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Article

Preliminary Study about the Origin of Trace Elements in the Atmospheric Deposition in Two Brazilian Subtropical Estuaries

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The atmospheric deposition of dissolved trace elements was investigated in two subtropical estuarine systems, located on the coast of Paraná, Southeast Brazil. The samples (n = 91) were collected in three periods, from May to September 2010, in four different areas. Trace elements concentrations (Al, Fe, Zn, Mn, Ba, Ca, Mo, V, As, Cu, Co, Ni, Cr and Pb) were determined for dissolved fraction using inductively coupled plasma-mass spectrometry (ICP-MS). pH measurements revealed the occurrence of a slightly acidic precipitation in the investigated points. Among the trace elements, Zn was the most abundant, followed by Al, Fe, Mn, Cu, Ba and V. The analysis of the enrichment factors enabled the identification of the different sources of the analysed elements. The origin of the Al and Fe elements were entirely continental, whereas Zn was primarily associated with human activities. Thus, the atmospheric deposition may be a primary route of exposure to anthropogenic Zn for estuarine biota.

Keywords: rainwater composition, trace elements, Paranaguá Estuarine Complex, Guaratuba Bay

Introduction

Monitoring the composition of the atmosphere is essential for understanding the biogeochemical cycles of chemical elements and the anthropic influence on them once the atmosphere plays an important role in transporting pollutants for continental and coastal ecosystems by the wet and dry deposition.[1-5]

The increase of industrialisation and the growth of urban populations have increased energy demands, which have resulted in higher emissions of pollutants to the atmosphere (aerosols, volatile organic compounds, NO_x, SO_2 and trace elements).[6-10]

The nitrogen oxides ($NO_x = NO + NO_2$) and sulfur dioxide (SO_2) are primarily emitted by the burning of fossil fuels and industrial activities, and are oxidized into nitric acid (HNO_3) and sulphuric acid (H_2SO_4), respectively, and can reduce the pH of the rainwater of 5.6,[11] leading to acidification of the soil and the surface water bodies, with consequent damage to the continental and coastal ecosystems.[10,12-15]

In coastal and oceanic zones, the atmospheric deposition of trace elements such as cadmium (Cd), mercury (Hg) and lead (Pb), even at low concentrations, have harmful effects on marine organisms.[16-19]

These elements are persistent in the environment and have high mobility, reactivity and solubility in rainwater (especially under conditions of low pH), which increases their bioavailability and biomagnification,[20] and indirectly affects humans.[21-23]

Therefore, the qualitative and quantitative characterisation of trace elements in rainwater, especially in industrialised coastal and densely populated regions, is of great importance to identify the different sources of these elements and to assess their potential impacts on marine ecosystems and human health.[24]

In the Paranaguá Estuarine Complex (PEC) and the Guaratuba Bay (GB), Paraná State, in the Southern of Brazil,

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the population growth, with a corresponding increase in tourist, agricultural, industrial and port activities, has been changing the conformation of the boundary of these two estuarine systems and generating problems that affect the environment and its natural support system.[25]

Recent studies have indicated sediment contamination by trace elements of the PEC, such as arsenic (As) and zinc (Zn),[26,27] and the water column by selenium (Se).[25] In the GB,[28] it was observed that the enrichment of Hg in recent sediments is deriving from agricultural activities in the region. Therefore, we hypothesized that human activities conducted in these two estuarine systems and their surroundings can be potential sources of trace elements to the local atmosphere, with subsequent deposition in these ecosystems.

The objective of this study was to evaluate comparatively the trace elements deposition in the two estuarine systems (PEC and GB) through measurements of pH and conductivity, and analysis of the trace elements in the dissolved fraction. In addition to looking at the relationship between the chemical composition of the precipitation and the meteorological factors, such as the wind direction and intensity, and consequently infer the possible sources of air pollution.

Experimental

Study area

The State of Paraná (southern region of Brazil) has a coastal plain located between the Serra do Mar and the South Atlantic Ocean. The climate of the coast, according to the Köeppen classification is Cfa type, which means that the area has a mesothermal humid subtropical climate with a hot summer.[29] The average annual temperature is 21.5 ºC, and the average rainfall may reach more than 2000 mm year^{-1}.[30] The predominant winds on the coastal region are originated from the east, southeast and south quadrants, with an average speed of 4 m s^{-1} and a maximum speed of 25 m s^{-1}.[31]

The continuity of the coastal plain is interrupted by two estuarine systems: in the north, the Paranaguá Estuarine Complex (PEC), and in the south, the Guaratuba Bay (GB). The north shore of these systems is covered with well-preserved mangrove areas, whereas the southern shore is densely populated (Figure 1).[32]

The PEC is located between the parallels 25°00'S and 25°35'S, and longitudes 48°15'W and 48°50'W, has an area of approximately 600 km^2, and is one of the largest estuarine systems of South Atlantic.[29] In the PEC lives in approximately 180,000 people distributed in the inner, middle and outer sectors of the system.[33] In the median sector of the PEC is the main urban, industrial and port center of this system, being the largest grain exporter of the country (Figure 1).

