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 nonpoint pollutant source and in urban environments contributes to aquatic ecosystem quality decay. Here, we examined the runoff characteristics on the export of total solids and total metals, as well as pH and conductivity responses during the rainfall evolution. In 2017 and 2018, 12 rain events in 4 sampling stations were monitored at a 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 was composed of Ca > K > Mg > Si > Al > Fe > Na > Zn > Mn > Sr > Ti > Mo > V > Cu > B > Pb > Ni > Ce > Sb > Cr > La > U > Th > Cd. Total solids, Al and Fe exceed Brazilian water quality standards. Principal components analysis identified the elemental clusters linked to the facility activity, soil, traffic/atmospheric related deposition. Our results show that the runoff characteristics could be differentiated by pollutant source. 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 consider to disentangle the elemental clusters and pollution source contributions. In winter, continental air masses were associated with higher concentrations heavy metals in the surface runoff. Spatial changes with no seasonal variation were observed for U, Th, La and Ce.

1. 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). In urban environments, the runoff is a significant source of diffuse pollution subject to confounding factors such as the season (Hilliges et al., 2017), land uses(Opher and Friedler, 2010), vehicle traffic(Berndtsson, 2013), industrial activities, rain event origin and intensity (Imfeld et al., 2020; Perera et al., 2019). Although extensive reviews(Gioda et al., 2021; M Huber et al., 2016; Müller et al., 2020; Rodak et al., 2020), there are still open questions about how does pollutants wash-off and what are the key influential rain variables over the pollutants wash-off process(Alias et al., 2014a, b). Several studies have been carried out presenting study cases (Sörme and 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) associated with storm water runoff.

In 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, 2021, 2009). 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. In the majority of countries including Denmark, Ireland, Malta, Netherlands, Norway, Slovakia, Sweden, Switzerland, water services include rainwater runoff management However, the EC/Directive 1991/ 271 requires the stormwater prevention of leaks and pollution limitation. Therefore the main actions are on the heavy metals reduction emission (Cd, Hg and Pb)(European Environment Agency, 2016). In Latin America and Brazil, no storm water runoff regulation is required at the moment. Even in São Paulo, a megacity, with a car fleet of 30,778,960 thousand units (IBGE, 2020), where the traffic-derived pollution is considered significant by several authors, no runoff regulation is 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 (CETESB, 2021; CETESB, 2021). 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 soil waterproofing by 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. Another line of action for surface runoff control applied conventional measures to promote the infiltration and temporary rainwater storage, to compensate the urbanization effects over the hydrological process. One of the options would be rainwater harvesting and re-use. However the water runoff through roofs, streets, and roads should not contain pollutants(Canholi, 2014; Righetto, 2009). Some studies identified pollutants like sediment, organic matter, bacteria, metals such as copper, zinc, manganese, iron, and lead that reached the water bodies through the runoff (Becouze-Lareure et al., 2015; Burton Jr and Pitt, 2001). Some of these pollutants originated in particulate matter airborne deposited first on surfaces and then were flushed during precipitation events. As a nonpoint pollutant source, runoff stormwater can be harmful to plants, animals, and people(Hilliges et al., 2017; Paz et al., 2004). One of the main ways to characterize the stormwater event is the first flush phenomenon, as it helps to find the main source in urban runoff in roads or roofs, from separated or combined discharge systems and receiving water flow(Deletic and Maksimovic, 1998; Hilliges et al., 2017). The first flush assesses if the mass emission rate is higher during the first portions (Bach et al., 2010; Barco et al., 2008). By the first flush it is 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. To be considered successful, the management of rainwater should be done judiciously. Thus, eliminating the first fraction and when appropriate prioritizing the monitoring and treatment for the effective use of water (Meland, 2016).

In the present study, we accessed 12 runoff events that occurred in São Paulo, inside the University of Sao Paulo and IPEN Campus IPEN. IPEN is a nuclear facility with training and research reactors, with radioisotopes production for diagnosis and therapy. This area corresponds to a green zone surrounded by intense traffic and under and under the influence of continental and oceanic air masses. Our main hypothesis 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 our hypothesis, we have monitored the concentrations of potentially toxic elements (PTE's) such as Cr, Cu, Cd, Ni, Pb, Sb, and Zn; major and trace elements (MTE) with natural soil occurrence like Al, Ca, Fe, K, Mn, Mg, Na, Si, Sr, and Ti; and elements related to the nuclear cycle process like U, Th, La, and Ce. The variability associated with the precipitation amount, the season changes, spatial distribution of sampling points and the backward atmospheric trajectory were disentangled by using general linear models.

