Potentially toxic elements and radionuclides contamination in soils from the vicinity of an ancient mercury mine in Huancavelica, Peru

M.A. Castillo Corzo[a(*)], V.A Peña Rodríguez[a], M.A. Manrique Nungent[b], E. G. Villarreyes Peña[a], P. Byrne[c], J. C. González [a], G. Patiño Camargo[a], C.H.W. Barnes[d], J.F. Sanchez Ortiz[a], J. Saldaña Tovar[e], L. De Los Santos Valladares[d(*)]

[a] Facultad de Ciencias Físicas, Universidad Nacional Mayor de San Marcos, P.O Box 14-0149, Lima, Peru.

[b] Universidad Nacional Autónoma de Huanta, Jr. Manco Cápac 497, Huanta, Ayacucho, Peru.

[c] School of Biological and Environmental Sciences, Liverpool John Moores University, Liverpool L3 3AF, UK

[d] Cavendish Laboratory, Department of Physics, University of Cambridge, J.J. Thomson Ave., Cambridge CB3 0HE, UK.

[e] Facultad de Ciencias Matemáticas, Universidad Nacional Mayor de San Marcos, P.O Box 14-0149, Lima, Peru.

(*) Corresponding authors emails: mcastilloc@unmsm.edu.pe (M. Castillo Corzo) and ld301@cam.ac.uk (L. De Los Santos Valladares)

Supplementary Information

Section 1S. Points of sample collection

Table 1S. Point of collections and initial details of the samples collected from the Huancavelica, Peru. h.a.s.l: height above sea level. *D*: Distance to the Ichu River.

Samples	Place of collection	Latitude	Longitude	*D* (m)	Height (h.a.s.l)	Characteristics
M1	Quintanilla Pampa	12°46'59.29''S	74°59'17.78''W	106.31	3709	approximately 20 cm depth from the surface
M2	San Cristóbal	12°46'53.39"S	74°58'15.92"W	349.22	3709	approximately 20 cm depth from the surface. Near a thermal spring pond.
M3	Yananaco	12°47'15.51"S	74°58'44.79"W	92.44	3693	from abandoned house
M4	Santa Ana	12°47'9.13"S	74°58'7.19"W	120.00	3683	approximately 20 cm depth from the surface
M5	Asención	12°47'2.57"S	74°58'41.60"W	122.23	3687	approximately 20 cm depth from the surface

Fig. 1S. Place of collection of samples: M1, Quintanilla Pampa (a). M2, San Cristobal (b), M3, Yananaco (c). M4, Santa Ana (d), and M5, Asencion (e). The arrows show the exact point of sample collection

Section 2S. Transition metals

Figure 1S shows some photos taken of the sites during sample collection, whereas Table 2S lists the elemental composition, quantified in mg kg^{-1}, of the soil samples obtained by XRF. The most abundant elements are: Si, Ca, Al, K, Fe and Ti; as expected since the samples are soils, whose main composition are quartz (SiO_2), alumina (Al_2O_3) and aluminium silicates ($x Al_2O_3 . y SiO_2 . z H_2O$, where x, y and z can be Na, Ca and K) (Santos et al., 2022). In fact, according to the XRD analysis presented in a previous work (Castillo et al., 2022), the mineralogical composition for all the present samples contain quartz

(SiO_2) and the aluminium silicates Andradite ($Ca_2(Fe^{3+})_2(SiO_4)_3$), Sanidine ($KNa((SiAl)_4O_8$), Microcline ($KalSi_3O_8$), Augite ($Ca(Mg,Fe)Si_2O_6$), Muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$), Albite ($NaAlSi_3O_8$), Kaolinite ($Al_2(Si_2O_5)(OH)_4$ and Grossular ($Ca_3Al_2(SiO_4)_3$). Figure S2 shows the XRF spectra for all the samples. The plots are given in logarithmical scale in order to reveal also the minor peaks. Whereas, Fig. 3S depicts the comparison on the concentrations of the chemical elements with the sites of collection. In this way, the presence of Si, O, Ca, Al, K and Na in the table corroborate the presence of quartz and silicates minerals in all the samples. In the case of Fe, it is not only present as a silicate component but also as iron oxide (e.g., goethite and magnetite in sample M2), as it has been previously analyzed in detailed in our previous work (Castillo et al., 2022).

