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Geochemical Insights into Health Risks from Potentially Toxic Elements in Rural Aqueducts of Cocle, Panama: Unveiling Links to Local Geology

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Abstract: The El Valle Volcanic Complex, located in the province of Cocle, Panama, presents geological characteristics that could be linked to public health problems. This study focuses on the municipalities of San Juan de Dios, Pajonal, and Caballero, where water is consumed directly from springs (groundwater outcrops). The region has a high incidence of non-traditional chronic kidney disease (nt-CKD) that may be associated with the natural presence of potentially toxic elements (PTEs) in the water. This study aimed to analyze the concentration of PTEs in groundwater and assess the carcinogenic (CR) and non-carcinogenic (HQ) risk to human health from the direct ingestion of water. Sediments, rocks, and water samples were collected. Major ions and PTEs (As, Al, Ba, Co, Cu, Fe, Mn, Sr, Sb, Pb, V, and Zn) were measured, and the mineralogical composition of the rocks was analyzed. The results showed that Fe was the only PTE that exceeded the recommended concentration for drinking water, according to Panama regulations, and Pb according to USEPA. In Caballero and Pajonal, the acceptable threshold for CR and HQ was exceeded, a higher percentage than in San Juan de Dios. The PTEs that contribute most to the risk are Co, Cu, Pb, and As. This study suggests that the region's historical volcanic activity, involving the release of minerals rich in these PTEs, along with the interaction between groundwater and volcanic rocks, may be contributing to the presence of PTEs in the

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water. This geological phenomenon could be what has led to prolonged exposure to these elements, which correlates with the high prevalence of chronic kidney disease in the area. This is a novel study, the first conducted in Panama, as it seeks to uncover the relationship between the geology of the site, the presence of PTEs in the groundwater of springs for human consumption, and the implication of health risks, with the aim of generating new information for decision makers for the generation of public policies on health issues such as nt-CKD and cancer in the region.

Keywords: drinking water; geology; potentially toxic elements; risks to human health; non-traditional chronic kidney disease

1. Introduction

Underground sources supply water for human consumption in certain communities in the municipalities of San Juan de Dios, Pajonal, and Caballero. These groundwaters come from springs, from places where groundwater emerges to the Earth's surface [1,2], and their location is, in most cases, close to water bodies. Of the Sustainable Development Goals (SDGs), the one with the greatest relevance is number 6 (clean water and sanitation), which concerns the development of scientific research involving communities in order for them to know the state of their water quality [1]. This specific case concerns groundwater used for human consumption, which has been known to be one of the concerns of the inhabitants in this sector, who, through their organizations, have supported the development of this study.

In the Municipality of Caballero, the Instituto de Acueductos y Alcantarillados Nacionales (IDAAN) is where 96.1% of households obtain water for human consumption. The Institute of National Aqueducts and Sewers water treatment plant is administered by the Juntas Administrativas de Acueductos Rurales (JAAR) (eng. Boards of Directors of Rural Aqueducts), and in San Juan de Dios the number of households that obtain water for human consumption is 92.5% [2].

In terms of morbidity, diarrhea, gastroenteritis, and urinary tract infections are among the top five leading causes for both children and adults under 60 years of age in the province of Cocle [3]. The prevalence of non-traditional chronic kidney disease is 29 cases per 10,000 inhabitants [4]; the cancer mortality rate is 78.5 cases per 10,000 inhabitants, and the premature mortality rate for malignant neoplasms was 36.2 deaths per 100,000 inhabitants for the year 2021 [5]—diseases that may be related to the ingestion of water for human consumption.

The water quality index (WQI) and human health risk assessment (HHRA) are among the most used tools for categorizing and reflecting the state of the water and the health risk in a certain area [5]. Diatoms are good indicators of water quality; their abundance and diversity help to determine the gravity of the state and if there is environmental pollution. Phytobenthos and phytoplankton are the most numerous microalgae that, due to their biological and ecological characteristics, are good indicators of water quality [6]. The trophic state and environmental pollution in the water are determined by their abundance and diversity [6].

Although groundwater tends to be fresh and suitable for human consumption, it is necessary to evaluate its quality, since it may contain certain potentially toxic elements naturally present through the dissolution of salts from rocks that make up the aquifer or through human activities [7,8]; in this sense, it is important to study the geology of the area linked to the chemical composition of groundwater used for human consumption, as it can sometimes provide concentrations of heavy metals associated with the mineral

phases present in the rocks [9,10]. The Geoaccumulation Index (Igeo) is used to normalize the concentrations of elements in soils and sediments so that regional geological variations are reduced and the anthropogenic influence can be observed [11,12].

Studies have been carried out in countries such as Colombia [13] and Saudi Arabia [14], finding Cd, Cr, Cu, Pb, and Zn. In the case of Colombia, 84% of the groundwater samples analyzed represented a high risk to human health, establishing the need to implement water treatment systems, protect the areas of rural aqueducts, and implement a system to monitor water quality in order to reduce the morbidity and mortality rates associated with water consumption.

Potentially toxic elements (PTEs) found in rocks and sediments mobilize to waters and can pose risks to biota and humans as they bioaccumulate [15]. Studies and various literature reviews have established the relationship between environmental exposure to heavy metals, such as As, Co, Cu, Pb, and others, and the development of chronic kidney disease [16–21].

Epidemiological studies have shown evidence that arsenic can cause cancers of the skin, lung, liver, and bladder, among other tissues [22]. Gastrointestinal and bladder cancers are consistently associated with elevated Pb levels in biological samples such as blood, urine, nails, and hair [23]. Cobalt (Co^{2+}) is a trace element that can be found in the kidneys, along with other organs like the liver, heart, and spleen, while cobalt is an essential cofactor in the body. Too much cobalt can be toxic; cobalt induces cardiomyopathy and renal toxicity [24].

Copper is essential for people; its deficiency or excess in a diet can cause diseases. Ingesting high levels of copper, usually via drinking water, can cause vomiting, nausea, abdominal pain, and/or diarrhea, while daily and prolonged intake of higher-than-recommended amounts of copper, such as in water or copper supplements, can cause serious diseases, such as kidney and liver damage [25], chronic renal disease [26], and diabetic renal disease [27].

As part of the scientific support of the community, this study seeks to impact these communities through the hydrogeochemical study of groundwater used for human consumption and to relate the content of this water to the surrounding geology in order to determine its geochemical characterization and its chemical and biological quality and evaluate the risks to human health due to the presence of potentially toxic elements that the consumption of these waters may represent. This is a novel study, the first conducted in Panama, as it seeks to uncover the relationship between the geology of the site, the presence of PTEs in the groundwater of springs for human consumption, and the implication of health risks, with the aim of generating new information for decision makers for the generation of public policies on health issues such as nt-CKD and cancer in the region.

2. Materials and Methods

2.1. Study Area

Springs used for drinking water supply were selected in the municipalities of Caballero and San Juan de Dios, in the district of Antón, and the municipality of Pajonal, in the district of Penonome (Figure 1). The municipality of Caballero has an area of 41.7 km^2 and a population of 4132 inhabitants; San Juan de Dios has 56.1 km^2 and 5538 inhabitants; and Pajonal has 63.7 km^2 and 7678 inhabitants [28].

The district of Anton has certain plowable areas focused on the development of the agricultural and livestock sector; it also has rivers and streams that originate in the El Valle de Antón junction. The municipality of Pajonal also stands out for its citrus fruit, vegetable, and vegetable crops, as well as its livestock production [29].

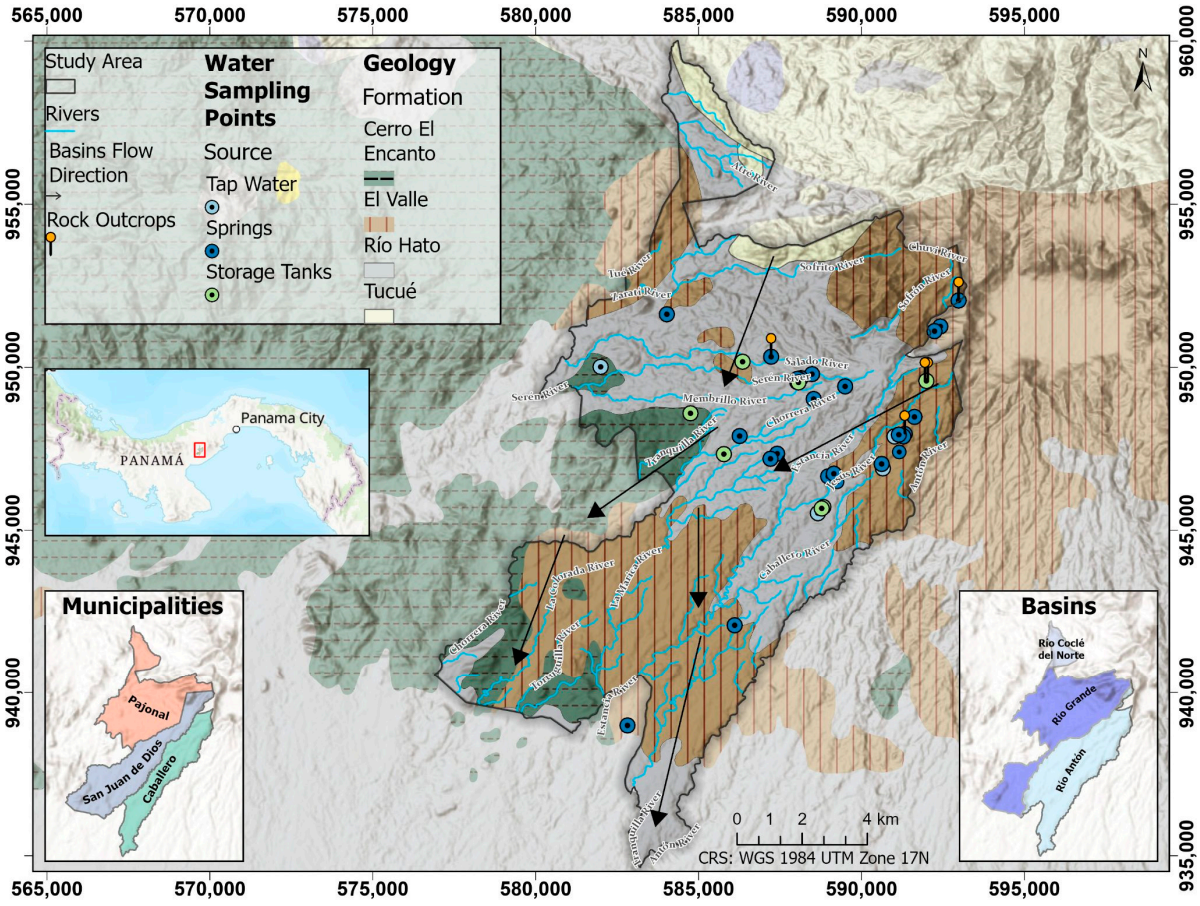


Figure 1. Study area and sampling sites.

The Caballero and San Juan de Dios municipalities belong to the Anton River basin, and Pajonal belongs to the Grande River basin. The direction of movement of the surface waters is from north to southwest, flowing into the Pacific Ocean [29]—the same flow orientation as the groundwater in the area according to isotopic modeling, where it flows directly from the Central Cordillera towards the base of the fan-shaped runoff [30]. The area is characterized by a sub-equatorial climate with a dry season, with an average annual rainfall of 2401–2700 millimeters and an average annual temperature of 25.6–26 degrees Celsius. In addition, the region has a forest cover of the intervened forest type and lowland stubble (0 to 500 m above sea level (masl) in the Caribbean Sea; 0 to 700 masl in the Pacific Ocean) [29].

Three geological formations converge in the study region. El Valle, occurring in the municipalities of Caballero, San Juan de Dios, and Pajonal, has volcanic formations of dacites, breccias, plugs, ignimbritic flows, pumices, fine tuffs, andesites, and basalts. Río Hato, distributed along Caballero, Pajonal, and San Juan de Dios, has sedimentary formations of conglomerates, sandstones, shales, tuffs, semi-consolidated sandstones, and pumice. And lastly, Cerro El Encanto, located mainly in San Juan de Dios and Pajonal, has volcanic formations of dacites, rhyodacites, ignimbrites, sub-intrusives, tuffs, and lavas [29]. The study area is within the El Valle Volcanic Complex and comprises a system of faults and/or fractures that affect the area with a main E-W direction.

