Atmospheric particulate matter as a source of metal nanoparticles contamination in aquatic ecosystems

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ABSTRACT

Air pollution is currently considered as one of the greatest health risks for humans and air pollution legislation and control worldwide is based on the size of particulate matter (PM) to evaluate the effects on health. Particulate matter ≤2.5 μm diameter is considered more dangerous than larger sizes (PM≤10). This study investigates the composition, stability, size and dispersion of atmospheric PM after transfer to an aqueous system. We aimed to understand the changes in the physical properties and characteristics that can contribute to increased metal uptake in humans and other biota to improve the safety regulations involving PM in the environment. Samples collected in an area affected by the steel industry influence were separated into 8 fractions (425 to ≤10 μm) and analysed physically by diameter light scattering (DLS), potential zeta and nanoparticle tracking analysis (NTA) for dispersion measurements and scanning electron microscope (SEM) for particle size characterization. The elemental composition (B, Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Rb, Sr, Y, Zr, Nb, Ag, Cd, Sn, Ba, La, Se, Ta, W, Hg, Hg, Pb and Bi) among the fractions were compared using X-ray and chemical analyses using ICP-MS. The PM composition was 80% of Fe, followed by Al, Mn and Ta. All particle fractions are formed by an agglomeration of nanoparticles ≤200 nm in aqueous medium. This study highlights that the environmental impact from atmospheric particulate matter contamination could be substantially higher than would be otherwise expected under atmospheric regulatory frameworks. These findings provide the important insights to future investigations on safety regulations involving atmospheric PM on the environment indicating the need to revise air pollution regulation and to create new legislation regarding atmospheric particulates in hydrological resources.

Keywords: Nanoparticle, particulate matter, air quality, emergent metallic contaminants, air

safety regulations.

1. INTRODUCTION

Steel industries are a major environmental pollution source as they release numerous contaminants as particulate matter (PM), gas, and vapour. Most PM wastes from these industries contain iron, carbon powder and silicon (Yan et al. 2010), and minor elements such as lead, aluminum, zinc, manganese, chromium, cadmium, copper, nickel, titanium, vanadium and other trace metals (Lima et al. 2001). Legislation for monitoring and controlling atmospheric contamination is usually based on the definition that PM is a complex mixture of solid and liquid particles of organic and inorganic substances suspended in air; fractions having a diameter of 10 μm or less (≤ PM10) can penetrate and lodge deep inside the lungs and those fractions having a diameter of 2.5 μm or less (≤ PM2.5) can penetrate the lung barrier and reach the blood system (WHO, 2016; WHO, 2005; CONAMA, 1990).

The International Agency for Research on Cancer considers that contaminants from iron melting and steel production are carcinogenic for humans, and PM with an aerodynamic diameter ≤ PM10 are more associated with cancer development (Alexandrina et al. 2019; Mohammed et al. 2017; WHO, 2005). The steel smoke and particles can cause several types of damage in the lung, with siderose the most common disease; for example, 30-40% of steel workers have smoke fever or steel flu caused by exposure to the discharged metals (Lima, 2001).

The different PM sizes released in the atmosphere during smelting are dependent on the alloys produced, the original ore and industrial process due to high melting temperature or additives used in the process (Badillo-Castañeda et al. 2015). The PM released in smoke can be coarse, fine, ultrafine and nanoparticle (NPs) size (at least in one dimension ≤100nm) which have high potential to reach the respiratory system (Arick et al. 2015). Furthermore, metallic

NPs has been widely used in steel production to improve weld strength but this may increase their release to the environment (Kumar et al. 2018). NPs are continuously used in numerous industries, including the steel ones but, as yet there are no established environmental regulations as their action is not fully understood.

The PM can disaggregate into fine and nanoparticles (NPs) which can be assimilated in cells, tissues and the bloodstream (Panzarini et al. 2018; Bakand and Hayes, 2016; Gnach et al. 2015; Zhao and Stenzel, 2018). Souza et al. (2019) showed that the atmospheric PM collected surrounding Vitória city, in the State of Espirito Santo, Brazil, was formed by particle agglomerates of approx. 100 μm and some of them were composed by Ti nanoparticles varying from 17 to 193 nm. Once dissociated into water, these NPs were incorporated into different tissues of a native estuarine fish species (*Centropomus parallelus*) living in this region (Souza et al., 2019).

Although the above studies cast doubt on the validity of the current legislation for atmospheric PM based only in restricted fine particle size (Laux et al., 2018), this creates more questions regarding their fate and effects following dissociation and fragmentation in aqueous media (Goswami et al. 2017).

As the above represents uncertainties for human and environmental safety in creating legislation based only on the PM size (≤ PM10), the present work focuses on the size, composition, stability and properties of atmospheric PM from a steel industry area after entering the aqueous system. We aimed to verify changes in the atmospheric PM properties and characteristics in aqueous medium to support improvements in the safety regulations involving atmospheric PM in the environment. Hence the hypothesis tested here is that particle sizes other than those emphasised in the legislation pose a major environmental threat. The analysis involved comparing the size and elemental composition of PM in the air and in water.

