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Heavy metals and their impact on surface waters of the Mantaro river basin, Junin, Peru

Abstract

In the Mantaro river basin, located in Central Peru, an agricultural activity developed, even supplying the capital of Peru. An intense mining activity took place in the headwaters of this basin, and the La Oroya Metallurgical Complex was built a century ago. Mining activity has left mining environmental liabilities, which directly impact the quality of the water and the soil. In this sense, it is very important to investigate the presence of heavy metals and identify the geochemical associations present in surface waters to assess the real impact on the environment. For this purpose, 30 water samples were analyzed, collected from the Mantaro River and the channels that derive water for irrigation and animal consumption. The samples were analyzed by ICP-MS techniques, inductively coupled plasma-mass spectrometry, and ICP-AES, inductively coupled plasma-optical emission spectrometry. For the evaluation of the main physicochemical parameters, the ECA has been used, as the environmental quality standard of Peru, according to the Ministry of the Environment (2017); while for the chemical quality of surface water, the quality standards of the WHO, World Health Organization, were taken as a reference, according to the WHO guide (2017), being the elements considered: Al, As, Mn, Pb, and Zn. Investigations results show that the waters of some sectors have concentrations of As and Pb, which exceed the standards established by WHO, and there are also some specific cases (Muqui canal) in which Al and Mn exceed the WHO standard. In the case of Zn, its concentrations are much lower than the WHO standard.

Keywords: heavy metals, surface water, environmental impact, geochemical associations, mining environmental liabilities

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Jorge Chira,[1] Luis Vargas,[2] César Calderón,[3] Freddy Arcos,[4] Mayra Mogrovejo,[5] César De La Cruz[6]

[1]Coordination of Geology and Laboratories, Geological, Mining, and Metallurgical Institute – INGEMMET, Canada avenue 1470, San Borja, Lima, Perú
[2]Directorate of Laboratories, Geological, Mining, and Metallurgical Institute – INGEMMET, Canada avenue 1470, San Borja, Lima, Perú
[3]Directorate of Mineral and Energy Resources, Geological, Mining, and Metallurgical Institute – INGEMMET, Canada avenue 1470, San Borja, Lima, Perú
[4]Directorate of Mineral and Energy Resources, Geological, Mining, and Metallurgical Institute – INGEMMET, Canada avenue 1470, San Borja, Lima, Perú
[5]Directorate of Laboratories, Geological, Mining, and Metallurgical Institute – INGEMMET, Canada avenue 1470, San Borja, Lima, Perú
[6]Directorate of Mineral and Energy Resources, Geological, Mining, and Metallurgical Institute – INGEMMET, Canada avenue 1470, San Borja, Lima, Perú

Correspondence: Jorge Chira, Coordination of Geology and Laboratories, Geological, Mining, and Metallurgical Institute – INGEMMET, Canada avenue 1470, San Borja, Lima, Perú, Tel 51987934591, Email jchiraf@unmsm.edu.pe

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Introduction

Surface waters of the Mantaro River, which runs through the central Andes of Peru, show an appreciable content of heavy metals as a consequence of impact generated by the mining environmental liabilities located in the headwaters of the basin, in the town of La Oroya,[1] where an old metallurgical plant is located. Similar investigations have been developed in Ecuador by Oviedo et al.[2] who also determined the impact on the soil; Bhuyan et al.[3] carried out a similar investigation in Bangladesh, identifying values that exceed the WHO standards in Fe, Ni, and Al. On the other hand, Giri et al.[4] evaluated the surface water quality, determining that dissolved metals show greats seasonality, with the lowest concentrations in the rainy season. Bouguerne et al.[5] applied multivariate statistical techniques to evaluate temporal variations in surface water quality over ten years, identifying geochemical associations important.

