

INCIDENCE OF HEAVY METALS IN WATER, SOIL, ALFALFA (MEDICAGO SATIVA L.) AND SHEEP (OVIS ARIES L.) ALONG THE QUILCA - VITOR - CHILI BASIN IN AREQUIPA, PERU

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Abstract: The concentration of heavy metals (Cd, Cu, Cr, Fe, Hg, Pb, Zn) and arsenic was determined in water, soil and alfalfa samples in three sites (Congata, Uchumayo and Vitor) located along the Quilca - Vitor - Chili River, near the city of Arequipa, Peru. The content of these elements was also analysed in samples of alfalfa at different times of being planted (1 to 3 months) in Congata. Alfalfa planted in three other locations (Quiscos, Yarabamba and La Joya) upstream and downstream of the first three was also analysed. To determine the concentration of heavy metals in sheep, measurements were made on liver and kidney samples from animals farmed in the first three sites. The concentration of metals and arsenic in the water samples was lower than the Peruvian environmental quality standards, except for Hg in Vitor (0.0001 mg L⁻¹). The Cd content in the soil at all three sites (62.01 - 381.94 mg kg⁻¹) was well above the EQS for agricultural, commercial or industrial soils. The Cd content in the alfalfa samples grown in the same soils was higher than that observed in the samples from Quiscos, Yarabamba and La Joya. The estimated daily intake values (EDI) for metals detected in sheep kidneys and liver (Fe, Cu, Zn) were below the provisional maximum tolerable daily intakes (PMTDI) for children and adults, while the target hazard quotient (THQ) and total THQ of these elements were less than 1, indicating that their consumption would not have an adverse health effect.

Keywords: heavy metals, alfalfa, copper, mining, meat

1. INTRODUCTION

Heavy metals occur in varying concentrations in the water, soil and air of the planet, and can accumulate in living beings through the food chain. They have different origins, and can also come from human activities such as agriculture (fertilisers), sewage treatment sludge, mining, commerce and industry (International Programme on Chemical Safety, 1992, Bampidis et al., 2013). Some of these metals such as Fe, Cu and Zn are essential for biological processes (JECFA, 2011b). In plants and animals exposed to high concentrations of heavy metals, these can occur in higher concentrations depending on the organ or tissue (Damian et al., 2019a), as well as the specie. Due to the toxic characteristics of some of these metals such as Cd, Hg and Pb, the exposure of the population through water, air and food must be monitored. Toxic heavy metals

such as Cd and Pb are known to accumulate in the tissues (particularly the liver and kidney) of terrestrial and aquatic animals, especially those that feed on detritus (JECFA, 2011b). Consumption of or chronic exposure to Pb can lead to increased systolic pressure and decreased IQ (intelligence quotient), while Cd is a carcinogen associated with lung cancer mainly by inhalation and inorganic As is also carcinogenic and mostly naturally present in food and water due to geochemical conditions (JECFA, 2011a). Also, the levels of Cr, Co, Ni, Cu, Zn, As, Cd and Pb in river sediments may be higher than the geochemical background values (Maftei et al., 2019b).

Alfalfa (*Medicago sativa*) is a plant of the legume family used as a medicinal plant and as food for animals. In Peru, it is commonly used to feed sheep and cattle, as well as guinea pigs (*Cavia porcellus*). Sheep (*Ovis aries* L.) are the third largest source of mammal meat in the province, after cattle

and pigs. Its consumption is mainly associated with small livestock and subsistence farming, which is why part of the slaughtering is not done in established slaughterhouses but is done in part of the slaughtering is not done in established slaughterhouses but is done in 86.21% of the cattle population (León Hinostroza, 2019). Most cattle production is carried out in a technified manner, in stables with controlled feeding conditions, while sheep are the main livestock of small farmers and are raised freely, feeding mainly on fodder and grasses grown on the same farms. This would make them good indicators of contamination.

In the case of Peru, accidents and suspected contamination with heavy metals by industry and mining have generated conflicts between companies and populations. For this reason, government agencies and other organisations carry out specific monitoring to evaluate the concentration of these elements in nearby or declared areas within the impact area of mining and industrial activities. Peru has established maximum permissible limits (MPLs) for the discharge of mining or metallurgical liquid effluents (DS N° 010-2010-MINAM, 2010) and maximum allowable values (MAVs) for non-domestic wastewater discharged into the sewer system (DS N° 021-2009-VIVIENDA, 2009), for the oil industry (DS N° 037-2008-PCM, 2008), and tanneries (DS N° 003-2002-PRODUCE, 2002). There are no MPLs for heavy metal concentration in wastewater treatment plant effluents (DS N° 021-2009-VIVIENDA, 2010). Environmental quality standards (EQS) are also established for surface water, water for irrigation and animal drinking (DS N° 004-2017-MINAM, 2017), and soil from agricultural, domestic, commercial, and industrial activities (DS N° 011-2017-MINAM, 2017). In central Peru, the concentration of Zn in sheep liver was related to the distance to a nearby Zn smelter, although the concentration of Cu in more distant areas was higher (Reif et al., 1989). In southern Peru, the concentration of Cd and Hg in the urine of the population near a copper mine increased compared to the pre-exploitation period (Astete et al., 2014). As the apparent half-life of Cd in human kidneys is about 15 years, a steady-state would be reached after more years of exposure (JECFA, 2011b). Therefore, the analysis of heavy metal and As in water, soil, plants and animals in the area is useful to identify levels above those established by the standards and their uptake in the food chain.

Previously, the hydrographic basin of Arequipa was studied to evaluate the effect of urbanisation on water quality and its impact on human health. A direct correlation was found

between urbanisation and a decrease in water quality and an increase in the incidence of gastrointestinal diseases (Villena Carpio & Fath, 2011). High levels of As in drinking water have also been observed in the localities of Congata and Tiabaya (Diaz-Rodriguez et al., 2015). The purpose of this study was to evaluate the level of heavy metal contamination in the water of the Quilca - Vitor - Chili River, soils of alfalfa fields irrigated with river water, alfalfa and viscera of sheep raised in alfalfa fields. Congata, Uchumayo, and Vitor were established as study areas because they are places where agriculture is reduced in extension and mainly dedicated to family and local consumption, as well as close to the contaminating influence of the city. The heavy metal content of alfalfa grown far from the river was also analysed, as well as the heavy metal content during alfalfa growth.

2. MATERIAL & METHODS

2.1. Location and study area

The Quilca - Vitor - Chili River basin is located in the Arequipa Region in southern Peru. The river provides water to the city of Arequipa, in the province of the same name, in addition to the irrigation of La Joya and the Vitor Valley. The Yura River joins the Chili River to form the Vitor River. The basin empties into the Pacific Ocean and its flow varies from 5 to 24 m³ s⁻¹ (Falcón, 2009). Congata and Uchumayo are traditional districts near the city of Arequipa with a presence of small-scale agriculture and livestock, mainly for local consumption and sale, as are Vitor and Yarabamba, which are further away from the city. Quiscos is a small farming town even further away from the city and located upstream. La Joya is a more modern irrigation system mainly dedicated to the production of agricultural products for export. The average temperature of the Chili River near Uchumayo and Congata is 18°C and the average pH is 7.65 (Torres-Franco et al., 2019). The average pH of the river sediments in Uchumayo and Congata is 7.12 and 7.31 respectively (Monge Quispe, 2018). The hydraulic works along the basin include dams, canals and irrigation tunnels that are only recently being modernized. The wet months in the basin area are from December to April, while the dry climate predominates in the rest of the year (Abarca Romero et al., 2015).