2. MATERIAL AND METHODS

2.1 Study area and sampling

Atmospheric PM was collected in the Ilha do Boi (20º17′03.8″S and 40º14′24.9″W), in Vitória city, state of Espírito Santo, Brazil, only 14 km from the Tubarão Complex, an important steel industrial area (Figure 1). Ilha do Boi was originally an island poorly accessible to the mainland and with very low local traffic and contamination by mobile sources as road traffic. Ilha do Boi receives direct impact from the PM released by the Tubarão Complex all year round, with April and November having a higher PM deposition (Santos et al., 2017). Airborne gravimetric sampling was carried out by JUNTOS SOS Ambiental in April 2018.

2.2 Particulate matter characterization in solution

The atmospheric PM was fractionated into 8 different sizes: 425-250 µm, 250-150 µm, 150-75 µm, 75-45 µm, 45-32 µm, 32-22 µm, 22-10 µm and ≤10 µm (known as PM10). The first six sizes were separated using an EML DIGITAL PLUS Test Sieve Shaker (Haver & Boecker, Germany), and the lowest two sizes were obtained using a precision sieve Advanced Sonic Sifter (Advantech Manufacturing, USA). From 1 kg of collected PM there was on average 1g of PM≤10.

The PM was characterized in relation to particle size, agglomeration potential and surface loads. Characterization involved preparing a concentrated solution in ultrapure water (100 µg mL^{-1}) which was sonicated for 30 minutes in an ultrasonic bath (40 kHz frequency, Q335D, QUIMIS, Brazil) of each PM fraction size. Thereafter, samples from each solution were diluted in ultrapure water at concentrations of 10 and 40 µg mL^{-1} for PM characterization. The PM hydrodynamic sizes and zeta potential were measured using a light scattering spectrophotometer (DLS, Diameter Light Scattering, Zetasizer Nano ZS90 Malvern Panalytical Instruments, Westborough, MA, USA). A NanoSight for Tracking Analysis (NTA, NS300, Malvern Panalytical Instruments, Westborough, MA, USA) using light scattering and Brownian motion properties gave the particle size distribution in the liquid suspension samples.

2.3 Chemical analyses

The chemical analysis was conducted as described by Souza et al (2019). PM from each fraction (0.1 g dry weight each) were digested according Chappaz et al. (2012) with 3 mL of nitric acid and 500 µL of hydrochloric acid (ultrapure, sub-boiling grade) and 500 µL of hydrogen peroxide Suprapur (30% analytical grade - Merck) and, filtered with 0.45 µm nitrocellulose filter according to EPA (1994). Controls were prepared with only reagents used in digestion following the same procedure. All digested samples were stored at 4°C until analyses.

Twenty seven elements were measured (B, Al, V, Cr, Mn, Fe56, F57, Ni, Cu, Zn, As, Se, Rb, Sr, Y, Zr, Nb, Ag, Cd, Sn, Ba, La, Se, Ta, W, Hg201, Hg202, Pb, Bi), in triplicate, in ICP-MS according to 200.8 (USEPA, 2009). Quality control and assurance were accessed using a certified reference material (MESS-2, estuarine sediment) and recoveries were 92 ± 8%. The repeatability of ICP-MS measurements was generally ≥ 96.8%.

2.4 X-ray, and Scanning and Transmission Electron Microscope (STEM) Analyses

To determine the phases of each PM fraction, X-ray diffraction was performed according to Souza et al. (2019). The SEM microanalyses were conducted as described by Souza et al

(2019), using aluminum studs in which the PM samples were glued on copper double-face tap e sputtering with platinum. The particles present in each PM fraction were characterized using a scanning and transmission electron microscope (MAGELLAN 400 FEG 100, FEI Technologies Inc., USA) with a secondary electron (SE) and an electron backscatter detector (BSE). The chemical elements were identified applying Electron Dispersive Spectroscopy (EDS). Images at different magnifications were taken to correlate with physical characterization in solution.

2.5 Statistical analysis

One-factor ANOVA ($p \leq 0.05$) analysis was conducted to detect differences among fraction sizes (Tukey test). Shapiro-Wilk test and means for Variances-Levene (ADM) analysis were used to check normal distribution and homogeneity of variance, respectively. The data are reported as mean and 95% confidence intervals. Canonical Discriminant Analysis (CDA) was performed to assess differences among matrices regarding its total metal constitution ($p \leq 0.05$). Zr, Sn and Hg were not included in the CDA analysis due to being lower than the detection limit in some fraction sizes.

3. RESULTS AND DISCUSSION

The PM fractions collected in Ilha do Boi were all mainly formed of hematite and quartz (Figure 2). Hematite is a mineral phase that contains 70% of Fe and impurities which is typical from Brazilian iron mining and is the main material used in the Tubarão Complex industries. Hematite is used to produce iron pellets, a raw material for the steel industry that also adds other metals (eg. Cr, Cu and Ti) to produce different alloys, according to the market demand. Quartz is a common mineral found in PM samples likely derived from dust.