Likewise, Nnorom et al.[6] investigated groundwater and surface water sources, determining Al and Fe as dominant contaminants in water bodies, coming from the shale of southeastern Nigeria. On the Chinese Loess Plateau, Xiao et al.[7] determined that the poor quality of river water is mainly related to high alkalinity and the danger of salinity, while the main contaminants in drinking well water were As, Cr and B. Chao-yang et al.[8] studied the distribution of Zn, Cd, Cu, Cr and As in Lake Honghu, indicating that these are below quality standards, denoting that Cr and As are derived mainly from industrial effluents. Using surface water and sediment samples from the upper Tigris River, Varol[9] determined that all concentrations of total nitrogen, total phosphorus, As, Cd, Co, Cr, Fe, Mn, Ni, Pb, and Zn in water samples were lower than the maximum concentration allowed for the protection of aquatic life, with Cu being the metal that exceeded the allowed threshold.

Mantaro area, Oncevay (2013) reports that the surface waters contain high contents of iron and total suspended solids, as a result of the presence of mine effluents. Custodian et al. (2019, 2020) evaluated the presence of Cu, Pb, Fe, Zn, and As in surface waters of the aforementioned basin, using multivariate methods, revealing that “the Mantaro River continues to be a sink for discharges of mining waste and runoff of liabilities miners in the headwaters of the Mantaro basin”. On the other hand, Orellana et al.[10] investigated soils and pastures, indicating that although the water contains leads at high levels, this does not imply a risk for the agriculture, since the bioconcentration factors were not significant. Aylas et al.[11] showed that the water of the Chanchas river (Mantaro basin) presents a higher concentration of pollutants during the afternoons, in alkaline pH conditions (8.69), being within the environmental quality standards for human consumption, but not for irrigation.

The water that flows downstream of the town of La Oroya[12] also does so through irrigation canals of the soils for agricultural use, which produce different vegetables that supply both the town of Huancayo and the city of Lima, the capital of Peru. In this way, it is necessary to evaluate the distribution of heavy metals and how they are associated with surface waters, identifying the most environmentally impacted areas. Results investigation mean a contribution principal to the knowledge of the environmental impact due to the heavy metals in surface waters in consequence of liability mining presence environmental.

Material and methods

In the collection of samples were used bottles of polyethylene with double lids. The samples were preserved with nitric acid (1:1) to ensure a pH lower than 2. The determination of metals was performed using the ICP-MS and ICP-OES techniques. Likewise, in situ readings of pH, electrical conductivity, and dissolved oxygen were taken at each sampling point, using HANNA 9828 multi-parameter equipment. ICP was developed for optical emission spectrometry (OES) by Wendt and Fassel at Iowa State University in the United States, and by Greenfield et al. at Albright & Wilson, Ltd. in the UK in the mid-1960s.[13] Inductively coupled plasma (ICP) mass spectrometry (MS) is commonly used in various research fields, such as earth sciences, food, chemical materials, and nuclear industry, among others. The high density of ions and high temperature in a plasma provide an ideal medium for atomization and ionization for all types of samples and matrices introduced by a variety of specialized devices.[14]

Instruments and reagents

The content of heavy metals in surface water samples was determined using the ICP-MS equipment, Perkin Elmer model Nexion 300D; and ICP-AES, Agilent Technologies model 735-ES. In the laboratory of the Geological, Mining and Metallurgical Institute of Peru, the samples were digested with high purity nitric acid (60-62%) and high purity hydrochloric acid (30-32%), through a digestion system of the hot block (SCP Science DigiPREP) under controlled conditions of pressure and temperature, according to EPA methods, U. S. Environmental Protection Agency, 200.7, determination of metals and trace elements in water and wastewater by inductively coupled plasma atomic emission spectrometry,[15] and EPA 200.8, Determination of Metals and Trace Elements in Water and Wastewater by Inductively Coupled Plasma - Mass Spectrometry.[16]

Results

Physicochemical parameters in surface waters

Based on a strategic sampling, water samples were collected in 30 places located in the Mantaro River, streams, and irrigation canals; pH, electrical conductivity, and dissolved oxygen readings were taken in each one (Table 1). On the other hand, in the laboratory of the Geological, Mining, and Metallurgical Institute, the concentrations of total metals were determined (Table 1). The pH ranges between 7.3 and 8.8, which to a certain extent favors the formation of metal hydroxides due to their insolubility in alkaline media.[17] According to the ECA (6.5 – 8.5), it identified that in four streams and three irrigation canals, said the standard was exceeded (Table 1). The electrical conductivity (EC) ranged from 111 to 853 µS/cm and did not exceed the ECA (2500 µS/cm), see Table 1. In the case of dissolved oxygen (DO), the ECA (≥4 mg/L) was exceeded in all the places sampled, except for the irrigation channel of the San Lorenzo district, in which this parameter is 7.58 mg/L (Table 1). From the applied multi-element techniques (ICP-MS and ICP-AES), a series of metals were quantified. However, the results of those that deserve special attention will be presented, given their environmental implications and their concentrations for the quality environmental standards considered.

