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RESEARCH

Contamination characteristics in runoff fractions from a nuclear facility in São Paulo, Brazil

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Abstract The stormwater runoff may act as a non-point pollutant source and contributes to aquatic ecosystem quality decay in urban environments. The aim of this work was to evaluate the runoff characteristics on the transport of total solids and total metals, as well as pH and conductivity responses during the rainfall evolution. During 2017 and 2018, 12 rain events were monitored in 4 sampling stations at a car parking lot located at Nuclear and Energy Research Institute (IPEN/CNEN) in São Paulo/Brazil. A 4-chamber integrated collector allowed the sequential/temporal runoff evolution assessment. The runoff composition, in decreasing order of quantities, was Ca > K > Mg > Si > Al > Fe > Na > Zn > Mn > Sr > Ti > Mo > V > Cu > B > Pb > Ni > Ce > Sb > Cr > La > U > Th > Cd. The amount of total solids, Al, and Fe exceeded the Brazilian water quality standards. Principal component analysis (PCA) identified the elemental clusters linked to the facility activity, soil, and traffic/atmospheric-related deposition. The results show that the runoff characteristics could be differentiated by pollutant source. Factors such as seasonal variation, rain event intensity, air mass from oceanic or continental origin, spatial distribution inside the monitoring area, and the intensity of the first flush must be considered in order to disentangle the elemental clusters and pollution source contributions. In winter, continental air masses were associated with

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higher concentrations of heavy metals in the surface runoff. Spatial changes with no seasonal variation were observed for U, Th, La, and Ce.

Keywords Runoff · Air and water pollution · Stormwater · Heavy metals

Introduction

Urban stormwaters became a key factor to assure the quality and safety of receivers' water bodies, once a significant amount of pollutants can reach the drainage system by runoff (Collins et al., 2010; Joshi et al., 2020; Müller et al., 2020; Zhang et al., 2015). The runoff is a significant source of diffuse pollution in urban environments, subject to confounding factors such as the season (Hilliges et al., 2017), land uses (Opher & Friedler, 2010), vehicle traffic (Berndtsson, 2013), industrial activities and rain event origin, and intensity (Imfeld et al., 2020; Perera et al., 2019). There are still open questions about how does pollutants wash-off and what are the key influential rain variables over this process (Alias et al., 2014a, 2014b), despite extensive reviews being published (Gioda et al., 2021; Huber et al., 2016; Müller et al., 2020; Rodak et al., 2020). Several studies have been carried out associated with storm water runoff presenting cases (Sörme & Lagerkvist, 2002; Souza Castro et al., 2020), source tracking, correlation to traffic density (Du et al., 2019), and demands of hazardous control (Shi et al., 2021; Yoo et al., 2014).

In the USA, stormwater discharges from industrial activities regulate total solids, nutrients, chemical oxygen demand, and only three heavy metals (Cu, Zn and Pb)(National Research Council, 2008; USEPA, 2009, 2021). In Europe, sustainable water management is discussed in the water framework directive (European Community, 2000, 1991), and the governance of water services is regulated by each country. Water services include rainwater runoff management in the majority of countries, including Denmark, Ireland, Malta, Netherlands, Norway, Slovakia, Sweden, Switzerland. The EC/Directive 1991/271 requires the stormwater prevention of leaks and pollution limitation as well. Therefore, the main regulations are related to heavy metals reduction emission (Cd, Hg and Pb) (European Environment Agency, 2016). In Latin America including Brazil, there are no storm water runoff regulations at the moment. São Paulo, a megacity in Brazil, with a car fleet of 30,778,960 units (IBGE, 2020), where the traffic-derived pollution is considered significant by several authors, has no runoff regulation in power (Canteras et al., 2019; CETESB, 2020a; de Miranda et al., 2012; Lange et al., 2018). CETESB — Companhia Ambiental do Estado de São Paulo, Environmental Agency of São Paulo State, monitors the air and water quality; however, the stormwater or drainage runoff has no systematic monitoring. In Brazil, the accelerated urban growth and the absence of permanent environmental planning contributed to an increase in surface runoff and flash flood events. One of the main causes is the waterproofing of the soil due to bitumen and cement roads and sidewalks. For decades, traditional interventions aimed at the urban drainage system expansion, transferring the runoff downstream of the river basin. Conventional measures have been applied to promote the infiltration and temporary rainwater storage, to compensate the urbanization effects over the hydrological process. One of the solutions would be the rainwater harvesting and re-use. However, the water runoff through roofs, streets, and roads would not contain pollutants (Canholi, 2014; Righetto, 2009). The pollutants have been identified as sediment, organic matter, bacteria, and metals (Cu, Zn, Mn, Fe, Pb), which reached the water bodies through the runoff (Becouze-Lareure et al., 2015; Burton & Pitt, 2001). Some of these pollutants originated from particulate matter airborne deposited first on surfaces and then flushed during precipitation events. As runoff stormwater can be harmful to plants, animals, and people (Hilliges et al., 2017; Paz et al., 2004), it is classified as a nonpoint pollutant source. One of the main ways to characterize a stormwater event is the first flush phenomenon, indicated as a peak of elemental concentration observed on time during the rain event. This phenomenon helps to find the main source of pollution in urban runoff in roads or roofs, as it allows the source identification from separated or combined discharge systems and receiving water flow (Deletic & Maksimovic, 1998; Hilliges et al., 2017). The first flush assesses if the mass emission rate is higher during the first or later portions of the rain event (Bach et al., 2010; Barco et al., 2008). It is also possible to monitor the pollutant "wash-off" process (named final washing or simply washing) by dividing the event into several stages or slices, each

stage being analyzed separately. Usually, the first rainwater has poor quality; the management of rainwater should be done judiciously to be considered successful. So the strategy is to eliminate the first fraction and when appropriate to prioritize the monitoring and treatment for the effective use of water (Meland, 2016).