The hydrogeological map of Panama has a scale of 1:1,000,000, which, in order to determine the type of aquifer, is based on the physical characteristics of the rocks in different geological formations, with the theoretical possibility of being able to contain groundwater. It is a purely qualitative criterion, which raises different hypotheses, such as alluvial sediments needing to form an aquifer layer; igneous rocks and fractured limestones constituting

aquifer networks; and igneous rocks, massive and not fractured, not containing groundwater [31]. The El Valle and Río Hato geological formations are predominantly intergranular aquifers, continuous, generally unconsolidated, of variable permeability, and of moderate productivity, with flow rates of 3 to 10 m^3 h^{-1}, with aquifers of variable extension [32]. The El Valle geological formation, made up of fragmented volcanic products of variable granulometry, has an unconfined aquifer, while the Río Hato geological formation, made up of consolidated and poorly consolidated clastic sediments, may have unconfined or confined aquifers [32].

2.2. Sample Collection

In this study, samples were taken from springs close to water bodies used as a source of water for human consumption. The springs were made into a concrete chamber, where the water from the ground is stored and sent through PVC pipes by gravity to houses or to larger reservoir tanks and then to the houses. A reservoir tank can receive water from different springs. These rural aqueduct systems do not have a treatment plant; only a chlorine tablet is administered every 15 days in a small chamber after the storage tank and before the water is delivered to the houses.

A total of 5 rock outcrops samples, 36 water samples (see Supplementary Table S1) (24 groundwater samples from springs, 1 surface water intake sample, 7 storage tanks, and 4 household taps from the groundwater from the springs), and 23 sediment samples from spring and surface water intakes (see Supplementary Table S2) were collected in the municipalities of Caballero, San Juan de Dios, and Pajonal of Cocle, Panama, during the months of October 2023 to February 2024. The samples taken from the household taps come from different springs and from different distribution networks. Three were taken in the municipality of Caballero and one in the municipality of Pajonal.

Physicochemical parameters such as pH, electrical conductivity (EC), temperature, salinity, total dissolved solids (TDSs), and dissolved oxygen (DO) were measured with multiparametric field probes (Bante 820 and Apera PC60) according to the instructions for in situ sampling of the Standard Methods for Examination of Water and Wastewater, 22nd Edition [33]. Water samples were collected in plastic containers at each water intake visited for laboratory analysis.

To determine the biological quality of the water, further portions of water samples were collected by taking a plastic container and using a brush to scrape the walls, rocks, and pipes inside the intakes to collect environmental samples for possible diatoms and filamentous algae. Then, the samples were stored in a 100 mL container, and an alcohol cap was placed on it for preservation.

Sediment samples were collected with a plastic scoop and were stored in plastic bags and identified for transport to the laboratory [34]. The rocks were taken from the outcrop sites and placed in plastic bags with their field identification data. At each of these points, data such as site coordinates, photographs, and field observations were taken.

2.3. Sample Preparation

Water and sediment samples were taken to the laboratory of the Faculty of Civil Engineering of the Universidad Tecnológica de Panamá for preparation.

A 250 mL plastic container was prepared with a portion of the sample unacidified and unfiltered for chromatographic analysis of ions (fluoride, chloride, bromide, nitrite, nitrate, phosphate, and sulfate) and alkalinity. A 100 mL plastic container was prepared with a portion of the sample acidified with nitric acid to a pH of less than two and filtered for metal assay (Al, As, Ba, Ca, Co, Cu, Fe, K, Mg, Mn, Na, Pb, Sb, Sr, V, and Zn) by the

ICP-MS technique. These tests were carried out at Activations Laboratories Ltd. (Ancaster, ON, Canada).

Sediment samples were dried in an oven at 60 °C for 24 h, then disaggregated with a wooden roller and passed through a 2 mm sieve for further analysis [34].

2.4. Laboratory Analysis

2.4.1. Macroscopic Petrographic Description

Macroscopic analysis of the rocks was performed by an expert petrographer through visual and magnifying glass inspection.

2.4.2. Sediment Analysis

Mineralogical Analysis

Ten samples were sent to Activations Laboratories Ltd. (Canada) for quantitative X-ray diffraction analysis. A portion of each powdered sample was mixed with corundum and loaded into a standard holder. Corundum was added as an internal standard. X-ray diffraction analysis was performed on a Bruker D8 endeavor diffractometer equipped with a Cu X-ray source and operating at the following conditions: 40 kV and 40 mA; range 4–70 deg 2 θ; step size 0.02 deg 2 θ; time per step 0.5 s; fixed divergence slit, angle 0.3°; and sample rotation 15 rpm. The PDF4/Minerals ICDD database was used for mineral identification. The quantities of the crystalline mineral phases were determined using the Rietveld method. The Rietveld method is based on the calculation of the complete diffraction pattern from crystal structure data. The amounts of crystalline minerals were recalculated based on the known percentage of corundum, and the remainder, up to 100%, was poorly crystalline and amorphous material.

Physicochemical Analysis

Physicochemical analyses were conducted on the sieved sample; in particular, pH, total dissolved solids (TDSs), and electrical conductivity (EC) were determined in a 1:5 suspension (w/v) [35] with a multiparameter RCYAGO. Organic matter (OM) was established by weight loss at 440 °C [36] in a Hobersal HD150 furnace. Tests of particle size distribution in soils were performed according to ASTM D 7928 [37], and a permeability test of granular soils by the constant load method was conducted [38].

All the sieved samples were sent to Activations Laboratories Ltd. (Canada). Metals (n = 23) were determined by partial digestion with aqua regia using a microprocessor hotbox to analyze pseudo-total concentrations [39–41]. In the extracts, the metals Al, As, Ba, Ca, Cd, Co, Cr, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, V, and Zn were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with certified reference materials Oreas 922 and Oreas 907, which were also digested and analyzed in duplicate. In terms of accuracy, the certified reference materials had recovery percentages of 90–100%. Carbonates and sulfates (n = 10) were determined by Infrared with the certified reference material RTS-3a, with recovery percentages ranging from 95 to 100%. For quality control, blanks, controls, and duplicates were also analyzed in all the analyses. In terms of precision, the relative standard deviation (RSD) for all replicates was <10%. The limits of quantification (LQs) for the different tests are pH = 0.01, EC = 0.001 dS m^{-1}, OM = 0.01 %, $CaCO_3$ = 0.02%, SO_4 = 0.05%, Al = 0.01%, As = 0.50 mg kg^{-1}, Ba = 1.00 mg kg^{-1}, Ca = 0.01%, Cd = 0.10 mg kg^{-1}, Co = 0. 10 mg kg^{-1}, Cr = 1.00 mg kg^{-1}, Cu = 0.20 mg kg^{-1}, Fe = 0.01%, Hg = 0.01 mg kg^{-1}, Mn = 1.00 mg kg^{-1}, Ni = 0.10 mg kg^{-1}, Pb = 0.10 mg kg^{-1}, Sb = 0.10 mg kg^{-1}, Se = 0.50 mg kg^{-1}, V = 2.00 mg kg^{-1} and Zn = 1.00 mg kg^{-1}.

2.4.3. Water Analysis

Physicochemical Analysis

The samples (n = 36) were sent to Activations Laboratories Ltd. (Canada) for the analysis of metals (Al, As, Ba, Ca, Co, Cu, Fe, K, Mg, Mn, Na, Pb, Sb, Sr, V, Zn) by ICP-MS, with certified reference material IV-STOCK-1643, of anions (chlorides, sulfates, and nitrates) by ion chromatography [42] with IC Ref Std, and of alkalinity by potentiometric titration. In terms of accuracy, the certified reference materials had recovery percentages of 95 to 100%. For quality control, blanks, controls, and duplicates were also analyzed in all the analyses. In terms of precision, the relative standard deviation (RSD) for all replicates was <10%. The limits of quantification (LQs) for the different tests are pH = 0.01, TDS = 0.01 mg L^{-1}, OD = 0.01 mg L^{-1}, Na = 0.01 mg L^{-1}, Ca = 0.70 mg L^{-1}, Mg = 0.01 mg L^{-1}, K = 0.03 mg L^{-1}, Cl = 0.03 mg L^{-1}, NO_3 = 0.01 mg L^{-1}, SO_4 = 0.03 mg L^{-1}, CO_3 = 1.00 mg L^{-1}, HCO_3 = 1.00 mg L^{-1}, Al = 2.00 µg L^{-1}, As = 0.03 µg L^{-1}, Ba = 0.10 µg L^{-1}, Co = 0.01 µg L^{-1}, Cu = 0.20 µg L^{-1}, Fe = 10.00 µg L^{-1}, Mn = 0.10 µg L^{-1}, Pb = 0.01 µg L^{-1}, Sb = 0.01 µg L^{-1}, Sr = 0.04 µg L^{-1}, V = 0.10 µg L^{-1} and Zn = 0.50 µg L^{-1}.

Microbiological Analysis of Water

A part of the water samples, 10 out of 24, from the springs and stream samples, were selected for microbiological analysis to determine the presence of diatoms as an indicator of the biological quality of the water [43–45]. This selection was made based on the samples that were sent for sediment mineralogy analysis, selecting 3 to 4 samples per municipality from the different rural aqueduct boards. This analysis was carried out at the Technological University of Panama, with a microscope (Euromex iscope, Euromex Microscopen BV, Duiven, The Netherlands) with objectives 4, 10, and 40 used to analyze them. Two to three drops of the sample were taken with an eyedropper on a slide, and a coverslip was placed on the slide to place it under the microscope and analyze five different portions of each sample.

2.5. Methods

2.5.1. Geocumulation Index

Muller presented the concept of the Igeo, which is used to assess different pollution levels in soil and sediments [46]. Igeo is measured by Equation (1).

$$\text{Igeo} = \log 2 \frac{\text{Cn}}{1.5\ \text{Bn}} \quad (1)$$

In Equation (1), Cn shows measured metal contents in samples, Bn symbolizes reference or background values of metal, and 1.5 is a factor that is used to calculate possible changes in background value. In this study, the reference values used were Al = 0.64%, As = 0.025 mg kg^{-1}, Ba = 33 mg kg^{-1}, Ca = 0.20%, Cd = 0.05 mg kg^{-1}, Co = 5.8 mg kg^{-1}, Cr = 7. 0 mg kg^{-1}, Cu = 12.4 mg kg^{-1}, Fe = 3.70%, Hg = 0.05 mg kg^{-1}, Mn = 240 mg kg^{-1}, Ni = 5.0 mg kg^{-1}, Pb = 1.3 mg kg^{-1}, Sb = 0.05 mg kg^{-1}, Se = 0.8 mg kg^{-1}, V = 76 mg kg^{-1}, and Zn = 43 mg kg^{-1}. These values correspond to the sediment sample from the Árbol de Pan spring (code APY11-23S), which belongs to the Río Hato geological formation. In general terms, this sample shows the lowest metal concentrations in the study area, making it a useful reference for assessing the enrichment levels of the elements of interest in the studied municipalities (Table S2).

According to Müller [11], the Igeo values are divided into classes that represent a type of sediment quality, the definitions for which are listed in Table 1.

Table 1. Classification of Geoaccumulation Index by Müller.

Igeo	Class	Sediment Quality
<0	0	Uncontaminated
0–1	1	Uncontaminated to moderately contaminated
1–2	2	Moderately contaminated
2–3	3	Moderate to heavily contaminated
3–4	4	Heavily contaminated
4–5	5	Heavily to extremely contaminated
>5	6	Extremely contaminated

2.5.2. Hydrochemical Characterization

The Piper hydrochemical diagram was made using the Diagramme program, which made it possible to classify and characterize the water samples, highlighting the anion and cation contents. The Piper diagram, widely used in hydrochemical studies, facilitates the representation of the hydrochemical facies of the samples.

