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Potentially Toxic Elements (PTEs) Dispersion in Alluvial Deposits from Abandoned Mining Sites

Julián Martínez [1], Rosendo Mendoza [1], María José de la Torre [2,*] and M. Carmen Hidalgo [2]

[1] Mechanical and Mining Engineering Department and CEACTEMA, Higher Polytechnic School of Linares, Technological Scientific Campus, University of Jaen, 23700 Linares, Spain; jmartine@ujaen.es (J.M.); rmendoza@ujaen.es (R.M.)

[2] Geology Department and CEACTEMA, Higher Polytechnic School of Linares, Technological Scientific Campus, University of Jaen, 23700 Linares, Spain; chidalgo@ujaen.es

* Correspondence: mjtorre@ujaen.es

Abstract: In the watersheds of abandoned mining districts, it is common to find remains of former facilities and waste dams on stream banks and slopes—a situation that results in the transport and accumulation of metal(loid)s in alluvial deposits. To analyze this problem, an area of the former mining district of Linares–La Carolina (southern Spain) was selected to evaluate the contents and distributions of Ag, As, Ba, Cu, and Pb as potentially toxic elements (PTEs) found in the mineral paragenesis. Specifically, this study focused on the Siles Stream, which runs through a sector where underground mining for the exploitation of galena veins generated abundant mining wastes, mainly waste rock and tailings. Thirty-four sediment samples from the stream bed of the Siles Stream and two sediment samples from the Guadiel River, of which it is a tributary, were analyzed. Floodplain sediments were sampled in the stream banks at the middle and lower reaches (11 samples), as well as the riverine soils developed at the mouth of the Siles Stream (22 samples). The analyzed samples presented high levels of PTEs, in most cases with values much higher than the generic reference levels established by European and regional legislation for PTEs in soils. In the case of Pb, the main metal mined in this district, contents of up to 27,074 mg·kg^{-1} were observed in the stream bed sediments. Very high concentrations of Pb also appeared in the floodplain sediments, with maximum values in the middle course of the stream, where the concentration reached 43,692 mg·kg^{-1}. With respect to the sediments of the Guadiel river bed, the Pb content was 699 mg·kg^{-1} before the confluence with the stream and 2537 mg·kg^{-1} downstream, which clearly reflects the influence of the contributions from the Siles Stream. The enrichment factors (EFs) show that the sediments present a severe to very severe anthropogenic influence for Ag, As, Ba, Cu, and Pb. The geoaccumulation index (Igeo) indicates that the entire basin is extremely polluted by Pb, to which As and Ag are added in the middle course of the stream. The potential ecological risk index (RI) and pollution load index (PLI) based on the contamination factor (CF) suggested that metal loads far exceeded the reference values. Selective chemical extraction methods were used to assess the potential bioavailability of these elements in sediment and soil samples. The results showed high concentrations of Pb in the exchangeable fraction, which poses a significant ecological risk and potential human health risks.

Keywords: lead mining; pollution; metal(loid)s; bioavailability; alluvial sediments; riverine soils

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1. Introduction

With the metal crisis of the 1970s, many mining districts were forced to close, mainly due to the low price of raw materials and sometimes due to the depletion of reserves. Abandonment was quick, without the necessary time or resources to carry out corrective measures to protect the natural environment, which has had serious environmental consequences that persist decades later [1,2].

Mining activities, both extractive and those of concentration and smelting, produce waste materials that are accumulated in the vicinity of the facilities themselves, sometimes on the banks of rivers and streams due to the ease that slopes offer for emptying. The metals and metalloids present in these wastes are mainly responsible for the contamination of soils and surface waters—an effect that can sometimes extend for kilometers downstream of the emission source [2,3]. In the United Kingdom, the basins and floodplains of many rivers that run through former mining areas are affected by the mobilization of pollutants from waste deposits into river beds [4,5]. In China, there are numerous examples of river basins contaminated by mining activities, such as the Baoshan area (southwest China), where high contents of potentially toxic elements (PTEs) related to lead and zinc mining carried out 40 years ago were measured [1,6]. A study carried out in the Sinú River (northern Colombia) on agricultural soils affected by mining activities shows that metal(loid) content is well above the values of the regional geochemical background [7]. In Tunisia, a combination of environmental geochemical indices was used to study the state and sources of metal(loid) contribution that affect the sediments of the Oued Rarai basin in the northwest of the country, showing a high level of potential ecological risk from Sb, As, Pb, Hg, and Ag [8]. Additionally, in Europe, affected areas are described, for example, in southeastern Poland, where the Pb–Zn mining developed in Olkusz–Trzebinia has affected the waters and sediments of the Chechlo, Biala Przemsza, and Sztola rivers [9]. In Spain, the same phenomenon occurs in different mining districts, such as Cartagena–La Unión [10–12] and Linares–La Carolina [13,14].

PTEs are part of the elements that make up the Earth's crust, and many of them are beneficial for humans, being required by the body in small amounts. However, overexposure to some of them (e.g., As, Cd, or Pb) is detrimental to health. Soil contamination by mining waste is related to problems observed in the surrounding ecosystems, such as scarcity of vegetation in areas close to tailings impoundments and high metal contents in tree species [15,16]. Furthermore, exposure to metal(loid)s present in soils can have serious effects on human health. In fact, high metal(loid) contents have been found in blood, hair, and urine in populations near mines and metallurgical industries in Russia [17], Mexico [18], China [19], and Spain [20]. For this reason, different environmental agencies have focused on mining activity that can cause soil pollution, developing legislation that establishes reference levels for the contents of different PTEs [21–24].

The mining district of Linares is located in the province of Jaen (Andalusia, Spain), characterized by the presence of filonian deposits of lead and copper sulfides [25]. Mining operations in Linares date back to pre-Roman times; however, the first industrial activities began in the 1820s, reaching the highest levels of production between the years 1880 and 1920, a period in which the district became the world's leading producer of Pb, reaching 1011 active mining concessions [26]. The exploitation system was constructed by underground mining using the chamber-storage method, generating wastes that were deposited in piles. These are made up of heterometric granitic materials, presenting significant metal(loid) contents [27] such as those observed in the Siles Stream basin. The mined ore was treated by gravimetric separation using the sink-float method to obtain a concentrate that was sent to the smelter to extract the lead. This intense industrial activity generated large volumes of waste, sometimes with high mineral grades, which were deposited in the vicinity of the mining facilities [28].

In this mining district, 32 flotation ponds and tailings dams have been inventoried, and the total metal(loid) content is very significant, especially for Pb, Zn, and As [13,29–31]. Therefore, it is considered an area of interest to analyze the mobilization of PTEs, studying the scope of the different dispersion mechanisms and the degree of contamination that may exist three decades after the mining operations were abandoned. This investigation focused on the Siles Stream basin. To analyze the mobility and persistence of PTEs in sediments and soils, different environmental factors were estimated and the degree of contamination presented by different types of alluvial deposits was defined. Finally, selective metal(loid) extraction tests were carried out to evaluate the bioavailability and the potential risk of affecting the crops.

2. Materials and Methods

2.1. Study Area

The study site is located in the province of Jaen (Andalusia, Spain), where the historic mining district of Linares is located. Within the hydrographic network that runs through the study site, the subbasin of the Siles Stream (Figure 1) was selected, a channel that runs dry for much of the year. This stream, approximately 5 km long and with an average slope of 2.8%, is a tributary of the Guadiel River, which in turn flows into the Guadalquivir River, the largest in Andalusia. The drainage basin of the Siles Stream is occupied by lands that currently have agricultural uses, mainly olive groves and pastures for sheep farming (Figure 2A). Remains of former mining operations are found along the river, among which the La Gitana and San Antón mines stand out, and numerous mining wastes (Figure 1A). There is also a restored tailings pond in the lower course of the stream, next to the confluence with the Guadiel River (Figure 1B). The closest major urban area is Linares, which has a population of 58,000 inhabitants and is located 6 km from the studied sector.