Fe had the highest concentration in all PM fractions, consisting approximately 80-90% of total metals analysis by ICP-MS (Table 1), followed by Al which varied from 7.5 to 14% and in minor proportion, manganese and titanium. There was no clear pattern of metals concentration and distribution among the eight-fraction sizes analyzed. The PM≤10 and PM32-45 had the highest metal concentration values while the PM250-425 and PM250-150 had the lowest values for almost all analyzed metals (Table 1). However, CDA showed no differences among the fraction sizes (r^2= 1).

Despite high Fe and Al concentrations, another 19 metals were quantified (Table 1) and 6 (Ta, Z, W, Ag, Cd, As, Se) metals were detected but were below detection limits. It is important to highlight the presence of emerging metallic contaminants, not yet evaluated in monitoring programs and without pre-established limits in the legislation, such as Bi, Ti, Zr, Y, La, Nb, Ba, Sn, Sr and Ce (Table 1). All these metals are used in new metal alloys for the growing electronics, light alloys and anticorrosive steel. These rare elements dispersed in the atmosphere contaminate not only the air but also the aquatic environment and, passively, be incorporated by the local biota (Souza et al. 2018b, Souza et al. 2019).

The SEM analyses of PM fractions demonstrated that each one was constituted by an agglomeration of nanoparticles (Figure 3). SEM with nano-size magnification showed that all PM ranging from 1 to 425 μm in size were formed by agglomerates of nanoparticles varying approximately from 14.2 to 69 nm (smaller dimensions) and 100 to 467 nm (larger dimensions) (Figure 3). In general, larger particles are transported in the air by surface creep (>2000 μm) and resuspended (60 – 2000 μm), being responsible for most of the mass movement at local scale (Stout and Zobeck 1996; Ravi et al 2011). Conversely, smaller particles (≤60 μm) are transported as an atmospheric suspension, and are liable for long-range transport at regional, continental, and global scales (Chadwick et al 1999; Prospero et al 2002).

Additionally, SEM analyses show that in all PM fractions occurred agglomerates of NaCl between metal nanoparticles (Figure 4). Santos et al. (2017) reported that the main contribution of PM in Ilha do Boi resulted from metallurgical activities, including the ore stockpiles, iron-pellet stockpiles and the main furnaces. Steel industries require large water volume and easy access to ports to export their product, thus, these companies are usually installed in coastal areas and/or estuaries. It is suggested here that the presence of NaCl agglomerates is due to maritime spray and high humidity; once released in the atmosphere, the metallic nanoparticles form agglomerates with salt, silicon, and heavy metals.

Once in aqueous solution, the agglomerates can be dispersed, and the nanoparticles become available being easily internalized in the biota (Oberdörster et al. 2005). After PM dispersion into water, the particle characterization obtained from NTA and DLS analyses agreed with the SEM results, showing that the hydrodynamic diameter of all fraction sizes of PM analyzed (from 10 to 425 μm) was in the nanoscale ranging between 100 to 250 nm (Table 2 and Figure 5). The polydispersity index (PdI) values (0.4 to 0.8) indicated that the NP agglomerates/aggregates were in suspensions (Table 2) and the Zeta potentials, in which values higher +30 mV and below -30 mV indicate particle stability in aqueous systems, were between −19.2 mV and − 29.8 mV (Table 2). This shows that the analyzed samples probably were composed of different types of particles, each one with different stabilities.

At present, each country has applied specific regulations to outdoor and indoor environments to minimize and prevent health problems. The atmospheric PM limits recommended by the World Health Organization (WHO) for coarse particles (PM≤10) in the atmosphere is a maximum of 50 μg m^{-3} in 24 h but, considering the value calculated for one year, the daily mean cannot exceed 20 μg m^{-3} in the same period; for fine particulate (PM≤2.5), it is a maximum of 25 μg m^{-3} in 24 h and daily mean of 10 μg m^{-3} in in the same period (WHO, 2005; Bourdrel et al. 2017). The analysis of air quality usually quantifies PM≤10 and PM≤2.5 filtered from air by 24 h and captured in a membrane; the difference between the membrane mass before and after sampling process is considered as the total amount of PM in the air (Cereceda-Balic, 2017). The mass difference is considered the main parameter to classify air quality. In our study, we found that for each 1000 g of total PM collected, we sieved 1g of PM≤10 μm showing that the worldwide government rules are based on usually 0.1% of the total PM released in the atmosphere.

Larger atmospheric PM sizes (>10 μm) receive little attention and usually have no emission limits determined or flexible limits by governmental regulations (WHO, 2005). Considering that all larger PM fractions are liable to dissociate in smaller ones, even in nanoparticles, in water, these regulations can be inaccurate. Moreover, atmospheric PM can obscure a complex chemical composition depending on sources and interactions with the surrounding environment (Bourdrel et al. 2017). Recent studies in the same Brazilian estuarine areas as that studied here, and using carbon, nitrogen, strontium, and lead stable isotopes and titanium nanocrystallography, concluded that an important source of contamination of these aquatic estuarine ecosystems was metals present in atmospheric PM which were accumulated and transferred to the upper level of the trophic chains by bioaccumulation (Souza, 2017; Souza et al. 2018b, 2019).

