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Contamination of Water Supply Sources by Heavy Metals: The Price of Development in Bolivia, a Latin American Reality

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Abstract: Like other Latin American countries, Bolivia is in the race towards development, which has caused many economic activities to be carried out without due consideration for the care of the environment. At this point, it is essential to carry out environmental inventories to preserve the quality of ecosystems and natural resources, such as water. As water is vital, it needs to be adequately monitored and managed to prevent its degradation. This research presents the results of monitoring the main sources of water supply in two continuously growing departments of Bolivia, La Paz, and Tarija. The main objective of this study was to evaluate the suitability of the water to which the population has access, with particular attention to heavy metals with concentrations that exceed the permitted limits. The metals found were arsenic, chromium, mercury, manganese, iron, zinc, and tin in the Milluni area, and lead, iron, and manganese in the Guadalquivir area. Exposing the presence of metals in water sources implies immediate attention by decision-makers to take action to reduce the risk to public health. In addition, this study exposes a Bolivian reality that could encourage other countries in similar contexts to conduct similar studies on their water sources.

Keywords: water sources; heavy metals safe water; sustainable development

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1. Introduction

Water is essential for the balance of the environment, the economic development, and the social well-being of nations; therefore, the preservation of its quality is necessary [1]. Among the different water contaminants, metal ions stand out due to their acute toxicity and carcinogenic nature, denoting a threat to the environment and public health [2,3]. Heavy metals are described as elements having atomic weights between 63.5 and 200.6 and a density greater than 5 g per cubic meter [4]. Some metals such as copper (Cu), zinc (Zn), manganese (Mn), iron (Fe), and cobalt (Co) play essential roles in biochemical processes in the human body. However, excessive exposure to these ions can lead to dangerous impacts [5]. Other heavy metals such as arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg), and chromium (Cr) are toxic, even at trace levels (parts per billion, ppb), and because they are non-degradable, they can enter the food chain and bioaccumulate in major human body systems [6,7]. Under normal circumstances, the human body can tolerate small amounts of metal ions without experiencing severe problems. However, long-term exposure to heavy metals can cause high levels of toxin accumulation in the body, leading to the failure of body systems and eventual fatality [8,9].

The contamination of freshwater bodies by heavy metals is a global concern [10]. Water with a concentration of metal ions above the Maximum Concentration Limit (MCL), stipulated by international organizations such as the World Health Organization (WHO), is not safe for human use or consumption. So, the presence of heavy metals in water storage dams is dangerous since this water is the main source of supply for population centers [11,12]. In this sense, there is a pressing need to seek strategies and mechanisms to monitor the concentrations of heavy metals and identify the risk to public health in certain areas.

Water Problem in Bolivia

Developing countries, such as Bolivia, have high rates of poverty and greater vulnerability to environmental degradation [13]. Many of the main economic activities in Bolivia, such as mining, agriculture, and livestock, have used and continue to use natural resources without sustainable planning, generating a negative impact on the environment. Water pollution due to anthropogenic activities in different basins is observed both in the east and in the west of Bolivia. The study by [14] exposes the contamination of the Lake Titicaca basin caused by uncontrolled population expansion. A similar situation occurs in transboundary basins, such as the Amazon basin, in which Bolivia participates with five other countries. The Amazon basin currently suffers from the negative impacts of anthropogenic pollution, and [15,16], among others, exposes this water problem.

In Bolivia, migrations were and are an important population phenomenon to achieve the coexistence of the various production systems [17]. As [18] indicates in his study, population displacements affect local dynamics, which in Bolivia has caused different activities to settle in different regions. A culture oriented towards migration to achieve a certain development not only has repercussions at a social and economic level, as exposed in [19] but also leads to a depletion of the different natural resources. It should be noted that an important part of environmental degradation is caused by the contamination of water resources [20].

According to the World Health Organization, diseases associated with a lack of drinking water and adequate sanitation and hygiene continue to be one of the main causes of mortality for millions of developing countries [21]. That is why the sustainable and affordable supply of water of adequate quality is one of the most complex challenges of the century, not only in developing countries but throughout the world [22]. Drinking water is linked to public health, and this in turn to sustainable development [23]. For this reason, the water issue is a priority in Goal 6, "Clean water and sanitation", within the Sustainable Development Goals (SDG), which frame the 2030 agenda [24].

Bolivia has participated in international water forums as a pioneer of the Declaration of Human Rights of Water before the United Nations General Council [25]. However, Bolivia still faces several challenges related to water management in practice. The report of the Spanish Agency for International Development Cooperation (AECID) indicates that the lack of adequate access to drinking water in sufficient quantity and quality is one of the main factors in the increase in diseases in the Bolivian population [26]. The WHO states that only 50% of Bolivia has access to clean water [27]. There are also other problems related to the supply of drinking water; for example, the state of the water supply infrastructure in Bolivia shows that the water storage capacity is only 56 m^3 per inhabitant; between 42% and 61% of drinking water is not accounted for by local operators due to deficiencies in the control and operation systems; the systems are characterized by poor house connections and distribution systems, often due to the age of the pipes; and the most alarming problem is that the main sources of water supply are affected by serious and growing pollution [21].

This research presents new information on the state of water sources in two ever-growing Bolivian cities, La Paz and Tarija. The objective is to evaluate the suitability of the water to which the population has access, making visible the problem of contamination of water sources in Bolivia that requires urgent attention. The impact of this study is to expose the environmental price of unsustainable development, a reality in Bolivia and many Latin American countries.

2. Materials and Methods

In this section, the study basins are introduced. The design of the water quality monitoring program and the steps during its implementation are then detailed. Finally, the methodology for the identification of contamination and the degrees of affectation in the study areas are described.

2.1. Study Areas

The basin is recognized as the most suitable territorial unit for the efficient management of water resources [28]. However, the political/administrative limits do not always coincide with the territorial limits of the hydrological basins, making the process of taking advantage of the hydrological cycle difficult in many cases [29]. Hydrographic basins are complex socio-ecological systems since the water resources within them are managed according to the needs of the populations that inhabit them [30,31]. The study, management, and policy development of river basins require reliable information on human and environmental linkages [32]. Figure 1 shows the location of the study basins.

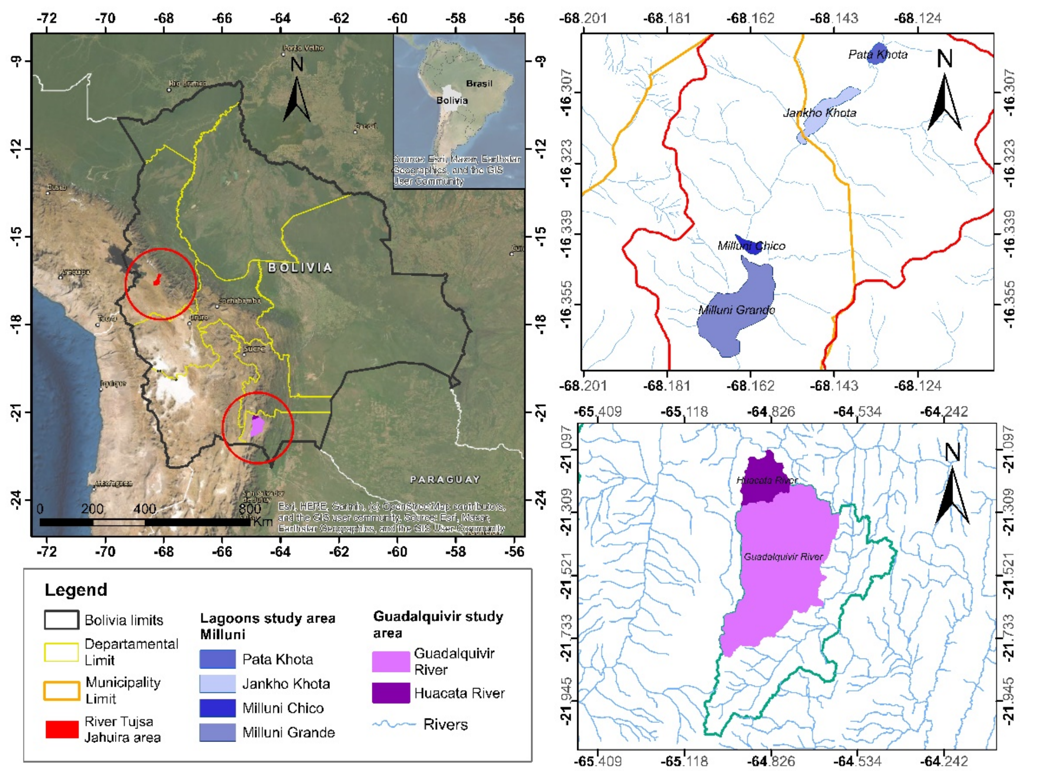


Figure 1. Study Basins.

