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# Assessment of metals, emerging contaminants, and physicochemical characteristics in the drinking water and wastewater of Cuenca, Ecuador

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ABSTRACT

*Background:* Traditional drinking water and wastewater treatments used in Latin-American and Caribbean countries are meant to improve the organoleptic, and microbiological characteristics and to remove nutrients. However, to be effective, treatments need to process potential threats from natural or anthropogenic origins.
*Objective:* to evaluate emerging contaminants and metals in drinking water and wastewater from traditional water treatment systems, in the city of Cuenca, in the Ecuadorian Andes.
*Methods:* samples were taken from the water plants of Cuenca, from its wastewater treatment plant, and from domestic houses. The physical-chemical characteristics and 15 metals (ICP-OES) were analyzed in samples from the drinking water plant and from the houses. A heavy metal pollution index (HPI) was calculated. The wastewater samples were also analyzed for 7 emerging contaminants (ECs) (GC-MS).
*Results:* Our results show that the treated water depends on the quality of the incoming water, and that the available treatments are not capable of removing unexpected pollution, such as aluminium, which could be due to natural sources, such as ashes from the Sangay volcano might contaminate Cuenca's water sources. The HPI varied from 0.44 to 0.59, which indicates that water distribution systems have low metal contamination. The wastewater plant was not capable of removing emerging contaminants such as caffeine.
*Conclusions:* Natural and anthropogenic contamination in the water must be considered in the treatments due to the potential risk that they represent.

## 1. Introduction

According to the United Nations (UN), access to basic water and sanitation services are fundamental human rights mentioned in Sustainable Development Goals 6. UN indicators for the year 2020 show that 26 % of the world's population lacked safely managed drinking water services, 46 % lacked safely managed sanitation services, and 44 % of household wastewater was not safely treated [1]. According to UNESCO (2019), 80 % of the world's wastewater is still released into the environment without treatment. Developing countries, such as Ecuador, lack universal adequate sanitation infrastructures [1,2]. For instance, only the cities of Cuenca, Guayaquil and Quito are accredited to satisfy international standards for drinking water quality, while in other parts of the country, such as the Ecuadorian Amazon region, only 25 % of the wastewater is subjected to some type of treatment, and 56 % of the wastewater is discharged directly into the rivers untreated. Additionally, the few existing sewage treatment plants include only primary and secondary treatments, focusing on the removal of nutrients, microbial contaminants, heavy metals, and other regulated compounds such as pesticides [3].

To identify inadequate water sources or possible flaws in the water treatment plants (WTPs), the water quality needs to be monitored in the implemented systems; apart from eutrophication, chemical contamination, which includes emerging contaminants (ECs), should also be constantly evaluated [4]. Conventional widely implemented water treatments include coagulation and flocculation, sedimentation, filtration, adsorption, and disinfection. Those physical-chemical processes

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diminish turbidity, organic matter, and pathogens [5]. Nevertheless, these processes are ineffective in removing other compounds naturally present in Ecuador's water sources, such as metals, or emerging contaminants [4,6–10].

The presence of metals in the drinking water in developing countries is increasing due to a lack of facilities for wastewater treatment before they are released into natural waters [4]. About half of the 34 studies from developing countries that were reviewed by Chowdhury et al. (2016) reported toxic metals in drinking waters and identified mining, agricultural, and industrial activities as the main pollution sources [11]. However, natural sources may also play a role in metal contamination. In the Andean region of Ecuador, trace metals are probably naturally present in concentrations harmful to the consumers [12]. High concentrations of As, Al, Ge, and Mn are common in areas close to volcanic zones, or even affected by ash [13–15]. Metals in water sources have been widely studied because of their toxicity to living organisms. Most of them cannot be eliminated from the human body, and their accumulation increases health risks [16].

In addition to metals, there is a worldwide concern about ECs present in water sources and drinking water. ECs are chemical compounds, including antibiotics, pesticides, surfactants, caffeine, and illegal drugs, among other substances, that are not eliminated by conventional wastewater treatments and, therefore, contaminate water sources when released into the environment [7,17,18]. ECs such as endocrine disruptors are related to cancer in human beings and hormonal alterations in fish and mammals, while antibiotics are related to bacterial resistance [6,7].

The efficiency of wastewater treatment in removing both metals and ECs before releasing them into the environment in Ecuador is inconclusive, as both groups of substances have been detected in the watercourses near urban areas [6,19].

The wastewater treatment of waste stabilization ponds (WSPs) is the most used system to treat sewage in Latin America and the Caribbean (Latam) [20]. Stabilization ponds are generally rectangular, shallow excavations that seek to remove organic matter and pathogenic microorganisms from the domestic wastewater that is deposited and kept for several days. It is generally composed of single or multiple anaerobic, facultative, or maturation ponds [4]. The facultative pond operates aerobically in the upper part, facultative in the intermediate part, and anaerobically in the lower part. Other types of ponds may be added to the original systems. For example, aerated ponds, whose main functions are to remove organic matter and nutrients, tend to decrease the residence time and the size of the lagoon in comparison with the traditional facultative ponds, but energy use increases. The main advantage of WSPs is their efficiency, design simplicity, and low operation and maintenance costs compared to other technologies. Its disadvantages are the emissions of greenhouse gases, the need for large plots of land, sludge generation, bad odors, and the low effectiveness in removing more complex contaminants such as metals and emerging contaminants [21,22].

