Total metals in stormwater runoff at the Nuclear and Energy Research Institute (IPEN), São Paulo – Brazil.

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***Abstract*—Stormwater quality allows to evaluate if any pollutants load happens within its runoff. This work aims stormwater temporal and spatial profile characterization to assess environmental risk and to identify chemical tracers. Thus, a specific collector was built to sample collection, with four separate PVC tubes, and the collector allowed single event temporal and sequential evaluation, as long as each compartment was fulfilled. The collector was installed in the runoff direction in order to have maximum collection volume. Two collections were carried out in summer (January 2017) at two IPEN stations, in urban areas. Total metals analysis were performed, in addition to physicochemical data, such as pH, temperature and conductivity. The results had aluminum, iron and manganese present, and some elements, such as zinc, had a temporal distribution, with a decrease concentration within the collected volume. The preliminary results have as objective to assist the studies of urban water management.**

Keywords—Stormwater, runoff, metals

I. INTRODUCTION

When rainwater flows to the catchment surface, it carries pollutants such as toxic elements and bacteria [1].

Recent studies [2, 3] have demonstrated that urban water quality has become a key element in the assessment of receiving watercourses. These studies have been widely conducted in several countries whose concern is to improve water quality in their water resources linked to improved sanitation in urban areas [4, 5, 6, 7, 8].

These evaluations and their respective discussions have been used to characterize the baseline event and water quality parameters, focusing on the precipitation characteristics and surface runoff, such as Event Mean Concentrations (EMC) of the pollutant and precipitation intensity and characteristics of the rain [9].

The first flush is the most important phenomenon in the runoff process and urban stormwater management. The term first flush is used to indicate whether the mass emission rate is higher during the first portions of flow, than during its last portion [9]. Bach et al. (2010) proposed a new method, different from the traditional one that redefined the first phenomenon caused by the discharge of rainwater. One of the highlights of this method is that the "wash-off" process of the pollutant (final washing or simply washing) is divided into

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several stages or slices, each stage being analyzed separately [9, 10].

In order to establish the best collection conditions and which parameters are determinants of surface runoff, this study was carried out in the Metropolitan Region of São Paulo (SP, Brazil), at the IPEN station, located within the facilities of the University of São Paulo campus, at the Nuclear and Energy Research Institute (www.ipen.br).

With a four-stage collector, this paper aims to demonstrate the rainfall behavior from the surface runoff in urban areas. Two collections were carried out in summer (January 2017) at two IPEN stations, upper station (23°33'42''S – 46°44'23''W) and lower station (23°33'42''S – 46°44'24'' W), to analyze the metals content that can be found in the region.

II. STORMWATER RUNOFF COLLECTOR

The integrated collector was built with four PVC tubes, adapted following the reference [1, 9], showed in Fig. 1. Each tube has an 850 mL capacity. This system can collect a single temporal event of stormwater runoff in a sequential way.

Fig. 1. Integrated Collector built with PVC tubes (adapted from [1, 9]).

The collector was installed in the direction of the street slope to captured surface water runoff. Two collections were carried out in summer 2017 at two IPEN stations. Fig. 2 shows the installed collector in the street, fixed on the metal grid.

Fig. 2. Integrated collector installed in the street

III. METALS ESSAY

A. Metal Essay

All sample were digested by using microwave furnace MDS-2000 (CEM) with time and power following the EPA method. All quality control was carried out and it is elsewhere described [11, 12].

Cadmium were analyzed by Graphite Furnace Atomic Absorption Spectrometer GF-AAS (AAnalyst, Perkin Elmer) and zinc, aluminum, iron, manganese, cooper, chromium, nickel and uranium Inductively Coupled Plasma Optical Emission Spectrophotometer - ICP-OES (SpectroArcos, Spectro) [11].

B. Physicochemical Essay

All physicochemical essays were performed at the sample collection. The pH and temperature analysis used a calibrated potentiometer (model PG 2000, GEHAKA©) and the electrical conductivity used a standard conductivity cell (model 150, ORION©).

IV. STUDY AREA

The study area is located at the Nuclear and Energy Research Institute (IPEN), specifically at the Chemistry and Environment Center (CQMA). This urban area has a dense vegetation cover and for this reason has large amounts of organic matter in the street that was observed in Fig. 3.

Fig. 3. Runoff area after stormwater

V. RESULTS AND DISCUSSION

A. Physicochemical

In TABLE I and TABLE II, pH, temperature and conductivity data from two collections are presented.