As mentioned in the text of the manuscript, the mercury mining activity in Huancavelica finished in 1970 and the currently main activities are agriculture and cattle raising. The agricultural zones in Huancavelica are located nearby the sites of sample collection, at the North and South edges of the city (see Figure 1 in the manuscript). The identified primary macronutrients are K and P whereas the secondary macronutrient Ca is identified in the five areas of study (see Table S1). The largest quantity of K has been found in samples M5 and M4 and in lower quantities in samples M1 and M3. K is an essential component of plants nutrition, especially for strengthening during their early growth. It also plays a role in helping the plant to retain water and increases drought resistance. It helps to open and close stomata facilitating the absorption of carbon dioxide in the leaves and it is also found in commercial fertilizers in the form of potassium chloride (KCl, Sylvite) (Dmitrenko et al., 1999; Elouear et al., 2016; Kiiski et al., 2000; Prakash et al., 2016; Webb, 1939). The levels of K reported in Table S1 indicate that the Sites M5 and M4 are more agricultural fertile than the sites M1 and M3. This is corroborated in the corresponding photos of the areas presented in Figure S1, in which plants grow more easily. However, since KCl is also one of the main components of potassium chloride fertilizers (Dmitrenko et al., 1999; Elouear et al., 2016; Kiiski et al., 2000; Prakash et al., 2016; Webb, 1939), it is not clear whether the K found in this work comes from natural or from rest of fertilizers.

Phosphorous has been identified in all the samples with the highest amount in sample M5 and lowest amount in sample M4. Native phosphorus is usually found in the form of natural phosphate $(PO_4)^{3-}$ and apatite ($Ca_{10}(PO_4)_6(OH, F, Cl)_2$); and its natural cycle develops when it is released through the processes of weathering, leaching and erosion (Alguacil et al., 2010). The phosphate released from apatite is absorbed by plants and microbial biomass, then it is incorporated into the organic matter of the soils and again deposited as a slightly soluble mineral form. It is possible that there are still rests of phosphorus from fertilizers used by the local farmers.

In the case of calcium, it is identified in all samples with the highest quantities in Yananaco (M3) and Quintanilla Pampa (M1), while the lowest amounts are found in San Cristobal (M2) and Santa Ana (M4). As secondary macronutrient, Ca helps to create cell walls making the plant strong and rigid, to keep upright and to protect them from disease. It is also required for plant metabolism, to help the plant to absorb nitrogen from the soil. The highest amount of calcium in the collection point M3 should be related with the highest presence of calcite ($CaCO_3$) in the area, as it has been revealed in our previous work (Castillo et al., 2022). Calcite, as the main source of calcium in soils, has been also found in other Peruvian areas and it comes from limestones found throughout catchment headwaters in Andean Rivers (Santos et al., 2022). As it is discussed in the next section, the fact that M3 presents the highest levels of Hg and Cd might be related to the highest amount of calcite present in the area of collection since has been reported that calcite immobilizes heavy metals (Wang et al., 2019; Peña et al., 2013; Sasamoto et al., 2022; Xie et al., 2021). Similarly, the presence of Mn has also been detected in all the samples, with the highest amounts in samples M2 and M5. This element constitutes a micronutrient for plants, but it is also likely to form alloys with heavy metals such as As and Pb, as it is discussed in more detail in the manuscript.

Table 2S. X-ray fluorescence analysis of soils samples collected from five neighborhoods in Huancavelica City, Peru. Quintanilla Pampa (M1), San Cristóbal (M2), Yananaco (M3), Santa Ana (M4) and Asencion (M5). Units: 10^{+3} mg kg^{-1}.