The two study basins of this research and the water problems that exist within them are presented below.

2.1.1. Milluni Basin

Milluni is located at approximately 4600 m.a.s.l., this 40 km^2 area is part of the Altiplano basin system, which presents extreme climatic conditions typical of the area [33]. The Milluni territory has been and continues to be negatively impacted by past, current, and illegal mining activity, with it being the main economic activity in the area [34–36]. The water resources of the upper part of the Milluni Basin are sources of fresh water for the cities of La Paz and El Alto, essential cities in Bolivia, with approximately 450,000 inhabitants [37]. The water treatment plants that treat the waters of Milluni do not have specific treatments for the elimination of heavy metals; in this sense, the quality of the water is not guaranteed [12].

The Milluni basin is part of the Katari macro-basin, defined as a strategic basin by the Bolivian National Basin Plan [38]. The Katari Basin Management Unit has been in charge of monitoring Milluni from 2006 to the present. An analysis of historical monitoring data from Milluni determined some inconsistencies in the applied program. The most important were: a non-uniform monitoring frequency, the variation in the location of the monitoring points, and the variation in the parameters to be analyzed [39]. This implies little representative data of contamination in the surface bodies of Milluni, denoting the need for more profound water quality studies in the area.

2.1.2. Guadalquivir Basin

The Guadalquivir basin is also known as the central valley basin of Tarija and covers the municipalities of San Lorenzo, Cercado, and Padcaya with approximately 247,000 inhabitants [37]. The Guadalquivir River has a length of 70 km that rises in the upper part of the Serranía de Sama, Trancas River, to the narrow of San Luis and the basin with an area of 1540 km^2 [40]. The central valley of Tarija is of lacustrine origin affected by the erosion of un-stabilized sediments [41]. It is characterized by a semi-arid climate, where rainfall is concentrated between October and April [42].

The upper basin of the Guadalquivir River is the most populated urban area in the department of Tarija. During recent decades, it has experienced great economic income, bringing a disproportionate population and real estate growth, causing pollution and environmental degradation. The leading causes of surface water contamination in the basin are essential of agricultural and domestic origin [43]. Likewise, other anthropic activities such as the disposal of wastewater with little or no treatment process, solid waste on the banks of the river, and overexploitation of aggregates are processes that have generated the degradation of water and resources in the Central Valley of Tarija [44].

2.2. Design of a Water Quality Monitoring Program

There can be as many monitoring programs as targets, water bodies, pollutants, and water use [45]. The Water Quality Monitoring Program (WQMP) was designed for the Milluni and Guadalquivir basins due to natural water sources vulnerable to anthropogenic contamination, which must be monitored. Two international standards were taken to determine the components that the WQMP should have; the standards were: the “Practical guide for the design and implementation of studies and monitoring programs of freshwater quality” [46] and the protocol “ISO 5667-1: 2006 Water quality—Sampling—Part 1: Guidance on the design of sampling programs and sampling techniques” [47]. It was essential to consider the particularities of each basin so that the proposed WQMP could be aligned and be part of the macro management system in both study areas. A functional monitoring program ensures the generation of valid information about contaminants [48].

Implementation of the Monitoring Program

The implementation of the program was carried out in two stages, a first of coordination (2018) and a second of fieldwork (2019). Coordination before fieldwork was carried out with the entities in charge of management in each basin, with the aim of not interfering or hindering the work they carry out and seeking to optimize the available resources. For Milluni, the coordination was made with the Katari Basin Management Unit (UGCK). For the Guadalquivir basin, work was carried out with the Universidad Católica Boliviana-Tarija in cooperation with the Cooperativa de Servicios de Agua y Saneamiento (COSAALT by its acronym in Spanish) and the protected area’s office in Tarija (SERNAP, acronym in Spanish). The temporality of both basins defined the months of fieldwork due to the existence of two marked seasons, the dry season and the wet season. The dynamics of pollutants during a hydrological year were observed by monitoring the wet and dry seasons.

The fieldwork included three tasks. The first was the measurement of in situ parameters, pH, and conductivity, with an HQ40D portable multimeter and turbidity with a 2100Q Handheld Turbidimeter, both brand HACH and made in the USA [49,50]. The second one was sampling, transport, and storage, following the protocol established in ISO 5667-1 [47] and ISO 5667-4 [51], to avoid contamination of the samples. The third one was the analytics of the ex situ parameters (heavy metals); these were analyzed with a Model 7700x Inductively Coupled Plasma Mass Spectrometer (ICP-MS), brand Agilent Technologies, made in the USA. The measurement mode used was the He, and Low matrix [52].

The program's implementation during a hydrological year identified the pollutants in the surface bodies in both study basins.

2.3. Methodology for the Identification of Contamination and Degrees of Affectation in the Study Areas

Figure 2 shows the steps to follow to identify the contamination and the degree of affectation on the water resources of the study basins.

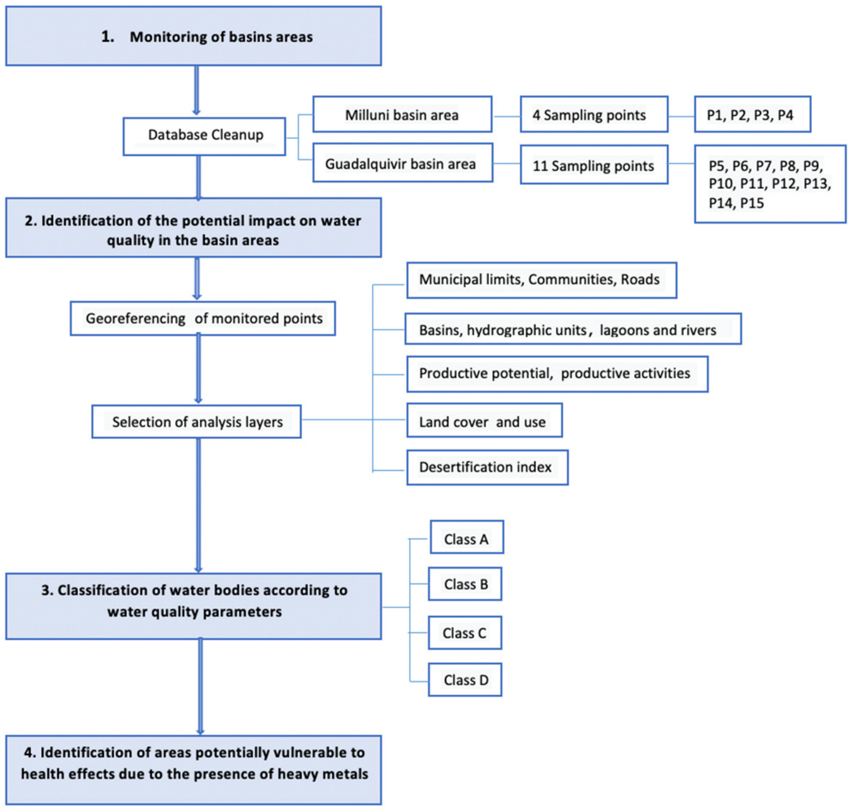


Figure 2. Methodological Scheme.

After monitoring both study basins, valid data for stage two were selected as the first stage. In the second stage, layers of geographic information were extracted in Shape and Raster format; these were: municipal limits, limits of main basins, limits of hydrographic units, populations, road limits, productive activities, the productive potential of the soil, coverage, and use of the earth and index of desertification. The geodata portal "Geobolivia" [53] was used for data processing for the map layers. In stage three, the classification of water bodies was carried out according to the quality parameters of Law 1333—Bolivia, according to its Water Pollution Regulation [54]. The fourth stage was the combination of the results of the monitored points with the geographic information layers to analyze the potential vulnerability in public health due to heavy metals outside the permitted limits. For the evaluation of the health risk, the following were used: Bolivian Standard 512 [55], Guide for the Quality of Drinking Water of the WHO [56], and the Environmental Protection Agency of the United States, Standards for the Health of the Bodies of Water [57].

3. Results

This section identifies the potential impact on water quality and the classification of water resources in each study basin. Finally, the potentially vulnerable areas to health effects from the presence of heavy metals are exposed.

3.1. Milluni Basin Monitoring

The Milluni Basin is located within the Katari Macro-basin in the Tujsa Jahuira River hydrographic unit of exorheic type. The monitored points are presented in Figure 3.