Despite the lack of standardized water treatment in most Ecuadorian cities, in the survey conducted by the INEC in 2012, people's perception indicates that the city of Cuenca has one of the best water quality in the country [4,23]. Cuenca represents an adequate case study as the water supply comes from an Andean paramo area with elevated natural metal concentrations, which may increase during ashes deposition from the nearby volcanic activities. Although water quality standards are often monitored, the efficiency of water treatment systems for the removal of toxic metals and ECs from traditional systems of drinking water and wastewater treatment is still to be evaluated. Thus, the objective of this research was to assess the concentrations of metals and ECs in water samples of drinking water in the city of Cuenca and in the inlet and outlet of the drinking and wastewater treatment plants.

## 2. Methods

### 2.1. Sampling site

Cuenca is an inter-Andean city with an average altitude of 2560 m.a.s.l. and average temperatures of 15°C. According to the INEC (2022), Cuenca's population is 636.996 inhabitants. The average precipitation is 98.4 mm/year, being August the month with the lowest precipitation average (35 mm) and March the month with the highest (157 mm). Cuenca is considered one of the Ecuadorian cities with the best living standards due to the quality of its basic services. The municipal company ETAPA oversees treating and supplying drinking water and treating the city's wastewater. The water that supplies Cuenca comes from the Cajas National Park, where water is captured for purification and distribution. ETAPA supplies drinking water to 96 % of the city, with 120.000 cubic meters/day of the reserve [24].

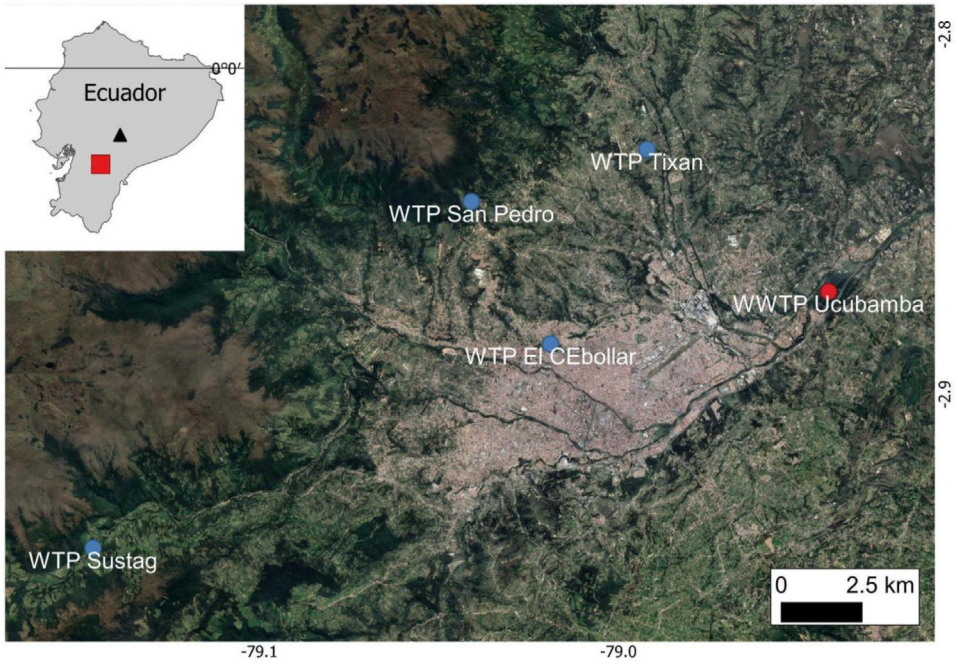


**Fig. 1.** Location of the water treatment plants in Cuenca. Blue dots show the drinking water treatment plants (DWTP), while the red dot indicates the wastewater treatment plant (WWTP). The optical satellite image in the background shows the extension of Cuencas' urban area. In the upper map, the red square shows the study area location, and the black triangle shows the location of the Sangay volcano.