The atmospheric PM consists of chronic and diffuse contamination in which only one source may spread particles to a large area (Tiwary and Williams, 2018). During the rainy season the atmospheric PM can be dispersed and dissociated in the nanoscale and percolate into the subsoil and affect groundwater until it reaches rivers, lakes and oceans. Then, to exclude the possibility of overexposure to nanoscale particles in areas in which the atmospheric PM can contaminate hydrological resources, additional tests should be incorporated in environmental analyses related to atmospheric PM dispersion in aqueous system and size measurements, for example, NanoSight for Nanoparticle Screening (NTA). Thus, the effects of atmospheric particulate emissions for aquatic biota can be understood more accurately with this newly-observed process.

Thus, despite the aerial animals and human exposure to atmospheric pollution, a second contamination pathway should be evaluated as the aquatic system can be direct or indirect, the main receptor of larger and smaller atmospheric PM. Nanoparticles present in the atmospheric PM incorporated by aquatic biota can be transferred to humans by consumption of food (Xing et al, 2017). Hence, it is necessary to show the correlation between atmospheric PM and aquatic biota contamination, since only few studies have focused on this contamination pathway and most environmental regulations remain unclear about this issue and its impact on several organisms, populations and communities.

We hypothesized that in humans and terrestrial animals, the internalization of fine PM, via the respiratory system, by direct contact with the humid lung epithelial surface may be higher with the particle disaggregation in NP size in body fluids (e.g. human mucous or blood). However, experiments are required to explore this hypothesis once, as emphasized by Kettiger et al. (2015) those particles can interact and promote damage to tissues.

In recent few years, concerns regarding air pollution have been increasing due to large-scale health effects involving premature deaths, pulmonary diseases, respiratory infections, and cancer. Currently, 91% of the world population are living in places with low air quality leading the World Health Organization (WHO) to consider air pollution as the biggest health human problem (Andreão et al. 2018; WHO, 2016, WHO, 2018). Material Science has made substantial progress in the recent years with the emergence of innovative characterization technologies, complex synthesis, and many materials being commercialized on a global scale. Despite this, legislation adaptation and updating accounting for these advanced techniques are still poorly included in government policies.

CONCLUSIONS

The air pollution impact on health increases each year and indicates the importance of adopting more restrictive air quality standards. Our results show that PM is an agglomeration of nanoparticles and particles $\leq$200 nm. New data here showing the composition presented by ICP-MS, size characteristics (SEM) and dispersion (DLS and NTA) is essential to implementing, monitoring and evaluating environmental policies that help to tackle air pollution while also protecting health. Thus, this paper demonstrates that particles separated by size do not correspond in solution to the exact size as a dry form, which can lead to an environmental impact. These results highlight the need to revise the actual regulatory framework for air pollution and create new legislations regarding atmospheric particulate matter contamination in water environments, considering that the only use of size particles may not be sufficient as an parameter for atmospheric pollution regulations.

Therefore, a review of air quality standards is necessary, thus, we present this research as a starting point for update atmospheric laws regulations, with the inclusion of dispersion particles, eg. NTA (preferentially) or DLS, and analysis to identify nanoparticle form, such as the use of scanning microscopy. We propose these analyses should be made at least once a year by defining the environmental conditions for industries operation to check the particles real size.

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FIGURE CAPTIONS

Figure 1. State of Espírito Santo in Brazil, South America, showing the sampling site Ilha do Boi (A) and the industrial area Tubarão Complex (B).

Figure 2. X-Ray analyses of atmospheric particulate matter fractions collected in Ilha do Boi, Espitrito Santo, Brazil. Red triangle: Hematite Fe_2O_3 phase; Blue square: Quartz SiO_2 phase.

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Figure 5. NanoSight for Nanoparticle Screening (NTA) analysis of different particulate matter (PM) fractions. a) ≤10 µm; b) 10-23 µm; c) 23-32 µm; d) 32-45 µm; e) 45-75 µm; f) 75-150 µm; g) 150-250 µm; h) 250-425µm. The black line indicates the mean value of all NTA measurements, and the red area represents the +/-1 standard error of the mean.

