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Halogen (and Species) Determination in Surface Water by Inductively Coupled Plasma Mass Spectrometry and Ion Chromatography

Determinação de Halogênios (e suas Espécies) em Águas Superficiais Usando Espectrometria de Massa com Plasma Indutivamente Acoplado e Cromatografia de Íons

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An investigation was carried out to evaluate the contribution of the activities and effects of a University Campus on the waters that are part of its natural environment, by focusing on the determination of halogens. This case study was undertaken on the Federal University of Santa Maria campus, Santa Maria city, where teaching and research activities occur, in addition to the main regional Hospital and University Residence inside the campus. Composite sampling was carried out over 12 h at five strategic points, from the stream's entrance to the exit of the university campus. Chlorine, bromine, and iodine were determined by inductively coupled plasma mass spectrometry (ICP-MS) and fluoride, chloride, bromide, and iodide species were determined by ion chromatography (IC). Results revealed that among the activities developed on the university campus, those carried out at the hospital have the greatest impact on halogen concentrations. Nonetheless, a comparison of the analyte concentrations in the inlet and outlet streams, showed that they are generally similar or smaller to those in other streams except for iodine.

Keywords: Halogens; speciation analysis; surface water; ion chromatography; ICP-MS.

1. Introduction

Water is a necessary resource for humans and can be used in different ways, from domestic to industrial applications. However, contamination of water resources can occur due to human activities. For example, the release of inadequately treated wastewater into the environment can lead to aquatic ecosystems degradation. Plants and organisms exposed to these contaminated waters can be affected which can harm individual species and impact the natural biological communities.[1]

Water contamination has received great attention from the scientific community, especially regarding organic contaminants, their determination and research on their removal/degradation.[2–4] In addition to organic contaminants in aqueous environmental matrices, elements such as metals and halogens and their species can also pollute water bodies. Inorganic contaminants can include minerals and their acids, inorganic salts, trace elements, metals, organometallic complexes, cyanides, and sulfates.[5] Generally, inorganic water pollutants, such as phosphates, nitrates, chloride, and fluoride, are persistent and non-biodegradable. Hence, halogens determination in environmental samples is highly relevant as these elements have an ambiguous effect on human health.[6] They are characterized by being essential to living beings; nevertheless higher concentrations can cause various health problems, which in some cases can be toxic.[7]

Halogens include fluorine, chlorine, bromine, and iodine. Their toxicity and reactivity decrease from fluorine to iodine. These nonmetals are used in various commercial and industrial applications to improve material performance. Synthetic halogenated compounds, especially fluorides, bromides, and chlorates, are commonly used as pesticides, disinfectants, solvents, drugs, and flame retardants.[8] In addition, they are widely used in household products, which have received increasing concern, since the incineration of products containing halogenated organic compounds leads to the formation of highly carcinogenic, migratory, and chronically toxic products.[9] Despite halogenated organic compounds have been commonly identified in water, only a few halogenated inorganic species are regularly determined.[7,10,11]

Fluorine is widely distributed and has a strong metallogenic capacity; its main forms are cryolite (Na_3AlF_6), fluorite (CaF_2), fluorapatite ($Ca_5(PO_4)_3F$), topaz ($Al_2SiO_4(F,OH)_2$), and amphibole ($NaCa_2(Mg,Fe)O_{10}(OH,F)_2$). The dissolution of fluorine-containing minerals is an important source of fluoride in water. In addition, anthropogenic inputs, including agricultural irrigation, phosphate fertilizers application, electroplating, metallurgical activities, and coal burning also promote fluoride enrichment in water.[12] Fluoride enrichment can form a series of soluble complexes with iron (Fe^{3+}), aluminum (Al^{3+}), magnesium (Mg^{2+}), sodium (Na^+), calcium (Ca^{2+}), and hydrogen (H^+). Fluoride concentrations in water can change due to fluoride-containing minerals, ion exchange, residence time, dilution, temperature, pH, and salinity. Fluoride at concentrations between 0.5 and 0.9 mg L^{-1} is beneficial for preventing dental cavities in humans. However, in quantities between 2 to 4 mg L^{-1}, it can cause tooth discoloration. In addition, concentrations above 4 mg L^{-1} can induce bone damage.[5,12]