The city of Arequipa has approximately one million inhabitants and its main economic activities are services, commerce, agro-industrial production, brewing, tanneries, textile manufacturing, boron, cement and mining. Copper is the main mineral extracted in the province, and the open-pit mine

(approximately 2650 meters above sea level) is located near 16 km from the centre of the city. There is not always a clear separation between the city limits and agricultural and industrial areas, and wastewater from activities such as tanneries in the Rio Seco Industrial Park can infiltrate the groundwater that runs through streams that discharge near the Uchumayo sector (Trujillo Vera, 2007). The National Water Authority has also identified up to 9 municipal solid waste dumps in riverbeds, mainly near the city (National Water Authority, 2012), while in the Vitor sector agricultural effluent discharges are the most important (Falcón, 2009). The main crops near the river are vegetables such as onions, garlic, potatoes, as well as alfalfa to feed the cattle and sheep. Farmers practice monoculture for 2-3 seasons, followed by the cultivation of alfalfa or grass and a 6-month rest for the land (Villena Carpio & Fath, 2011). The wastewater from the city has a very high concentration of total suspended solids ($743 \text{ mg TSS L}^{-1}$) and organic material ($821 \text{ mg BOD}_5 \text{ L}^{-1}$) (Caceres & Alca, 2016) and is treated at two wastewater treatment plants (La Enlozada and La Escalerilla) using physical and biological methods. Some of the treated water is then discharged into the Chili River.

Cárdenas (1960) distinguished in the Arequipa area the basement constituted by metamorphic rocks (Charcani gneiss), sedimentary rocks represented by Jurassic clastic and carbonate rocks (Yura group) and intrusive rocks of La Caldera batholith that emerge in the southern part of the city. On top of this basement, the rocks have been little studied and they correspond to andesites and basalts that surface in the Cincel bridge area, which are overlain by the "Sencca" ignimbrite. Núñez de Prado et al., (2001) also identified the "Salmon" stratified tuff, which is arranged in layers (separated according to particle size) that follow the underlying topography, are of a rhyolitic composition and great uniformity, lack quartz and have pozzolanic properties, occupying an extensive area in the triangle formed by the Yura and Chili rivers. The best exposures of this unit are observed in the cut of the Chili River between Chilina and Charcani, on the right bank where it is associated with layers of pumice stone. The geology map of the study area is shown in Figure 1.

2.2. Sampling locations and procedure

The sampling sites are presented in Figure 2, using a copper mine as a geographical reference. In order of linear distance from the open-pit mine, they sampling sites were: Congata (10.3 km, 2080 m a.s.l.), Yarabamba (13.5 km, 2480 m a.s.l.), Uchumayo (14.7 km, 1950 m a.s.l.), La Joya (36.1

km, 1250 m a.s.l.), Vitor (36.5 km, 1150 m a.s.l.) and Quiscos (40.4 km, 2920 m a.s.l.). Three samples of river water, soil, and alfalfa samples were taken in Congata, Uchumayo, and Vitor in May 2017. Sheep liver and kidney samples were taken in October 2017 from slaughtered animals (all adult females) that were raised in the alfalfa fields corresponding to these three locations. The sheep were free of apparent disease until the time of their slaughter in the Camal Metropolitano de Arequipa. Commercial samples of sheep liver and kidney were obtained from a market in the city of Arequipa in the same month. Three samples of kidney (approximately 80 g) and three samples of liver (approximately 130 g) were collected in HDPE containers previously rinsed with distilled water and analysed within 24 hours of acquisition.

To study the variation of heavy metal concentration in alfalfa according to the time of growth of alfalfa, samples from Congata were used, from September to November 2018. Three alfalfa samples were also taken from locations upstream of the river (Quiscos, 40.4 km, 2920 a.s.l.), near a tributary of the Chili River (Yarabamba, 13.5 km, 2480 m a.s.l.), and downstream in an irrigation system far from the main river course (La Joya, 36.1 km, 1250 m a.s.l.) in May 2019.

The water samples were obtained using an HDPE bucket that collected surface running water in the middle of the river, in each of the locations (Congata, Uchumayo and Vitor). They were stored in closed polyethylene containers of 500 mL and refrigerated at $4 \text{ }^\circ\text{C}$ until analysis. Soil samples were taken from the surface part refrigerated at $4 \text{ }^\circ\text{C}$ until analysis. Soil samples were taken from the surface part (rhizosphere), up to a depth of 15 cm using a hard plastic shovel. Approximately 1000 g were obtained from each area, which were stored in polyethylene bags at 22.7°C until analysis. Stones, gravel and woody materials were removed from the soil samples, according to Khanum et al., (2017). For the alfalfa samples, the tops of the plants were cut off above 10 cm above the ground. Approximately 335 g of alfalfa were collected from each area, which were also stored in polyethylene containers at 22.4°C until analysis. The bucket, containers and shovel were carefully washed with deionised water before use. All samples were taken for analysis within 24 hours of collection.

2.3. Heavy metals and arsenic analysis

The water samples were analysed for the metals cadmium (Cd), copper (Cu), chromium (Cr), iron (Fe), mercury (Hg), lead (Pb) and zinc (Zn) by Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS), following EPA method 6020A revision

1.0 (US EPA, 2007a). The metalloid arsenic (As) was analysed using the same method. Results were expressed as $\mu\text{g L}^{-1}$. Soil samples were previously treated with the digestion procedure described in EPA method 3050B revision 2.0 (US EPA, 1996a) before being analysed by ICP-MS, except for

mercury (Hg) which was treated and analysed according to EPA method 7471B revision 2.0 (US EPA, 2007b). This method had a detection limit of 0.1 and 0.005 mg kg^{-1} for As and Hg, respectively. In the case of alfalfa samples from Congata, Vitor and Uchumayo, they were analysed by atomic absorption