2. Materials And Methods

2.1. Study area

The study area was located inside the University of São Paulo campus, in a parking lot at IPEN, nearby the Centre of Chemistry and Environment (-23,566268 S, -46,737629 W). That 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 km². 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 1,450 mm, with summers prone to thunderstorms. The main traffic corridors (Marginal do Rio Pinheiros and Avenida Politécnica) were distant 6.7 km from the collection site. IPEN performs a series of nuclear activities, among them, short-lived radioisotopes production for medical applications, radiation metrology and monitoring with radioprotection and dosimetry, nuclear reactors operation with partial activities of the fuel cycle, and several multidisciplinary activities that varied teaching, research, and development, and innovation program (SANTOS, 2017). Therefore, air quality is regularly self-monitored, as well as monitored at Cidade Universitaria station by CETESB - State of São Paulo Environmental Company. CETESB has several other stations in São Paulo as presented in Fig. 1

The collection sites (*P0*, *P1*, *P2*, and *P3*) cover 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 a significant green area coverage. P0 (-23°56'16.98" S, -46°73'97.50" W) and P1 (-23°56'15.93" S, -46°74'02.00" W) are located respectively in front of the lower and upper parking lots of the deactivated and dismantled nuclear fuel cycle reprocessing unit (CELESTE). P2 (-23°56'13.65" S, -46°73'96.80" W) 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" S, -46°73'94.25" W) was located in front of the Laser and Applications Centre, 150 m apart from 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).

2.2. Meteorological data

Two stations provided meteorological data: 1) IPEN/Cidade Universitaria Station (De Molnary, 2018) and 2) National Institute of Meteorology (INMET, 2019), which correspond to the nearest and the reference stations respectively. The sampling period started on January 2017 and ended in September 2018. The rain intensity by event date is 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).

In 2017, the yearly accumulated rain in Sao Paulo was 1,414 mm, which was close to the 20-year historical average. However, that 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. While April, May, and August were much rainier (CETESB, 2018a, 2018b) than the average. That was explained by a situation of neutrality of oceanic and atmospheric conditions in the Equatorial Pacific concerning the phenomenon of global scale El Niño-South Oscillation (ENOS) (CETESB, 2018a). As the atmospheric blocks were formed, both in the Pacific Ocean and the Atlantic Ocean, as well as high-pressure systems on the continent that influence 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 value reached 1,223 mm, which was 14% below 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). In 2018, in the first quarter, the 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 ENOS phenomenon were observed and that lasted until mid-September when an indication of warming in the waters of the Equatorial Pacific was identified.

2.3. Backward atmospheric trajectory

The particulate backward trajectories were obtained at the NOAA'S HYSPLIT platform for each rain event (Stein et al., 2015a) along with the atmospheric pressure during this period. To be effective, the particulate matter trajectory had the endpoints as the sampling stations considered the 24 hours before the precipitation time. Thus, the air mass origin of the trajectories with altitude, speed, and directions of deposited particles were identified. Then, the trajectories were classified by the prevalent direction and associated with each rain/runoff event and classified as continental and oceanic according to their origin.

2.4. Sequential sampler and sampling campaign

Three sequentially integrated samplers were built, with four sampling chambers. The collector design was adapted from (Righetto, 2009). One collector had 850 mL and two others had 1,000 mL total capacity (Figure S1). The EPA protocol for stormwater monitoring was used (USEPA, 2009). For this study, 12 rain events 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).

2.5. Chemical analysis

pH and electrical conductivity (EC) were analyzed *in situ* (APHA;AWWA;WEF, 2017). The total solids (TS) were analyzed gravimetrically. For metals analysis, all samples were acidified by adding 0.5 mL concentrated nitric acid (pH < 2) and microwave digested with a mixture of nitric and hydrochloric acid, with time and power following the method 3015A. After the digestion, Ce, Cr, Cu, Cd, La, Ni, Pb, U, Sb, and Th were measured by ICP-MS (Model 7700, Agilent, USA) following the method 6020D (USEPA, 1998). While 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).