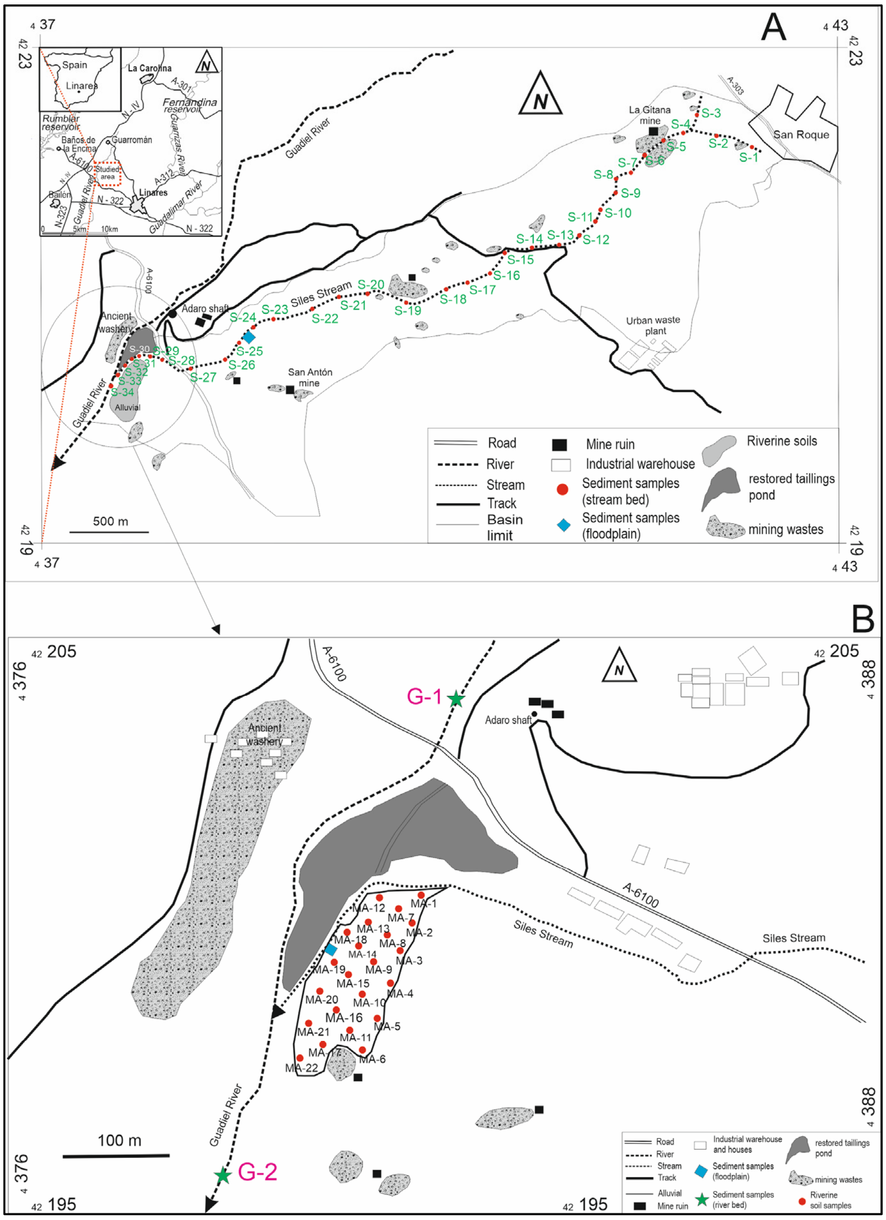

Figure 1. (**A**) Spatial distribution of the sampling points in the Siles Stream. (**B**) Spatial distribution of the sediment samples in the Guadiel River and the riverine soil samples at the mouth of the Siles Stream.

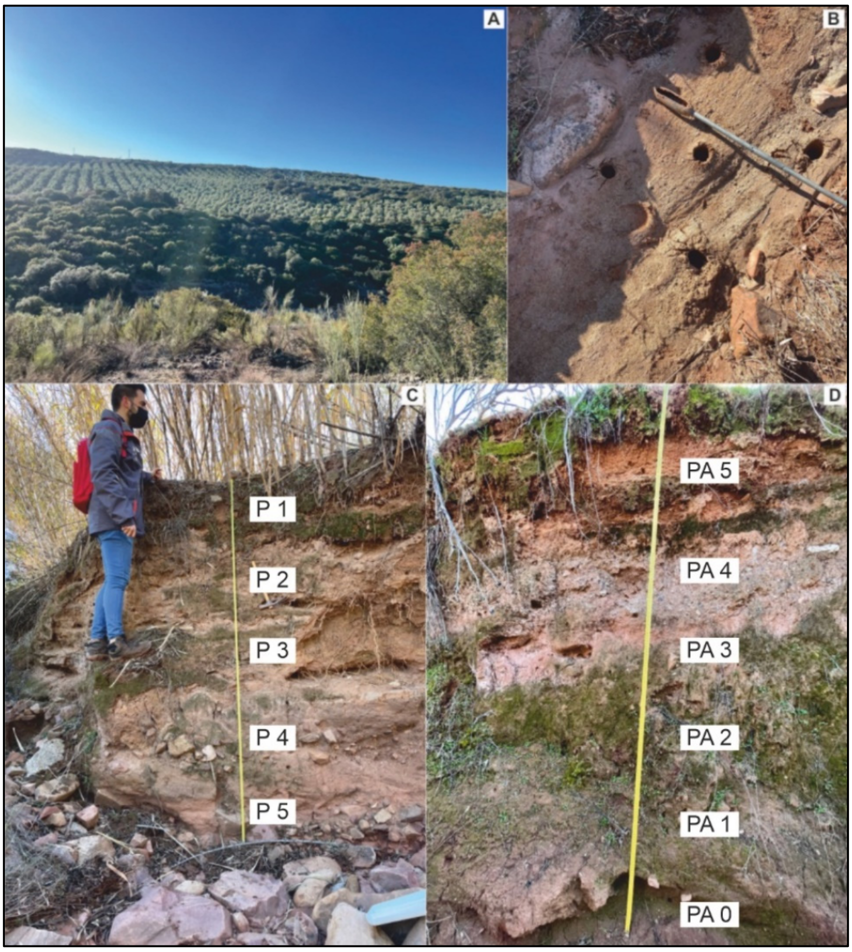

Figure 2. (**A**) Overview of the Siles Stream basin with a developed olive grove. (**B**) Sediment sampling with an Edelman auger in the stream bed of Siles Stream. (**C**) Sampling in the stream bank at the middle course (blue diamond in Figure 1A). (**D**) Profile in the floodplain sediments of the stream bank at the lower course (blue diamond in Figure 1B).

The regional geology is characterized by the presence of a basement consisting of metamorphic rocks (Palaeozoic phyllites with quartzite intercalations) where a granite intrusion occurred. Embedded in the granite basement are hydrothermal veins rich in sulfides, such as galena (PbS), chalcopyrite ($CuFeS_2$), and sphalerite (ZnS), as well as sulfides and sulfoantimonides of Ag, which drove the underground mining developed in the district. On the Palaeozoic materials, there is a sedimentary cover of sands and clays from the Triassic, which outcrops in most of the region [25].

2.2. Sampling and Analytical Methods

To study the behavior of metal(loid)s in different types of river deposits, a sampling network was designed that included stream bed sediments, floodplain sediments, and riverine soils. Thirty-four sampling points were distributed along the stream bed of the Siles Stream (S-1 to S-34, Figure 1A) and another two in the Guadiel River, the latter located upstream and downstream of the confluence with the stream (G-1 and G-2, Figure 1B). Each sediment sample was made up of five subsamples collected according to a Greek cross-sampling method with a spacing of one meter [32] (Figure 2B). The first 20 cm of the soil was collected with an open-face "Edelman" sampler until approximately 2 kg of soil was available, which was deposited in plastic bags for transfer to the laboratory.

The stream channel is embedded with floodplain sediments, which are scoured by erosion and develop steep stream banks. Two vertical sediment sampling profiles were performed on two stream bank erosion zones located in the middle (Figures 1A and 2C, samples P1 to P5) and lower reaches of the Siles Stream (Figures 1B and 2D, samples PA-0 to PA-5). Added to this were 22 samples distributed in grid formation in the riverine soils developed at the mouth of the stream (Figure 1B, samples MA-1 to MA-22).

Once in the laboratory, the samples were dried, homogenized, quartered, sieved, and ground. The samples were sieved (in a PVC sieve and bottom) to separate the fraction smaller than 2 mm. For the determination of the total metal(loid) content, the fraction <2 mm was ground in an agate ball mill (Retsch PM 100) to a size of less than 50 microns. The chemical analysis was carried out on 1 g of the ground sample by means of a complete microwave digestion (model MARS Xpress of CEM), using as reagents HNO_3 with the addition of H_2O_2 to facilitate the complete oxidation of the organic matter [33]. The analysis of metal(oids) (Al, P, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Ag, Cd, Sb, Ba, and Pb) was carried out by ICP–MS in the laboratories of the Scientific-Technical Instrumentation Center of the University of Jaen, with a mass spectrometer with a plasma torch ionization source and quadrupole ion filter (model 7900 Agilent, Santa Clara, CA, USA).

