geosciences

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Metal(loid)s Transport in Hydrographic Networks of Mining Basins: The Case of the La Carolina Mining District (Southeast Spain)

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Received: 2 September 2020; Accepted: 21 September 2020; Published: 28 September 2020

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Abstract: This study analyses the distribution of the total metal(loid)s content accumulated in the sediments of the Grande River, the most important river course that runs through the old mining district of La Carolina (Jaén, Spain), whose waters are collected in an urban supply reservoir. In total, 102 sediments samples were taken along the river, 51 in the live-bed channel and another 51 in the floodplain. The samples analysed have high metal(loid)s content, sometimes much higher than the reference levels established by European and regional legislation for soils, especially Pb, As and Ba, with average values of 5452 mg/kg, 116 mg/kg and 2622 mg/kg, respectively. The statistical analysis of the values obtained allows the distribution of the contents of the different elements along the river to be characterized and the associations and dispersion patterns in the sediments of the metal(loid)s coming from the environmental liabilities of the numerous dumpsites and tailings dams generated by mining activity to be defined. In both cases, the high metal(loid)s content identified as well as the resulting values of various environmental indices (the enrichment factor, contamination factor, geoaccumulation index, potential ecological risk index and pollution load index), confirmed that 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.

Keywords: contaminated soils; sediments; live-bed; floodplain; statistical techniques; kriging

1. Introduction

At the end of the last century, the mineral reserves of many deposits were depleted, causing a metal price crisis that led to the closure of many mining operations worldwide. These circumstances occurred in a context where the environmental protection laws of many countries were poorly developed or non-existent, so the necessary remediation measures were not adopted to mitigate environmental damage after abandonment.

Metallic mineral mining and its associated pyrometallurgical practices are one of the main causes of heavy metal contamination of soil and water resources worldwide [1,2], affecting up to several kilometres from the pollution source [3]. The main transport agent is water, both by infiltration and erosion in tailings deposits and by drainage of mining holes [4]. This has been demonstrated by the Environment Agency of England and Wales in the rivers that flow through old mining districts in the United Kingdom, where after more than 4000 years, the rivers have been contaminated by lead, zinc and copper and many other metals and metalloids, including iron, tin, arsenic and silver, from dumpsites and tailings dams that have contributed solid contaminants to live-bed channels and floodplains of the rivers for decades after their closure [2,4–6]. This has been equally evident in other mining districts of the world [7–12].

The effect is manifested with greater intensity in the fine fraction of the sediment, composed of clay and silt with particle sizes below 63 μm [13], generally by the metalloids associated with the minerals that had been mined. To determine this impact, the measured contents are compared with the geochemical background values and with the maximum allowable levels established for the regulations of the region and/or country using statistical methods and contamination indices [8–11].

In recent decades, scientists, ecologists, politicians and society in general have demonstrated greater awareness regarding the existing problems related to the extensive contamination of soils and the corresponding environmental consequences [14]. Therefore, the different environmental agencies have taken an interest in evaluating, informing and acting on these affected areas through the development of laws and projects with the aim of protecting both the environment and the health of living beings [4,5,15]. The concern is greater when the land is used for agriculture because of the risk of the transfer of metal contamination to humans through food consumption, affecting their health, especially that of the young [7,16,17].

The study area is located in the old metallogenic district of Linares-La Carolina (Southern Spain), which is characterized by the presence of vein deposits of lead and copper sulphides. This district, abandoned today, was the object of intense exploitation through underground mining from pre-Roman times, and was one of the most important lead producers the world in for a long time [18,19]. As a result of this intense activity, very large volumes of waste were generated from the extraction, concentration and smelting activities, sometimes with high ore grades due to the technical limitations of these processes [20]. Given the orography of the region, these wastes accumulate on the margins of the river channels that run through the sector, whose waters flow into the Rumblar reservoir, destined for human consumption (Figure 1).

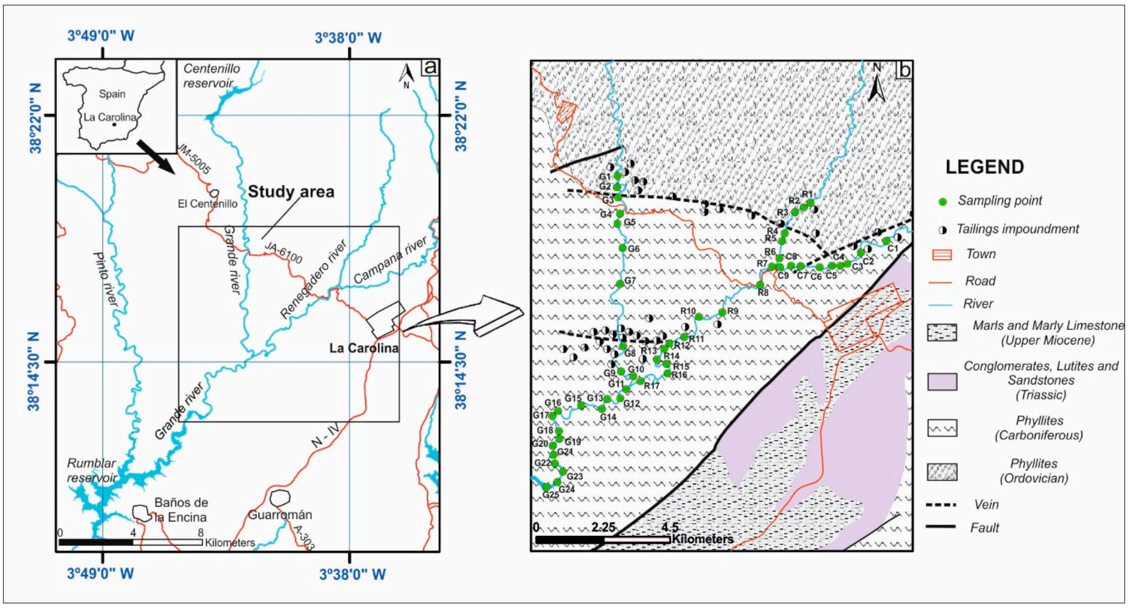

Figure 1. (**a**) General situation of the study area. (**b**) Spatial distribution of the sampling points and location of tailings impoundments.

This study is based on sampling performed in the sediments of the main river of the fluvial network of the mining district of La Carolina, specifically in the Grande River (Figure 1a,b). For this, a geochemical study was conducted in two sedimentary environments, a live-bed channel and a floodplain [21,22]. Through statistical techniques and environmental factors the distribution of the metal(loid)s contents was qualitatively and quantitatively evaluated from the different pollution sources derived from the mining activities. In addition, the distribution of Pb, As and pollution load index (PLI) has been modeled along the course of the affected rivers in this mining basin using the geostatistical kriging tool, giving information on the areas of greatest impact on their sediments. To determine the degree of contamination of this mining district, the generic reference levels established by the regional and Dutch regulations for each trace element according to soil use were compared. Finally, groups and associations of elements were defined according to their natural or anthropogenic origin, estimating the extent of the condition [15,23–25].

2. Materials and Methods

2.1. Study Area

The study area is located on the southeast slope of Sierra Morena within the Hesperic massif (southeastern Spain) in the old mining district of La Carolina. The area corresponds to the hydrographic basin of the Grande River and its two main tributaries, Campana and Renegadero (Figure 1a,b), which, with an approximate area of 100 km^2, collect the waters of the mining district until discharging them to the Rumblar supply and irrigation reservoir.

The climate of the region is continental Mediterranean, with cold winters and warm summers, so the flows that run throughout the year are very reduced and even disappear during the summer. The average annual precipitation is 613 mm, and the average annual temperature is 15.8 °C [26].