2.5.3. Water Quality Index

The WQI was calculated using the weighted arithmetic index technique, using thirteen significant physicochemical parameters (pH, TDS, DO, Al, As, Ba, Cu, Fe, Mn, Na, Pb, Sb, Zn) comparing these in relation to their suitability for human consumption, based on the values established in the Panamanian drinking water standard [47], using the formula of Tiwari et al., (2015) [48,49], by Equations (2)–(5).

$$qi = \frac{Vi}{Si} \times 100 \quad (2)$$

where qi is the quality rating scale of ith parameter, Vi is the concentration of ith parameter, and Si is the standard permissible value of ith parameter.

$$K = \frac{1}{\sum(1/Si)} \quad (3)$$

where K is the proportional constant, and Si is the standard permissible value of ith parameter.

$$wi = \frac{K}{Si} \quad (4)$$

where wi is the unit weight factor of ith parameter, K is the proportional constant, and Si is the standard permissible value of ith parameter.

$$WQI = \sum_{i=1}^{n} wi \times qi \quad (5)$$

where WQI is the water quality index, wi is the unit weight factor of the ith parameter, and qi is the quality rating scale of the ith parameter.

The quality of water based on a WQI may be categorized into five categories, including excellent, good, poor, very poor, and unfit, as shown in Table 2 [49].

Table 2. Categories of water quality index: value, ratings and usage.

WQI Value	Water Quality Ratings	Usages
0–25	Excellent	Drinking, irrigation, and industrial
26–50	Good	Domestic, irrigation, and industrial
51–75	Poor	Irrigation
76–100	Very Poor	Restricted use for irrigation
>100	Unfit, unsuitable for drinking	Proper treatment required before use

2.5.4. Human Health Risk Assessment

The assessment of human health risks is a fundamental tool in decision-making processes aimed at minimizing adverse effects. In this study, a probabilistic approach was used for risk evaluation. This approach generates a distribution of potential exposure values. In this methodology, parameters are described by their distributions, accounting for the randomness and uncertainty inherent in the data.

The potential risks were quantified in terms of non-carcinogenic and carcinogenic risks. A residential scenario was considered, where both adults and children were exposed through water ingestion and dermal contact. The average daily dose (ADD) was estimated using the equations proposed by the United States Environmental Protection Agency [50] in Equations (6) and (7).

$$\mathrm{ADD_{ingestión}} = \frac{\mathrm{C_i} \times \mathrm{EF} \times \mathrm{IR} \times \mathrm{ED}}{\mathrm{AT} \times \mathrm{BW}} \quad (6)$$

$$\mathrm{ADDI_{dermal\_contact}} = \frac{\mathrm{C_i} \times \mathrm{EF} \times \mathrm{ET} \times \mathrm{ED} \times \mathrm{SA} \times \mathrm{kp}}{\mathrm{AT} \times \mathrm{BW}} \quad (7)$$

where C_i is the PTE concentration in water (μg/L); EF is the annual exposure frequency (days/year); IR is the ingestion rate of water (L/day); ED is the life exposure duration (years); ET is the exposure time in the shower (h/day); SA is the skin surface area exposed (cm^2); kp is the skin permeability constant (cm/h); AT is the averaging time (days); and BW is the body weight (kg). The values of the parameters and the probability distributions used for the probabilistic risk assessment are given in Table 3. Regarding PTE concentration in waters, the probability distributions were generated in R language by bootstrap resampling, obtaining a dataset of size 1000. The probability distributions, as well as the specific exposure values, were integrated into risk equations to calculate the probabilistic ADD by ingestion of water and dermal contact with water for each recipient.

The non-carcinogenic risk was quantified in terms of Hazard Quotients (HQs) using Equation (8). The Hazard Index (HI), which represents the cumulative non-carcinogenic risk, was estimated by the sum of the HQs. The carcinogenic risk (CR) was estimated according to Equation (9), and the total carcinogenic risk (TCR) was estimated by the sum of the CRs. For HI > 1 and TCR > 1×10^{-5}, the safe exposure threshold is exceeded [51]. The values of Reference Dose (RfD) and Slope Factor (SF) used in this study (Table 3) were collected from Risk Assessment Information System (RAIS) website [52]. The cancer risk was assessed for As and Pb, which have slope factors reported.

$$\mathrm{HQ} = \frac{\mathrm{ADD}}{\mathrm{RfD}} \quad (8)$$

$$\mathrm{CR} = \mathrm{ADD} \times \mathrm{SF} \quad (9)$$

Table 3. Parameters and values used for the probabilistic assessment.

Symbol	Parameters	Point Estimate Values and Probability Distributions	References
EF	Exposure frequency—adults and children	Triangular 345 (180–365) days $year^{-1}$	[53]
ED_a	Exposure duration—adults	30 years	[54,55]
ED_c	Exposure duration—children	6 years	
ET	Exposure time of adults and children	Uniform (0.12–0.28) h day^{-1}	[56]
SA_a	Skin surface area—adults	Normal (18,400 ± 2300) cm^2	[55,55]
SA_c	Skin surface area—children	Normal (6800 ± 600) cm^2	
Bw_a	Body weight—adults	Normal (72 ± 15.9) kg	[56]
Bw_c	Body weight—children	Normal (15.6 ± 3.7) kg	[57,58]

Table 3. *Cont.*

Symbol	Parameters	Point Estimate Values and Probability Distributions	References
IR_a	Ingestion rate of water—adults	2.04 L day^{-1}	[55]
IR_c	Ingestion rate of water—children	1.28 L day^{-1}	
AT_{nc}	Averaging time—non-carcinogen	365 × ED	[51]
AT_{ca}	Averaging time—carcinogen	365 × 70	[51]
K_p	Permeability constant (cm $hour^{-1}$)	Al, As, Ba, Cu, Fe, Mn, Pb, Sr, and V = 0.001, Co = 0.0004, and Zn = 0.0006	[59]
RfD	Reference dose (mg kg^{-1} day^{-1})	Al = 1, As = 0.0003; Ba = 0.20, Fe = 0.7, Co = 0.0003, Cu = 0.04; Mn = 0.14, Pb = 0.0035; Sr = 0.60, V = 0.01, Zn = 0.3	[59]
SF	Slope factor (kg day mg^{-1})	As = 1.5, Pb = 0.0085	[59]

2.5.5. Data Processing

Microsoft 365 (office) Excel spreadsheets were used to manage the results, and the Minitab 15 program was used to analyze the statistical parameters of the analytical results. Multivariate analysis was performed by applying factor analysis and principal component analysis (PCA). The maps were produced using ArcGIS Pro 3.3.0 software.

3. Results

3.1. Rocks

Figure 2 shows the rock outcrops found near the water intakes, which are located next to faulted water bodies in the study area. Table 4 shows a macroscopic petrographic description. According to the macroscopic petrographic description, the rocks correspond to tuffs, dacite, and andesite that belong to the Rio Hato and El Valle Formations, and within this to the Rio Mar (50 thousand years) and Mata Ahogado (34 thousand years) eruptions, which are recent eruptions of the El Valle Volcanic Complex [60].

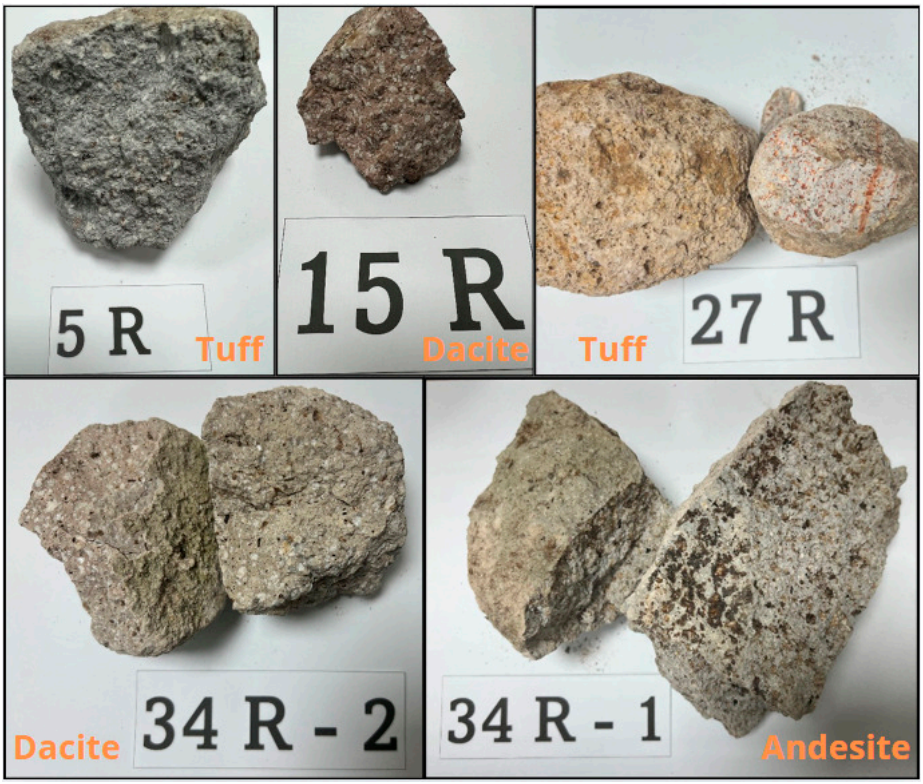


Figure 2. Images of rock outcrops near the water intakes.

Table 4. Macroscopic petrographic description of the rock outcrops.

Sample	Municipality, Site	Rock Type	Macroscopic Description
5 R	Caballero, Las Claritas	Tuff	It is an igneous rock, color N8 (very light gray); clastic structure, pyroclastic texture, with pumice fragments, little magnetite and minerals such as mica (biotite) and quartz. It has a hardness of 3 and is slightly weathered.
15 R	San Juan de Dios, La India	Dacite	Rock of volcanic origin, color 10R 6/2 (pale red); clastic structure, texture, presents mica and plagioclase. It has a hardness of 3 and a degree of weathering.
27 R	Pajonal, La Mina	Tuff	It is an igneous rock, color 10YR 8/2 (very pale orange); clastic structure, pomiseous scoriaceous texture, with presence of pumice, hematitic oxidations and minerals such as mica and quartz. It has a hardness of 1 and is moderately weathered.
34 R1	Caballero, Campana	Andesite	Igneous rock, color N8 (very light gray); clastic structure, texture, made up of plagioclase crystals, hornblende and biotite. It has a hardness of 6 and is slightly to moderately weathered.
34 R2	Caballero, Campana	Dacite	Rock of volcanic origin, color 5R 8/2 (grayish pink); fine-grained structure, porphyritic texture, with quartz, hornblende and plagioclase. It has a hardness of 3 and a degree of weathering.

3.2. Sediments

3.2.1. Mineralogical Analysis

Figure 3 shows the box plot for the abundance of sediment minerals in the water intakes. As can be seen, the most abundant mineral is plagioclase with a percentage abundance between 26.6% and 73.4%; quartz is in second place, with a percentage abundance between 17.4% and 36. 0%; third place is amorphous with abundance between 5.0% and 33.6%; feldspar with a maximum value of 6%, and then amphibole with abundance between 2.8% and 6.5%; and, in lower abundance, magnetite (0.5 to 1.1%), serpentine (trace to 5.0%), and mica (trace to 0.5%). Magnetite may include other spinel minerals.

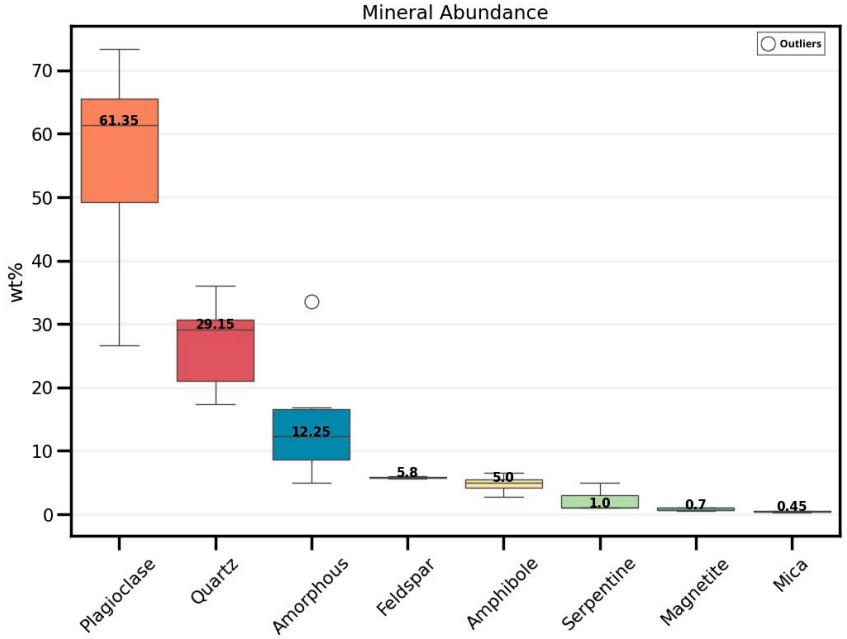


Figure 3. Box plot for the abundance of sediment minerals in the water intakes.