Table 1 Physicochemical parameters and metals

Id	Sample	North	East	Zone	Drainage	Locality	EC (µS/cm)	DO (mg/L)	pH	Al (mg/L)	As (mg/L)	Mn (mg/L)	Pb (mg/L)	Zn (mg/L)
1	24l-002	8701899	433973	18	Molino stream	Molino	425	2.38	8.8	0.049	0.001	0.0051	0.0003	0.002
2	24l-003	8695044	443705	18	Mantaro river	Yauyos	768	1	8.03	0.269	0.012	0.2671	0.0024	0.046
3	24l-004	8697295	439151	18	Mantaro river	Parco	776	2.47	8.04	0.41	0.012	0.3017	0.0028	0.053
4	24m-003	8674902	476646	18	Zárate Huayccoc stream	Hullahoyo	248	1.83	8.54	0.11	0.001	0.0211	0.0003	0.002
5	24m-004	8685635	470036	18	Ingenio stream	Ingenio	390	1.68	8.68	0.03	0.013	0.0031	0.0003	0.009
6	24m-005	8689266	461045	18	Apata stream	Apata	181	2.26	8.09	0.406	0.004	0.0297	0.0003	0.003
7	24m-006	8691508	463024	18	Seco stream	Apata	146	1.18	8.49	0.016	0.002	0.0035	0.0003	0.003
8	24m-007	8702473	447657	18	Puyhuan stream	Pancan	140	0.78	8.2	0.041	0.002	0.0777	0.0003	0.006
9	24m-008	8697291	455974	18	Masma stream	Masma	113	1.24	8.37	0.04	0.002	0.0208	0.0003	0.003
10	24m-009	8692677	445400	18	Casa Blanca stream	Casa Blanca	358	2.55	8.7	0.307	0.002	0.0127	0.0019	0.006
11	24m-010	8696002	451224	18	Yacus stream	Ataura	709	2.66	8.46	0.1	0.01	0.1181	0.0025	0.029
12	24m-011	8694804	446333	18	Mantaro river	Yauyos	823	0	8.15	0.102	0.012	0.2615	0.002	0.044
13	24m-012	8684831	458978	18	Canal	Sincos	853	3.98	8.57	0.043	0.005	0.008	0.0003	0.039
14	24m-013	8673983	468977	18	Canal	Sicaya	809	2.96	8.51	0.224	0.013	0.1708	0.004	0.051
15	24m-014	8700011	452199	18	Julcan stream	Julcan	135	2.61	7.36	0.025	0.002	0.339	0.0003	0.006
16	24m-015	8702530	447865	18	Puyhuan stream	Molinos	111	1.81	7.65	0.1	0.002	0.0506	0.0005	0.004
17	24m-016	8692147	458653	18	Seco stream	Pampas	127	2.91	7.5	0.325	0.002	0.1051	0.0007	0.005
18	24m-016a	8691350	458858	18	Canal	San Lorenzo	623	7.58	8.05	0.1	0.006	0.0979	0.0013	0.01

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Table Continued...

