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Articles

Assessing critical water quality indicators in raw and drinking waters of the main treatment plants in the city of Cuenca, Ecuador

Evaluación de indicadores críticos de calidad del agua en el agua cruda y potabilizada de las principales plantas de tratamiento de la ciudad de Cuenca, Ecuador

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Abstract

Ecuador is a tropical country with wet and dry periods. The seasonality of water resources leads to water availability and quality variability. This study investigated the variability of physical-chemical characteristics (pH, colour, turbidity, and conductivity), aluminum content, residual free chlorine, and caffeine levels in the inlets and outlets, and in the distribution networks of the three main drinking water treatment plants in the city of Cuenca: El Cebollar (Tomebamba River), Sustag (Yanuncay River), and Tixan (Machangara River). Samples were collected from May 2023 to December 2024. The average values for each parameter fell below regulatory limits. No caffeine was detected. There were isolated instances of values exceeding the regulatory standard for aluminum in inlet and distribution samples. A deficiency of free chlorine was also observed at some points in the distribution system, which might be due to the distance from the treatment plant and the state of the pipes. These findings indicate the quality of Cuenca's drinking water. However, more

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water quality controls should be implemented throughout the distribution network.

Keywords: water quality, drinking water, water treatment, water supply, water resources, chemical analysis, pollutants, Ecuador.

Resumen

Ecuador es un país tropical con periodos húmedos y secos. La estacionalidad de los recursos hídricos genera variabilidad en la disponibilidad y calidad del agua. Este estudio investigó la variabilidad de las características físico-químicas (pH, color, turbidez y conductividad), el contenido de aluminio, el cloro libre residual y los niveles de cafeína en las entradas y salidas, y en las redes de distribución de las tres principales plantas de tratamiento de agua potable de la ciudad de Cuenca: El Cebollar (río Tomebamba), Sustag (río Yanuncay) y Tixán (río Machangara). Se recolectaron muestras entre mayo de 2023 y diciembre de 2024. Los valores promedio de cada parámetro se situaron por debajo de los límites reglamentarios. No se detectó cafeína. Se observaron casos aislados de valores que superaron la norma reglamentaria para el aluminio en las muestras de entrada y distribución. También se observó una deficiencia de cloro libre en algunos puntos del sistema de distribución, lo que podría deberse a la distancia de la planta de tratamiento y al estado de las tuberías. Estos hallazgos indican la calidad del agua potable de Cuenca. Sin embargo, se deberían implementar más controles de calidad del agua en toda la red de distribución.

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Palabras clave: calidad del agua, agua potable, tratamiento del agua, abastecimiento de agua, recursos hídricos, análisis químico, contaminante, Ecuador.

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Introduction

Ecuador is located on the equator, or zero parallel, between the Tropic of Cancer and the Tropic of Capricorn; it does not experience hot and cold seasons but has two distinct periods, the wet and dry periods. In this country, water source, quality, and availability vary by region. For instance, The Sierra or Andean region is characterized by its páramo biomes, which supply water to the cities (Hofstede *et al*., 2023). The availability and quality of water resources vary throughout the year depending on the period, wet and dry, and other large-scale phenomena such as El Niño, La Niña, and climate changes (Hidalgo-Proaño, 2017).

Access to clean and safe drinking water is a fundamental human right. This is reflected in the United Nations Sustainable Development Goal (SDG) 6, which calls for "Ensuring the availability of water and its sustainable management and sanitation for all" (UN, 2022). However, water insecurity plagues our planet. Therefore, it is essential to monitor water quality to detect any contamination that could present a human

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health risk if consumed (Alcocer-Yamanaka *et al*., 2004; Arias-Muñoz *et al*., 2025).

During heavy rainfall events, runoff that contains large amounts of dissolved and particulate matter enters surface water sources, presenting challenges for drinking water treatment. These include membrane fouling, increases in chemical demands, and the formation of various disinfection by-products (Delpla *et al*., 2023). In Andean páramos of volcanic origin, there might also be leaching of metals (Arcentales-Ríos *et al*., 2022). During periods of drought, there is a risk of water shortages.

In addition to natural sources of variation in water quality, anthropogenic activity also plays a role. These activities release chemical and biological contaminants into the environment, including metals like arsenic, lead, chromium, and salts like fluorides and nitrates, as well as emerging contaminants such as pharmaceuticals, pesticides, and microplastics (WHO, 2023). Notably, caffeine stands out as an indicator for emerging contaminants due to its widespread presence in surface waters globally (Pinos-Vélez *et al*., 2019).

Given the evidence of high levels of contaminants, ensuring water quality at sources that supply treatment plants, the effectiveness of the treatment itself, and the maintenance of water quality during distribution is crucial. Therefore, this study aimed to evaluate the critical physical and chemical parameters in the source water and treated water of the three main water treatment plants in the Andean city of Cuenca, Ecuador. For each sample, we analyzed the aluminum content, free chlorine, color, pH, conductivity, turbidity, caffeine concentration, and acute ecotoxicity using *Daphnia magna*. We compared the levels of these critical parameters with regulatory standards and evaluated the variability of water quality

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between the three plants, between the two seasonal periods, and at various locations throughout the system from the source to the end of the distribution network.