The GB, a small estuarine system, is located between the parallels 25°47'S and 25°52'S and longitudes 48°39'W and 48°45'W and has an area of approximately 48.57 km^2 (Figure 1).[33] This bay belongs to the city of Guaratuba, which has a population of approximately 32,000 inhabitants

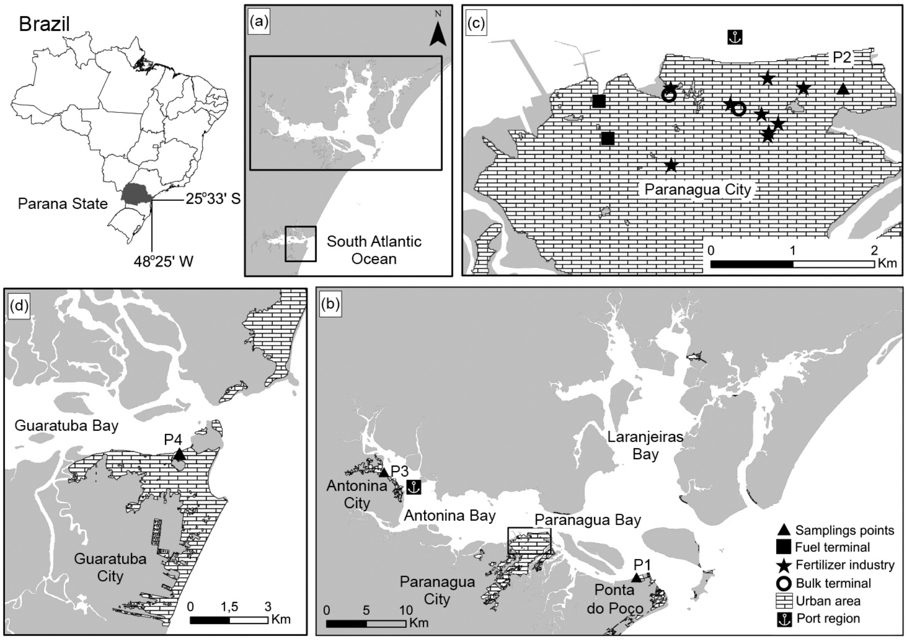

Figure 1. Location map of study area: (a) to the north, the PEC, and to the south, the GB; (b) PEC, with three sample points situated in the external sectors (P1), middle (P2) and internal (P3); (c) city of Paranaguá, with the locations of the P2 point, fertiliser industries and fuel terminals and bulk; (d) GB, with a sample point (P4) located at the mouth of this bay.

Table 1. Location and description of the sampling points

Sampling points	Geographic coordinates	Location area	Distance from the bay / m	Distance from the sea / km
Paranaguá Estuarine Complex (PEC)				
P1 (Marina club Ponta do Poço)	25°32'60"S 48°23'17"W	suburban	70	5
P2 (Container terminal of Paranaguá)	25°30'17"S 48°30'13"W	urban, industrial and port	381	16
P3 (Nautical club of Antonina)	25°26'09"S 48°42'25"W	suburban	10	37
Guaratuba Bay (GB)				
P4 (Yacht club Guaratuba)	25°52'27"S 48°34'46"W	urban	33	1.5

and experiences a significant increase in population during the summer.[32] Its main economic activities are tourism, fishing and more recently, mariculture. In the inner portion of the bay, rice and banana crops are predominant in the foothills of Serra do Mar.

Sampling

Sampling was carried out at three sites located in the external (P1), middle (P2) and internal (P3) sectors of the PEC and at the mouth of the GB (P4). The last one is approximately 50 km from the primary urban, industrial and port centre of the PEC (Figure 1). The description of the sampling points and their distances from the bay and the sea are presented in Table 1.

Three sampling campaigns were accomplished. The first collection was performed from May 26 to June 03, the second one between July 08 and 16, and the third one from September 23 to 30. At each sampling point, ten collectors for the bulk deposition were installed during the first two campaigns and five in the third one, and the collectors were displayed for eight days of each campaign. The replicate number was reduced because we verified no significant difference ($p > 0.05$) between them for all investigated elements. This is also evident due the low values of standard errors as showed in Table 2.