Id	Sample	North	East	Zone	Drainage	Locality	EC (µS/cm)	DO (mg/L)	pH	Al (mg/L)	As (mg/L)	Mn (mg/L)	Pb (mg/L)	Zn (mg/L)
19	24m-017	8687126	467826	18	Santa Rosa stream	Santa Rosa	308	1.04	8.07	0.079	0.005	0.0121	0.0003	0.005
20	24m-018	8683405	464301	18	Quichuay stream	Quichuay	379	0.37	8.05	0.048	0.014	0.0262	0.0007	0.009
21	24m-019	8680051	472008	18	Quilcas stream	Quilcas	127	0.87	7.99	0.23	0.008	0.0175	0.0003	0.003
22	24m-030	8688853	455127	18	Canal	Huancani	757	1.15	8.41	0.327	0.011	0.1156	0.0053	0.037
23	24m-031	8689686	454531	18	Canal	Huancani	774	1.17	8.3	0.344	0.012	0.1727	0.0057	0.046
24	24m-032	8692188	453316	18	Canal	Muqui	773	1.07	8.26	2.359	0.035	0.4966	0.1113	0.357
25	24m-033	8692676	453906	18	Canal	Muquiyauyo	770	1.43	8.26	0.2	0.012	0.2497	0.0035	0.034
26	24m-034	8694406	451484	18	Canal	Muquiyauyo	766	1.35	8.31	0.86	0.02	0.3408	0.0318	0.165
27	24m-035	8695222	446779	18	Canal	Huaripampa	777	1.46	8.17	0.228	0.012	0.2671	0.0029	0.043
28	24m-036	8696588	448755	18	Canal	Jauja	712	1.62	8.17	0.111	0.01	0.1724	0.0015	0.034
29	24m-037	8693708	453490	18	Canal	Huamaly	702	1.37	8.43	0.635	0.014	0.179	0.0128	0.079
30	24m-038	8689184	456405	18	Canal	San Lorenzo	716	1.82	8.65	0.499	0.017	0.0752	0.0164	0.086

EC: Electric conductivity.

DO: Dissolved oxygen

Chemical quality of surface water

For the evaluation of the chemical quality of the surface waters of the Mantaro river basin, the environmental quality standards established by the WHO (Table 2) for five elements have been taken into account: Al, As, Mn, Pb, and Zn (Figure 1–10). The highest content of aluminum (2.36 mg/L) is recognized in the channel of the Muqui locality (24m-032), which widely exceeds the WHO standard (Figure 1). With the exception of the channel of the town of Muqui (24m-032), the other samples show aluminum values lower than the WHO standard, including the water from the Muquiyauyo channel (24m-034), where the concentration of this metal is 0.86 mg /L (Figure 1). Regarding arsenic, it was evidenced that it is the metal that most frequently exceeded the WHO standard, in this case, 51% of the samples are greater than 0.01 mg/L (Figure 2). This undoubtedly denotes a characteristic hydrochemical pattern in the study area, expressed in the maximum statistical variability of the metals studied. The highest concentrations of arsenic occur in the canals of the towns of San Lorenzo (0.017 mg/L), Muquiyauyo (0.020 mg/L), and Muqui (0.035 mg/L), exceeding the WHO standard by up to 3.5 times (Figure 2). Manganese shows a behavior similar to aluminum, being for both cases the sample 24m-032, the one that exceeds the respective WHO quality standards (Figure 3).

Table 2 Water quality standards, WHO (2018)

Element	Quality standard - WHO (mg/L)
Aluminum (Al)	0.9
Arsenic (As)	0.01
Manganese (Mn)	0.4
Lead (Pb)	0.01
Zinc (Zn)	3

WHO: World Health Organization

The manganese contents closest to the WHO quality standard correspond to samples 24m-034 (0.34 mg/L), 24m-014 (0.34 mg/L), and 24l-004 (0.30 mg/L), as shown in Figure 3. It should be noted that the manganese variability pattern is the second-highest, after arsenic, both patterns being similar (Figures 2 and 3). As for lead, the values that exceed the WHO quality standard range from 0.013 to 0.111 mg/L (Figure 4), located in the channels of the towns of Muqui, Muquiyauyo, Huamaly, and San Lorenzo, respectively. As shown in Figure 4, except for the lead samples that exceed the WHO quality standard, it is evident that the concentrations of this metal describe a relatively stationary pattern, with a plateau of 0.006 mg/L, which is reflected in the minimum statistical variability of the investigated metals. Zinc is the only metal that did not pass the WHO quality standard (Figure 5). The maximum concentration is evidenced in sample 24m-032 (0.357 mg/L), located in the channel of the town of Muqui. The zinc average in the studied waters is of the order of 0.04 mg/L, with a standard deviation of 0.07 mg/L, which describes a lower variability than the patterns of As, Mn, and Al (Figure 5).

