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Characterization of soils from recreational parks in Pernambuco – Brazil

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Abstract

The Santana and Caiara Parks together with Maximiniano Campos, is part of the Recife City Hall project entitled "Capibaribe Melhor Project". This project seeks to integrate environmental education initiatives, lookouts and squares. Parks located in urban areas have amounts of metals, which can cause damages to human health, knowing that the main users of these areas are the elderly and children who are considered to be the most vulnerable to health problems. There are no reference values for all soil elements in Pernambuco; elements such as: Pb, Cu, Ni and Zn are described by the State Environment Agency. This work aims to characterize the soils of parks and squares in the Northern area of Recife, using the Energy Dispersion X-Ray Fluorescence (EDXRF) equipment for the determination of metals in soil samples collected by simple random distribution, with plastic spatulas. The results found in descending order of the trace elements in Caiara's Park were: Si>Al>Fe>K>Ca>Ti>Mn>Sr>Zn>Cu>Pb>Ga, and in Santana's Park were: Si>Al>Fe>K>Ti>Ca>Mn>Sr>Cu>Zn>Pb>Ga. Silicon and Aluminum exhibited the highest levels, followed by K, Ca and Mn, indicating that they were of crustal origin; while Fe was identified as being of atmospheric origin.

Keywords: Analytic analysis, environmental control, heavy metals, soil contamination.

Introduction

The Lancet Commission on Pollution and Health concluded that of air, water, soil and chemistry' pollution was responsible in 2016 for 940,000 deaths in children worldwide, and two-thirds of them were under five. Most were due to gastrointestinal and respiratory diseases caused by polluted air and water.

Pollution is also linked to multiple non communicable diseases (NCDs) in children, including low birth weight, asthma, cancer and neurodevelopmental disorders, and these diseases are on the rise. The list of pediatric NCDs attributed to pollution is likely to expand as the health effects of new chemical pollutants are better defined and additional associations between pollution and disease are discovered (FABIAŃSKA et al., 2019).

Soil contamination by toxic elements is one of the main environmental problems of recent years, as runoff takes these elements to water sources and food grown in agricultural land can also be hazardous when contaminated. Main sources of this contamination are industrial wastes, pesticides, chemical fertilizers (ALAMGIR et al. 2015) and the ubiquitous atmospheric pollution due to vehicles exhaust fumes. In tropical environments, the search for reference values is a continuous challenge for agriculture, vegetation, and estuarine soils (COSTA et al. 2016; MIOLA et al. 2016; PRESTON et al. 2016); the quality assessment of tropical soils and sediments is still under discussion, with efforts being made on the part of governmental agencies to establish reference values.

The term "trace metals" has been used in order to denominate elements having a density higher than 5,000 kg/m3 and having an atomic number higher than 20 (FABIAŃSKA et al., 2019). This classification includes not only metals but also semi-metals, and even those elements that are known as nonmetals. In order to define the toxicity levels of these elements, certain aspects such as concentration, type of organisms exposed, capacity of metals' assimilation, exposures' routes and other factors have to be taken into account (MARTINS et al, 2011). These elements play an important role in the development of organic structures and nutrients' assimilation. For this reason, local authorities throughout the world are intent on establishing the concentration of these trace metals in public areas as a subsidy for eventual remediation actions. The "Capibaribe Melhor" ("a better Capibaribe") Project was launched by the Municipality of Recife with the aim to promote the recovery, expansion, and requalification of Caiara and Santana parks, and in addition, to the creation of a brand-new recreation area in the vicinity, the Apipucos Maximiano Campos Park. The name of the project is a reference to the Capibaribe River, the City of Recife's main body of water, meandering through the urban area from west to east.

Santana's park built in 1985, with an original area of 26,000 m², Santana Park has been extended to 63,000 m² and caters for about 70,000 inhabitants, mostly from high income neighborhoods. The park's design forecasts the creation of an area where environmental education will be the main focus, with the idea of establishing the park as a public space for contemplation, recreational and cultural leisure. The area will also have a vantage point for viewing the Capibaribe River in its eastern part. This section will be called "Window for the Capibaribe" and will house the Recreational-Cultural Pole. "Capibaribe Melhor" will also benefit part of Recife's West Side by renovating the Caiara Park. This park is located in the Iputinga Neighborhood, populated mainly by lower-middle-class families, and has been renovated to provide the inhabitants in the vicinity, with a recreation area, to improve the life quality of some 115,000 people.