The height of the collectors varied between the sampling points due to the logistics of each collection location. The collector heights above the ground level were of approximately 22 m, 21 m, 2 m and 8 m, at P1, P2, P3 and P4, respectively.

The design of the total deposition collectors was based on the model of Casartelli *et al.*,[7] coupling a funnel to the top of a 3 L bottle, both of polyethylene (Figure 2). In the larger opening of the funnel, a saw-toothed part of polyethylene was attached to prevent birds landing on the funnels and contaminating the samples with faecal waste. A polyethylene cap with small openings was placed into the smaller opening of the funnel to allow the passage of rain water while simultaneously hindering the passage of insects. The area of the mouth of the collector funnel and its volume were 82 cm^2 and 280 mL, respectively.

Figure 2. Design of the total deposition collector (adapted from reference 7).

The collection bottles were coated with Tetra Pak material to minimise reactions mediated by microorganisms and photochemical changes likely to occur during the storage period of rainwater in the collector.

The material used for the collector assembly was carefully cleaned before each sampling, first with a sponge and tap water, and then rinsed with distilled/deionised water. Then, the funnels were immersed into a 10% solution of nitric acid (HNO_3) for at least 24 hours, and the bottles were then shaken vigorously with the same solution of $HNO_{3,}$ which remained in the bottles for the same time. After this step, the funnels and bottles were carefully rinsed with deionised water, and the electrical conductivity of the last water rinse was less than 1 µS cm^{-1}. Subsequently, the collectors were dried at 60 °C and stored in plastic bags until they were distributed in the field.[7]

To determine the influence of the meteorological factors on the chemical composition of the precipitation of the two estuarine systems, the rainfall, temperature, relative humidity, wind direction and intensity data were compiled for the period from May to September 2010. The meteorological data were provided by the Center for Marine Studies (CMS) of the Federal University of Paraná (the weather station of Pontal do Paraná), National Institute of Meteorology (INMET, weather station of Paranaguá) and the Meteorological System of Paraná (SIMEPAR, weather stations of Antonina and Guaratuba).

Analytical methodology and data quality

In the laboratory, the total volume of rain water from each collector was measured immediately. The pH and electrical conductivity of an unfiltered portion of each sample were measured using a pH meter (Analion®, model PM-602) and a conductivimeter (Oakton®, model CON-5), respectively. The pHmeter and the conductivimeter were calibrated with buffer solutions (Vetec®) that had pH values of 4.0 and 7.0 and a standard solution (Ms Tecnopon®) with a conductivity of 146.9 µS cm^{-1}, respectively.

For analysing the trace elements dissolved in the precipitation, an aliquot of each sample was filtered through a cellulose acetate membrane (Sartorius Stedim®) with a porosity of 0.45 µm, stored in polyethylene tubes, acidified to a pH < 2 using HNO_3 with an above pure grade (Merck®), refrigerated and have not suffered acid digestion before analysis.[7]

The analysis of the trace elements (Al, Fe, Zn, Mn, Ba, Ca, Mo, V, As, Cu, Co, Ni, Cr and Pb) was performed by inductively coupled plasma mass spectrometry (ICP-MS) using an instrument from Thermo Scientific® (model XSERIES 2). The detection limits were calculated according to the three standard deviations of the blank values, in µg L^{-1}: 5×10^{-4} to V and Co; 1×10^{-3} to Mn and Mo; 2×10^{-3} to Pb and Ga; 3×10^{-3} to Cu; 5×10^{-3} to Ni, 6×10^{-3} to Cr; 8×10^{-3} to As; 1×10^{-2} to Zn; 5×10^{-2} to Fe; 9×10^{-2} to Ba and 1×10^{-1} to Al. The accuracy of the analysis was less than 10% for all trace elements measured. The accuracy of the method was evaluated by the addition of an internal standard (Rh) to all samples, and the relative error was less than 2%.