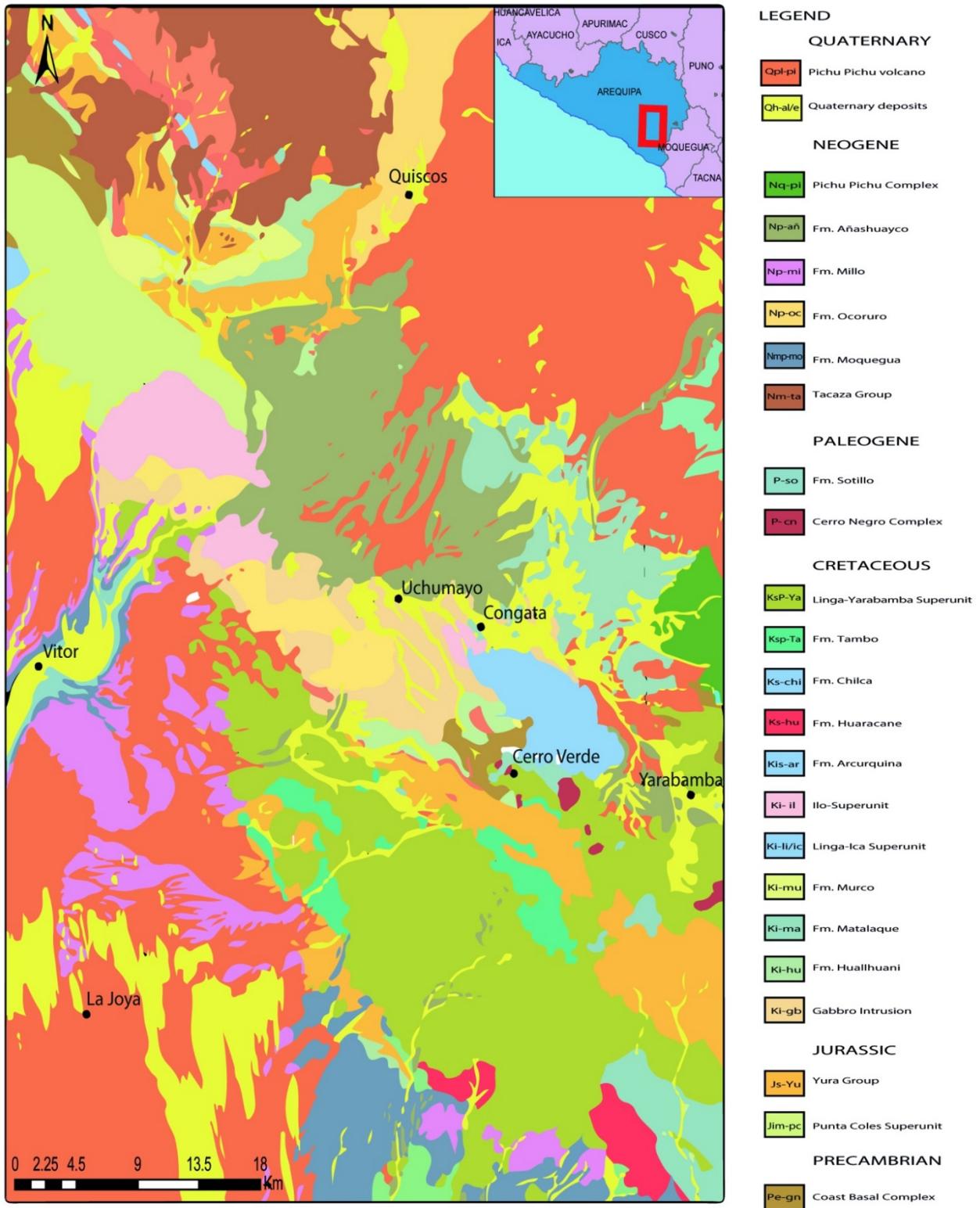


Figure 1. Geology map of the study area.

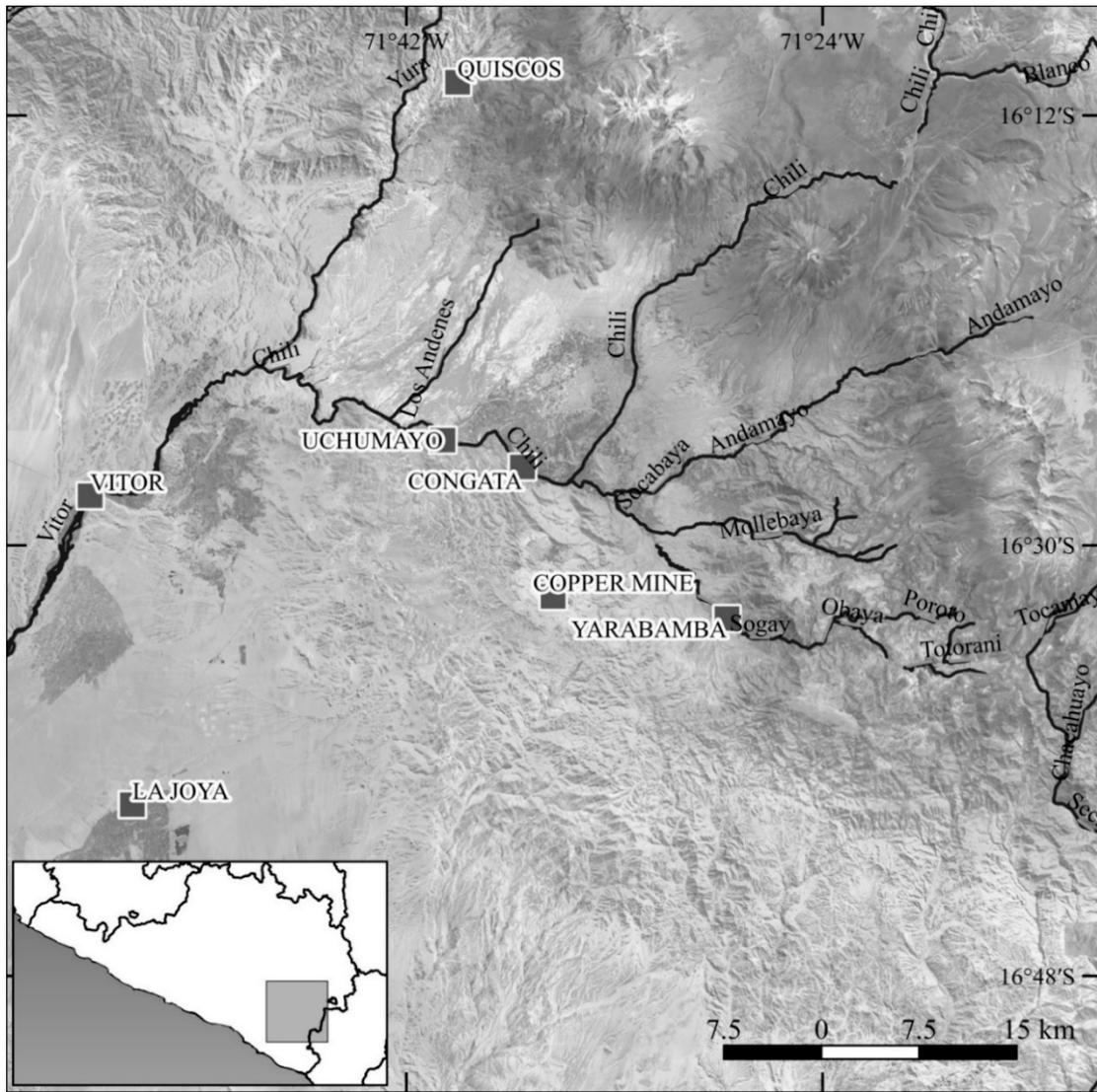


Figure 2. Location of the sampling sites and the Quilca – Vitor – Chili basin

spectrophotometry (AAS), with a detection limit for As, Hg and Cd of 0.1, 0.05 and 0.05 mg kg⁻¹, respectively. Samples from Quiscos, Yarabamba and La Joya were analysed by ICP-MS which had a detection limit for Hg of 0.005 mg kg⁻¹. Liver and kidney samples were also analysed by atomic absorption spectrophotometry and expressed as wet basis. The detection limits for As, Cd, Cr, Hg and Pb were 0.1, 0.05, 0.15, 0.05 and 0.2 mg kg⁻¹ respectively.