This work evaluated 12 runoff events that occurred in São Paulo, inside the University of Sao Paulo and IPEN Campus. IPEN is a nuclear facility containing training facilities, research reactors, cyclotrons, linear accelerators, and radiopharmaceutical production facilities for diagnosis and therapy application. This area corresponds to a green zone surrounded by intense traffic and under the influence of continental and oceanic air masses. The main hypothesis of this study is that the rainwater runoff from storm events can be used to identify the point and nonpoint potential pollution sources that are deposited in roofs and streets. These sources can be both external, that arrive at the site by dry and wet deposition, as well as, internal that could leak and escape from the facility during the normal operation. To test this hypothesis, the concentrations of (i) potentially toxic elements (PTEs) such as Cr, Cu, Cd, Ni, Pb, Sb, and Zn; (ii) major and trace elements (MTE) with natural soil occurrence such as Al, Ca, Fe, K, Mn, Mg, Na, Si, Sr, and Ti; and (iii) elements related to the nuclear cycle process such as U, Th, La, and Ce have been monitored. The variability associated with the precipitation amount, the season changes, the spatial distribution of sampling points, and the backward atmospheric trajectory was disentangled by using general linear models.

Materials and methods

Study area

The study area was located inside the University of São Paulo campus, in a car parking lot at IPEN, nearby the Centre of Chemistry and Environment (−23.566268, −46.737629). This area corresponds to an urban micro region with an extensive green area. The sampling site covers 3.76 km^2 of IPEN's total area of 544 km^2. The Sao Paulo climate is humid and sub-tropical, labeled as Cfa by Köppen-Geiger classification. The average temperature is 19.5 °C, and the yearly precipitation is 1450 mm, with summers prone to thunderstorms. The main traffic corridors (Marginal do Rio Pinheiros and Avenida Politécnica) are 6.7 km distant from the collection site. IPEN performs a series of nuclear activities; among them are short-lived radioisotope production for medical applications, radiation metrology and monitoring, radioprotection and dosimetry, nuclear reactor operation with partial activities of the fuel cycle, and several multidisciplinary activities that varied from teaching, research, and development, to an innovation program (Santos, 2017). Therefore, air quality is regularly self-monitored, as well as monitored by CETESB — State of São Paulo Environmental Company at one station located at Cidade Universitaria. CETESB has several other stations in São Paulo as presented in Fig. 1.

The collection sites (*P0*, *P1*, *P2*, and *P3*) covered the main runoff at the facilities of IPEN. The sampling was planned to get an integrated view of the runoff from an urbanized drainage area with significant green area coverage. P0 (−23°56′16.98″, −46°73′97.50″) and P1 (−23°56′15.93″, −46°74′02.00″) were located respectively in front of the lower and upper car parking lots of the deactivated and dismantled nuclear fuel cycle reprocessing unit (CELESTE). P2 (−23°56′13.65″, −46°73′96.80″) is located on the upper side, further ahead of the site P1. In August 2017, P2 was replaced by P1. The station P3 (−23°56′05.48″, −46°73′94.25″) was located in front of the Laser and Applications Centre, 150 m from the Prof. Almeida Prado Avenue and 2.7 km from Marginal Pinheiros, a route with intense transit of light and heavy vehicles. The selected points have asphalted streets with local pedestrian and vehicle transit (see Fig. 1).

Meteorological data

Two stations provided meteorological data: (1) IPEN/Cidade Universitaria Station (De Molnary, 2018) and (2) National Institute of Meteorology (INMET, 2021), which correspond to the nearest and the reference stations, respectively. The sampling period started on January 2017 and ended in September 2018. The present study assessed 12 rain events. The date, precipitation depth, and event classification of the sampled events are presented in Table S1. The events were classified as weak (up to 2.5 mm h^{-1}), moderate (from 2.5 to 7.5 mm h^{-1}), and strong (over 7.5 mm h^{-1}) (Imfeld et al., 2020).