Chlorine is commonly determined in water and is mostly naturally present. Natural chlorine sources include the oceans, atmospheric deposition, and the weathering of rocks and minerals. The most common anthropogenic sources of chlorine are fertilizers and water treatments, mainly in the chloride form. Although chlorides have mild effects on living organisms, their excessive intake can cause serious harm or poison to the living body and the recommended limit for chloride in water is 250 mg L^{-1}.[5]

Bromine occurs naturally in seawater and freshwater, with freshwater concentrations ranging around 0.5 mg L^{-1}.[7] Common forms of bromine in surface waters include its presence in soluble salts such as bromide, bromine, hydrobromic acid, and bromine oxyacids. High bromide concentrations in surface waters may be due to bromine leaching from natural soil organic matter.[13] The main anthropogenic factors that contribute to bromine or species in surface waters are the presence of wastewater, leaks in sewage systems, and pesticides use. It is also used as a disinfectant, in swimming pools, because its residues are less irritating to the eyes. Therefore, determining bromine concentrations in water samples is crucial.[7,13]

Iodine occurs naturally in many surface waters, although iodide and iodate are their only stable inorganic forms. Typical iodine concentrations in river waters are around 5 µg L^{-1}, but concentrations above 50 µg L^{-1} can be found in some surface waters due to saltwater intrusion or specific rock formations. The primary natural sources of iodine include those from the oceans, rock weathering, and plant decomposition. The iodinated contrast medium from medical wastewater is an anthropogenic source of iodine in surface waters.[14,15] Iodinated contrast media include common drugs of large molecular weight used to improve soft tissue imaging, such as in computed tomography and magnetic resonance imaging scans. In addition, iodinated contrast media are dosed at extremely large concentrations and designed to pass through the body without biotransformation. Nonetheless, these properties also enable them to remain intact during wastewater treatment, making hospital effluents potential polluting sources of this type of contaminant.[14–16]

Considering the determination of these elements, some difficulties are faced. Their determination is made difficult even by some well-established techniques, such as inductively coupled plasma mass spectrometry (ICP-MS) and ICP optical emission spectrometry (ICP OES).[17] Low mass/charge ratio for fluorine, chlorine and bromine in ICP-MS and low working wavelength for chlorine, bromine and iodine are the main challenges to overcome for the use of those techniques. Especially for fluorine, the determination using ICP-MS is uncommon due to its high ionization energy (17.4 eV), that means about 0.0009% of the fluorine is ionized in the Ar plasma (ionization energy: 15.8 eV).[18,19]

The Federal University of Santa Maria (UFSM) is located in the city of Santa Maria, Rio Grande do Sul State (29º 43' 02" S latitude and 53º 43' 4.2" W longitude). It is located in the region that constitutes one of the sources of the Vacacaí-Mirim River, whose basin is 65% occupied by the university campus. The waters of the hydrographic basin are part of the University's natural environment and - like any other element of nature - impact the space in which they are inserted and are also impacted by this environment.[20,21] Therefore, research is needed to understand the impact that the activities carried out at UFSM have on the quality of the composition of these waters, especially regarding the halogen concentration. Moreover, UFSM hosts the University Hospital of Santa Maria (HUSM), the largest hospital in the center of the State, being the hospital effluent a possible source of halogen contaminants for the river. Based on the aforementioned, in this study, the determination of halogens and their species in surface waters of the Vacacaí-Mirim River inside the university campus was performed.

2. Materials and Methods

2.1. Instrumentation

Chlorine, Br and I determination was performed by inductively coupled plasma mass spectrometry (ICP-MS, Elan DRC II, Perkin Elmer-SCIEX, Canada). The spectrometer was equipped with a concentric nebulizer (Meinhard Associates, USA), a cyclonic spray chamber (Glass Expansion, Inc., Australia), and a torch with a quartz injector tube (2 mm i.d.). Argon 99.996% (White Martins, Brazil) was used for plasma generation, nebulization, and as auxiliary gas for ICP-MS. Operational conditions for measurements by ICP-MS are listed in Table 1.