Table 1

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	Size fraction of particulate matter (PM)							
	PM <10 µm	PM 10-23 µm	PM 23-32 µm	PM 32-45 µm	PM 45-75 µm	PM 75-150 µm	PM 150-250 µm	PM 250-425 µm
B	535 a (526-544)	318 b (309-327)	244 d (235-253)	273 c (264-282)	262 cd (253-271)	244 d (235-253)	311 b (302-321)	276 c (267-285)
Al	16669 b (16331-17008)	14458 c (14120-14797)	8793 f (8454-9132)	24106 a (23768- 24446)	11194 d (10856- 11533)	10916 d (10578-11256)	10091 e (9752-10430)	9060.2 f (8721-9399)
Ti	873 (850-897) b	668 (645-692) c	406 (383-430) f	1290 (1267-1314) a	565 (542-588) d	570 (547-594) d	493 (470-517) e	398 (375-422) f
V	87 (85-89) b	63 (61-64) c	42 (41-44) f	103 (101-104) a	61 (59-63) c	52 (50-54) d	46 (45-48) e	39 (37-40) f
Cr	59 (57-60) b	63 (62-64) a	28 (27-30) e	50.7 (49.5-51.9) c	34 (33-36) d	21 (19-22) f	15 (14-16) g	8 (7-10) h
Mn	1267 a (1246-1289)	1035 c (1013-1056)	773 d (752-795)	1274 a (1253-1295)	1093 b (1072-1115)	1130 b (1109-1152)	780 d (759-802)	736 d (715-757)
Fe^{56}	192685 a (190437-194933)	91227 c (88979-93474)	91560 c (89312-93808)	87277 c (85029-89525)	161469 b (159221-163717)	72659 d (70411-74907)	71437 d (69189-73685)	54691 e (52444-56939)
Fe^{57}	194452 a (192982-195922)	91664 c (9094-93134)	91307 c (89837-92777)	87562 d (86092-89032)	161229 b (159759-162700)	72781 e (71311-74251)	71787 e (70316-73257)	54672 f (53202-56143)
Ni	31.(30.6-31.7) b	30.6 (30.0-31.2) b	15.8 (15.2-16.4) d	45.1 (44.4-45.6) a	19 (18-20) c	19.9 (19.3-20.5) c	20 (19-21) c	15.3 (14.8-15.9) d
Cu	495 (490-500) a	231 (227-237) c	113 (109-119) g	300 (296-306) b	149 (145-154) f	165 (161-171) e	206 (201-211) d	228 (223-233) c
Zn	79 (65-93) f	411 (397-426) b	128 (114-142) d	531 (517-546) a	101 (87-115) def	224 (210-239) c	90 (75-104) ef	118 (103-132) de
Rb	15.2 (14.8-15.6) b	11.4 (11.0-11.8) c	9.2 (8.8-9.6) e	17.9 (17.5-18.3) a	11.29 (10.98-11.77) c	11.5 (11.2-12.0) c	10.9 (10.5-11.3) cd	10.0 (9.7-10.5) de
Sr	111 (109-114) b	94 (91-96) c	68.31 (65-70) e	120.23 (118-123) a	86 (83-88) d	90 (88-92) cd	65 (63-67) e	65 (63 -67) e
Y	11.7 (11.4-12.1) b	8.8 (8.4-9.1) c	5.7 (5.4-6.0) g	13.0 (12.7-13.3) a	7.4 (7.1-7.8) de	7.8 (7.5-8.2) d	6.9 (6.6-7.2) ef	6.4 (6.1-6.8) f
Zr	<LOQ	2.5 (0.9-4.1) b	<LOQ	0.6 (-1.1-2.2) b	<LOQ	13 (11-14) a	<LOQ	<LOQ
Nb	5.1 (4.8-5.3) a	2.9 (2.6-3.1) b	1.2 (0.9-1.4) d	3.2 (2.9-3.4) b	2.1 (1.8-2.4) c	1.5 (1.2-1.7) d	1.7 (1.5-2.0) cd	1.1 (0.9-1.5) d
Sn	<LOQ	0.71 (0.1-1.2) a	<LOQ	<LOQ	<LOQ	<LOQ	0.3 (-0.3-0.8) a	<LOQ
Ba	1.01 (0.97-1.05) d	1.31 (1.27-1.35) b	0.67 (0.63-0.71) f	2.21 (2.17-2.25) a	1.19 (1.15-1.23) d	1.16 (1.12-1.20) c	0.86 (0.82-0.90) e	0.67 (0.62-0.70) f
La	24.2 (23.8-24.6) a	15.5 (15.1-15.9) c	9.2 (8.8-9.6) f	20.1 (19.7-20.5) b	12.9 (12.5-13.2) d	12.3 (11.9-12.7) d	10.8 (10.4-11.2) e	9.7 (9.3-10.0) f
Ce	43.5 (42.9-44.1) a	29.0 (28.4-29.6) c	16.7 (16.1-17.3) f	41.4 (40.8-42.0) b	24.1 (23.5-24.7) d	24.2 (23.6-24.8) d	20.0 (19.4-20.6) e	16.9 (16.3-17.5) f
Hg	2.8 (2.1-3.6) a	0.4 (-0.3-1.1) b	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Pb	89 (87-91) b	64 (63-67) c	32 (30-34) g	107 (105-108) a	50 (48-52) f	55 (53-57) de	57 (55-59) d	52 (50-54) ef

Table 1. Metal concentration (µg mL^{-1}) in the eight fraction sizes of atmospheric particulate matter collected in Ilha do Boi (Vitória, ES, Brazil). Media (95% confidence intervals). Different letters indicate significant difference among fraction ($p<0.05$, one-factor ANOVA, Tukey test).

Table 1. Dynamic Light Scattering (DLS) and zeta potential measurements in each fraction of settleable particulate matter (SPM).