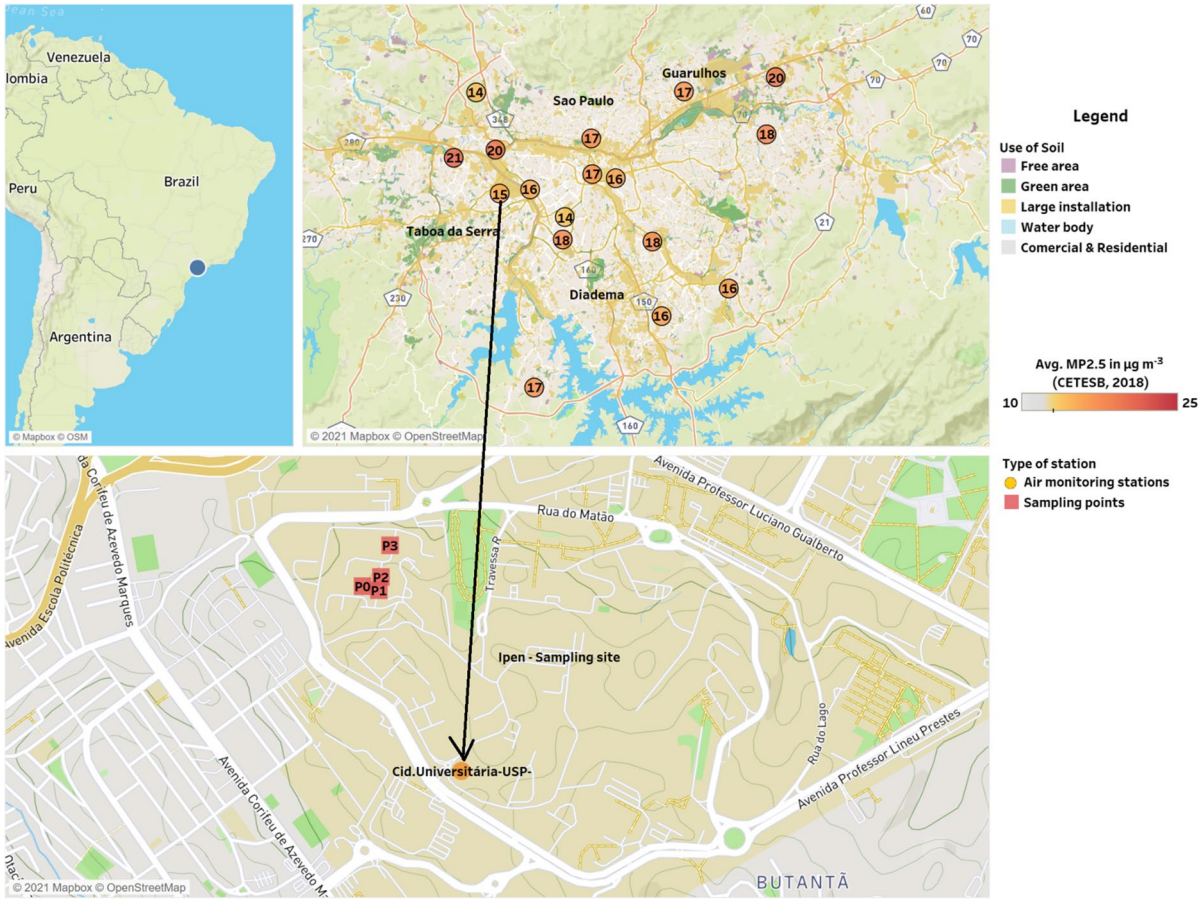

Fig. 1 Studied area with the land use, air monitoring stations with yearly average values of fine inhalable particles matter ($PM_{2.5}$) and sampling points P0 to P4

The 12 runoff sampled events were generated by a total of 113.4 mm (4%) of rain that occurred in 2017 and 2018. Details of the sampling campaign are presented in Table S2 in the supplementary material. The general precipitation pattern during the total period of our sampling campaign is presented by year. In 2017, the yearly accumulated rain in Sao Paulo was 1414 mm, which was close to the 20-year historical average. However, it was 33% higher than the precipitation observed in 2014, a critical year with severe drought. The precipitation events were quite irregular during the dry season from July to September and much drier than expected. April, May, and August had more rain than the average (CETESB, 2018a, b). This was explained by a situation of neutrality of oceanic and atmospheric conditions in the Equatorial Pacific concerning the phenomenon of global scale called El Niño-South Oscillation (ENOS) (CETESB, 2018a). Atmospheric blocks were formed, both in the Pacific Ocean and in the Atlantic Ocean, as well as high-pressure systems on the continent that influenced the rainfall regime, causing more intense rainy and drier/hot periods during the rainy and dry seasons in the State of São Paulo.

In 2018, the accumulated rain value reached 1223 mm, which was 14% lower than the previous 23 years average (CETESB, 2020b). In May, June, and July, the rain records were much lower than the respective climatological averages. In contrast, August had the largest contribution, and September was close to the respective climatological average. The lowest rainfall was observed in mid-June and lasted until the end of July (CETESB, 2020a). During the first quarter of 2018, the so-called La Niña phenomenon took place in the

Equatorial Pacific Ocean, with a peak in January and signs of weakening in March. In April, oceanic and atmospheric neutral conditions concerning the so-called ENOS phenomenon were observed and lasted until mid-September when an indication of warming in the waters of the Equatorial Pacific was identified.

Backward atmospheric trajectory

The particulate backward trajectories were obtained at the NOAA'S HYSPLIT platform for each rain event (Stein et al., 2015) along with the atmospheric pressure during this period. For the particulate matter trajectory calculations, the endpoints were the sampling station coordinates. The trajectories were calculated considering the 24 h prior the precipitation time. The air mass origin of the trajectories with altitude, speed, and directions of deposited particles was identified. The trajectories were then classified by the prevalent direction and associated with each rain/runoff event and classified as continental and oceanic according to their origin.

Sequential sampler and sampling campaign

Three sequentially integrated samplers were built, with four sampling chambers each one. The collector design was adapted from (Righetto, 2009). One collector had 850 mL, and two others had 1000 mL total capacity (See Fig. S1, in supplementary material). The EPA protocol for stormwater monitoring was used (USEPA, 2009). This study evaluated 12 rain events that were collected in 4 points, generating a total of 91 samples. This corresponded to two rainy and dry seasons in 2017 and 2018 (Table S2).

Chemical analysis

The pH and electrical conductivity (EC) of the samples were analyzed in situ (APHA;AWWA;WEF, 2017). The total solids (TS) were analyzed gravimetrically. The metals analysis started with the acidification of the samples to pH < 2 by adding 0.5 mL concentrated nitric acid (65% Suprapur, Merck, CAS: 7697–37-2, Darmstadt, Germany), and then, they were digested by microwave with a mixture of nitric and hydrochloric acid, with time and power following the method 3015A (USEPA, 1998). The elements Ce, Cr, Cu, Cd, La, Ni, Pb, U, Sb, and Th were measured by ICP-MS (Model 7700, Agilent, USA) after the digestion, following the method 6020D (USEPA, 1998). Other elements such as Al, Fe, K, Mg, Mn, Na, Sr, Ti, and Zn were measured by ICP-OES (Arcos, Spectro, Germany) following the method 6010 (USEPA, 2014). All samples were analyzed in triplicates. The method quantification limits (QL) were 0.5 μg L^{-1} for Ce, Cr, Cu, Cd, La, Ni, Pb, U, Sb, and Th; 10 μg L^{-1} for Al, Mn, Sr, Mg, and Zn; 100 μg L^{-1} for Fe and Ti; and 500 μg L^{-1} for Ca, K, and Na. All quality control was carried out, and it is elsewhere described (Faustino, 2016; Faustino et al., 2016). Details of the ICP-MS calibration curves are presented in the supplementary material. The reference material SRM 1643f (NIST, USA) containing trace elements in water was used for quality control; recovery details are presented in the supplementary material Fig. S4.