Materials and methods

Study area

Cuenca, Ecuador, is located in the Ecuadorian Andes, with an average temperature of 15 °C, and an altitude of 2 560 meters above sea level (masl) (INEC, 2022). The city has a seasonal variation of wet and dry periods with an average annual precipitation of 984 mm (Arcentales-Ríos *et al*., 2022). The Municipal Public Company (ETAPA EP) manages water treatment and supply, covering over 90 % of the population in ETAPA EP (2020). Cuenca has three main drinking water treatment plants: El Cebollar, Tixan, and Sustag. The oldest of the three main water treatment plants is El Cebollar (C), which began operations in 1949. Located in the northwest area at 2 639 masl, it draws water at 2 736 masl from the Tomebamba River (IC). This plant serves the central and south-central areas of the city, providing drinking water to roughly 200 000 residents (ETAPA EP, 2020). For flocculation, El Cebollar utilizes 35 mgl^{-1} of aluminum sulfate and 0.7 mg l^{-1} of a cationic polymer, while chlorine gas (1 mg l^{-1}) is used for disinfection (Ávila, 2013). The Tixan (T) drinking water treatment plant, located in the Chiquintad parish, utilizes water from the Machángara River (IT) at 2 690 masl. It began operations in 1994 (Ávila, 2013) and supplies the northern part of Cuenca (ETAPA EP, 2020). The Sustag (S) drinking water treatment plant is located in the

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Sustag area in San Joaquín, at an elevation of 2 920 masl. This plant sources water from the Yanuncay River (IS), at an elevation of 2 736 masl and provides drinking water to approximately 25 000 people in the southern part of the city (ETAPA EP, 2020).

Sampling points: For each of the three water treatment plants, samples were collected from seven sampling points: the source water inlet (I), the outlet after treatment (O), and five additional points within the distribution network (D1 through D5). Sampling points are numbered according to the proximity to the plant, with the lowest numbers closest to the plant. The points are located throughout the entire distribution network to determine if there are variations in parameters due to distance from the treatment plant. Details regarding specific distribution points can be found in Figure 1. The sampling was carried out during two distinct campaigns: May 2023 (representing the wet season, denoted by "Wet") and July 2023 (representing the dry season, denoted by "Dry"). For each sample, we analyzed aluminum content, free and total chlorine, colour, pH, conductivity, turbidity, and caffeine concentration. We collected a total of 450 samples, 150 from each of the three water treatment plants.

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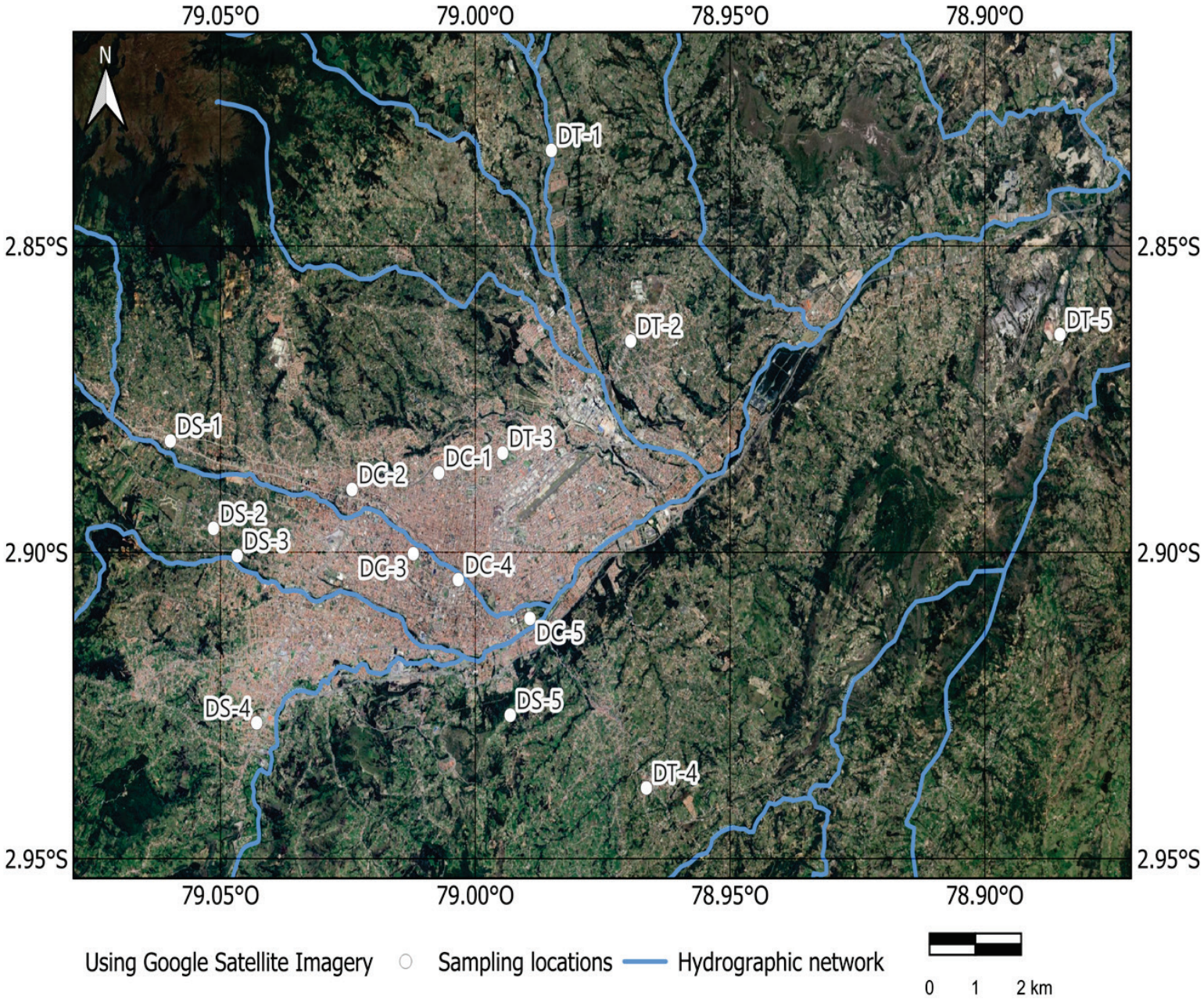

Figure 1. Sampling points for distribution (D) for El Cebollar (C), Sustag (S) and Tixan (T) systems.