2.4. Estimated daily intake (EDI)

The estimated daily intake (EDI, µg kg⁻¹ body weight day⁻¹) was determined according to Eq. 1 (adapted from Luo et al., (2018)) for the elements analysed in the sheep liver and kidney. In the equation, C is the metal concentration (mg kg⁻¹, fresh weight), FIR is the mean food intake rate (g day⁻¹) and BW is the reference body weight (kg body weight). The average per capita consumption of offal

in the Peruvian population is 3.5 kg year⁻¹ (Instituto Nacional de Estadística e Informática, 2002) and the offal from sheep represents 16.83% of the total offal production (León Hinostroza, 2019), so we have estimated the FIR as 3.5 kg year⁻¹ × 0.1683 × 365⁻¹ year day⁻¹ × 1000 g kg⁻¹ = 1.614 g day⁻¹, for both kidney and liver. The average weight of children aged 5 to 17.9 years was estimated at 32.3 kg from the averages reported for each sex by Cossio-Bolaños et al., (2020). The average weight of the adult Peruvian population of both sexes was estimated at 57.5 kg (Instituto Nacional de Estadística e Informática, 2002; Instituto Nacional de Salud, 2014).

$$EDI = \frac{FIR \times C}{BW} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{1000 \mu\text{g}}{1 \text{ mg}} \quad (1)$$

2.5. Target hazard quotient (THQ)

The non-carcinogenic risk from consumption of metals in sheep offal was estimated using the

Target Hazard Quotient (THQ). THQ (unitless) values were determined using Eq. 2 (Chien et al., 2002).

$$THQ = \frac{Efr \times ED_{tot} \times FIR \times C}{RfDo \times BW \times AT} \times 10^{-3} \quad (2)$$

Where EFr is the frequency of exposure (350 days year⁻¹, (US EPA, 1996b)), ED_{tot} is the duration of exposure (17.9 years for children, 74.6 years for adults (Instituto Nacional de Estadística e Informática, 2015)), RfDo is the oral reference dose (mg kg⁻¹ day⁻¹) and AT is the average exposure for non-carcinogens in a year (350 days year⁻¹ x years of exposure). The RfDo for Cu, Fe and Zn were 4 x 10⁻¹, 7.0 x 10⁻¹ and 3.0 x 10⁻¹ mg kg⁻¹ day⁻¹, respectively (US EPA, 2019). THQ values less than 1 indicate no adverse effect on human health. The total target hazard quotient (TTHQ) was determined by Eq. 3.

$$Total\ THQ\ (TTHQ) = THQ_{metal1} + THQ_{metal2} + \dots + THQ_{metal\ n} \quad (3)$$

2.6. Statistical analysis

The metal concentration data in the area of the river Chili closest to the city (Congata, Uchumayo and Vitor) were compared with the average of the metal concentration data obtained in the areas of the river farthest from the city of Arequipa (Yarabamba, La Joya, Quiscos) using the Welch t-test of the statistical environment R (version 3.4.4) (R Core Team, 2020).

3. RESULTS & DISCUSSION

3.1. Heavy metals and arsenic content

The concentrations of heavy metals and metalloid in water and soil, as well as samples of alfalfa, in the areas of Congata, Vitor and Uchumayo are reported in Table 1. On average, the main element present in the water was Fe, followed by Zn, As, Cr, Cu, Pb, Cd and Hg, with mean values of 144.0 ± 93.2, 28.3 ± 10.2, 19.140 ± 13.284, 12.523 ± 13.715, 5.83 ± 0.60, 0.68 ± 0.15, 0.113 ± 0.056 and 0.059 ± 0.038 µg L⁻¹, respectively. All measured values were below the maximum permissible levels (MPL) established by Peruvian regulations for water from industrial activities of cement, beer, tannery and paper (DS N° 003-2002-PRODUCE, 2002), as well as those established for liquid effluents from mining, metallurgical (DS N° 010-2010-MINAM, 2010) and hydrocarbon activities (DS N° 037-2008-PCM, 2008). They were also lower than the maximum permissible values for non-domestic wastewater discharges into the sewer system (DS N°

021-2009-VIVIENDA, 2009). All river water samples showed metal concentration values lower than those established by the Peruvian Environmental Quality Standard (EQS) (DS N° 004-2017-MINAM, 2017) for surface water intended for drinking water, recreation, cultivation of hydrobiological species, crop irrigation and animal drinking, as well as the EQS for lake and river water, except for the Vitor sample, where the Hg concentration was the same as the EQS established for these waters (0.0001 mg L⁻¹).

Table 1. Heavy metal content in water (µg L⁻¹), soil (mg kg⁻¹, db) and alfalfa (mg kg⁻¹, wet basis, wb)

Sample	Element	Site		
		Congata	Uchumayo	Vitor
Water	As	6.468	32.962	17.990
Water	Cd	0.159	0.130	0.050
Water	Cu	5.90	6.40	5.20
Water	Cr	27.610	9.150	0.810
Water	Fe	240.0	54.0	138.0
Water	Hg	0.026	0.050	0.100
Water	Pb	0.850	0.580	0.610
Water	Zn	40.0	21.0	24.0
Soil	As	BDL	BDL	BDL
Soil	Cd	255.88	62.01	381.94
Soil	Cu	31.49	29.64	35.34
Soil	Cr	33.55	17.14	15.06
Soil	Fe	27.38	15.63	17.01
Soil	Hg	BDL	BDL	BDL
Soil	Pb	4.02	9.82	1.41
Soil	Zn	53.08	48.28	45.31
Alfalfa	As	BDL	BDL	BDL
Alfalfa	Cd	0.29	0.15	0.19
Alfalfa	Cu	18.77	14.44	7.83
Alfalfa	Cr	1.21	0.61	1.08
Alfalfa	Fe	298.19	63.06	89.92
Alfalfa	Hg	BDL	BDL	BDL
Alfalfa	Pb	1.42	0.85	0.60
Alfalfa	Zn	52.48	35.71	22.84

BDL: Below detection limit

3.1.1. Water samples

The concentration of Fe, Zn and Pb were higher in the waters of Congata, to decrease in Uchumayo and increase near Vitor, where the most notable increase was in Fe. The Fe concentration in Uchumayo was higher than in Congata in previous years (321 - 635 µg L⁻¹) according to the National Water Authority (2011, 2012, 2014), although Velarde Paz (2016) and Torres-Franco et al., (2019) reported similarly higher average Fe values in Congata and Uchumayo, with high variability, during the period 2011 - 2015 (1161 - 1700 and 1600 µg L⁻¹, respectively). Pinto Paredes (2018) measured the Fe content at two nearby points 1.95 km downstream and

