composed of individual particles with sizes between 100 and 350 nm (Wilczynska-Michalik et al., 2014). The size distribution of these particles corresponds to pigmentary TiO_2, suggesting that they could be derived from paints and building material. Another study detected 200–300 nm TiO_2 in dust dry deposition in Daejeon and Seoul, Korea (Lee et al., 2016). A recent environmental fate modeling study suggested that stormwater runoff could result in high variability in TiO_2 concentrations in urban rivers (Parker and Keller, 2019). These studies suggested the occurrence of TiO_2 engineered particles in the urban environment based on measuring total Ti concentrations by elemental analysis, identifying few particles in a given sample using transmission electron microscopy (TEM), or based on environmental fate modeling. However, none of these studies provide measured quantitative data on the concentrations of TiO_2 engineered particles in the studied media including urban runoff.

The aim of this paper is to quantify the concentration of TiO_2 engineered particles in real urban runoff based on increases in the elemental ratios of Ti to Nb relative to their natural background elemental ratio.

2. Materials and methods

2.1. Sampling sites

Two wet weather runoff samples were collected from two bridges in Columbia, SC to evaluate the possible discharge of engineered particles from highways to surface water. The first bridge runoff sample (referred to as BR1) was collected during a rainy day (precipitation 0.5 mm) on January 28, 2018, from a bridge over Gills Creek on highway 760, known as Fort Jackson Blvd (33°59′31″N, 80°58′22″W). The main land use in the area is dominated by a small business district (commercial), and residential properties (City information viewer., 2019). The annual average daily traffic volume (AADT) was estimated at 10,000 in 2017 (SCDOT, 2017). The second bridge runoff sample (referred to as BR2) was collected on a rainy day (October 26, 2018, precipitation 0.8 mm) from a bridge on highway 176 known as Blossom Street in Columbia, South Carolina over the Congaree River (33°59′17″N, 81°2′48″W). The main land use in this area is residential with significant construction activity for additional residential buildings near the sampling site in 2018 (City information viewer., 2019). The AADT was estimated at 26,900 in 2017 (SCDOT, 2017).

Dry weather runoff samples were collected from Ballona Creek (34°0′43″N, 118°23′30″W) and Los Angeles (LA) River (34°07′48″N, 118°16′24″W) in Los Angeles, California on December 3rd, 2017. Ballona Creek and LA River were selected because they are designed for flood control and convey wet and dry runoff from urbanized areas to the Pacific Ocean. These samples were attributed to dry weather runoff from LA County because of the dry season and a lack of rainfall events preceding the water sampling day.

Ballona Creek is a 14 km-long waterway in southwestern LA County, California, USA. The Ballona Creek watershed receives runoff from the LA basin, which spans from the Santa Monica Mountain to the north, the Harbor Freeway (I-110) to the east, and Baldwin Hill to the South. Ballona Creek receives water from a 320 km^2 urban area with 82% developed, 61% impervious surface, and drains into Santa Monica Bay (Gold et al., 2015). Its land use consists of 64% residential, 8% commercial, 4% industrial, and 17% open space. The dry and wet weather runoffs in Ballona Creek are estimated at 10 and 70 million m^3 per year, respectively (Ackerman et al., 2005). The Ballona Creek banks are bordered by commercial, industrial, and residential properties, contributing dry-weather irrigation runoff from homes as well as runoff from industrial sites into the Creek.

The LA River starts in the Simi Hills and Santa Susana Mountains and flows through LA County, California, from Canoga Park in the western end of the San Fernando Valley, nearly 82 km southeast to its mouth in Long Beach. The river covers 2250 km^2 of watershed and winds through 14 cities. The LA River and its tributaries receive water from rainfall or snow melt during winter and irrigation runoff from LA County (2160 km^2) during summer, where the watershed is 49% developed and 30% impervious. The dry and wet weather runoffs in LA River are estimated at 32 and 623 million m^3 per year, respectively (LA's watershed protection, 2019).

2.2. Sample collection

Water samples from Ballona Creek and LA River were collected from the middle of the channel in a 1 L high-density polyethylene bottles (HPDE, Thermo Scientific, USA) following the USGS guidelines for collection of water samples (Wilde and Radtke, 1998). The sample locations in Ballona Creek and LA River are 5.6 km and 35 km into the downstream the point of origin. The typical chemical compositions of both waterbodies based on measurements for several months are summarized in Table S1. The bridge runoff samples were collected from drainpipes underneath the bridges in a 1 L high-density polyethylene bottles. Prior to use, bottles were soaked in 10% nitric acid (Acros Organics, Czech Republic) for at least 24 h followed by soaking in ultrapure water (UPW, PURELAB Option-Q, ELGA, UK) for 24 h, air dried, and then double-bagged. In the field, the sampling bottles were rinsed three times in the surface water before filling with the water sample. Samples were individually double-bagged and returned to the lab the same day, where they were stored at 4 °C in the dark until further analysis. All samples were digested with HF:HNO_3 (3:1) mixture (ACS grade acids distilled in the laboratory) and analyzed for total elemental concentrations using PerkinElmer NexION 350D ICP-MS according to the protocols described in detail in the supplementary information section (section S1 and S2) (Loosli et al., 2019a).

2.3. Particle extraction

To better understand the distribution of measured metals and particles among different size fractions, particles of different sizes (*e.g.,* <1000, <450, and <100 nm) from Ballona Creek water were extracted using ultrapure water (UPW) and $Na_4P_2O_7$ according to the previously established protocols (Loosli et al., 2018a). Ballona Creek water was first concentrated 24 times using an Amicon stirred cell (MilliporeSigma, USA) and 10 kDa Regenerated Cellulose membrane (EMD Millipore Corporation, USA, ~2 nm size cut-off), to ensure that the extracted suspensions contain sufficient particles for further analysis by ICP-MS and TEM. For UPW extraction, 1 mL of the concentrated natural water was transferred into a 15 mL polypropylene centrifuge tube (Fisherbrand, USA), and mixed with 9 mL UPW. For $Na_4P_2O_7$ extraction, 1 mL of the concentrated natural water was mixed with 8 mL of UPW and 1 mL of 100 mM $Na_4P_2O_7$ solution to achieve a final concentration of 10 mM $Na_4P_2O_7$. For all extractions, the pH was then adjusted to 10 using NaOH to enhance the disaggregation of natural hetero-agglomerates by inducing electrostatic repulsion (Loosli et al., 2018a), thus, the extraction protocols are referred to as NaOH- and $Na_4P_2O_7$-extractions. The mixed samples were stirred in a tube rotator (Fisher Scientific, China) at 40 rpm for 20 h, followed by a 60 min bath sonication (Branson, 2800, 40 kHz, Mexico) for better particle dispersion. Then, the samples were centrifuged (Eppendorf, 5810 R, Germany; 750 g for 5 min; 750 g for 30 min; and 3100 g for 130 min) to obtain suspension <1000, <450, and <100 nm, respectively assuming natural particle (clay) density of 2.5 g cm^{-3}. In each case, the top 8 mL were decanted and stored at 4 °C for further analysis. All samples were digested with HF:HNO_3 (3:1) mixture and analyzed for total elemental concentrations using PerkinElmer NexION 350D ICP-MS according to the protocols described in detail in the supplementary information section (section S1 and S2) (Loosli et al., 2019a).