In the first collection (TABLE I), pH ranged from 7.30 to 7.83, showing a slyly basic amount in samples. The second collection (TABLE II), pH ranged from 6.48 to 6.73, with an acidic presence in the sample.

The conductivity ranged from 36.3 to 42.3 $\mu S.cm^{-1}$, in the first collection and from 32.6 to 44.0 $\mu S.cm^{-1}$ in the second collection, this data indicates a low presence of dissolved salts in the samples.

TABLE I. Physicochemical results from upper station area

Upper station area	pH	Temperature °C	Conductivity µS.cm^{-1}	Date
Chamber 1 – U*	7.30	22.40	36.3	17/01/2017
Chamber 2 – U	7.83	22.50	40.5	17/01/2017
Chamber 3 – U	7.83	22.00	42.3	17/01/2017
Chamber 4 – U	7.68	21.90	36.5	17/01/2017

*U = upper station

TABLE II. Physicochemical results from lower station area

Lower station area	pH	Temperature °C	Conductivity µS.cm^{-1}	Date
Chamber 1 – L*	6.48	23.70	44.0	31/01/2017
Chamber 2 - L	6.62	23.40	42.7	31/01/2017
Chamber 3 - L	6.73	23.40	37.3	31/01/2017
Chamber 4 - L	6.72	23.30	32.6	17/01/2017

*L = Lower station

B. Metals

The analyzed metals were zinc, aluminum, iron, manganese, cadmium, cooper, chromium, nickel and uranium. No amount of uranium, nickel, cadmium and chromium was found above the quantification limit that can be observe in TABLE III.

TABLE III Quantification Limit

Elements	Quantification Limit (µg L^{-1})
Uranium	49
Nickel	29
Cadmium	1
Chromium	18

Manganese was present only in the lower station area, but only in the first and the second collector chambers, with a concentration of 63.3 and 31.1 µg.L^{-1}, respectively (Fig. 4.). The third and fourth chambers had no concentration above the quantification limit (10 µg.L^{-1}).

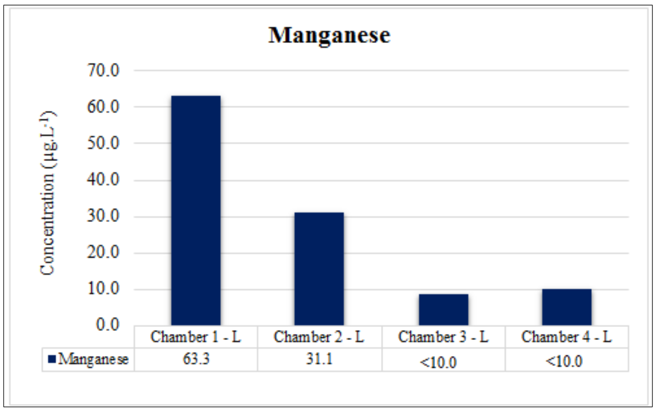

Fig. 4. Manganese concentration in lower station area.

As manganese, cooper was present only in the lower station area. Copper concentration decreased from 79 to 69 µg.L^{-1}, from first to second collector, respectively. In the third and fourth collector, similar copper concentrations were found (Fig. 5).

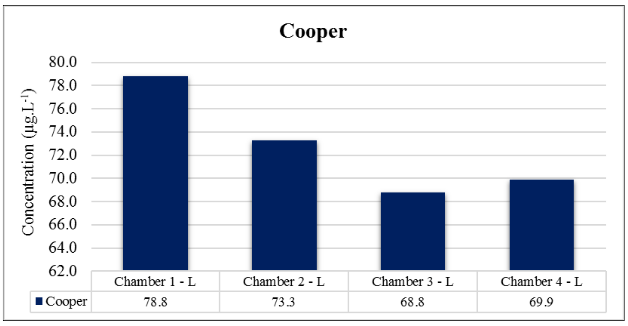

Fig. 5. Cooper concentration in lower station area.

Zinc results presented a temporal distribution, with a decrease concentration within the collected volume. In Fig. 6 and Fig. 7, zinc was present in both collections.

With a volume-monitoring collection, instead of a time-monitoring collection, it was possible to observe that the water collected from the runoff surface washes surrounded region and presents some elements concentration decrease.