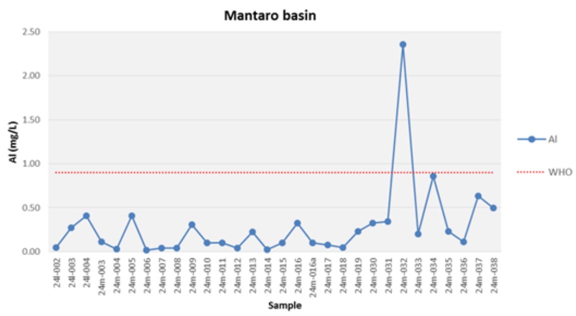

Figure 1 Aluminum in surface waters in the Mantaro basin.

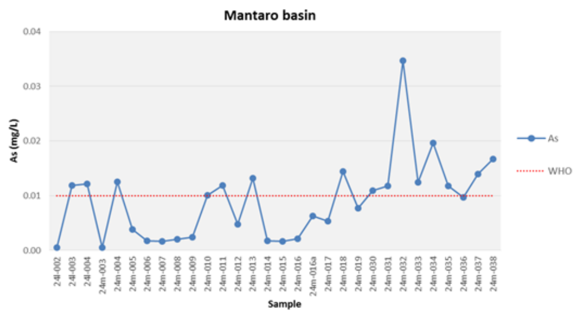

Figure 2 Arsenic in surface waters in the Mantaro basin.

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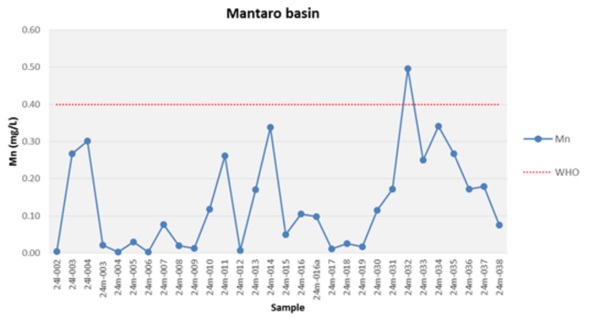


Figure 3 Manganese in surface waters in the Mantaro basin.

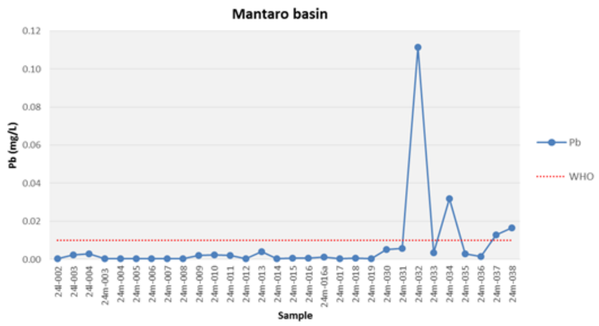


Figure 4 Lead in surface water in the Mantaro basin.

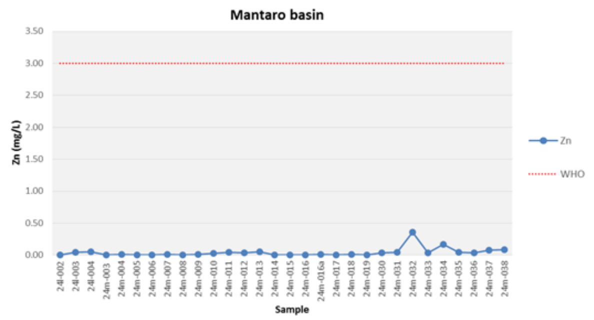


Figure 5 Zinc in surface waters in the Mantaro basin.