**Table 1**
The water source (inlet) for the WTP. Values indicate the mean ± standard deviations. The standard limits of TULSMA and USEPA are indicated as references for the measured parameters. Values in bold exceed either TULSMA or USEPA reference values.

| Parameters | USEPA[φ] | TULSMA[γ] | El Cebollar, T.I | Tixán, M.I | Sustag, Y.I | San Pedro, C.I |
|---|---|---|---|---|---|---|
| pH | - | 6-9 | 7.00 (0.00) | 7.90 (0.00) | 7.65 (0.07) | 7.30 (0.00) |
| Conductivity ($\mu scm^{-1}$) | - | - | 110.00 (0.00) | 70.00 (0.00) | 40.00 (0.00) | 80.00 (0.00) |
| Turbidity (UTN) | - | 100 | 5.00 (0.00) | 7.00 (0.00) | 3.50 (4.95) | 0.00 (0.00) |
| Temperature (°C) | - | Natural ±3 | 14.50 (0.00) | 17.30 (0.00) | 14.95 (0.64) | 16.40 (0.00) |
| DO ($mgL^{-1}$) | - | 6 | **7.75 (0.00)** | **7.03 (0.00)** | **7.59 (0.06)** | **6.53 (0.00)** |
| DO (%) | - | >80 | 78.32 (0.00) | 75.18 (0.00) | 77.41 (0.44) | 68.60 (0.00) |
| $Cl_2(mgL^{-1})$ | - | - | - | - | - | - |
| Al ($mgL^{-1}$) | - | 0.2 | **0.272 (0.08)** | **0.241 (0.01)** | 0.000 (0.00) | 0.000 (0.00) |
| As ($mgL^{-1}$) | 0.00002 | 0.05 | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Ba ($mgL^{-1}$) | 1 | 1 | 0.029 (0.00) | 0.018 (0.00) | 0.032 (0.00) | 0.018 (0.00) |
| Ca ($mgL^{-1}$) | - | - | 0.027 (0.00) | 0.023 (0.00) | 0.016 (0.00) | 0.020 (0.00) |
| Cd ($mgL^{-1}$) | 0.01 | 0.01 | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Co ($mgL^{-1}$) | - | - | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Cu ($mgL^{-1}$) | 1.3 | 1 | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Cr (VI) ($mgL^{-1}$) | 0.05 | 0.05 | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Fe ($mgL^{-1}$) | 0.3 | 1 | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Mn ($mgL^{-1}$) | 0.05 | 0.1 | 0.010 (0.00) | 0.089 (0.00) | 0.011 (0.00) | 0.006 (0.00 |
| Na ($mgL^{-1}$) | - | 200 | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Ni ($mgL^{-1}$) | 0.013 | - | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Pb ($mgL^{-1}$) | 0.005 | 0.05 | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Zn ($mgL^{-1}$) | 7.4 | 5 | 0.002 (0.00) | 0.011 (0.00) | 0.009 (0.01) | 0.000 (0.00) |
| Hg ($mgL^{-1}$) | 0.0001 | 0.001 | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |

[φ] [37,38] and γ: [33].

#### 2.1.1. Drinking water treatment system

The drinking water system of Cuenca has four subsystems named according to the rivers from which the water is taken: Tomebamba (T), Machángara (M), Yanuncay (Y), and Culebrillas (C). Each of them has its own catchment, conduction, treatment plants, reserve centers, and distribution networks. The water collected from the Tomebamba (T.I), Machángara (M.I), and Yanuncay (Y.I) rivers are directed to purification plants through pipes where they receive filtration, flocculation with the use of polymers, aluminum sulfate, and finally chlorination; the drinking water treatment plant (DWTP) of Tomebamba, Machángara and Yanuncay sub-system are respectively: El Cebollar (T.O), Tixán (M.O), and Sustag (Y.O) (ETAPA EP, Ministerio del Ambiente, 2018). The locations of the DWTP are shown in Figure. 1. The water coming from the Culebrillas river (C.I) is treated in the DWTP San Pedro (C.O) sub-system which includes catchment, conduction, flocculation, treatment in DAFFI module (coagulation/flotation/ filtration system), clear water tank (pressure flocculation), and disinfection [24].

#### 2.1.2. Wastewater treatment plant (WWTP)

The Ucubamba WSP system (U) treats 95 % of the city's domestic effluent. The WSP has been in operation since 1999 by the Municipal Company ETAPA EP (http://www.etapa.net.ec). The location of the WSP is shown in Figure 1. Ucubamba (see Fig. S1), consists of two independent parallel systems of three lagoons each. Every set contains an aerated lagoon (using mechanical floating aerators), a facultative lagoon, and a maturation pond. The average discharge influence on the system is 1.2 $m^3s^{-1}$. The total surface of the WWTP is 45 ha, and the hydraulic retention time (HRT) is 12 days [25].

### 2.2. Sampling

The sampling was carried out during the first week of December 2019, whose seasonality corresponds to a dry season. Two samples were taken at each sampling point: 1) 500 mL amber glass bottle for the analysis of emergent contaminants and 2) 100 mL plastic bottle for metals analysis. In each DWTP, 4 samples were taken, two at the inlet and two at the outlet. In addition, for each of the three principal subsystems (T, M, and Y), 5 samples were taken in their distribution zones in Cuenca city (D). For Ucubamba WWTP four samples were taken, two in the inlet and two in the outlet. All sampling points are listed in Table 1. In total, 8 samples of the inlet (I) and 8 of the outlet (O) of the DWTP, 15 samples in the Cuenca city (D) for the T, M, and Y sub-system, and 2 samples in the inlet, and 2 in the outlet of Ucubamba WWTP were taken during the campaign, see Table S1.