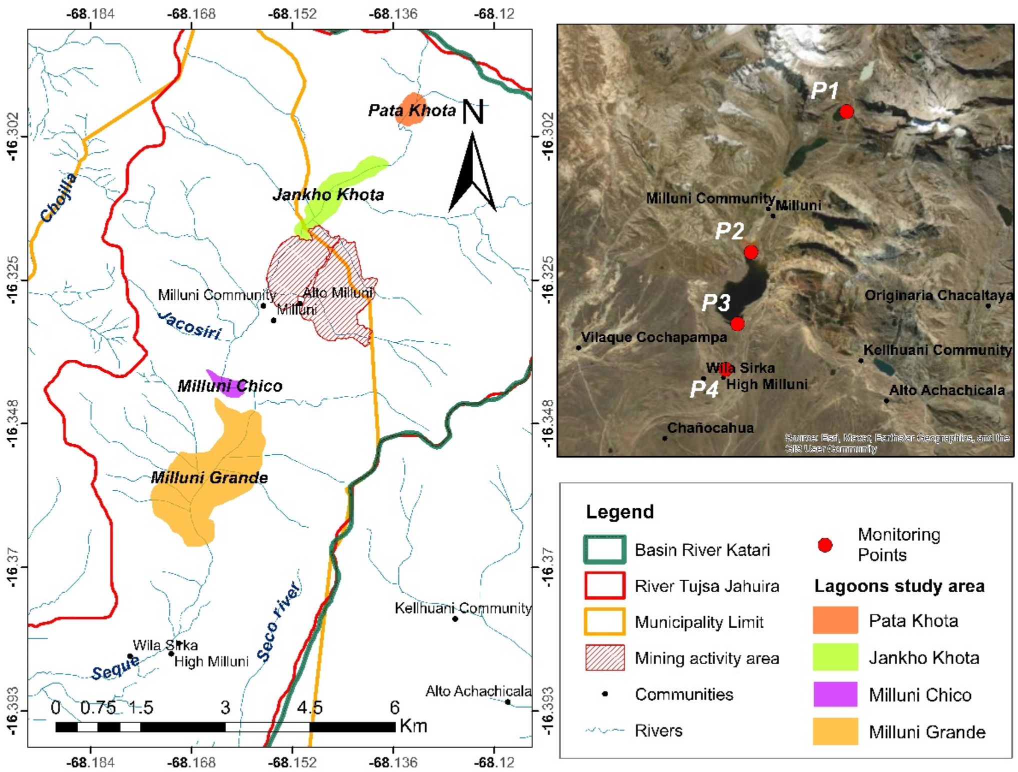


Figure 3. Map of monitoring points in Milluni.

In Milluni, there were four monitoring points. Point 1 (P1) was in the Pata Khota Lagoon; it identifies the initial conditions in the lagoon system since its tributaries come from the snow-capped Huayna Potosi. Point 2 (P2) was located in the effluents from Laguna Milluni Chico; it determines any signs of deterioration in water quality near a production area. Point 3 (P3) was in the Laguna Milluni Grande, where the storage dam is located; it states whether the body of water meets the desired quality standards. Point 4 (P4) was situated after the pretreatment to condition the Milluni waters; it evaluates the intervention's effectiveness in managing water quality.

3.1.1. Identification of the Potential Impact on Water Quality in the Milluni Basin

The areas of greatest vulnerability concerning water quality were identified considering factors such as land cover, degree of desertification, land use, and the type of productive activity around or near the monitored water bodies. In addition, it was considered that the areas that receive the most significant negative impacts from productive activities are the populations close to them. Figure 4 reveals the vulnerability areas against the factors analyzed in Milluni.

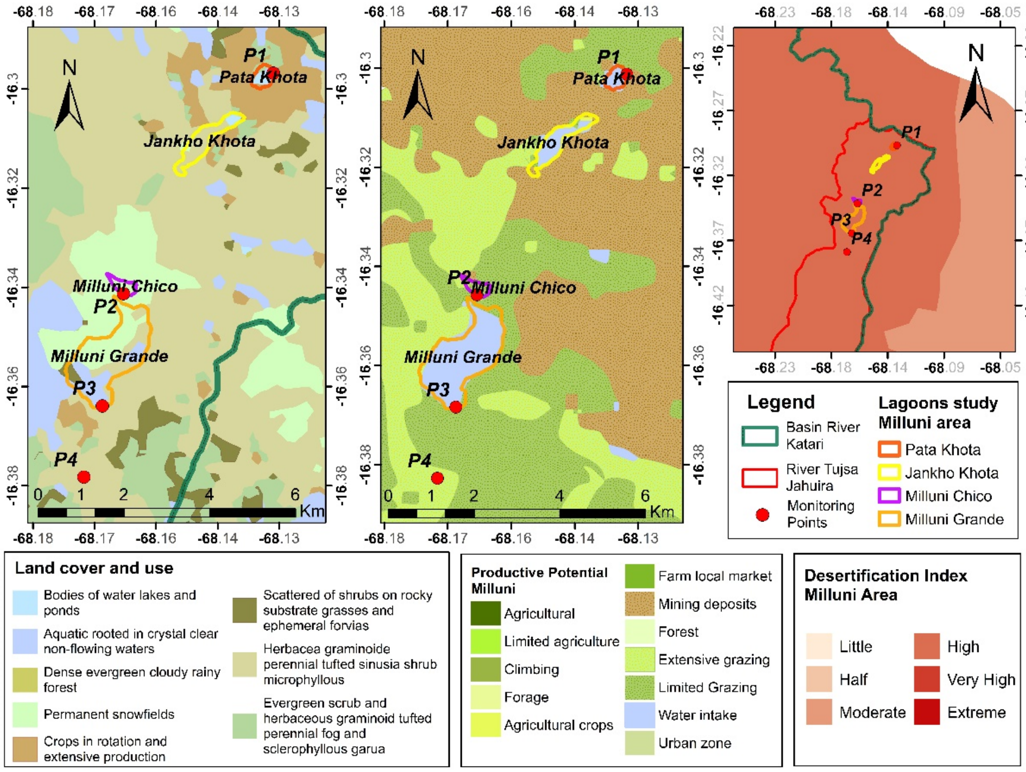


Figure 4. Identify the potential impact on water quality at the points monitored in the Milluni basin.

Water use according to its quality is represented in two registered activities, fish farming and the capture of water sources. According to the land cover and its productive capacity, the study area is characterized by extensive farming activities, limited agriculture, extensive grazing, and limited grazing. On the other hand, there is a high percentage of land suitable for the exploitation of mining deposits around the Jankho Khota lagoon. In this sector, there is a minimal scale of agricultural crops, making the area highly vulnerable to mining activity, which has prevailed over other minor productive activities due to its economic retribution.

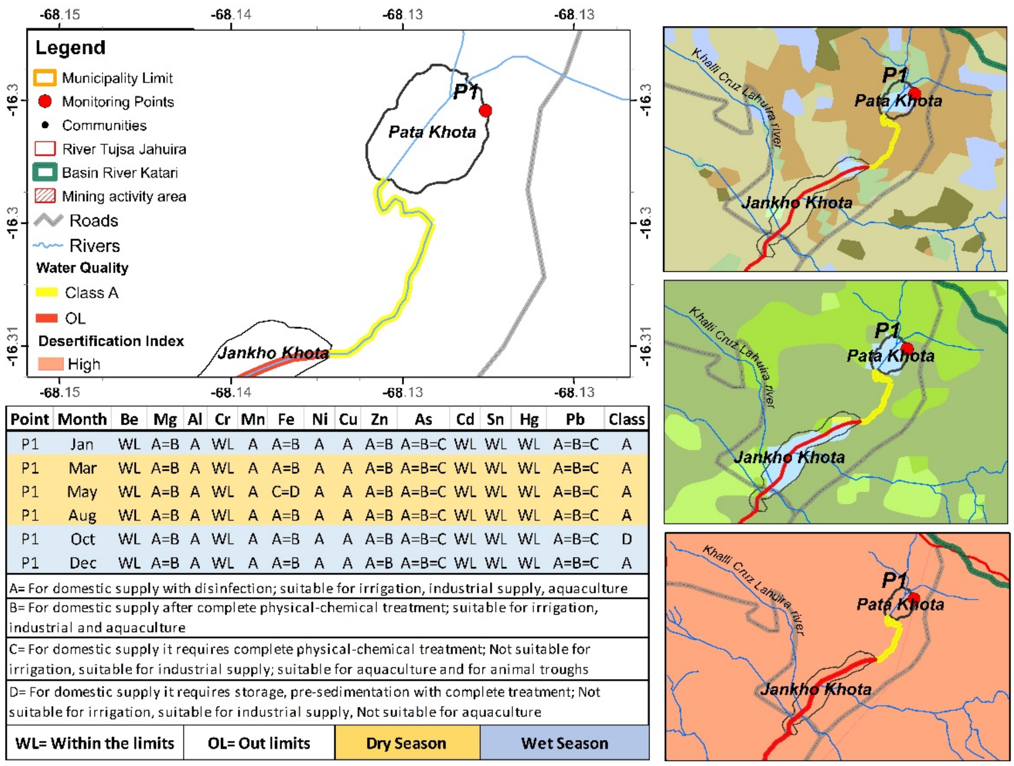
Regarding the degree of desertification, there is a high index for being an area with scattered bushes and rocky, grassy soil. This area has been impacted mainly by mining activity, extensive grazing, and extensive cultivation. This makes the entire Milluni area vulnerable to economic activities, which have generated a negative impact on its water resources.