3.2.2. Physicochemical Analysis

Table 5 shows the statistical summary of the concentrations of the physicochemical parameters analyzed in the sediment samples from the water intakes; the sample data

are presented in Table S2. The most abundant elements in these samples are Fe with a mean value of 3.82%, Al with 1.33%, and Ca with 0.41%. In lower concentrations, we have mean values of 354.45 mg kg^{-1} Mn, 82.35 mg kg^{-1} V, 63.30 mg kg^{-1} Ba, 62.65 mg kg^{-1} Zn, 23.83 mg kg^{-1} Cu, 9.65 mg kg^{-1} Cr, and 7.74 mg kg^{-1} Co. In mean trace values, we have 0.93 mg kg^{-1} Se, 0.31 mg kg^{-1} As, 0.05 mg kg^{-1} Sb, and 0.01 mg kg^{-1} Hg. As for anions, the samples contain $CaCO_3$ in a range of 0.01 to 1.82% and a SO_4 composition of 0.03%.

Table 5. Statistical summary of the concentrations of physicochemical parameters analyzed in sediment samples.

	pH	EC dS m^{-1}	OM %	$CaCO_3$ %	SO_4 %	Al %	As mg kg^{-1}	Ba mg kg^{-1}	Ca %	Cd mg kg^{-1}	Co mg kg^{-1}	Cr mg kg^{-1}	Cu mg kg^{-1}	Fe %	Hg mg kg^{-1}	Mn mg kg^{-1}	Ni mg kg^{-1}	Pb mg kg^{-1}	Sb mg kg^{-1}	Se mg kg^{-1}	V mg kg^{-1}	Zn mg kg^{-1}
Mean	6.87	0.036	1.70	0.47	<0.05	1.33	0.31	63.30	0.41	<0.10	7.74	9.65	23.83	3.82	0.01	355.45	8.94	1.88	<0.10	0.93	82.35	62.65
Min	5.78	0.009	0.20	<0.02	<0.05	0.64	<0.50	33.00	0.20	<0.10	1.70	2.00	12.40	0.96	0.01	124.00	2.10	1.00	<0.10	0.70	15.00	20.00
p95	7.59	0.082	4.78	1.37	<0.05	2.61	0.62	96.30	0.62	<0.10	15.29	22.6	38.25	8.38	0.02	578.50	21.34	3.14	<0.10	1.10	203.15	137.10
Max	9.12	0.196	7.60	1.82	<0.05	3.72	1.00	178.00	0.65	<0.10	30.30	34.0	41.0	16.9	0.03	1120.0	39.10	3.90	0.10	1.10	415.00	234.00
SD	0.65	0.038	1.79	0.54	0.00	0.76	0.18	31.52	0.14	<0.10	6.33	7.60	8.26	3.53	0.01	221.20	8.53	0.72	0.01	0.12	90.37	49.06
LQ	0.01	0.001	0.01	0.02	0.05	0.01	0.50	1.00	0.01	0.10	0.10	1.00	0.20	0.01	0.01	1.00	0.10	0.10	0.10	0.50	2.00	1.00

Notes: EC, electrical conductivity; OM, organic matter; SD, standard deviation; LQ, limit of quantification.

Panama does not have sediment quality standards, so we have compared the average sediment values from this study with the values presented in Table 6, which shows guide values for freshwater sediments in Ontario, Canada [61], and values from other sediment studies in Panama [62]. The mean values for As (0.31 mg kg^{-1}), Cd (0.05 mg kg^{-1}), Cr (9.65 mg kg^{-1}), Mn (355.45 mg kg^{-1}), Ni (8.94 mg kg^{-1}), Pb (1.88 mg kg^{-1}), and Zn (62.65 mg kg^{-1}) were lower than the Canadian sediments, while Cu (23.83 mg kg^{-1}) and Fe (3.82 mg kg^{-1}) were higher. For the study of sediments from the Santamaría River basin in Panama [62], the values of this study were lower but higher for Fe, Mn, Ni, Pb, and Zn than the study of Villarreal et al. (2018) [63] of La Villa River basin in Panama.

Table 6. Sediment guideline values in Canada and values from other sediment studies in Panama.

Parameter	Canada Standard [61]	Santamaría River [62]	La Villa River [63]
	mg kg^{-1}		
As	6	-	8.01
Cd	0.6	-	0.34
Co	-	-	-
Cr	26	-	78.5
Cu	16	46.16	26.4
Fe	2	-	1.73
Mn	460	-	46.1
Ni	16	13.8	2.44
Pb	31	4.57	1.78
Zn	120	114.24	59.8

Table 7 shows the summary statistics of the texture and permeability test of the samples studied. The sediment samples in this study were all sandy loam in texture, with mean values of 73.90% sand, 19.24% silt, and 1.82% clay.

The permeability coefficient (k) is a measure of how fast water passes through a unit of soil surface when there is a unit of hydraulic gradient, so it is a key factor in geotechnical engineering, as it affects the physical and mechanical properties of the soil [64]. In this study, k had a minimum value of 3.95×10^{-3} and a maximum value of 3.79×10^{-1}, which corresponds to a medium permeability degree typical of fine gravel to coarse gravel materials [65]; this agrees with the sandy loam texture of the sediments.

Table 7. Summary statistics for the texture and permeability test on the study samples. Abbreviations: k, permeability coefficient at 20 °C.

	Sand %	Silt %	Clay %	k cm seg^{-1}
Mean	73.90	19.24	1.82	8.47×10^{-2}
Min	55.30	12.90	0.10	3.95×10^{-3}
p95	85.70	30.78	9.82	3.07×10^{-1}
Max	85.70	33.50	15.20	3.79×10^{-1}
SD	10.33	5.59	3.66	1.64×10^{-1}

The soil texture of the study area is sandy loam with a high percentage of sand, which produces a soil permeability capacity of medium grade, typical of fine-to-coarse gravel materials [65] and typical of sedimentary soils with tuffs in the area [29], which allow for rapid infiltration; therefore, special care must be taken with the activities that take place near the water catchment area, because if there are anthropogenic activities on the surface, for example, the agricultural activities observed in the field work (planting vegetables), the fertilizers and products used will reach the soils and from there to the aquifers.

3.2.3. Multi-Elemental Analysis

Figure 4 presents the PCA of the relationships between potentially toxic elements (As, Co, Cu, Pb), minerals, and physicochemical parameters measured in ten (10) sediments of the water intakes. According to the table of the strength of the relationships (Table 8), the most significant relationships are as follows: for the first principal component (PC1), As (0.071) is positively related to feldspar (0.052) and negatively related to magnetite (−0.072); positively related to Co (0.159) with serpentine (0.115); positively related to Cu (0.085) with mica (0.098); positively related to Pb (0.271) with amorphous (0.254) and negatively related with plagioclase (−0.286) and amphibole (−0.259). In the second principal component (PC2), As has a negative relationship (−0.162) and is opposite to Mn (0.162) and Ni (0.163); Co (0.041) is positively related to Pb (0.049) and $CaCO_3$ (0.050); and Cu (0.333) is positively related to mica (0.300) and Ca (0.325).

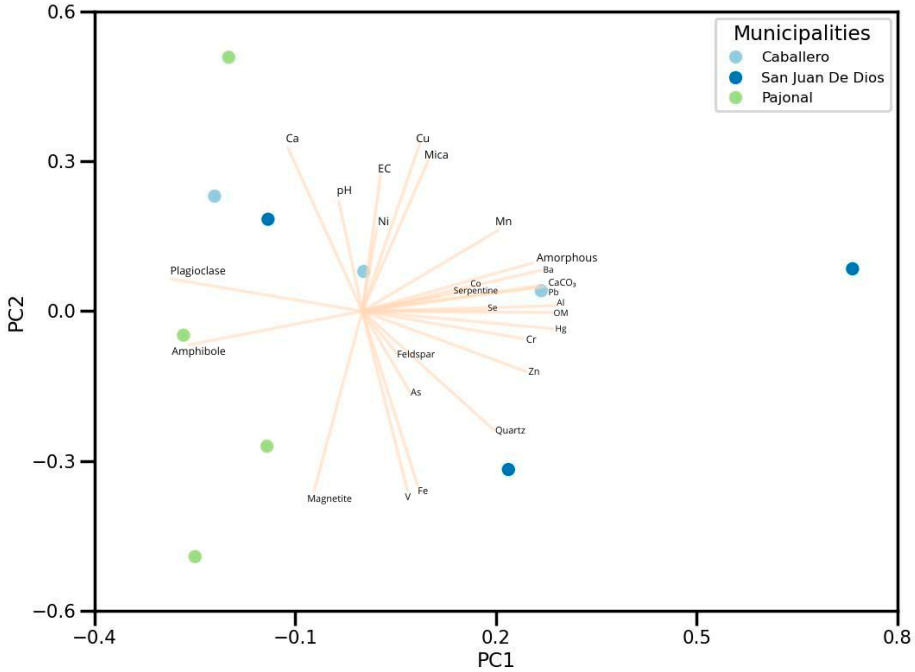


Figure 4. PCA of the relationships between potentially toxic elements (As, Co, Cu, Pb), minerals, and physicochemical parameters measured in the sediments of the water intakes.

Table 8. Principal component analysis matrix for the relationship between potentially toxic elements (As, Co, Cu, Pb), minerals, and physicochemical parameters in the sediments of water intakes. Bold numbers correspond to PC1 or PC2 and are more significant.

Variable	PC1	PC2
Quartz	0.197	−0.238
Plagioclase	**−0.286**	0.064
Feldspar	**0.052**	−0.085
Amphibole	**−0.259**	−0.067
Mica	**0.098**	**0.300**
Serpentine	**0.115**	0.031
Magnetite	**−0.072**	−0.359
Amorphous	**0.254**	0.097
pH	−0.035	0.218
EC	0.027	0.272
OM	0.285	−0.003
Texture	0.000	0.000
$CaCO_3$	0.265	**0.050**
SO_4	0.000	0.000
Al	0.289	0.011
As	**0.071**	**−0.162**
Ba	**0.267**	0.082
Ca	−0.111	**0.325**
Cd	0.000	0.000
Co	**0.159**	**0.041**
Cr	0.240	−0.055
Cu	**0.085**	**0.333**
Fe	0.082	−0.348
Hg	0.285	−0.035
Mn	0.203	**0.162**
Ni	0.021	**0.163**
Pb	**0.271**	**0.049**
Sb	0.000	0.000
Se	0.184	0.001
V	0.067	−0.357
Zn	0.245	−0.121

The relationships between minerals and PTEs (As, Co, Cu, Pb) shown in the PCA diagram are verified in the literature, where As is part of feldspar [66], Cu of mica [67], Co of serpentine [68], and Pb of amorphous [69]. The rock outcrops found near the water intakes correspond to tuffs, dacites, and andesites, which are formed among other minerals by feldspar and mica, and these minerals have been found in the sediments of the water intakes, while minerals such as serpentine and amorphous may come as a pluton process from the deep part or a hydrothermal process, according to the Bowen series [70], forming anomalies of little importance.

The PCA diagram shows how the samples are grouped according to their origin and municipality. It is observed that the Pajonal sediment samples are grouped in the lower left part, while those from Caballero and San Juan de Dios are distributed in the upper quadrants. A sample from Pajonal is different, being in the upper left quadrant; a sample from San Juan de Dios is different, being in the lower right quadrant.

3.2.4. Geocumulation Index

Igeo was used to observe in which zones there was greater geoaccumulation of the elements in order to associate them with the geological formations of the study area.