Data treatment and statistical evaluation

The event mean concentration (EMC_i) was applied to calculate pollutants' load in collected samples (Eq. 1), through the discharge flow at the time (t) in L min^{-1} (Q_t)/concentration of the corresponding pollutant at the time (t) in μg L^{-1} (C_t) (Erickson et al., 2010; Kaczala et al., 2012).

$$EMC_i = \frac{\sum_{t=1}^{t=T} Q_t C_t}{\sum Q_t} \quad (1)$$

The data matrix consisted of 91 samples (12 events collected in 4 sampling points) and 31 variables. Factorial ANOVA was used to assess the main controlling factors over the elemental content. The sample observed variability was assessed by the factors collector chamber (C), sampling point (P), rain events (E), seasonality (S), and wind direction (D). Principal components analysis (PCA) was performed with varimax standardized rotation factor. Principal components with eigenvalues over 1 (one) were considered to identify elemental covariations, similar to other studies (Huang et al., 2007; Porfírio et al., 2020; Tositti et al., 2018).

Results

Precipitation events

In 2017 and 2018, the total sampled precipitation was respectively 41.6 mm ($n=4$) and 71.8 mm ($n=8$), representing, approximately, 3% and 6% of the total yearly precipitation. Even though the precipitation coverage was low, it was considered sufficient for the runoff sampler assessment among the collector chambers, the sampling locations, the rain intensity classification, the seasons, and the trajectories. The number of events classified as weak ($n=5$) or moderate ($n=6$) was balanced and occurred in all seasons. As expected, the strong events occurred during summer, on January 17, 2017 (34.8 mm), and March 14, 2018 (42.8 mm). From 1930 to 2019, in Sao Paulo, the frequency of intense events (> 20 mm) increased, especially during summer. Even when this increase is considered, the frequency of weak/moderate/strong events agrees with the expected precipitation frequency in Sao Paulo (Marengo et al., 2020).

Physical–chemical results

The pH values ranged from 5.6 to 7.8 among all samples; therefore, no occurrence of acid runoff was observed. Considering the factorial ANOVA assessment (see Table S3 in the supplement material), the season/temperature, the sampling points, and the event class were statistically different factors, while log precipitation and trajectories were not significant over pH values. Figure 2 a shows the collection points and the seasons as dominant controlling