3.1.2. Classification of Water Quality in Milluni

The values obtained at the monitoring points were evaluated by the Regulation on Water Pollution of Law 1333 of Bolivia. Specifically, Table A-1 was used, where the classification of the water bodies is given according to their suitability for use based on the maximum admissible values in receiving bodies. The following sections present the maps of the water quality analysis for the points monitored in Milluni.

- Water quality in P1

Most of the months monitored in P1, located in the Pata Khota Lagoon, have Class A water quality, suitable for the supply of drinking water before disinfection. However, in the month of October, there is a Class D quality; this change may be related to a specific mining exploration event that only lasted a short time, but affected the quality of the water at point 1. Figure 5 presents the location of P1 and the parameters used to analyze its water quality.



Point	Month	Be	Mg	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Sn	Hg	Pb	Class
P1	Jan	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	A
P1	Mar	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	A
P1	May	WL	A=B	A	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	A
P1	Aug	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	A
P1	Oct	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	D
P1	Dec	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	A

A= For domestic supply with disinfection; suitable for irrigation, industrial supply, aquaculture

B= For domestic supply after complete physical-chemical treatment; suitable for irrigation, industrial and aquaculture

C= For domestic supply it requires complete physical-chemical treatment; Not suitable for irrigation, suitable for industrial supply; suitable for aquaculture and for animal troughs

D= For domestic supply it requires storage, pre-sedimentation with complete treatment; Not suitable for irrigation, suitable for industrial supply, Not suitable for aquaculture

WL= Within the limits	OL= Out limits	Dry Season	Wet Season

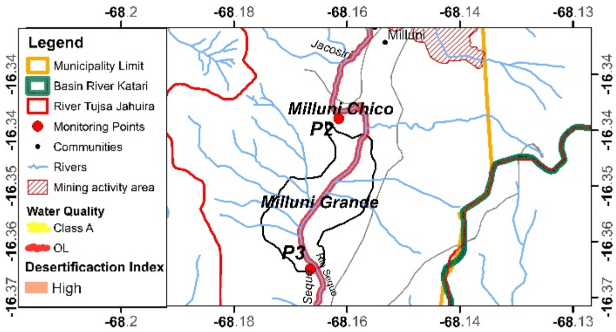
Figure 5. Water quality classification according to parameters monitored in P1—Milluni Basin.

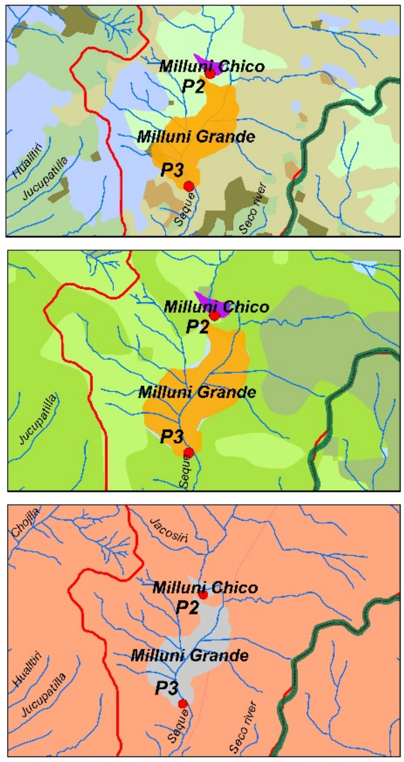
As complementary data to P1, the registered land use contributes to water quality not being highly affected, since cop activity is rotational (limited cultivation), which reduces a progressive and constant impact on the area. On the other hand, the ground cover is characterized by a concentration of graminoid herbaceous type and evergreen scrub due to the existing humidity conditions as it is close to a natural snow-capped mountain. The decrease in land cover, in this case, could be an indicator of the degradation of water quality in P1.

- Water quality in P2 and P3

It should be noted that the water quality is presenting changes from the Jankho Khota Lagoon, located after the Pata Khota Lagoon (P1) and before the Milluni Chico Lagoon (P2). In the second lagoon of the lagoon system, Laguna Jankho Khotase, reception points for polluting effluents from informal (illegal) mining activity have been identified. Acid mine drainage is enhanced by the geological composition of the area, which has generated mineral concentrations and an acidic pH that affects the water quality of the Laguna Milluni Chico (P2). Figure 6 presents the location of points P2 and P3 with the parameters used to analyze their water quality.

Point 2, located in the effluents of Laguna Milluni Chico, was identified as the point most affected by the mining waste concentrate. The results of the monitoring carried out in P2 show that, for the most part, concentrations of heavy metals and basic control parameters (dissolved oxygen, pH, and conductivity) are outside the permissible limits. Polluting agents, heavy metals, are quickly infiltrated by the type of soil cover and the effects of humidity in the area, which affects the ecosystems surrounding the Laguna Milluni Chico.





Point	Month	Be	Mg	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Sn	Hg	Pb	Class
P2	Jan	OL	A=B	OL	OL	OL	OL	B=C=D	B=C=D	OL	OL	OL	WL	OL	A=B=C	OL
P3	Jan	OL	A=B	OL	OL	OL	OL	B=C=D	B=C=D	OL	D	OL	WL	OL	A=B=C	OL
P2	Mar	OL	A=B	OL	WL	OL	OL	B=C=D	B=C=D	OL	OL	OL	WL	WL	A=B=C	OL
P3	Mar	OL	A=B	OL	WL	OL	OL	B=C=D	B=C=D	OL	A=B=C	OL	WL	WL	A=B=C	OL
P2	May	OL	A=B	OL	WL	OL	OL	B=C=D	B=C=D	OL	OL	OL	WL	WL	A=B=C	OL
P3	May	OL	A=B	OL	WL	OL	OL	B=C=D	B=C=D	OL	A=B=C	OL	WL	WL	A=B=C	OL
P2	Aug	OL	A=B	OL	WL	OL	OL	B=C=D	B=C=D	OL	OL	OL	WL	WL	A=B=C	OL
P3	Aug	OL	A=B	OL	WL	OL	OL	B=C=D	B=C=D	OL	A=B=C	OL	WL	WL	A=B=C	OL
P2	Oct	OL	A=B	OL	WL	OL	OL	B=C=D	B=C=D	OL	OL	OL	WL	WL	A=B=C	OL
P3	Oct	OL	A=B	OL	WL	OL	OL	B=C=D	B=C=D	OL	D	OL	WL	WL	A=B=C	OL
P2	Dec	OL	A=B	OL	WL	OL	OL	B=C=D	B=C=D	OL	OL	OL	WL	WL	A=B=C	OL
P3	Dec	OL	A=B	OL	WL	OL	OL	B=C=D	B=C=D	OL	D	OL	WL	WL	A=B=C	OL
P3	Dec	OL	A=B	OL	WL	OL	OL	B=C=D	B=C=D	OL	D	OL	WL	WL	A=B=C	OL

A= For domestic supply with disinfection; suitable for irrigation, industrial supply, aquaculture

B= For domestic supply after complete physical-chemical treatment; suitable for irrigation, industrial and aquaculture

C= For domestic supply it requires complete physical-chemical treatment; Not suitable for irrigation, suitable for industrial supply; suitable for aquaculture and for animal troughs

D= For domestic supply it requires storage, pre-sedimentation with complete treatment; Not suitable for irrigation, suitable for industrial supply, Not suitable for aquaculture

WL= Within the limits	OL= Out limits	Dry Season	Wet Season

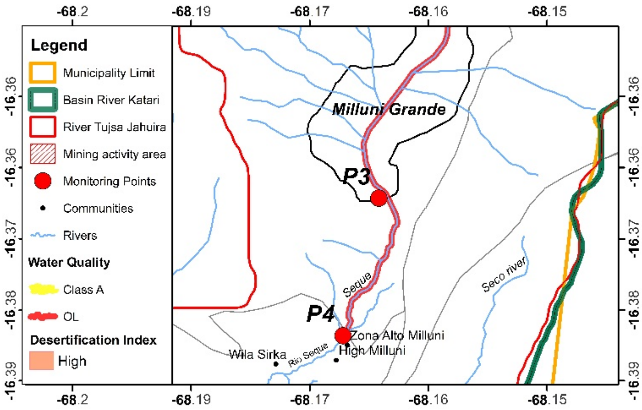
Figure 6. Water quality classification according to parameters monitored in P2 and P3—Milluni Basin.