Samples	M1	M2	M3	M4	M5
Fe	40.80(25)	56.43(5.2)	12.01(1.1)	24.49(36)	57.42(2.2)
Si	26.89(1.4)	15.73(27)	25.76(2.1)	61.51(4.8)	47.12(4.3)
Ca	12.94(68)	6.31(51)	54.45(4.1)	8.41(11)	10.16(67)
Al	9.40(4)	4.14(88)	7.34(61)	19.98(1.9)	20.13(2.4)
K	2.76(2)	3.59(19)	3.19(17)	5.36(11)	5.42(11)
Ti	2.07(3)	1.04(8)	1.11(19)	2.71(21)	3.82(29)
P	1.17(11)	0.52(11)	0.97(1)	0.43(3)	1.55(6)
Mn	1.07(2)	4.87(49)	0.44(3)	0.13(1)	2.14(5)
Cu	0.35(1)	0.02(1)	0.01(1)	0.01(1)	0.72(2)
Zn	0.20(1)	1.10(9)	0.08(1)	0.08(1)	0.37(1)
Cl	0.16(5)		0.03(1)	0.68(12)	0.21(10)
As	0.16(1)	0.38(2)	0.17(1)	0.06(1)	0.33(2)
Ce	0.15(1)				0.19(1)
Ni	0.07(1)	0.09(1)	0.01(1)	0.00(1)	0.09(1)
Cr	0.05(1)	0.02(1)	0.01(1)	0.03(1)	0.13(1)
Pb	0.05(1)	0.73(5)	0.04(1)	0.02(1)	0.14(1)
Sr	0.04(1)	0.02(1)	0.18(1)	0.25(2)	0.07(1)
Rb	0.02(1)	0.02(1)	0.02(1)	0.03(1)	0.05(1)
Hg			0.14(1)		0.02(1)
Ba			0.13(1)	0.38(2)	