In order to compare the results and identify halogenated anionic forms, fluoride, chloride, bromide and iodide were determined using an ion chromatography (IC) system (MagIC Professional 850, Metrohm Ion Analysis, Switzerland), with an anion-exchange column (Metrosep A Supp 5, polyvinylalcohol with quartenary ammonium groups, 250 x 4 mm i.d.), a guard column (Metrosep A Supp 4/5

Table 1. Instrumental conditions for F, Cl, Br and I determination by ICP-MS and IC

Parameter	ICP-MS	IC
RF power (W)	1300	-
Plasma flow rate (L min^{-1})	15.0	-
Auxiliary gas flow rate (L min^{-1})	1.20	-
Nebulizer gas flow rate (L min^{-1})	1.15	-
Spray chamber	cyclonic	-
Nebulizer	concentric	-
Sampler and skimer cones	Pt	-
Ion lens	Auto lens on	-
Dwell time (ms)	50	-
Isotopes (m/z)	^{35}Cl, ^{79}Br, and ^{127}I	-
Mobile phase	-	3.2 mmol L^{-1} Na_2CO_3 + 1.0 mmol L^{-1} $NaHCO_3$
Flow rate (mL min^{-1})	-	0.7
Sample loop (µL)	-	100

Guard), a chemical suppressor module, and a conductivity detector. A 100 µL sample loop and a mixture of Na_2CO_3 and $NaHCO_3$ solutions were used as the mobile phase.

All statistical treatments were made using the GraphPad InStat software (GraphPad InStat Software Inc., Version 3.00, 1997) with a confidence level of 95%.

2.2. Reagents

All reagents used were of analytical grade or better. Water was obtained from a Milli-Q system (18.2 MΩ cm, Millipore, USA) and used to prepare the reference solutions, mobile phase, and sample dilutions.

Fluorine, Cl, Br, and I standard reference solutions (1000 mg L^{-1}) were prepared by dissolution of NaF, NaCl, KBr and KI salt (Merck, Germany), respectively, in water. These solutions were sequentially diluted to obtain standard analytical solutions for calibration of chlorine, bromine and iodine by ICP-MS (1 to 10 mg L^{-1} for chlorine, 1 to 10 µg L^{-1} for bromine, and 0.1 to 1 µg L^{-1} for iodine) in 10 mmol L^{-1} NH_4OH, and for IC (10 to 100 µg L^{-1} for fluoride, chloride, and bromine and 250 to 1000 µg L^{-1} for iodide) in water.

2.3. Sampling

Samples were collected at five strategic points along the stream that runs through the university area. The first collection point was the entrance of the stream to the university, as this point is not influenced by the activities developed at UFSM. Point 2 is located next to the university's industrial college (CTISM). Point 3 is located near the gas station at UFSM, as well as the release of untreated urban sewage from the urban neighborhoods. Point 4, is the release of the hospital effluent that has been microbiologically treated. The last one, point 5, is the limit of the University Campus. A map with the five points is presented in Figure 1. The sampling consisted of 12 h collections, conducted at a rate of one sample per hour (12 sub-samples), which made up a composite sample at the end of the sampling period. Each sub-sample was transferred to the appropriate recipient, homogenized, kept in a thermal box while transported to the laboratory, and stored at 4 to 8 °C until analysis (within 24 - 48 h). Strict safety precautions were taken due to the possible toxicity of the samples. Sampling was carried out in January, 2019 and all the sampling was done in the same day. Additionally, the samples were characterized for color, turbidity, chemical oxygen demand (COD), pH, and nitrate.

2.4. Sample preparation by filtration

Sample preparation was carried out as usually performed for this type of sample, using simple filtration. In this study, an additional evaluation was performed to check the influence of filtration on the results. Filter membranes containing different composition and porosity were used. For this evaluation, seven filter types were investigated: polyethersulfone (PES, ϕ 0.45 µm and ∅ 25 mm), polytetrafluoroethylene (PTFE, ϕ 0.20 µm ∅ 25 mm, ϕ 0.22 µm ∅ 25 mm and ϕ 0.45 µm ∅ 13 mm), nylon polyamide (PAN, ϕ 0.45 µm ∅ 25 mm), cellulose acetate (CA, ϕ 0.45 µm ∅ 25 mm), polyvinylidene difluoride (PVDF, ϕ 0.22 µm ∅ 25 mm and ϕ 0.45 µm ∅ 13 mm), mixed cellulose ester (MCE, ϕ 0.22 µm ∅ 25 mm and ϕ 0.45 µm ø 13 mm) and polypropylene (PP, ϕ 0.22 µm ∅ 25 mm). Standard solutions (25 mL) containing F^-, Cl^-, Br^-, I^-, ClO_3^-, BrO_3^-, IO_3^-, and ClO_4^- were filtered through each membrane (manual filtration) and solutions after filtration were analyzed by IC.