During the sampling, the Sangay volcano (located 120 km, NE from Cuenca; 2.002° S; 78.341° W) was releasing ashes that had reached Cuenca. The Sangay Volcano is one of the most active volcanoes in Ecuador, maintaining constant eruptive activity since 1628.

### 2.3. Physicochemical analysis

The measurement of pH, conductivity, dissolved oxygen, and the temperature was carried out in situ using an HQ40D portable multimeter HACH and PRO 3-in-1 pH, EC, TDS Combo Meter brand Milwaukee MW802. Residual chlorine and turbidity were measured with the HACH DR /850 colorimeter.

### 2.4. Metal analysis

For the determination of total metal content, samples of 100 ml were taken and stored in plastic bottles. They were acidified in situ with 0.5 ml of nitric acid $HNO_3$ of 0.7 M. Later, they were conserved at 4°C and transported to the laboratory. Wastewater samples were digested according to the method (EPA 3050b.) previous to the analysis; fresh and drinking water were analyzed directly. Next, the following metals were analyzed: aluminum, arsenic, calcium, sodium, chromium, copper, cobalt, nickel, barium, cadmium, manganese, zinc, lead, and iron through an inductively coupled plasma atomic emission spectrometer ICP-OES (Thermo Scientific iCAP 7400) at the Laboratory of Environmental Engineering Universidad San Francisco de Quito (LIA USFQ). To do this, calibration curves of a Merck-Millipore ICP multi-element standard solution mixed with various analytes were prepared at a concentration of 100 $mgL^{-1}$ (Certipur grade for ICP, Merck-Millipore). The limits of detection (LOD) and quantification (LOQ) were calculated by analyzing at least 12 independent replicas of blank samples and multiplying the standard deviation by three and by ten to obtain the LOD and LOQ, respectively, the values shown in Table S2. The concentrations of each metal were corrected according to the recovery percentage for each analyte, ranging from 91% to 100 %. Each sample was measured in triplicate.

Mercury quantification was done using a direct mercury analyzer Milestone (DMA 80) based on the method EPA 7473 by thermal decomposition; a 10 $mgL^{-1}$ mercury standard (Inorganic Ventures) was used to perform the calibration curve.

### 2.5. Emerging Contaminants (ECs)

Water samples taken in the WWTP were treated by solid-phase extraction (SPE) using a vacuum pump (Millipore, WP6111560), a manifold (27 × 17 × 9.5 cm), and Waters OASIS HLB cartridges with a capacity of 200 mg and 6 mL, respectively, according to the Glassmeyer et al. (2017) protocol. The quality control performed includes field banks (bottles with distilled water to detect interferences) and spiked blanks (mean concentration level to evaluate the recovery percentage of each component). The samples were analyzed using a GC-MS (Agilent 7890/5977) under EI mode. The column used was a DB-5 ms. the temperature ramp was 5°C for 2 min, 28°C/min up to 170°C, 4.9°C/min up to 280°C, 6.3°C/min up to 30°C/min, and then 300°C for 10 min, LOQ, and LOD values are included in Table 3.

### 2.6. Determination of toxicity

the toxicity tests were carried out by calculating the index of contamination by toxic metals (Chaturvedi, et al, 2019; Mahato, et al, 2014). This index allows identifying the quality of drinking water considering its content of toxic metals. It is calculated by the following equation (1):

$$HPI = \sum_{i=1}^{n} HPI_i \tag{1}$$

Where n is the number of heavy metals; HPI *i* is the partial contamination index of heavy metals for the nth metal. Calculating the partial contamination index of heavy metals is carried out using equation (2); for the calculation of the metal subscript, the following equation (3) is used; for the calculation of the unit weighting factor, the following equation (4) is used. Where $W_i$ is the unit weighting factor, $Q_i$ is the metal subscript, Mi is the measured concentration, Si is the maximum allowed concentration, and I is the maximum admissible concentration [26–28]:

$$HPI_i = \frac{\sum_{i=1}^{n} W_i \times Q_i}{\sum_{i=1}^{n} W_i} \tag{2}$$

$$Q_i = \sum_{i=1}^{n} \frac{[M_i - I_i]}{[S_i - I_i]} \times 100 \tag{3}$$

$$W_i = \frac{1}{S_i} \tag{4}$$

For the calculations corresponding to the toxicity index of metals, the formulas expressed above were applied in such a way that the weighting factor of the unit and the metal subscript were obtained to determine the HPI considering for 13 metals; HPI was obtained for the drinking water collected within the city of each of the three main drinking water systems; cobalt and calcium have not been considered since they do not have a maximum concentration allowed in the Ecuadorian technical standard *NTE INEN 1108 (2020)* and for the WHO [29–31].