The Igeo values of all sampling sites and elements of this study are presented in Figure 5. Elements with an Igeo < 0 are As, Cd, Fe, Hg, Sb, Se, V, and most of the Cr, Co, Mn, Ni, Pb, and Zn; many of them have certain anomalous values, above zero. Elements

with Igeo < 1 are Al, Ba, Ca, Cu, and part of Mn, Ni, Pb, and Zn. Elements that present a small fraction Igeo < 2 are Al, Ca, Cu, Mn and Ni.

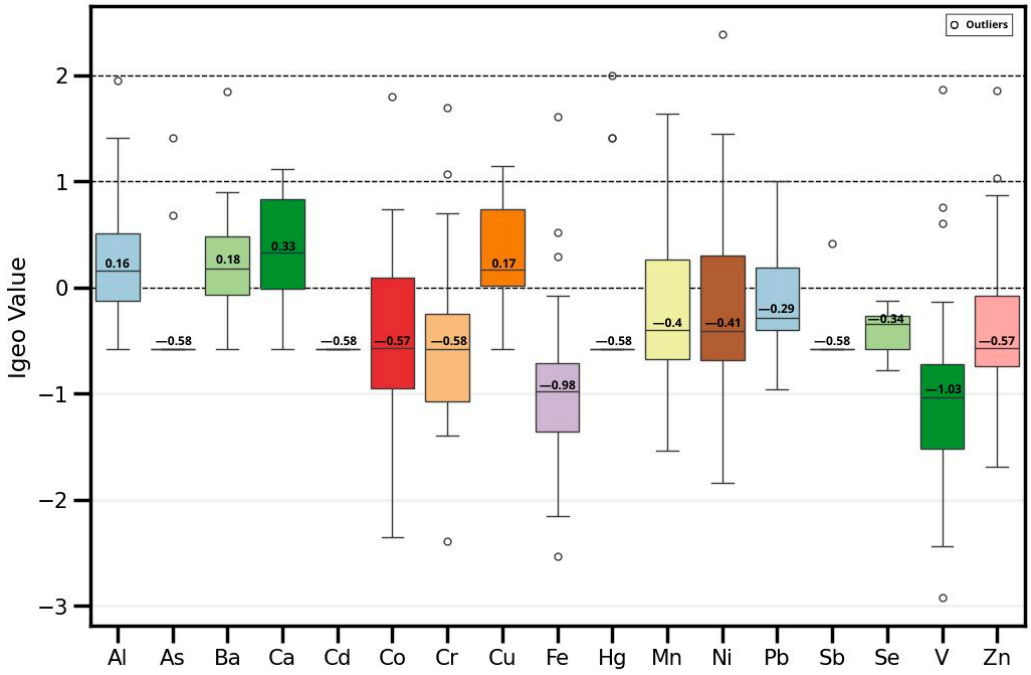


Figure 5. Box plot for the Igeo value for the elements of the study in sediments. Black lines represent sediment quality classes: <0 uncontaminated, <1 uncontaminated to moderately contaminated, <2 moderately contaminated.

Figure 6 shows the spatial distribution of the mean value of Igeo for As, Co, Cu, and Pb in the municipalities of Caballero, San Juan de Dios, and Pajonal. These elements are potentially toxic and come from the erosion of natural deposits [71] typical of the geology of the El Valle Volcanic Complex. For the calculation of the Igeo, a sediment sample from the municipality of Pajonal, belonging to the Río Hato formation, was used as a background. As shown in Figure 6, the El Valle formation in the northeastern part of the study area, and close to the volcano crater, is the most enriched in Co and Pb, while Cu is enriched in both formations (Rio Hato and El Valle), and As anomalies appear in the El Valle formation.

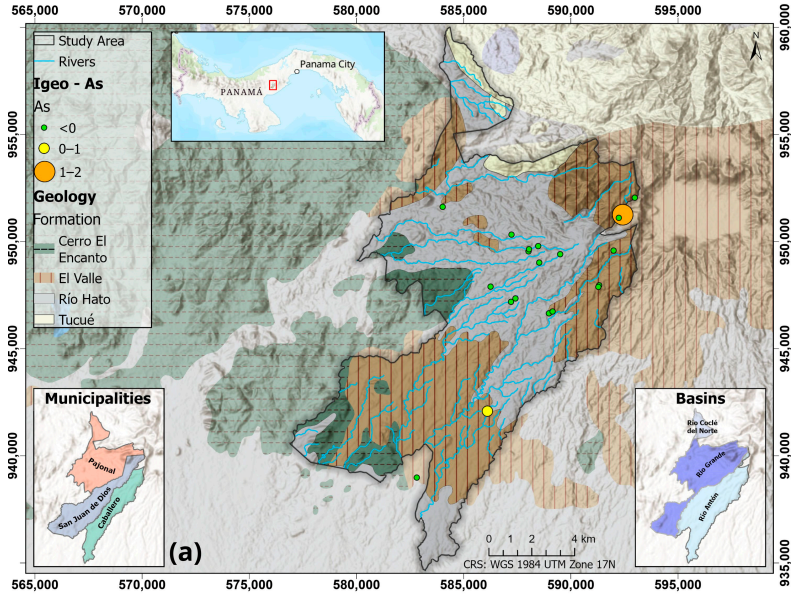


Figure 6. *Cont.*

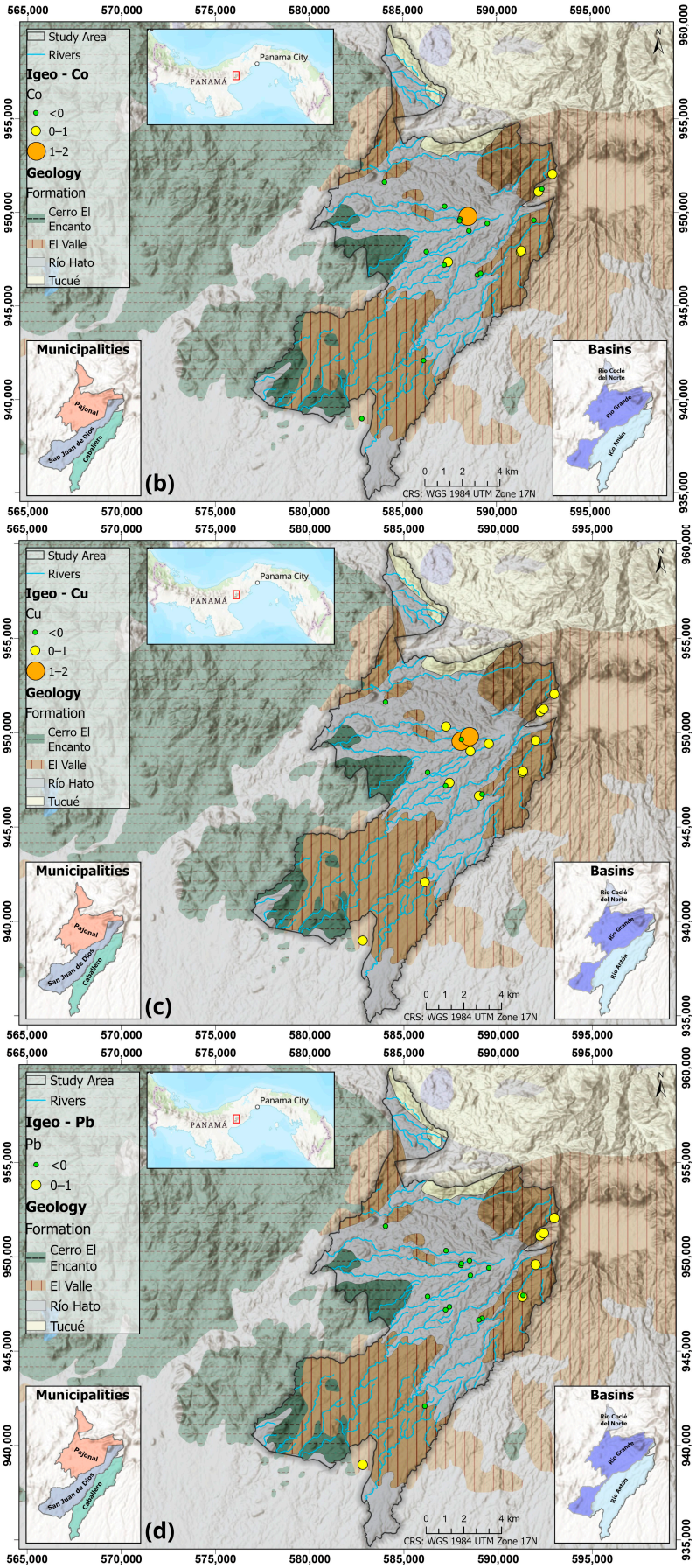


Figure 6. Spatial distribution of mean values of Igeo for (**a**) As, (**b**) Co, (**c**) Cu, and (**d**) Pb in the municipalities of Caballero, San Juan de Dios, and Pajonal.

3.3. Water

3.3.1. Physicochemical Analysis

Table 9 shows the statistical summary of the concentrations of the physicochemical parameters analyzed in the water samples of this study; the sample data are presented in Table S1. Table 10 shows the guideline values of Panamanian standards for drinking water [72] and other uses [73,74] and international standards for drinking water from the World Health Organization (WHO) [75] and the U.S. Environmental Protection Agency (USEPA) [71]

Table 9. Statistical summary of the concentrations of physicochemical parameters analyzed in water samples.

	pH	TDSs	OD	Na	Ca	Mg	K	Cl	NO_3	SO_4	CO_3	HCO_3	Al	V	Mn	Fe	Cu	Co	Zn	Sr	As	Sb	Ba	Pb
						mg L^{-1}												μg L^{-1}						
Min	6.03	60.50	2.83	6.08	4.60	0.82	0.79	3.01	0.02	0.08	<1.00	43.00	6.00	0.80	< 0.10	< 10.00	1.10	<0.01	1.70	90.90	<0.03	0.02	4.60	0.03
p50	6.45	85.63	6.11	11.85	8.75	2.10	3.14	3.92	0.15	0.38	<1.00	58.50	21.50	1.75	1.70	20.00	2.10	0.02	5.05	190.50	0.10	0.03	48.70	0.25
p95	7.34	111.50	8.76	14.75	12.93	3.75	4.19	5.50	0.36	0.70	<1.00	74.30	88.75	2.75	10.65	197.50	9.08	0.07	16.30	272.50	0.18	0.06	79.55	1.42
Max	8.08	325.00	9.30	15.60	14.60	4.03	4.49	5.51	0.45	0.75	<1.00	77.00	214.00	5.00	22.20	470.00	17.70	0.24	90.20	307.00	0.22	0.09	100.00	5.04
SD	0.46	42.48	1.81	2.11	2.38	0.88	0.98	0.91	0.13	0.24	0.00	10.70	38.85	0.73	4.47	94.10	3.23	0.04	14.55	54.97	0.04	0.01	23.31	0.87
LQ	0.01	0.01	0.01	0.01	0.70	0.01	0.03	0.03	0.01	0.03	1.00	1.00	2.00	0.10	0.10	10.00	0.20	0.01	0.50	0.04	0.03	0.01	0.10	0.01

Notes: TDSs, total dissolved solids; DO, dissolved oxygen; SD, standard deviation; LQ, limit of quantification.

Table 10. Water quality guide values for Panamanian and international standards.