2.5. Procedure for ICP-MS determination

As mentioned, the samples were kept under refrigeration, and for ICP-MS determination, samples were initially left

Figure 1. Representation of sampling points in the surface water that runs through the UFSM area.

to stabilize at room temperature. In the sequence, they were centrifuged and then filtered with a membrane filter. All samples were diluted in 10 mmol L^{-1} NH_4OH, the same as the calibration curve.

2.6. Procedure for IC

After reaching room temperature, the samples were centrifuged and filtered with a membrane filter. All samples were diluted in ultrapure water and analyzed immediately.

3. Results and Discussion

3.1. Samples characterization

Initially, the characterization of the five sampling points was carried out (Table 2). At all points evaluated, in terms of color, the samples presented the maximum limit of the instrument (70 mg L^{-1} Pt/Co). Regarding to turbidity, the values determined ranged from 4.81 to 15.8 NTU, and the highest turbidity value was determined at the point near to the HUSM. The increase in turbidity may be due to the sampling point being made when the hospital effluent is released (after biological treatment).

As for pH, there was no significant variation, and values ranging from 6.94 to 7.62 were determined. For COD, the values were in the range of 7.2 to 16 mg L^{-1} of O_2; again, the highest concentrations were for the sampling points near the hospital. The NO_3^- concentrations ranged from 1.35 to 5.63 mg L^{-1}.

3.2. Sample preparation by filtration

Since filtration is a common approach before chromatographic analysis, especially when analyzing liquid samples without a previous sample preparation step (e.g. surface waters), some membrane types were investigated in this study.

For this, standard solutions were filtered and further analyzed; thus, the results were compared before and after the filtration. The results showed no difference (t-test, 95% confidence level) to the results obtained for standard solutions that did not undergo the filtration step. In this way, no contaminations or interconversions were linked to this step. On that basis, any of the filters can be chosen for this step. Figure 2 shows the results for the multispecies reference solution that went through the filtration step, using a concentration of 500 µg L^{-1} for each species (Cl^-, Br^-, I^-, ClO_3^-, BrO_3^-, IO_3^-, and ClO_4^-). It is worth noting that the determination was made by ICP-MS, so the reference values represent the sum of the species in the solution.

Table 2. Characterization of surface water samples investigated in this study

Sampling point	Color, mg L^{-1} Pt-Co	Turbidity, NTU	COD, mg of O_2 L^{-1}	pH	NO_3^-, mg L^{-1}
1	> 70	6.54	7.28	7.19	3.12
2	> 70	5.44	7.20	7.30	2.94
3	> 70	6.97	8.48	7.25	5.63
4	> 70	15.8	16.0	6.94	-
5	> 70	4.81	7.20	7.62	1.35