The water in the Grande River carries high concentrations of metal(loid)s, especially in low water periods and during the first autumn rainfall, so that it exceeds the maximum concentration limits for Cd, Pb and Zn established by environmental quality regulations for surface waters. When considering La Campana River, As is also added to these three elements. On average, discharges from mine adits located in the headwater catchment area account for the entry into surface waters of more than 20 tons of Fe, several tons of Mn, and hundreds of kilograms of As per year, which are transported downstream to the Rumblar reservoir [27]. During the wet season, especially during periods of flooding, there is a dilution of mining spills, so the stream water entering the reservoir presents good chemical quality and low mineralization. Despite this seasonal dilution effect, contents in As, Cu and Pb have been detected in the waters at the tail-end of the reservoir that exceed the maximum admissible limits for human consumption.

Geologically, two large groups stand out at the regional level: a Paleozoic basement and a posthercynian sedimentary cover (Figure 1b). The Paleozoic basement is made up of metamorphic rocks, basically phyllites with quartzite intercalations, that were intensely folded during the Hercynian orogeny and subsequently affected by a granitic intrusion. The intense folding and fracturing tectonics that affected the Paleozoic set resulted in a wide network of fractures, many of which were later mineralized by a hydrothermal fluid enriched in metallic sulphides, consisting mainly of galena, sphalerite, chalcopyrite and pyrite, with quartz, ankerite and calcite as accompanying minerals. The orientation of these veins, which have a subvertical disposition, is N 70°–110° E y N 30° E, highlighting those of “Los Guindos”, “Ojo Vecino” and “El Sinapismo”, among others [28]. Discordantly on the Palaeozoic basement and fossilizing these mineralizations, the posthercynian cover appears, which is subhorizontally arranged. The cover is made up of Triassic materials (red shales and conglomerates), Miocene (marls with levels of sandstones, silts and/or breccia at the base) and quaternaries (silts, sands and gravels associated with the filling of the channels) [18,19,29].

In this mining district, extraction was achieved by underground mining using the method of shrinkage stoping, for which it was necessary to excavate wells and galleries that generated a large amount of waste that accumulated in the vicinity. Everything obtained was treated through numerous concentration operations with the aim of obtaining a high-grade ore. The concentration processes were carried out by gravimetric techniques and by flotation, wet processing in both cases, generating a brine of treatment water that was poured directly into the channels and solid waste that was accumulated in dumps and in fine tailings ponds (Figure 1b), where the waters separated after the decantation of the solids were also drained into the nearby channels. Finally, the sulphide concentrates obtained were smelted in the metallurgical plants that were installed in the region to obtain metals of industrial interest, generating gaseous, liquid and slag waste [18,20,28].

In this district, up to 32 tailings ponds and dams have been counted (Figures 1b and 2c) with significantly high total metal(loid)s content, especially, Pb, Zn and As [30], with the common assumption that all these wastes were deposited without any prior adaptation of the site for environmental mitigation [10,31]. In addition, the orography of this district, of valleys and hills sometimes with steep slopes and a well-developed hydrographic network, facilitates the mobilization of mining waste with high contents of metals and metalloids towards the drainage network [32].

Figure 2. (**a**) Sediment sampling with Edelman auger in the floodplain of the Grande River, at the tail-end of the reservoir. (**b**) Four sub-samples arranged in a cross with a spacing of 1 m were collected at each sampling point. (**c**) Mining wastes deposited near the banks of the Renegadero River.

2.2. Sampling and Analysis

For the study, 51 sampling points were selected along the river (Figure 1a,b) as follows: in the main channel of the Grande River (samples G1 to G25), in its tributary the Renegadero River (samples R1 to R17) and in the Campana River, a tributary of the Renegadero River (samples C1 to C9). The sampling was designed after the geological and mining cartographies of the area and previous field work were reviewed. The selection of the sampling sites ensured they were consistently spaced along the channel and that they sampled sedimentation zones, natural traps, meanders, bars, etc., downstream of the old mining operations, dumpsites and tailings ponds.

At all the selected points, two samples were taken, one in the channel bed and the other in the floodplain, to compare the distributions of the contents in both sedimentary environments [10,33].

Each sample consisted of four subsamples collected in the shape of a Greek cross with a spacing of 1 m (Figure 2a,b), taking the first 20 cm of the soil with an open-face "Edelman" auger (Figure 2a), which was subsequently placed in plastic bags in which they were mixed and stored, with an average weight of 1.5–2 kg.

Once in the laboratory, the samples were physically prepared for analysis, which consisted of drying and homogenization, quartering, sieving and grinding. The samples were sieved (PVC sieve and bottom) to separate the <2 mm fraction, classifying the fine fractions by sedimentation according to the UNE 103101:1995 standard.

For the determination of the total metal(loid)s content, the <2 mm fraction was ground in an agate ball mill until a size of less than 50 microns was obtained (Retsch PM 100). Chemical attack was performed on 1 g of the milled sample by total microwave digestion [34], using HNO_3 as reactants with the addition of H_2O_2, which facilitates the complete oxidation of organic matter [35]. The analysis of the solutions obtained was performed by ICP-MS (inductively coupled plasma mass spectrometry) in the laboratories of the Center for Scientific and Technical Instrumentation of the University of Jaén in a mass spectrometer with a plasma torch ionization source and an AGILENT model 7900 quadrupole ion filter. The samples with a Pb concentration exceeding the limit allowed by the analytical method (10,000 mg/kg) were analysed with portable X-ray fluorescence equipment (Niton XLT 792) according method 6200 (US EPA 1998). Three measurements were performed on the sample for 60 s, and the mean value was calculated [36,37].

2.3. Evaluation of the Heavy Metal Content in Sediments

To identify metalloid enrichment in the analysed sediments, values of the naturally occurring geochemical background are required to serve as a reference level. In this study, Clarke values and acid igneous rocks were used [38–40] for the calculation of different environmental factors and indices.

The enrichment factor (EF) assesses the impact of anthropogenic sources of heavy metals in the sediment using the following equation [41]:

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

where $(C_M/C_P)_{sample}$ is the ratio of the heavy metal concentration (C_M) to the phosphorus concentration (C_P) in the sediment sample and $(C_M/C_P)_{background}$ refers to the background values for each metal in Clarke values and acid igneous rocks. A value of EF close to 1 suggests natural weathering processes, EF > 1.5 indicates human influence and EFs of 1.5–3, 3–5, 5–10 and >10 are considered evidence of minor, moderate, moderately severe, and severe enrichment, respectively [42–44].

The geoaccumulation index (I_{geo}) defines the level of contamination in the sediment by the following relationship [45]:

$$I_{geo} = \mathrm{Log}_2\left[\frac{C_n}{1.5\ B_n}\right] \tag{2}$$

where C_n is the average concentration of the metal in the sediment and B_n represents the average values for trace elements of acid igneous rocks [40]. A factor of 1.5 is introduced to minimize the possible variations in the background data that may be due to lithological variations. Seven levels of I_{geo} are established: uncontaminated (<0), uncontaminated to moderately contaminated (0–1), moderately contaminated (1–2), moderately to strongly contaminated (2–3), strongly contaminated (>3), strongly to extremely strongly contaminated (3–4) and extremely contaminated (>4) [46].

Another index analysed in this work is the ecological risk potential ($E_r{}^i$ and RI), which estimates the potential ecological risk of each metal ($E_r{}^i$) and potential ecological risk index (RI) for the set of metals/metalloids in the sediment [47]:

$$E_{r^i} = T_{r^i} \times \frac{C^i}{C_{n^i}} \quad (3)$$

$$RI = \sum_{i=1}^{n} E_{r^i} \quad (4)$$

where $T_r{}^i$ is the toxic factor of a metal/metalloid for As, Cd, Co, Cr, Cu, Mn, Ni, Pb, V and Zn with a value of 10, 30, 5, 2, 5, 1, 5, 5, 2 and 1, respectively [11,47]. C^i is the average concentration of metal i in the sediment samples, and $C_n{}^i$ is the background value of heavy metal i in acid igneous rocks [40].