2.2 km upstream of Congata during 2017, reporting annual averages of 4121.97 and 4262.13 $\mu\text{g L}^{-1}$. Before the closure of an old wastewater treatment plant, a collector discharged the treated water near Congata, with a concentration of As, Cd, Cr, Cu, Fe, Hg, Pb and Zn of 147.6, 11.8, 16016, 206.5, 32374, 1.1, 212.6 and 515.5 $\mu\text{g L}^{-1}$, respectively (National Water Authority, 2011). Laura Ticona (2018) reported a Fe content (376.9 $\mu\text{g L}^{-1}$) closer to ours on a bridge located 2.2 km upstream of Congata in December 2017. In this area, the Fe content during the flood period of the river is up to 3 times higher than it would be during the baseflow period (Yupanqui Mendoza & Bernabé Ortiz, 2018). The Zn content in Congata is usually higher than the values reported for Vitor (National Water Authority, 2012), although in 2011 the average Zn concentration in Uchumayo was even higher (78.5 $\mu\text{g L}^{-1}$) (National Water Authority, 2011, 2012). At the Congata site, the Zn content during river flooding is up to 10 times higher than during the baseflow period (Yupanqui Mendoza & Bernabé Ortiz, 2018). The concentration of Zn in Congata is in the annual range reported by Pinto Paredes (2018) (40.22 - 49.28 $\mu\text{g L}^{-1}$) for two nearby points, also in 2017. In August 2011 the Pb content in Uchumayo was less than 3 $\mu\text{g L}^{-1}$ (National Water Authority, 2012) and in October of the same year it rose to 11 $\mu\text{g L}^{-1}$ (National Water Authority, 2011). The Pb concentration in Congata was lower than that reported by Pinto Paredes (2018) in March 2017 on a bridge 2.2 km upstream of Congata (2.6 $\mu\text{g L}^{-1}$) but similar to that reported by Laura Ticona (2018) in December of the same year (0.82 $\mu\text{g L}^{-1}$) on the same bridge. In July 2017 Pinto Paredes (2018) reported a Pb concentration of less than 0.2 $\mu\text{g L}^{-1}$ at two points downstream and upstream of Congata.

The content of As and Cu was higher in Uchumayo than in Congata but then decreased in Vitor where the content of As was higher than that of Congata. In 2011 Vitor presented higher As values (22 $\mu\text{g L}^{-1}$) than Uchumayo (National Water Authority, 2011, 2012), while in 2015 the concentration of As in Congata (19.31 $\mu\text{g L}^{-1}$) reported by Velarde Paz (2016) was similar to that reported by the National Water Authority (2014) for Uchumayo in 2014 (19.2 $\mu\text{g L}^{-1}$). In 2015, Diaz-Rodriguez et al. (2015) obtained high values of As in the drinking water of Congata (24.72 $\mu\text{g L}^{-1}$), since drinking water in that area is obtained from underground wells. In 2015 the water from an underground stream (approximately 6 meters deep) draining from the surroundings of the copper mine to Congata had an average annual concentration of Cu, Pb, Cr and Hg of 30, 1.85, 2 and 0.3 $\mu\text{g L}^{-1}$, respectively (Ramos Vizcarra, 2018). The

concentration of As in Congata was close to the value measured 1.95 km downstream in March 2017 (6.73 $\mu\text{g L}^{-1}$), while 2.2 km upstream the concentration of As (26.1 $\mu\text{g L}^{-1}$) was significantly higher (Pinto Paredes, 2018). The concentration of As in Uchumayo was higher than that reported by Laura Ticona (2018) in December of the same year 2.2 km upstream of Congata (29.03 $\mu\text{g L}^{-1}$). In August 2011 the concentration of Cu in Uchumayo (6 $\mu\text{g L}^{-1}$) reported by the National Water Authority (2012) was similar to this study, while in October of that year the concentration rose to 28 $\mu\text{g L}^{-1}$ (National Water Authority, 2012). The Cu concentration 1.95 km downstream of Congata in 2017 ranged from 0.03 (July) to 91.54 $\mu\text{g L}^{-1}$ (January), while 2.2 km upstream varied from 0.03 (September) to 91.61 $\mu\text{g L}^{-1}$ (January) (Pinto Paredes, 2018).

The concentration of Cd and Cr decreased with the advance of the river from Congata to Vitor, although Cr had a more notable decrease. In Uchumayo, the National Water Authority (2011) reported a Cr concentration of 28 $\mu\text{g L}^{-1}$ in October 2011, while in August of the same year the concentration was less than 6 $\mu\text{g L}^{-1}$ (National Water Authority, 2012). The highest Cr concentration 1.95 km downstream of Congata in 2017 was 27.1 $\mu\text{g L}^{-1}$ (March), while 2.2 km upstream was only 2.4 $\mu\text{g L}^{-1}$ (Pinto Paredes, 2018). Only the Hg content of the water rose along the course of the river. The average annual Hg concentration in 2017 of two locations upstream and downstream of Congata was always less than 0.03 $\mu\text{g L}^{-1}$ (Pinto Paredes, 2018).

3.1.2. Soil samples

In the analysed soils the main metal found was Cd, followed by Zn, Cu, Cr, Fe and Pb, with average values of 233.28 ± 161.16 , 48.89 ± 3.92 , 32.16 ± 2.91 , 21.92 ± 10.13 , 20.21 ± 6.42 and 5.08 ± 4.30 mg kg^{-1} , respectively. The concentration of As and Hg in the soils analysed was below the detection limit of the method used. The Cd concentration at all three sites was well above the maximum Peruvian EQS value for agricultural (1.4 mg kg^{-1}), urban (10 mg kg^{-1}), commercial and industrial soils (22 mg kg^{-1}) (DS N° 011-2017-MINAM, 2017). The concentration of Cu and Zn was below the limit value for soils (100 and 200 mg kg^{-1} , respectively) in Finland (Government Decree 214/2007, 2007). The Pb concentration was lower than the Peruvian EQS for agricultural, urban, commercial, industrial and extractive soils (DS N° 011-2017-MINAM, 2017). The Cr concentration on all three sites was lower than the Peruvian EQS for urban (400 mg kg^{-1}), commercial and industrial soils (1000 mg kg^{-1}) as well as the limit value for Cr (100 mg kg^{-1}) in Finnish soils (Government Decree

214/2007, 2007). All the concentrations obtained for Cu, Pb and Zn were much lower than those reported by Damian et al., (2019b) for anthropic and eutricambosol soils near a lead smelter in Romania at different soil depths, although the concentration of Cd in the present study was much higher than those reported by these authors (0.1 – 34 mg kg⁻¹).