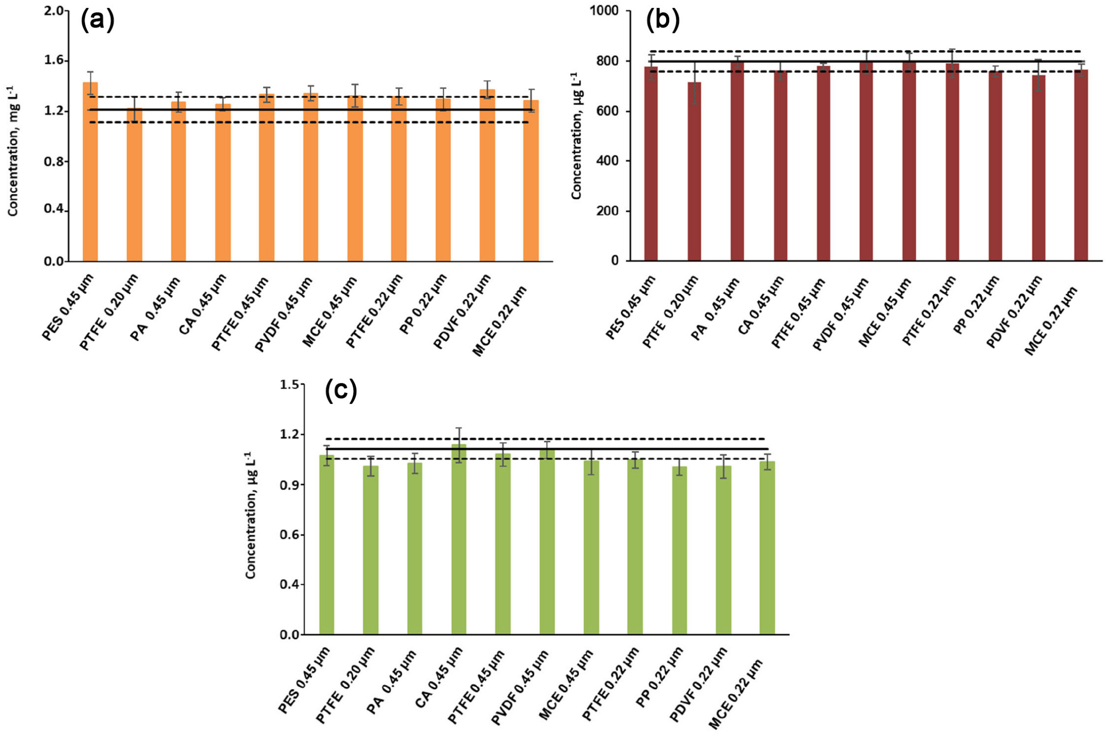

Figure 2. Chlorine (a), bromine (b), and iodine (c) concentration after filtration of a reference solution (500 µg L^{-1}) using different membrane types. Black and dotted lines represent the reference values and their standard deviation, respectively. Determinations by ICP-MS, n = 5.

3.3. Halogen and species determination in surface waters

Regarding the fluorine concentrations, it was not feasible to determine the total content by ICP-MS due to the poor sensitivity of this technique for this analyte. Hence, fluoride was determined by IC at concentrations of 320 to 362 µg L^{-1} (Figure 3 (a)), except at the collection point after the HUSM, where the content was higher (634 µg L^{-1}).

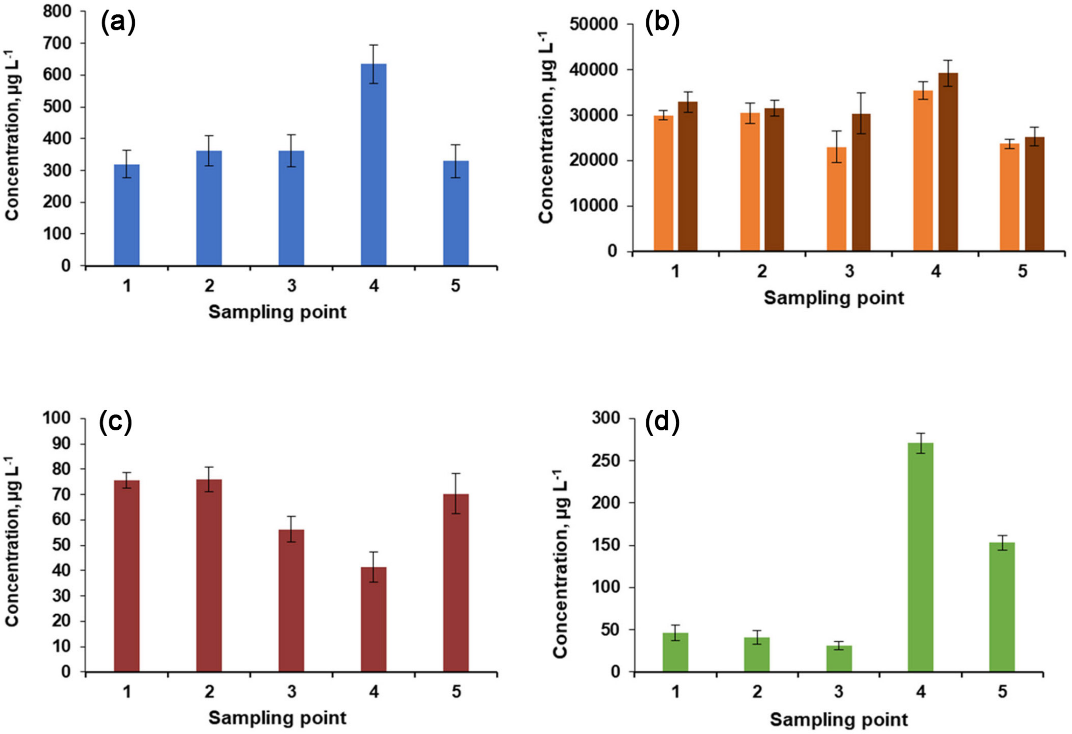

Figure 3. (a) Fluoride, **(b)** chlorine (🟧) and chloride (🟫), **(c)** total bromine, and **(d)** iodine concentrations determined at each of the 5 sampling points.