2.4. Calculation of total TiO_2 engineered particle concentration

Ti in surface water is expected to occur solely in solid phases because of the very low solubility TiO_2 (Antignano and Manning, 2008). Naturally occurring TiO_2 particles contain other elements such as Nb, Ta, W, Zr, Fe, U, Pb, and Ba (Gondikas et al., 2014). On the other hand, all TiO_2 engineered particles, except TiO_2 used as a food additive, contain 1%–15% of artificial coatings by weight, most commonly oxyhydrates and oxides of silicon and aluminum (Working Group on the, 2010). Additionally, TiO_2 engineered particle contain trace amount of Nb, which was below the ICP-MS detection limit (*e.g.,* < 7 ng L^{-1}) as demonstrated for two commercially available TiO_2 engineered particles (Table S2). Therefore, we used elemental ratio of Ti to Nb to differentiate natural Ti-containing particles from TiO_2 engineered particles in urban runoff because natural Ti-containing minerals have been shown to be the dominant carrier (>90–95% of whole rock content) for Nb (Nakashima and Imaoka, 1998; José and Wyllie, 1983). Elemental ratios (*e.g.,* Ti to Nb) have been recently implemented to quantify the total concentration of TiO_2 engineered particles in surface waters impacted by sewage spills (Loosli et al., 2019a). The concentration of TiO_2 engineered particles was calculated according Eq. (1) assuming that all Ti occur in particulate form and that anthropogenic Ti occur as pure TiO_2 particles

$$[TiO_2]_{engineeredparticles} = \frac{TiO_{2MM}}{Ti_{MM}}\left[Ti_{sample} - Nb_{sample}\cdot\left(\frac{Ti}{Nb}\right)_{background}\right] \quad \text{(Eq.1)}$$

Where, $[TiO_2]_{\text{engineered particles}}$ is the concentration of TiO_2 engineered particles, Ti_{MM} and $TiO_{2\,MM}$ are the molar masses of Ti and TiO_2, Ti_{sample} and Nb_{sample} are the concentrations of Ti and Nb in a given sample, $Ti/Nb_{background}$ is the natural background elemental concentration ratio of Ti to Nb. Here, we used two background elemental ratios of Ti to Nb, to account for the uncertainties in the natural Ti to Nb elemental ratios, including **1)** the average crustal value, which was in good agreement with uncontaminated soils measured near the sampling sites in South Carolina and California (*e.g.,* Ti/Nb = 320) (Loosli et al., 2019b; Yi et al., 2019; Smith et al., 2013), and **2)** the average of eight water samples collected in Columbia, SC (Loosli et al., 2019a), assuming that the elemental ratios of the reference water samples were similar in SC and CA. This is a reasonable assumption given the similarity in the soil elemental ratios near the sampling sites.

2.5. Particle analysis by transmission electron microscopy

Ballona Creek, the LA River, and the bridge runoff from highways 760 (BR1), as well as the <450 nm extracted suspension from Ballona Creek, were examined by scanning transmission electron microscopy (STEM) to gather information about the average size and morphology. STEM analysis was performed using a LaB_6 JEOL 2100 TEM (JEOL USA Inc., MA, USA) operated at 200 keV and equipped with a JEOL EX-230 Silicon Drift Detector (SDD; JEOL USA Inc., MA, USA) for Energy Dispersive X-ray Spectroscopy (EDS) analysis. TEM samples were prepared according to method described elsewhere (Loosli et al., 2019a) and is summarized in the supplementary information section (section 4).

3. Results and discussion

3.1. Identification and quantification of TiO_2 engineered particles

The total concentrations of Ti in wet runoff (BR1 and BR2) were 140–200 μg L^{-1} and those in dry runoff were 15–195 μg L^{-1} (Fig. 1a). The Ti concentrations measured in this study were higher than those measured in river waters (Markus et al., 2018), and those measured in urban runoff (*e.g.,* 10–15 μg L^{-1}) following the release of TiO_2 particles from exterior facades (Kaegi et al., 2008). High Ti concentrations (150–1600 mg kg^{-1}) were reported in different road-environment samples (*e.g.,* road dust, sludge from storm drains, and roadside soil), which were suspected to be of anthropogenic origin (*e.g.,* use of alkali metal titanates as inorganic fillers for the purpose of stabilizing the friction coefficient) (Adamiec, 2017). High Ti concentration in surface waters was also shown to be linked to urban land use and industrial activities relative to rural/pristine backgrounds (Neal et al., 2011).

The elemental ratios of Ti to Nb in all runoff samples were higher than the average crustal Ti to Nb ratio and higher than the Ti to Nb ratio in reference water samples (320 and 266 g g^{-1}, respectively) measured in Columbia, SC (Fig. 2a) (Loosli et al., 2019a). The higher Ti to Nb ratio is an indication of anthropogenic titanium contamination. STEM-EDS analysis of BC and LA

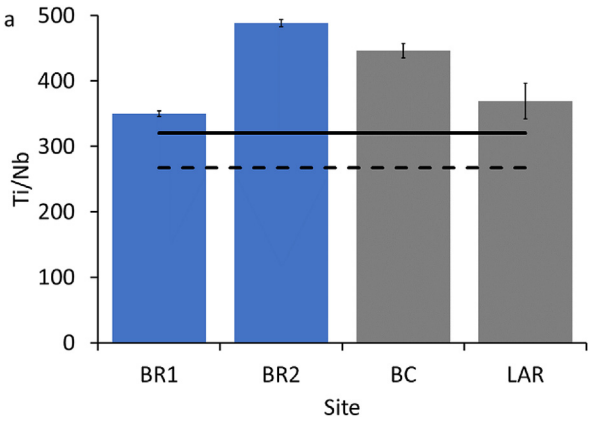

Fig. 2. Elemental ratios of Ti to Nb in wet- and dry-weather runoff. BR1, and BR2 refer to Bridge 1 and Bridge 2 in Columbia, South Carolina. BC and LAR refer to Ballona Creek and LA River, California. The solid and dashed lines indicate the average crustal (320) and average background reference water samples (267) elemental ratios of Ti to Nb. The error bars represent the standard deviation of three independent replicates.

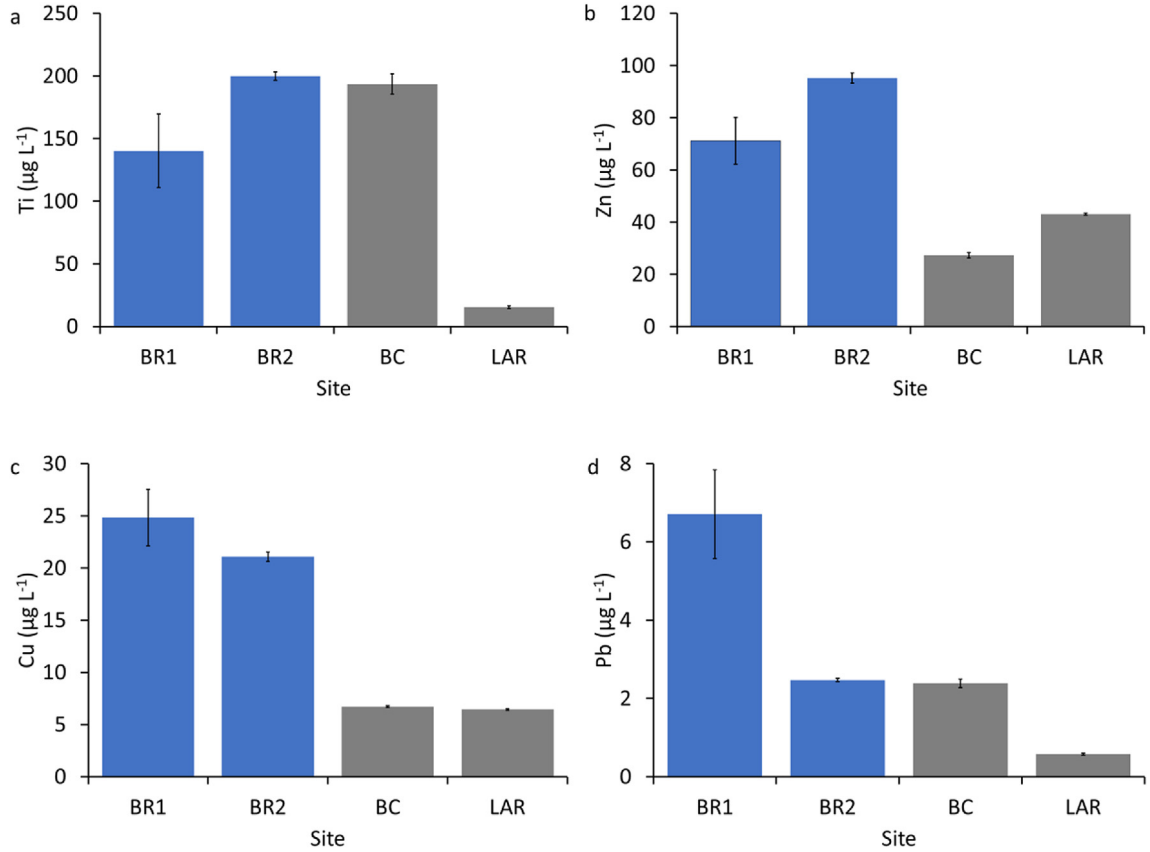

Fig. 1. Concentration of (a) Ti, (b) Zn, (c) Cu, and (d) Pb in wet-weather runoff collected from Bridge 1 (BR1) and Bridge 2 (BR2) in Columbia, South Carolina and in dry-weather runoff from Ballona Creek (BC) and Los Angeles River (LAR), California. The error bars represent the standard deviation of three independent replicates.