In a selection of 11 samples, a selective metal(loid) extraction was performed by the multi-element super trace method in four steps to determine the elements associated with the mobile, exchangeable, reducible, and oxidizable fractions of the sediment. These analyses were carried out in the ALS Minerals laboratories in Vancouver (ON, Canada). The mobile fraction was extracted with deionized water leaching; the exchangeable fraction was formed by cations adsorbed by clay and elements coprecipitated with carbonates and was extracted using a solution of ammonium acetate ($C_2H_7NO_2$) in acetic acid (CH_3COOH); the reducible fraction was composed of Fe and/or Mn oxides and hydroxides and extracted using a 0.1 M hydroxylamine solution in 0.01 nitric acid (HCl-NH_2OH); and finally, the oxidizable fraction was formed by elements adsorbed by organic matter and/or sulfides and was extracted using a 0.1 M sodium-pyrophosphate solution ($Na_4P_2O_7$). The obtained solutions were analyzed using inductively coupled plasma–mass spectrometry (ICP–MS) to determine the total concentrations of the selected elements.

2.3. Diagnosis of Contamination

Based on Clarke and Mason geochemical background values for acidic igneous rocks [34], different contamination indices were estimated.

Enrichment factor (EF): evaluates the anthropogenic influence on the metals present in the sediment using the following formula [35].

$$EF = \frac{(C_M/C_P)_{sample}}{(C_M/C_P)_{background}} \quad (1)$$

where $(C_M/C_P)_{sample}$ is the ratio of the concentration of metals (C_M) and of phosphorus (C_P) in the sediment sample, and $(C_M/C_P)_{background}$ is the ratio of the values of the geochemical background. An EF value close to 1 suggests natural weathering processes, EF > 1.5 is considered indicative of human influence, and EFs of 1.5–3, 3–5, 5–10 and >10 are considered evidence of minor, moderate, and severe and very severe alteration, respectively [36,37].

Geoaccumulation index (I_{geo}): evaluates the level of contamination in the sediment.

$$I_{geo} = Log_2\left[\frac{C_n}{1.5B_n}\right] \quad (2)$$

where C_n is the mean concentration of the metal in the sediment and B_n is the mean value for trace elements in acid igneous rocks. The factor 1.5 minimizes possible variations in background values that can be attributed to lithogenic effects. Seven levels of I_{geo} are established: uncontaminated (<0), uncontaminated to slightly contaminated (0–1), moderately contaminated (1–2), contaminated (2–3), heavily contaminated (3–4), and extremely contaminated (>4) [38].

Ecological risk (E_r^i) and environmental risk potential (RI): estimates the ecological risk of each element (E_r^i) and the sum of the elements (RI) in the sediment [39].

$$E_r^i = T_r^i \times \frac{C^i}{C_n^i} \tag{3}$$

$$RI = \sum_{i=1}^{n} E_r^i \tag{4}$$

where T_r^i is the toxicity value for an element, C^i is the mean concentration of metal i in the sediment samples, and C_n^i is the geochemical background value for element i. According to the E_r^i values, the following classes are considered: very high risk ($E_r^i > 320$), high risk ($160 \leq E_r^i \leq 320$), considerable risk ($80 \leq E_r^i < 160$), moderate risk ($40 \leq E_r^i < 80$), and low risk ($E_r^i < 40$).

RI is the sum of E_r^i and defines four levels of ecological risk: very high (RI > 600), considerable ($300 \leq RI \leq 600$), moderate ($150 \leq RI < 300$), and low ecological risk (RI < 150).

Pollution load index (PLI): defined as the nth root of the multiplications of the contamination factor of metal(loid)s (CF).

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{1/n} \tag{5}$$

where CF is calculated from the relationship between the measured concentration and the natural abundance of a metal, $CF_{metal} = C_{metal}/C_{background}$. Depending on the value of CF, four degrees of metal(loid) contamination load are defined: low degree (CF < 1), moderate degree ($1 \leq CF < 3$), considerable degree ($3 \leq CF < 6$), and very high degree ($CF \geq 6$) [40]. PLI values less than 1 indicate that there is no contamination, while PLI = 1 suggests that it is around the background value, and PLI greater than 1 indicates deterioration due to contamination. In the latter case, the site is considered to be contaminated and would require intervention measures.

2.4. Statistical Analysis

Univariate and multivariate statistical techniques were used to determine the relationship and variability of the 18 elements analyzed using SPSS 22 software developed by IBM. Cluster analyses were performed to separate the elements that appeared grouped using the proximity criterion and the Ward distance measurement strategy, techniques used in other environmental and soil contamination studies [41–43].

To analyze the spatial distribution of the contents of selected elements and the pollution load index (PLI), ordinary kriging was performed using the spherical semivariogram model. The information was processed with ArcGIS 10.6 software, developed by Esri, to produce distribution maps for Ag, As, Ba, Cu, and Pb in the Siles Stream basin.

3. Results

3.1. Total Element Concentrations

Table 1 shows the total contents of the metal(loid)s analyzed (Al, P, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Ag, Cd, Sb, Ba, and Pb) in the sediments and riverine soils of the Siles Stream and in the river bed of the Guadiel River. Values that exceed the generic reference levels (GRL) set by the Andalusian regional government are highlighted in bold, which correspond to 275 mg·kg^{-1} for Pb, 36 mg·kg^{-1} for As, 595 mg·kg^{-1} for Cu, and 25 mg·kg^{-1} for Co, referring to agricultural land uses. Especially noteworthy are the high Pb contents in all the samples analyzed, with values well above the limits set by the Andalusian and Dutch regulations for other land uses, which would indicate possible effects on humans and ecosystems.

Table 1. Total concentrations (mg·kg^{-1}) of selected elements in sediment and soil samples from the Siles Stream (stream bed sediments, floodplain sediments, and riverine soils) and the Guadiel River. The concentrations above the generic reference levels in Andalusia (GRL) are in bold.