The values of $E_r{}^i$ are grouped into the following classes: 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 defined as the sum of $E_r{}^i$ and is classified as very high ecological risk (RI > 600), considerable ecological risk (300 ≤ RI ≤ 600), moderate ecological risk (150 ≤ RI < 300) and low ecological risk (RI < 150) [11].

Finally, the pollution load index (PLI) and contamination factor (CF) were considered, where the PLI is defined as the root of the multiplication of the metalloid CF [48]:

$$CF_{metals} = \frac{C_{metal}}{C_{background}} \quad (5)$$

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{1/n} \quad (6)$$

where CF is the relationship between the average concentration (C_{metal}) and the background values ford each metal ($C_{background}$). Four classes define the contamination of a metal: low (CF < 1), moderate (1 ≤ CF < 3), considerable grade (3 ≤ CF < 6) and very high (CF ≥ 6) [49,50]. A PLI value of zero indicates no background concentration, a value of one indicates the presence of only a baseline level of contaminants, and values greater than one indicate a progressive deterioration of the quality of the site [48].

2.4. Statistical Analysis

Univariate and multivariate statistical techniques were used to determine the interrelation and variability of each metal(loid)s to determine the presence of anomalies. The data processing was performed using SPSS 22 software developed by IBM.

The mean, median, range, standard deviation, variance, skewness and kurtosis were calculated, generating the histograms, normality plots and box and whisker plots [51,52].

In multivariate statistics, a principal component analysis is performed with the objective of transforming a set of original variables into a new set of variables, called factors, which are characterized by being correlated with each other. The first factor or component explains the largest variance in the data set, the second factor or component explains the second largest variance in the data set, and so on for the rest of the factors [53]. For its interpretation, the rotation of the components (axes) is used. Varimax rotation is the most commonly used approach in geochemistry, which is adequate when the number of components is small. This technique has been used in different environmental scenarios [21,54–56].

Geostatistical analysis through an ordinary kriging of a spherical semivariogram model was used to predict the contents of Pb and As and the PLI along the entire course of the sampled rivers, since this technique provides the best spatial prediction for unsampled locations [57]. The information was processed to develop distribution maps using arcGIS 10.6 software developed by ESRI.

3. Results and Discussion

The different regulatory standards concerning contaminated soils establish generic reference levels (GRL) that indicate possible impacts on humans and/or ecosystems if they are exceeded. The concentrations of 17 metal(loid)s (Ag, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Sr, V and Zn) in the 102 samples collected in the live-bed channel and in the floodplain (Table 1) were analysed. In Table 1, the values that exceed the limit set by the Andalusian regional standard and the Dutch standard are highlighted in bold. Note that in the case of Pb, only sample R1, taken in the live-bed channel, and samples R1 and R2, taken in the floodplain, have contents that are below the norm values.

Table 2 shows the main statistical parameters for the metal(loid)s studied in the samples taken in the floodplain as well as the GRL established by the regional government [15] and Dutch regulations [25]. In bold the values that exceed these reference limits are highlighted. The average values obtained for the concentrations of Pb and As stand out clearly exceeding the GRL of Andalusia and the Dutch standards and Ba exceeds the intervention value established in the most restrictive Dutch standard.

Figure 3 shows the variation in the Pb and As contents in the hydrographic basin studied both in the live-bed channel and in the floodplain and compares them with the limits established by the Andalusian and Dutch regulations. In the three rivers Grande Renegadero and Campana practically all the samples collected present Pb and As values above the GRL in the two sedimentary environments although the maximum concentrations of Pb and As are recorded in the vicinity of the old abandoned mining operations and extend downstream in both cases with greater intensity in the floodplain. The Pb concentration peaks greatly vary in both sedimentary environments which indicates its low mobility being more homogeneously distributed in the live-bed channel with an increase towards the tail of the Rumblar reservoir (samples G23 to G25). As presents a lower spatial variability than Pb with a similar response in both sedimentary environments although at a lower intensity in the live-bed channel. Only 14 samples are below the intervention levels for As: the first four samples in the headwaters of the Renegadero River (R1, R2, R3, R4 and R5) in both sedimentary environments and sample R6 in the live-bed channel located upstream of the mining works sample C4 in the floodplain of the Campana River and samples G22 and G24 in the live-bed channel all located far from mining liabilities (Figures 1 and 3). In the case of Ba the intervention value is exceeded in most of the samples analysed especially in the floodplain.

Table 2 shows the maximum and minimum values mean median standard deviation variance kurtosis and asymmetry of the metal(loid)s studied. The concentrations of Pb As and Ba (elements related to the mineral paragenesis of the ore of interest) present different mean and median values. In addition the standard deviations and variances are high together with kurtosis and positive asymmetry due to the presence of extreme values which indicates a high degree of heterogeneity and dispersion along the channel.

Table 1. Total concentrations (mg/kg) of selected elements in the sediment samples. Concentrations above the reference values are in bold.

Samples	Ag	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sr	V	Zn
Floodplain																	
G1	4.8	**136**	502	1453	1.9	18	12	101	24,453	1461	1990	24	488	**4035**	18	11	293
G2	6.4	**84**	**987**	1053	4.1	16	15	60	25,156	1283	2313	22	417	**5294**	25	17	481
G3	7.3	**179**	**1248**	762	1.6	15	11	340	26,640	1049	1062	18	482	**6312**	35	10	240
G4	8.1	**178**	**2148**	1685	5.0	**31**	16	432	31,229	1620	4492	46	568	**7680**	29	19	546
G5	7.2	**157**	**1081**	890	2.6	20	11	307	25,222	1061	1573	23	474	**6558**	50	10	329
G6	3.4	**85**	602	613	1.4	14	12	147	26,791	1477	933	24	461	**3152**	60	12	276
G7	4.4	**98**	**1242**	835	1.7	16	12	166	25,384	1392	1075	22	473	**4828**	55	12	263
G8	4.5	**129**	**800**	1510	4.7	15	15	68	26,592	2494	1093	32	536	**4365**	18	18	491
G9	9.2	**143**	**6139**	3225	5.1	13	13	99	24,682	2625	1038	27	558	**13,585**	67	16	504
G10	3.3	**132**	**942**	1096	3.0	12	11	72	23,880	2122	831	26	498	**4674**	18	12	501
G11	3.2	**103**	**1036**	2484	3.4	14	**22**	54	32,980	3248	894	31	643	**3642**	26	23	**857**
G12	2.6	**84**	577	1851	3.9	12	16	42	24,977	2879	760	26	565	**3894**	13	17	619
G13	3.1	**126**	**1345**	2690	3.4	15	19	63	31,604	3201	1028	30	644	**4226**	29	19	**836**
G14	3.5	**153**	**1680**	3093	3.8	15	15	71	31,494	3027	1091	29	621	**4646**	32	16	**838**
G15	3.5	**138**	**1209**	2893	3.8	15	19	68	32,674	3233	1103	32	664	**4674**	28	20	**821**
G16	2.9	**94**	**670**	1711	3.8	11	14	53	30,990	2864	880	26	588	**4531**	14	16	607
G17	3.8	**155**	**1471**	2921	4.1	15	15	86	32,516	3056	1129	28	643	**5254**	30	14	**865**
G18	2.4	**124**	**916**	2010	2.9	14	17	61	32,329	3186	876	31	614	**3989**	22	18	688
G19	1.9	**110**	469	1383	2.7	15	**20**	56	34,025	3100	749	34	624	**3226**	18	24	597
G20	3.1	**157**	**1455**	2240	3.4	14	14	71	31,616	2918	991	27	610	**4588**	29	14	**767**
G21	2.8	**137**	**1317**	2251	3.4	14	15	69	32,406	2928	1018	29	631	**4078**	27	16	**779**
G22	6.8	**122**	**2205**	2214	4.7	10	12	51	18,736	2076	714	18	357	**8084**	27	13	495
G23	4.0	**116**	**1262**	1890	4.1	11	14	47	21,335	2291	711	21	424	**5547**	21	16	538
G24	8.4	**160**	**3321**	3193	6.3	12	15	54	25,211	2704	890	23	550	**9328**	38	15	685
G25	9.4	**143**	**2773**	3498	6.2	14	16	60	25,720	2974	1027	25	590	**10,270**	32	15	668
R1	0.1	10	**626**	918	0.2	12	**21**	16	27,860	2751	444	25	408	**367**	21	18	72
R2	0.1	9	**649**	545	0.1	10	**20**	14	28,946	2744	326	22	400	**358**	16	17	72
R3	5.9	16	**8027**	2077	5.2	11	16	311	30,981	2437	630	21	493	**7674**	48	13	475
R4	1.0	18	**1513**	935	2.1	11	19	21	29,921	2778	668	26	431	**1759**	27	17	583
R5	1.5	19	**4697**	970	3.0	10	**21**	34	33,116	3025	580	25	448	**2134**	62	18	551
R6	3.6	**105**	**3965**	2481	2.9	11	19	55	28,601	2705	582	22	611	**4027**	54	18	642
R7	4.8	**140**	**2193**	1271	1.9	16	17	78	28,330	2011	795	27	488	**7697**	27	17	445
R8	11.8	**192**	**5537**	3768	11.1	20	18	112	37,114	2583	1155	29	719	**11,258**	87	18	**1694**
R9	6.2	**145**	**3950**	5417	5.9	18	**22**	76	32,889	3595	1108	32	797	**5777**	60	22	**987**