River samples showed the presence of titanium oxide particles (Figs. 3, 4a, and S1) in the 50–200 nm size range. Fig. 3a shows an aggregate of particles in Ballona Creek water. Elemental maps, obtained by STEX-EDS, illustrate that this aggregate is composed of several particles containing Al, Si, P, S, Mg, Ca, Ti, Fe, and Zn. The extracted elemental maps of the Ti-rich particle in Fig. 3 with the region of interest restricted to the Ti-rich particle illustrate that Ti and O are spatially correlated within this Ti-rich particle (Fig. S1), and thus suggest that this particle is a titanium oxide particle. Fig. 4a shows an aggregate of particles in the LA River. Elemental maps, obtained by STEX-EDS, illustrate that this aggregate is composed of several particles containing Si, F, Cl, K, Ca, Ti, Fe, Zn, and Pb. The extracted elemental maps of his aggregate illustrate that Ti, Pb, and O are the major constituents of this aggregate (Fig. S2) and that Ti and O (Figs. S2c and d, respectively) are spatially correlated within the Ti-rich particle, and thus suggest that this particle is a titanium oxide particle. The size and morphology of these particles are very similar to the size and morphology of white pigments detected in façade and urban storm water runoff (Kaegi et al., 2008), construction landfill leachate (Kaegi et al., 2017), and sewage spills (Loosli et al., 2019a). It is worth noting here that the large majority of analyzed particles occurred as aggregates of particles with few individual particles. This is because TiO_2 are susceptible to aggregation in the presence of multivalent cations in surface waters (Loosli et al., 2015; Perstrimaux et al., 2015).

Using STEM, one titanium oxide particle was observed in the BC bulk water (Fig. 3e) and another particle was observed in LA River bulk water (Fig. 4a. However, the occurrence of titanium oxide engineered particles in BC was further confirmed by the detection of 20 titanium oxide particles in the extracted particle suspensions from BC water (see section 3.2). No titanium oxide particles were detected in BR1, which does not necessarily indicate the absence of titanium oxide particles in this sample, but rather highlights the difficulty in detecting engineered particles in natural environmental samples by TEM. The detection of few titanium oxide particles by TEM is expected due to the presence of numerous natural and anthropogenic particles in urban runoff. This is consistent with previous studies reporting the detection of few engineered particles in environmental samples (Loosli et al., 2019a; Kaegi et al., 2017; Gondikas et al., 2018). For instance, using autoSEM (automated imaging and analysis) and TEM, only 6 out of 2351 particles and 1 out of 1605 particles were identified as titanium oxide in the Old Danube Lake during and after the bathing season, respectively (Gondikas et al., 2018). In another study, only 29 titanium oxide particles were detected in 14 surface water samples impacted by

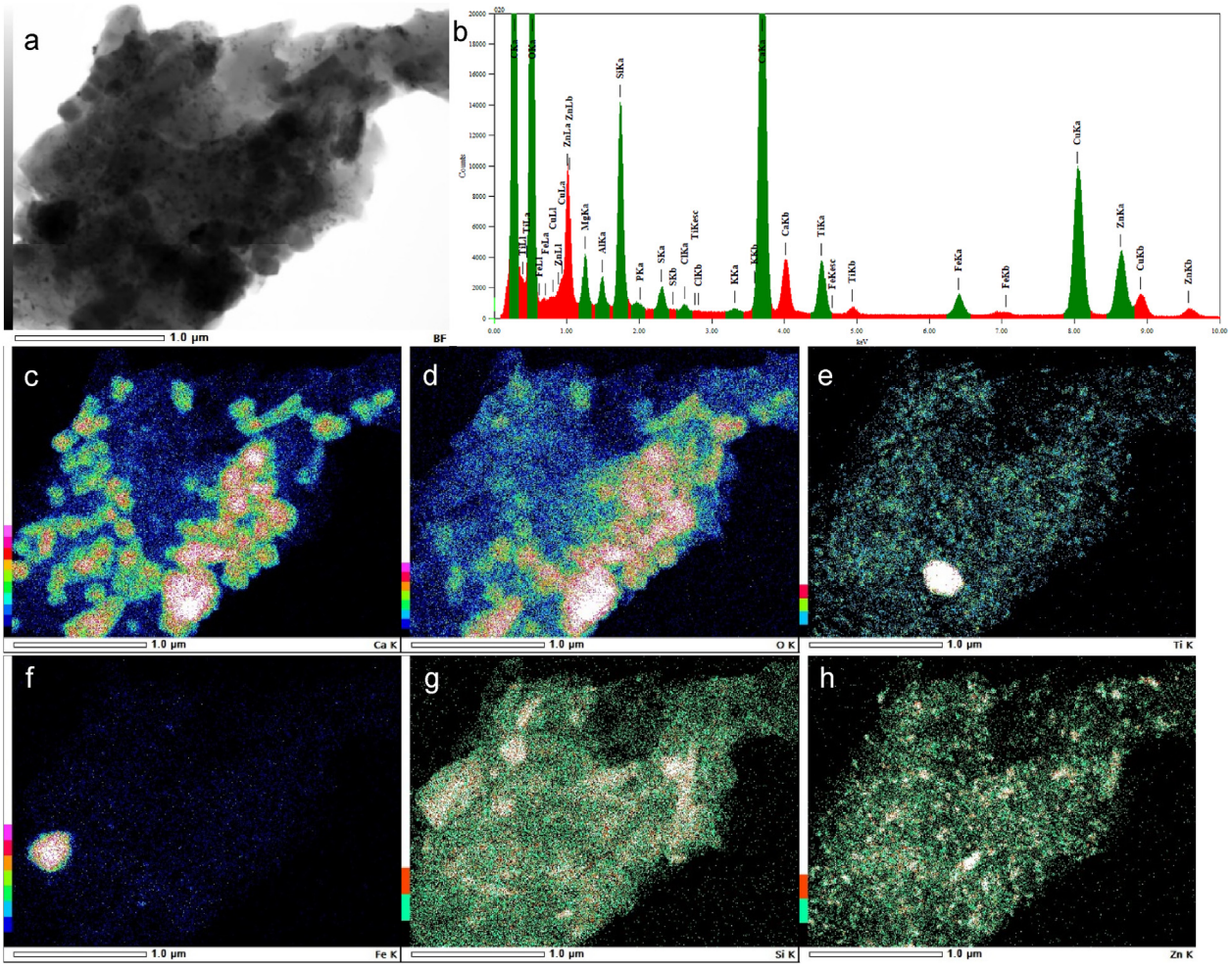

Fig. 3. Elemental maps together with the elemental spectra of particles present in Ballona Creek bulk water obtained by X-ray energy dispersive spectroscopy (EDS) coupled with scanning transmission electron microscopy (STEM): (a) bright field micrograph, (b) EDS spectrum of the overall aggregate, (c–h) map of all elements detected in the imaged particle aggregate, (c) map Ca K, (d) map of O K, (e) map of Ti K, (f) map of Fe K, (g) map of Si K, and (h) map of Zn K. The spectral lines used for the maps are highlighted in dark green. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