Samples	Al	P	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Ag	Cd	Sb	Ba	Pb
Stream bed sediments—Siles Stream																		
S1	11,570	366	2043	139	9.7	359	12,143	5.0	5.1	46	35	9	0.1	0.6	0.1	0.0	1700	**3649**
S2	15,901	432	9513	68	11.6	1112	15,080	7.5	8.6	99	101	**94**	1.5	3.1	0.7	0.2	1795	**11,889**
S3	24,71	332	3356	187	17.8	676	18,042	9.0	11.2	89	68	**60**	0.5	2.9	0.4	0.5	1818	**15,763**
S4	23,041	141	20,923	71	19.0	521	16,780	6.9	10.9	68	36	**55**	0.2	1.5	0.2	0.3	1956	**5170**
S5	21,548	237	12,004	85	16.9	1310	17,831	11.4	12.7	155	86	**81**	0.8	4.5	0.5	1.0	2105	**11,706**
S6	10,711	213	5893	96	8.5	614	11,388	6.3	5.7	57	56	**39**	0.2	0.7	0.3	0.3	1633	**3673**
S7	24,752	234	19,419	80	15.5	3339	22,716	**34.7**	19.6	**750**	114	**111**	3.2	6.4	0.5	0.9	3582	**27,074**
S8	10,374	218	6572	84	8.2	587	10,760	6.9	5.3	70	59	26	0.2	0.8	0.1	0.1	1025	**3530**
S9	23,704	120	3580	91	22.2	548	23,001	6.3	10.3	31	26	30	0.2	0.4	0.1	0.1	727	**2041**
S10	10,898	188	5252	177	8.4	544	10,394	6.6	5.2	73	44	24	0.3	0.5	0.1	0.1	712	**2858**
S11	10,528	213	5845	121	8.5	493	10,422	6.2	5.1	49	33	24	0.3	0.5	0.1	0.1	1281	**3737**
S12	12,589	239	11,081	164	9.2	1038	11,795	11.6	7.6	120	39	**44**	0.9	1.9	0.1	0.5	1137	**7807**
S13	9991	217	8914	73	7.8	734	10,427	7.7	6.1	72	44	**40**	0.3	0.7	0.1	0.1	3494	**3789**
S14	17,275	293	40,142	116	13.0	2809	17,310	11.1	9.9	115	69	**71**	2.1	3.9	0.2	1.1	3533	**12,800**
S15	8432	207	8210	105	6.4	553	8704	6.8	4.1	52	31	30	0.2	0.6	0.1	0.1	1997	**3193**
S16	9417	210	8340	135	7.5	570	8849	7.0	4.9	64	31	17	0.4	0.4	0.1	0.1	1052	**2505**
S17	11,406	253	8559	97	9.6	675	11,151	7.6	5.7	59	37	26	0.2	0.7	0.1	0.1	2630	**6124**
S18	9715	206	9719	134	7.1	649	9662	7.1	5.6	59	57	**69**	0.8	1.4	0.1	0.5	4392	**10,436**
S19	8655	222	11,637	102	6.7	835	9469	6.8	4.8	62	31	28	0.3	1.0	0.1	0.2	2611	**5980**
S20	9060	215	8103	99	6.5	843	9390	5.7	4.6	62	30	35	0.3	1.4	0.1	0.3	4659	**8373**
S21	12,360	259	8567	90	9.7	802	11,523	7.2	5.9	79	38	32	0.4	1.1	0.1	0.3	4020	**6358**
S22	7981	187	7896	134	6.0	607	8203	4.7	3.7	66	26	21	0.3	1.2	0.1	0.1	3740	**7310**
S23	10,447	206	8103	122	7.5	542	9568	5.8	4.8	41	27	14	0.2	0.5	0.1	0.1	1611	**3615**
S24	9856	246	9436	139	7.5	780	10,779	11.3	8.4	79	33	**56**	2.9	4.0	0.1	0.3	4135	**15,841**
S25	7518	203	8109	126	6.8	729	9613	7.6	4.9	62	24	**50**	1.5	1.8	0.1	0.2	3893	**10,970**
S26	10,219	194	8517	135	7.7	620	9675	5.5	4.8	62	29	22	0.4	2.1	0.1	0.2	4214	**6915**
S27	8350	198	7116	109	6.5	660	8282	5.9	4.7	47	24	26	0.3	0.9	0.1	0.2	2944	**4625**
S28	9937	188	6488	98	6.9	532	8575	4.7	4.4	43	24	18	0.3	0.5	0.1	0.1	2845	**3637**
S29	9068	187	7555	111	7.8	650	8634	6.8	5.0	61	26	**40**	0.4	1.1	0.1	0.1	3451	**7234**
S30	9150	174	7075	117	6.7	518	8547	4.9	4.2	39	23	11	0.2	0.4	0.1	0.1	1687	**2963**
S31	10,793	189	7255	123	7.5	551	8947	5.1	4.7	49	33	**37**	1.2	1.2	0.1	0.1	4174	**8563**
S32	14,914	277	8934	161	11.9	622	12,707	7.2	7.0	91	36	**69**	1.7	2.3	0.1	0.3	4466	**12,155**
S33	9121	224	8725	116	6.9	652	9496	8.3	6.4	156	27	26	0.3	0.9	0.1	0.2	4342	**7227**
S34	8895	175	7696	113	6.6	700	8614	6.5	4.5	50	23	13	0.4	0.5	0.1	0.1	3328	**3999**
Mean	11,711	225	9429	115	9.6	817	11,720	7.9	6.7	90	42	**40**	0.7	1.5	0.2	0.3	2726	**7456**
Median	10,374	213	8160	114	7.8	650	10,408	6.9	5.3	62	33	31	0.3	1.1	0.1	0.2	2738	**6241**
Floodplain sediments (middle course)—Siles Stream																		
p1	12,673	322	19,623	99	9.6	1800	13,998	9.2	7.7	113	46	**47**	1.2	2.3	0.3	0.4	3033	**12,808**
p2	14,553	322	33,185	128	10.8	3054	18,615	14.4	10.5	187	76	**70**	1.5	4.1	0.3	0.4	2652	**20,256**
p3	16,466	272	31,725	86	10.8	3609	23,282	14.4	10.6	231	99	**99**	2.0	6.1	0.4	0.3	3162	**29,100**
p4	21,303	490	5670	160	15.1	824	15,128	9.2	9.5	168	43	**41**	0.5	5.2	0.1	0.5	1294	**43,693**
p5	18,964	266	5265	110	13.1	348	12,836	6.7	8.4	210	33	18	0.1	5.7	0.1	0.4	653	**35,789**
Mean	16,792	334	19,094	117	11.9	1927	16,772	10.8	9.3	182	59	**55**	1.1	4.7	0.2	0.4	2159	**28,329**
Median	16,466	322	19,623	110	10.8	1800	15,128	9.2	9.5	187	46	**47**	1.2	5.2	0.3	0.4	2652	**29,100**
Riverine soils—Siles Stream																		
MA1	7363	192	10,600	124	5.9	863	8971	6.3	4.5	59	26	25	0.6	1.2	0.1	0.2	3462	**6983**
MA2	8682	227	12,016	135	7.1	871	9310	8.4	7.0	49	28	17	0.5	0.6	0.1	0.1	2971	**3853**
MA3	9049	228	10,045	121	7.5	873	9293	6.4	4.8	49	28	20	0.4	0.7	0.1	0.1	3505	**4570**
MA4	9725	219	7948	116	8.2	775	9748	6.0	5.0	96	40	21	0.4	0.7	0.1	0.1	3033	**4663**
MA5	8259	194	9764	130	7.2	894	8687	5.9	4.8	48	25	14	0.3	0.4	0.1	0.1	1940	**3059**

Table 1. *Cont.*

Samples	Al	P	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Ag	Cd	Sb	Ba	Pb
MA6	10,385	200	9635	109	9.3	803	10,145	5.7	5.6	49	31	15	0.2	0.5	0.1	0.1	1480	**3160**
MA7	9609	219	7888	77	7.6	759	9359	7.4	5.4	52	27	19	0.3	0.8	0.1	0.1	3308	**5231**
MA8	9133	197	7357	93	8.5	759	8262	5.5	5.0	42	24	17	0.4	0.9	0.1	0.1	2097	**3821**
MA9	10,115	231	9780	73	8.6	852	9948	6.6	5.5	50	30	25	0.4	0.7	0.1	0.1	2603	**4439**
MA10	9247	191	14,048	82	8.3	940	9367	5.2	5.2	45	26	14	0.2	0.6	0.1	0.1	2781	**2679**
MA11	10,360	219	11,199	166	8.9	867	10,358	6.2	5.8	49	43	17	0.3	0.6	0.1	0.1	2518	**3557**
MA12	8479	202	6947	112	7.2	606	7878	4.6	4.2	57	24	13	0.2	0.7	0.1	0.1	1437	**2506**
MA13	12,169	274	11,669	109	10.8	938	11,765	7.4	6.9	86	36	23	0.4	0.8	0.1	0.1	2308	**4644**
MA14	9057	231	8026	109	7.4	783	8970	6.0	4.7	52	25	18	0.4	0.6	0.1	0.1	2990	**3677**
MA15	8062	194	12,093	131	7.4	823	8867	4.8	4.7	52	24	15	0.3	0.5	0.1	0.1	2362	**3034**
MA16	9391	184	8622	121	7.8	748	9124	5.4	4.8	46	28	13	0.3	0.5	0.1	0.1	2036	**3307**
MA17	7631	175	9725	118	6.5	713	7892	5.0	4.3	40	24	13	0.3	0.6	0.1	0.1	2724	**3300**
MA18	9982	231	9500	115	8.3	763	9978	5.5	5.5	62	28	23	0.5	0.8	0.1	0.1	2783	**5416**
MA19	12,186	261	10,115	154	10.5	861	11,391	8.1	7.8	111	32	19	0.4	0.7	0.1	0.1	2028	**4472**
MA20	12,444	273	9451	141	10.0	889	11,873	7.2	6.2	70	33	26	0.4	0.9	0.1	0.1	2390	**5110**
MA21	12,147	236	9724	122	10.1	864	11,449	7.1	6.3	60	32	20	0.5	0.7	0.1	0.1	1962	**4346**
MA22	16,102	251	14,434	103	13.7	936	13,968	7.2	8.7	73	38	21	0.3	1.0	0.2	0.3	4221	**5078**
Mean	9981	219	10,027	116	8.5	826	9846	6.3	5.6	59	30	18	0.4	0.7	0.1	0.1	2588	**4132**
Median	9500	219	9745	117	8.3	857	9363	6.1	5.3	52	28	18	0.4	0.7	0.1	0.1	2561	**4099**
Floodplain sediments (lower course)—Siles Stream																		
PA5	13,622	199	51,900	104	13.6	2485	16,345	6.4	11.3	55	56	26	0.7	1.4	0.3	0.1	6542	**4556**
PA4	19,111	225	4575	106	21.0	502	13,992	6.2	13.5	32	32	13	0.2	0.4	0.1	0.2	669	**2822**
PA3	15,803	264	2877	80	14.8	374	11,082	5.9	8.7	52	27	12	0.2	0.8	0.1	0.5	681	**11,632**
PA2	19,454	206	3041	82	17.6	378	13,400	6.2	11.1	57	29	13	0.2	0.4	0.1	0.2	542	**3914**
PA1	11,190	188	6445	137	9.8	537	9928	5.7	6.3	59	25	**58**	0.7	2.0	0.1	0.2	4257	**9466**
PA0	15,473	306	10,158	149	12.0	1049	14,586	8.5	7.4	82	40	25	0.4	1.1	0.2	0.2	1550	**6420**
Mean	15,776	231	13,166	110	14.8	888	13,222	6.5	9.7	56	35	24	0.4	1.0	0.2	0.2	2374	**6468**
Median	15,638	216	5510	105	14.2	520	13,696	6.2	9.9	56	30	19	0.3	1.0	0.1	0.2	1116	**5488**
River bed sediments—Guadiel River																		
G1	15,867	233	14,508	102	18	432	11,430	4.4	13	22	37	12	0	1	0	0	1366	**699**
G2	9887	198	6768	124	9.6	455	9179	4.6	6.4	23	25	11	0	0	0	0	459	**1199**

Pb concentrations in the stream bed sediments show a large dispersion, with a minimum of 2041 mg·kg^{-1} (S9) and a maximum of 27,074 mg·kg^{-1} (S7). The mean value (7456 mg·kg^{-1}) is similar to the results obtained in riverbed sediments studies in other Pb sulfide mining areas in Spain [12]. Similar figures were also obtained by Mendoza (2020) [14] in the sediments of the Grande River, the most important water course that runs through the studied mining district, with average values of 5452 mg/kg, 116 mg/kg, and 2622 mg/kg, for Pb, As, and Ba, respectively. The results obtained by Cortada (2019) [13] in the sediments of the Baños Creek (at 10 km from the Siles Stream) exhibited even higher Pb content, with a maximum of 75,912 mg/kg, which is associated with a waste rock heap very nearby.