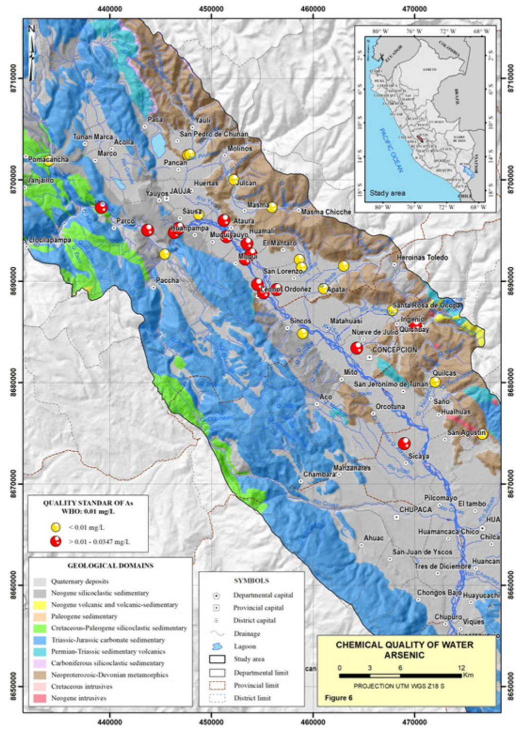
Statistical correlations

Table 3 shows the Pearson correlation indices, which show that the highest positive correlations occur between Pb-Zn (0.97), Pb-Al (0.97), Al-Zn (0.95), and As-Zn (0.87), As-Al (0.79) and As-Pb (0.87). These indices allow us to postulate a geochemical association composed of Al, As, Pb, and Zn, under alkaline pH conditions.

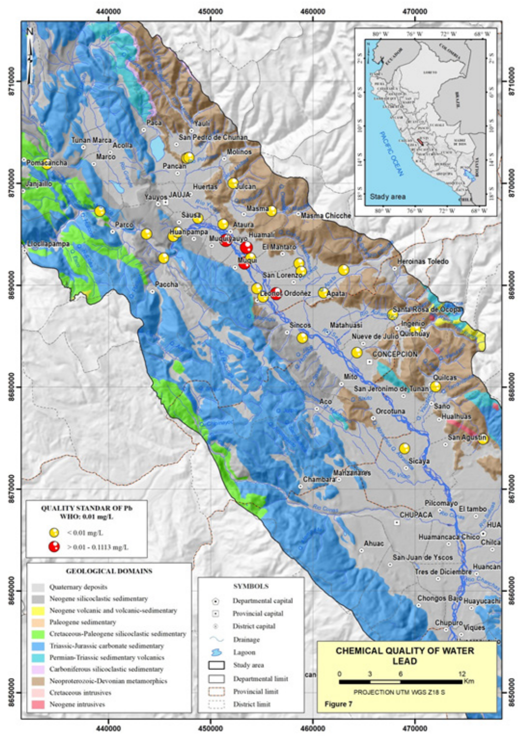
Table 3 Pearson correlation indexes

	pH	EC	DO	Al	As	Mn	Pb	Zn
pH	1	0.336	-0.034	0.038	0.14	-0.309	0.071	0.106
EC	0.336	1	0.078	0.322	0.66	0.541	0.297	0.486
DO	-0.034	0.078	1	-0.138	-0.239	-0.13	-0.142	-0.155
Al	0.038	0.322	-0.138	1	0.788	0.633	0.966	0.953
As	0.14	0.66	-0.239	0.788	1	0.678	0.785	0.868
Mn	-0.309	0.541	-0.13	0.633	0.678	1	0.615	0.713
Pb	0.071	0.297	-0.142	0.966	0.785	0.615	1	0.967
Zn	0.106	0.486	-0.155	0.953	0.868	0.713	0.967	1

pH: Hydrogen potential. EC: Electric conductivity. DO: Dissolved oxygen



The arsenic contents that exceeded the WHO quality standard (0.01 mg/L), are distributed between the localities of Parco and Sicaya, controlled by the surrounding alkaline environment, related to the Triassic-Jurassic carbonate formations and environmental liabilities mining, the product of the exploitation of polymetallic deposits in the headwaters of the basin. Between the towns of Muquiyauyo and Muqui, there are the highest concentrations of this metal. In the Ranra River (24m-004) and the ravine of the town of Concepción (24m-018), tributaries of the Mantaro River, the arsenic content that exceeds the quality standard can be attributed to anthropic factors and the metamorphic units of the Neoproterozoic-Devonian.