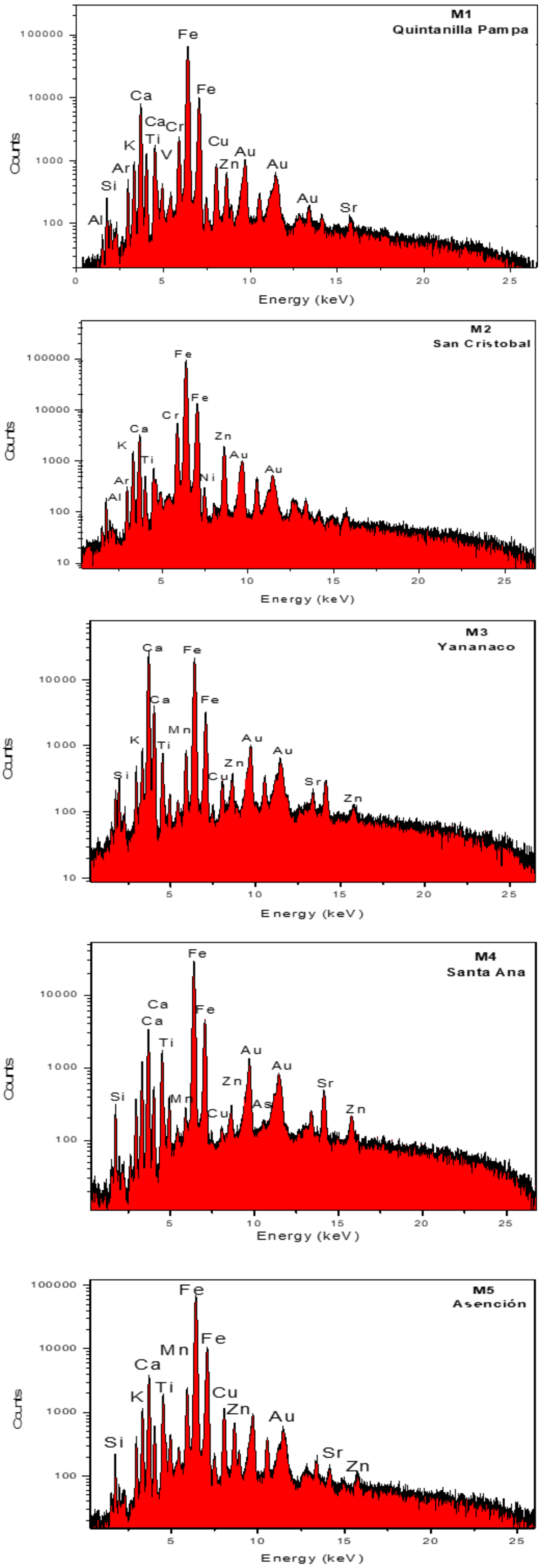

Fig. 2S. XRF spectra of soil samples collected from an ancient contaminated area, Huancavelica, Peru.

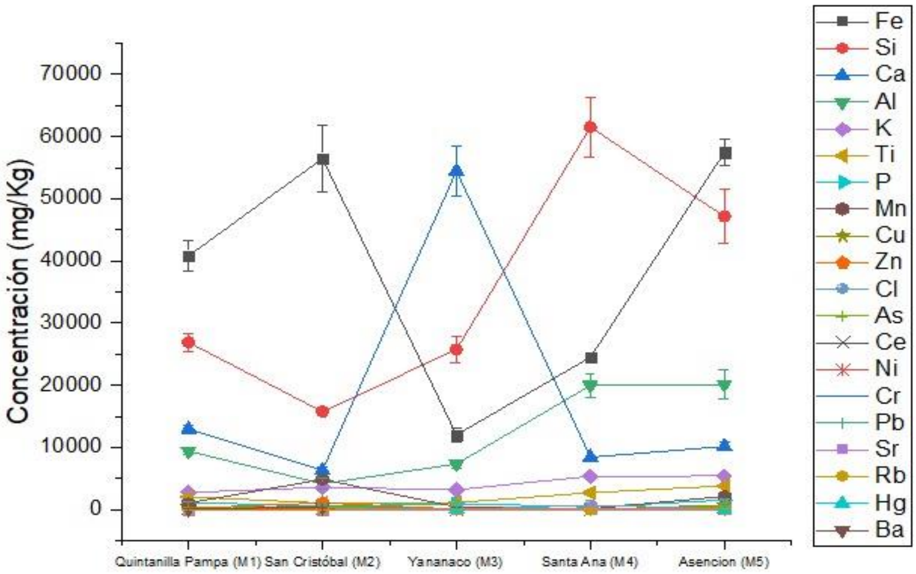

Fig. 3S. Comparison plot of the concentration (in mg/Kg) of elements found by XRF in soil samples collected from different sites in Huancavelica, Peru.

Section 3S. Peruvian standards

Table 3S. Environmental quality standards for the clasification of soils in 2017 in Peru (in Spanish "Estándares de Calidad Ambiental", ECA) (in mg.kg-1) (Ministerio del Ambiente (MINAM), 2017).

Nro	Material	Agricultural soils	Urban soils	Industrial soils	Method
1	Arsenic	50	50	140	EPA 3050 EPA 3051
2	Barium total	750	500	2000	EPA 3050 EPA 3051
3	Cadmium	1.4	10	22	EPA 3050 EPA 3051
4	Chromium total	**	400	1000	EPA 3050 EPA 3051
5	Chromium VI	0.4	0.4	1.4	EPA 3060/EPA 7199 ó DIN EN 15192
6	Mercury	6.6	6.6	24	EPA 7471 EPA 6020 ó 200.8
7	Lead	70	140	800	EPA 3050 EPA 3051
8	Cyanide free	0.9	0.9	8	EPA 9013 SEMWW-AWWA-WEF 4500 CN F o ASTM D7237 y/ó ISO 17690-2015