Every month of monitoring in P2 presents Poor Quality Water (PQW) type. This type of water is unsuitable for domestic water supply, irrigation, or animal watering holes and requires complete decontamination.

Point 3, located in the storage dam, has characteristics in the soil cover of the tufted graminoid herbaceous type and water quality of type PWQ, the same as Point 2. The water quality in P3 is not suitable for its use and consumption without an exhaustive and complete treatment. In P3, there are parameters such as Be, Al, Mn, Fe, Ni, Zn, As, Cd, and Pb out of limits and an acidic pH that varies from 2 to 3.

- Water quality in P4

Monitoring point 4 presents parameters outside the permissible limits in the same elements as point P3, Be, Al, Mn, Fe, Ni, Cu, Zn, As, Cd, Hg, acid pH that ranges between 2.8 and 4.5, which represents that the quality of the water at this point is still not suitable for consumption. The results of the parameters monitored in P4 reveal that the water to which the downstream communities are exposed is not safe, with the Alto Milluni community being the closest. Figure 7 shows the location of P4 with the parameters used for analyzing its water quality.



Point	Month	Be	Mg	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Sn	Hg	Pb	Class
P4	Jan	WL	A=B	OL	WL	OL	OL	A	B=C=D	OL	A=B=C	OL	WL	OL	A=B=C	OL
P4	Mar	WL	A=B	OL	WL	OL	OL	A	B=C=D	OL	A=B=C	OL	WL	WL	A=B=C	OL
P4	May	OL	A=B	OL	WL	OL	OL	B=C=D	B=C=D	OL	A=B=C	OL	WL	WL	A=B=C	OL
P4	Aug	OL	A=B	OL	WL	OL	OL	B=C=D	B=C=D	OL	D	OL	WL	WL	A=B=C	OL
P4	Oct	OL	A=B	OL	WL	OL	OL	A	B=C=D	OL	A=B=C	OL	WL	WL	A=B=C	OL
P4	Dec	WL	A=B	OL	WL	OL	OL	A	B=C=D	OL	A=B=C	OL	WL	WL	A=B=C	OL

A= For domestic supply with disinfection; suitable for irrigation, industrial supply, aquaculture

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WL= Within the limits | OL= Out limits | Dry Season | Wet Season

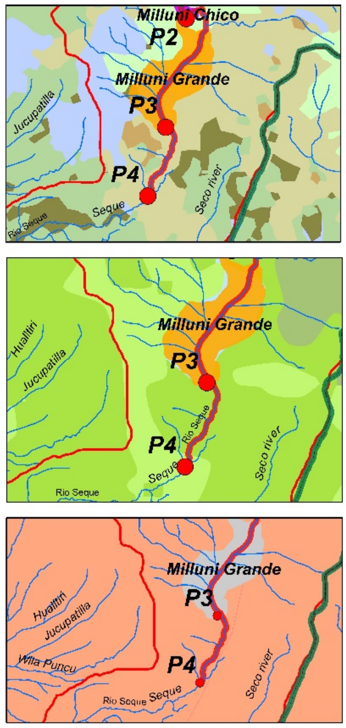


Figure 7. Water quality classification according to parameters monitored in P4—Milluni Basin.

3.2. Guadalquivir Basin Monitoring

The monitoring of the Guadalquivir area was located in the Guadalquivir River Basin, specifically in its level 5 hydrographic units, Guadalquivir River and Huacata. Their areas cover the municipalities of Tarija, Villa San Lorenzo, and a small extension of Tomayapo (El Puente). The monitored points are presented in Figure 8.

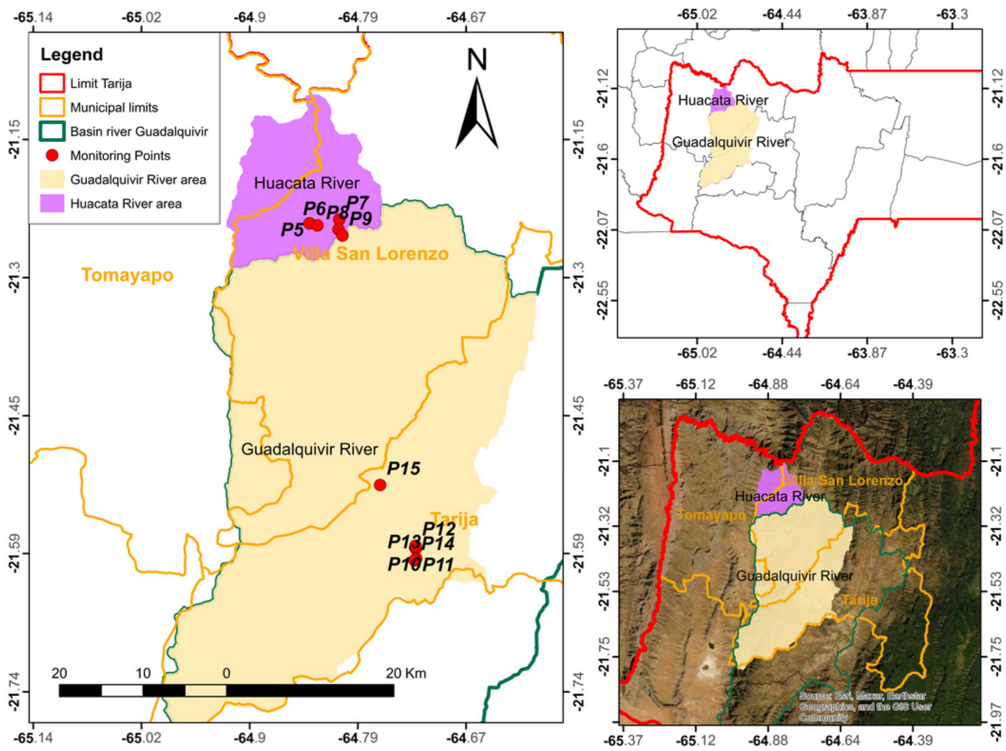


Figure 8. Map of the monitored points in the Guadalquivir Basin.

The points monitored in the Guadalquivir Basin were assigned the recognition code that continued with the monitoring coding in Milluni. The 11 points were located in two areas, Embalse Huacata and Emblase San Jacinto (the central area of the Guadalquivir Basin).

In the Huacata area, there were five monitoring points. Point 5 (P5) was located on the Huacata River, specifically at the height of the Huacata Bridge, which is a contribution (transfer) to the dam. Point 6 (P6) was on the Huacata River transfer reservoir. Point 7 (P7) was on the left side upstream of the Huacata dam, near where the transfer comes from the Huacata River. Point 8 (P8) was located near the transfer intake Corana River, and water is taken to be transferred to the Guadalquivir basin by the Corana River. Point 9 (P9) was located at the exit of the transfer tunnel to the Guadalquivir River through the Corana River.

In the Central Guadalquivir area, there were six monitoring points. Point 10 (P10) was in the intake (pumping) work that supplied drinking water to the city of Tarija. Point 11 (P11) was about 200 m from the intake work on the left side. Point 12 (P12) was about 200 m from the intake work to the right side. Point 13 (P13) was located near the dam's hydroelectric plant feeding tunnel. Point 14 (P14) was near the dam, an area with many food stalls and tourists sensitive to pollution. Point 15 (P15) was located in the drinking water intake work in the Las Tips area on the Guadalquivir River; it is a surface water source for Tarija.

3.2.1. Identification of Potential Impact on Water Quality in the Guadalquivir Basin

For the analysis of the affectation regarding the water quality of the monitored points, the degree of desertification, the productive activities in the area, the coverage, and the use of surrounding land were identified. The identification of the potential affectation of water quality is presented in Figure 9.