Table 1. *Cont.*

Samples	Ag	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sr	V	Zn
								Floodplain									
R10	3.8	**160**	**4383**	3745	3.1	15	**33**	76	30,665	3853	843	31	680	**4374**	68	38	592
R11	7.3	**125**	**4958**	3954	7.0	15	17	68	34,018	3489	1192	28	663	**7584**	48	18	**924**
R12	4.9	**124**	**5105**	4036	4.9	16	**22**	102	39,019	3744	1033	34	738	**5471**	74	25	**1029**
R13	5.8	**137**	**5425**	4475	5.2	16	20	222	38,069	3653	1077	33	694	**6302**	77	23	**1010**
R14	10.0	**137**	**3865**	3723	8.2	16	19	75	33,385	3398	1240	29	750	**11871**	47	20	**985**
R15	5.0	**116**	**1717**	3364	4.3	18	19	71	35,769	3586	981	33	657	**5777**	30	23	**911**
R16	5.9	**156**	**3173**	5432	5.3	18	20	76	35,435	3918	1264	33	674	**6788**	48	23	**1003**
R17	2.9	**114**	349	1522	3.0	13	**24**	60	28,607	2935	711	36	814	**3222**	20	32	554
C1	2.8	**186**	**1240**	3215	4.3	12	15	41	22,977	2693	785	20	532	**3254**	24	18	687
C2	3.1	**105**	**2907**	4713	3.7	12	**31**	44	23,681	2985	643	32	738	**3873**	51	21	582
C3	4.5	**109**	**4189**	3011	3.6	11	20	48	19,725	2395	689	18	465	**4826**	56	13	583
C4	9.5	**45**	**11762**	2395	12.5	15	19	59	39,207	3195	1167	26	482	**15,533**	172	18	**1794**
C5	3.9	**120**	**2610**	3678	3.7	12	**25**	58	24,780	3029	627	27	689	**4566**	41	17	693
C6	3.4	**93**	**3762**	2015	2.7	10	**20**	35	20,338	2434	590	19	482	**3295**	53	17	422
C7	2.8	**91**	**2702**	2972	3.3	10	**24**	46	21,273	2693	481	22	757	**2925**	43	18	596
C8	2.9	**95**	**2891**	3022	3.2	10	**24**	46	20,201	2503	517	21	710	**3066**	47	17	558
C9	4.2	**100**	**4141**	2974	3.9	10	**26**	43	21,364	2526	544	24	708	**3838**	60	19	588
								Live-bed									
G1	3.2	**113**	432	910	1.2	14	14	109	19,747	1412	1205	20	396	**2644**	13	15	212
G2	3.8	**100**	474	601	2.1	12	12	46	21,064	1089	1303	18	358	**3598**	13	15	342
G3	3.7	**180**	**908**	549	1.2	12	11	329	22,189	1114	962	20	378	**3007**	16	12	270
G4	8.8	**180**	**1149**	3132	5.8	**32**	17	361	28,782	1988	4660	47	585	**7391**	27	19	593
G5	4.1	**197**	575	504	1.2	13	12	223	26,245	1198	736	22	462	**3599**	14	13	309
G6	4.4	**126**	**2244**	1022	1.8	19	17	244	31,657	1855	1542	36	518	**3579**	34	18	329
G7	3.4	**132**	**1138**	848	2.5	17	16	200	27,020	1672	1501	33	451	**4589**	23	18	343
G8	3.4	**110**	**719**	1009	2.7	11	18	53	26,541	3065	712	28	538	**3909**	17	22	354
G9	4.3	**100**	**655**	2235	2.9	11	16	35	19,156	2696	702	24	548	**5983**	21	21	303
G10	2.6	**92**	233	1393	1.7	11	12	46	21,387	2412	545	25	513	**3942**	12	13	269
G11	6.7	**105**	**801**	2280	4.3	14	19	59	39,565	3076	1124	31	636	**6940**	21	21	**942**
G12	4.1	**88**	499	1777	4.4	13	15	54	29,017	2778	840	27	575	**4246**	12	18	635
G13	4.4	**125**	486	2318	3.0	14	16	103	33,253	2892	843	32	723	**5083**	19	20	695
G14	2.8	**104**	377	1751	3.4	14	15	50	33,853	2862	933	30	639	**3922**	12	17	**781**
G15	2.5	**118**	**866**	1872	2.7	12	**21**	51	32,584	3049	806	30	635	**3584**	27	25	640
G16	7.6	**161**	**2881**	3255	6.7	13	16	61	27,353	2869	1116	25	591	**8816**	35	18	706