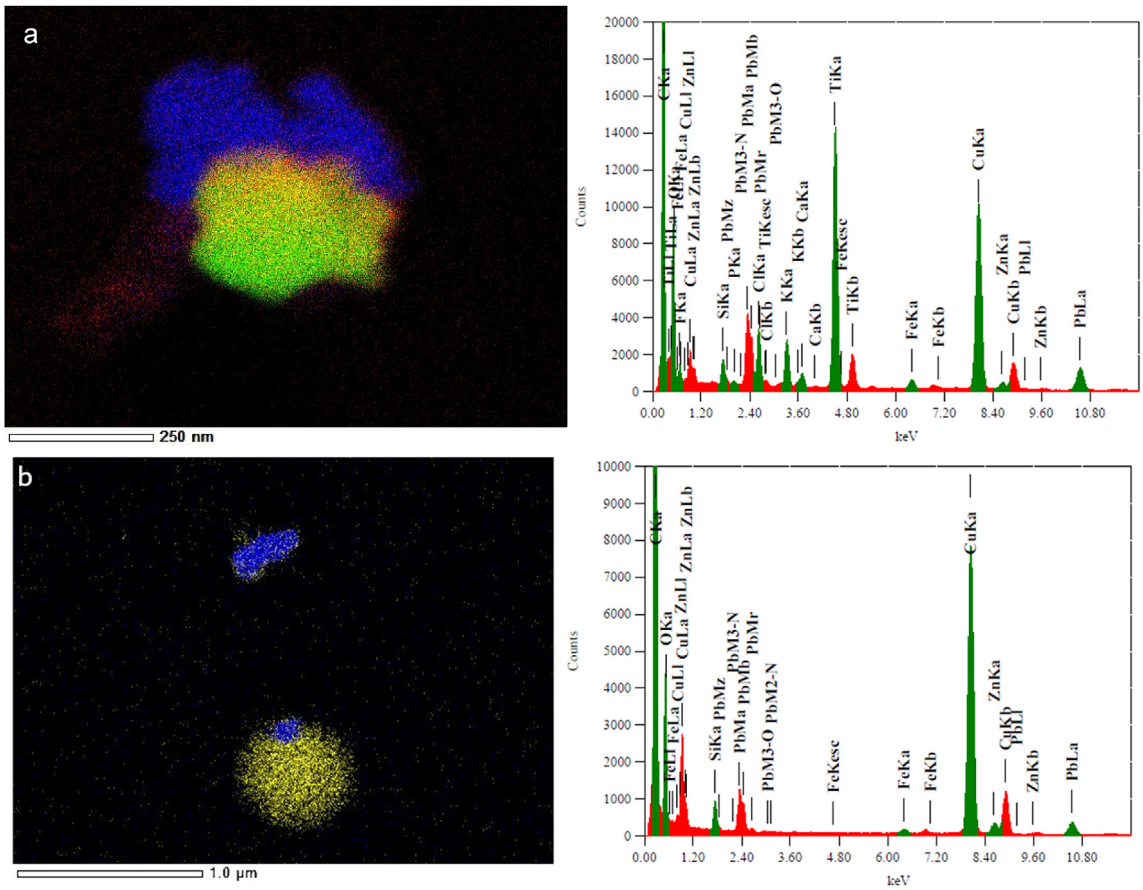

Fig. 4. Elemental maps together with the elemental spectra of particles present in LA River bulk water obtained by X-ray energy dispersive spectroscopy (EDS) coupled with scanning transmission electron microscopy (STEM): (a) map of Ti K (green), Pb L (blue), and O K (red), and (b) map of Pb L (yellow) and Zn K (blue). The spectral lines used to generate the elemental maps are highlighted in green in the EDS spectra. The individual elemental maps of the elemental overlay in a are presented in Fig. S2. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

sewage spills (Loosli et al., 2019a). Practical limitations for TEM analysis, including the demanding operator time, the presence of high concentrations of natural particles, the poor statistical power due to limited number of particles that can be imaged and analyzed within a reasonable time and cost frame, hamper the use of TEM as a standalone technique to quantify engineered particle concentrations in complex matrices (Gondikas et al., 2018). Therefore, pragmatically, TEM should be used to provide complementary (qualitative) evidence to support other analytical approaches such as total elemental analysis performed in this study.

Elemental ratios of Ti to Nb calculated based on total metal concentrations in the water samples were used to calculate the total concentrations of TiO_2 engineered particles in the water samples, by estimating the Ti attributed to natural and engineered TiO_2 particles (Fig. 5). The concentration of TiO_2 engineered particles varied between 5 and 150 μg L^{-1} and was highest in BR2 and lowest in LA River. These concentrations are higher than the predicted concentration of TiO_2 engineered nanoparticles in surface waters (Gottschalk et al., 2009). Additionally, these concentrations are higher than those experimentally determined concentrations of TiO_2 engineered particles in surface waters (*e.g.,* 0.4–110 ng L^{-1} in Clear Creek in Golden, Colorado (Reed et al., 2017); 1.7–27.1 μg L^{-1} in the Old Danube lake water, Switzerland (Gondikas et al., 2014); and <1.6 μg L^{-1} River Dommel Netherlands (Smith et al., 2013). Nonetheless, similar TiO_2 concentrations to those estimated in this study were measured in surface waters impacted by sewage spills in Columbia, South Carolina, USA (Loosli et al., 2019a).

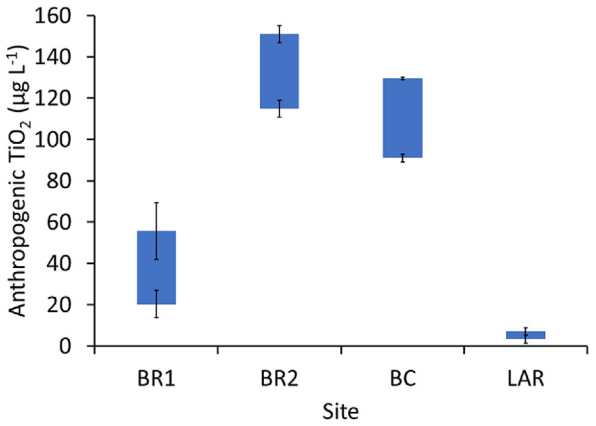

Fig. 5. Estimated concentration of TiO_2 engineered particles in wet- and dry-weather runoff. TiO_2 concentration was calculated assuming that all anthropogenic Ti occur in the form of TiO_2 engineered particles. The lower and upper TiO_2 concentrations were estimated using Ti/Nb ratios of 267 and 320, respectively to account for natural background ratio uncertainty. BR1, and BR2 refer to Bridge 1 and Bridge 2 in Columbia, South Carolina. BC and LAR refer to Ballona Creek and LA River, California. The error bars represent the standard deviation of three independent replicates.

The higher concentration of anthropogenic TiO_2 in BR2 relative to that measured in BR1 might be attributed to the higher traffic volume on highway 176 (AADT = 26,900) compared to that on

highway 760 (AADT = 10,000) (SCDOT, 2017). It is worth noting that the highways investigated in this study are relatively small (4 lanes) with low traffic density (AADT of 10,000 to 26,900) compared to those (*ca.* AADT of up to 400,000) in major cities in the United States. Thus, TiO_2 concentrations in urban runoff from larger highways with higher traffic density are likely to be much higher than those reported in this study (Traffic Volumes on Califo, 2016). The higher concentration of TiO_2 in BC compared to that in the LA River can be attributed to differences in land use, discharge origin, and natural attenuation of contaminants. The BC watershed has more impervious surfaces than the LA watershed – resulting in higher TiO_2 release per unit area. The BC receives only dry weather runoff during the sampling period, whereas the LA River receives both runoff and natural waters resulting in dilution of urban runoff in LA River relative to BC. Natural attenuation of TiO_2 by sorption and deposition on riverbed may result in lower TiO_2 concentrations in the water column. TiO_2 occurred as heteroaggregates (*e.g.,* aggregates of natural and engineered particles) and is concentrated in the large size fraction (ca. >1000 nm) (Clavier et al., 2019), which are more prone to sedimentation. Based on the typical water composition (Table S1), LA River is characterized by higher concentrations of dissolved solids or electrical conductivity, which promote particle aggregation. The sedimentation of TiO_2 engineered particles is likely to be more significant in the LA River relative to BC due to the longer (approximately 7 times) distance traveled.