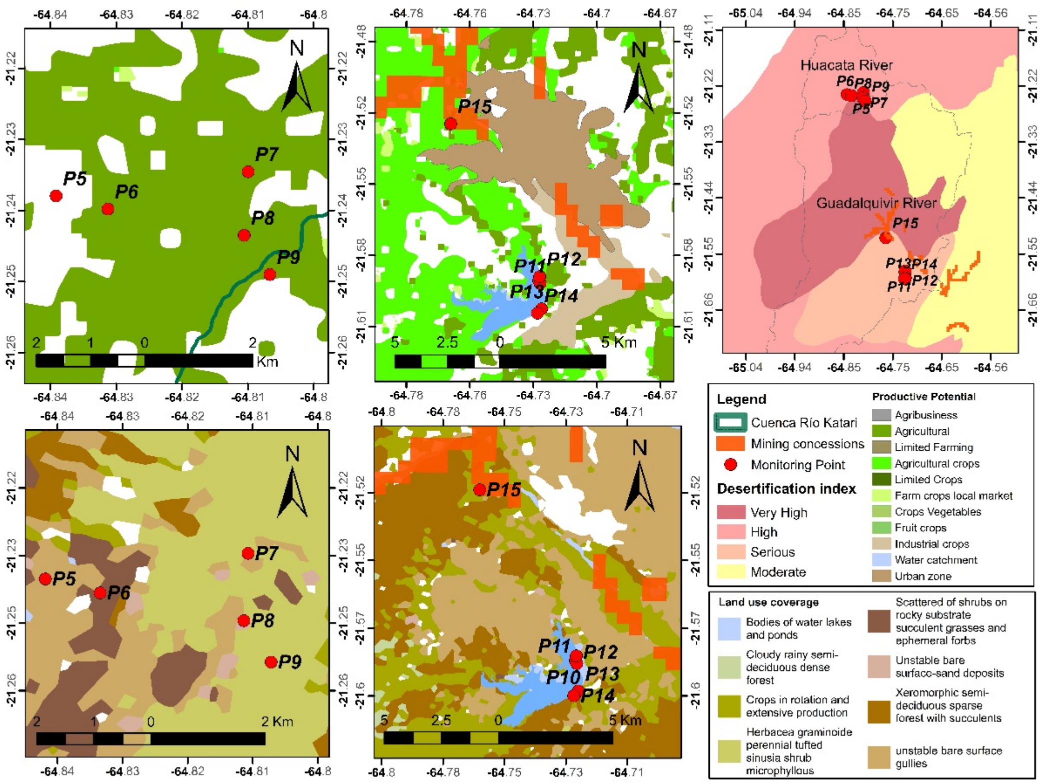


Figure 9. Identify the potential impact on water quality at the monitoring points in the Guadalquivir Basin.

The Guadalquivir Basin is generally characterized by having perennial tufted graminoid herbaceous soil covered with microphyllous shrubby sinuses, in some areas covered by dense cloudy semi-deciduous rainy forest and scattered shrubs on rocky substrate accompanied by grasses and ephemeral forbs. However, a percentage of soil within the study area is also characterized by an unstable bare surface with sand deposits and gullies.

The productive activities according to the use and type of soil within the Guadalquivir Basin are, in the Huacata area, limited agricultural production activity of farming crops, and in the Guadalquivir area, it presents aptitude for consumption and sale in the local market, and a higher percentage of the area carries out limited-type agrarian production. Another productive activity is verifying the mining concessions settled in the area of the municipality of Villa San Lorenzo that intersects the Guadalquivir Basin.

The desertification index identified for the monitored points, P5, P6, P7, P8, and P9, is high to very high. Points P10, P11, P12, P13, P14, and P15 are located in areas with a severe desertification index, revealing one of the factors that most affect the area's water quality due to its direct relationship with the recharge of aquifers and the soil degradation. Finally, according to the type of soil, the type of production, and the desertification index, Las Tipas (P15) was identified as the point with the most significant threat of affecting water quality. The P15 is located in the central area of the study basin and is an essential source of drinking water, so its conservation is vital for the area.

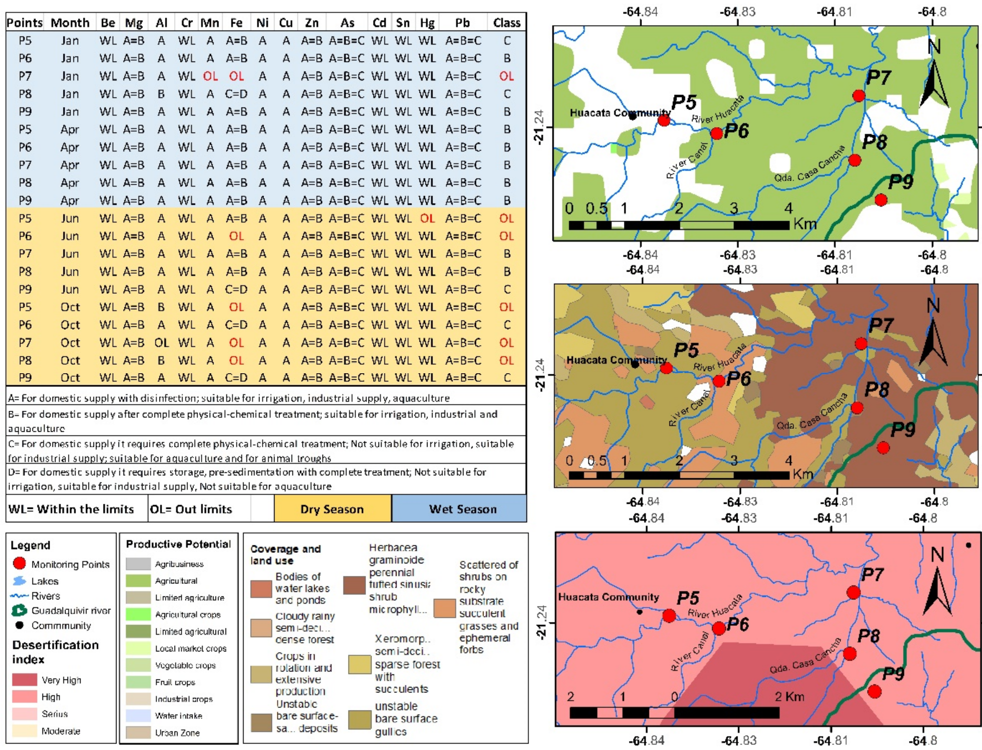
3.2.2. Classification of Water Quality in the Guadalquivir Basin

Like the analysis for Milluni, the values obtained by monitoring in the Guadalquivir were evaluated by the Regulation on Water Pollution of Law 1333 of Bolivia. Table A-1 was used, where the classification of the water bodies is given according to their suitability for use. The following sections present the water quality analyses for the monitored points in the second study basin.

- Water quality in the Huacata area

The five control points have made it possible to establish that during the months monitored in the Huacata area, the water contains heavy metals such as Pb, Mn, and Fe with concentrations higher than current regulations. Although there are months where a decrease in the attention of the parameters is observed, the permanence in the sludge establishes an increased risk for health. The water quality at these analyzed points ranges from Class B to Class D, which should not be used for domestic consumption, irrigation, or animal watering troughs if they are fully treated.

Figure 10 presents the distribution of the monitored points and the water quality analysis. Specific findings stand out in the monitored attributes. In P5, during the wet season, it did not present concentrations of heavy metals outside the permissible limits, and the water quality ranged between the Class B and Class C categories. However, in the dry season in P5, the concentrations of Fe and Hg were outside the permissible limits, but the pH remained in the range of 6.3 to 7.2. P6 in the rainy season presented a Class B type water quality. In the dry season, there were Fe concentrations outside the permissible limits, and the water had a type C classification; the pH remained between 7 and 8. In the rainy season, the P7 presented concentrations of Mn and Fe outside the permissible limits; something similar happened in the dry season, with concentrations of Fe exceeding the allowable limits. However, in P7, the pH remained at 7 (neutral). P8 presented Class C to B water in the wet season, but in the dry season, there were Fe concentrations outside the permissible limits, but a pH of 6.5 to 7 was maintained.