2.6. Data treatment and statistical evaluation

The Event Mean Concentration (EMC_i) was applied to calculate pollutants' load in collected samples (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). Thus, the pollutants' mean concentration was obtained (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 by collector chamber (C), sampling point (P), rain events (E), seasonality (S), and wind direction (D) was assessed. Principal components analysis (PCA) with varimax standardized rotation factor. Principal components with eigenvalues over 1 (one) was considered to identify elemental covariations, similar to other studies(Huang et al., 2007; Porfírio et al., 2020; Tositti et al., 2018).

3. Results

3.1. Precipitation events

In 2017 and 2018, the 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, we considered the precipitation amount

sufficient for the runoff sampler assessment among the collector chambers, the sampling locations, 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 17th, 2017 (34.8 mm), and March 14th, 2018 (42.8 mm). From 1930 to 2019, in Sao Paulo, the frequency of intense events (> 20mm) 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).

3.2. Physical-chemical results

pH ranged from 5.6 to 7.8 among all samples, therefore no occurrence of acid runoff was observed. For pH, the location of collection points and the seasons were the dominant controlling factors over trajectories and the event class as presented in Fig. 2a.

EC and TS ranges were from 10.2 to 308 μS cm^{-1} and from 20 to 1,760 mg L^{-1}, respectively. For EC, the precipitation amount effect was dominant, 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). That is associated with the dilution caused by the precipitation increase and it was similar as described in other studies (Hilliges et al., 2017; Maximilian Huber et al., 2016; Makineci et al., 2015; Valtanen et al., 2015a). Regarding the sampling points, higher EC values were observed at P3, even when it is considered comparable TS values among all sampling points. We have considered the dense traffic in the surrounding P3 explains 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 (Maximilian Huber et al., 2016; Valtanen et al., 2015b; Westerlund and Viklander, 2006). TS in all seasons exceeded the benchmark value for construction site runoff in Switzerland of 20mg/L (Meland, 2016).

3.3. Runoff elemental characteristics

A total of 19 elements were present in the runoff samples above the quantification limit and the decreasing 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 limit on effluent conditions to be released in surface water bodies (CONAMA, 2011). Aluminium in all seasons and iron in winter events were elements exceeding the Brazilian regulatory limits.

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	$\mu g\ L^{-1}$	43	**1337.5**	267.8	**841.0**	723.1	**2566.6**	1950.9	**1762.7**	1746.3	100[a]
Sb	$\mu g\ L^{-1}$	48	0.7	0.1	1.5	2.6	3.7	6.8	1.0	0.4	5[b]
Cd	$\mu g\ L^{-1}$	17	0.6	0.0	0.7	0.1	1.7	1.2	0.7	0.1	200[b]
Pb	$\mu g\ L^{-1}$	84	5.6	2.7	7.9	5.7	15.7	11.1	9.2	7.4	500[b]
Cu	$\mu g\ L^{-1}$	84	14.6	6.7	9.8	3.5	22.1	23.4	24.3	12.8	1000[a]
Cr	$\mu g\ L^{-1}$	80	2.9	1.7	2.5	2.7	3.9	2.7	2.9	1.9	1100[c]
Fe	$\mu g\ L^{-1}$	43	692.5	246.3	737.8	572.2	**2273.3**	1555.1	828.9	625.3	1500[a]
Mn	$\mu g\ L^{-1}$	34	44.1	5.0	47.4	14.9	116.3	95.6	64.2	12.3	1000[b]
Ni	$\mu g\ L^{-1}$	79	2.3	0.8	2.2	1.6	5.2	5.2	3.7	2.8	2000[b]
U	$\mu g\ L^{-1}$	59	1.0	0.5	2.5	1.7	2.1	2.0	3.3	2.7	20[b]
Zn	$\mu g\ L^{-1}$	43	59.0	12.2	100.9	62.4	156.3	114.4	83.5	55.0	5000[b]
Ca	$\mu g\ L^{-1}$	43	5094.9	278.3	5186.3	1711.1	9669.6	7529.0	6427.1	1823.4	-
Ce	$\mu g\ L^{-1}$	81	6.1	4.2	3.1	2.3	7.5	6.1	6.9	5.3	-
K	$\mu g\ L^{-1}$	39	4488.9	386.9	4209.0	2331.0	7931.3	6742.0	8611.8	2167.0	-
La	$\mu g\ L^{-1}$	74	2.2	1.6	1.6	1.1	3.1	2.4	2.7	1.8	-
Mg	$\mu g\ L^{-1}$	47	761.8	55.5	1228.4	803.5	1225.6	1317.7	853.2	454.1	-
Na	$\mu g\ L^{-1}$	26	294.7	28.0	452.1	94.4	1283.8	307.5	995.6	117.3	-
Sr	$\mu g\ L^{-1}$	38	26.9	2.0	24.1	7.1	41.8	31.2	27.6	9.8	-
Ti	$\mu g\ L^{-1}$	21	29.1	8.4	26.6	13.7	110.1	60.2	39.7	20.7	-