Parameter	Drinking Water [72]	Recreational Use (Direct Contact) [73]	Irrigation Water [74]	Aquaculture Water [74]	Drinking Water According to the WHO [75]	Drinking Water According to the USEPA [71]
	mg L^{-1}					
pH	6.5–8.5	6.5–8.5	6.0–9.0	6.0–9.0	-	-
TDS	500	<500	-	-	-	-
OD	-	>7.0	-	>5.0	-	-
NO_3	10	-	-	-	50	10
SO_4	250	-	350	-	500	-
Na	200	-	35%	-	200	-
K	-	-	-	-	3000	-
Cl	250	-	200	-	250	-
Al	0.2	-	5.0	0.1	0.1–0.2	-
V	-	-	0.1	-	-	-
Mn	0.1	-	0.2	-	0.4	-
Fe	0.3	-	5.0	0.3	2.0	-
Cu	1.0	-	0.002	0.002	2.0	1.3
Co	-	-	0.05	-	-	-
Zn	5.0	-	2.0	0.03	3.0	-
As	0.01	<0.1	0.1	0.05	0.01	0.05
Sb	0.05	-	-	-	0.02	0.006
Ba	0.7	-	4.0	-	1.3	2.0
Pb	0.01	<0.05	5.0	0.002	0.01	0.0

For pH, the samples ranged from 6.03 to 8.08, with some samples below the pH range established for drinking water (6.5 to 8.5); for TDS, the maximum value was 325 mg L^{-1}, so they all comply with the standard for drinking water in Panama. Low dissolved oxygen (DO) values were observed at the intakes (2.83 mg L^{-1}), whereas, as its gravity flows down to the storage tanks, the DO rises to 9.30 mg L^{-1}. The rest of the parameters comply with the values established in the Panamanian drinking water standard (human consumption and animal consumption in contact with humans and for human consumption) [72], as well as by the USEPA [71] and the WHO [75], except for Fe in Los Pozos (0.47 mg L^{-1} Fe) and El Barnizal (0.31 mg L^{-1} Fe) water intakes in the municipality of Caballero, where they exceed the value of 0.30 mg L^{-1} Fe for the Panamanian drinking water standard [72]. Pb in all samples exceeds the safety value above which no risk to human health is expected, which is zero mg L^{-1} from the USEPA [71].

As for other uses that can be given to these waters, the samples comply with the standard for recreational use with direct contact [73] and the standard for irrigation waters of Panama [74]. For aquaculture use [74], some samples do not comply with the established limit for Al (0.1 mg L^{-1}), Fe (0.3 mg L^{-1}), Cu (0.002 mg L^{-1}), Zn (0.030 mg L^{-1}), and Pb (0.002 mg L^{-1}).

3.3.2. Hydrochemical Characterization

Figure 7 shows the Piper diagram, where it can be observed that the water from the water intakes in the municipality of Pajonal is of the sodium bicarbonate type, while those in the municipalities of San Juan de Dios and Caballero are of the calcium and magnesium bicarbonate type.

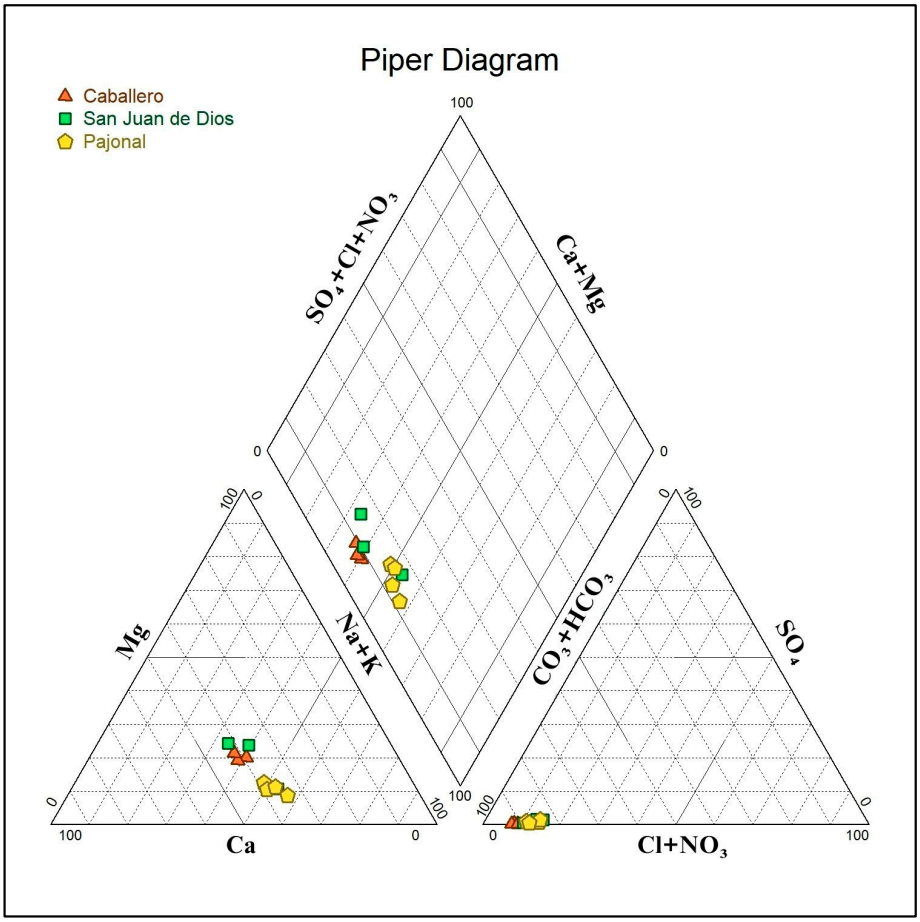


Figure 7. Hydrochemical composition of water using the Piper Diagram for each municipality.

3.3.3. Multi-Elemental Analysis

Figure 8 presents the PCA of the relationships between potentially toxic elements (As, Co, Cu, Pb) and physicochemical parameters measured in water for human consumption (n = 36). According to the table of the strength of the relationships (Table 11), the most significant relationships are as follows: for the first principal component (PC1), As (0.126) is negatively related to pH (−0.119), and positive relationships are presented between Co (0.354) and TDS (0.336); Cu (0.150) and Sb (0.162); and Pb (0.317) and V (0.320) and Fe (0.322). In the second principal component (PC2), As (−0.330) has a negative relationship with DO (0.339); Co (0.178) has a positive relationship with Fe (0.172); and Cu (−0.081) has a negative relationship with Pb (0.090).

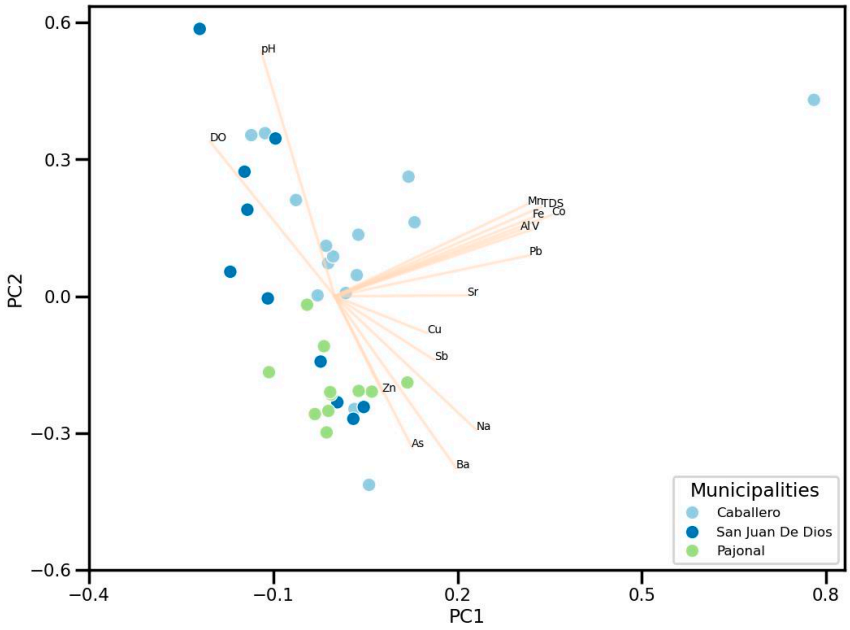


Figure 8. PCA of the relationships between potentially toxic elements (As, Co, Cu, Pb), and physicochemical parameters measured in water for human consumption.

Table 11. Principal component analysis matrix for the relationship between potentially toxic elements (As, Co, Cu, Pb) and physicochemical parameters in water for human consumption. Bold numbers correspond to PC1 or PC2 and are more significant.

Variable	PC1	PC2
pH	**−0.119**	0.535
TDS	**0.336**	0.196
DO	−0.203	**0.339**
Al	0.303	0.145
As	**0.126**	**−0.330**
Ba	0.198	−0.377
Cu	**0.150**	**−0.081**
Co	**0.354**	**0.178**
Fe	**0.322**	**0.172**
Mn	0.314	0.202
Na	0.230	−0.293
Pb	**0.317**	**0.090**
Sb	**0.162**	−0.140
Sr	0.216	0.002
V	**0.320**	0.146
Zn	0.077	−0.210

The PCA diagram shows how the samples are grouped by municipality. The samples from Pajonal are grouped in the two lower quadrants; most of the water samples from Caballero are grouped in the two upper quadrants, while those from San Juan de Dios are grouped in the upper left quadrant, and another part in the lower quadrants with similarity to those from Pajonal. This can be explained by location, since the municipality of San Juan de Dios is located between Caballero and Pajonal.

From the principal component analysis, it is observed that the slightly acidic pH of the waters promotes the increase in the dissolution of salts, dissolving elements that are abundant in the sediments such as Fe and linked to the dissolution of Fe; potentially toxic elements such as Co, Pb, Cu, and As are dissolved. On the other hand, a negative relationship between DO and As is observed, inferring that the oxygenation of the water promotes a decrease in the presence of As. It also highlights the difference between the

group of samples by municipality and their grouping according to the hydrographic basin, with the Pajonal samples from the Rio Grande Basin being different from the Caballero samples found in the Rio Anton Basin, while the samples from San Juan de Dios, which shares territory in both basins, are spaced between the two groups in the PCA diagram.

3.3.4. Microbiology Analyses

As for the biological quality of the water, we used the observation of the presence of microorganisms such as diatoms and based our analysis on the richness and abundance of these to estimate their quality [76]. Ten samples selected from the water intakes of the three municipalities were analyzed, and only one species of diatom belonging to the genus *Pinnularia* sp. was identified; the rest of the material observed was debris or residual organic matter. Due to the low diversity and abundance of diatom species and individuals observed, the type of diatom (*Pinnularia* sp.) indicates that the environment is disturbed and, qualitatively, that the biological quality of the environment is slightly contaminated.

According to the microbiological analysis of diatoms in water intakes, little diversity and abundance was found; the identified species, *Pinnularia* sp., survives in disturbed environments with slight contamination [77], which can be explained by the presence of PTEs (As, Co, Cu, Pb) that affect the proliferation of other diatom species.

3.3.5. Water Quality Index

Figure 9 shows the geospatial location of the Water Quality Index (WQI) results calculated for the different sites where water samples were taken for this study. The set of samples from the three municipalities of the study, Caballero, San Juan de Dios, and Pajonal, show an Excellent WQI [46], with a minimum value of 3.27 at the Campana water intake and a maximum value of 23.72 at the Bella Vista water intake, both from the municipality of Caballero. Two water intakes exceed the value of 25, having good water quality; these are the Chorrerita #1 water intake in San Juan de Dios with a value of 25.89 and the Los Pozos water intake in Caballero with a value of 30.10.

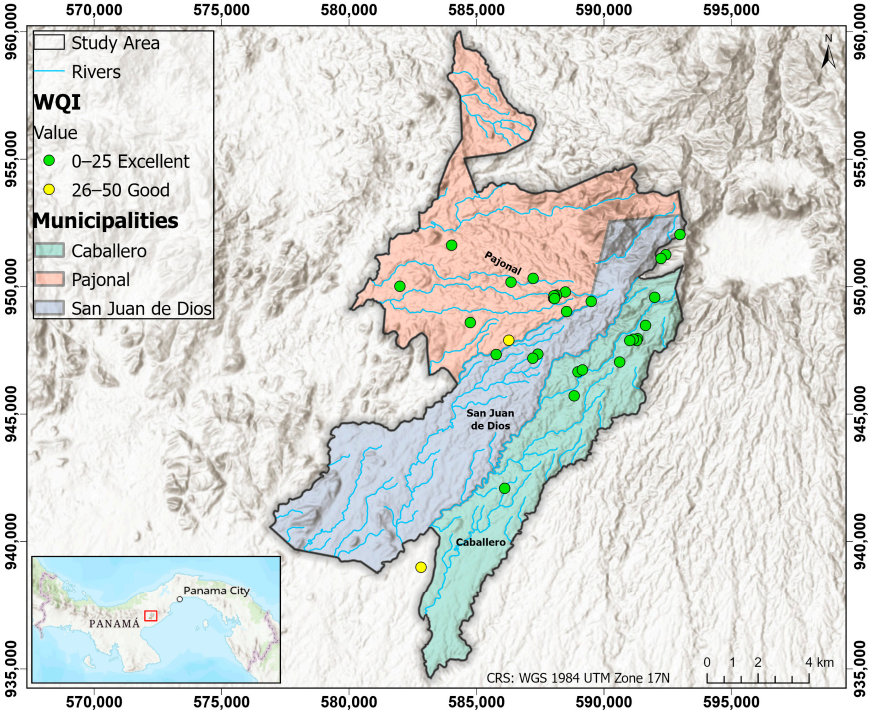


Figure 9. Geospatial location of the water quality index (WQI) results calculated for the different sites where water samples were taken for this study.