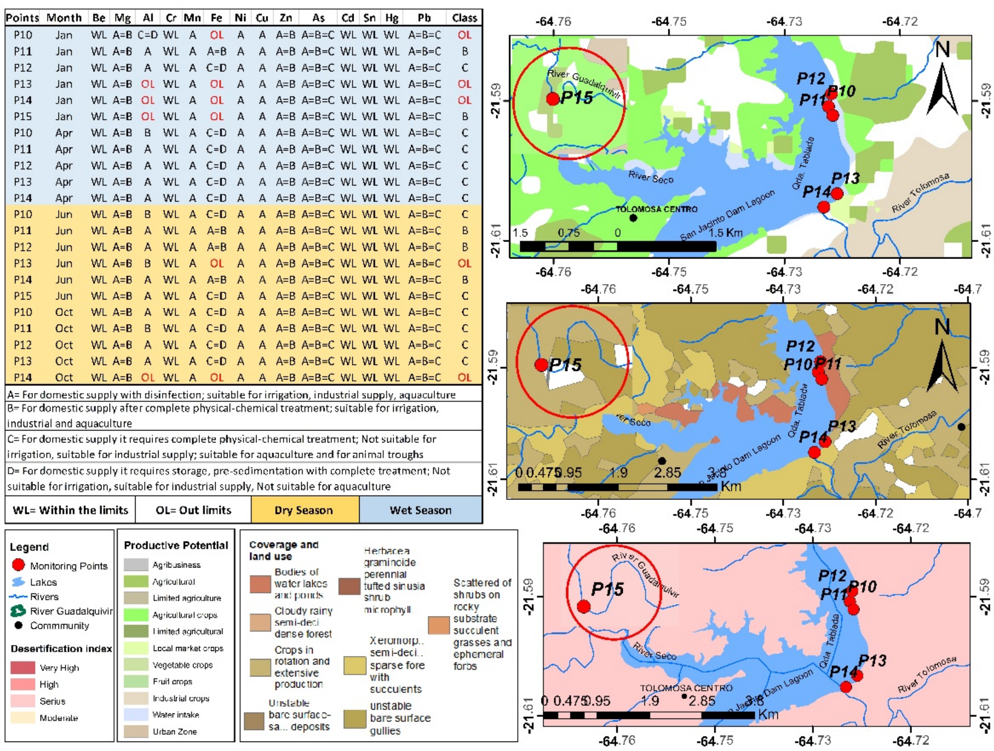
Points	Month	Be	Mg	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Sn	Hg	Pb	Class
P5	Jan	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C
P6	Jan	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	B
P7	Jan	WL	A=B	A	WL	OL	OL	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	OL
P8	Jan	WL	A=B	B	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C
P9	Jan	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	B
P5	Apr	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	B
P6	Apr	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	B
P7	Apr	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	B
P8	Apr	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	B
P9	Apr	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	B
P5	Jun	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	OL	A=B=C	OL
P6	Jun	WL	A=B	A	WL	A	OL	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	OL
P7	Jun	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	B
P8	Jun	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	B
P9	Jun	WL	A=B	A	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C
P5	Oct	WL	A=B	B	WL	A	OL	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	OL
P6	Oct	WL	A=B	A	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C
P7	Oct	WL	A=B	OL	WL	A	OL	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	OL
P8	Oct	WL	A=B	B	WL	A	OL	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	OL
P9	Oct	WL	A=B	A	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C

A= For domestic supply with disinfection; suitable for irrigation, industrial supply, aquaculture
B= For domestic supply after complete physical-chemical treatment; suitable for irrigation, industrial and aquaculture
C= For domestic supply it requires complete physical-chemical treatment; Not suitable for irrigation, suitable for industrial supply; suitable for aquaculture and for animal troughs
D= For domestic supply it requires storage, pre-sedimentation with complete treatment; Not suitable for irrigation, suitable for industrial supply, Not suitable for aquaculture
WL= Within the limits | OL= Out limits | Dry Season | Wet Season

Figure 10. Water quality classification in the monitored points in Huacata.

- Water quality in the Central Guadalquivir area

In this area, six points were monitored, which can be seen in Figure 11.



Points	Month	Be	Mg	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Sn	Hg	Pb	Class
P10	Jan	WL	A=B	C=D	WL	A	OL	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	OL
P11	Jan	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	B
P12	Jan	WL	A=B	A	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C
P13	Jan	WL	A=B	OL	WL	A	OL	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	OL
P14	Jan	WL	A=B	OL	WL	A	OL	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	OL
P15	Jan	WL	A=B	OL	WL	A	OL	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	B
P10	Apr	WL	A=B	B	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C
P11	Apr	WL	A=B	A	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C
P12	Apr	WL	A=B	A	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C
P13	Apr	WL	A=B	A	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C
P14	Apr	WL	A=B	A	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C
P10	Jun	WL	A=B	B	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C
P11	Jun	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	B
P12	Jun	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	B
P13	Jun	WL	A=B	B	WL	A	OL	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	OL
P14	Jun	WL	A=B	A	WL	A	A=B	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	B
P15	Jun	WL	A=B	A	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C
P10	Oct	WL	A=B	A	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C
P11	Oct	WL	A=B	B	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C
P12	Oct	WL	A=B	A	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C
P13	Oct	WL	A=B	A	WL	A	C=D	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	C
P14	Oct	WL	A=B	OL	WL	A	OL	A	A	A=B	A=B=C	WL	WL	WL	A=B=C	OL

A= For domestic supply with disinfection; suitable for irrigation, industrial supply, aquaculture
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D= For domestic supply it requires storage, pre-sedimentation with complete treatment; Not suitable for irrigation, suitable for industrial supply, Not suitable for aquaculture
WL= Within the limits | OL= Out limits | Dry Season | Wet Season

Figure 11. Water quality classification in the monitored points in the Central Guadalquivir area.

P10 had water quality between Class B and D in the wet season due to Fe concentrations outside the permissible limits. In the dry season, P10 presented a Class C quality characteristic. The pH was between 6.3 and 7.43. P11, both in the wet and dry seasons, gave Class B to Class C quality, but in the dry season, it gave Fe concentration outside the permissible limits. The pH was between 7 and 8. The P12 in most of the monitored months presented Class C quality, without metal concentrations outside the boundaries and with a pH of 6 to 7. P13 had a Class C quality in most months, but with Al and Fe concentrations outside the limits, the pH remained close to 7.5. The P14 presented high concentrations of Al and Fe in the months of January and October; in the other months, the quality of Class B and C was presented. The pH remained in the range of 6 to 7. The P15 had a Class B quality most of the year, without concentrations of heavy metals outside the permissible limits, and the pH was kept between 6 and 7.

3.3. Potentially Vulnerable Areas to Health Effects from the presence of Heavy Metals

As seen in the previous sections, both the Milluni and Guadalquivir basins have been affected by the presence of some toxic heavy metals. Unsustainable anthropogenic activities generated these metals. It should be mentioned that the water resources studied are natural sources of water for consumption. However, these waters go through treatment plants before being distributed. Still, these plants do not have specific processes to guarantee the total removal of heavy metals, which would not guarantee safe water if anthropogenic activities continue to impact water sources negatively—studied water sources. Figures 12 and 13 reveal the vulnerable areas of both study basins concerning the presence of heavy metals, these areas are colored in red and correspond to the sectors where the water has a quality outside the permitted limits (OL = Out of Limits).

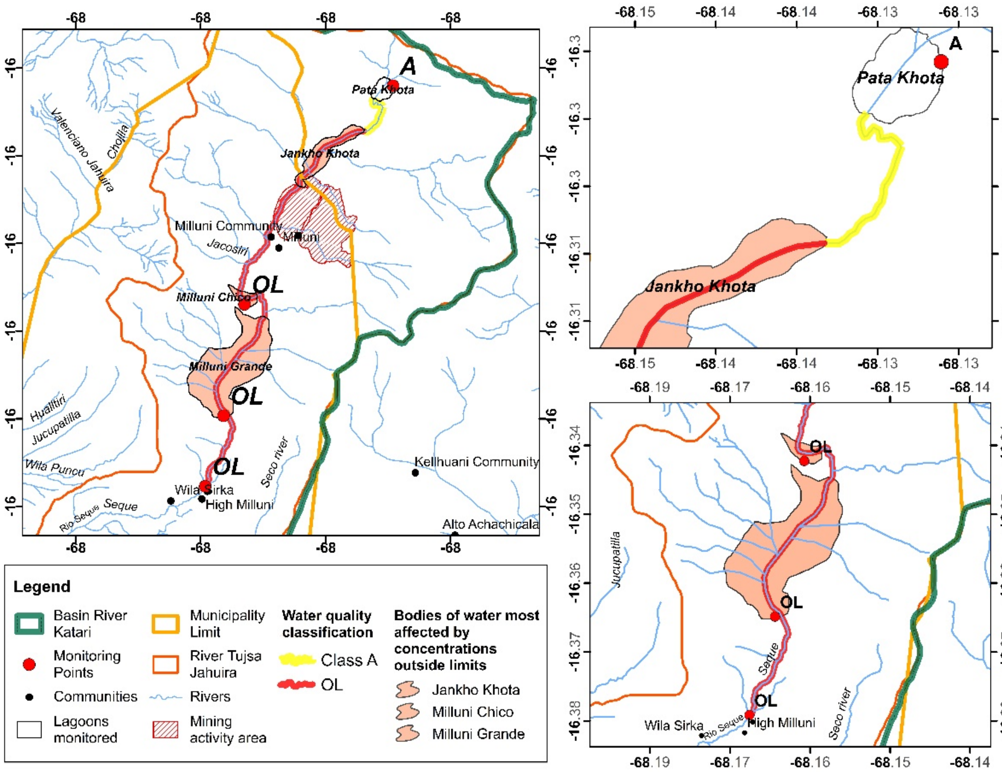

Figure 12. Vulnerable areas to the concentration of heavy metals in Milluni.