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Analysis

Aluminum analyses: 100 ml of each water sample was stored in a plastic container and transported to the IRCMA laboratory facilities, where the samples were analyzed the same day. To measure aluminum in the water samples, we used a Hanna Instruments HI93712-01 caloric method test kit (with a detection range of 0.00 to 1.00 mgl^{-1}). Briefly, reagent A was added to 50 ml of the drinking or inlet water sample. Once homogenized, the contents of B were added, stirring until dissolved. The set was divided into two 10 ml cuvettes. Reagent C was added to one of the cuvettes to obtain the blank. We waited 15 minutes. Next, both cuvettes were analyzed using a spectrophotometer (HI883305 Multiparameter Photometer for Boiler & Cooling Tower, Hanna Instruments) to determine the Al^{3+} and Al_2O_3 content in mgl^{-1}.

Residual-free chlorine analyses: The residual-free chlorine was measured in situ. For the analysis, a Hanna Instrument HI38017 DPD (N, N-diethyl-p-phenylene-diamine) and a colorimetric method test kit were used (with a detection range of 0.00 to 5.00 mgl^{-1} of Cl_2). Briefly, 10 ml cuvette of distilled water was used as blank in a spectrophotometer. Then, 10 ml of the sample and a/the reagent was poured into a separate cuvette and mixed for 20 seconds for free chlorine, and for three minutes for residual chlorine before measuring in the spectrophotometer.

The pH and conductivity (range 0.00 to 20.00 $mScm^{-1}$ EC, electrical conductivity) were measured in situ for each sample using a Hanna Instruments meter, model HI98130. To determine colour, we used the Hach hexachloroplatinate method. To measure turbidity, we used nephelometry and Hach method 10258. This involved placing 10 ml of the

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sample in a cuvette, mixing it with the provided reagent, and then measuring the solution in a spectrophotometer to obtain a turbidity reading in nephelometric turbidity units (NTU).

Caffeine analyses: 1 000 ml of each water sample were stored in a glass container to be transported in a cooler to the IRCMA laboratory facilities, where the samples were analyzed in the same week. The analytical method was taken from previous work carried out in the group (Cipriani-Avila *et al*., 2023; Jara-Negrete *et al*., 2023). Caffeine analysis involved a solid phase extraction process using Strata C-18 cartridges. These cartridges were first conditioned by passing 10 ml of methanol through them at a controlled flow rate of $5E^{-8}$ m^3s^{-1}. Subsequently, 900 ml of the water sample was passed through the cartridges using a vacuum manifold, ensuring a slow drip speed (less than or equal to one drop per second). After drying the cartridges with the vacuum pump for 5 minutes, the concentrated sample was eluted with 2 ml methanol. Each sample was analyzed in duplicate for accuracy. A blank sample was prepared by eluting 900 ml of distilled water through the cartridge. The samples were analyzed in an Azura brand HPLC-DAD. The injection volume was 30 µl of sample. The mobile phase/elution liquid comprised 40 % milliQ water and 60 % HPLC grade methanol. The total analysis time per sample was 6.5 minutes. A calibration curve for caffeine was established using a Sigma Aldrich standard, and the detection limit was set at 0.025 μgl^{-1}.

***Daphnia magna* bioassay**: For this test, the European Union regulations were followed: Test No. 202: *Daphnia* sp. Acute Immobilization Test (OECD, 2004). 100 ml of each water sample were stored in a glass container and transported to the IRCMA laboratory. To determine ecotoxicity, we placed five *Daphnia magna* neonates (less than

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24 hours old) in a 35 ml sample of dechlorinated water, for each test of each sample. After 48 hours, we counted the number of immobilized *Daphnia magna* (Pinos-Vélez *et al*., 2023). All bioassays were conducted in duplicate.

Statistical analysis

Descriptive statistics were calculated for the data set to find the median, mean, and standard deviation of parameters by sampling point or type of sample (*i.e*., Inlet, Outlet, or Distribution). Homoscedasticity and normality were assessed. As these assumptions were not met for all data sets, non-parametric inferential tests (Wilcoxon Test and Kruskal-Wallis Test) were employed with a significance level of 0.05. The Wilcoxon Test was used to determine statistically significant differences between parameters by period (dry (D) or wet (W)). A Kruskal-Wallis Test was used to determine differences between parameters by plant or by type of sample, and if significant, a one-tailed post hoc test was applied. For multivariate statistics, a Cluster analysis (k-means) using Euclidean distance, and a Principal Component Analysis with scaled data and their combination were performed using the R packages FactoMineR and factoextra. The R (Version 4.4.0) software package with an R-Studio interface was used for statistical analyses.

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Results and discussion

We analyzed 450 samples, 150 from each treatment plant. As shown in Table 1, results for raw water samples were compared to the limits established by the Ecuadorian standard TULSMA (MAE, 2018). For drinking water samples, the comparison was made with the NTE INEN-1108:2020 standard, except for aluminum, which was evaluated according to the limits set by the World Health Organization (WHO, 2003; WHO, 2023). All median values across the monitoring points were within the permissible limits, though variations related to seasonal changes and distribution networks were noted.

Table 1. Medians [min/max] of aluminum, chlorine, and physical-chemical parameters in samples from the inlet (I), outlet (O), and distribution (D) at El Cebollar (C), Sustag (S), and Tixan (T) treatment plants during wet (Wet) and dry (Dry) periods.