SPM Fraction	Hydrodynamic size (nm)	PdI[a]	Zeta Potential (mV)
<10 µm	330.2 ± 75.1	0.849 ± 0.238	-22.6 ± 2.0
10-23 µm	205.9 ± 95.9	0.686 ± 0.154	-25.6 ± 1.8
23-32 µm	150.1 ± 33.1	0.694 ± 0.192	-23.9 ± 1.1
32-45 µm	234.9 ± 19.5	0.668 ± 0.145	-26.9 ± 0.2
45-75 µm	169.4 ± 39.5	0.680 ± 0.255	-29.8 ± 3.1
75-150 µm	234.1 ± 25.3	0.698 ± 0.161	-21.3 ± 1.5
150-250 µm	251.8 ± 37.8	0.372 ± 0.028	-19.9 ± 0.2
250-425µm	242.2 ± 41.5	0.451 ± 0.102	-19.2 ± 0.4

[a] PdI = polydispersity index.

Figure 1
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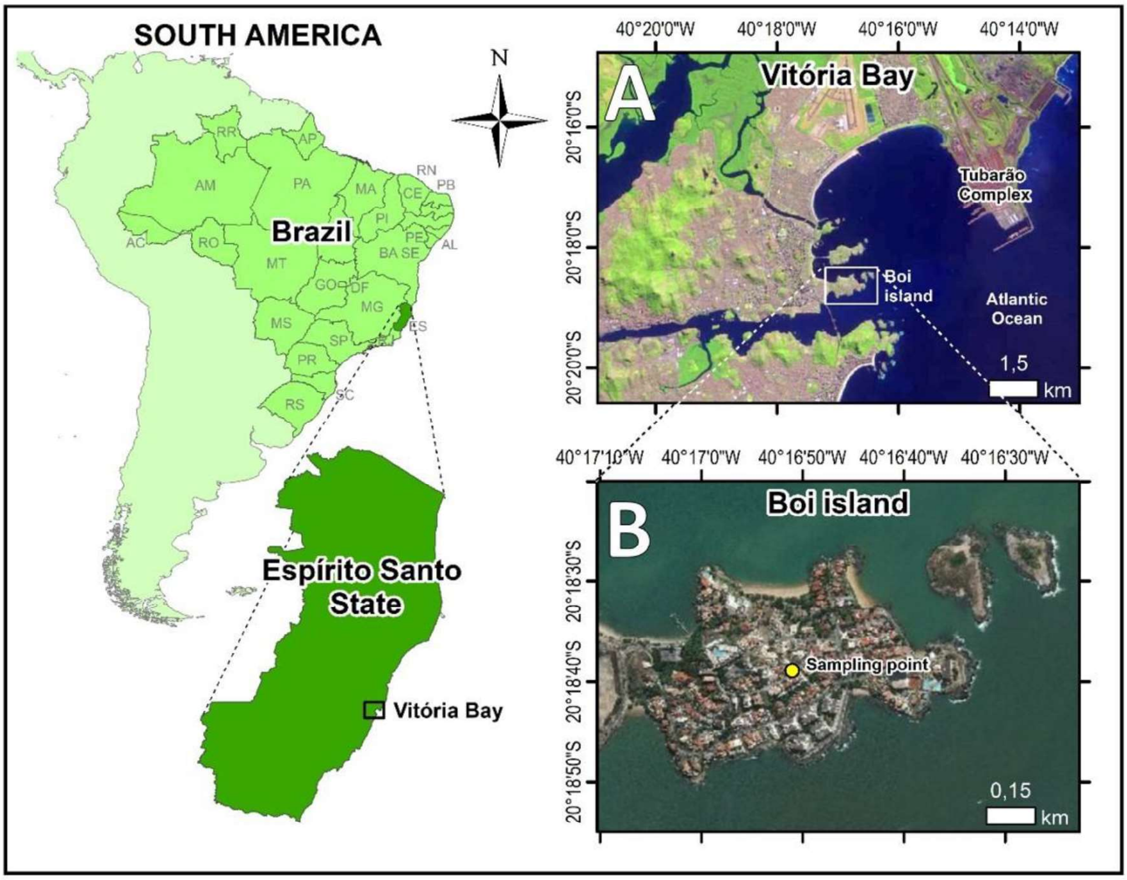