Point 4 reflects the impact of activities carried out by HUSM on the stream (sampling point 4). This higher value, compared to the other points, may be caused by the use of fluorine-based substances, such as radiopharmaceutical sodium fluoride (18-F).[22] It is important to highlight that 20% of the drugs on the market have the presence of one or more fluorine atoms in their composition.[23] It is important to point out that this concentration is below the allowed by legislation according to the National Environmental Council (CONAMA) Resolution No. 357, of March 17, 2005, that establishes maximum allowed values as 1.4 mg L^{-1} for total fluoride.[24]

Total chlorine was determined by ICP-MS from 23.0 to 35.5 mg L^{-1} (Figure 3 (b)). The chloride concentrations measured by IC presented no statistical difference by the t-test (confidence level of 95%) compared to the total chlorine, indicating that the most significant contribution for Cl content is from salts instead of organic forms. High concentrations in surface water have also been reported elsewhere and are commonly related to sewage discharge.[25,26] A study by Corsi *et al.*[25] reported that chloride concentrations in urban rivers in the northern United States increased as urban development also increased. Nonetheless, the concentrations found in all the points are below the value established by CONAMA, where the values for total chloride (250 mg L^{-1}) are mentioned.[24]

Relatively low bromine and bromide concentrations were measured and in some samples were close to the limit of quantification by IC (60 µg L^{-1}). Total bromine content by ICP-MS ranged from 41.5 to 76.1 µg L^{-1} (Figure 3 (c)). In general, total bromine and bromide concentrations showed reasonable agreement considering the uncertainty of the IC data at low concentrations. Therefore, the dominant chemical form of bromine in samples was mainly bromide. According to El-Said *et al.*,[27] bromide was the most abundant halogenated species in Lake Mariout in Egypt. Furthermore, Soltermann *et al.*[28] have shown that the chemical industry and municipal incineration wastes are primarily responsible for the increased bromide concentration in rivers.

As shown in Figure 3 **(c)**, points 1, 2, and 5 showed slightly higher bromine concentrations, whereas points 3 and 4 remained in the range of bromine concentrations naturally found (approximately 50 µg L).[7] In these points (1, 2, and 5), the activities developed in the neighborhood possibly influenced the bromide concentrations in the surface water, one of them being the release of urban sewage, thereby corroborating the study by Soltermann *et al.*[28] Other activities in the area may also have an effect, including the gas station, car washing, and farms, where the use of pesticides is common and can also have some influence.

Results for total iodine concentrations (Figure 3 (d)) were about 46.6 µg L^{-1} in the first collection point and similar in the others, with concentration determined near the HUSM (sampling point 4, 271 µg L^{-1}). At the exit point, despite some reduction observed, the concentrations were still higher than the initial concentration (153 µg L^{-1}). It is possible to see that hospital's activities must significantly influence the iodine content. With regard to iodide, it was not detected by IC due to the poor limit of quantification (270 µg L^{-1}).

Iodine is used in various activities carried out in hospitals. Its use ranges from disinfecting agents to diagnostic reagents (contrasts for X-rays). In addition to these uses, radioactive iodine (^{131}I) is administered at relatively high doses (100 and 200 mCi) in treating thyroid carcinoma.[29] On average, 80% of the dose is not absorbed by the treated organ and is eliminated in the first 48 h in the urine of patients undergoing treatment.[30] The uncontrolled release of this specific effluent releases a contaminant into the sewage collection network with the potential to modify the characteristics of the environment through which it passes.[15]

4. Conclusions

From these results, it is possible to perceive that among the activities developed in the university city, those carried out at the HUSM have the most significant impact on the concentrations of halogens. It is known that the effluents generated by hospital services correspond to a considerable fraction of the different types of wastewater that cause environmental impact. Among the main sectors involved in effluent generation in hospitals, clinical analysis services, radio and chemotherapy sectors, laundries, intensive care units and beds of different classes of accommodation stand out. The numerous activities carried out lead to the consumption and disposal of large amounts of compounds (mainly pharmaceuticals) at a single point. For this reason, the impact of this type of wastewater was investigated, especially considering that there is no legislation (nationally and regionally) for all the analytes investigated, especially if halogen species are of concern. Nevertheless, most studies have focused on determining organic compounds. Thus, this study contributes to an important area that has been little explored regarding halogen concentrations in a sampling point hospital effluents are discharged. In contrast, when comparing the analyte concentrations in the inlet and outlet streams, they were generally similar to or lower than those in other streams. Further investigations covering other halogenated species must be conducted many products are formulated containing halogens.

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