[a]Dissolved form | [b]Total form | [c] 100 ug/L as Cr^{+6} and 1000 as Cr^{+3}- No guidance value

	Units	N samples > LQs	Spring		Summer		Winter		Autumn		CONAMA Res. 430/11
			Mean	SD	Mean	SD	Mean	SD	Mean	SD	
Th	$\mu g\ L^{-1}$	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	$\mu S\ cm^{-1}$	-	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	-

[a]Dissolved form | [b]Total form | [c] 100 ug/L as Cr^{+6} and 1000 as Cr^{+3}- No guidance value

Copper, Cr, Ni, and Pb were the most frequently detected elements, present in 88–94% of all samples. Zinc was in a higher concentration but present in less than 50% of samples. All samples agreed with the values reported by USEPA urban runoff range for Cu (from 10 to 400 µg/L), Pb (from 10 to 1,200 µg/L), and Zn (from 10 to 2,900 µg/L), which classify these elements as the most prevalent priority pollutants found in urban runoff (USEPA, 2021). The high prevalence of these elements was associated with vehicle traffic by fuel combustion 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 inferior to the surface runoff from the road to the Ganges river in India (2016 to 2019)(Siddiqui and Pandey, 2021).

In our study, 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 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.

3.4. Controlling factors over the runoff composition

Some factors influence the concentration variability observed in the present study, 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. Even for the elements with no significant statistical difference among the seasons, winter was the season with the maximum observed values, like for Fe, Mn, U, and Sr. We have associated this trend 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). 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. While dust and soil elements (like Fe, Mn, Al, and Ca) had no difference by sampling point or by collection chamber (Figure S2). Therefore, no first flush effect was noted for soil formation elements.

The rain event intensity affected significantly the concentration of most elements. For weak events, the concentrations were higher 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. Figure 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., 2015b; Zhou et al., 2021). The continental trajectories were prevalent among the events regardless 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). Again that was observed for the majority of measured elements. However, uranium had a different spatial distribution. U was high during winter, as other dust and soil originated elements, but P0 had higher values than other stations, once P0 was the closest sampling point to the U reprocessing unity inside IPEN. To confirm the local influence of U, we have observed no statistical difference between air mass trajectories, once its source is not external to IPEN facility.

3.5. Principal component analysis

For the factor analysis, five principal components were identified with eigenvalues > 1 able to explain 89.8% of total matrix variability. presents these factors' eigenvalues, explained variability per component, and total explained variability.

Factor 1 explained 44.0% of the system variability (Fig. 4a). Factor 1 was associated with elements such as Na, K, Fe, Sr, Ca, Zn, Mg, Mn, Ti, and Al. Therefore the increase of these elements was associated inversely with pH and collection points. By the characteristics of these elements factor 1 was associated with the soil formation elements. Factor 2 explained 19.9% of the system variability. This factor was associated to EC and TS inversely related to U, Th, and Al. These two factors associated clearly differentiated P0 and P3. As discussed previously, because P0 had higher U and Th values and P3 had higher concentrations from other elements from other origins than the soil.

Factor 3, explains 14.9% of the system variability. In this factor the variables withheld were Pb, Sb, Ce, U, Cr, Ni, La, and Th (Fig. 4c). Uranium and Th are correlated to the activities of IPEN, located near the P0 station (Fig. 4d), Pb, Sb, Ce, Ni, and Cr linked to car traffic.

4. Implications For Runoff Monitoring And For The First Flush Treatment

The results indicate that stormwater monitoring requires meteorological, chemical, and spatial information for its 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 provide environmental protection or improvement. Sequential sampling like the four chamber collector used in this study indicates the initial 2 to 3 mm of each rain event are critical for pollutant load reduction. (Barco et al., 2008) suggested the retention and treatment of a small portion of the runoff can be more effective and economical. In a nuclear facility like IPEN, the runoff sampling, analysis, and eventually retention can act as another protection line.