If HPI has a value lower than 15 it is determined as low contamination: if HPI value is between 15 and 30 it is medium contamination and if HPI value is greater than 30, it is considered high contamination [28].

### 2.7. Data analysis

The values of the physical-chemical parameters and the metal concentration were compared with national and international standards to verify if they were within the recommended limits. For the verification of the freshwater used at the inlet of the water treatment plants, the respective norms from the national Unified text of secondary environmental legislation (TULSMA) and U.S. Environmental Protection Agency (US EPA) regulations were used. For drinking water, the respective norms of the Ecuadorian Standardization Service (INEN) and the recommendations of the World Health Organization (WHO) were used. Finally, for treated wastewater, the results were compared with the Ecuadorian TULSMA standard for discharge water norm, and with the international finance corporation (IFC) recommendations.

The data was analysed to determine whether there are significant differences between the physicochemical parameters and the concentration of each metal in the water before (I) and after (O and D) the treatment for each plant and without discriminating between plants, in a total of 16 samples. Prior to the analysis data normality and homoscedasticity were determined. The data normality test for small samples, Shapiro Wilk, considering a significance level of 5 %, revealed a normal distribution ($p > 0.05$) for the parameters pH, barium, and calcium, while it found a non-normal distribution in the rest of them ($p < 0.05$). The Levene test applied to establish homogeneity and homoscedasticity revealed that only conductivity, temperature, barium, calcium, iron, manganese, and zinc had a homogeneous behavior in terms of their variances. When verifying the lack of normality and homoscedasticity, non-parametric Kruskal Wallis and Wilcoxon tests were used. A determination coefficient of 0.05 was established. Statistical analyses were performed with the software R version 4.1.0 with the R studio interface [32].

## 3. Results and discussion

### 3.1. Drinking water treatment plants (DWTP)

Inlet water: values of the physicochemical parameters pH, conductivity, turbidity, temperature, and dissolved oxygen were in accordance with the limits established in the TULSMA regulation for natural water that can be treated for human consumption and USEPA for natural water (Table 1) [33]. The percentage of dissolved oxygen (DO) was below the 80 % indicated by TULSMA. This is assumed to be because the sampling was carried out in the dry season when the temperature oscillates between 9 °C and 17 °C. When temperature increases, the water flow decreases, causing the percentage of oxygen to decrease as well [34]. Another study has also reported a DO of 77% in the Machángara and Yanuncay systems, below the limit established by the TULSMA [35]. Although the differences in DO compared to the standard limits seem not to be relevant, monitoring is necessary to detect the reasons that could be affecting the DO in these DWTPs. Regarding the metals, except for Al in T.I and M.I, all the other metals complied with the TULSMA established limits (Table 1). The water that supplies the city of Cuenca stands out for being of low hardness and good organoleptic and physicochemical properties [36].

Outlet and Distribution of DWTP: when comparing the physicochemical parameters obtained from the outlet treated water in each one of the systems and from the samples collected in distribution sources, we found that both waters comply with the water quality standards established by INEN 1108: 2020 and WHO for drinking water [30,31]. Thus, our results show that the physicochemical parameters of the incoming water meet the optimal conditions and that the treatment given in the four plants is sufficient to achieve the necessary parameters to be considered suitable for consumption. The concentration of metals complies with the INEN standard 1108: 2020 and WHO. At some points of the distribution, the concentrations of Zn were higher compared with their respective outlets; also, Cu from M.O. to M.D., Ca from M.O. to M.D., and from Y.O. to Y.D.

Aluminium is not contemplated in the INEN standard 1108: 2020 norm, but it does in WHO (Table 2) [31]. Considering the WHO, Al content in T.O., T.D., M.O., and Y.D., were above the recommended limits. The concentration of Al found in drinking water around can vary between 0.1 to 2.7 ($mgL^{-1}$) [29]. The Al concentration in the drinking

**Table 2**
Drinking water treatment plants, Outlet (O), and the distribution (D) of each treatment plant. Values indicate the mean ± standard deviations. Values in bold exceed either INEN or WHO reference values.