Code	Al_2O_3 mgl^{-1}	Al^{3+} mgl^{-1}	Free Cl_2 mgl^{-1}	Colour Pt-Co	pH	Conductivity µS	Turbidity NTU
IC.Wet	0.00 [0.0/0.17]	0.00 [0.00/0.17]	0.05 [0.00/0.10]	11.2 [10/15]	8.1 [7.7/8.50]	115 [74/158]	2.6 [1.58/4.2]
OC.Wet	0.05 [0.0/0.17]	0.04 [0.00/0.08]	1.20 [0.85/1.26]	1.25 [0/5.0]	7.41 [6.8/8.29]	114 [81/167]	1.0 [0.26/2.75]
DC.Wet	0.05 [0.0/0.23]	0.05 [0.00/0.12]	1.20 [0.01/1.36]	< LD	7.70 [7.1/8.26]	110 [52/129]	1.3 [0.00/2.3]
IC.Dry	0.06 [0.0/0.23]	0.04 [0.03/0.12]	0.05 [0.00/0.10]	10.0 [0.0/30]	7.78 [7.15/7.9]	119 [108/155]	2.00 [1.0/2.6]

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Code	Al_2O_3 mgl^{-1}	Al^{3+} mgl^{-1}	Free Cl_2 mgl^{-1}	Colour Pt-Co	pH	Conductivity µS	Turbidity NTU
OC.Dry	0.07 [0.0/0.2]	0.04 [0.0/0.10]	1.23 [0.9/1.40]	< LD	7.28 [6.7/8.2]	114 [87/161]	1.00 [0.3/2.0]
DC.Dry	0.11 [0.0/0.3]	0.06 [0.00/0.2]	1.26 [1.20/1.40]	0.0 [0.0/2.5]	7.50 [7.1/8.3]	111.0 [101/125]	1.25 [0.3/2.4]
IS.Wet	0.03 [0.0/0.1]	0.01 [0.0/0.1]	0.05 [0.00/0.10]	22.5 [7.4/50]	8.11 [7.4/8.3]	67.0 [17/124]	2.09 [4.0/4.7]
OS.Wet	0.02 [0.0/0.11]	0.02 [0.0/0.06]	1.32 [0.8 /1.57]	0.00 [0.0/5]	7.32 [5.6/7.7]	83.3 [51/129]	0.75 [0.19/1.0]
DS.Wet	0.07 [0.0/0.3]	0.03 [0.0/0.14]	1.26 [0.0/1.4]	0.00 [0.0/10]	7.45 [6.6/7.9]	77.00 [51/124]	1.00 [0.0/5.2]
IS.Dry	0.02 [0.0/0.1]	0.01 [0.0/0.07]	0.06 [0.0/0.10]	20.0 [0.0/75]	7.96 [7.2/8.5]	68.5 [45/98]	2.34 [1.2/6.4]
OS.Dry	0.00 [0.0/0.9]	0.00 [0.0/0.05]	1.30 [1.00/1.44]	0.00 [0.00/5]	7.68 [5.8/8.1]	76.5 [51/107]	1.00 [0.33/2.0]
DS.Dry	0.050 [0.0/0.3]	0.03 [0.0/0.1]	1.26 [1.2/1.36]	0.0 [0.0/12.5]	7.50 [7.1/8.0]	87.00 [66/132]	1.00 [0.4/2.6]
IT.Wet	0.05 [0.0/0.34]	0.03 [0.0/0.26]	0.08 [0.0/0.1]	13.8 [5/20]	8.08 [7.1/8.5]	92.0 [68/130]	2.19 [1.0/7.0]
OT.Wet	0.00 [0.0/0.23]	0.00 [0.0/0.12]	1.23 [0.5/1.6]	< LD	7.60 [7.1/8.0]	104.5 [90/138]	0.64 [0.2/1.5]
DT.Wet	0.02 [0.0/0.3]	0.01 [0.0/0.18]	1.26 [0.0/1.4]	0.00 [0.00/5]	7.79 [7.0/8.3]	94 [86/103]	0.75 [0.0/3.6]
IT.Dry	0.11 [0.0/0.4]	0.06 [0.0/0.20]	0.05 [0.0/0.1]	17.5 [0.00/65]	7.72 [7.2/8.2]	97 [72/111]	1.85 [1.0/13]
OT.Dry	0.04 [0.0/0.2]	0.02 [0.0/0.09]	1.26 [1.0/1.4]	0.00 [0.0/15]	7.40 [6.6/8.6]	104 [79/122]	0.48 [0.0/1.1]

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Code	Al_2O_3 mgl^{-1}	Al^{3+} mgl^{-1}	Free Cl_2 mgl^{-1}	Colour Pt-Co	pH	Conductivity µS	Turbidity NTU
DT.Dry	0.06 [0.0/0.43]	0.03 [0.0/0.23	1.26 [1.2/1.4]	< LD	7.50 [7.2/8.0]	94 [78/108]	0.89 [0.3/2.0]
TULSMA†	-	0.2	-	-	6.0–9	-	100
INENæ	-	-	0.3–1.5	15	6.5–8	-	5
WHOø		0.2					-

< LD: Below detection limit.

†Ministerio del Ambiente. (2015) for raw water.

æINEN (2020) for drinking water.

øWHO (2023) for drinking water.

Aluminum content

The mean aluminum concentration across all treatment plants and sampling points was 0.04 mgl^{-1}, indicating the consistent presence of aluminum from the source (I) at all locations throughout the distribution network. While aluminum levels typically remained within the permissible limits set by TULSMA and WHO standards (0.2 mgl^{-1}), isolated cases showed marginal exceedances at three samples in El Cebollar, with an average of 0.24 mgl^{-1}, five points in Sustag, with an average of 0.24 mgl^{-1}, and 7 points in Tixan, with average of 0.32 mgl^{-1}. In Tixan, most of those exceedances were at points within the distribution network, with only two in the inlet. These findings suggest occasional challenges in managing residual aluminum levels at Tixan, potentially linked to high-turbidity conditions in the source water.

During periods of elevated turbidity, commonly observed in raw water during the wet season, the increased application of aluminum-

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based coagulants, such as aluminum sulfate, becomes imperative for managing sediment and suspended particles. Although higher coagulant dosages effectively control turbidity, they simultaneously increase the risk of residual aluminum in treated water if dosing is not meticulously calibrated (Spînu & Racoviteanu, 2014). Aluminum sulfate, a widely used coagulant, may lead to increased residual aluminum due to the formation of aluminum hydroxide precipitates. These precipitates capture suspended particles but may also inadvertently elevate aluminum concentrations post-treatment (Cogollo, 2011).