3.3.6. Probabilistic Human Health Risk Assessment

A human health risk assessment was conducted to evaluate the potential risks to inhabitants exposed to elevated concentrations of potentially toxic elements (PTEs) in groundwater used for domestic purposes or direct consumption. Both non-carcinogenic and carcinogenic risks were assessed, expressed in terms of hazard quotients (HQs) and cancer risk (CR), respectively. Probabilistic methods were used, considering both ingestion and dermal exposure pathways for children and adults in the localities of Caballero, San Juan de Dios, and Pajonal (Figure 10).

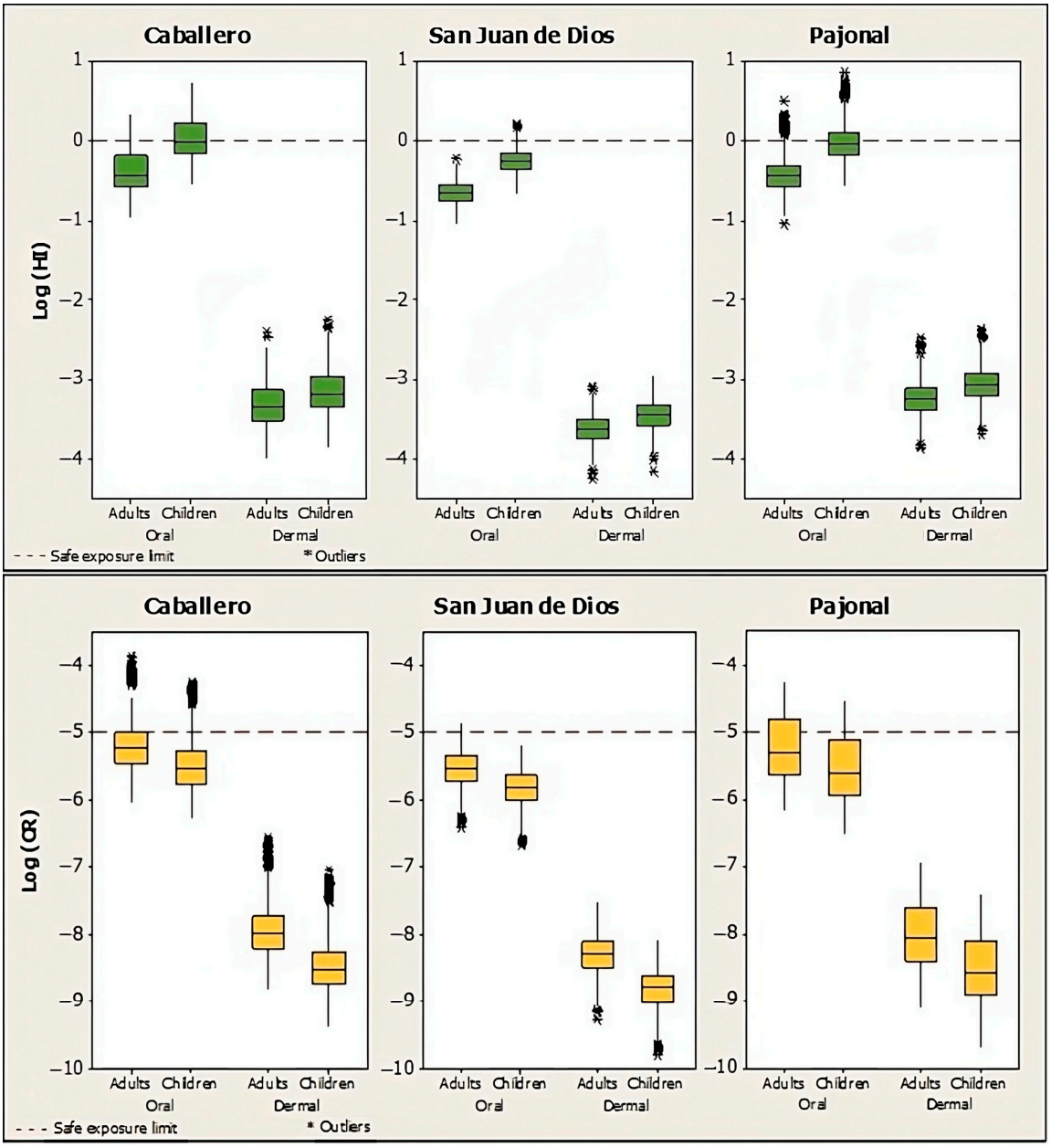


Figure 10. Non-carcinogenic (HQ) risk and carcinogenic (CR) risk by exposure route and receptor in Caballero, San Juan de Dios, and Pajonal. The red line represents the safe exposure threshold.

The results indicated that both non-carcinogenic and carcinogenic risks in Caballero and Pajonal exceeded the acceptable threshold, with water intake being the primary exposure route for both adult and child receptors. By contrast, San Juan de Dios only exhibited risk values above the safe exposure threshold for carcinogenic risk related to water ingestion.

The findings showed that both carcinogenic and non-carcinogenic risks were primarily associated with water ingestion in both age groups. Dermal exposure did not significantly contribute to either the carcinogenic or non-carcinogenic risk in children or adults at the assessed locations. The PTEs contributing to non-carcinogenic risk, in descending order, were Co > Cu > Pb > As, while Sr, Mn, Al, Zn, V, Ba, and Fe were negligible contributors to the hazard index (HI).

In Caballero, HQ values for adults ranged from 1.06×10^{-1} to 2.17 for ingestion and from 1.03×10^{-4} to 3.99×10^{-3} for dermal contact. For children, HQ values ranged from 2.19×10^{-1} to 5.28 for ingestion and from 1.42×10^{-4} to 5.49×10^{-3} for dermal routes. Regarding carcinogenic risk, CR for ingestion ranged from 9.67×10^{-7} to 1.32×10^{-4} in adults and from 5.25×10^{-7} to 5.79×10^{-5} in children, while CR for dermal contact ranged from 1.54×10^{-9} to 2.86×10^{-7} in adults and from 4.33×10^{-10} to 9.13×10^{-8} in children.

In San Juan de Dios, HQ for adults ranged from 9.03×10^{-2} to 5.86×10^{-1} for ingestion and from 5.78×10^{-5} to 8.08×10^{-4} for dermal exposure. For children, HQ values ranged from 2.13×10^{-1} to 1.60 for ingestion and from 7.19×10^{-5} to 1.09×10^{-3} for dermal exposure. For carcinogenic risk, CR for ingestion ranged from 4.06×10^{-7} to 1.40×10^{-5} in adults and from 2.15×10^{-7} to 6.40×10^{-6} in children, while CR for dermal contact ranged from 5.63×10^{-10} to 3.17×10^{-8} in adults and from 1.68×10^{-10} to 8.53×10^{-9} in children.

In Pajonal, for non-carcinogenic risk, HQ for adults ranged from 9.10×10^{-2} to 1.31 for ingestion and from 3.32×10^{-3} to 1.38×10^{-3} for dermal exposure. In children, HQ values ranged from 2.59×10^{-1} to 7.11 for ingestion and from 2.10×10^{-4} to 4.37×10^{-3} for dermal exposure. For carcinogenic risk, CR for ingestion ranged from 6.81×10^{-7} to 5.64×10^{-5} in adults and from 3.18×10^{-7} to 2.93×10^{-5} in children, while CR for dermal contact ranged from 8.08×10^{-10} to 1.16×10^{-7} in adults and from 2.01×10^{-10} to 4.16×10^{-8} in children.

The cumulative probability distributions for the HI and TCR for both receptors are shown in Figure 11. The risk levels determined by Caballero and Pajonal follow a similar trend. The HI exceeded the threshold at approximately the 55th percentile, indicating that at least 45% of child receptors are exposed to non-carcinogenic risk. For adults, the HI was above the safe limit at the 92nd percentile, meaning that 8% of adults are exposed to non-carcinogenic risk.

Regarding cancer risk, the TCR exceeded the safe exposure limit at the 92nd and 82nd percentiles for children and at the 75th and 70th percentiles for adults in Caballero and Pajonal, respectively. This indicates that in Caballero, at least 8% of children receptors are exposed to levels of cancer risk higher than acceptable, while in Pajonal, 18% of children receptors are exposed to such risks. For adults, at least 30% of the population in both locations exceeds the safe exposure threshold. On the other hand, San Juan De Dios is the locality with the lowest levels of risk for the population; fewer than 3% of adult and child receptors exposed to PTEs could develop adverse health effects from consuming groundwater. Regarding carcinogenic risk, although the risk is high in both receptors, a more significant risk is observed in adults. Although the risk of cancer in children is relatively lower, their vulnerability to the effects of carcinogens at early stages of life can have long-term consequences, making it important to monitor both age groups in the areas studied. The greater cumulative exposure in adults could explain why the carcinogenic risk is higher in this group.

Overall, the potential health risks associated with continued exposure to PTEs, particularly Co, Cu, Pb, and As, in the studied areas are evident, as both cancer and non-cancer risk values exceed the acceptable limits. Safe drinking water is a fundamental requirement for a healthy lifestyle. However, in many regions, the presence of PTEs in water poses

a significant health risk to the population. In this regard, it is crucial to establish public policies that monitor water quality, implement optimal treatment systems, communicate potential risks, and ensure the health and safety of consumers.

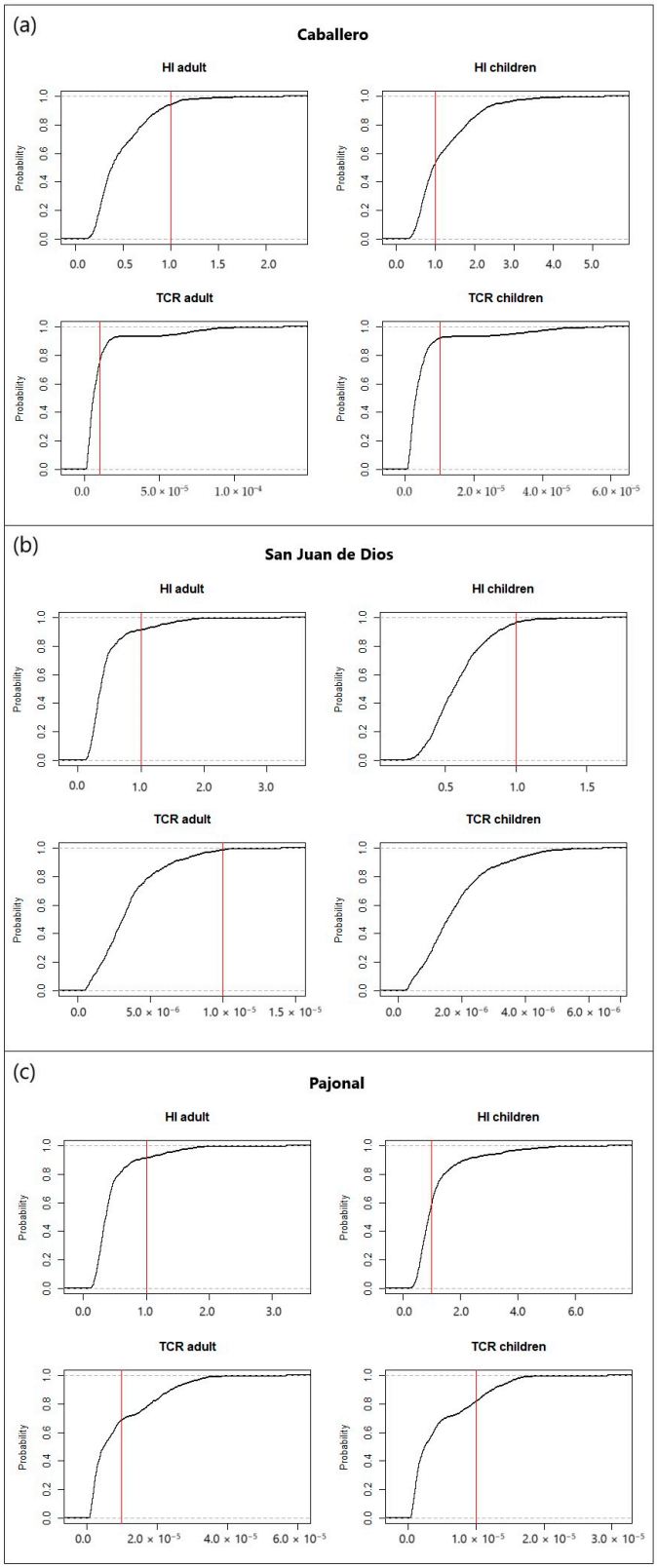


Figure 11. Cumulative probability distributions for the hazard index (HI) related to PTEs in groundwater for both receptors in (**a**) Caballero, (**b**) San Juan de Dios, and (**c**) Pajonal. The red line represents the safe exposure threshold.