The Maximiano Campos Park is located in Apipucos, a high-profile area in Recife, which also has an outstanding historical value. Still not heavily affected by the so-called urban speculation that has severely destroyed the character of most neighborhoods in Recife, Apipucos is dominated by houses built decades ago and high rises that are the trademark of other districts are rarely seen. As expected, its inhabitants are keen on preserving their environment, and they welcomed the new park as a place where children can play and the elderly may exercise conveniently and safely.

The accomplishment of these interventions aims to enable the public collective use of the banks of the Capibaribe River; increase the population's access to urban infrastructure and essential services; reduce the environmental degradation of canals and the Capibaribe River caused by the inappropriate use and occupation of its banks; promote the physical integration of the left and right banks of the river in the densest section of its basin in Recife.

EDXRF (Energy dispersive X-ray fluorescence) is a reliable technique to quantify chemical elements, including in geological materials. Terrigenous elements (Al, Fe, Si, and Ti), nutrients (Ca, Fe, K, Mg, Mn, Ni, and Zn) and pollutants (Mn, Ni, Pb, and Zn) can be confidently determined, depending on the concentration. This method is relatively simple, provided that reference materials are available, not costly (when compared to ICP-MS, for example), and with analytical uncertainties comparable to instrumental neutron activation analysis (INAA) (FERNÁNDEZ et al., 2017). The applicability of EDXRF was demonstrated for tropical soils from the State of Pernambuco, Brazil, characterizing terrigenous chemical elements, nutrients, and pollutants. EDXRF is also a potential analytical technique for quantifying diverse chemical elements in geological material without chemical treatment, primarily when it is performed at an appropriate metrological level (FERNÁNDEZ et. al, 2017).

The work aims to collaborate with a larger project, in partnership with other units of CNEN (National Nuclear Energy Commission), on the environmental monitoring of urban soils in parks and squares used for recreational purposes, characterizing the soil of Caiara's Park and Santana's Park regarding the presence of chemical elements.

Methods

Soil samples were collected at four different points (totaling 20 samples) around Santana's Park and 16 samples in Caiara's Park with a plastic spoon according to Tables 1 and 2. This is a simple random distribution scheme, which can be applied in cases where little prior information from the area is available and it is an irregular distribution of the contaminated areas is assumed (CETESB, 1999). Soil collections were performed with the aid of a spatula, where each duct was 6 to 7 cm deep and 6 cm apart from each other, the samples were stored in plastic bags and labeled. Upon arrival at the laboratory, the samples were dried, crushed in a mortar, sieved in thin series of sieves (2, 1, 500, 250, 125, 63 mm/μm) and packed in plastic bottles.

The determination of organic matter and carbonate in the samples was carried out in an exhaust hood using H_2O_2 PA and 10% hydrochloric acid, respectively. The determination of trace metals was performed by EDXRF that uses an X-ray beam to promote excitation of the electrons of the trace metals in the samples. This

excitation provides the emission of characteristic X-rays that are detected and through the generated spectra; the chemical elements were identified and quantified.

The EDX-720 equipment from Shimadzu was calibrated from the energy and resolution calibration standards, A-750 and SUS. Samples were transferred to polyethylene capsules specific for EDXRF analysis and sealed with polypropylene films. The determination of trace elements in the samples was performed from analytical curves obtained by reference materials (SOUSA et al., 2013). For the quality control of the analytical procedure, SRM 2711 certified reference material was analyzed together with the samples.

For the validation of the analytical procedure, the number En was used and for the achievement of the 95% confidence level, the appropriate range for the results the number En should be between [-1 and 1], as recommended by ISO 13528/2005. The number En allows the comparison of the value obtained with the certificate value, considering the expanded uncertainties of both values. The number En between [-1 and 1] are considered as admissible value (Table 3) that ensure the accuracy and reliability of the analytical method.