5. 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. For soil formation elements, no significant difference was observed by collection points or collection chamber, as expected. While traffic related elements had a higher concentration on the collection point close to the intense road traffic, and higher concentration, as well as, 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 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, Ce were susceptible to spatial variability by 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 masse trajectory, seasons, spatial distribution, and runoff process/number of collection chambers. At the study site, no environmental risk was associated with runoff during the monitored period.

However, in a nuclear facility subjected to radiological and environmental risks, any action that improves and expands the surveillance and monitoring are desired.

Declarations

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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Data availability

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

Authors contribution

Mainara Generoso Faustino and **Maria Aparecida Faustino Pires** – Conceptualization, funding acquisition, methodology, sample collection, analysis, project administration, Statistical analysis, manuscript writing;

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Lucilena Rebêlo Monteiro – Statistical analysis and writing;

Walter dos Reis Pedreira Filho, **Roberta Granja Gonzaga** and **Marycel Elena Barboza Cotrim** – Chemical analysis, writing.

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Figures

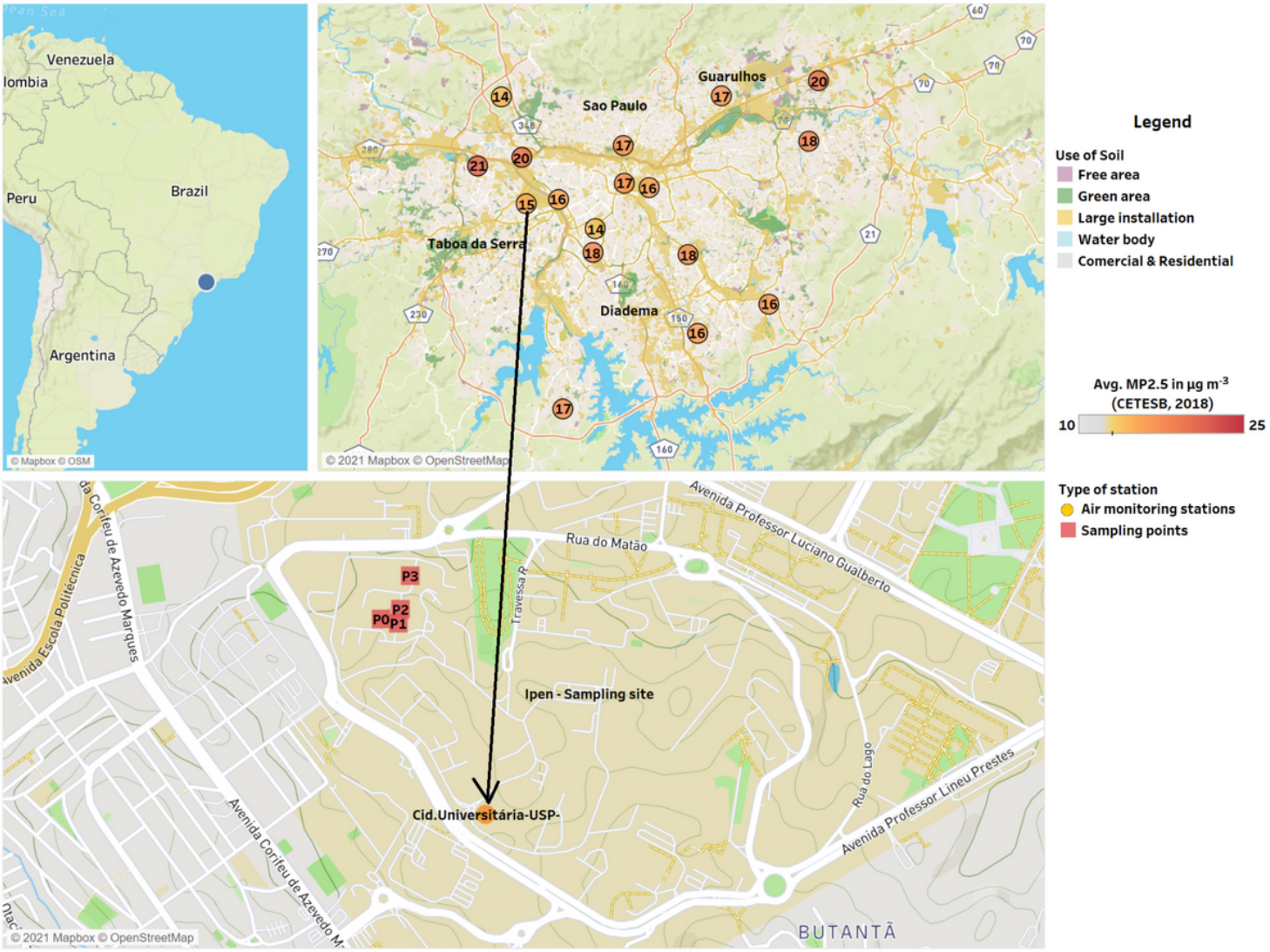

Figure 1

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.

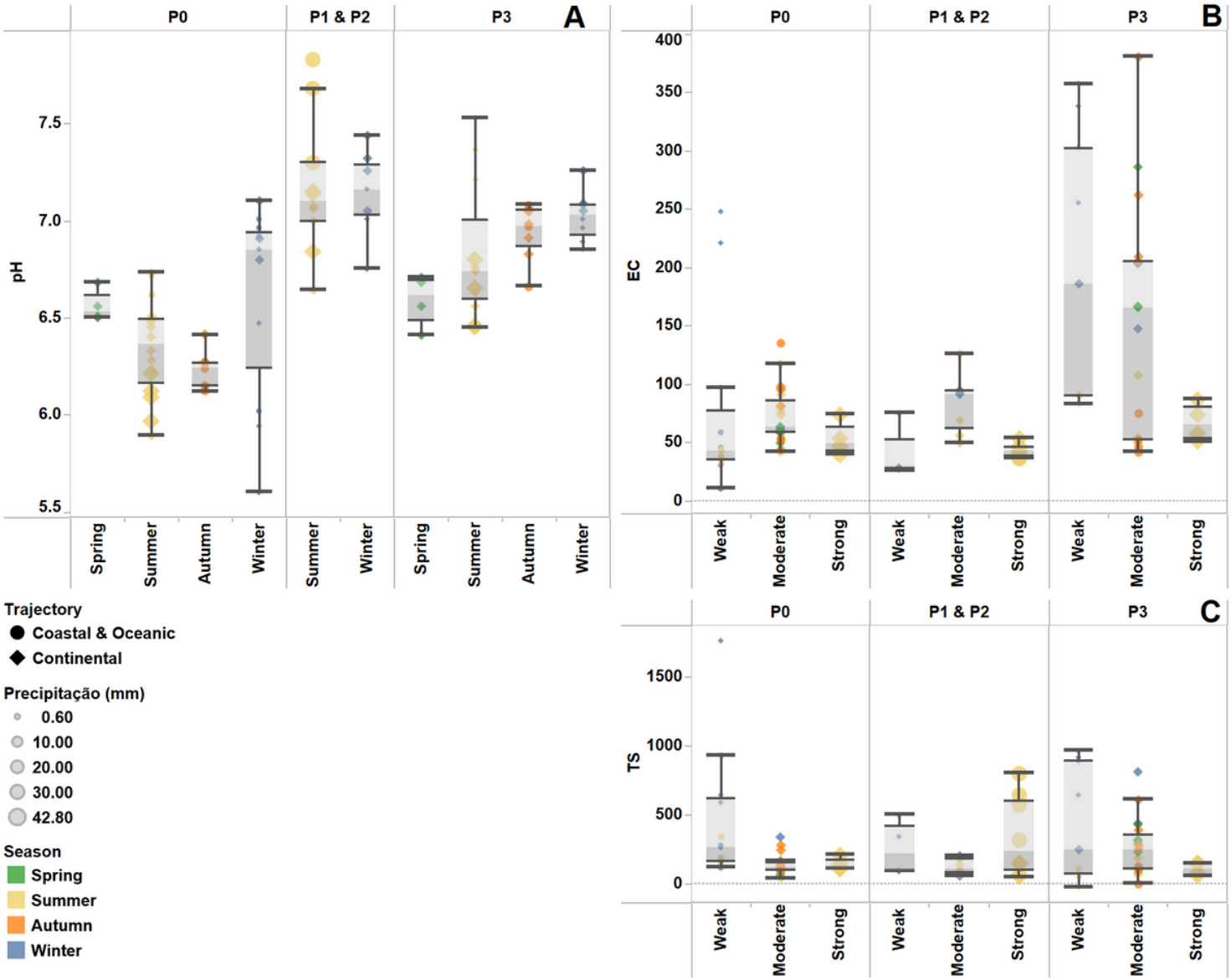

Figure 2

pH(a), EC(b) and TS(c) by point, event intensity and air mass trajectory.