The floodplain sediments from the middle course of the stream are those that generally present the highest values for this element, between 12,808 mg·kg^{-1} (P1) and 43,693 mg·kg^{-1} (P4). The samples obtained in the second profile of the floodplain sediments, at the lower course of the stream, also appear enriched in Pb, although in somewhat lower concentrations, from 2822 mg·kg^{-1} (PA4) to a maximum of 11,632 mg·kg^{-1} (PA3).

The riverine agricultural soils sampled in the final section of the alluvium present Pb contents between 2506 mg·kg^{-1} (MA-12) and 6983 mg·kg^{-1} (MA-1), with an average value of 4132 mg·kg^{-1}. Finally, in the two samples collected in the bed of the Guadiel River, concentrations of Pb of 699 mg·kg^{-1} (sample G1) and 1199 mg·kg^{-1} (sample G2) were obtained upstream and downstream, respectively, from the confluence with the Siles stream.

The level of As also reached the highest concentrations in the sediment samples from the headwaters of the stream, with a maximum concentration of 111 mg·kg^{-1} in sample S7. As with Pb, the As contents in the sediments of the floodplain are high, with a maximum value of 99 mg·kg^{-1} (P3). Sample S7 from the Siles Stream should be highlighted due to the high concentrations of not only Pb but also As, Co, Cu, Mo, and Zn. These alluvial deposits are found downstream from the La Gitana mine, whose tailings were deposited on the banks of the stream. On the other hand, the middle course receives contributions of sediments from the San Antón mine, located on the slopes of the basin, which would contribute to this considerable increase in the metal content of the deposits. The lower course of the stream is affected by all the contributions of the basin, and although the values for the Pb content are high, these values are more attenuated than those in the head and middle courses of the stream where most of the mining activity was concentrated.

3.2. Selective Extraction Analysis

To evaluate the bioavailability of these PTEs, a geochemical speciation analysis was carried out on samples of the different groups of sediments and soils studied. A selective extraction of metal(loid)s was carried out in a sample of riverine soil (MA-15), three samples from the stream bed (S-2, S-18 and S-32), a set of sediment samples from the floodplain (P-1 to P-5), and the Guadiel River bed sediments (G-1 and G-2). Table 2 shows the results obtained for the different fractions analyzed (mobile, exchangeable, reducible, and oxidizable) for Ag, As, Pb, Ba, and Cu.

Table 2. Ag, As, Pb, Cu, and Ba contents of the mobile, exchangeable, reducible, and oxidizable fractions in the alluvial deposits of the Siles Stream.

	Fractions (mg·kg^{-1})	**MA-15**	**S-2**	**S-18**	**S-32**	**P-1**	**P-2**	**P-3**	**P-4**	**P-5**	**G-1**	**G-2**
Ag	Mobile	0.01	0.10	0.02	0.05	0.05	0.05	0.02	0.02	0.04	0.01	0.02
	Exchangeable	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
	Reducible	0.05	0.03	0.02	0.04	0.18	0.38	0.72	0.15	0.39	<0.002	0.058
	Oxidizable	0.00	0.37	0.02	0.28	0.25	0.47	0.49	1.11	0.47	0.023	0.002
	Total	0.5	3.1	1.4	2.3	2.3	4.1	6.1	5.2	5.7	0.7	0.2
As	Mobile	0.26	0.64	0.38	0.31	0.56	0.66	0.36	0.18	0.23	0.44	0.47
	Exchangeable	1.18	2.62	1.54	1.56	2.19	2.63	1.71	3.01	2.57	1.42	1.10
	Reducible	0.04	0.15	0.08	0.10	0.08	0.07	0.06	0.09	0.06	0.18	0.06
	Oxidizable	1.09	3.54	1.85	2.68	3.14	5.20	9.98	7.13	3.65	2.21	1.32
	Total	15.00	94.00	69.00	69.00	47.00	70.00	99.00	41.00	18.00	11.9	11.1
Pb	Mobile	17	79	63	62	108	101	49	109	238	6.25	6.16
	Exchangeable	1655	>5000	>5000	>5000	>5000	>5000	>5000	>5000	>5000	325	629
	Reducible	1.065	1600	4080	2870	2730	3210	>5000	>5000	>5000	5.8	405
	Oxidizable	866	>5000	4090	>5000	>5000	>5000	>5000	>5000	>5000	158	251
	Total	3034	11,889	10,436	12,155	12,808	20,256	29,100	43,693	35,789	699	1199
Cu	Mobile	0.34	2.43	0.91	2.18	1.91	1.88	0.87	0.83	1.97	0.72	0.33
	Exchangeable	9.06	19.35	10.75	22.70	21.30	35.50	42.40	25.70	43.90	7.19	6.99
	Reducible	3.59	0.62	0.59	0.84	3.52	9.27	18.50	3.63	12.70	0.07	1.91
	Oxidizable	3.98	30.90	6.49	28.30	23.60	42.00	41.20	78.90	84.60	8.33	3.46
	Total	52	99	58	91	113	187	231	168	209	22	23
Ba	Mobile	12.25	6.37	25.40	12.50	12.40	9.65	10.10	6.45	6.77	5.84	1.69
	Exchangeable	309	173	345	236	221	175	225	134	207	137	107.5
	Reducible	110.00	72.20	72.20	57.60	59.40	67.80	63.70	31.10	60.00	58.8	67.4
	Oxidizable	33.80	53.00	38.90	43.30	33.10	28.30	31.40	40.10	64.40	22.8	20.3
	Total	2361	1795	4392	4466	3033	2652	3162	1294	653	1366	459

The metal(loid)s present in the mobile fraction are weakly bound and therefore easily removable. This fraction and the exchangeable fraction are considered the most mobile and potentially bioavailable in soils. The reducible fraction is relatively stable under environmental conditions, just as the metal(oid)s associated with the organic phase; however, the latter can be mobilized under oxidizing conditions that degrade organic matter.

4. Discussion

4.1. Statistical Analysis

The cluster for the elements analyzed in the soils and sediments of the Siles Stream is shown in Figure 3, where the association of Ag, As, and Pb, elements of the paragenesis of the deposits of the studied district, can be seen, among others. These metal(loid)s were selected for further discussion in this paper, together with Ba and Cu, as the elements of environmental significance related to mining activity.

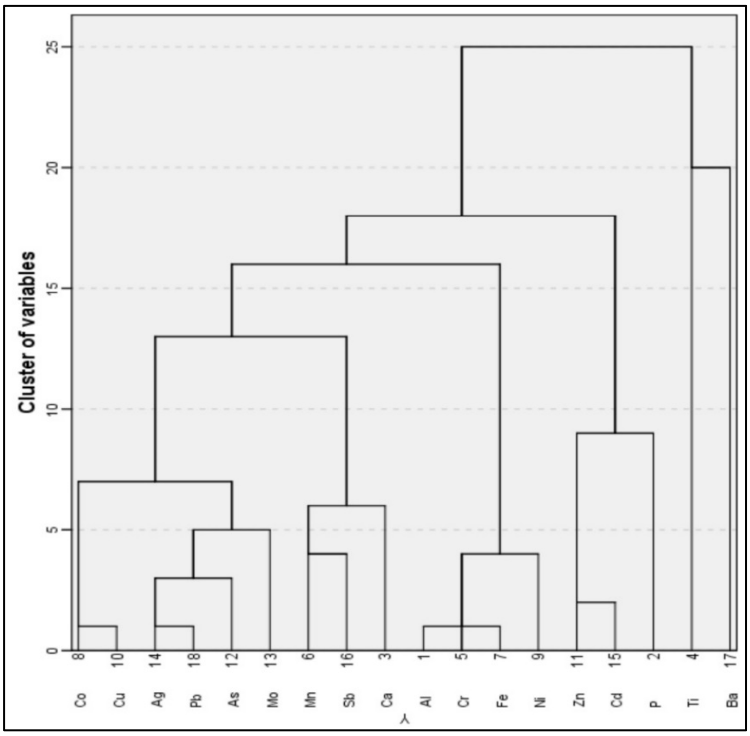

Figure 3. Cluster of the elements analyzed in soils and sediments.