Table 1. *Cont.*

Samples	Ag	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sr	V	Zn
Live-bed																	
G17	1.7	**129**	218	1184	2.4	12	17	39	28,185	2606	666	25	579	**2378**	12	20	522
G18	2.9	**106**	304	1355	2.7	13	18	50	33,025	2656	740	29	622	**3582**	13	20	649
G19	2.3	**102**	346	1499	3.0	14	18	47	35,642	2937	864	33	632	**3364**	14	19	709
G20	2.6	**156**	237	1284	2.5	13	**20**	61	33,697	2767	680	31	614	**3490**	15	25	608
G21	2.0	**92**	129	975	1.8	12	16	54	24,534	2490	552	24	551	**2285**	10	18	463
G22	1.9	**67**	193	891	2.4	8	10	34	20,390	1935	456	20	419	**2531**	7	12	409
G23	2.0	**77**	149	893	2.7	9	11	35	25,326	2032	546	23	471	**2785**	6	13	465
G24	2.0	**65**	224	1057	3.2	10	13	27	22,784	2341	705	22	515	**2640**	9	15	436
G25	2.4	**78**	324	1158	2.9	9	12	49	24,535	2497	571	23	557	**3005**	10	14	418
R1	0.1	18	**904**	434	0.1	11	**23**	18	37,278	3277	330	27	483	**309**	18	19	81
R2	0.7	15	**1649**	522	0.3	10	**22**	14	31,087	2902	296	26	400	**1125**	27	19	88
R3	8.2	**59**	**12671**	1542	4.3	15	19	81	34,753	2899	692	27	465	**10,511**	173	17	619
R4	3.2	23	**10310**	1365	2.6	10	**21**	23	34,266	3193	615	28	467	**5433**	146	19	635
R5	0.7	20	**1592**	630	2.3	10	**22**	19	35,946	3337	528	28	482	**1677**	25	18	619
R6	1.3	23	**8966**	1523	4.4	13	20	20	29,753	2616	1233	28	460	**2568**	115	20	**830**
R7	3.3	**85**	**1531**	1709	2.4	10	19	49	28,013	2716	417	26	727	**3164**	26	17	567
R8	4.1	**115**	**3591**	5159	5.2	16	**28**	59	31,304	3690	954	32	989	**3607**	61	26	**912**
R9	4.7	**85**	**1446**	4053	3.9	14	**22**	56	33,905	4047	886	32	728	**3696**	28	24	**760**
R10	4.1	**147**	**3125**	4603	4.6	16	**23**	85	32,557	4054	1052	32	798	**4998**	51	25	**723**
R11	10.9	**174**	**3440**	6098	9.0	18	10	83	37,289	3852	1855	28	606	**10,606**	40	12	**1350**
R12	3.9	**95**	**1046**	2595	7.0	17	20	58	39,933	3268	1516	38	712	**4413**	22	24	**1087**
R13	3.6	**107**	**862**	3361	5.2	16	**22**	57	40,213	3645	1022	36	713	**4995**	22	25	**1038**
R14	4.6	**90**	**1850**	2997	5.0	12	19	43	25,852	3166	823	23	573	**5312**	26	19	673
R15	4.2	**104**	**1848**	3310	5.3	15	**21**	56	36,510	3522	1061	34	709	**4584**	33	24	**975**
R16	3.2	**100**	537	2492	4.0	17	19	49	31,106	3235	1007	33	645	**3423**	14	20	**865**
R17	4.1	**118**	348	3874	3.3	17	19	60	28,578	3629	946	39	856	**5243**	23	24	520
C1	6.7	**168**	**5579**	1163	2.3	14	14	98	28,353	1898	686	28	481	**10,282**	66	17	462
C2	3.2	**231**	**1122**	1819	5.0	12	13	53	27,583	2288	765	24	532	**3916**	18	15	**805**
C3	3.1	**119**	**2491**	3822	4.7	13	**37**	48	18,652	2399	454	30	1111	**3634**	50	20	642
C4	3.8	**110**	**4669**	5346	4.6	9	**44**	61	19,855	3019	407	32	1251	**4631**	74	19	688
C5	3.6	**148**	**2767**	5043	7.1	13	**63**	57	22,207	3058	689	39	1575	**4784**	57	20	**888**
C6	6.4	**197**	**8727**	5604	7.7	9	**38**	59	22,070	2354	415	21	839	**7022**	128	15	**911**
C7	5.4	**144**	**7741**	2693	6.8	11	**27**	58	23,684	2387	545	24	805	**4071**	105	18	**781**
C8	4.6	**105**	**10539**	2704	5.4	8	**36**	36	21,741	2145	313	28	526	**4211**	136	17	582
C9	3.1	**93**	**3735**	2754	3.7	8	20	45	17,753	2346	393	19	560	**2824**	54	15	490

Table 2. Descriptive statistics of total concentrations: minimum maximum median range standard deviation (all data in mg kg) variance skewness and kurtosis. Enrichment factors referred to crust Clarke values and acid rocks are showed. Generic reference levels (GRL) established by the regional government (Junta de Andalucía 2015) and the Dutch soil standard (Dutch Ministry 2013) are also included. Concentrations above the reference values are in bold.

Element	Min.	Max.	Mean	Median	Range	Std. Deviation	Variance	Skewness	Kurtosis	Crust Clarke Values	Acid Rocks
Ag	0	12	5	4	12	3	7	0.78	0.33	0.10	0.15
As	9	**192**	**116**	124	182	44	1.978	−0.92	0.71	5	2
Ba	349	**11,762**	**2622**	1717	11,414	2203	4,852,462	1.85	4.92	260	830
Ca	545	5432	2472	2395	4887	1243	1,544,183	0.42	−0.39	36,300	-
Cd	0	12	4	4	12	2	5	1.69	4.92	0.15	0.10
Co	10	**31**	14	14	21	4	13	2.09	8.31	23	5
Cr (III-VI)	11	**33**	18	18	22	5	23	0.83	1.09	200	25
Cu	14	**432**	90	63	418	85	7196	2.62	6.72	70	30
Fe	18,736	39,207	28,724	28,607	20,471	5308	28,173,431	0.03	−0.79	50,000	-
Mg	1049	3918	2704	2778	2869	705	497,429	−0.69	0.15	20,900	-
Mn	326	4492	999	894	4166	611	373,780	4.08	21.61	1000	600
Ni	18	46	27	26	28	5	29	0.74	1.44	80	8
P	357	814	583	590	457	115	13,332	0.03	−0.98	180	700
Pb	**358**	**15,533**	**5452**	4646	15,175	3010	9,061,307	1.36	2.40	16	2
Sr	13	172	42	31	159	28	759	2.66	10.77	300	300
V	10	38	18	17	27	5	25	1.66	4.97	150	40
Zn	72	**1794**	659	596	1723	318	101,411	1.36	3.94	132	60

Element	Enrichment Factor (crust)	Enrichment Factor (acid rocks)	Generic Reference Levels in Andalucia			Dutch Regulations for Standard Soils Intervention Value
			Industrial	Urban	Others	
Ag	94	37	-	-	-	-
As	47	93	40	36	36	76
Ba	20	3.79	10,000	10,000	10,000	625
Ca	0.14	-	-	-	-	-
Cd	54	48	750	75	25	13
Co	1.24	3.39	250	25	24	190
Cr (III-VI)	0.18	0.87	10,000–100	10,000–20	10,000–20	180–78
Cu	2.60	3.60	10,000	3130	595	190
Fe	1.16	-	-	-	-	-
Mg	0.26	-	-	-	-	-
Mn	2.02	2.00	-	-	-	-
Ni	0.68	4.04	10,000	1530	1530	100
P	1	1	-	-	-	-
Pb	689	3272	2750	275	275	530
Sr	0.28	0.17	-	-	-	-
V	0.24	0.54	3650	365	50	-
Zn	10	13	10,000	10,000	10,000	720