Source: *DS N° 011-2017-MINAM.*

Section 4S. Possible formation of natural Pb in soils

In contact with water, it forms PbO or lead (II) sulfide (PbS, galena) minerals which are also insoluble in water:

$$PbS_{(s)} \leftrightarrow Pb^{2+} + S^{2-}$$

$$PbCO_{3(s)} \leftrightarrow Pb^{2+} + {CO_3}^{2-}$$

Nevertheless, following these reactions, the resultant S^{2-} and CO_3^{2-} easily react with water (Baird et al., 2012)

$$S^{2-} + H_2O \leftrightarrow HS^- + OH^-$$

$${CO_3}^{2-} + H_2O \leftrightarrow {HCO_3}^- + OH^-$$

Thus, the concentration of the original anions decreases, increasing the dissolution of the PbS and $PbCO_3$ minerals. This is enhanced in contact with acidic water because the HS^- converts to H_2S through the reaction:

$$HS^- + H^+ \leftrightarrow H_2S \quad (9)$$

Therefore

$$PbS_{(s)} + 2H^+ \leftrightarrow Pb^{2+} + H_2S_{ac}$$

Table 4S. Maximun permisible levels of heavy metals in agricultural soils (in mg kg^{-1}) around the world (. In the case of UK, the values correspond to Predicted Effect Level (PEL) of sediment quality criteria (Hudson, et al., 2008; Kabata et al., 1992; Kabata et al., 2007; Belmonte et al., 2010).

Metal	Austria	Polonia	Germany	Holland	Canada	Japan	UK	European Union
Arsenic	50	30	40	-	25	15	17	-
Berilium	10	10	10	-	-	-	-	-
Cadmiun	5	3	2	-	8	-	3.53	3
Cobalt	50	50	-	-	25	50	-	-
Chromium	100	100	200	100	75	-	90	-
Copper	100	100	50	20	100	150	197	100
Mercury	5	5	10	-	0.3	-	2	-
Molibdenum	10	10	-	-	2	-	-	-
Nickel	100	100	100	50	100	100	35.9	50
Lead	100	100	500	50	200	400	91.3	100
Zinc	300	300	300	200	400	250	315	300

Section 5S. Further discussion about Hg

In contrast to organic contaminants, mercury vapour does not condense in cool weather, and it is not soluble in water (Gworek, 2020). It permanently circulates in the air in the form of Hg^0 until it re-oxidates again to Hg^{2+} by interacting with OH or O_3. The half-life-time of gaseous Hg^0 is one year, enough time to oxidate to Hg^{2+} which is soluble in water and falls with rain, far away from the emission region. If that occurred in the present work, Hg would have immobilized by other minerals (e.g calcite).

Other form of emitted Hg^{2+} is in the form of $HgCl_2$ (mercury (II) chloride) possibly formed during combustion of carbon in the mine, by reaction of Hg^0 with different chlorine gasses (Cl, Cl_2, HCl) following the form (Baird et al., 2012)

$$Hg^{2+}(carbon) \xrightarrow{flame} Hg^0(g) \xrightarrow{Cl_x} HgCl_2(g) \quad (5)$$

which is soluble in water.

Mercury forms inorganic compounds in both Hg(I) and H(II) valent states (Greenwood et al., 1997), and it is the Hg (II) the most stable in soils and the most encountered (Steinnes, 1995; Schlüter, 1993; Brussels, 1993). In contrast to the electronical neutral Hg^0 which spread from the lungs to the blood and can easily penetrate the brain-blood barrier, metal Hg_2^{2+} it is not much toxic since it combines in the stomach with the Cl ion to form insoluble Hg_2Cl_2. However, inorganic mercury can be methylated by abiotic and microbial to monomethyl mercury with the general formula CH_3HgX (e.g. CH_3HgCl and CH_3HgOH) which is very toxic. This toxin is stronger than Hg^{2+} salts because is soluble, mobile, and accumulates in fat tissues. The half-life time of methylmercury in the human body is around sixty days and once it is ingested, X transforms to amino acids containing sulphur and can penetrate the blood-brain barrier and the placenta to transform in Hg^{2+} (Schlüter, 1993; Brussels, 1993; Steinnes, 1995; Agency for Toxic Substances and Disease Registry, 1999).