Table 1: Geographic coordinates of the sampling points' at Santana Park

Point	Latitude (S)	Longitude (W)
1	8°02'29.6"	34°55'04.4"
2	8°02'29.7"	34°55'04.1"
3	8°02'29.0"	34°55'04.1"
4	8°02'29.1"	34°55'03,6"

Table 2: Geographic coordinates of the sampling points' at Caiara Park

Point	Latitude (S)	Longitude (W)
1	8°02'22.2"	34°55'39.8"
2	8°02'22.6"	34°55'39.7"
3	8°02'22.6"	34°55'40.0"
4	8°02'22.2"	34°55'39.9"

Table 3: Chemical elements' concentrations observed in SRM 2711 standard

METALS	SRM 2711 Mensured Mean(mg/kg)± uncertainty	SRM 2711 certificated values Mean(mg/kg)± uncertainty	En
Si	294332 ± 4	304400 ± 1900	-0,94
Al	62284 ± 5	65300 ± 900	-0,93
Fe	28088 ± 2	28900 ± 600	-0,96
K	23470 ± 3	24500 ± 800	-0,95
Ca	27618 ± 4	28800 ± 800	-0,92
Ti	3008 ± 61	3060 ± 230	-0,18
Mn	570 ± 23	638 ± 28	-0,50
Sr	261 ± 6	245,3 ± 0,7	0,87
Zn	396 ± 12	350,4 ± 4,8	0,95
Cu	121 ± 21	114 ± 2	0,26
Pb	1059 ± 15	1162 ± 31	-0,64
Ga	15 ± 14	15 ± 3	-0,04

Results and Discussion

The calculation of soil moisture in Santana Park is shown in Table 4. The values show a variation between 1.75 and 2.57%. In Caiara Park soil moisture ranged from 0.74 to 5.3% (Table 5).

Table 4: Soil moisture in Santana Park

Soil moisture	(average value)% ± sd
Sample Point 1	2.08 ± 0.32
Sample Point 2	2.09 ± 1.00
Sample Point 3	2.57 ± 0.28
Sample Point 4	1.75 ± 0.43

Table 5: Soil moisture in Caiara Park

Soil moisture	(average value)% ± sd
Sample Point 1	0.74 ± 0.22
Sample Point 2	5.30 ±1.46
Sample Point 3	1.02 ± 0.24
Sample Point 4	1.05 ± 0.26

Table 6 shows carbonate's figures for Caiara Park; these values ranged from 0.39 to 0.88%. It can be observed in Table 7 shows that OM content in Santana Park varies from 0.56 to 1.19%.; Sediment samples collected in Ceará-Brazil ranged from 4.55 to 95.0%, thus corroborating former studies reporting values of 0.2 - 95%. The values for Apipucos' Park (analyzed in previous studies) ranged from 1.66 to 30.5%, being close to the mentioned values. However, the values found in Santana and Caiara parks were much lower.

Table 6: Carbonate results for Caiara Park

Carbonate	(average value)% ± sd
Sample Point 1	0.77 ± 0.074
Sample Point 2	0.84 ± 0.100
Sample Point 3	0.88 ± 0.220
Sample Point 4	0.39 ± 0.0095

Table 7: Organic matter content, Caiara Park

Organic matter	(average value)% ± sd
Sample Point 1	1.19 ± 0.022
Sample Point 2	1.04 ± 0.400
Sample Point 3	0.99 ± 0.004
Sample Point 4	0.56 ± 0.0014

The values in Table 8 ranged from 0.25 to 0.36% in the playground area, however for the samples collected along the Capibaribe River the values are around 1.0%. In Table 9, we observed the values for the organic matter at Santana Park; the values ranged from 0.48 to 0.81% in the children's playground, whereas the samples collected near the Capibaribe River showed figures around 4.4%. Studies involving lake sediments, at Olho D'água Lagoon in Pernambuco-Brazil, also supplied OM figures of 0.6-4.8% (LIMA et al., 2017). According to Aguiar et al. (2007), the values for organic matter on the Brazilian continental platform varied from 0.05 to 0.39%. Studies carried out at Ibirapuera Park (São Paulo, Brazil), issued OM figures around 70%, much higher than those found in the parks of Recife. The results for OM content reported by Lange (2018) in others parks ranged from 0.6 to 3%.

Table 8: Carbonate values for Santana Park

Organic Matter	(Average Value)% ± sd
Sample 1	0.71 ± 0.040
Sample 2	0.81 ± 0.0021
Sample 3	0.79 ± 0.0058
Sample 4	0.48 ± 0.060
Capibaribe	4.38 ± 0.160

Table 9: Organic Matter content in Santana Park

Organic Matter	(Average Value)% ± sd
Sample 1	0.71 ± 0.040
Sample 2	0.81 ± 0.0021
Sample 3	0.79 ± 0.0058
Sample 4	0.48 ± 0.060
Capibaribe	4.38 ± 0.160

Values expressed in Table 10 represent the guiding values for soils in Pernambuco State Environment Agency (CPRH, 2014), assuming a non-impacted area. The standards are to be taken as reference to element concentrations for contamination control and management of contaminated areas under investigation.