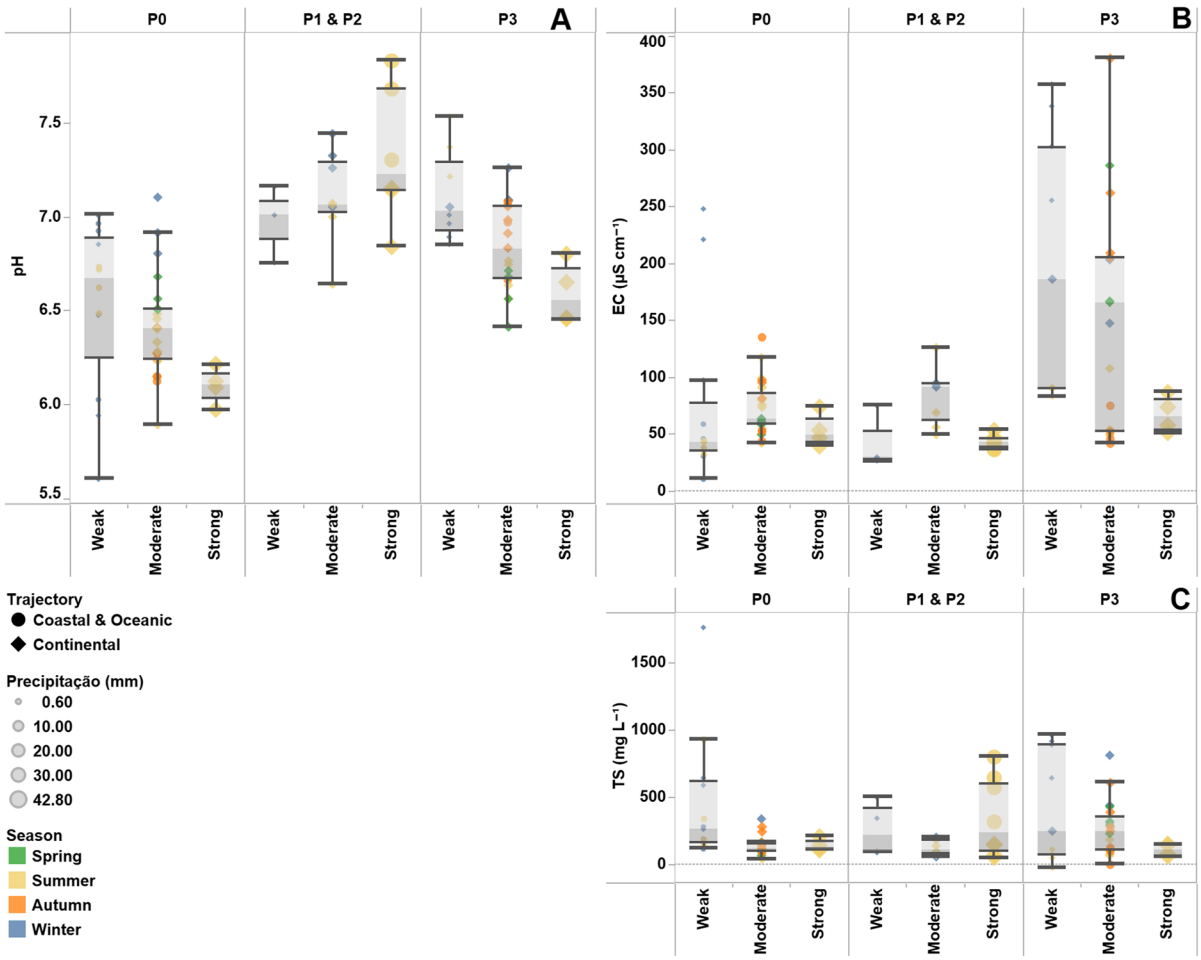

Fig. 2 pH (**A**), EC (**B**), and TS (**C**) by point, event intensity class, seasons (by color), and air mass trajectory (shape)

factors over trajectories for the pH results and the event class as presented in Fig. 2a. Strong precipitation events during summer led to lower and narrower pH range for runoff samples at P0 and P3. These pH values were also closer to precipitation pH. For P1 and P2, pH had a wide range and high values, on strong summer events. That behavior was attributed to the sharp slope hill close to P1 and P2 that contributed more with soil components leading to a more alkaline sample.

EC and TS varied from 10.2 to 308 μS cm^{-1} and from 20 to 1760 mg L^{-1}, respectively. The precipitation amount effect was dominant for EC results, with higher EC values for the weak and moderate precipitation amounts when compared with the strong events (Fig. 2b). The same was observed for TS, except for one collection at P2 (Fig. 2c). This is associated with the dilution caused by the precipitation increase, and it was similar as described in other studies (Hilliges et al., 2017; Huber et al., 2016, Makineci et al., 2015; Valtanen et al., 2015). Regarding the sampling points, higher EC values were observed at P3, even when comparable TS values are considered among all sampling points. The dense traffic in the surrounding of P3 may explain the higher EC values.

Regarding TS, weak events presented higher values (see Fig. 2c), because these events occurred after some long dry periods as typically happens in autumn and winter. Strong events occurred in summer and did not drag much solid material due to the large dilution effect and frequent rains (Huber et al., 2016, Valtanen et al., 2015; Westerlund & Viklander, 2006). TS in all seasons exceeded the benchmark value of 20mg/L for construction site runoff in Switzerland (Meland, 2016).

Runoff elemental characteristics

A total of 19 elements were present in the runoff samples above the quantification limit and the decreasing concentration (in μg L^{-1}) order was the following: Ca > K > Mg > Si > Al > Fe > Na > Zn > Mn > Sr > Ti > Mo > V > Cu > B > Pb > Ni > Ce > Sb > Cr > La > U > Th > Cd. Table 1 presents the mean and standard deviation values by season and the Brazilian regulatory limits on effluent conditions to be released in surface water bodies (CONAMA, 2011). Aluminum in all seasons and iron in winter events were elements exceeding the Brazilian regulatory limits.

Copper, Cr, Ni, and Pb were the most frequently detected elements, present in 88 to 94% of all samples. Zinc had higher concentrations but was present in less than 50% of samples. All results were in accordance with the values reported by USEPA urban runoff range for Cu (from 10 to 400 μg L^{-1}), Pb (from 10 to 1,200 μg L^{-1}), and Zn (from 10 to 2,900 μg L^{-1}), which classified these elements as the most prevalent priority pollutants found in urban runoff (USEPA, 2021). The high prevalence of these elements was associated with fuel combustion from vehicle traffic or breaks (Cu) and tire wear (Zn), rubber products, and other car parts (Canteras et al., 2019; Hwang et al., 2016; Lange et al., 2018; Rocha, 2015). Zinc concentrations in summer and winter and Cd values in winter exceeded the Swedish benchmark set for road construction (Meland, 2016). In 2017 and 2018, during all seasons in Sao Paulo, the runoff values of Cr, Cu, Cd, Zn, Ni, and Pb were lower than the surface runoff from the road to the Ganges River in India (2016 to 2019)(Siddiqui & Pandey, 2021).

The values of Ce, Cd, and Mn were lower or comparable to the values observed in low-depth groundwater samples from one impounded vehicle scrapyard susceptible to breaks, tires wear, and metal car parts pollution, located in Sao Paulo/Brazil (Lange et al., 2018). However, a comparison with the same location indicates that Fe, Mn, Ni, Zn, Cu, and U values were higher, most probably because IPEN was more exposed to atmospheric deposition and the U ores processed at the location.

Controlling factors over the runoff composition

Some factors influence the concentration variability observed in the present study and the detailed results of ANOVA test are presented in the supplementary material. Figure 3 presents some elements variability by year, rain event intensity classification, trajectory origin, season, and sampling point (see also Table S3). Even though the number of sampled events was different in 2017 and 2018, no significant difference was observed for all elements by year. However, the seasons presented a significant effect over the concentration of Zn, Cu, and Pb. Winter was statistically different from other seasons presenting higher concentrations for these three elements. Winter was the season with the maximum observed values for Fe, Mn, U, and Sr, even for the elements with no significant

Table 1 Elemental average concentration and standard deviation with correspondent Brazilian legal limit (CONAMA, Resolution 430/2011)