| | | | El Cebollar | | Tixán | | Sustag | | San Pedro |
|---|---|---|---|---|---|---|---|---|---|
| Parameter | INEN$^{\eta}$, 2020 | WHO$^{\phi}$, 2017 | T.O | T.D | M.O | M.D | Y.O | Y.D | C.O |
| pH | 6.5 -8 | 6.5 -8 | 6.80 (0.00) | 6.84 (0.11) | 7.40 (0.14) | 7.24 (0.13) | 6.95 (0.07) | 6.88 (0.22) | 7.10 (0.00) |
| Conductivity ($\mu scm^{-1}$) | - | - | 150.00 (0.00) | 98.00 (4.47) | 85.00 (7.07) | 84.00 (5.48) | 65.00 (7.07) | 94.00 (20.74) | 80.00 (0.00) |
| Turbidity (UTN) | 5 | 5 | 0.00 (0.00) | 0.80 (1.79) | 0.50 (0.71) | 0.00 (0.00) | 0.00 (0.00) | 2.60 (3.29) | 0.00 (0.00) |
| Temperature (°C) | - | - | 15.70 (0.00) | 19.32 (1.34) | 16.00 (0.57) | 20.94 (0.30) | 15.70 (0.00) | 21.06 (3.15) | 16.00 (0.00) |
| $Cl_2(mgL^{-1})$ | 0.3-1.5 | 0.3-1.5 | 0.79 (0.00) | 0.44 (0.16) | 1.07 (0.12) | 0.41 (0.24) | 1.07 (0.20) | 0.23 (0.31) | 0.55 (0.00) |
| Al ($mgL^{-1}$) | - | 0.1 | **0.39 (0.00)** | **0.35 (0.07)** | **0.36 (0.17)** | 0.080 (0.19) | 0.004 (0.00) | **0.24 (0.24)** | 0.000 (0.00) |
| As ($mgL^{-1}$) | 0.01 | 0.01 | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Ba ($mgL^{-1}$) | 1.3 | 0.7 | 0.026 (0.00) | 0.026 (0.00) | 0.019 (0.00) | 0.018 (0.00) | 0.030 (0.00) | 0.028 (0.00) | 0.014 (0.00) |
| Ca ($mgL^{-1}$) | - | - | 0.030 (0.00) | 0.026 (0.00) | 0.020 (0.00) | 0.023 (0.00) | 0.016 (0.00) | 0.022 (0.01) | 0.020 (0.00) |
| Cd ($mgL^{-1}$) | 0.003 | 0.003 | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Co ($mgL^{-1}$) | - | - | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Cu ($mgL^{-1}$) | 2 | 2 | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.004 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Cr(VI) ($mgL^{-1}$) | 0.05 | 0.05 | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Fe ($mgL^{-1}$) | - | - | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Mn ($mgL^{-1}$) | - | 0.4 | 0.004 (0.00) | 0.003 (0.00) | 0.122 (0.02) | 0.019 (0.01) | 0.010 (0.01) | 0.003 (0.00) | 0.000 (0.00) |
| Na ($mgL^{-1}$) | - | - | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Ni ($mgL^{-1}$) | 0.07 | 0.07 | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Pb ($mgL^{-1}$) | 0.01 | 0.01 | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |
| Zn ($mgL^{-1}$) | - | - | 0.000 (0.00) | 0.001 (0.04) | 0.007 (0.00) | 0.016 (0.01) | 0.013 (0.00) | 0.369 (0.26) | 0.000 (0.00) |
| Hg ($mgL^{-1}$) | 0.006 | 0.006 | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) | 0.000 (0.00) |

$^{\eta}$ [30] and $\phi$ [31].

water sample could be attributed to the natural characteristics of the water in the region [35]. In Table 1 it can be seen that T.I. and M.I. already have Al concentrations higher than those recommended by the WHO. In second place due to the treatment with aluminium sulfate since Al has increased its concentration in the treated samples (Table 2). Alternatively, the high Al concentrations could be attributed to ash contamination from the Sangay volcano that reached the water sources during the sampling week, according to reports from the national institutions [39]. High Al concentrations are common in areas close to volcanic zones [13]. In fact, volcanic ashes may be composed mainly of oxides of silicon, aluminium, iron, and, to a lesser extent, alkali, and alkaline earth metal oxides [13]. Despite the origin of the Al that reached the water that is distributed to the Cuenca's population additional studies on the long-term exposure to higher Al concentrations are needed since high concentrations of Al might be related to many brain disorders including Alzheimer's disease, Parkinson's disease, and multiple sclerosis [40].

Due to the different sources of aluminium, it is recommended that the source waters arrive through pipes to the water treatment plant and not through open channels as is currently the case; in this way, the water is prevented from leaching minerals along the way and from being affected by contamination such as volcanic ash. In addition, during the treatment, the use of aluminium sulfate must be optimized to avoid traces remaining in the finished water. Alternatively, treatments that remove aluminium and other metals, such as electrocoagulation [41], could be applied.

DWTP system: The analysis of the differences between the physicochemical parameters at inlet (Table 1) and outlet of the WTP (Table 2), showed significant differences in pH ($p = 0.003$), turbidity ($p = 0.007$), and chlorine ($p = 0.0004$). Specifically, the source waters C.I. and Y.I. had low turbidity values. Some locations had high concentrations of chloride (YD.1 and YD.3, Table S1), which may be due to the storage of water from the municipal network in a cistern before being distributed to the pipes. No statistically significant differences were found between the metal content of the inlet and outlet water, confirming that this process does not serve to remove them. No differences were found in Al concentrations as well, which could be since the source water of the T and M systems already contained an important amount of Al input. Comparing the three distribution systems, statistically, significant differences were found. The pH between M and T systems ($p = 0.034$), and Ba and Mn content between systems of M and T ($p = 0.017$, 0.024) and M and Y ($p = 0.024$, 0.024) due to M having a lower content of Ba and higher content of Mn, see Table 2.