For each trace element, we calculated the volume-weighted mean concentration (VWM) and the volume-weighted standard error (VWSE), to minimize the effects of very high concentrations of trace elements in poor rains and heavy rainfall dilution.[34] The VWM concentration was estimated using the equation:

$$\mathrm{VWM[X]} = \sum_{i=1}^{n} [\mathrm{X}]_i \mathrm{V}_i \Big/ \sum_{i=1}^{n} \mathrm{V}_i$$

VWSE was calculated from the formula of the VWM variance:[35]

$$\mathrm{Var(VWM)} = \mathrm{n} \Big/ \left(\sum_{i=1}^{n} \mathrm{V}_i\right)^2 \times \left[\left(\mathrm{n}\sum_{i=1}^{n} [\mathrm{X}]_i^2 \mathrm{V}i^2 - \left(\sum_{i=1}^{n} [\mathrm{X}]_i \mathrm{V}_i^2\right) \Big/ \mathrm{n(n-1)}\right)\right]$$

where $[X]_i$ is the concentration of the ion in the precipitation in µeq L^{-1}, V_i is the total volume (L) of precipitation of each sample and n is the number of samples.

The VWM value of the pH for the study period was determined by the VWM concentration of H^+, i.e., pH = –log [H^+],[34] and the ions H^+ were estimated by the following equation:[36]

$$[\mathrm{H^+}] = 10^{-\mathrm{pH}} \times 10^6 \text{ in µeq L}^{-1}.$$

Results and Discussion

Meteorological factors

Based on 10 years of meteorological data obtained for the coast of Paraná, the total rainfall for the period from May to September (2000 to 2010) was approximately 840 mm.[37] The cumulative rainfall during the study period (May to September, 2010) in P1, P2, P3 and P4 was approximately 548, 606, 782 and 888 mm, respectively.

The highest values observed for P3 (PEC) and P4 (GB) are likely due to the proximity of the Serra do Mar, which acts as a barrier for the oceanic air masses coming from the Atlantic Ocean, which results in the condensation of water vapour and consequent precipitation.

Table 2 presents the data of accumulated rainfall, predominant wind direction, average wind speed, temperature and relative humidity during the collection days, including one day before each sampling period (weekly, n = 27).

The predominant wind direction during the collection days in P1, P2, P3 and P4 was S-WSW, E-SSE, E-SSE/W-NNW and E-SSE, respectively, that is, from the ocean towards the continent in the two estuarine systems.

Furthermore, in P1, at the mouth of the PEC, we observed a higher wind speed (3.2 m s^{-1}) compared to the other study areas, which favoured the horizontal dispersion of the ionic concentrations in the atmosphere and in the precipitation. P3 and P4 presented the highest values of rainfall and relative humidity due to the proximity of the Serra do Mar (Table 2).

Table 2.Weather conditions during the collection days (n = 27). Accumulated rainfall (mm), predominant wind direction (%), average wind speed (m s^{-1}), temperature (°C) and relative humidity (%) of the air at investigated points (weather data provided by CMS, INMET and SIMEPAR)

Local	Accumulated precipitation / mm	Wind direction / %				Wind speed / (m s^{-1})	Air temperature / ºC	Relative humidity / %
		N-NE-ENE	E-SE-SSE	S-SW-WSW	W-NW-NNW			
P1	129.4	11.1	11.1	74.1	3.7	3.2	19.2	89.0
P2	143.5	11.1	48.2	29.6	11.1	1.6	19.1	87.8
P3	262.2		40.7	18.6	40.7	0.3	18.1	94.8
P4	254.2	22.2	40.7	14.9	22.2	1.9	18.2	91.2

Variation of pH and electrical conductivity

During the study period, the pH of the precipitation in the two studied systems ranged from 4.64 (22.9 µeq L^{-1})-6.40 (0.40 µeq L^{-1}), as shown in Figure 3. The VWM of H$^+$ was 8.1 µeq L^{-1}, which corresponds to the pH value of 5.09 VWM (Table 3).

This value was close to those reported for the cities of São Paulo (5.19),[38] and Ilha Grande-RJ (5.22),[11] lower than the values reported for the basin of the Guaíba River (South of Brazil) (6.06),[39] and the industrial zone of Rio Grande (6.1),[7] and higher than the values reported for the basin of the Piracicaba River (Southeast of Brazil) (4.5),[40] and Central Amazon (4.7).[41]

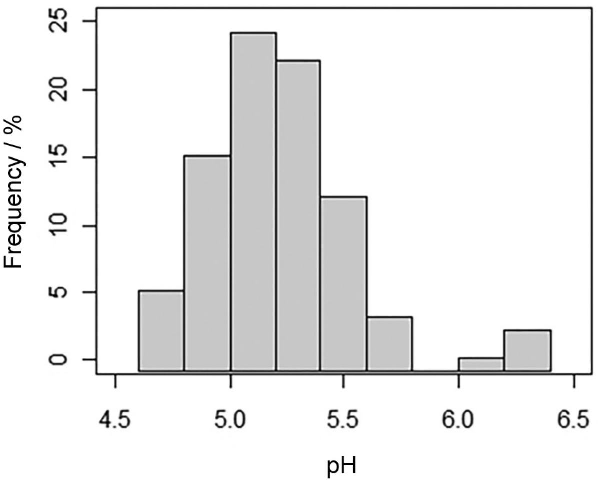

Figure 3. Histogram of pH values of the rainfall on the coast of Paraná (n = 91).