It is noteworthy that elevated aluminum levels were detected not only in the treated water but also at the inlet of the Tixan treatment plant before any treatment chemicals were applied. This finding suggests that the presence of aluminum in the source water could primarily result from natural sources, such as mineral leaching within the Machangara River watershed, particularly during the wet season. The aluminum concentration in natural waters varies depending on physicochemical and mineralogical factors. Dissolved aluminum concentrations in waters vary from 0.001 to 0.05 mgl^{-1} at neutral pH and from 0.001 to 0.5-1 mgl^{-1} in acidic waters (WHO, 2003). High turbidity values recorded at the inlet further support this hypothesis, as such conditions are typical of Andean rivers flowing through mineral-rich soils. This situation highlights the critical importance of precise coagulant dosing and continuous monitoring to ensure compliance with health standards (Gonzalez *et al*., 2013) while effectively managing the natural influx of aluminum from the watershed. Overall, aluminum levels in drinking water depend on the concentration occurring in the source water and the doses of aluminum-based coagulants applied during water treatment (WHO, 2003).

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Free chlorine content

According to INEN-1108:2020, the allowable concentration of residual free chlorine in water distribution systems should range between 1.2 and 1.6 mgl^{-1}. However, in some instances, residual free chlorine levels were undetectable. Specifically, 4 % of samples from El Cebollar, 6.6 % from Tixan, and 5 % from Sustag fell below the permissible limit for residual free chlorine, with these lower levels observed at points farther from the plant, particularly towards the extremities of the distribution network. These findings align with other research that has reported that physical parameters, including pipeline distance, diameter, and flow velocity, significantly influence chlorine decay, though initial chlorine concentration remains the most influential factor (Kwio-Tamale & Onyutha, 2024). Additionally, another study determined that the rate of free residual chlorine decay is affected by travel time and the presence of organic matter. This underscores the importance of monitoring these variables to maintain safe chlorine levels throughout the network (Oliveira *et al*., 2022).

Physical-chemical parameters

The average pH value of the analyzed samples was 8, which is considered neutral and falls within the range required by the NTE INEN 1108-2020 water quality standard. However, the pH of certain samples fell outside of the compliance range. Specifically, samples from points OS11 and OS18 had values lower than recommended, and 45 samples had pH values

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above the standard, 16 in El Cebollar (18 % in I, 6.6 % O, and 75.4 % in D). This variability in pH is likely influenced by differences in water sources and treatment processes. For instance, the Yanuncay River, a source for the Sustag DWTP, is known for its high levels of humic and fulvic acids derived from wetland-originated organic matter. Humic and fulvic acids can form in wetlands through the decomposition of organic matter. These compounds can also enter rivers during periods of increased runoff, such as after rainfall or storm events, when they are transported from soils into surface waters (Ngumba *et al*., 2016; Mahler *et al*., 2021). This process can contribute to pH fluctuations, as these organic acids can lower the pH when present in significant concentrations. This is consistent with the pH values observed at two samples at Sustag compared to samples at the other DWTPs.

The average values of samples collected from the inlets of all three plants were ~15 Pt-Co units for colour, ~100 µS cm-1 for conductivity, and ~1 NTU turbidity. Colour levels tended to be higher during the wet season, likely due to the increased presence of dissolved organic matter from rainwater runoff. For instance, the inlet points at the Sustag plant (IS.Wet: 22.5 Pt-Co) showed notably elevated colour levels during the wet season. In contrast, outlet points and distribution networks consistently showed lower colour values, often below detectable limits (< LD), indicating that the colour removal treatment (coagulation and flocculation) used by all three plants is effective in both seasons.

Conductivity measurements indicated a trend towards higher conductivity in the dry season across most samples, especially at inlet points. For example, at the El Cebollar plant, conductivity at the inlet during the dry season (IC.Dry: 119.0 ± 7 µS cm-1) was higher than in

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the wet season (IC.Wet: 115 µS cm-1). In the Sustag plant, although seasonal conductivity differences were less pronounced, a slight increase was observed in the dry season. Turbidity also showed notable seasonal variation, with higher turbidity levels observed during the wet season at most inlet points, likely due to increased sediments from rainfall. For instance, turbidity at the El Cebollar plant inlet point during the wet season (IC.Wet: 2.6 NTU) was higher than in the dry season (IC.Dry: 2 NTU), which aligns with typical sediment influx from Andean rivers during periods of rain. In the distribution systems, however, turbidity levels remain consistently low in both seasons, reflecting the effectiveness of treatments at clarifying water before distribution.

Overall, by examining the data according to seasonal and locational differences, a clearer pattern emerges in the physical-chemical behaviors of colour, pH, conductivity, and turbidity.

Caffeine

Analyses showed no traces of caffeine in the water for any plants according to our methods' detection limits. These findings are inconsistent with other studies conducted on the coast and in the Amazon region of the country (Capparelli *et al*., 2021; Jara-Negrete *et al*., 2023). This difference may be due to the different origins of the source water. In our study, source water originates from the Andean highlands, while source water along the coast travels through populated areas where it is more susceptible to contamination from inadequate wastewater treatment or illegal landfills. This suggests that caffeine could be considered anthropogenic (Spongberg *et al*., 2011). However, it is possible that

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caffeine also comes from environmental sources. Coffee and tea contain caffeine and are commonly cultivated on the coast, while the Amazon region is known for growing tea and guayusa, another caffeinated plant.

Wet and dry periods

Results of the comparison between parameters by period are shown in Table 2. We used a Wilcoxon test with a significance level of 0.05 to compare between the wet and dry periods for all three plants.

Table 2. p-values from Wilcoxon tests for the wet and dry periods at all three plants. Blue represents instances when the values in the wet period were significantly higher, and orange represents when values for the dry period were significantly higher.