3.2. Identification of other anthropogenic nanoparticles

In addition to titanium oxide engineered particles, other anthropogenic particles (*e.g.,* Pb and Zn-rich particles) were identified by STEM-EDS and thus are briefly discussed here. The total concentrations of Zn, Cu, and Pb are presented in Fig. 1b–d. The bridge runoff samples (*e.g.,* BR1 and BR2) exhibited higher concentrations of Zn, Cu, and Pb than those measured in Ballona Creek and LA River, all indicating anthropogenic contamination, likely from traffic related emissions. These findings are supported by previous reports on heavy metals contamination, including Zn, Cu, and Pb, in highway and urban runoff (Wu et al., 1996; Lee and Bang, 2000; Sansalone and Buchberger, 1997).

STEM-EDS analysis provided further evidence on the occurrence of other types of nanoparticles in urban runoff (Figs. 3 and 5). Fig. 3h illustrates the occurrence of Zn-rich nanoparticles aggregated with other particles (*e.g.,* Si, Ca, Ti and Fe-rich particles, Fig. 3c–g) in Ballona Creek water. Fig. 4a illustrates an aggregate of Ti and Pb rich particles from the LA River. The absence of other natural particles such as Al and Si-rich particles suggest that this is an aggregate of anthropogenic particles. Fig. 4b shows Pb and Zn rich particles in LA River water, most likely from anthropogenic sources. Sansalone and Buchberger found that lead (Pb) in urban roadway storm water was mostly associated with suspended solids during storm events whereas Cu and Cd were mainly in the dissolved fraction (Sansalone and Buchberger, 1997). Marsalek and Marsalek showed that Pb, Cu, and Zn are strongly associated with smaller particles in sediments from a storm water management pond (Marsalek and Marsalek, 1997). Fig. S3 shows an aggregate of particles that contain a significant number of Zn-rich nanoparticles. Thus, STEM-EDS analysis illustrates that Ballona Creek and LA River waters contain a mixture of engineered and anthropogenic particles.

3.3. Particle and metal extraction

In general, the elemental concentrations in the $Na_4P_2O_7$ extracted suspensions were higher than those measured in the NaOH-extracted suspensions (Fig. S4) for all size fractions (*e.g.,* <1000, <450, and <100 nm). This is in good agreement with the previous studies demonstrating the extraction of higher concentrations of natural and engineered particles by $Na_4P_2O_7$ than by NaOH (Loosli et al., 2018a; Loosli et al., 2018b). Pyrophosphate ($Na_4P_2O_7$) is a metal chelator, which sequesters metal ions, thus reducing free multivalent ion concentrations in the extracted NP suspensions. This in turn, enhances NP surface charge by removing multivalent cations from solution and reduces NP aggregation via bridging mechanism (Philippe and Schaumann, 2014) and/or cation specific adsorption (Jolivet, 2000). For NaOH extraction, the percentage of extracted elements was approximately 1–6%, 2–14%, and 3–32% of the total elemental concentration for the <100, <450 and < 1000 nm size fractions, respectively. For $Na_4P_2O_7$ extraction, the percentage of extracted elements ranged from 8 to 55%, 9–53%, and 10–59% of the total elemental concentration for all elements for the <100, <450 and < 1000 nm size fractions, respectively. The <100 nm $Na_4P_2O_7$ extractable Ti was approximately 10%, whereas the <100 nm $Na_4P_2O_7$ extractable Cu and Zn were approximately 30 and 40%, respectively. The low Ti concentration in the <100 nm size fraction is likely due to the occurrence of natural Ti in large particles and/or the occurrence of anthropogenic Ti-rich particles in the large size fractions (*e.g.,* aggregates, or encased with polymers), which would have been removed during the particle separation process by centrifugation. The high Zn concentration in the <100 nm size fraction is in good agreement with their occurrence in the nanosized form as illustrated by STEM-EDS (Figs. 3c and S3h).

The calculated TiO_2 concentrations in the extracted suspensions are presented in Fig. 6. For the same extractant, the concentration of TiO_2 engineered particles increased with the increase in the extracted suspension size cutoff, suggesting that the extracted TiO_2 engineered particles are either a mixture of engineered nanomaterials (ENMs, *e.g.,* <100 nm) and pigments (e.g., 100–300 nm) and/or occurred as both individual particles and heteroaggregates of natural and engineered particles. For the same size fraction, the concentration of TiO_2 engineered particles in the $Na_4P_2O_7$-extracted suspensions were higher than those in the NaOH-extracted suspensions (Fig. 6). In all cases, the extracted TiO_2 engineered particles represented a small fraction (*e.g.,* <20% in the $Na_4P_2O_7$ extracted <1000 nm suspension) of the total TiO_2 concentration in bulk Ballona Creek water. The low recovery of TiO_2 engineered particles can be attributed to the heteroaggregation of TiO_2 particles with natural particles, and/or to their attachment to polymer matrices from painted surfaces (Shandilya et al., 2014a; Gohler et al., 2010; Shandilya et al., 2014b). The low recovery of TiO_2 engineered particles is in agreement with our previous study demonstrating that only <15% of P25–TiO_2 engineered nanoparticles were recovered in the <100 nm size fraction from a TiO_2-clay mixture using $Na_4P_2O_7$ due to particle aggregation (Loosli et al., 2018a). Nevertheless, these extractions demonstrate the occurrence of TiO_2 as primary engineered nanoparticles (*e.g.,* <100 nm) in urban runoff.

The occurrence of titanium oxide engineered particles in the extracted suspensions (<450 nm) from Ballona Creek was further confirmed by STEM-EDS analysis. Figs. 7 and 8 show aggregates of particles with different contrasts. The elemental maps, obtained by STEM-EDX, illustrate that the dark particles are Ti-, Al-, Si-, and Fe-rich particles (Fig. 7) and Ti-, and Si-rich particles (Fig. 8). The Ti rich particles are also rich with O (Fig. 7b and c and Fig. 8 b and c), suggesting that these Ti-rich particles are titanium oxide particles. The primary particle diameter of the Ti-rich particles varied between 50 and 200 nm.

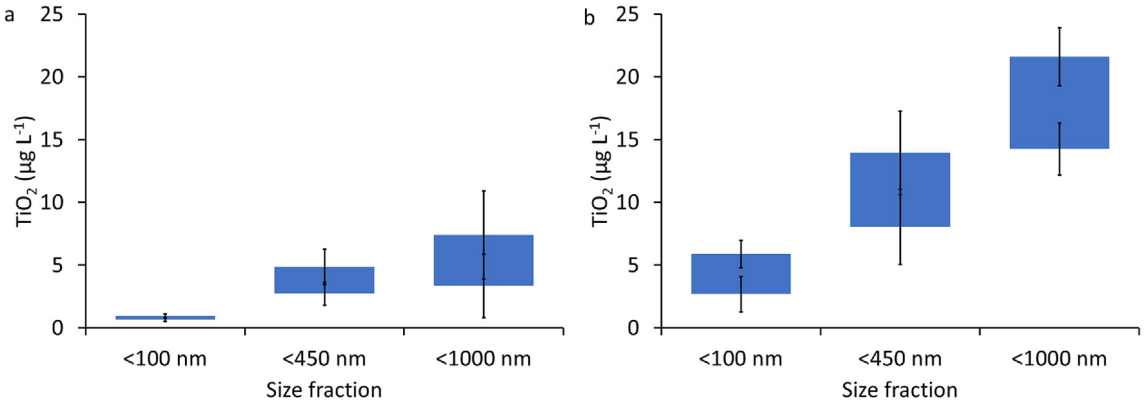

Fig. 6. Concentration of TiO_2 engineered particles in the extracted suspensions in Ballona Creek using (a) NaOH and (b) $Na_4P_2O_7$. TiO_2 concentration was calculated assuming that all anthropogenic Ti occur in the form of TiO_2 engineered particles. The lower and upper TiO_2 concentrations were estimated using Ti/Nb ratios of 267 and 320, respectively to account for natural background ratio uncertainty. The error bars represent the standard deviation of three independent replicates.