Approximately 23.1 and 91.2% of the pH values of the precipitation in the investigated region were less than 5.0 and 5.6, respectively, and only 8.8% of the values were greater than 5.6 (Figure 3). Therefore, the pH values were predominantly lower than 5.6, the reference pH value of the rain in equilibrium with the atmospheric CO_2,[38] which allows the precipitation of the region to be characterised as acid.

The electrical conductivity in the precipitation samples ranged from 3.1 to 72.2 µS cm^{-1}, with a VWM of 16.0 µS cm^{-1} (Table 3). This value was slightly higher than the value reported for the basin of the Guaíba River (South of Brazil, 12.6 µS cm^{-1}),[39] and the central region of São Paulo (13.0 µS cm^{-1}),[38] and also higher than the values reported for the Central Amazon (6.5 µS cm^{-1}),[41] and the Candiota region - RS (South of Brazil) (6.6 µS cm^{-1}).[42]

The VWM value of the electrical conductivity in the rainwater from P1 (26.6 µS cm^{-1}) was higher compared with P2 (15.7 µS cm^{-1}) and P3 (9.2 µS cm^{-1}), which reveals a higher contribution of marine aerosols in the precipitation in this region because of its proximity to the coast.

As expected, the electrical conductivity showed a correlation inversely proportional to the total volume of the rainwater samples in the four investigated areas, in agreement with other studies.[43]

However, only in P2 (Paranaguá) was a significant correlation between the electrical conductivity *vs.* rainfall ($R = -0.99$; $R^2 = 0.97$, $p < 0.001$, n = 91), electrical conductivity *vs.* pH ($R = 0.90$; $R^2 = 0.80$, $p < 0.001$, n = 91) and pH *vs.* rainfall ($R = -0.90$; $R^2 = 0.81$, $p < 0.001$, n = 91) observed. This result demonstrates the relative predominance of alkaline species to a lower volume of rain with consequent dilution of these compounds with the increasing of the amount of precipitation and the decrease of the electrical conductivity.[38,44]

Trace elements in the atmospheric precipitation

Table 3 presents the arithmetic and weighted by the volume (µg L^{-1}) mean concentrations and the minimum, maximum and volume-weighted standard error of the dissolved trace elements in the precipitation of the four investigated points. The majority of the values (> 50%) for the elements Ga, Mo, As, Co, Ni, Cr and Pb were below the detection limit; therefore, these values are not presented in Table 3.

The VWM concentrations (µg L^{-1}) of the trace elements in the rain water for all of the study areas followed the order: Zn (41.2) > Al (25.7) > Fe (17.4) > Mn (9.7) > Cu (3.4) > Ba (1.9) > V (0.7). Zn was the most abundant element in the majority of the investigated points and had

Table 3. pH and electrical conductivity (EC in µS cm^{-1}), arithmetic mean (AM) concentrations and weighted by the volume (VWM) in µg L^{-1}, minimum, maximum and volume-weighted standard error (VWSE) of the trace elements dissolved in the precipitation of the four investigated points in the PEC and the GB from May to September 2010 (n = 91)