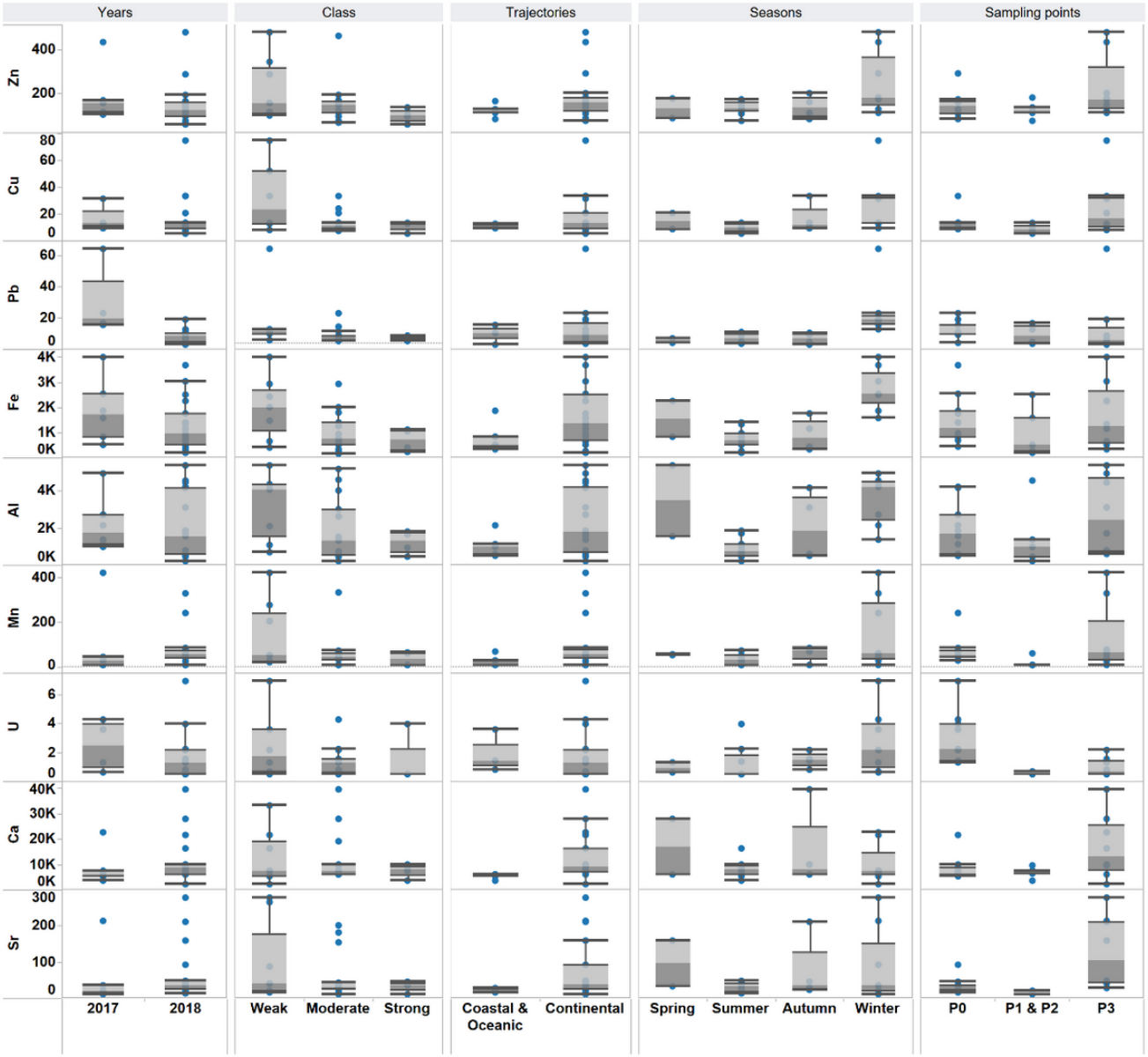

Figure 3

Variability of Zn, Cu, Pb, Fe, Al, Mn, U, Ca and Sr by years, event class, trajectory origin, seasons and sampling points.