Milluni presents concentrations of heavy metals detected as As, Pb, Cr, Hg, Cd, and Zn in all the monitored points. Other light toxic elements, such as Be, and elements that evolve to taste and smell, such as Fe, Mn, and Mg, are also detected, making the sources unsuitable for consumption.

In the Guadalquivir study area, concentrations of Pb, Mn, Fe, and Al were identified as parameters that exceed permissible limits and are a threat to water quality and, therefore, the health of nearby populations.

Considering that heavy metals in the water carry a certain risk to public health, Table 1 presents the effects of heavy metals that were identified in the study basins.

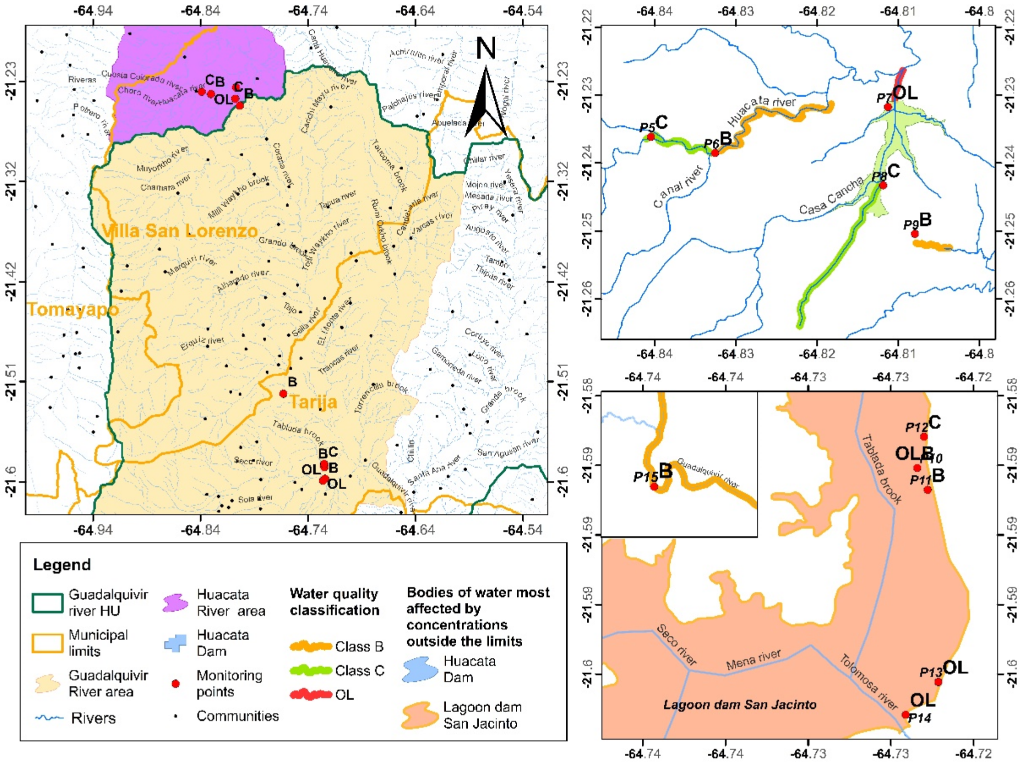

Figure 13. Vulnerable areas to the concentration of heavy metals in Guadalquivir.

Table 1. Health effects of heavy metals.

Heavy Metal Detected	Water Quality Limits			Health Effects
	EPA	NB 512	RMCH	
	g/m^3	g/m^3	g/m^3	
Be	0.004	NE	0.001	Intestinal injuries are the first effect on health,
Al	0.05–0.2	0.1	0.2	damage to the central nervous system, dementia, loss of memory, apathy, and severe tremors.
Mn	0.05	0.1	0.1	Damage to the central nervous system, dementia, loss of memory, apathy, and severe tremors.
Fe	0.3	0.3	0.3	In general, it does not present a health hazard. However, it can change the taste of water, cause reddish-brown stains on clothing, and cause buildup problems in pipes, pressurized tanks, and even water softeners.
Ni	NE	0.05	0.05	High probability of developing cancer of the lung, nose, larynx and prostate. Sickness and dizziness after exposure to nickel gas. Pulmonary embolism. Respiratory failures.Birth defects, asthma, and chronic bronchitis. Allergic reactions such as skin rashes, mostly from jewelry. Heart disorders.
Zn	5	5	0.2	Loss of taste and lack of appetite. It can affect the immune and enzyme systems of children.
As	0.1	0.1	0.05	Long-term exposure to arsenic through the consumption of contaminated food and water can cause cancer and skin lesions. It has also been associated with developmental problems, cardiovascular disease, neurotoxicity, and diabetes.
Cd	0.005	0.005	0.005	Eating food or drinking water with very high levels of cadmium can cause severe stomach irritation, leading to vomiting and diarrhea, and sometimes death. Ingesting lower levels of cadmium over a long period of time can lead to accumulation of cadmium in the kidneys.
Hg	0.002	0.001	0.001	Loss of peripheral vision, tingling sensations, usually in the hands, feet, and around the mouth, lack of coordination of movements, dysfunction of speech, hearing, and ability to walk, muscular weakness.
Pb	0.015	0.01	0.5	It can cause brain and kidney damage and can affect the production of red blood cells that carry oxygen to all parts of the body.

Source: Own elaboration based on [54,55,57].

4. Discussion

The water sources for the supply of the studied areas, Milluni and Guadalquivir, present contamination by heavy metals, which is mainly due to the unsustainable anthropogenic activities that have been developed around them. This confirms that population centers in developing countries face rapid waves of social transformation and economic development in which the environment is largely neglected [14]. The results of this research add to the scientific evidence that human activities have affected the environment, especially water [58–60]. The importance of water lies in the fact that it is indisputably linked to public health, and these to sustainable development, as established [23]. For this reason, preserving the water supply resources is essential to guarantee the development of the different nations in the world.

Heavy metals are considered priority pollutants due to their mobility in aquatic ecosystems and their toxicity to higher life forms [61,62]. Thus, the presence of heavy metals in drinking water sources represents an imminent risk to public health. For this reason, the removal of heavy metals from water for supply has become the challenge of the century to be addressed [62]. Despite scientific and technological advances [63–66], the most efficient treatment alternatives are also the most expensive, which limits their application in all contexts. Currently, you will find treatments with high efficiencies and affordable costs co-invested as a priority. More studies are needed such as [67,68], which focus on reducing the energy costs of different treatment systems, which would encourage their application. More alternatives are also required for the generation of clean energy that can be input into water treatment [69,70].

Finally, a focus on the different basins as complex socio-ecological systems contributes to a better understanding of the relationships between water and society in congruence with the study [71]. Therefore, the techniques to detect dangerous contaminants and prevent their dispersion into the environment must start from the engineering sciences but be linked to the social area. The foregoing will allow rational and conscious knowledge about the presence of heavy metals in the environment and thus establish strategies for their control, in addition to consolidating water management aimed at the shape of water systems.

5. Conclusions

Water is vital for living beings, so it is necessary to control the different sources of contamination. Special attention should be paid to concentrations of heavy metals that exceed permissible limits in water supplies because they represent risks to public health, as shown in Table 1. Heavy metals can be derived from the different economic activities of each region. The analysis of the potential impact of economic activities on water resources carried out shows the vulnerability of water to contamination with heavy metals in the study basins. It is highlighted that the development in both areas is not sustainable and affected the quality of their water resources, finding heavy metals with concentrations outside the permissible limits. In Milluni, the metals found were arsenic, chromium, mercury, manganese, iron, zinc, and tin, and there were also acidic pH values and high conductivities. The metals found in the Guadalquivir were lead, iron, and manganese; however, the pH ranges remained close to neutrality, which shows that the concentration of metals would not be excessive. Both study areas, despite having marked wet and dry seasons, had different results. For Milluni, regardless of the time of year, metals predominated with dangerous concentrations; on the other hand, for Guadalquivir, there were concentrations that exceeded the permissible limits in the dry season and not in the wet season, reflecting the phenomenon of dilution of contaminants during the season with greater volume of water, coming from the rains.

The problem of water sources being contaminated is not an isolated or punctual case since it is observed in other parts of Bolivia and the world. The first step to conserving source water is to conduct water quality inventories in all areas that may be vulnerable to the impact of contamination. Constant monitoring is a tool that helps identify the dynamics of the contaminants present and thus seeks techniques and/or technologies to eliminate them from the environment. Future research should prioritize the development of methods of continuous and affordable monitoring to ensure the control of water sources vulnerable to contamination by heavy metals and other contamination, to avoid ecological and public health disasters.

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

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