Figure 4 shows the variation in the Ag, As, and Pb contents in the samples taken in the stream bed, indicating the Andalusian GRL and Duch intervention value, together with the histograms, normality, and box-and-whisker graphs.

The Pb concentrations in all the stream bed samples were much higher than the GRL set by both the Andalusian regional standard and the Dutch regulation for soil quality. Samples S7, S14, S18, S24, and S25 stand out, related to contributions from mine tailings, along with S31 and S32, located at the foot of a restored tailings pond. With respect to As, it presents values higher than the GRL at the head of the stream and in the middle course, but it remains below the normative limit both in the rest of the stream bed and in the alluvial soils, and also in the samples of the Guadiel River. Nevertheless, the As mean value was 40 mg·kg^{-1} in the stream bed sediments, greater than those values found in other contaminated mining areas [8].

The Andalusian standard does not establish reference values for Ag; however, the Dutch standard does set a maximum content of 15 mg·kg^{-1} for this element. All the samples analyzed have Ag concentrations lower than this figure.

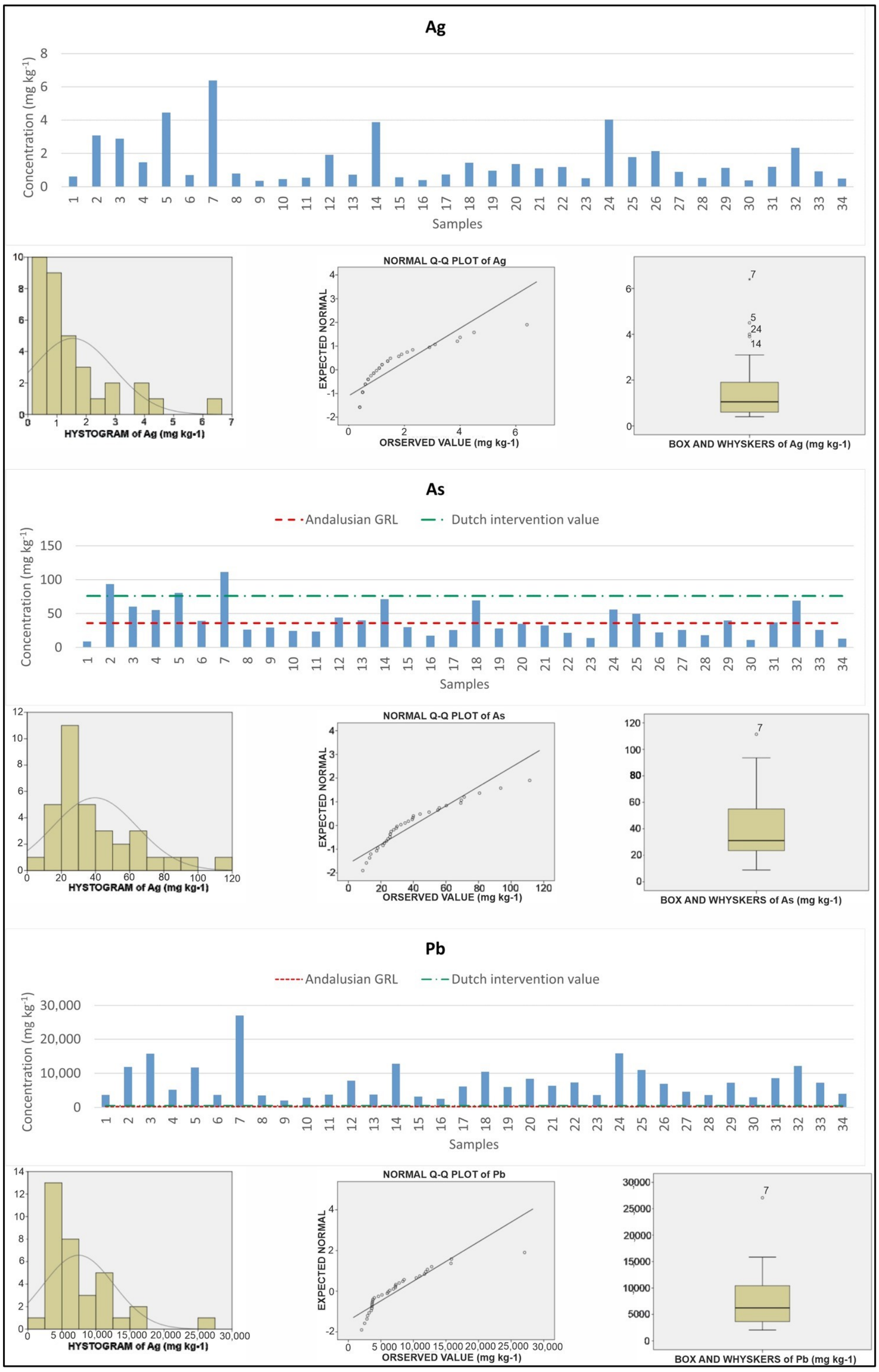

Figure 4. Distributions, histograms, box−and−whisker plots, and normality curves for Ag, As, and Pb contents in sediments from the Siles Stream (GRL: generic reference levels in Andalusia).

These three elements (Ag, As, and Pb) associated with the mineral paragenesis exhibit asymmetric histograms and lognormal distributions, with values that deviate from the normal line in the Q/Q plots (Figure 4).

As seen in the box plots, the three elements present similar graphs and are characterized by a highly asymmetric distribution, with the median shifted towards the lower values. For Ag, samples S5, S7, S14, and S24 are identified as outlier values. These are samples related to contributions from the mine tailings. The S7 sample, also marked as an outlier in the As and Pb box plots, is located in the La Gitana mine at the head of the stream, which stands out as one of the sectors most enriched in PTEs.

4.2. Environmental Indices

From the metal(loid) content, environmental indices were calculated for the different groups of sediments and soils (Table 3). Those factors that present high values (considering the reference levels included in Section 2.3) are marked in bold. Diagnosis of contamination are marked in bold, as well as the elements that present at least one high factor (Ag, As, Pb, Ba, and Cu). In Figure 5, the spatial distributions of Ag, As, Ba, Cu, and Pb (the five elements for which significant values of the contamination indices were obtained) in the stream bed of the Siles Stream is represented.

Table 3. Calculated values for enrichment factor (EF), geoaccumulation index (Igeo), ecological risk (**E_r^i**), environmental risk potential (RI), contamination factor (CF), and pollution load index (PLI). Those factors that present high values appear in bold, as well as the elements that present at least one high factor.

	Element	Background (mg·kg^{-1})			Factors					
		Acid Rocks [34]	**Triassic Local Background [42]**	**Average Value (mg·kg^{-1})**	**EF**	**Igeo**	**E_r^i**	**RI**	**CF**	**PLI**
Stream bed	Al	81,300		12,440		−3.3				
	P	700		225		−2.2				
	Ti	2300		115		−4.9				
	Cr	25		10		−2	1			
	Mn	600		817		−0.1	1			
	Co	5		8		0.1	8			
	Ni	8		7		−0.8	4			
	Cu	30	49	907	0	1	15	**18,983**	**1.8**	**1.7**
	Zn	60	56	42	2.3	−1.1	1		0.7	
	As	1.5	16	40	**7.7**	**4.1**	**264**		**2.5**	
	Ag	0.15	0.3	1.5	**15.9**	2.8	0		**5.1**	
	Cd	0.1	0.3	0.2	1.7	0.1	48		0.5	
	Ba	830	750	2726	**11.3**	1.1	0		**3.6**	
	Pb	2	525	7456	**44.1**	**11.3**	**18,640**		**14.2**	
Floodplain (middle course)	Al	81,300		16,792		−2.9				
	P	700		334		−1.7				
	Ti	2300		116.51		−4.9				
	Cr	25		12		−1.7	1			
	Mn	600		1927		1.1	3			
	Co	5		11		0.5	11			
	Ni	8		9		−0.4	6			
	Cu	30	49	182	**7.8**	2	30	**71,314**	**3.7**	**2.1**
	Zn	60	56	59	2.2	−0.6	1		**1.1**	
	As	1.5	16	55	**7.2**	**4.6**	**366**		**3.4**	
	Ag	0.15	0.3	5	**32.6**	**4.4**	0		**15.6**	
	Cd	0.1	0.3	0.2	1.7	0.7	73		0.8	
	Ba	830	750	2158	**6**	0.8	0		2.9	
	Pb	2	525	28,329	**112.9**	**13.2**	**70,823**		**54**	
Riverine soils	Al	81,300		9981		−3.6				
	P	700		219		−2.3				
	Ti	2300		116		−4.9				
	Cr	25		9		−2.1	1			
	Mn	600		826		−0.1	1			
	Co	5		6		−0.3	6			
	Ni	8		6		−1.1	3			
	Cu	30	49	59	**3.8**	0.4	10	**10,507**	**1.2**	**1.6**
	Zn	60	56	30	1.7	−1.6	0		0.5	
	As	1.5	16	19	**3.7**	**3**	123		**1.2**	
	Ag	0.15	0.3	0.7	**7.6**	1.7	0		**2.4**	
	Cd	0.1	0.3	0.1	1.1	−0.5	32		0.4	
	Ba	830	750	2588	**11**	1.1	0		**3.5**	
	Pb	2	525	4132	**25.1**	**10.4**	**10,330**		**7.9**	