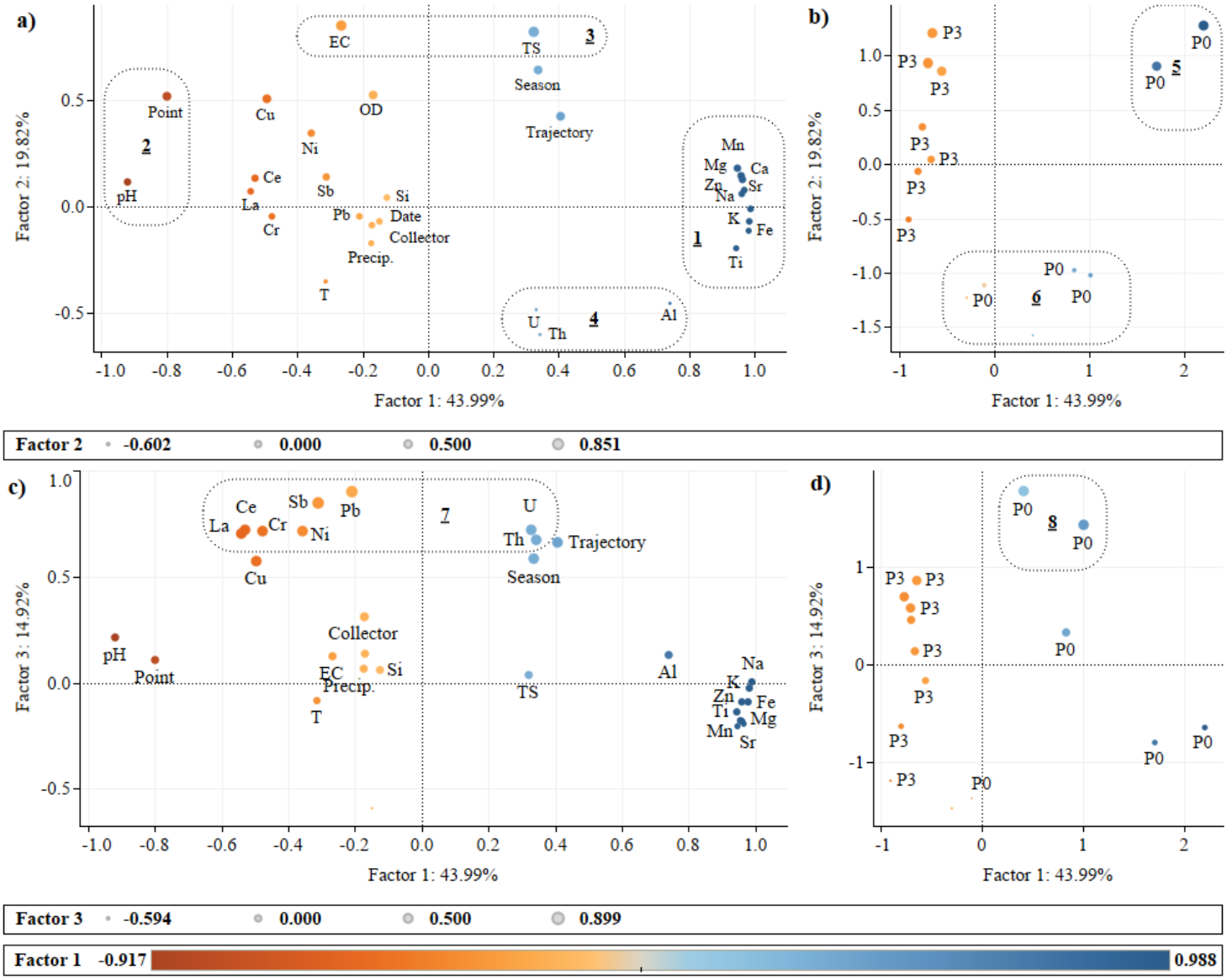

Figure 4

Projection of the variables and case on the factor-plane 1 x 2 (a | b) and 1 x 3 (c | d)

Supplementary Files

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