	Al_2O_3	Al^{3+}	Cl_2	Colour	pH	Conductivity	Turbidity
C.I					$8E^{-5}$****		
C.O				0.006**			
C.D			0.01*				
S.I							
S.O					0.01*		0.02*
S.D				0.027*		0.009**	
T.I					0.003*		
T.O							
T.D	0.003**	0.01*			0.037*		

* = p < 0.05
** = p < 0.01
*** = p < 0.001
**** = p < 0.000

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No differences in the aluminum oxide and aluminum concentrations were observed at El Cebollar and Sustag DWTPs. At the Tixan DWTP, statistically significant differences were found in the amount of aluminum oxide and the concentration of aluminum in the distribution water, with higher concentrations during the dry period. This may be due to a lower river flow, thus lower input to the plant, leading to excessive amounts of aluminum oxide being delivered to the plant producing higher concentrations of aluminum. For free chlorine, differences were only identified in the distribution water/system of the Tixan plant, with the highest values observed during the dry period. This may be due to the higher temperatures during this period (Guerrero *et al*., 2017). During the wet period, pH values were significantly higher in raw water for El Cebollar and Tixan DWTPs. This might be caused by the presence of more organic matter during that time. Compared to the dry period, the source water during the wet period typically contains more organic matter, which reacts with chlorine, giving rise to compounds such as trihalomethanes (Delpla *et al*., 2023; Mahler *et al*., 2021). When we measured conductivity, we found that there was significantly higher conductivity in the distribution water at Sustag during the dry period.

Daphnia magna

In general, D. magna survived in all inlet water samples and all water treated after 24 h of chlorine removal. The only statistically significant differences in medians were for the live D. magna in samples from the distribution water, with more live D. magna present in the wet period

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(Figure 2). This is a direct consequence of higher concentrations of aluminum in the water, and possibly trihalomethanes.

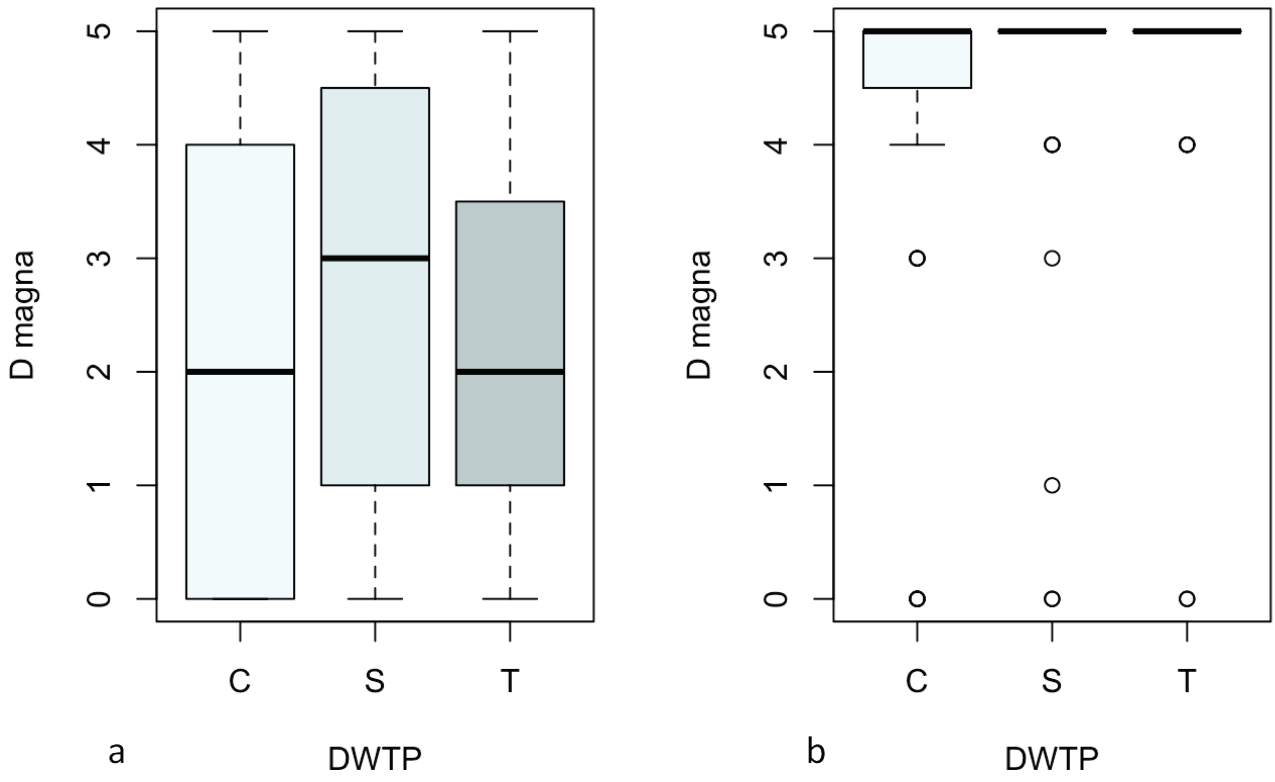

Figure 2. Box plot of the number of surviving D. magna by type of water and water treatment plant during (a) the dry period, and (b) the wet period.

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Comparison between plants by inlet, outlet, and distribution

Table 3 shows results from the Kruskal-Wallis test (with a significance level of 0.05) between plants by inlet, outlet, and distribution.

Table 3. p-values for the Kruskal-Wallis test for plant in inlet (I), outlet (O), and distribution (D).

	I		O		D	
	p	**post hoc**	**p**	**post hoc**	**p**	**post hoc**
Al_2O_3	0.01*	C < T; S <T	0.03*	C>S	-	
Al^{3+}	0.03*	C<T; S<T	0.03*	C>S	-	
Cl_2	-		0.02*	C<S	-	
Colour	0.003**	C<S; C<T	-		$2E^{-6}$****	S>T
pH	-		-		-	
Conductivity	$1E^{-8}$****	C>S; C>T	$2E^{-8}$****	C>S; C>T	$1E^{-12}$****	C>S; C>T
Turbidity	-		0.009**	C>T	$1E^{-4}$***	C>S>T

* = $p < 0.05$.