Around 1–3 % of the total mercury on the surface soils is in the methylated form and the rest is predominantly Hg(II) compounds (Kabata et al., 2007). Monomethylated mercury compounds are most likely to be found in soil as a result of natural microbial transformation of inorganic mercury (Agency for Toxic Substances and Disease Registry, 1999), but it is volatile and, due to their relatively high mobility compared with inorganic forms, they are the most important mercury species for environmental pollution (Schlüter, 1993; Agency for Toxic Substances and Disease Registry, 1999). Whereas, dimethyl mercury [$Hg(CH_3)_2$], a common constituent in microorganism, is also highly toxic and volatile compound.

Table 5S. Amount of mercury (in mg/kg) found in soil samples collected from Huancavelica, Peru obtained in this work and by other authors.

Sample	This work (mg/kg)	Hagan			Robins			Standard Peru
		Adobe brick	soil	dust	Adobe	Soil	dust	6.6 for agricultural soil
M1 Quintanilla	4.5							
M2 San Cristobal	2.7	8 a 1070	3.06 a 926	0.02 a 9.69	21.6 a 944	16.7 a 839	9.6 a 153	
M3 Yananaco	6.2				26.3 a 1072	19.2 a 926	26.3 a 1072	
M4 Santa Ana	1.7				8 a 243	3.1 a 66.4	8 a 243	
M5 Asencion	3.8				9.9 a 763	16 a 833	17.3 a 413	

Section 6S. Further discussion about Cd and Zn

Since elevated Cd and Zn in soils can be dangerous to human health and wildlife, some strategies have been suggested to minimize them in soils. Most of the approaches consist of adding soil amendments such as clays (González et al., 1994; Angove et al., 1997; Yavuz et al., 2002), goethite (Christophi et al., 2000), hydroxyapatite (Mandjiny et al., 1995), calcareous soils (Cavallaro et al., 1978; Fuller et al., 1987), slags and sludges (Lee et al., 2001), biochar and lime (Ramtahal et al., 2019), phosphorous doses (Sánchez et al., 2011), *Streptomyces* (Revoredo et al., 2017), *Aspergillus* and *Trichoderma* (Guerra et al., 2014) and Mycorrhizae (Mohamed et al., 2017). One interesting approach consists on adding calcium carbonate to the soils since cadmium and zinc can be adsorbed on it via chemisorption to form $CdCO_3$ (otavite) and $ZnCO_3$ (smithsonite) (Sasamoto et al., 2022). In the case of otavite, the mechanism has been explained by Horner et al. (2011), which proposed that Cd replaces Ca in the calcite crystal and the Cd isotope fractionation factor becomes 0.9990(1) < 1, indicating that calcite is preferentially enriched with light Cd isotopes and without being affected with temperature (Horner et al., 2011). In the environment, the coprecipitation process of otavite strongly affects the mobility of Cd. The precipitation is mediated by bicarbonate, Na^+, Ca^{2+} and Mg^{2+} in water, as well as organic matter. Because it is cheap and available at large quantities, calcium carbonate has been also recently proposed to adsorb other potential toxic elements, such as Hg and Pb (Wang et al., 2019; Peña et al., 2013; Sasamoto et al., 2022; Xie et al., 2021; Gilg et al., 2008; Yavuz et al., 2007). Thus, it is possible that in addition to the past mining activities, the presence of calcite found in the soils from the *Yananaco* area (Castillo et al., 2022) might have immobilized Cd and Zn and thus presenting the highest concentration.

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