The concentration of Cd, Cu and Fe in Uchumayo soils was lower than in Congata and lower than in Vitor soils. Uchumayo and Congata have in common their proximity to the Añashuayco Formation (Neogene) while Vitor lies between the Moquegua Formation (Neogene) and the Sotillo Formation (Palaeogene) (Fig. 1). The higher amount of Cd in the soils of Congata (4.13 times more) and Vitor (6.16 times more) with respect to Uchumayo could be because of more intense agricultural activity since Cd is an impurity of the phosphate rock used as fertiliser that would accumulate in the soil and to a lesser extent could leach into the river. The presence of Cd above the geochemical background was reported by Maftei et al. (2019a) at 3 sampling points in the peri-urban and urban area of Slănic-Moldova city. The high concentration of this and other elements in river sediments above background was associated with anthropogenic sources (Maftei et al., 2019b). The application of sewage sludge from the treatment plant as fertiliser can also be a significant source of Cd (International Programme on Chemical Safety, 1992). However, Monge Quispe (2018) determined the concentration of Cd in sediments upstream (0.54 km) and downstream (1.44 km) of Uchumayo, finding that the concentration in April (wet season) was lower than that measured in September (dry season) in 2017 and that the concentration of Cd in sediments downstream in April was 0.43 mg kg⁻¹, while upstream it was 0.38 mg kg⁻¹. This same author also measured the concentration of Cd in the river sediment at Congata, which was also higher in September (0.69 mg kg⁻¹) than in April (0.57 mg kg⁻¹). The Cu concentration in Congata was very similar to that reported by Yupanqui Mendoza & Bernabé Ortiz (2018) for the uncultivated agricultural soils (30.9 mg kg⁻¹) and those used for onion cultivation (35.6 mg kg⁻¹), further showing that the Cu content in the fields closest to the irrigation canal was higher than in the more distant fields. Yupanqui Mendoza & Bernabé Ortiz (2018) also reported lower Fe contents in the uncultivated soils and those used for onion cultivation in Congata (13.1 and 18.44 mg kg⁻¹, respectively) than in the present study.

The content of Zn and Cr decreased from Congata to Vitor. The Zn concentration in Congata was among the values reported by Yupanqui

Mendoza & Bernabé Ortiz (2018) for uncultivated (46 mg kg⁻¹) and cultivated (61.5 mg kg⁻¹) soils with onions, where the fields closer to the irrigation canal showed higher Zn levels than those further away. Pb concentration was higher in Uchumayo compared to Congata and Vitor. This was probably due to the proximity of the entrance toll to the city and heavier vehicle traffic and interprovincial transport. However, Bolivar Rosas (2014) reported a Pb content of 50 mg kg⁻¹ in the soil of an onion field in Congata in 2012. The behaviour of Cd, Zn, Cu and Pb concentration differs from that of river waters near the same locations, while Cr and Fe were similar.

3.1.3. Alfalfa samples

In the alfalfa analysed in the three sites the main metal found was Fe, followed by Zn, Cu, Cr, Pb and Cd, with mean values of 150.39 ± 128.70, 37.01 ± 14.86, 13.68 ± 5.51, 0.96 ± 0.32, 0.96 ± 0.42 and 0.21 ± 0.07 mg kg⁻¹, respectively. The concentration of As and Hg in alfalfa was below the detection limit of the method used at all three sites. The concentrations of Fe, Cd and Cr were lower in the Uchumayo samples than in the Congata and Vitor samples. The content of Zn, Cu and Pb decreased along the river from Congata to Vitor. Paredes et al. (2018) analysed the content of Cr, As, Cd, and Pb of the alfalfa leaves sold in markets in the city of Arequipa as a medicinal plant in May 2015, reporting lower values than those reported in this study. Similarly, Quispe Cruz (2019) observed lower concentrations of Cd, Cr and Pb in several vegetables grown in Congata (*Allium schoenoprasum*, *Mentha spicata*, *Coriandrum sativum*, *Allium sativum*), although they detected As and Hg levels up to 0.113 and 0.019 mg kg⁻¹, respectively. Bolivar Rosas (2014) reported a Pb content in Congata grown onions of 0.2 mg kg⁻¹, while Yupanqui Mendoza & Bernabé Ortiz (2018) also determined the Fe (98 - 700 mg kg⁻¹), Zn (12.9 - 133 mg kg⁻¹) and Cu (4 - 29.3 mg kg⁻¹) content in Congata grown onions, showing that the content of these elements in the onions grown in fields next to the irrigation canal varied according to the part of the plant and was similar to or slightly higher than that of the fields farther from the canal. The behaviour of Cd, Cu, Cr and Pb concentrations differed from that of the water and soil samples, while Zn was similar to that of the soil samples and Fe concentration varied in the same way as for the water and soil samples at the three sites.

The heavy metal content of the alfalfa samples collected from three sites far from the city (Yarabamba, La Joya and Quiscos) is presented in Table 2. The main metal present in these alfalfa samples was Fe, followed by Zn, Cu, Cr, Pb, As and Cd with mean values of 134.85 ± 38.30, 18.796 ±

6.403, 0.74142 ± 0.28325 , 0.3458 ± 0.1455 , 0.27783 ± 0.17203 and 0.01599 ± 0.00526 mg kg⁻¹, respectively. The presence of Hg was below the detection limit of the method. Alfalfa samples from Quiscos had the lowest metal content analysed compared to the other two sites. Waters from the Yura River measured downstream of Quiscos, had lower As, Cd, Cu, Cr, Fe, Hg, Pb and Zn contents than river water at Congata, Uchumayo and Vitor (National Water Authority, 2012, 2014). In the samples from La Joya, the highest concentrations of Zn, Cr, Pb, As and Cd were obtained in comparison with the other two sites. This could be explained by its location in the roadway and its exposure to more intense use of fertilisers. Alfalfa samples from Yarabamba had the highest Fe and Cu content compared to the other two sites. The As content in all three sites was higher than that observed for Congata, Uchumayo and Vitor, probably because the value measured was close to the detection limit of the method (AAS). The mean Fe, Zn, Cu, Pb content of alfalfa samples from the Yarabamba, La Joya and Quiscos sites was similar to the mean Fe, Zn, Cu, Pb content in Congata, Uchumayo and Vitor. On the other hand, the mean concentration of Cr and Cd in Yarabamba, La Joya and Quiscos was different ($p < 0.05$) and lower than the concentration of alfalfa samples in Congata, Uchumayo and Vitor.

Table 2. Heavy metal content (mg kg⁻¹, wb) of alfalfa in different sites

Element	Site		
	Yarabamba	La Joya	Quiscos
As	0.28578	0.44575	0.10196
Cd	0.01625	0.02112	0.01060
Cu	11.702	11.702	6.907
Cr	0.79609	0.99336	0.43482
Fe	163.54	149.66	91.36
Hg	BDL	BDL	BDL
Pb	0.4024	0.4545	0.1806
Zn	17.128	25.867	13.392