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Figure 2
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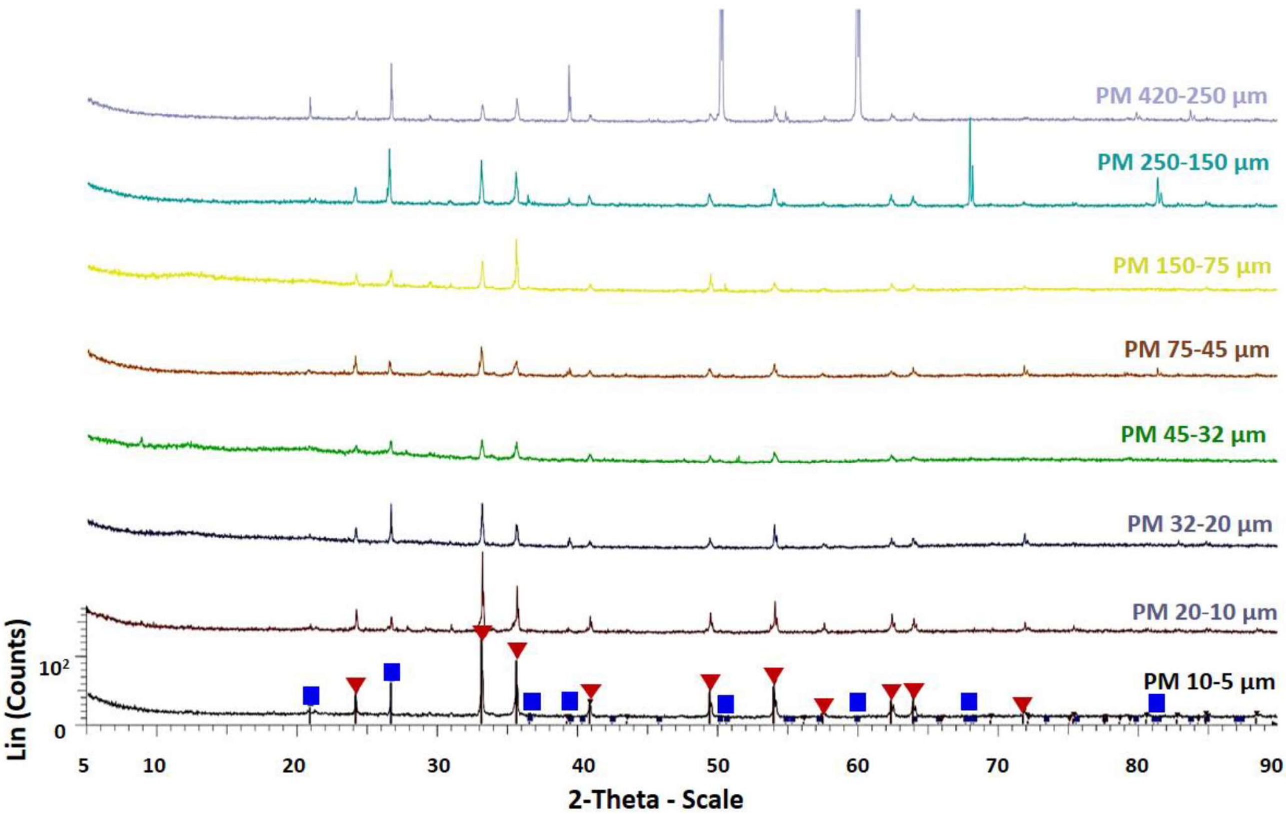

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Figure 4

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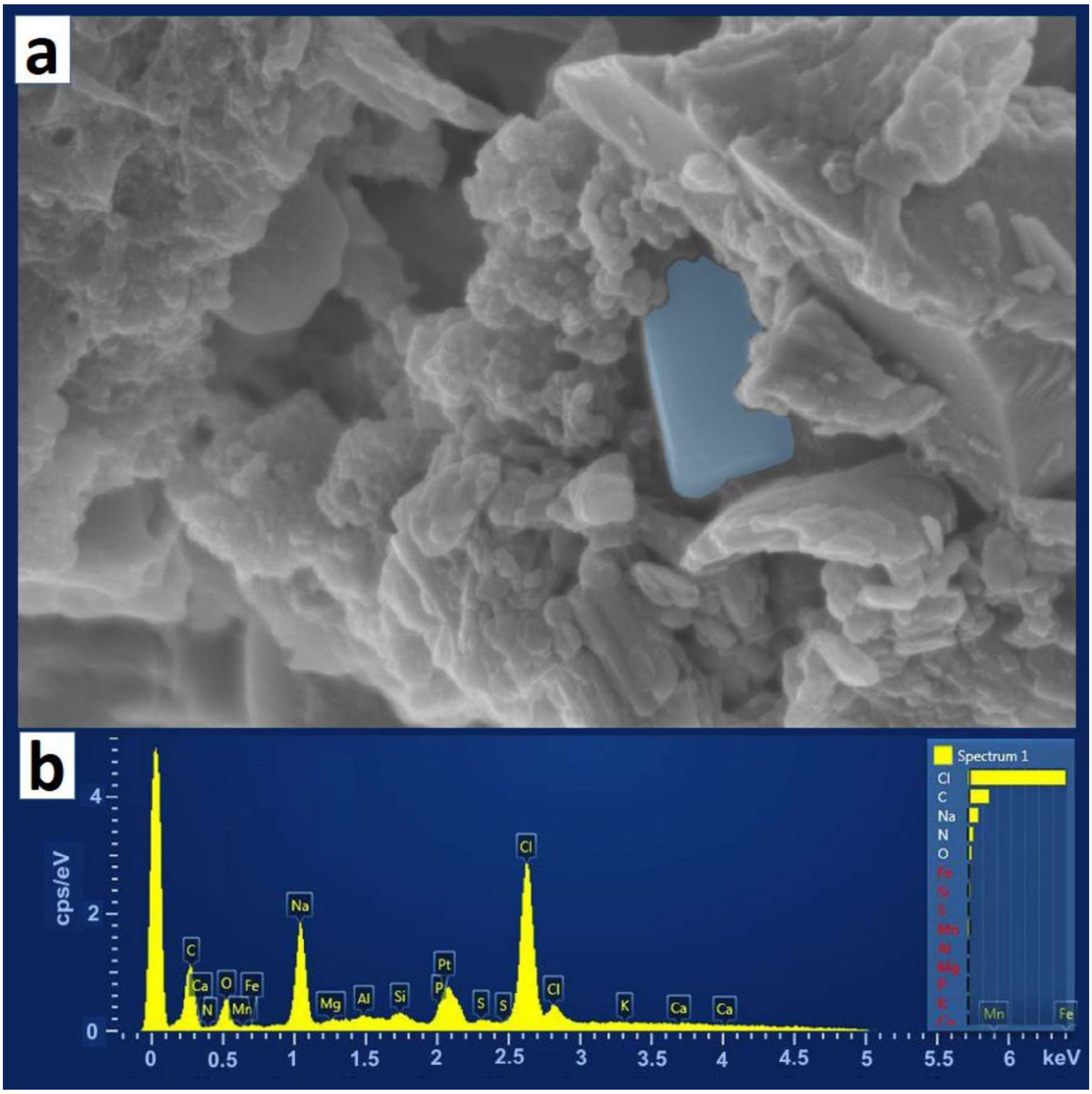