Table10: Guiding values for Pernambuco' soils

Element	Values (mg/kg)
Pb	13
Cu	5
Ni	9
Zn	35

Source: Adapted from the State Environmental Agency - CPRH.

Table 11: Chemical elements' concentrations in Santana Park

METALS	Sample 1Mean(mg/kg) ± combined uncertainty (mg/kg)	Sample 2 Mean (mg/kg) ± combined uncertainty (mg/kg)	Sample 3 Mean (mg/kg) ± combined uncertainty (mg/kg)	Sample 4 Mean (mg/kg) ± combined uncertainty (mg/kg)	AVERAGE VALUE (mg/kg)
Si	293694 ± 4	322392 ± 3	265452 ± 4	311314 ± 3	298213
Al	83857 ± 4	128952 ± 3	72787 ± 5	79459 ± 4	91264
Fe	16728 ± 3	14521 ± 4	46244 ± 1	16296 ± 3	23447
K	9512 ± 7	8699 ± 8	5464 ± 12	12596 ± 6	9068
Ti	5863 ± 5	5186 ± 5	5895 ± 5	5144 ± 5	5522
Ca	2613 ± 36	2810 ± 33	1837 ± 51	3498 ± 27	2690
Mn	175 ± 80	180 ± 75	154 ± 89	221 ± 64	183
Sr	139 ± 14	125 ± 16	125 ± 16	173 ± 12	144
Cu	56 ± 47	49 ± 52	52 ± 51	49 ± 52	52
Zn	42 ± 75	58 ± 55	43 ± 71	46 ± 68	47
Pb	37 ± 190	44 ± 161	66 ± 118	24 ± 281	42
Ga	11 ± 25	10 ± 25	12 ± 23	10 ± 23	11

Table 12: Chemical elements' concentrations in Caiara Park

METALS	Sample 1 Mean (mg/kg) ± combined uncertainty (mg/kg)	Sample 2 Mean (mg/kg) ± combined uncertainty (mg/kg)	Sample 4 Mean (mg/kg) ± combined uncertainty (mg/kg)	AVERAGE VALUE (mg/kg)
Si	269041 ± 4	234258 ± 5	292141 ± 4	264393
Al	89319 ± 4	178852 ± 2	100631 ± 3	123199
Fe	30833 ± 2	48131 ± 2	21588 ± 3	33122
K	24836 ± 3	13294 ± 5	14792 ± 5	18115
Ca	11088 ± 9	6701 ± 14	5597 ± 17	8463
Ti	5372 ± 4	7638 ± 4	4315 ± 5	5805
Mn	581 ± 26	303 ± 44	285 ± 45	392
Sr	259 ± 8	141 ± 12	196 ± 9	213
Zn	90 ± 35	64 ± 43	66 ± 44	78
Cu	53 ± 44	ND	57 ± 40	55
Pb	26 ± 226	26 ± 191	29 ± 199	27
Ga	10 ± 18	10 ± 17	9 ± 21	10

The values presented in Tables 11 and 12 are the results of elemental analyses carried out at Santana and Caiara Park. As it can be seen, at Caiara Park: Si > Al > Fe > K > Ca > Ti > Mn > Sr > Zn > Cu >Pb> Ga. And at Santana Park: Si > Al > Fe > K > Ti > Ca > Mn > Sr > Cu > Zn > Pb > Ga. It was also found that the presence of the more hazardous elements, namely Al, Zn, Cu and Pb, tends to increase with depth, while for major elements such as Fe, K, Ca and Si the influence of depth was not significant. The mean value of the parks for Zn (Caiara = 78 mg/kg and Santana = 47 mg/kg) is higher than the guiding values for soils in PE, CPRH (2014).

The mean value for Cu is 55 mg/kg in the investigated parks; this value is higher than the suggested value by the CPRH (2014). The values for Fe, in soils reach 26,000 mg/kg, in Santana Park, a figure close to the world average for soils, whereas in Caiara Park the value found is over 33,000 mg/kg. Lange (2018) observed an

over Fe contents (4.0 to 4.7%), close to the average value observed in the superficial soil (4.0%). Pb values vary from 27 mg/kg, in Caiara Park, to 42 mg/kg, in Santana Park, these values are higher than the suggested value by the CPRH (2014), that was 13 mg/kg, and then, we concluded that Pb is an element considered as a contaminant. However, the indicated value from Pb in soil, around the world, is 29 mg/kg. In previous studies in Apipucos neighborhood, the values found for lead in sediments demonstrated the incorporation of lead from atmospheric aerosols in these sediments.