	pH	EC / (µS cm^{-1})	H$^+$	Al	Fe	Mn	Cu	Zn	Ba	V
PEC, Ponta do Poço (P1) (n = 25)										
AM / (µg L^{-1})	5.10	27.1	9.0	16.1	5.2	5.4	0.13	8.2	0.47	0.25
VWM / (µg L^{-1})	5.05	26.6	9.0	16.0	5.2	5.2	0.19	7.2	0.54	0.21
VWSE	–	0.33	0.21	0.46	0.18	0.14	0.01	0.16	0.03	0.01
Minimum	4.64	21.3	2.5	3.2	0.82	1.2	< DL	1.2	< DL	< DL
Maximum	5.61	38.2	22.9	47.0	22.1	14.1	0.64	21.9	1.7	0.71
PEC, Paranaguá (P2) (n = 18)										
AM / (µg L^{-1})	5.49	23.6	4.6	11.4	9.0	6.1	1.2	26.6	2.4	1.8
VWM / (µg L^{-1})	5.27	15.7	5.4	10.9	9.1	6.7	0.86	27.6	1.8	0.93
VWSE	–	0.28	0.22	0.26	0.37	0.21	0.05	0.76	0.05	0.03
Minimum	5.02	10.0	0.40	5.9	2.8	1.8	0.20	11.2	0.61	0.47
Maximum	6.40	72.2	9.6	16.0	17.0	11.8	5.1	47.4	10.6	11.3
PEC, Antonina (P3) (n = 24)										
AM / (µg L^{-1})	5.24	12.6	6.6	7.3	4.5	2.5	2.2	10.7	0.40	0.16
VWM / (µg L^{-1})	5.24	9.2	5.8	7.6	5.4	2.3	4.0	8.2	0.56	0.05
VWSE	–	0.29	0.16	0.33	0.27	0.08	0.34	0.26	0.04	0.003
Minimum	4.94	3.1	0.89	1.5	0.43	1.1	< DL	1.4	< DL	< DL
Maximum	6.05	20.9	11.5	15.2	15.4	4.4	11.8	26.1	1.4	0.64
GB, Guaratuba (P4) (n = 24)										
AM / (µg L^{-1})	5.15	16.6	8.7	7.1	5.2	1.9	0.09	13.4	0.24	< DL
VWM / (µg L^{-1})	4.98	16.1	10.5	6.9	5.7	1.8	0.05	14.8	0.17	< DL
VWSE	–	0.29	0.40	0.22	0.27	0.04	0.004	0.72	0.01	< DL
Minimum	4.78	11.2	1.8	1.5	0.08	0.50	< DL	4.4	< DL	< DL
Maximum	5.75	27.8	16.6	15.4	17.5	4.8	0.49	48.8	1.1	< DL
All the samples (n = 91)										
AM / (µg L^{-1})	5.23	19.8	7.4	10.5	5.8	3.8	0.87	13.9	0.78	0.47
VWM / (µg L^{-1})	5.09	16.0	8.1	9.3	6.3	3.5	1.2	14.9	0.68	0.25
VWSE	–	0.10	0.10	0.08	0.08	0.03	0.04	0.20	0.01	0.005
Minimum	4.64	3.1	0.40	1.5	0.08	0.50	< DL	1.2	< DL	< DL
Maximum	6.40	72.2	22.9	47.0	22.1	14.1	11.8	48.8	10.6	11.3

(–): not determined; < DL: lower than the detection limit. In calculating the AM, the VWM- and the VWSE, values lower than the detection limit were assumed to be half the value of the detection limit of each trace element.[45,46]

higher VWM concentrations in the rain of P2 (27.6 µg L^{-1}) and P4 (14.8 µg L^{-1}) in relation to P1 (7.2 µg L^{-1}) and P4 (8.2 µg L^{-1}). The presence of this element in the precipitation of these urban areas is primarily associated to vehicular traffic, by dissolving zinc oxide emitted from the tire tread,[47] and from the burning of fossil fuels,[45,48] or both.[10,49] This influence may be particularly important for the P2 due to the heavy traffic of trucks around the Paranaguá Port. This is important year-round, but is higher at the time of the soybean crop.

A similar enrichment of Zn was also observed in the precipitation from the urban area of the city of Mersin (Northeastern Mediterranean) and in the basin of the Guaíba River (BGR, South of Brazil; Table 4). In these regions (Mersin and BGR), the high concentration of this element has been attributed to human activities, such as the incineration of hospital waste, industrial, agricultural activities and automotive emissions from vehicles and landfill areas.[39,46]

Similar to Zn, Cu and V are primarily associated with anthropic activities that involve low and high temperature combustion processes, such as metal extraction and industrial uses, waste incineration, burning of fossil fuels, among others.[10,19,47,50-52]

The VWM concentration of Cu in the precipitation of P3 was higher than the other investigated areas (Table 3). This may be related to industrial activities from the old Pig Iron of Paraná (disabled), with tailings deposited in the vicinity; the harbor activities of Baron Teffé Terminal (active), with coal deposits in the vicinity; to improper disposal of solid waste in open landfills; and, to use and management of chemicals in agricultural areas near the municipality ofAntonina.[53] In addition, winds coming from the east/southeast quadrant (Table 2) may have carried small particles enriched with this element to the internal sector of the PEC, which subsequently deposited via wet deposition.[54,55]

The Al, Fe, Mn and Ba elements are normally associated with the natural composition of the Earth's crust and are introduced into the atmosphere through the resuspension of ground dust.[2,10,46,56]

Specifically, in the region of the Ponta do Poço (P1), the concentrations of Al, Fe and Mn exhibited a significant negative correlation with the pH ($R > -0.70$, $p < 0.001$, $n = 91$), which indicates a higher solubility of these elements (in their ionic forms) under conditions of low pH (VWM value of 5.05). In the study by Hou *et al.*,[45] in Tsukuba, Japan, the pH of the total precipitation samples (VWM value of 5.0) was the primary controlling factor for the dissolution of minerals that contain Al during precipitation events.