	Units	*N* samples > LQs	Spring		Summer		Winter		Autumn		CONAMA Res. 430/11
			Mean	SD	Mean	SD	Mean	SD	Mean	SD	
Al	μg L^{-1}	43	**1337.5**	267.8	**841.0**	723.1	**2566.6**	1950.9	**1762.7**	1746.3	100[a]
Sb	μg L^{-1}	48	0.7	0.1	1.5	2.6	3.7	6.8	1.0	0.4	5[b]
Cd	μg L^{-1}	17	0.6	0.0	0.7	0.1	1.7	1.2	0.7	0.1	200[b]
Pb	μg L^{-1}	84	5.6	2.7	7.9	5.7	15.7	11.1	9.2	7.4	500[b]
Cu	μg L^{-1}	84	14.6	6.7	9.8	3.5	22.1	23.4	24.3	12.8	1000[a]
Cr	μg L^{-1}	80	2.9	1.7	2.5	2.7	3.9	2.7	2.9	1.9	1100[c]
Fe	μg L^{-1}	43	692.5	246.3	737.8	572.2	**2273.3**	1555.1	828.9	625.3	1500[a]
Mn	μg L^{-1}	34	44.1	5.0	47.4	14.9	116.3	95.6	64.2	12.3	1000[b]
Ni	μg L^{-1}	79	2.3	0.8	2.2	1.6	5.2	5.2	3.7	2.8	2000[b]
U	μg L^{-1}	59	1.0	0.5	2.5	1.7	2.1	2.0	3.3	2.7	20[b]
Zn	μg L^{-1}	43	59.0	12.2	100.9	62.4	156.3	114.4	83.5	55.0	5000[b]
Ca	μg L^{-1}	43	5094.9	278.3	5186.3	1711.1	9669.6	7529.0	6427.1	1823.4	-
Ce	μg L^{-1}	81	6.1	4.2	3.1	2.3	7.5	6.1	6.9	5.3	-
K	μg L^{-1}	39	4488.9	386.9	4209.0	2331.0	7931.3	6742.0	8611.8	2167.0	-
La	μg L^{-1}	74	2.2	1.6	1.6	1.1	3.1	2.4	2.7	1.8	-
Mg	μg L^{-1}	47	761.8	55.5	1228.4	803.5	1225.6	1317.7	853.2	454.1	-
Na	μg L^{-1}	26	294.7	28.0	452.1	94.4	1283.8	307.5	995.6	117.3	-
Sr	μg L^{-1}	38	26.9	2.0	24.1	7.1	41.8	31.2	27.6	9.8	-
Ti	μg L^{-1}	21	29.1	8.4	26.6	13.7	110.1	60.2	39.7	20.7	-
Th	μg L^{-1}	49	0.9	0.4	1.5	1.3	1.8	1.6	3.0	1.5	-
pH	-	-	6.6	0.1	6.8	0.5	6.9	0.4	6.6	0.4	5 to 9
EC	μS cm^{-1}	-	126.9	78.5	63.8	24.1	122.4	103.1	121.6	96.2	-
TS	mg L^{-1}	-	212.5	119.9	184.5	198.8	402.7	379.5	218.6	137.3	-

Bold values correspond to those that exceeded Brazilian regulatory. -no limits guidance value

[a]Dissolved form

[b]Total form

[c]100 μg/L as Cr^{+6} and 1000 as Cr^{+3}

statistical difference among the seasons. This trend may be associated to the accumulation in dust and particulate matter that is prevalent in the dry seasons in several Brazilian cities (de Miranda et al., 2012).

The seasonal effect was more intense for elements associated with road traffic than for soil formation elements. The pollutant source affected the elemental concentration by sampling point and per collection chamber (see figure S2 in the supplementary material). The elements associated with traffic activities (Zn, Cu, Pb) had higher concentrations at P3, the closest station to the intense traffic area, and in the 1st collection chamber as one effect of the first flush. Dust and soil elements (like Fe, Mn, Al, and Ca) had no difference by sampling point or by collection chamber (Fig. S2). Therefore, no first flush effect was noted for soil formation elements.

The rain event intensity affected significantly the concentration of most elements. The concentrations were higher for weak events than for moderate and strong events, due to the dilution associated with the rain depth effect.

The last assessed effect was associated with the air mass trajectory. Fig. S3 presents the backward trajectories obtained for the monitored events in 2017 and 2018. These trajectories were considered as the pathway of the air masses and particulate matter deposited at the collection site (Stein et al., 2015; Zhou et al., 2021). The continental trajectories were prevalent among the events regardless