Toxicity: HPI value of T.O was 0.44, M.O was 0.53, and Y.O was 0.59. In all cases, the HPI value is lower than 15, indicating that the three systems have low contamination and that the water is suitable for drinking purposes. In comparison with other Ecuadorian cities, the cities of Guayaquil (HPI: 10 - 400), Quito (HPI: 10 - 490), and Ibarra (HPI: 21.4 - 21.8) have higher reported HPI values [42].

### 3.2. Wastewater treatment plant

All the parameters comply with the limits established by Ecuadorian standard for environmental quality and effluent discharge (TULSMA, 2017); (Table 3). TULSMA (2017) only establishes the control of physicochemical parameters and metal content, but ECs are not yet considered in this information.

Regarding the ECs evaluated, caffeine was detected both at the inlet and outlet of the wastewater treatment plant. Caffeine is a widely consumed psychoactive substance in the world that is part of daily beverages as part of free trade medication [44–45], thus it ends up daily in the wastewater. The high occurrence of caffeine in wastewater with or without treatment has made this a ubiquitous compound in surface water worldwide and a source-specific indicator for wastewater discharged [46,47]. With few exceptions where caffeine occurrence is due to natural origin due to coffee bean production [48]. Caffeine is frequently found in surface waters due to its high solubility in water (13 $gL^{-1}$), very low octanol-water coefficient (log Kow = – 0.07), very low volatility, and a half-life of about 10 years. In humans' caffeine is rapidly metabolized by the liver and most of the ingested caffeine is converted to one or more secondary metabolites; thus, about 0.5 % to 10 % is excreted through urine and feces that end in sewage [44]. As in this study, an investigation in the north of Ecuador found caffeine in wastewater without treatment but in high a concentration ranging from 4444.3 to 5597.0 $\mu L^{-1}$ [19]. Table 3 shows a 50 % reduction in caffeine concentration when the wastewaters are treated, demonstrating that traditional WWTPs, such as waste stabilization ponds, are not able to eliminate caffeine efficiently [7]. Other studies in American countries that used this system have found caffeine in the WWTP inlet ranged between 0.5 – 50 $\mu L^{-1}$ [49–50]. Even advanced WWTPs for secondary treatment are

**Table 3**
The Wastewater treatment plant Ucubamba, before (inlet) and after (outlet) treatment. Values indicate the mean ± standard deviations. Values in bold exceed either INEN or WHO reference values.

| PARAMETERS | IFC[λ] | TULSMA[ν] | U.I | U.O |
|---|---|---|---|---|
| pH | 6-9 | 5-9 | 7.10 (0.00) | 8.00 (0.00) |
| Conductivity ($\mu scm^{-1}$) | | - | 540.00 (0.00) | 550.00 (0.00) |
| Turbidity (UTN) | | - | 166.00 (0.00) | 67.00 (0.00) |
| Temperature (°C) | | <35°C | 20.40 (0.00) | 23.60 (0.00) |
| DO ($mgL^{-1}$) | | - | 4.19 (0.00) | 13.50 (0.00) |
| DO (%) | | - | 47.54 (0.00) | 162.28 (0.00) |
| $Cl_2(mgL^{-1})$ | | 0.5 | 0.00 (0.00) | 0.00 (0.00) |
| Al ($mgL^{-1}$) | | 5 | 3.539 (0.23) | 1.659 (0.17) |
| As ($mgL^{-1}$) | | 100 | 0.000 (0.00) | 0.000 (0.00) |
| Ba ($mgL^{-1}$) | | 2 | 0.114 (0.01) | 0.080 (0.00) |
| Ca ($mgL^{-1}$) | | - | 0.046 (0.00) | 0.048 (0.00) |
| Cd ($mgL^{-1}$) | | 0.02 | 0.000 (0.00) | 0.000 (0.00) |
| Co ($mgL^{-1}$) | | 0.5 | 0.000 (0.00) | 0.000 (0.00) |
| Cu ($mgL^{-1}$) | | 1 | 0.034 (0.00) | 0.016 (0.00) |
| Cr(VI) ($mgL^{-1}$) | | 0.5 | 0.005 (0.01) | 0.011 (0.00) |
| Fe ($mgL^{-1}$) | | 10 | 0.001 (0.00) | 0.001 (0.00) |
| Mn ($mgL^{-1}$) | | 2 | 0.365 (0.01) | 0.250 (0.00) |
| Na ($mgL^{-1}$) | | - | 0.039 (0.00) | 0.035 (0.00) |
| Ni ($mgL^{-1}$) | | 2 | 0.000 (0.00) | 0.000 (0.00) |
| Pb ($mgL^{-1}$) | | 0.2 | 0.000 (0.00) | 0.000 (0.00) |
| Zn ($mgL^{-1}$) | | 5 | 0.1629 (0.01) | 0.042 (0.00) |
| Hg ($mgL^{-1}$) | | 0.005 | 0.000 (0.00) | 0.000 (0.00) |
| Caffeine ($\mu L^{-1}$) | | - | **1.05 (0.5)** | **0.55 (0.18)** |
| Nicotine ($\mu L^{-1}$) | | - | <0.14 | <0.14 |
| Ibuprofen ($\mu L^{-1}$) | | - | <0.14 | <0.14 |
| Acetaminophen ($\mu L^{-1}$) | | - | <0.4 | <0.4 |
| Triclosan ($\mu L^{-1}$) | | - | <0.14 | <0.14 |
| Trimethoprim ($\mu L^{-1}$) | | - | <2.8 | <2.8 |
| Estradiol ($\mu L^{-1}$) | | - | <0.14 | <0.14 |