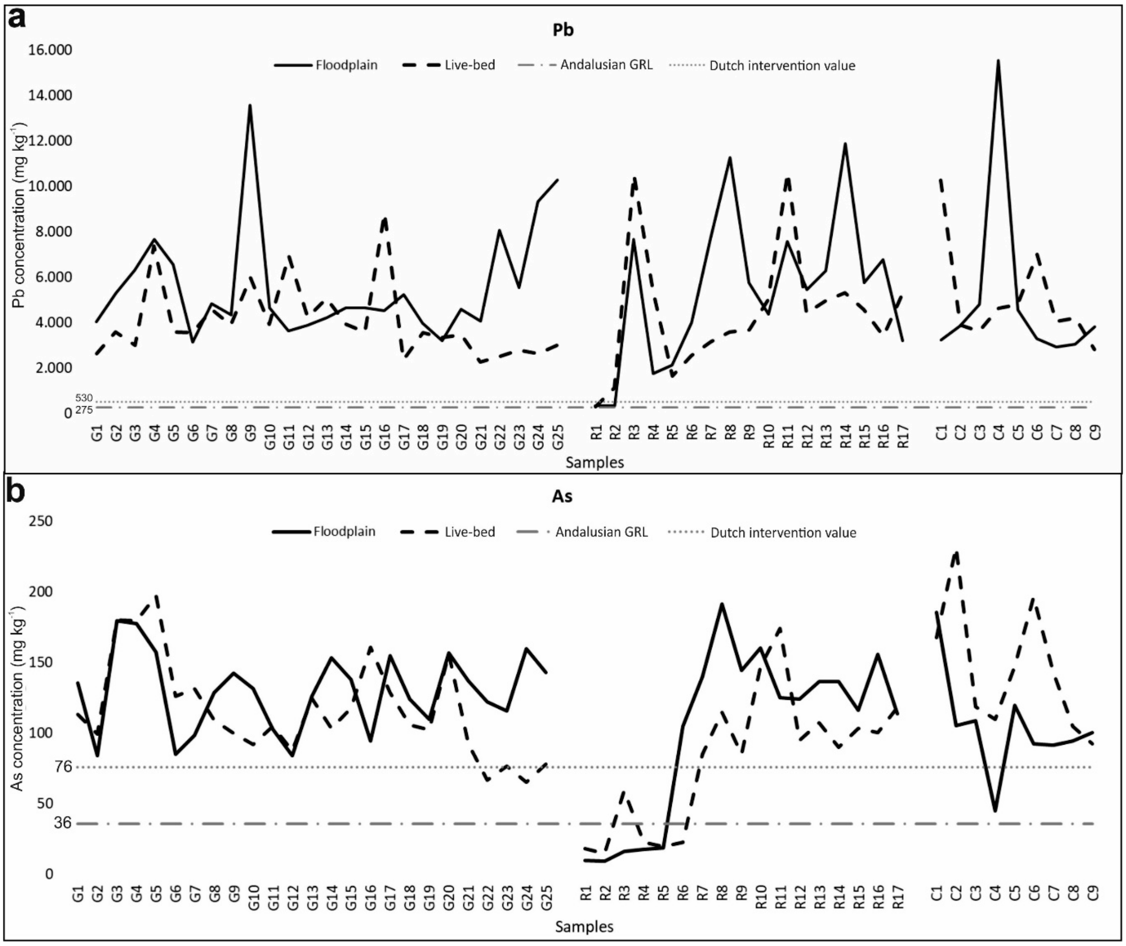

Figure 3. Distribution of Pb and As contents in sediments from La Carolina mining district. (**a**)—Pb; (**b**)—As. Generic reference levels (GRL) established by the regional government of 275 mg/kg for Pb and 36 mg/kg for As (Junta de Andalucía 2015) and Dutch intervention values of 530 mg/kg for Pb and 76 mg/kg for As (Dutch Ministry 2013) are showed.

Figure 4 shows the histograms box and whisker plots and normality plots for the concentrations of Pb, As and Ba in the samples taken in the live-bed and in the floodplain. For Pb the histograms are similar in the two sedimentary environments skewed to the right by extreme values. Additionally the box and whisker plots are similar in both situations showing numerous extreme values with a lognormal distribution as shown in the Q/Q plots of Figure 4. For As the live-bed histogram is symmetric but not the histogram of the floodplain which presents two families of values. The box and whisker plots are similar in both sedimentary environments with lower extreme values referring to the headwaters of the Renegadero River. The distribution is normal as shown in the Q/Q normality plots except for low values. The histograms of Ba for both environments are asymmetric to the right. The box and whisker plots for Ba show numerous extreme values presenting a lognormal distribution.

A multivariate analysis by principal components with varimax rotation was performed for the sediment samples obtained in the live-bed channel and in the floodplain. The total variance explained by the four components is 80.2% in the live-bed channel and 83.1% in the floodplain. In the live-bed channel (Table 3a) the following groupings are identified: component 1 which represents 21.9% of the variance and includes Mn Co Cu and As elements associated with the mineralization of this mining basin; component 2 which represents 20.35% of the variance and is composed of Fe Mg V Ni and Zn (elements naturally related to the soil); component 3 which represents 19.6% of the variance and is associated with P Cr Ca and Cd natural components of rocks and soils; and finally component 4 which represents 18.4% of the variance and groups Ba Sr Pb and Ag which is associated with the mineral paragenesis of the studied environment and therefore with the mining activities performed.

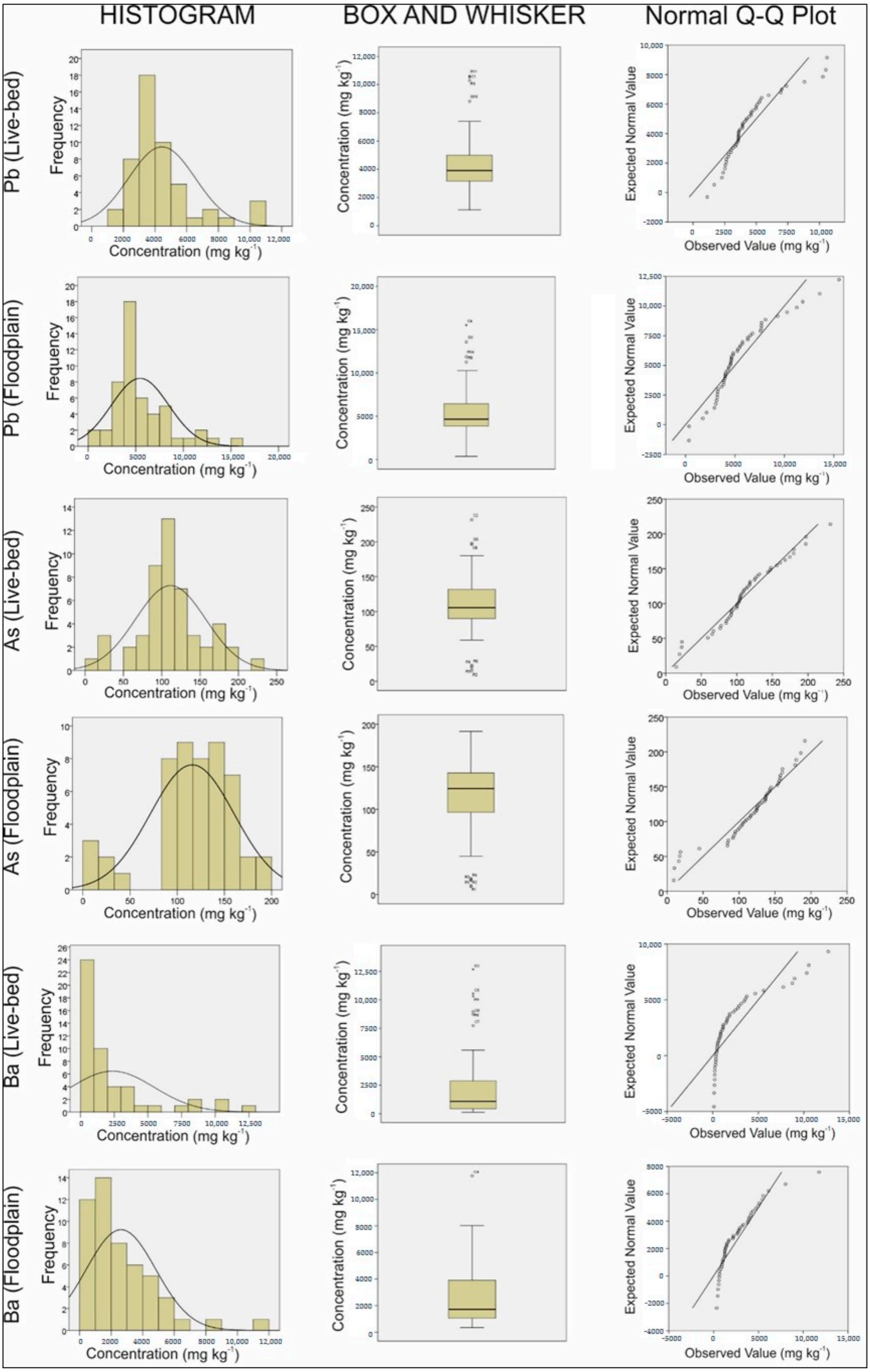

Figure 4. Histograms box-and-whisker plots and normality curves for Pb As and Ba.