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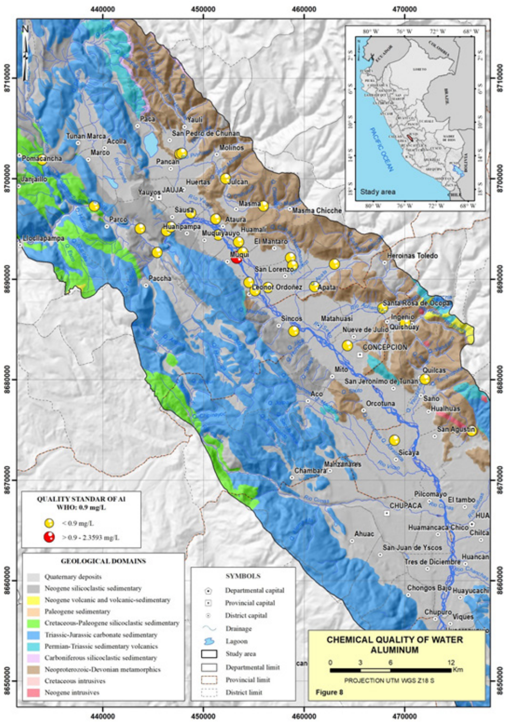
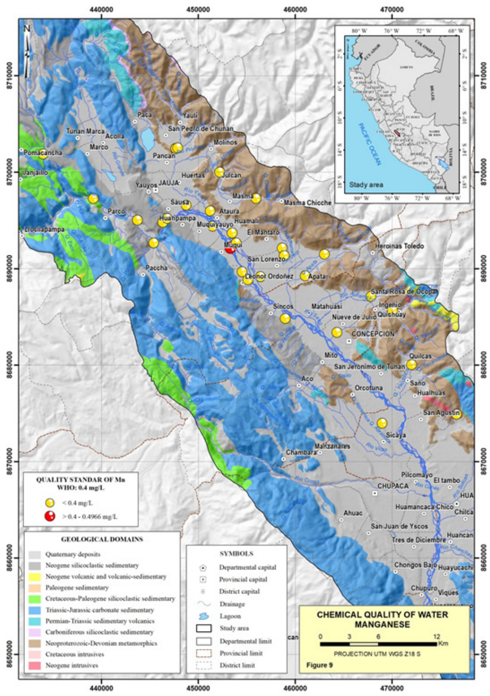
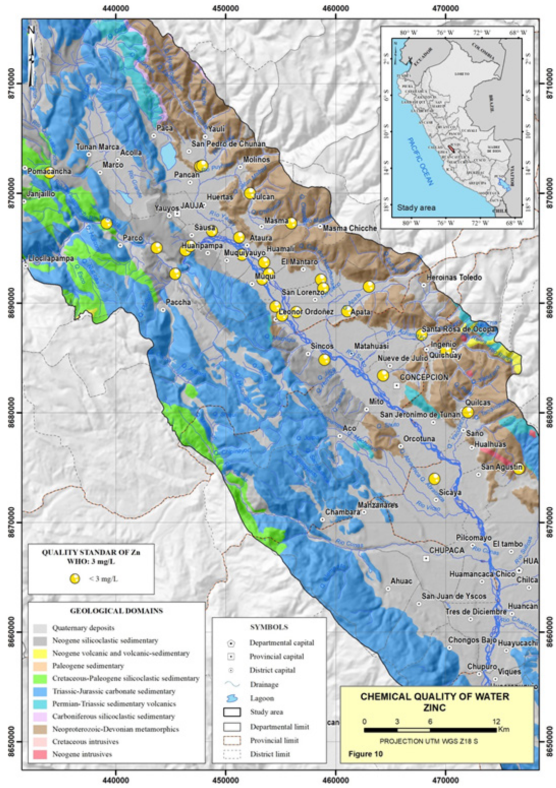
Lead is the second metal that exceeded the WHO quality standard (0.01 mg/L) in agricultural irrigation canal water, specifically between the towns of Muquiyauyo and San Lorenzo. It is not ruled out that this metal would come from the effluents discharged into the waters of the upper Mantaro river basin, and that in the study area they are used for irrigation through canals. In the channel of the town of Muqui, this metal exceeds the WHO quality standard by more than 11 times.