** = $p < 0.01$.

*** = $p < 0.001$.

**** = $p < 0.000$.

For the inlet samples, differences were found in the water colour between the three plants. In all inlet samples, the El Cebollar DWTP colour values were lower compared to the Tixan and Sustag plants. This is because the source waters of those two plants, the Yanuncay and

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Machángara rivers, have higher organic matter content in comparison to the Tomebamba river, which is the source for the El Cebollar plant. There were also differences in the Al_2O_3 and Al content, and the conductivity in the inlet samples between the three plants, which indicates that the aluminum and other metals come from the páramo. In the outlet samples, we observed differences in the aluminum content between the El Cebollar and Sustag DWTPs, which indicates that the aluminum at El Cebollar DWTP is introduced during the treatment. It should be noted that the El Cebollar DWTP is the oldest plant. At the outlets, the El Cebollar DWTP had lower chlorine content in comparison to the Sustag DWTP. Unlike at the inlet where the El Cebollar DWTP exhibited lower values relative to the other DWTPs, the outlet and distribution samples from the El Cebollar DWTP had the highest values for conductivity and turbidity.

A principal component analysis (PCA) was performed and PCA-means were calculated to determine which parameters could be grouped to explain the results in treated (O and D) and untreated water (I). Figure 3 shows the PCA results and in all cases, regardless of plant or period, turbidity and colour are part of the same component and are opposite to the chlorine variables. Component 1 (PC1) is associated with the changes due to water treatment, such as loss of colour, and lower turbidity and chlorination, while Component 2 (PC2) is associated with the aluminum and pH variables related to the characteristics of water when it arrives from the source (I) and how it changes during treatment (O and D). The first two components explain ~60 % of the variability for each plant and season. Component 1 explains between 34 and 43 %, and component 2 explains 23 to 30 % of the variability. Based on a cluster analysis by plant (Figure 4), the raw water (I) samples were different from the treated

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water samples (O and D), which did not differ from each other for any of the plants; that is, in the ordination plot the samples from the plant outlet were mixed in with those from the distribution, indicating that the water properties do not change in the distribution. This shows that the treatment in the plant is responsible for the changes observed in the water. These changes include decreases in colour, turbidity, chlorination, and, in some cases, aluminum. In addition, the characteristics of the treated water at the outlet and at the distribution points are generally maintained/consistent. This is true for both the wet and dry periods.

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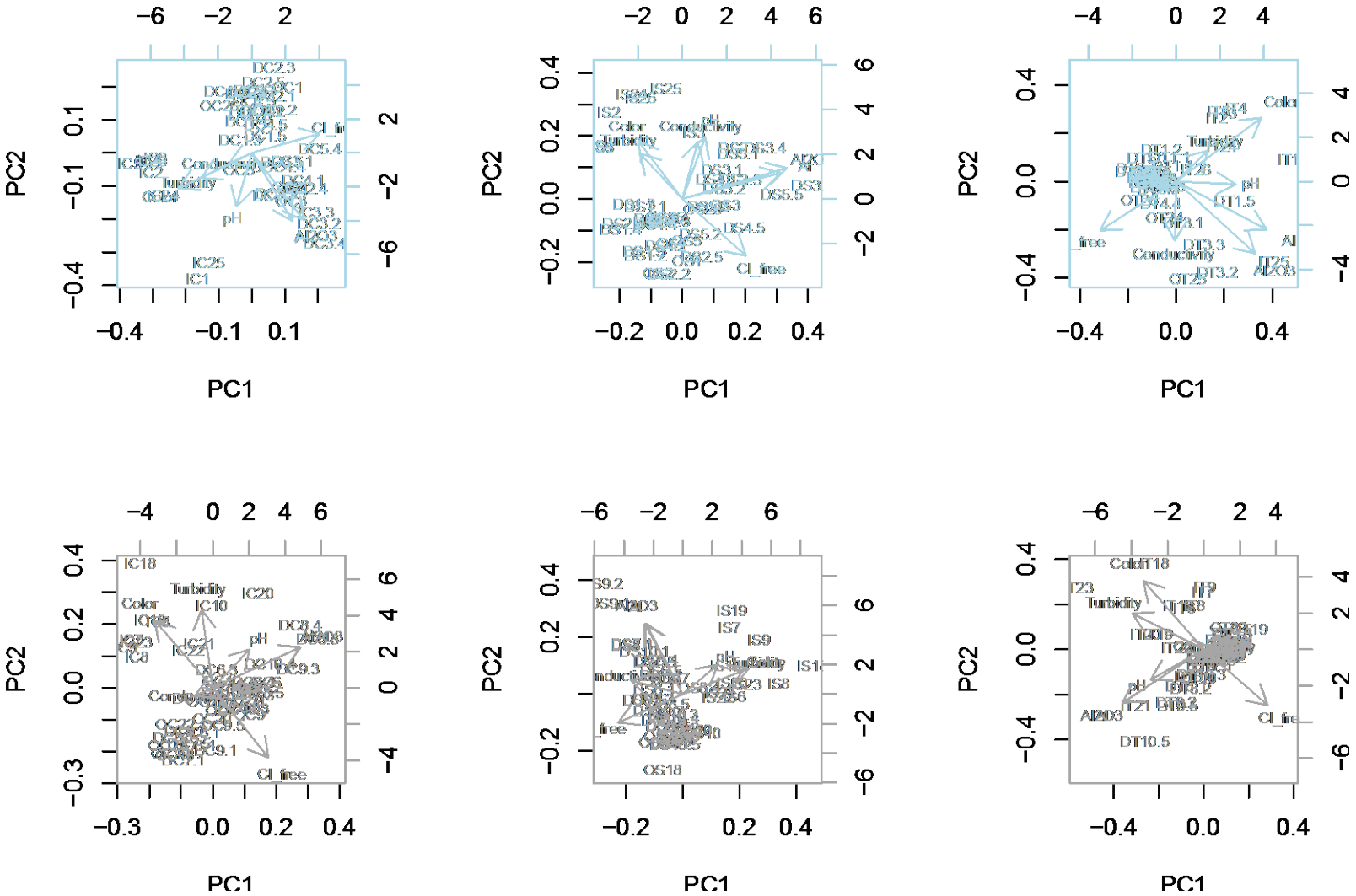

Figure 3. Principal component analysis of the measured parameters for each plant in the wet period (blue) and dry period (gray) at El Cebollar, Sustag, and Tixan DWTPs (suplefrom right to left).