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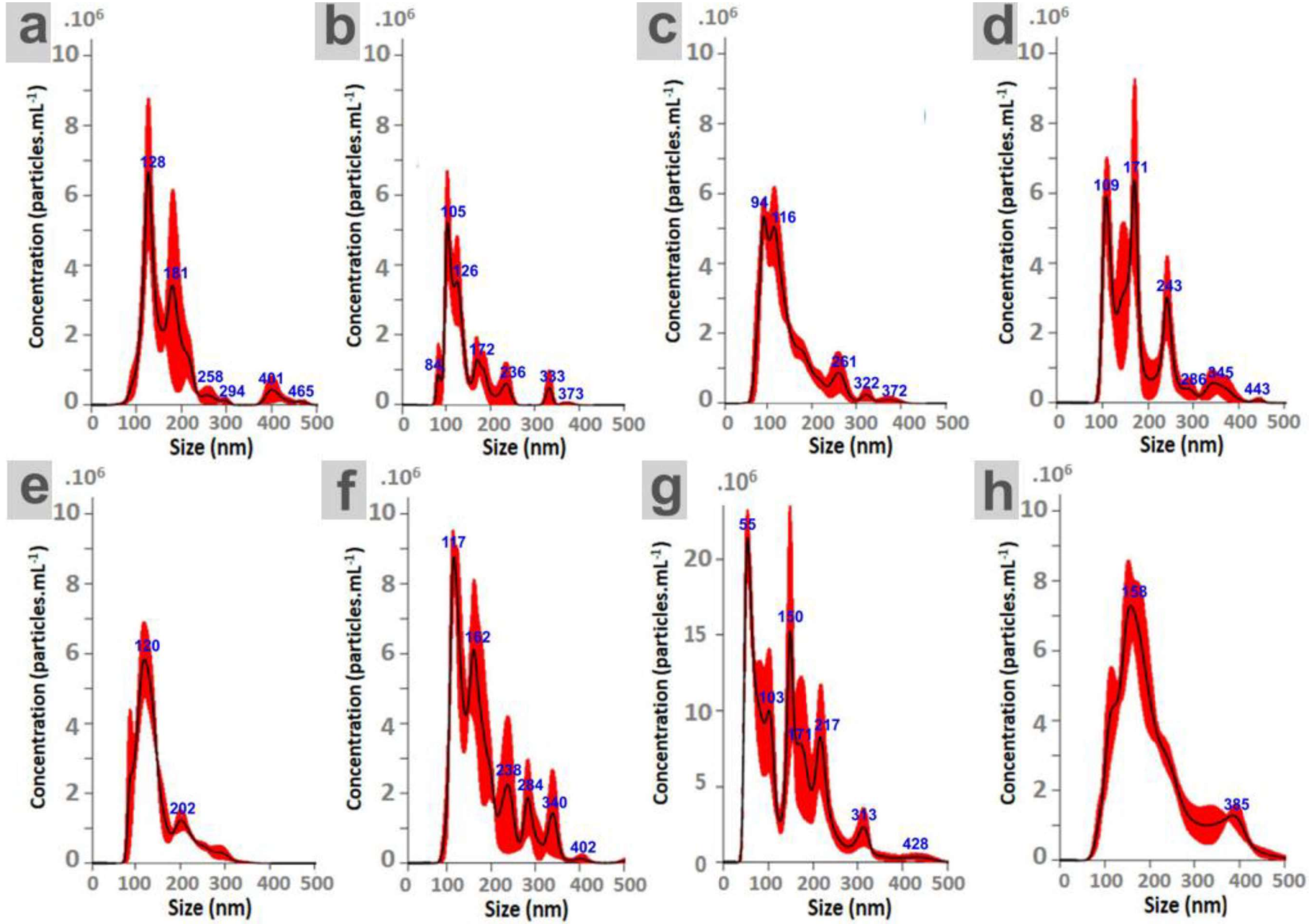

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*conflict of Interest Statement

Declaration of interests

☒ 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.