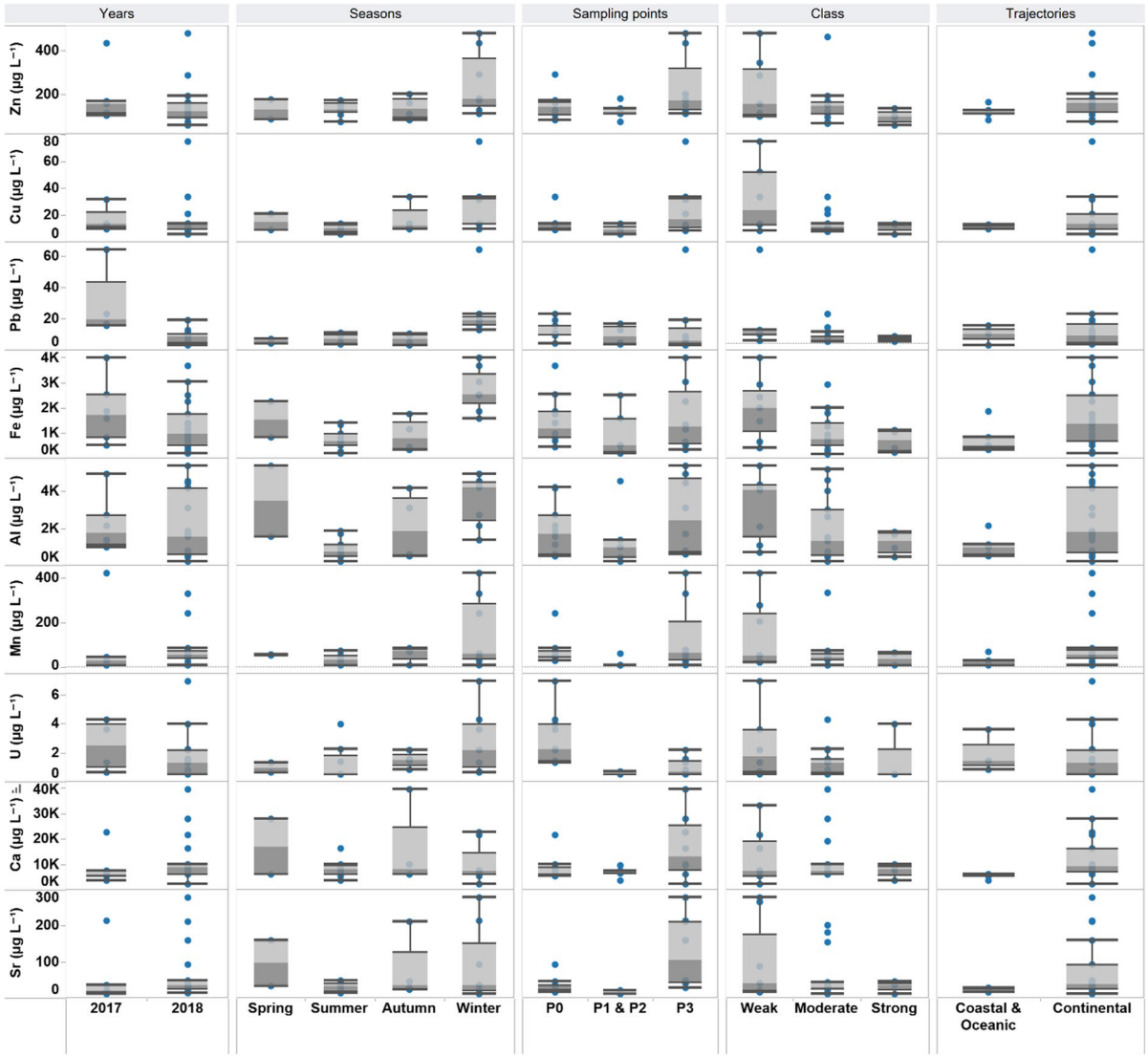

Fig. 3 Variability of Zn, Cu, Pb, Fe, Al, Mn, U, Ca, and Sr (µg L^{-1}) by years, event class, trajectory origin, seasons, and sampling points

of the season. Three events were classified as oceanic and one coastal. Among oceanic and coastal events, the concentrations were smaller than compared with continental trajectories. The continental air masses usually bring more particulate matter and black carbon to Sao Paulo during winter. This is a well-known phenomenon until 2019, when during the winter season; NW continental air masses that arrived in Sao Paulo with extreme pollutant load were reported as a "black rain" event (Pereira et al., 2021). That was observed again for the majority of measured elements. However, uranium had a different spatial distribution, high during winter, as other dust and soil originated elements, but P0 had the higher values than other stations, because P0 was the closest sampling point to the U reprocessing unity inside IPEN. No statistical difference was observed between air mass trajectories, so it was confirmed that the source of U is not external to IPEN facility.

Principal component analysis

For the PCA, the rotated varimax method was used and five principal components were identified with eigenvalues > 1 able to explain 89.8% of total matrix variability. PCA is an information reduction method that helps to identify parameters associations that explain the system variability. By using the factors plot, it is possible to identify variables that are associated and covariate. PCA was used as a confirmatory statistical technique once ANOVA was already applied and discussed.

Factor 1 explained 44.0% of the system variability (Fig. 4), being associated with soil naturally occurring elements such as Na, K, Fe, Sr, Ca, Zn, Mg, Mn, Ti, and Al. The increase concentration of these elements was inversely associated with the pH and collection points. The behavior presented by factor 1 was attributed to runoff samples with lower pH values increased the cation exchange releasing these elements.

Factor 2 explained 19.9% of the system variability and was associated to EC and TS influenced by the season and trajectory and inversely related to U, Th, and Al. By this factor, it was possible to identify the nuclear related component associated with U and Th that did not change significantly by year or by air mass trajectory, once it is associated with Ipen nuclear activity and that should not and was not associated with these externally associated variables like weather or vehicle traffic. The U and Th concentration in runoff samples increased during winter season only because this is the driest season, with larger