BDL: Below detection limit

3.2. Variation of heavy metals and arsenic content in alfalfa grown for three months

The heavy metal content of the samples of alfalfa grown in Congata and taken at three different times after planting is shown in Table 3. With respect to time, the concentration of Zn and Cd increased in the second month, although the concentration of Zn decreased in the third month while the concentration of Cd remained the same. In the case of Cu, Cr, Hg and Pb, the concentration decreased in the second month but that of Cu and Cr increased slightly in the third

month. Hg concentration increased above the value of the first month and Pb concentration remained constant. Only the As content increased from the first to the third month of cultivation. During the three months of the test the main metal found was Zn (53.29 ± 8.01 mg kg⁻¹), followed by Cu (13.6 ± 0.4 mg kg⁻¹), Cr (0.82 ± 0.28 mg kg⁻¹), As (0.7 ± 0.2 mg kg⁻¹), Pb (0.5 ± 0.4 mg kg⁻¹), Hg (0.19 ± 0.04 mg kg⁻¹) and Cd (0.06 ± 0.01 mg kg⁻¹). The average concentration of Cu, Cr and Pb during this experiment was not different from the average of the alfalfa samples from Congata, Uchumayo and Vitor, nor from those from Yarabamba, La Joya and Quiscos. The average concentration of As was higher in the samples from these sites than in the other alfalfa samples from the other sites, including Congata. This could be due to an increase in the concentration of As in the water or particles in the air during the growing period. Similarly, only in this experiment was the Hg concentration above the detection limit. However, Paredes et al. (2018) reported a lower content of Hg (0.011 mg kg⁻¹), Cr (0.07 mg kg⁻¹) and Pb (0.16 mg kg⁻¹) for samples of alfalfa acquired in markets in the city of Arequipa in May 2015. The As content of 1-month-old alfalfa was similar to that reported by the same authors for alfalfa from the market (0.65 mg kg⁻¹), while the Cd concentration was higher than that of alfalfa from the market during the three months. The As, Cr, Hg and Pb content of alfalfa samples analysed during the three months was higher than that reported by Quispe Cruz (2019) for four short-stemmed plant species grown in Congata for five months between 2018 and 2019, as was the Cd content of the 2- and 3-month-old alfalfa samples. The mean Cd content was higher ($p < 0.05$) than the mean Cd content of the samples from Yarabamba, La Joya, and Quiscos, but lower than the mean observed in the first experiment in Congata, Uchumayo, and Vitor. The mean Zn content was significantly higher ($p < 0.05$) than the mean Zn content of the Yarabamba, La Joya and Quiscos samples, while it was very close to the Zn content reported in the first experiment for alfalfa from Congata.

Table 3. Heavy metal content (mg kg⁻¹, wb) in alfalfa samples at different growth times in Congata

Element	Time		
	1 month	2 months	3 months
As	0.6	0.7	0.9
Cd	BDL	0.07	0.07
Cu	13.9	13.1	13.7
Cr	1.11	0.55	0.81
Hg	0.20	0.15	0.23
Pb	0.9	0.3	0.3
Zn	48.15	62.52	49.20

BDL: Below detection limit

3.3. Heavy metal content in offal

3.3.1. Kidney samples

The metal content of the sheep kidney samples is shown in Table 4. The main metal detected at all three sites was Fe, followed by Cu and Zn, with mean values of 54.84 ± 24.56 , 32.61 ± 29.44 and 24.54 ± 24.09 mg kg⁻¹, respectively. The concentrations of As, Cd, Cr, Hg and Pb were below the detection limit. In an analysis of 2074 results of As content in offal, 52.84% reported values below the limit of detection (JECFA, 2011a). The concentration of Fe and Cu in the three sites was higher than that of the market sample, while the concentration of Zn from the kidneys of Congata and Uchumayo was lower. The Vitor samples had the highest Cu and Zn levels, while the Congata samples had the highest Fe concentration. The Fe concentration of the three sites was similar to the range reported by Bortey-Sam et al., (2015) for sheep kidneys near gold mines in Ghana (24.8 - 80.6 mg kg⁻¹), while Abou-Arab (2001) reported an average Fe content of 38.1 mg kg⁻¹ for sheep kidneys from industrial areas in Egypt. The concentration of Cu in sheep kidneys from the three sites was in the range reported by Bilandžić et al., (2010) for sheep in rural areas of Croatia (0.95 - 228.9 mg kg⁻¹), although higher than their geometric mean (4.24 mg kg⁻¹). Bortey-Sam et al., (2015) and Abou-Arab (2001) also reported lower mean Cu concentrations (2.89 and 3.8 mg kg⁻¹, respectively). The Zn concentration of the Congata and Uchumayo samples were below the range reported by Bortey-Sam et al., (2015) for sheep kidneys in Ghana (18.1 - 28.1 mg kg⁻¹) and the mean observed by Abou-Arab (2001) for sheep from rural areas of Egypt (11.4 mg kg⁻¹), while in Vitor the concentration was in the range reported by Chessa et al., (2000) for sheep kidneys raised near a Pb and Zn smelter in Italy (31.27 - 52.08 mg kg⁻¹).

Table 4. Heavy metal content (mg kg⁻¹, wb) in ovine kidney

Element	Site			
	Market	Congata	Uchumayo	Vitor
As	BDL	BDL	BDL	BDL
Cd	BDL	BDL	BDL	BDL
Cu	1.52	19.01	12.44	66.39
Cr	BDL	BDL	BDL	BDL
Fe	23.41	81.50	33.15	49.86
Hg	BDL	BDL	BDL	BDL
Pb	BDL	BDL	BDL	BDL
Zn	22.85	6.72	14.95	51.94

BDL: Below detection limit

3.3.2. Liver samples

The main metal detected in the livers of sheep at

the three sites (Table 5) was Fe, followed by Zn and Cu, with mean values of 93.52 ± 29.70 , 34.90 ± 7.05 and 23.58 ± 14.05 mg kg⁻¹, respectively. Concentrations of As, Cd, Cr, Hg and Pb were below the detection limit. The concentration of Fe and Zn in the livers of the three sites was higher than that of the market samples. Only the Cu concentration of the Vitor sample was lower than that of the market. The Congata livers had the highest Fe and Cu concentration, while the Uchumayo livers had the highest Zn concentration. The Fe concentration was in the range reported by Bortey-Sam et al., (2015) for sheep livers from areas near a gold mine (55.4 - 294.1 mg kg⁻¹) and was slightly lower than the average reported by Abou-Arab (2001) for sheep raised in industrial areas of Egypt (96.3 mg kg⁻¹). Reif et al., (1989) reported a higher range of Zn concentration in sheep liver for sheep raised near a Zn smelter in central Peru (86.87 - 316.04 mg kg⁻¹), while near another Zn and Pb smelter in Sardinia, Italy, Chessa et al., (2000) reported Zn concentrations (33.97 - 44.73 mg kg⁻¹) closer to those in Uchumayo and Congata. The Vitor and market samples showed a lower Zn content than the average observed by Abou-Arab (2001) for sheep livers from industrial areas of Egypt (36.8 mg kg⁻¹), but higher than that of rural areas (20.7 mg kg⁻¹). The Cu content of the Uchumayo and Congata samples was in the range reported by Reif et al., (1989) for livers from sheep raised near a Zn smelter in central Peru (22.29 - 38.92 mg kg⁻¹), while Bortey-Sam et al., (2015) reported a wider range for livers from sheep raised near gold mines in Ghana (7.9 - 224.3 mg kg⁻¹). Abou-Arab (2001) did not observe a large difference between the mean Cu contents in the livers of sheep raised in rural (46.9 mg kg⁻¹) and industrial (48.6 mg kg⁻¹) areas of Egypt.

3.4. Health Risk Assessment

Table 6 shows the EDI values for children and adults from the kidney and liver samples tested. All EDI values for Cu and Zn from children and adults were below the FAO/WHO provisional maximum tolerable daily intakes (PMTDI) (500 µg kg⁻¹ day⁻¹ for Cu and 300 - 1000 µg kg⁻¹ day⁻¹ for Zn, according to JECFA (1982)). Similarly, no EDI of Fe for children or adults was higher than the PMTDI of 800 µg kg⁻¹ day⁻¹ established by FAO/WHO (JECFA, 1983).