[λ] [43] and ν: [33].

not capable of removing caffeine. For instance, in Ecuador, high concentrations have already been reported (31.5 $\mu L^{-1}$) in the outlet of an advanced WWTP [6]. This fact is worrying because caffeine-containing nitrogen groups are decomposed to form toxic fumes of nitrogen oxides [51]. Then, studies on chronic caffeine exposure are necessary to evaluate its impact on the environment [52].

That caffeine has not been removed may be an indicator that other more complex compounds could not be removed, and they are present in the water, such as antibiotics that are related to bacterial resistance and endocrine disruptors that are related to cancer and hormonal changes in fish and mammals [53,54]. Considering their effectiveness, advanced oxidation processes with technologies based on Fenton, electrochemical oxidation, ozonation, ultrasound, photolysis (UV), and their combinations may be the most viable alternative because, in addition to their effectiveness in eliminating contaminants such as caffeine, they can contribute to water disinfection [55,56]. Other methods have been evaluated but may not be feasible to implement in the study system. Adsorbent methods have been evaluated with good results but with the disadvantage that being based on transport from one phase to another, not being a final solution for the contamination in our study system [57,58]. Advanced oxidation processes achieve the mineralization of these pollutants, but with the disadvantage of difficult implementation difficulty and high costs [59–61]. Therefore, it is essential to consider tertiary treatments to eliminate emerging contaminants, such as caffeine, so the water released in the natural matrix would contain lower contaminants concentration.

## 4. Conclusions

We found that the traditional water purification treatment has been sufficient to improve the physicochemical parameters of the water, but not in removing metals and caffeine. The concentration of Al above the threshold limit both in the source water and in the distribution deserves special attention. The Machángara and Tomebamba rivers have concentrations of aluminium over 0.1 mg per liter recommended by WHO. This content is partly explained by the Andean zone through which they cross, rich in metals that are leached. Although we cannot track back its main sources, we hypothesized that one of the possible contamination sources could be volcanic activity. The results in the treated waters show that more than eliminating aluminium, the potabilization process increases its content, therefore, higher concentrations are found in the waters coming from the mentioned rivers already loaded with aluminium and in the water from the Sustag DWTP whose Inlet waters did not contain this metal.

HPI index indicates that Al does not represent a problem for public health in the concentrations found in our study, thus the effects of chronic exposure to Al are still inconclusive and need to be better investigated. Regarding the wastewater plant efficiency, it complied with the physicochemical parameters, but it was also found that it is not capable of eliminating contaminants emerging such as caffeine.

Most cities in Latin America are not prepared to treat wastewater and drinking water that contain metals and ECs, but the city of Cuenca is an exception in this context.

Ternary treatment should be more implemented due to its efficiency for removal ECs, such as advanced oxidation processes, with the advantage of being able to eliminate recalcitrant organic compounds but with the disadvantage of their operating costs and the need for personnel specialized. Although studies on aluminium in drinking water and caffeine as emerging contaminants indicate a priori that they do not represent a serious public health problem for the environment, these studies focus more on acute cases than chronic ones, so more studies are recommended on the effects of these contaminants for a population exposed daily to them. A complete assessment such as ours could be implemented in other cities to build a better picture of the status of water distribution and treatment.

## 5. Ethical Statement

his manuscript has not been published. It has also not been sent to another journal for review.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## CRediT authorship contribution statement

**R. Arcentales-Ríos:** Formal analysis, Investigation, Writing – original draft. **A. Carrión-Méndez:** Formal analysis, Investigation, Writing – original draft. **I. Cipriani-Ávila:** Conceptualization, Funding acquisition, Methodology, Writing – review & editing. **S. Acosta:** Investigation. **M. Capparelli:** Validation, Writing – review & editing. **G.M. Moulatlet:** Writing – review & editing. **V. Pinos-Vélez:** Funding acquisition, Writing – original draft, Writing – review & editing.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jtemin.2022.100030.

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