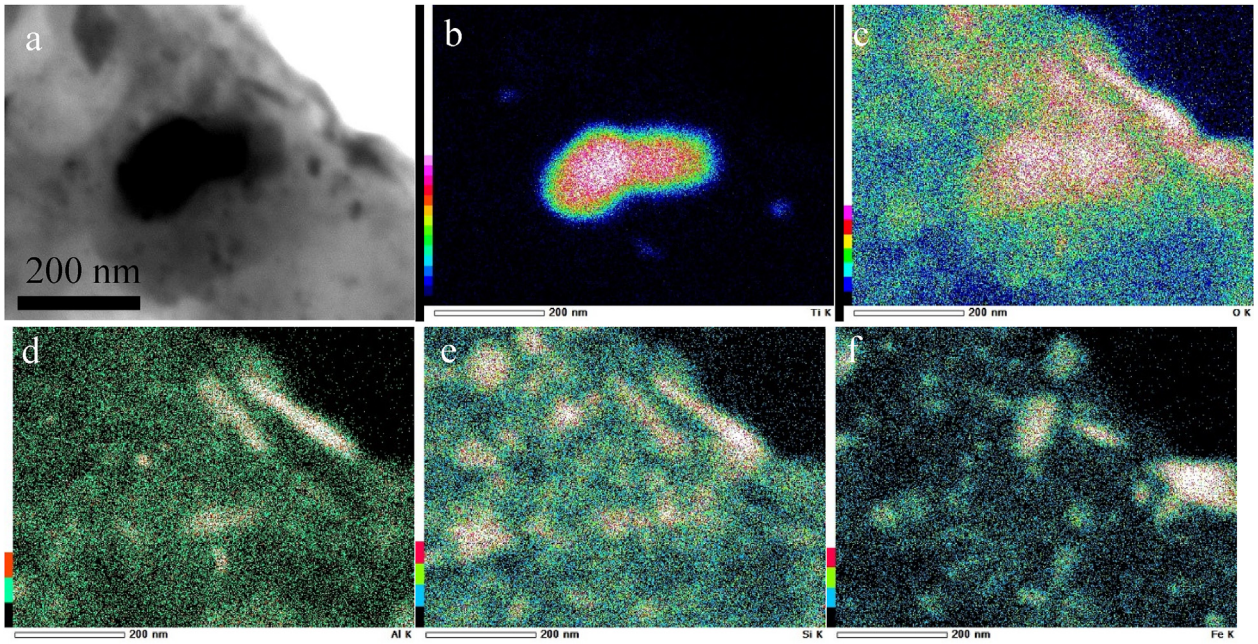

Fig. 7. TEM micrograph and elemental maps of particles present in the extracted particle suspension (e.g., <450 nm) from Ballona Creek water obtained by X-ray energy dispersive spectroscopy (EDS) coupled with transmission electron microscopy (TEM): (a) bright field micrograph, (b, c, d, e, and f) maps of Ti K, O K, Al K, Si K, and Fe K, respectively.

3.4. Discussion of analytical strategies to measure engineered particles

In this study, increases in the elemental ratios of Ti to Nb relative to the average crustal and reference water elemental ratio of Ti to Nb were used to identify and quantify the concentrations of titanium oxide engineered particles in urban runoff. Mass-balance calculations were implemented to estimate the total concentrations of the released TiO_2 engineered particles. Extraction of arbitrarily defined suspensions was used to provide further evidence on the occurrence of engineered nanoparticles (e.g., <100 nm). Additionally, STEM-EDS analysis was implemented to gather visual evidence of the presence of titanium oxide particles.

The total TiO_2 engineered particle concentrations, calculated using the elemental ratio approach, refers to the sum of all TiO_2 particles that do not contain Nb, including TiO_2 ENMs, pigments, and potentially other Ti-rich particles that are not associated with Nb. The use of Nb as a tracer of natural TiO_2 particles implies the assumptions that the measured Nb concentrations do not contain any anthropogenic Nb. This assumption is reasonable given the small production (approximately 70,000 metric tons annual world production) and use of Nb relative to the production and use of TiO_2 (approximately 6.1 million metric tons world production in 2016) (Mineral Commodity S, 2019). The presence of anthropogenic Nb in a given sample will result in underestimation of the calculated titanium oxide concentrations when titanium oxide is present at high concentrations and/or misleadingly not identifying titanium dioxide contamination if titanium oxide is present in a given sample at low concentrations. Additionally, the elemental ratio of Ti to Nb might vary from one region to another, and thus further research is needed determine the elemental ratio of Ti to Nb across different regions. In this study, we assumed that the elemental ratios of the reference water samples were similar in SC and CA. The assumption is reasonable given that the elemental ratio of Ti to Nb in uncontaminated soils near the sampling sites in SC and CA were very similar and close to the average crustal value (*e.g.*, Ti/Nb = 320)

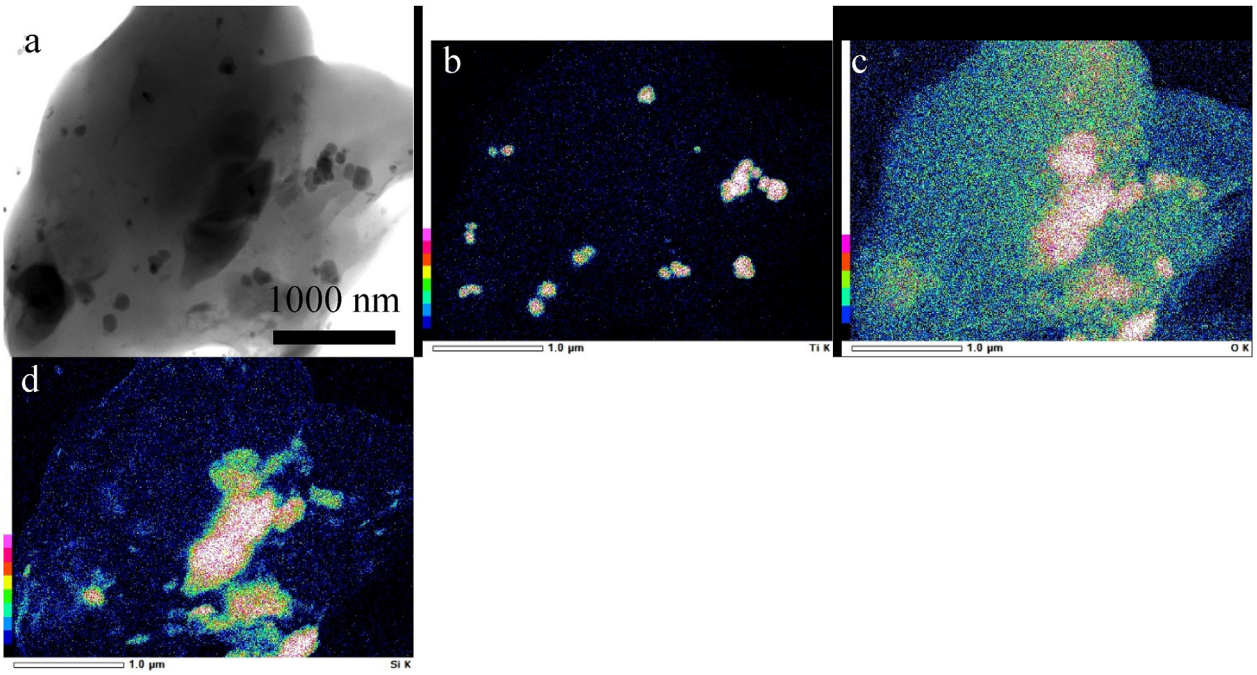

Fig. 8. TEM micrograph and elemental maps of particles present in the extracted particle suspension (e.g., <450 nm) from Ballona Creek water obtained by X-ray energy dispersive spectroscopy (EDS) coupled with transmission electron microscopy (TEM): (a) bright field micrograph, (b, c, and d) maps of Ti K, O K, and Si K, respectively.