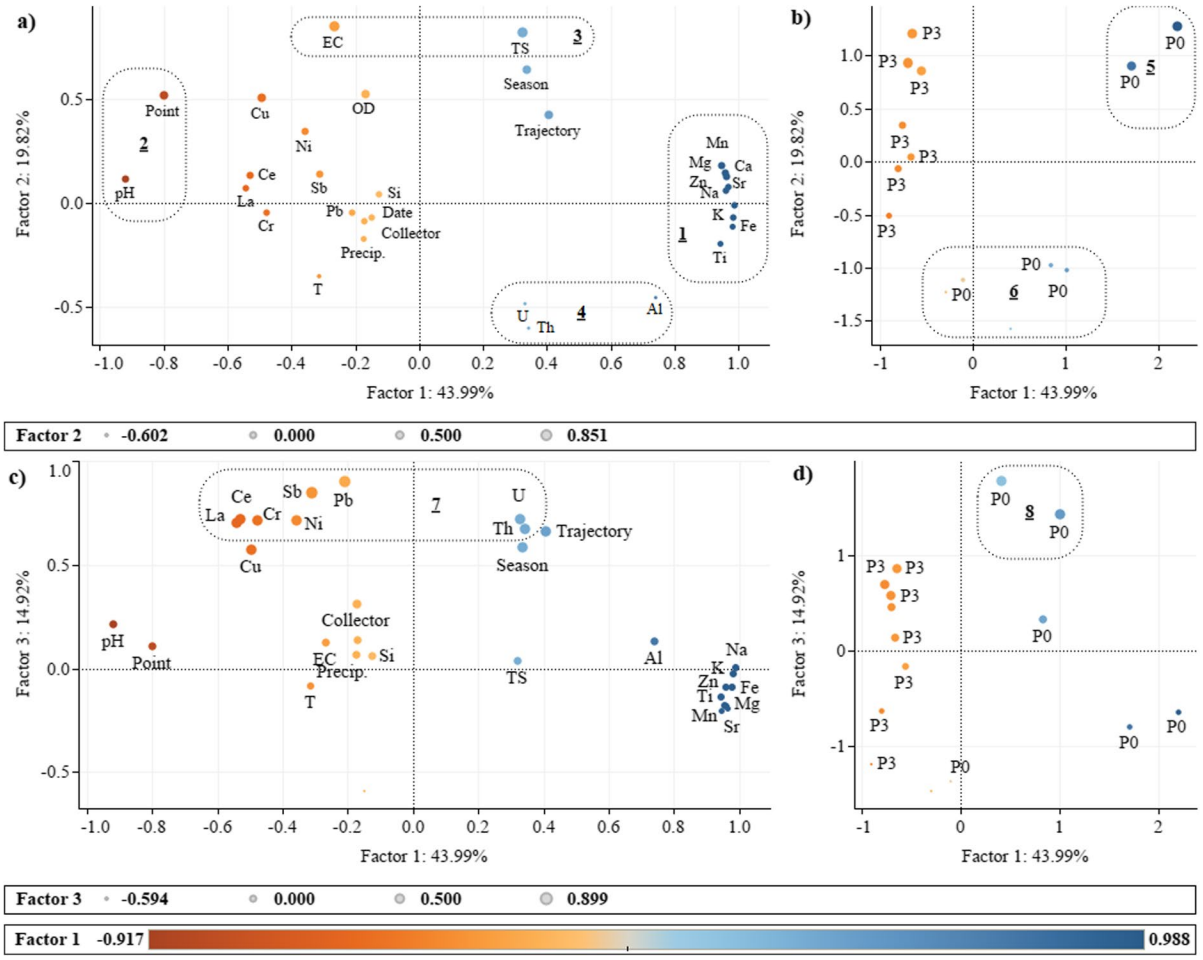

Fig. 4 Projection of the variables and case on the factor-plane 1×2 (**a**, **b**) and 1×3 (**c**, **d**)

local dust residence in the pavement. The association of these factors (F1 × F2) mainly differentiated P0 and P3 (see Fig. 4b) because P0 had higher U and Th values than P3, as P0 is the closest station to the nuclear fuel reprocessing unity.

Factor 3 explained 14.9% of the system variability being associated with Ce, Cr, Cu, La, Ni, Pb, and Sb (Fig. 4c); these elements were linked to car traffic once P3 was the closest station to a road with intense vehicular traffic. These elements were associated with car traffic due its use in car breaks, fuel catalyzers, and its occurrence in car exhaust emissions.

Implications for runoff monitoring and for the first flush treatment

The results indicate that stormwater monitoring requires meteorological, chemical, and spatial information for a proper assessment. Several areas with sensitive land use, such as industrial zones (Mamun et al., 2020; Porfírio et al., 2020), roads, or car parks (Meland, 2016; Poudyal et al., 2021), where contaminated surface runoff could escape and affect external water bodies, require first flush collection and treatment. The retention and treatment of the first stormwater portion likely provides environmental protection or improvement. Sequential sampling like the four chamber collector used in this study indicates that the initial 2 to 3 mm of the rain event are critical for pollutant load reduction. Barco et al. (2008) suggested that the retention and treatment of a small portion of the runoff can be more effective and economical. The runoff sampling, analysis, and eventually retention can act as another protection line in a nuclear facility like IPEN.

Conclusion

The present study provided an overview of stormwater runoff as an environmental monitoring assessment at the IPEN campus. The different pollution sources presented distinct runoff evolution. The elemental concentration varied with the precipitation amount, seasons, spatial distribution inside IPEN campus, and with the runoff process itself depending on its source. No significant difference was observed by collection points or collection chamber for soil formation elements, as expected, while traffic-related elements had a higher concentration on the collection point close to the intense road traffic and in the 1st collection chamber.

This response is typically associated with the first flush phenomena, for pollutants deposited in large surfaces like roads, rooftops, and car parking lots. External sources to IPEN campus, like traffic-related elements, had higher concentrations when the origin of the air mass was continental when compared with coastal or oceanic air masses. Elements associated with U ores processing, such as U, Th, La, and Ce, were susceptible to spatial variability but were not affected by the air mass trajectory origin. During this study, only Al and Fe exceeded limits from Brazilian legislation for untreated effluent release in surface water bodies. The sequential runoff sampler proved to be an effective monitoring tool when considering the usual source of variability such as air mass trajectory, seasons, spatial distribution, and runoff process/number of collection chambers. No environmental risk was associated with runoff during the monitored period at the study site. Any action that improves and expands the surveillance and monitoring is desired in a nuclear facility subjected to radiological and environmental risks such as IPEN.

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Data availability The datasets generated during the current study are available from the corresponding author on request.

Declarations

Ethics and responsibilities All authors have read, understood, and have complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors and are aware that with minor exceptions, no changes can be made to authorship once the paper is submitted.

Competing of interest The authors declare no competing interests.

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