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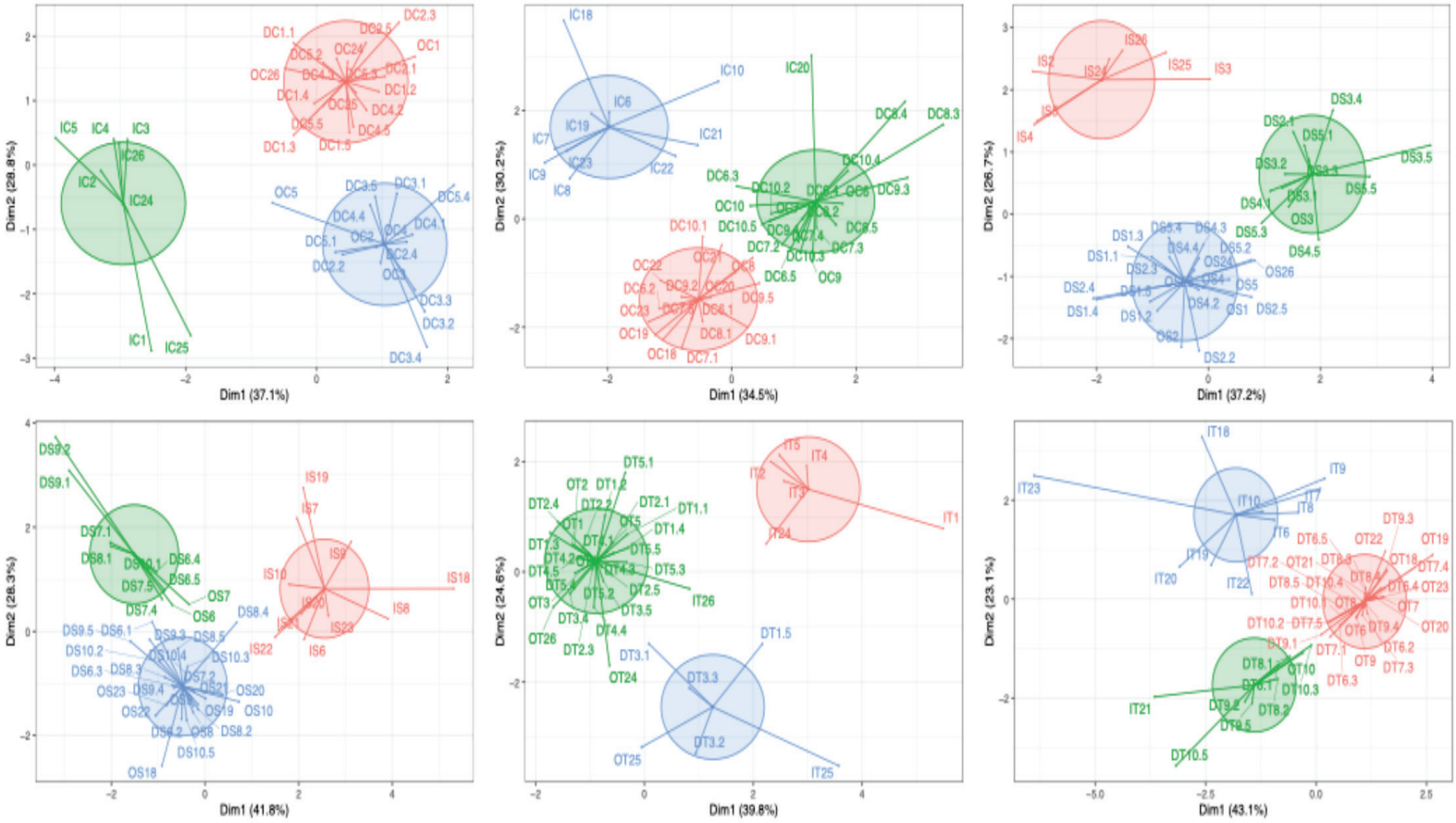

Figure 4. K-means cluster analysis of PCA values for each plant in the wet period (above) and dry period (below), for El Cebollar (left), Tixan (center) and Sustag (right). Each colour represents a separate cluster.

Conclusions

The study revealed significant reductions in colour and turbidity between the raw (inlet) water and treated (outlet and distribution) drinking water in all cases. These reductions are positive indicators of efficient water purification, as lower values of these parameters are considered safest for human consumption (ideally zero or close to zero). Physical-chemical

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properties across treatment plants and between wet and dry periods showed low variability and generally met the established standards (TULSMA for raw water and INEN/WHO for drinking water) with some exceptions. No caffeine was detected in any of the analyzed samples. This could be attributed to Cuenca's water supply source —the city's highlands— which are less susceptible to anthropogenic or natural pollutants compared to other water sources. Based on the analyzed physical-chemical parameters, including residual free chlorine, aluminum, and caffeine, the drinking water from the three treatment plants serving Cuenca complies with regulations for the considered parameters. However, strategies should be implemented to address potential chlorine loss at distribution points further away from the treatment plants. Given these results and the impact drinking water quality has on human health, it is important to continue with similar types of studies to identify if any by-products, such as trihalomethanes, caused by the reaction of chlorine with the organic matter, are present in the water.

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