Table 3. Principal component loadings obtained in principal component analysis of the element concentrations in the live-bed (**a**) and in the floodplain (**b**).

(a) Live-Bed					(b) Floodplain				
Variable	Component				Variable	Component			
	1	2	3	4		1	2	3	4
Mn	0.860	0.233	−0.113	−0.002	Ba	0.919	−0.055	0.143	−0.113
Co	0.855	0.413	−0.023	−0.019	Sr	0.893	−0.047	0.261	−0.164
Cu	0.822	−0.260	−0.125	−0.099	Cd	0.890	0.181	−0.038	0.270
As	0.667	−0.292	0.350	0.054	Pb	0.825	0.218	−0.251	0.273
Fe	0.130	0.866	−0.251	0.096	Zn	0.784	0.200	0.259	0.230
Mg	−0.214	0.837	0.308	0.127	Ag	0.769	0.283	−0.214	0.421
V	−0.037	0.755	0.313	−0.139	Co	0.176	0.928	0.097	0.197
Ni	0.451	0.675	0.327	−0.106	Mn	0.124	0.917	−0.186	0.115
Zn	0.117	0.609	0.426	0.395	Cu	0.108	0.884	−0.111	0.121
P	−0.016	0.186	0.943	−0.022	Ni	−0.049	0.842	0.443	0.112
Cr	−0.200	0.029	0.860	0.161	Fe	0.358	0.527	0.508	−0.147
Ca	0.182	0.280	0.783	0.356	V	−0.042	0.215	0.820	0.037
Cd	0.245	0.277	0.579	0.552	Mg	0.210	−0.038	0.819	0.143
Ba	−0.209	−0.059	0.097	0.875	Cr	−0.052	−0.186	0.786	−0.087
Sr	−0.214	−0.033	0.172	0.842	P	0.068	0.144	0.657	0.596
Pb	0.468	0.140	0.047	0.727	As	0.100	0.374	−0.099	0.845
Ag	0.641	0.070	0.105	0.667	Ca	0.414	−0.030	0.431	0.692
% Var	21.92%	20.25%	19.56%	18.42%	% Var	27.91%	23.05%	19.79%	12.31%

In the case of the floodplain (Table 3b) the following groups were obtained: component 1 (27.9% of the variance) groups Ba Sr Cd Pb Zn and Ag all elements of mineral paragenesis and therefore with anthropogenic influence linked to mining; component 2 (23.1% of the variance) composed of Co Mn Cu Ni and Fe associated with the mineralization of this mining basin; component 3 (19.8% of the variance) composed of V Mg Cr and P elements that are present in the rock matrix; and the fourth component which represents 12.3% of the variance and groups Ca and As. In both sedimentary contexts Pb is associated with Ba Sr and Ag.

Based on the values of the metal(loid)s content of the sediments the environmental factors and indices mentioned in the methods section were calculated. In the case of the EF of the 17 metal(loid)s analysed Zn As Ag Cd Ba and Pb have high values (>10) compared to their Clarke values in the Earth's crust. The EF of Pb increases when the geochemical background values for acid rocks are used as a reference which indicates that there is a very severe anthropogenic influence (Table 2).

The CF presents very high values for Zn As Ag Cd and Pb with values of 10.3 74.3 25.9 37.4 and 2216.3 respectively. Note the case of Pb which is the main ore of the mining basin with a CF 30 times higher than those of the rest of the metal(loid)s. In addition other elements such as Mn Co Ni Cu and Ba reach significant values with CF values of 1.5, 2.6, 3.5, 2.5 and 2.9 respectively.

The values obtained for the geoaccumulation index (I_{geo}) show an extremely high level of contamination in the case of As Ag Cd and Pb with values of 5.6, 4.1, 4.6 and 10.5 respectively. The Zn content in the sediments with a value of 2.8 presents a moderate to strong level of contamination. Moderate levels of contamination by Co Ni Cu and Ba are also present with values of 0.8, 1.2, 0.7 and 0.9 respectively for I_{geo}.

The potential ecological risk (E_r^i) values calculated for V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd and Pb are 1, 2, 1, 13, 18, 12, 10, 743, 1123, and 1,1081 respectively highlighting a very high risk for As, Cd and Pb with respect to the rest of the metal(loid)s studied. Considering the set of elements analysed a value of 13,006 is obtained for the RI so there is a very high ecological risk in the study area.

The PLI obtained for all metal(loid)s is 2.8 indicating a strong deterioration of the environmental quality of this mining area. This index estimated for each sample in both the floodplain and the live-bed channel (Figure 5) indicates that in both environments all the sediment samples analysed are contaminated (PLI > 1). In the live-bed channel (Figure 5a) although there is a wide variation the maximums are observed in the central section of the three channels (Grande Renegadero and Campana) decreasing towards the lower section of the Grande River which is the furthest away from mining activity. In the floodplain (Figure 5b) there are high PLI values in the middle and lower reaches of Renegadero with values between 3 and 4 which could be associated with scouring due to large flooding events and the formation of wide bars in the channel. In the Campana River higher values for PLI appear in the live-bed channel (between 2 and 4) than in the floodplain (between 2 and 3). Although the sediment values in the Grande River remain between 2 and 3 a maximum is observed in sample G4 (as in the live-bed channel) and in samples G24 and G25 located at the tail of the Rumblar reservoir.

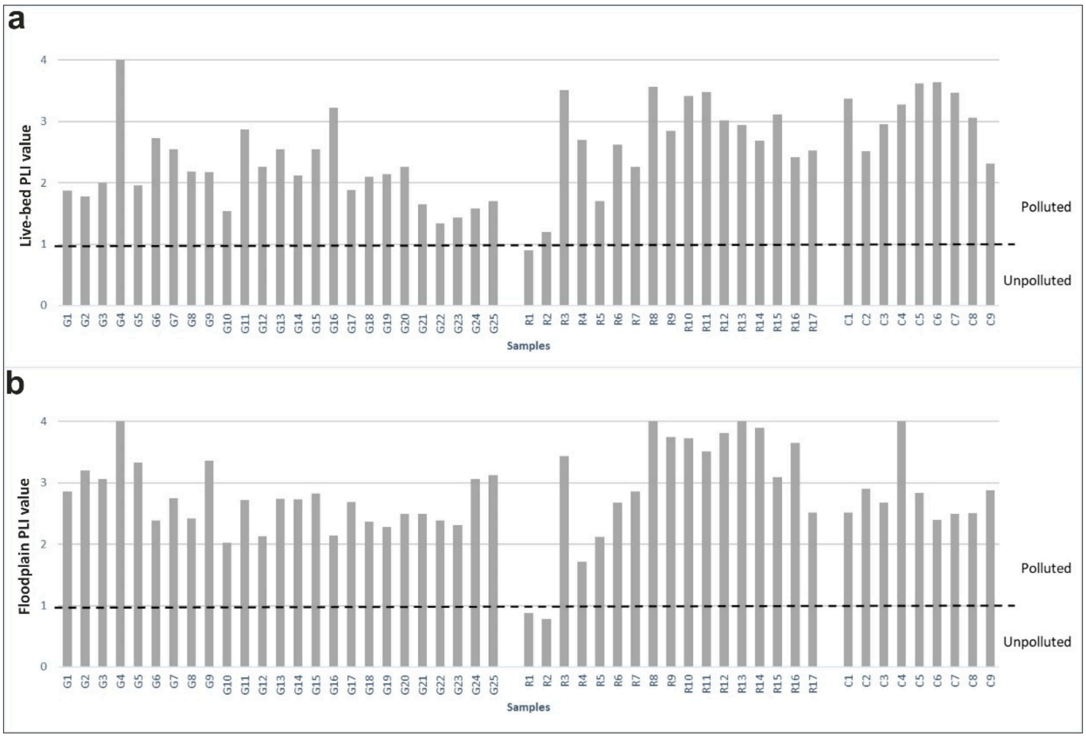

Figure 5. Distribution of pollution load index (PLI) values along the rivers of the La Carolina mining district. (**a**)—live-bed PLI value; (**b**)—floodplain PLI value.