Table 7 shows the THQ values of sheep offal. The THQ for Cu of Vitor sheep kidney presented the highest value for children and adults. All values were below 1, indicating no adverse effect on human health. The TTHQ values for children corresponding to the market kidney samples, Congata, Uchumayo and Vitor were 0.0074, 0.0306, 0.0204 and 0.0952,

while for adults they were 0.0041, 0.0172, 0.0114 and 0.0535, respectively.

Table 5. Heavy metal content (mg kg⁻¹, wb) in ovine liver

Element	Site			
	Market	Congata	Uchumayo	Vitor
As	BDL	BDL	BDL	BDL
Cd	BDL	BDL	BDL	BDL
Cu	1.52	19.01	12.44	66.39
Cr	BDL	BDL	BDL	BDL
Fe	23.41	81.50	33.15	49.86
Hg	BDL	BDL	BDL	BDL
Pb	BDL	BDL	BDL	BDL
Zn	22.85	6.72	14.95	51.94

BDL: Below detection limit

For livers, the TTHQ values for children from the market samples, Congata, Uchumayo and Vitor were 0.0308, 0.0557, 0.0503 and 0.0199, while for adults they were 0.0173, 0.0314, 0.0282 and 0.0112, respectively. All TTHQ values were also less than 1, showing that the estimated kidney and liver intake of sheep from the sites studied would not have an adverse effect on the health of children and adults.

3.5. Summary

The river water samples analysed had the highest mean concentration (in decreasing order) of Fe, followed by Zn, As, Cr, Cu, Pb, Cd and Hg. The values were within

the limits of the legislation, considering that external factors and seasonality may cause the concentration of some of them to vary. As for the agricultural soil samples close to the water sampling points, the metals in highest concentration were Cd, Zn, Cu, Cr, Fe and Pb. In all cases, the concentration of Cd was above the limits of the legislation. This could be a health hazard for people in the surrounding area, as Cd can affect the lungs over time through dust. To investigate whether Cd and other heavy metals would appear in high concentrations in the alfalfa consumed by sheep farmed on these agricultural lands, as well as to assess whether there was accumulation in the viscera of these sheep, other analyses were carried out. In the case of alfalfa, the concentration of metals in samples grown in one site (Congata) was monitored for three months, to compare it with the concentration of alfalfa samples grown in the other two sites (Uchumayo and Vitor) and those grown in places far from the city of Arequipa (Quiscos, Yarabamba and La Joya). The latter showed similar or lower concentrations than the first three sites, and Cd accumulation during alfalfa growth was only observed above the detection limit after the second month. As for the kidney and liver samples, the concentration of toxic elements such as Pb, Cd, Hg and As was below the detection limit, the key metals detected being Fe, Cu and Zn. This could show that there is no bioaccumulation in sheep of the high soil Cd concentrations.

Table 6. Estimated daily intake (µg kg⁻¹ day⁻¹) of Cu, Fe and Zn in sheep offal

Sample	Site	Cu		Fe		Zn	
		Child	Adult	Child	Adult	Child	Adult
Kidney	Market	0.0760	0.0427	1.1698	0.6571	1.1418	0.6414
Kidney	Congata	0.9499	0.5336	4.0725	2.2877	0.3358	0.1886
Kidney	Uchumayo	0.6216	0.3492	1.6565	0.9305	0.7470	0.4196
Kidney	Vitor	3.3174	1.8635	2.4915	1.3995	2.5954	1.4579
Liver	Market	0.9134	0.5131	2.8362	1.5932	1.1708	0.6577
Liver	Congata	1.6415	0.9221	6.3551	3.5699	1.6855	0.9468
Liver	Uchumayo	1.5231	0.8556	3.5478	1.9929	2.1217	1.1918
Liver	Vitor	0.3703	0.2080	4.1165	2.3124	1.4241	0.8000

Table 7. THQ values (unitless) of Cu, Fe and Zn in sheep offal

Sample	Site	Cu		Fe		Zn	
		Child	Adult	Child	Adult	Child	Adult
Kidney	Market	0.0019	0.0011	0.0017	0.0009	0.0038	0.0021
Kidney	Congata	0.0237	0.0133	0.0058	0.0033	0.0011	0.0006
Kidney	Uchumayo	0.0155	0.0087	0.0024	0.0013	0.0025	0.0014
Kidney	Vitor	0.0829	0.0466	0.0036	0.0020	0.0087	0.0049
Liver	Market	0.0228	0.0128	0.0041	0.0023	0.0039	0.0022
Liver	Congata	0.0410	0.0231	0.0091	0.0051	0.0056	0.0032
Liver	Uchumayo	0.0381	0.0214	0.0051	0.0028	0.0071	0.0040
Liver	Vitor	0.0093	0.0052	0.0059	0.0033	0.0047	0.0027

4. CONCLUSION

Heavy metal and arsenic content were determined from water samples from the Quilca - Vitor - Chili River, as well as from soil and alfalfa in three sites near the river and close to the city of Arequipa and a copper mine. Metals and As concentrations tested in the water were below Peruvian environmental quality standards (EQS) for surface water used for irrigation of crops and drinking of animals, except in the case of Vitor water. In general, the metal and As content in the water was similar to that previously reported, although it varies historically in periods of river flooding and baseflow, as well as groundwater seepage.

Variations in the concentration of metals such as Fe, Zn, Pb and Cr in river water previously reported in the literature in different months could be due to the fact that the water may carry silt, scrap metal and other debris close to the river bank. Uncontrolled discharges can also affect the concentration of metals in the water.

The soils of Congata, Uchumayo and Vitor presented a high Cd content, above the Peruvian EQS for agricultural, commercial and industrial soils, especially in Vitor. This may represent a hazard if Cd is inhaled through soil dust particles. The concentration of Cd in the air that may come from the Copper mine activities has not been measured, but, likely, part of the Cd is also explained by the use of fertilisers where Cd is an impurity, such as phosphate rock or sewage sludge, over several years.

The Cd content was low in the alfalfa samples from all sites, although higher in those near the city and the mine (Congata, Uchumayo and Vitor), which would indicate that the Cd is not well absorbed by the alfalfa. However, the As content of the alfalfa grown in Congata during three months increased from the second month of cultivation, probably because of the As content of the river and underground sources. The content of Cu, Cr and Pb was not very different among all the alfalfa samples analysed.

The main metals detected in the sheep offal were Fe, Cu and Zn, while the content of toxic heavy metals and As in the sheep offal was below the detection limits. The content of these metals in the commercial samples was lower than that of the samples from Congata, Uchumayo and Vitor, except for the Zn content of kidney and the Cu content of liver from Congata and Vitor, respectively, which were lower than the commercial samples. EDI values were below PMTDI for detected metals, and THQ and TTHQ values less than 1 indicate that the current consumption of this offal would not be harmful to the health of children and adults. However, it is

recommended that the consumption of offal by rural populations in southern Peru be specifically studied, as well as the metal content of other animals fed alfalfa on small farms, such as guinea pigs, and small animals that may ingest higher contents of Cd-contaminated soil, such as chickens.

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