The mean concentrations of the trace elements in the precipitation of the investigated areas are within the range reported in other regions of the world (Table 4). The values of Al and Fe were lower than those reported for the basin of the Guaíba River and Chesapeake Bay. The concentration of Mn was very close to the values reported for the BGR and city of Mersin (Northeastern Mediterranean) but lower than those reported for the city of Tsukuba. The contents of Zn, Cu and Ba were lower when compared with those of Mersin; however, the concentration of V was slightly higher than that reported for the city of Newark (USA).

Although this study constitutes a preliminary monitoring, the data reported here suggest that the atmospheric precipitation can be an important entry way of Zn in the two investigated estuaries.

Origins of trace elements in the rainwater

To estimate the contribution of the different natural and anthropogenic sources in the concentration of Fe, Mn, Ba, V, Cu and Zn elements, crustal enrichment factors (CEF) were calculated using Al as the reference element for the Earth's crust,[3,45,46,51,57] by the following equation:[2,45,46,49]

$$\text{CEF} = (X/\text{Al})_{\text{sample}} / (X/\text{Al})_{\text{crustal}}$$

where X is the VWM concentration of the element of interest in μg L^{-1}.

The CEF values for the trace elements are presented in the Table 5. In this reasoning, the CEF value near the unity for a determined element is an indicator that the weathering of the Earth's crust is an important source of that particular element. However, the CEF values between 1 and 10 are not considered enriched due to the differences between the chemical composition of the local soil and the referential crustal composition. The CEF values between 10 and 100 are considered moderately enriched, which indicates sources other than the continental origin whereas CEF values greater than 100 are highly enriched and indicate significant contamination due to human activities.[51]

In all of the investigated points, the CEF values for Fe were close to 1, which indicates the continental origin of this element, whereas the CEF values for Mn and the

Table 4. Summary of mean concentrations of the trace elements (μg L^{-1}) in the precipitation in other regions of the world

Localization	Country	Year	Study area	Al / (μg L^{-1})	Fe / (μg L^{-1})	Mn / (μg L^{-1})	Zn / (μg L^{-1})	Cu / (μg L^{-1})	V / (μg L^{-1})	Ba / (μg L^{-1})
PEC and GB, PR(this study)	Brazil	2010	coast/various areas	10.5	5.8	3.8	13.9	0.87	0.47	0.78
BGR, RS[39]	Brazil	2002	interior/various areas	25.1	25.7	3.5	33.6	2.6		
Porto Alegre, RS	Brazil		interior/metropolis		7.97		17.3	2.17		
Chesapeake Bay, Stillpond[56]	USA	1995-1996	east coast/estuary	30.0	18.0	1.6	9.0	1.1		
Tsukuba, Ibaraki[45]	Japan	2001-2002	Interior/suburban	34.0	7.5	11.0	18.0	2.5		
Newark, New Jersey[e57]	USA	2006-2007	east coast/metropolis	9.5	8.4		6.6	2.8	0.28	
Mersin[46]	Turkey	2003-2005	coast/various areas	6.5	3.2	3.2	36.9	1.6		1.6
A Coruña[2]	Spain	2011-2012	coast/suburban	49.4	11.4	6.4	55.7	2.1	0.83	15.2
Cape Point, CapeTown[52]	South Africa	2007-2009	coast/nature reserve	9.9	31.8	1.8	68.5	0.81		
Xi'an City[10]	China	2007-2008	interior/urban	50.7	30.7	11.0	60.8	2.9		

Table 5. Mean ratios of the trace elements (μg L^{-1}) in relation to the Al on the earth's crust and in the rainwater of the study areas, along with the CEF