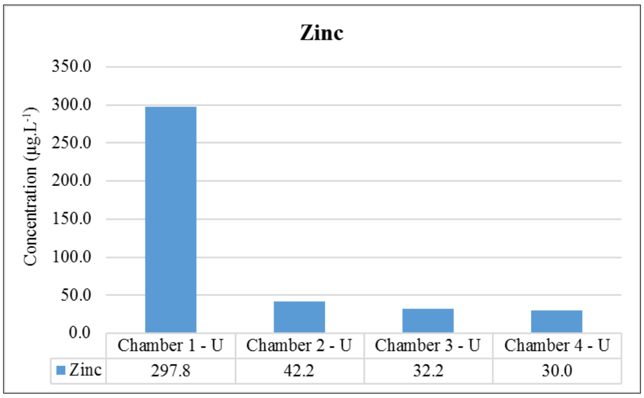

Fig. 6. Zinc concentration in upper station area

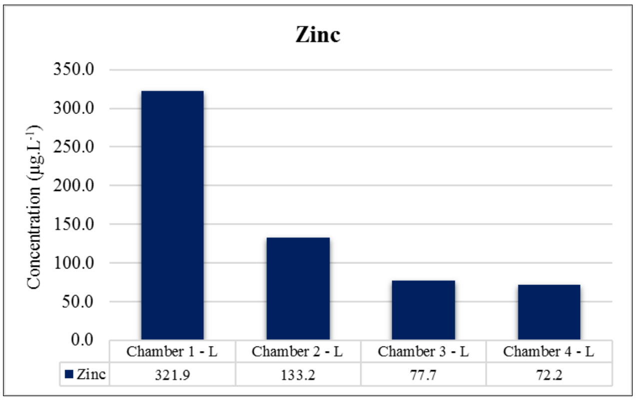

Fig. 7. Zinc concentration in lower station area

Iron and aluminum in lower station area had the same behavior as zinc, with a decreased concentration. At the upper station area, the behavior was more linear with little variation from the first to the last collector. Data from iron and aluminum can be observed in Fig. 8 and Fig. 9, respectively.

Aluminum is the most abundant element in the earth's crust, after oxygen and silicon [13], its solubility is low in pH between 5.5 and 6.0 [14]. Aluminum dissolved in neutral pH waters range from 1 to 50 µg.L^{-1}, but could increase up to 0.5 to 1 mg.L^{-1} in more acidic or organic matter rich waters.

Iron is mainly present in groundwater, but in surface water its level increases in rainy seasons, because of soil loading [15].

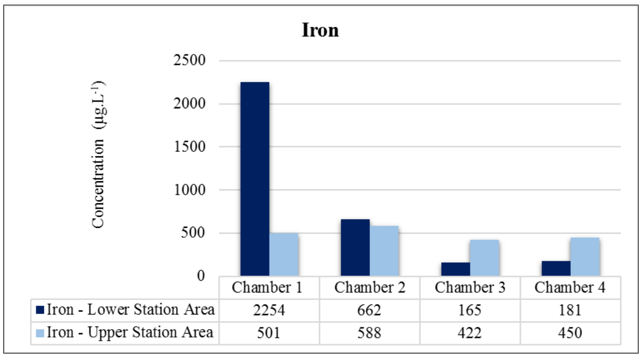

Fig. 8. Iron data from upper and lower station area

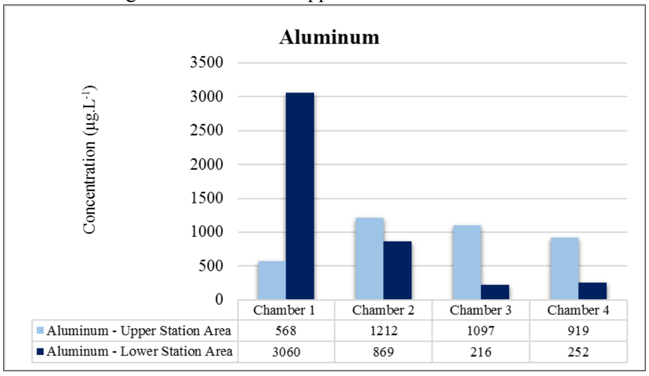

Fig. 9 Aluminum data from upper and lower station area

VI. Conclusion

With an integrated collector, metal behavior in the runoff water from the IPEN region was measured and demonstrated that the rain falling in the area washes and carries elements present in the surroundings.

The present study, considered preliminary, found no harmful or significant concentration that could affect the nearby streams and rivers, but showed that metals, although in small amount, are present in the region.

In this article, the runoff water quality was specifically addressed to summer 2017 of natural rainfall events in the city of Sao Paulo, based on high intensity medium and long duration of average precipitation. The water quality was considered as an independent variable of the precipitation event characteristics. The water quality forecast from runoff can contribute to know the impact over hydrographic basins health quality and to improve the treatment design to mitigate water quality in major cities.

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