Table 3. *Cont.*

	Element	Background (mg·kg^{-1})		Average Value (mg·kg^{-1})	Factors					
		Acid Rocks [34]	Triassic Local Background [42]		EF	Igeo	E_r^i	RI	CF	PLI
Floodplain (lower course)	Al	81,300		15,775		−3				
	P	700		231		−2.2				
	Ti	2300		110		−5				
	Cr	25		15		−1.3	1			
	Mn	600		887		0	1			
	Co	5		6		−0.2	6			
	Ni	8		10		−0.3	6			
	Cu	30	49	56	**3.5**	0.3	9	**16,399**	**1.1**	**1.7**
	Zn	60	56	35	1.9	−1.4	1		0.6	
	As	1.5	16	25	**4.6**	**3.4**	163		**1.5**	
	Ag	0.15	0.3	1	**10.1**	2.2	0		**3.3**	
	Cd	0.1	0.3	0.1	1.4	−0.2	40		0.4	
	Ba	830	750	2373	**9.6**	0.9	0		**3.2**	
	Pb	2	525	6468	**37.3**	**11.1**	**16,171**		**12.3**	

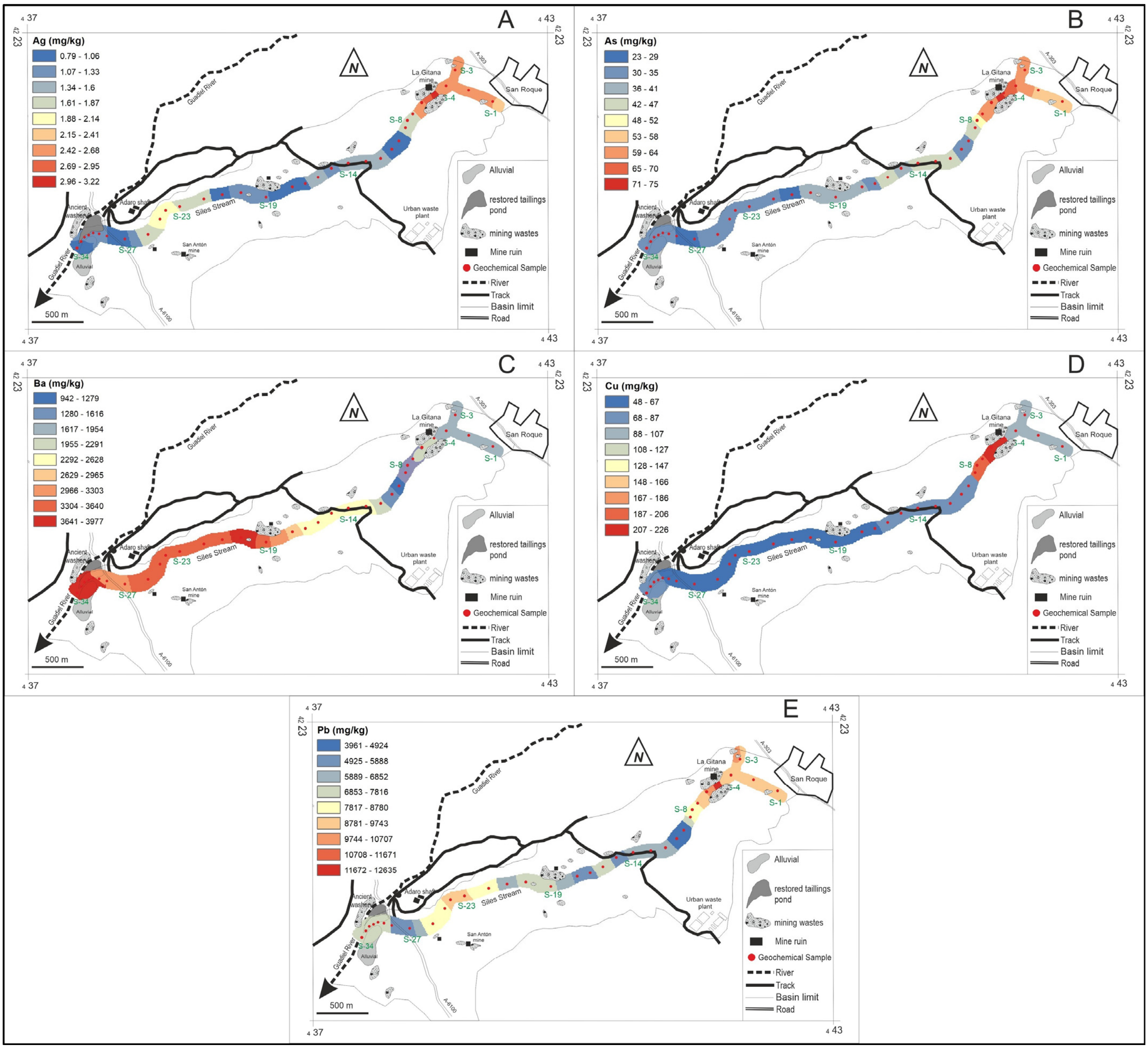

Figure 5. Spatial variation in the concentrations of Ag (**A**), As (**B**), Ba (**C**), Cu (**D**), and Pb (**E**) in the sediments of the Siles Stream.

In the case of the enrichment factor (EF), the value of the local geochemical background for Triassic materials was used as a reference value [42] since it is a very geochemically enriched area. There is a severe to very severe anthropogenic influence for Ag, As, Ba, and Pb in the three deposit environments studied; however, the EF for Pb is especially alarming, with very high figures. The maximum value for Pb corresponds to an EF of 112.9 in the middle section of the floodplain. It is also striking that even the lowest EF, estimated for the riverine soils of the final section, is 25. Cu is added to these elements, with EF values that indicate a severe alteration in the middle section of the floodplain, which downgrades to moderate in the final section of the creek.

Regarding the geoaccumulation index (l_{geo}), a soil is considered extremely contaminated when it presents values higher than 4 relative to Clarke's value for acid rocks. The highest values appear again on the floodplain sediments, with 4.6 for As, 4.4 for Ag, and 13.2 for Pb. In the stream bed sediments, the I_{geo} for Ag is less than 4 (heavily contaminated); however, the sediments are also considered extremely contaminated by both As and Pb, with values of 4.1 and 11.3, respectively. In other streams of the Linares–La Carolina mining district [14], the sediment samples were moderately to highly contaminated over extensive areas of the basin studied, with the greatest intensity and extent in the floodplain sediments. In the final section of the stream, both in the floodplain sediments and in the riverine soils for agricultural use, only Pb contamination is observed, with an I_{geo} of 11.1 and 10.4, respectively. The same degree of contamination in river bed sediments, ranging from heavily to extremely contaminated for As and Pb, were obtained for I_{geo} values in similar abandoned Spanish mine sites [12].

Regarding the potential ecological risk (E_r^i), values between 160 and 320 indicate a high risk, which becomes very high when the value exceeds 320. This index again reaches a maximum value of 70,823 for Pb in the deposits of the intermediate floodplain section, together with an E_r^i of 366 for As. These high concentrations in the floodplain sediments can indicate that there was important mobilization of Pb and As during overflow episodes.

In the rest of the sediments, only Pb maintains very high-risk values, with a minimum of 16,171 in the lower course floodplain profile. These figures are much higher than those calculated in stream sediments from other Pb polymetallic mining areas, e.g., the Baosan drainage basin in southwest China [1].

The ecological risk index (RI) was calculated for all the metal(loid)s that were studied. Values above 600 are considered very high, a figure that is exceeded in all sectors of the stream. The distribution of values reflects the results obtained for the other indices, with a maximum RI of 71,314 in the profile of the floodplain in the middle course of the stream. The lowest value appears again in the riverine soils at the mouth of the stream, with an RI of 10,507.