	Crustal[a]	Ponta do Poço (P1)		Paranaguá (P2)		Antonina (P3)		Guaratuba (P4)	
		Rain water	CEF	Rain water	CEF	Rain water	CEF	Rain water	CEF
Fe/Al / (μg L^{-1})	0.744	0.325	0.44	0.835	1.12	0.711	0.96	0.826	1.11
Mn /Al / (μg L^{-1})	0.0127	0.325	25.6	0.615	48.4	0.303	23.9	0.261	20.6
Ba/Al / (μg L^{-1})	0.0047	0.034	7.23	0.165	35.11	0.074	15.68	0.025	5.23
V/Al / (μg L^{-1})	0.0016	0.013	8.13	0.085	53.13	0.0066	4.13	–	–
Cu/Al / (μg L^{-1})	0.00081	0.012	14.81	0.079	97.53	0.526	649.4	0.0072	8.89
Zn/Al / (μg L^{-1})	0.0019	0.450	236.8	2.53	1.331.6	1.08	568.4	2.14	1.126.3

(–) Not determined, the concentrations of V were below the detection limit. [a]Calculation based on the crustal average abundance of Clarke.[58]

Zn were considered moderately and highly enriched, respectively (Table 5).

In P1 (PEC) and P4 (GB), the concentrations of Mn exhibited a significant correlation with Al, with correlation coefficients of 0.89 ($R^2 = 0.78$, $p < 0.001$, n = 91) and 0.81 ($R^2 = 0.64$, $p < 0.001$, n = 91), respectively, which suggests that the enrichment of Mn in the precipitation of these points was due to natural processes, such as the previous dissolution of Mn in relation to the Al during the event of the precipitation, rather than to anthropogenic contamination.[45]

In P2 and P3, the concentration of Mn exhibited a lower percentage of explanation compared to Al; therefore, the enrichment of Mn in the precipitation of these points may be related to sources other than those of continental origin. However, the CEF value for Mn should be used with caution because the $Mn/Al_{crustal}$ ratio may change significantly between locations due to variations in the conditions for the oxidation of the surface soils.[3,56]

Although in other coastal regions of Brazil marine aerosols represent an important source of trace elements such as Ba, V, among others,[59-61] in P1 (CEP) and P4 (BG) did not observe an enrichment of these elements in rainwater (Table 5). This may be related to weather conditions: (*i*) higher wind intensity at the mouth of the CEP (Table 2), favoring the transport of small particles to the internal sector of this complex; and, (*ii*) greater cumulative rainfall at the mouth of the BG (Table 2), with consequent dilution of the concentrations of trace elements. This behavior has also been observed in other coastal regions of the world, in North America and Europe.[62]

In P2, Ba, V and Cu were moderately enriched in the precipitation, indicating the contribution of other sources: marine and/or anthropic. In P3, the high enrichment of Cu in the precipitation can be related mainly to human activities developed in this place (previously described); and, with winds coming from the east/southeast quadrant, which may have transported fine particles enriched with this element from the middle to the internal sector of the PEC.

In all of the study areas, the CEF values for Zn were high, especially in the urban areas of Guaratuba (P4) and the industrial and port area of Paranaguá (P2) (Table 5), indicating contamination due to human activities, such as tire tread and burning of fossil fuels by vehicular fleet. Atmospheric deposition may be, therefore, a primary route of exposure to anthropogenic Zn for estuarine biota.

Conclusions

The measured pH values of the atmospheric precipitation in the two subtropical estuaries of the coast of Paraná revealed the occurrence of slightly acidic rainwater, where 91% of the analysed samples exhibited pH values less than 5.6, which is the reference pH value of rainwater in equilibrium with the atmospheric CO_2.

The electrical conductivity, inversely proportional to the total volume of the rainwater, varied from 3.1 to 72 μS cm^{-1}, with the VWM of 16 μS cm^{-1}.

At the investigated points, Zn was the most abundant, followed by Al, Fe, Mn, Cu, Ba and V. The analysis of the crustal enrichment factor enabled a preliminary assessment of the different sources of the investigated elements in the precipitation. Zn was primarily associated with human activities. One potentially important source of this element for PEC is the intense traffic of trucks associated with port activities, although others sources as open landfills and chemical industries in the vicinity of the Port of Paranaguá could not be disregarded. Due to its high concentrations, atmospheric deposition of anthropogenic Zn constitutes an important potential contamination source for these ecosystems.

The presence of Mn, Ba, V and Cu in the precipitation of P2 may be related to sources (marine and/or anthropic) other than those of continental origin. In P3, the high enrichment of Cu in the precipitation is due probably to human activities developed in this place as agriculture, burning of fossil fuels and from waste and from landfills.

Moreover, the predominant winds coming from the east/southeast quadrant may have transported fine particles enriched with this element from Paranaguá city to the internal sector of the PEC.

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