4. Discussion

4.1. Potential Health Effects of PTE Exposure

The results of the carcinogenic and non-carcinogenic risk analysis indicate that, in the Caballero district, consumption of water with concentrations of As, Co, Cu, and Pb could lead to significant adverse health effects in both children and adults. On the other hand, in the districts of San Juan de Dios and Pajonal, it was observed that As represents a risk of carcinogenic effects, while Co is associated with non-carcinogenic risks, such as effects on the cardiovascular and renal systems.

As is widely recognized for its ability to induce cancer in several organs, including the liver, lungs, skin, and urinary tract. Chronic exposure to As has been established to lead to cellular alterations that increase the likelihood of genetic mutations and, consequently, the risk of cancer [22]. Similarly, Pb has been linked to gastrointestinal cancers, such as stomach and bladder cancer, in addition to its well-known neurotoxic and cardiovascular effects [23]. In children, Pb exposure can interfere with brain development and cause delays in physical and mental development, while in adults, it can cause hypertension and kidney diseases [71]. Co, although less studied compared to As and Pb, has a high toxicity potential, particularly on the heart and kidneys. It has been documented that Co can induce cardiomyopathy and renal damage, emphasizing the importance of monitoring its presence in drinking water [24]. Likewise, Cu, although essential in small amounts for the body, can cause adverse effects if consumed in excess, such as short-term gastrointestinal discomfort and long-term liver or kidney damage [71].

The presence of these PTEs in drinking water, even at relatively low concentrations, poses a serious health risk for exposed populations. For instance, several studies have shown a link between even low levels of As (<10 µg/L) in drinking water and an increased risk of cancer [78–80]. Therefore, the presence of arsenic in water supply systems is a major public health concern [81]. In Latin America, As pollution of water has been reported in countries such as Argentina, Bolivia, Brazil, Chile, Colombia, Cuba, Ecuador, El Salvador, Guatemala, Honduras, Mexico, Nicaragua, Peru, and Uruguay [82]. In the study area, the correlation between the presence of these PTEs and the high incidence of chronic non-traditional renal diseases in the study region is alarming. The province of Coclé reports the highest hemodialysis rate in Panama, along with the highest age-adjusted mortality rate due to chronic renal diseases compared to other provinces [83,84].

Regarding the health statistics provided by the Ministry of Health (MINSA) for the Coclé Region during the 2019–2023 period [85,86], a high prevalence of gastroenteritis and colitis was observed in the pediatric population (0 to 9 years old). San Juan de Dios reported 106 cases, followed by Pajonal with 76 and Caballero with 20 cases. These episodes of gastroenteritis, particularly in children, may be linked both to poor hygiene practices and the presence of pathogenic bacteria, such as total coliforms and E. coli, in the water, indicating deficiencies in the drinking water chlorination system in some areas.

Additionally, urinary tract infection cases, more prevalent in adults aged 35 to 64 years, could be related to exposure to PTEs present in the water, as groundwater contamination with these pollutants may predispose individuals to recurrent infections. In the study municipalities, 93 cases were recorded in San Juan de Dios, 81 in Pajonal, and 26 in Caballero, reflecting a concerning trend.

The highest incidence of chronic non-traditional renal disease was reported in the 35 to 64 age group. The total number of cases of chronic kidney disease between the ages of 0 to 65 years and older were 204 cases in Pajonal, 116 in Caballero, and 56 in San Juan de Dios. A concerning incidence was also noted in the pediatric population, especially in Pajonal, where 31 cases were reported, highlighting the urgent need to address water quality in the region. The statistical trend for kidney disease is consistent with the probabilistic risk

analysis for non-cancer diseases, where the risk is higher in Pajonal and Caballero and lower in San Juan de Dios.

The analysis of cancer cases in Panama from 2015 to 2020 also shows that 14% of diagnosed cancers were gastrointestinal, 9% skin cancer, and 5% lung cancer. This distribution is consistent with the known carcinogenic effects of arsenic and lead, suggesting that exposure to these elements may be contributing to the prevalence of these types of cancer in the local population [5].

4.2. Origin of PTEs in the Study Area

In the study area, PTEs such as As, Co, Cu, and Pb are naturally present, meaning they have a geogenic origin, coming from the minerals that make up the volcanic rocks of the El Valle Complex. These rocks, a product of the historical volcanic activity in the region, contain a variety of minerals that, when exposed to weathering processes, release these elements through mineral alteration [7]. When volcanic rocks weather, the PTEs are released and become part of the soil and sediments. These potentially toxic elements dissolve into the groundwater, which predominantly comes from springs. This dissolution process is favored by the local geochemical conditions, including a slightly acidic pH in the water, which facilitates the release of PTEs into the water resources used for human consumption.

According to the results of the principal component analysis (PCA) conducted on the sediments and water, it was identified that the presence of As is primarily associated with the mineral feldspar, a common mineral in the volcanic rocks of the region. Co is predominantly found in serpentine, a metamorphic rock associated with volcanic environments. Cu is linked to mica, a mineral commonly found in igneous and metamorphic rocks, while Pb is associated with amorphous minerals, which are often products of mineralogical alterations. The PCA results from the water samples indicate that the presence of Pb, Cu, and Co is closely related to Fe, suggesting that the processes of mineralization and oxidation of Fe in volcanic rocks contribute to the release of these PTEs into groundwater. These oxidation processes, coupled with the increased solubility of metals at a slightly acidic pH, favor the dissolution and transport of these elements into drinking water, thereby increasing the concentration of these contaminants in the region's springs [87,88].

4.3. Implications for Water Management and Public Policy

Since the PTEs in the region have geogenic origins, it is essential to conduct additional studies evaluating both the temporal and spatial variability of their concentration in the springs. This monitoring would provide a better understanding of how these contaminant levels fluctuate over time, particularly in relation to seasonal changes and potential climate shifts. Identifying seasonal variations could offer key insights into the factors affecting the presence of PTEs in the water and help develop more effective management strategies. Furthermore, further investigation into the interaction between PTEs and other environmental factors, such as soil quality and biogeochemical processes, is recommended. Such research would allow for a more precise understanding of the mechanisms of release and transport of these contaminants into groundwater sources. This in-depth knowledge would facilitate the development of appropriate mitigation strategies and public policies aimed at protecting public health in the region.

Although drinking water quality standards provide guidelines for the maximum allowed values of certain components, it is essential to perform a comprehensive risk assessment of the long-term consumption of water contaminated with PTEs. Even if the concentrations of these elements are within the established limits, the cumulative effects of prolonged exposure over time could have significant negative impacts on human health,

which are not always immediately evident [89,90]. Therefore, it is recommended to implement longitudinal studies assessing chronic exposure to these contaminants, considering both carcinogenic and non-carcinogenic risks. It is essential that these studies focus particularly on vulnerable populations, such as children, the elderly, and individuals with pre-existing conditions, who may be more susceptible to harmful effects. Such studies could help identify safe exposure thresholds and provide the necessary scientific basis for revising and adjusting water quality regulations, if needed. Finally, it is crucial to consider the interaction between the various PTEs present in the water, as the combined effects of these contaminants could be more harmful than the risks associated with individual exposure. In this regard, continuous and detailed water quality assessments, complemented by long-term risk studies, should be a priority for health authorities. Only through this approach can effective protection of the health of exposed populations be ensured.

5. Conclusions

This study highlights the significant health risks associated with the consumption of groundwater from springs close to water bodies in the communities of San Juan de Dios, Pajonal, and Caballero, located within the El Valle Volcanic Complex. The presence of potentially toxic elements, particularly As and Co, is linked to the local geology and poses both carcinogenic and non-carcinogenic risks to the population. The study suggests that the region's historical volcanic activity, involving the release of minerals rich in these PTEs, along with the interaction between groundwater and volcanic rocks, may be contributing to the presence of PTEs in the water. This geological phenomenon could be leading to prolonged exposure to these elements, which correlates with the high prevalence of chronic kidney disease in the area.

Arsenic has been associated with skin, lung, liver, and urinary tract cancers, while excess cobalt can affect the kidneys. Moreover, long-term exposure to other heavy metals like Cu and Pb can result in liver and kidney damage.

The results show that non-carcinogenic risks primarily affect children, while adults are more vulnerable to carcinogenic effects, especially from ingestion. The municipalities of Caballero and Pajonal are more affected than San Juan de Dios due to the higher concentrations of these toxic elements in the groundwater. The importance of corrective measures cannot be overemphasized in this situation.

We recommend that authorities and decision makers implement drinking water treatment systems that eliminate the presence of heavy metals and PTEs such as As, Co, Cu, and Pb before the water is distributed to homes. Regular monitoring of these elements in the water is also essential. Ensuring the microbiological safety of water is crucial to reduce cases of gastroenteritis, which may be related to the presence of total coliforms.

It is crucial to protect water catchment areas from all anthropogenic activities to ensure both the quantity and quality of available water. It is suggested to extend this research to other environmental matrices and contaminants that might be related to the development of non-traditional chronic kidney disease (nt-CKD) in the region.

Finally, preventive health programs and ongoing population monitoring should be implemented to prevent the proliferation of CKD, thereby improving public health and the quality of life for affected communities.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/w17010110/s1, Table S1: Assay data measured in water samples for human consumption for the municipalities of Caballero, San Juan de Dios, and Pajonal; Table S2: Assay data measured on sediment samples for the Caballero, San Juan de Dios, and Pajonal municipalities.

Author Contributions: Conceptualization, A.C.G.-V., S.J.-O., and R.R.; methodology, A.C.G.-V., S.J.-O., J.A., and R.R.; software, A.C.G.-V., S.J.-O., J.A., T.C., F.S., A.D., and M.V.-L.; validation, A.C.G.-V., and S.J.-O.; formal analysis, A.D., A.C.G.-V., S.J.-O., J.M.-C., J.A., C.F., E.G., L.M., F.S., T.C., J.O., H.S., R.R., E.M., L.A.-G., C.V.-C., M.V.-L., and C.N.; investigation, A.C.G.-V., S.J.-O., A.D., and F.S.; resources, A.C.G.-V., S.J.-O., A.D., and J.A.; data curation, A.C.G.-V. and S.J.-O.; writing—original draft preparation, A.D., A.C.G.-V., S.J.-O., J.M.-C., J.A., C.F., E.G., L.M., F.S., T.C., J.O., H.S., R.R., E.M., L.A.-G., C.V.-C., M.V.-L., and C.N.; writing—review and editing, A.C.G.-V. and S.J.-O.; visualization, A.C.G.-V. and S.J.-O.; supervision, A.C.G.-V. and S.J.-O.; project administration, A.D. and A.C.G.-V.; funding acquisition, A.D., A.C.G.-V., R.R., and S.J.-O. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Laboratory analysis data generated in this study are available in the Supplementary Materials.

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Conflicts of Interest: The authors declare no conflicts of interest.

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