Mn was near 183 mg/kg, in Santana Park, this value is lower than 300 mg/kg, while, in Caiara Park, Mn was near 392 mg/kg and both values are higher than the recommended value for soils (DORIA et al., 2017). In surface soils were observed values between 240 and 480 mg/kg by Lange (2018), however, in the Santana and Caiara Parks these values was between 183 and 392 mg/kg. And, as expected, Si and Al exhibited the highest content followed by, K, Ca and Mn, indicating their crustal origin (WATTS et al., 2017).

Lange (2018) found values of manganese between 240 to 480 mg/kg, these values, are similar to the average value observed herein for the superficial soils (≅ 356 mg/kg). Pernambuco's urban soils were enriched in strontium (Sr) presenting maximum value near 400 mg/kg. Comparing our results with other studies in urban area soils (LANGE, 2018), is observed that, there are many similarities. For example, Lange (2018) found 61 mg/kg for Cu, vs. ca. 55 mg/kg for both Santana and Caiara parks. In the case of Pb, the values were between 19.7 and 50 mg/kg in the samples analyzed by Lange (2018), whereas in Santana and Caiara parks figures between 27 and 42 mg/kg were found. The same applies to Zn: 22.7 to 89 mg/kg (Lange, 2018) vs. 47 to 78 mg/kg. The presence of Pb, Zn and Cu can be attributed to incorrectly discarded car batteries and lamps (Wu et al., 2013).

The total concentrations in ambient air particles are directly related to the density of traffic in certain places in the urban environment and the driving of vehicles. Caiara's Park is located on Avenue Maurício de Nassau, where there is a high traffic of motor vehicles. Although phosphates have not been determined in the samples, it is known that a higher emission of organic phosphates is generally found at a "crossroads" and in places where traffic is denser and vehicle stops and starts are more frequent. Residential areas are less exposed to phosphate emissions. These phosphate concentrations show exponential correlations with each other and human exposure to these compounds increases exponentially with increasing traffic density (Fabiańska et al., 2019).

Correlating carbonate with the elements "in the statistical program" it could be seen that Ga, Fe and Ca have a positive correlation in the presence of carbonate, been these chemical elements are more bioavailable; just as the presence of organic matter also has a positive correlation with carbonates. While Si and Pb demonstrated an inversely proportional relationship in the presence of carbonates, they remain less bioavailable for animals and plants. When carried out the process of correlating organic matter with analyzed elements, it presents a positive response regarding Ga, Ca and Mn. Si and Pb shown a response inversely proportional to organic matter.

If an element-by-element correlation is performed for Si, a positive correlation with Pb will showed it linked to the crustal material. While, Fe, Ti, Al and Ga were the elements that were correlated negatively with silicon. For what is a positive relationship with Fe and Ti, aluminum is linked to iron oxides, bioavailable to the environment, and characterizing these elements that are of crustal origin. It has negatively with Si, Sr and K which can also be of crustal origin. Regarding the Fe element, a positive correlation with Al and Ti is identified, and a negative one when related to Si and Pb.

However, when observing K, it is positively related to Ca, Mn, Sr and Zn and negatively to Al. Ti has a positive correlation with Fe, Al and Ga and negatively with Si and Pb. In the case of Ca, it has a positive correlation with Zn, K, Mn, Sr and Ga. Regarding Mn, note that it has a positive correlation with K, Ca, Sr and Zn. For Sr, observe whether a relationship is proportional to K, Ca, Mn and Zn and is proportional to Al and Fe. To observe Zn has a positive correlation with K, Ca, Mn and Sr. However for the element Pb we have a positive correlation with Si and a negative relationship of this element with Fe, Ti and Ga. And in the case of Ga, we will have a positive relationship with Fe, Ti and Ca and negatively with Si and Pb.

Conclusions

More toxic metals found were: Al, Zn, Cu, and Pb, while the major elements were Fe, K, Ca, and Si. Lead values in both Parks were higher than the suggested value (13 mg/kg) by CPRH (2014), wherefore; Fe could be considered a contaminant. Silicon and Aluminum exhibited the highest content, followed by K, Ca and Mn, indicating their crustal origin. It is suggested that with the exhaust of public transport vehicles with the tallest pipe, avoid must atmospheric contamination, so that the health of the population is improved

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