(Loosli et al., 2019b; Yi et al., 2019; Smith et al., 2013).

The extraction of particle suspensions of different sizes facilitated the identification of TiO_2 ENMs in urban runoff. However, the estimated TiO_2 ENM concentration represented only <5% of the total TiO_2 engineered particle concentration. This is likely to be an underestimation of the actual TiO_2 ENM concentration in Ballona creek due to poor extraction of TiO_2 from natural environmental media. In fact, the occurrence of TiO_2 engineered particles in the size fractions >100 nm can be attributed to those of large primary particles (*e.g.,* pigment sized TiO_2), or those of aggregates of smaller primary particles (*e.g.,* TiO_2 ENMs). Future studies should focus on extraction protocols that may enhance ENM disaggregation from heteroaggregates to enhance the recovery of primary ENMs.

TEM was implemented pragmatically to gather qualitative visual evidence of the presence of TiO_2 engineered particles in urban runoff, to further support other analytical approaches such as total elemental concentration and particle extractions. This is because practical limitations of TEM such as the demanding operator time and the poor statistical power hamper the application of TEM as a standalone technique to quantify ENM concentrations in complex matrices (Gondikas et al., 2018). Nonetheless, the ability of TEM to provide information (*e.g.,* size, morphology, elemental composition, and structure) on single particles across the entire nanoscale range make it an essential tool to underpin other analytical approaches such as total concentration and particle extraction.

4. Conclusions and prospects

This study demonstrated the applicability of the elemental ratio (*e.g.,* Ti to Nb) approach to quantify the concentrations of titanium oxide engineered particles in urban runoff. Using this approach, we demonstrated, for the first time, that urban runoff is a hot spot of TiO_2 engineered particle (*e.g.,* ENMs and pigments, 5–150 µg L^{-1} TiO_2) release into the environment. Furthermore, this study demonstrated that wet and dry weather urban runoff contains other anthropogenic nanoparticles (*e.g.,* Zn and Pb rich particles), warranting further investigations on the discovery, quantification, and environmental fate and effects of various engineered and anthropogenic particles that may be present in urban runoff. Urban runoff is a global issue that continues to increase in occurrence intensity and significance with increased urbanization worldwide. For instance, the total annual urban runoff volume in the USA is estimated at 38,112 billion liters (Environmental Protect, 2004). This results in a total discharge of approximately 190 to 5700 tons of TiO_2 engineered particles per year to receiving surface waters in the USA through urban runoff. However, the actual concentration of TiO_2 engineered particles in urban runoff might be higher than the highest concentration reported in this study due to the time-dependent changes in concentration of contaminants in urban runoff. Typically, contaminants are more concentrated in the first flush and become less concentrated later during the storm event. Moreover, freeze-thaw occurrences in winter weathers can also contribute to the differences in discharge of urban runoff and can increase the released particle concentrations during snow-plowing efforts. This situation warrants further comprehensive evaluation of TiO_2 and other engineered particles in urban runoff and the resulting environmental fate modeling, exposure to organisms, and toxicity. In particular, investigating the effect of land use, storm intensity and duration, antecedent dry period, traffic volume and composition, freeze-thaw and snow-plowing intensity (in winter weather) on the occurrence and concentrations of TiO_2 and other engineered particles could inform policy and management methods to reduce exposure.

Declaration of competing interest

The authors declare no competing interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2020.126070.

Author contributions section

Dr. Baalousha conceived the overall idea of the study. Drs. Baalousha, Mohanty, Afrooz, and Aich discussed the overall strategy of the study and designed the sampling strategy. Mr. Nabi and Dr. Wang collected the bridge runoff samples in Columbia, South Carolina and performed all chemical analysis. Dr. Mohanty collected the runoff samples in California. Dr. Cantando performed transmission electron microscopy analysis. All authors contributed to writing, proof reading, and revision of the manuscript.

References

Ackerman, D., Stein, E., Schiff, K., 2005. Modeled wet weather trace metal loads to Ballona creek, California. Proc. Water Environ. Fed. 2005, 1526–1541.

Adamiec, E., 2017. Road environments: impact of metals on human health in heavily congested cities of Poland. Int. J. Environ. Res. Publ. Health 14, 697.

Antignano, A., Manning, C.E., 2008. Rutile solubility in H2O, H2O–SiO2, and H2O–NaAlSi3O8 fluids at 0.7–2.0 GPa and 700–1000 °C: implications for mobility of nominally insoluble elements. Chem. Geol. 255, 283–293.

ASTMASTM D7942 15, 2015. Standard Specification for Thermoplastic Pavement Markings in Non Snow Plow Areas. ASTM.

Baalousha, M., Yang, Y., Vance, M.E., Colman, B.P., McNeal, S., Xu, J., Blaszczak, J., Steele, M., Bernhardt, E., Hochella Jr., M.F., 2016. Outdoor urban nanomaterials: the emergence of a new, integrated, and critical field of study. Sci. Total Environ. 557–558, 740–753.

Buffle, J., Van Leeuwen, H., 1992. Environmental Particles. Lewis, Boca Raton, FL.

Christian, P., Von der Kammer, F., Baalousha, M., Hofmann, Th, 2008. Nanoparticles: structure, properties, preparation and behaviour in environmental media. Environ. Toxicol. Chem. 17, 326–343.

City Information Viewer, 2019. https://gis.columbiasc.gov/cocinfo/.

Clavier, A., Praetorius, A., Stoll, S., 2019. Determination of nanoparticle heteroaggregation attachment efficiencies and rates in presence of natural organic matter monomers. Monte Carlo modelling. Sci. Total Environ. 650, 530–540.

Coatingsworld, 2019. U.S. Demand for Paint & Coatings to Reach 1.4 Billion Gallons in 2019.

U.S.Environmental Protection Agency (USEPA). reportReport to Congress on Impacts and Control of Combined Sewer Overflows and Sanitary Sewer Overflows. EPA 833-R-04-001. 2004. Washington, D.C.: Office of Water., USEPA.

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

Gold, M., Hogue, T., Pincetl, S., Mika, K., Radavich, K., 2015. Los Angeles Sustainable Water Project: Ballona Creek Watershed (Full Report).

Gondikas, A.P., von der Kammer, F., Reed, R.B., Wagner, S., Ranville, J.F., Hofmann, T., 2014. Release of TiO2 nanoparticles from sunscreens into surface waters: a one-year survey at the Old Danube recreational lake. Environ. Sci. Technol. 48, 5415–5422.

Gondikas, A., von der Kammer, F., Kaegi, R., Borovinskaya, O., Neubauer, E., Navratilova, J., Praetorius, A., Cornelis, G., Hofmann, T., 2018. Where is the nano? Analytical approaches for the detection and quantification of TiO2 engineered nanoparticles in surface waters. Environ. Sci. Nano. 5, 313–326.

Gottschalk, F., Sonderer, T., Scholz, R.W., Nowack, B., 2009. Modeled environmental concentrations of engineered nanomaterials (TiO2, ZnO, Ag, CNT, fullerenes) for different regions. Environ. Sci. Technol. 43, 9216–9222.

Gottschalk, F., Sun, T., Nowack, B., 2013. Environmental concentrations of engineered nanomaterials: review of modeling and analytical studies. Environ. Pollut. 181, 287–300.

Grand View Research, 2018. https://www.grandviewresearch.com/industry-analysis/traffic-road-marking-coatings-market/request.

Jolivet, J.P., 2000. Metal Oxide Chemistry and Synthesis. From Solution to Solid State. Wiley, West Sussex, England.

José, C.G., Wyllie, P.J., 1983. Ilmenite (high Mg, Mn, Nb) in the carbonatites from the Jacupiranga complex, Brazil. Am. Mineral. 68, 960–971.

Kaegi, R., Ulrich, A., Sinnet, B., Vonbank, R., Wichser, A., Zuleeg, S., Simmler, H., Brunner, S., Vonmont, H., Burkhardt, M., Boller, M., 2008. Synthetic TiO_2 nanoparticle emission from exterior facades into the aquatic environment. Environ. Pollut. 156, 233–239.