Unlike arsenic and lead, aluminum content did not exceed the WHO quality standard (0.9 mg/L), except in the irrigation canal of the town of Muqui, where it exceeded the quality standard by more than two times. It is related to the low relative mobility of this metal in alkaline conditions and its possible leaching as a result of irrigation, especially in the agricultural land of the aforementioned locality.



Manganese shows a behavior similar to aluminum, so the irrigation canal in the town of Muqui was the only place that exceeded the quality standard determined by the WHO (0.4 mg/L). It is probably influenced by its low relative mobility in basic media and its possible leaching from the irrigation of agricultural land in the town of Muqui.



Unlike the metals described above, zinc shows the lowest relative mobility in alkaline media, in this case very low. Zinc concentrations did not exceed the WHO quality standard (3 mg/L), with the maximum concentration being around 0.357 mg/L, located in the irrigation channel of the town of Muqui.

Discussion

Based on the findings found, heavy metal content was found in the waters of the Mantaro River, some tributaries, and irrigation canals, with arsenic being the metal with the highest occurrence of concentrations that exceed the WHO standard (0.01 mg/L) these concentrations denote a range from 0.011 to 0.035 mg/L (Figure 6). Lead is next in importance, whose contents exceeded the WHO standard (0.01 mg/L), specifically in the canals of the towns of Muqui (0.111 mg/L), Muquiyauyo (0.032 mg/L), Huamaly (0.012 mg/L). L) and San Lorenzo (0.017 mg/L), as shown in Figure 7. Aluminum (2.36 mg/L) and manganese (0.50 mg/L) only exceeded the WHO standards in the channel of the Muqui locality (Figures 8 and 9). As for zinc, its concentrations do not exceed the WHO standard (3 mg/L), as shown in Figure 10. The impact of heavy metals in the waters of the Mantaro basin describes a predominantly fluvial pattern consistent with some geochemical factors such as mobility, pH, and adsorption, in addition to the main anthropic variable, in this case, the mining environmental liabilities located upstream of the investigated area. The fluvial course impacted by arsenic has an approximate length of 35 km between the towns of Parco and Leonor Ordóñez; while lead impact approximately 10 km of the river course between the towns of Ataura and Leonor Ordóñez. It is important to mention that 75% of the sampled irrigation canals are impacted by at least one of the metals under study.

It is evident that the hypotheses of authors such as Arce (2017) and Custodio et al. (2019, 2020), who state that the mining liabilities located in the headwaters of the Mantaro basin are the cause of the metals present in the waters of the Mantaro River and the channels studied. Likewise, it is shown that the waters studied are predominantly alkaline, with pH values from 7.3 to 8.8, denoting a physicochemical similarity with the alkaline and polluted scenario of the Chachas River, described by Aylas et al. (2021). Bivariate statistics determined the Al-As-Pb-Zn association, which would be related to the main polymetallic ores in central Peru. Undoubtedly, it is necessary to expand the investigations regarding heavy metals in the Mantaro river basin to correlate the geochemical dispersion in other matrices such as soils and sediments.[18–22]

Conclusion

The waters of the Mantaro River and the main agricultural irrigation canals between the towns of Parco and Leonor Ordoñez show metallic contents that exceed the WHO standards in at least one of the chemical elements studied. Arsenic is the metal that predominantly impacts the waters of the study area, this is explained by its greater relative mobility in alkaline media, related to the Triassic-Jurassic carbonate formations. Given the arsenic dispersion pattern, it is postulated that it comes from mining environmental liabilities located in the headwaters of the Mantaro basin. The same-origin is attributed to lead, which exceeded the quality standard in the irrigation canals located between the towns of Muquiyauyo and San Lorenzo. The only sample (24m-032) where aluminum and manganese exceeded the WHO quality standard is located in the irrigation channel of the town of Muqui. For both metals, this scenario is consistent with their low relative mobility in basic environments and their possible leaching as a result of agricultural irrigation. The highest concentration of zinc was identified in sample 24m-032 (0.357 mg/L), although it did not exceed the WHO quality standard. The metallic contents studied to define a marked hydrochemical association under alkaline conditions, made up of Al, As, Pb, and Zn, which suggests that these metals come from mining residues, a product of the exploitation of polymetallic deposits housed mainly in the carbonated units of the center from Peru.

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Conflicts of interest

There are no conflicts of interest.

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