Regarding the contamination factor (CF), values higher than 6 are considered very high, such as those obtained for Ag and Pb, with values of 15.6 and 54, respectively, in the profile of the middle section of the floodplain. In addition, a considerable degree ($3 \leq CF < 6$) of contamination for Cu and As is registered in this group of sediments.

CFs obtained in the sediments of the stream bed and the lower section of the floodplain are quite similar, with moderate contamination ($1 \leq CF < 3$) for Cu and As, considerable for Ag and Ba, and very high for Pb (13 on average).

The riverine soils show the lowest values of CF; however, they also present a moderate degree of contamination for Ag and Ba, and CFs are still very high for Pb (7.9). In comparison with other mining regions, these values of CF in agricultural soils are higher than those reported in different soils collected in the Sinú River (Colombia), along the Jishui River (China), and in agricultural soils in northern Bangladesh [7].

In Figure 5, the spatial distributions of Ag, As, Ba, Cu, and Pb (the five elements for which significant values of the contamination indices were obtained) in the channel of the Siles Stream is represented. In general, the contents decrease from the head to the end of the stream; however, for Ba, they increase from the middle section to the end given the influence of the San Antón mine. Ag and Pb also show relative maximums towards the final section of the stream—increases that are explained by the mining activity of the former San Antón and El Tesoro concessions.

In other streams of the Linares–La Carolina mining district [13], Cu, Pb, and Ag exhibit a low mobility, and their concentrations quickly decrease by some hundred meters from the pollution source. The presence of additional waste rock heaps and tailings some kilometers downstream lead to increases of these PTEs. A similar pattern is shown in the bed sediments of the Siles Stream, where downstream relative maximum concentrations are related to San Antón mine and waste rock piles. The mining sites and numerous waste dams located along the stream seem to be the main source of these elements transported throughout the channel bed. Despite the elevated contents of Pb, Ag, and As, significant attenuation can be observed as the distance from the main sources of pollution increases. Mechanical transport of particles from the main contamination sources to the watershed seems to be controlling the distribution of PTEs total contents in the stream bed.

Finally, the pollution load index (PLI), which indicates a deterioration in environmental quality due to metal(loid) contamination when its value is higher than 1, was calculated. This reference value was exceeded in all the sediment groups analyzed, and the variation in the PLI in the stream bed sediments is shown in Figure 6.

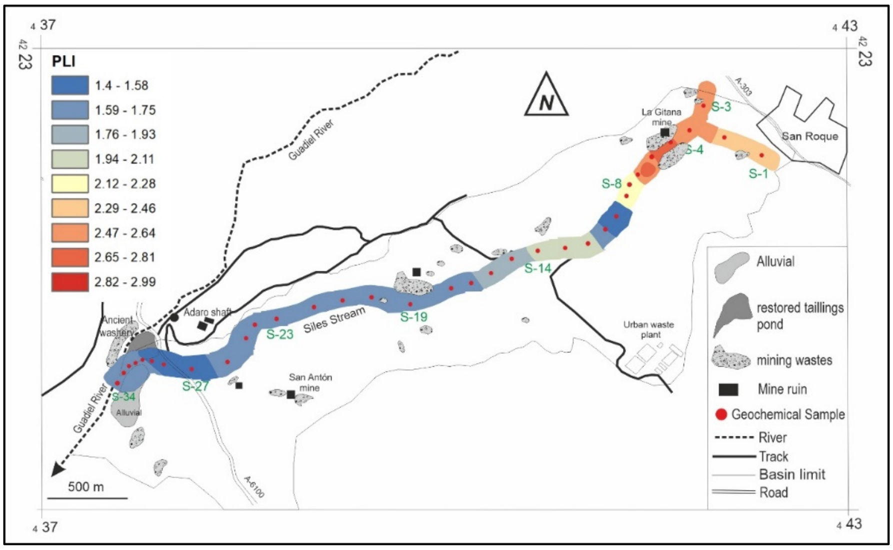

Figure 6. Distribution of the pollution load index (PLI) values along the Siles Stream.

Of the depositional environments studied, the maximum PLI value occurred in the floodplain sediments in the middle course of the stream. The results obtained for the PLI suggest the need to carry out intervention measures.

4.3. Geochemical Speciation

Figure 7 shows the distribution of Ag, As, Pb, Cu, and Ba in the mobile, exchangeable, reducible, and oxidizable fractions of the alluvial deposits from the Siles Stream.

Ba has a clear affinity for clays and carbonates, with a lower presence in the reducible and oxidizable fractions. Its distribution is very similar in all the samples analyzed, both in the stream and in the Guadiel River. The percentages of the bioavailable fraction with respect to the total content are 10%–15% in the sediments of the stream bed and in the lower levels of the floodplain, but they increase considerably in the riverine soils and in the Guadiel River (between 25 and 40% of the total).

In the case of Cu, the oxidizable fraction is the best represented in the samples from the head of the stream and from the most superficial zone of the floodplain. If considered together with the exchangeable fraction, they can reach approximately 60% of the total metal available in this type of sediment. In the riverine soils and the channel of the Guadiel

River, the Cu contents are much lower, and the best represented fraction corresponds to the exchangeable metal.

Figure 7. Distribution of Ag, As, Pb, Cu, and Ba in the mobile, exchangeable, reducible, and oxidizable fractions of alluvial deposits of the Siles Stream and the Guadiel River.

The results obtained for Pb are quite different. In the sediments of the stream bed, Pb appears to be mainly associated with exchangeable and oxidizable fractions, which together account for 80% of the total metal. The reducible fraction is also significant, accounting for 10%–20% of the total, which makes it possible to deduce very low values of the residual fraction. In the floodplain profile, an area in which the fasciculate roots of the olive tree develop, more than 5000 mg·kg^{-1} Pb was obtained for the exchangeable fraction (30%–40% of the total) up to a depth of 2 m. The distribution observed in riverine soils is similar; however, exchangeable and reducible fractions predominate. It is also these two fractions that experience a greatest increase in the Guadiel River downstream of the confluence of the stream. The relatively high percentages of Pb in the reducible fraction may be due to its tendency to be adsorbed on clay minerals and to coprecipitate with oxides.

5. Conclusions

PTEs in the stream bed sediments had extremely high contents of Pb (between 2000 mg·kg^{-1} and 16,000 mg·kg^{-1}), Cu (between 30 mg·kg^{-1} and 750 mg·kg^{-1}), and As (from 9 mg·kg^{-1}

to 111 mg·kg^{-1}), with values that vastly exceed the reference levels of current regulations (established at 275 mg·kg^{-1} for Pb, 595 mg·kg^{-1} for Cu, and 36 mg·kg^{-1} for As).

Especially noteworthy are the concentrations of Pb and As that appear in the profile sampled in the floodplain sediments (middle course), with mean values of 25,967 mg·kg^{-1} for Pb and 47 mg·kg^{-1} for As. It is in the bottom of this profile where the maximum Pb concentration (43,693 mg·kg^{-1}) of the entire study area was obtained. Additionally, the sediment samples taken in another profile of the floodplain (lower course) have high contents of Pb (5735 mg·kg^{-1} on average) and As (20 mg·kg^{-1} on average); however, they are somewhat more moderate than those in the previous sections.

The riverine soils developed around the mouth of the stream present more moderate contents of As (10 mg·kg^{-1} on average) and Pb (3782 mg·kg^{-1} on average); however, for the latter, the figure remains alarming.

The environmental indices indicate that the sediments of the Siles Stream basin are highly affected by Ag, As, Ba, Cu, and Pb. Specifically, the EF values reached for Pb and Ag correspond to a very severe anthropogenic influence in all the sediment groups analyzed. The geoaccumulation index (I_{geo}) presents values that classify the basin as extremely polluted with As and Pb. The same occurs with the potential ecological risk (E_r^i), which presents a high value for As in the upper and middle parts of the stream but stands out especially for Pb, with E_r^i being enormously high in the floodplain sediments (middle course). This leads to the ecological RI being considered very high for all the PTEs being studied. Finally, according to the PLI, there is deterioration of the environmental quality, which is more accentuated from the head to the middle section of the stream.

The selective extraction made it possible to differentiate the mobile, exchangeable, oxidizable, and reducible fractions. The percentage values obtained for the bioavailable fractions can be considered comparative indices of the mobility of each element and an indicator of the recent history of soil contamination. Thus, the results for Pb stand out: in addition to being the most abundant potentially toxic element, Pb is the element with the greatest mobility.

The results obtained show that this basin has been highly affected by many years of mining activity in which the waste generated was not properly managed. The problem persists after more than three decades since the closure of mining operations and has led to a very significant increase in the contents of As, Ag, and Pb in the sediments and soils of the environment, which represents a significant ecological risk given the agricultural and ranching use.

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