Kaegi, R., Englert, A., Gondikas, A., Sinnet, B., von der Kammer, F., Burkhardt, M., 2017. Release of TiO_2 (Nano) particles from construction and demolition landfills. NanoImpact 8, 73–79.

Kiser, M.A., Westerhoff, P., Benn, T., Wang, Y., Perez-Rivera, J., Hristovski, K., 2009. Titanium nanomaterial removal and release from wastewater treatment plants. Environ. Sci. Technol. 43, 6757–6763.

LA's watershed protection program, 2019. https://www.lastormwater.org/about-us/about-watersheds/ballona-creek/.

Lee, J.H., Bang, K.W., 2000. Characterization of urban stormwater runoff. Water Res. 34, 1773–1780.

Lee, P.K., Yu, S., Chang, H.J., Cho, H.Y., Kang, M.J., Chae, B.G., 2016. Lead chromate detected as a source of atmospheric Pb and Cr (VI) pollution. Sci. Rep. 6, 36088.

Loosli, F., Le Coustumer, P., Stoll, S., 2015. Effect of electrolyte valency, alginate concentration and pH on engineered TiO_2 nanoparticle stability in aqueous solution. Sci. Total Environ. 535, 28–34.

Loosli, F., Yi, Z., Wang, J., Baalousha, M., 2018a. Dispersion and Analysis of Natural Nanomaterials in Surface Waters as New Step towards Quantification of Engineered Nanoparticle in Environmental Systems. Wat. Res. submitted for publication.

Loosli, F., Berti, D., Yi, Z., Baalousha, M., 2018b. Toward a better extraction and stabilization of titanium dioxide engineered nanoparticles in model water. NanoImpact 11, 119–127.

Loosli, F., Wang, J., Rothenberg, S., Bizimis, M., Winkler, C., Borovinskaya, O., Flamigni, L., Baalousha, M., 2019a. Sewage spills are a major source of engineered titanium dioxide release into the environment. Environ. Sci. Nano. 6, 763–777.

Loosli, F., Yi, Z., Wang, J., Baalousha, M., 2019b. Improved extraction efficiency of natural nanomaterials in soils to facilitate their characterization using a multimethod approach. Sci. Total Environ. 677, 34–36.

Loosli, F., Yi, Z., Wang, J., Baalousha, M., 2019c. Dispersion of natural nanomaterials in surface waters for better characterization of their physicochemical properties by AF4-ICP-MS-TEM. Sci. Total Environ. 682, 663–672.

Luo, Z., Wang, Z., Li, Q., Pan, Q., Yan, C., Liu, F., 2011. Spatial distribution, electron microscopy analysis of titanium and its correlation to heavy metals: occurrence and sources of titanium nanomaterials in surface sediments from Xiamen Bay, China. J. Environ. Monit. 13, 1046–1052.

Markus, A.A., Krystek, P., Tromp, P.C., Parsons, J.R., Roex, E.W.M., Voogt, P.d., Laane, R.W.P.M., 2018. Determination of metal-based nanoparticles in the river Dommel in The Netherlands via ultrafiltration, HR-ICP-MS and SEM. Sci. Total Environ. 631–632, 485–495.

Marsalek, J., Marsalek, P.M., 1997. Characteristics of sediments from a stormwater management pond. Water Sci. Technol. 36, 117–122.

USGS. Mineral Commodity Summaries 2019: US Geological Survey. -200. 2019. U.S. Geological Survey.

Nakashima, K., Imaoka, T., 1998. Niobian and zincian ilmenites in syenites from cape ashizuri, southwest Japan. Mineral. Petrol. 63, 1–17.

Neal, C., Jarvie, H., Rowland, P., Lawler, A., Sleep, D., Scholefield, P., 2011. Titanium in UK rural, agricultural and urban/industrial rivers: geogenic and anthropogenic colloidal/sub-colloidal sources and the significance of within-river retention. Sci. Total Environ. 409, 1843–1853.

Parker, N., Keller, A.A., 2019. Variation in regional risk of engineered nanoparticles: nanoTiO2 as a case study. Environ. Sci. Nano. 6, 444–455.

Perstrimaux, C., Le Faucheur, S., Mortimer, M., Stoll, S., Aubry, F.B., Botter, M., Zonta, R., Slaveykova, V.I., 2015. Stability of titanium dioxide nanoparticle agglomerates in transitional waters and their effects towards plankton from Lagoon of Venice (Italy). Aquat. Geochem. 21, 343–362.

Philippe, A., Schaumann, G.E., 2014. Interactions of dissolved organic matter with natural and engineered inorganic colloids: a review. Environ. Sci. Technol. 48, 8946–8962.

Reed, R.B., Martin, D.P., Bednar, A.J., Montano, M.D., Westerhoff, P., Ranville, J.F., 2017. Multi-day diurnal measurements of Ti-containing nanoparticle and organic sunscreen chemical release during recreational use of a natural surface water. Environ. Sci. Nano. 4, 69–77.

Saharia, A.M., Zhu, Z., Aich, N., Baalousha, M., Atkinson, J.F., 2019. Modeling the transport of titanium dioxide nanomaterials from combined sewer overflows in an urban river. Sci. Total Environ. 696, 133904.

Sansalone, J.J., Buchberger, S.G., 1997. Characterization of solid and metal element distributions in urban highway stormwater. Water Sci. Technol. 36, 155–160.

SCDOT, 2017. Average daily traffic. https://www.scdot.org/travel/pdf/trafficcounts/2017/Richland.pdf.

Shandilya, N., Le Bihan, O., Morgeneyer, M., 2014a. A review on the study of the generation of (nano) particles aerosols during the mechanical solicitation of materials. J. Nanomater. 2014, 5.

Shandilya, N., Bihan, O.L., Bressot, C., Morgeneyer, M., 2014b. Evaluation of the particle aerosolization from n-TiO 2 photocatalytic nanocoatings under abrasion. J. Nanomater. 2014, 185080-185081-185080-14.

Smith, D.B., Cannon, W.F., Woodruff, L.G., Solano, F., Kilburn, J.E., Fey, D.L., 2013. Geochemical and Mineralogical Data for Soils of the Conterminous United States.

Tong, T., Hill, A.N., Alsina, M.A., Wu, J., Shang, K.Y., Kelly, J.J., Gray, K.A., Gaillard, J.F., 2015. Spectroscopic characterization of TiO2 polymorphs in wastewater treatment and sediment samples. Environ. Sci. Technol. Lett. 2, 12–18.

2016 Traffic Volumes on California State Highways. http://www.dot.ca.gov/

trafficops/census/docs/2016_aadt_volumes.pdf. 2019.
von der Kammer, F., Ferguson, P.L., Holden, P.A., Masion, A., Rogers, K.R., Klaine, S.J., Koelmans, A.A., Horne, N., Unrine, J.M., 2012. Analysis of engineered nanomaterials in complex matrices (environment and biota): general considerations and conceptual case studies. Environ. Toxicol. Chem. 31, 32–49.
Wilczynska-Michalik, W., Rzeznikiewicz, K., Pietras, B., Michalik, M., 2014. Fine and ultrafine TiO2 particles in aerosol in Krakow (Poland). Mineralogia 45, 65–77.
Wilde, F.D., Radtke, D.B., 1998. Handbooks for Water-resources Investigations: National field manual for the collection of water-quality data. Field Measurements. US Department of the Interior, US Geological Survey.
IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, Carbon Black, Titanium Dioxide, and Talc, IARC Monogr. Eval. Carcinog. Risks Hum., vol. 93 (2010), pp. 1.
Wu, J.S., Holman, R.E., Dorney, J.R., 1996. Systematic evaluation of pollutant removal by urban wet detention ponds. J. Environ. Eng. 122, 983–988.
Yi, Z., Loosli, F., Wang, J., Berti, D., Baalousha, M., 2019. How to distinguish natural versus engineered nanomaterials: insights from the analysis of TiO2 and CeO2 in soils. Environ. Chem. Lett. 18, 215–227.