Figure 6 maps the spatial variation in Pb and As. For Pb anomalies can be seen in the live-beds of the Renegadero and Campana channels clearly related to mining activity (Figure 6a) while in the floodplain the anomalies cover more area but less intense being located downstream in the final section of the Renegadero and middle part of the Grande River (Figure 6b). Anomalies for the As content of the sediments of the live bed are observed in the upper part of the Grande River and throughout the Campana River with intermediate values in the final sections of the Renegadero and lower reach of the Grande River (Figure 6c). In the floodplain As (Figure 6d) shows strong As concentration anomalies throughout the Grande River as well as in the middle and lower reaches of the Renegadero River and lower intensity anomalies in the Campana. Figs. 6e and 6f show the spatial distribution of the PLI values displaying similar behaviour in both sedimentary environments and presenting the highest contamination in the middle and upper reaches of the Grande River and the lower reaches of the Renegadero and in the Campana River with greater intensity and extent in the floodplain.

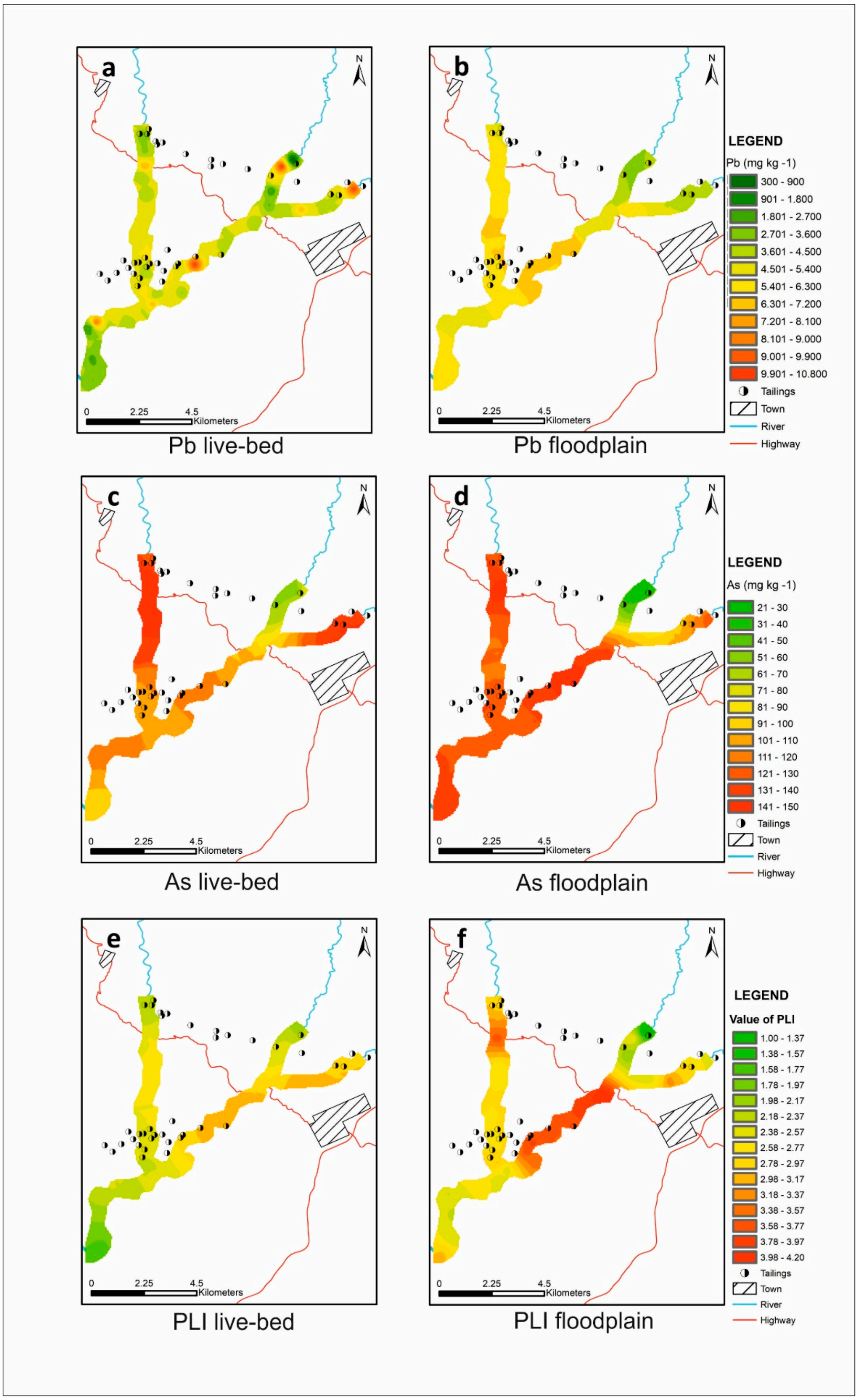

Figure 6. Spatial variation of the Pb and As contents and the pollution load index (PLI) values in the channel and floodplain of the rivers of the La Carolina mining district. (**a**)—Spatial variation of the Pb contents in live-bed; (**b**)—Spatial variation of the Pb contents in floodplain. (**c**) Spatial variation of the As contents in live-bed; (**d**)—Spatial variation of the As contents in floodplain. (**e**)—Pollution load index (PLI) values in live-bed; (**f**)—Pollution load index (PLI) values in floodplain.

4. Conclusions

The sediments of the Grande River and its tributaries Renegadero and Campana have high contents of Cd, Ag, Co, Ni, Cu, As, Zn, Ba and Pb with average values in the floodplain deposits of 4, 5, 14, 27, 90, 116, 659, 2622 and 5452 mg/kg respectively. These values are much higher than those of the regional geochemical background and those established in the generic reference levels of government regulations. Pb and As present the highest contents with maximum concentration values of 15,533 and 192 mg/kg respectively. These metal(loid)s come from the existing mining liabilities in the area (ruins of old mining facilities dumpsites and fines tailings dams). The average concentrations are somewhat higher in the samples taken in the floodplain than in the samples taken in the live-bed channel showing more variable Pb behaviour with numerous peaks that indicate great variability and low mobility. In contrast As has a more uniform distribution along the basin and its maximum concentrations generally do not coincide with those of Pb.

The mineral paragenesis elements of mining interest (group 1 of the principal component analysis for the floodplain and group 4 for the live-bed channel) especially Pb and Ba present heterogeneity and dispersion with lognormal behaviour and numerous extreme values.

The environmental indices calculated suggest a high degree of impact by metals in the basin sediments for the elements Ag, As, Ba, Cd, Pb, Zn of the mineral paragenesis classifying the existing contamination as moderate to high. For Pb anomalies occur in the live-bed channel both in the Renegadero River and in the Campana River clearly related to mining with more intense and extensive effects in the floodplain due to strong flooding creating areas used for cultivation [5] both in the final stretch of the Renegadero and in the middle stretch of the Grande River. As is present in the sediments of the entire basin both in the bed-live and in the floodplain presenting only low concentrations in the upper reaches of the Renegadero River. The distribution map of the PLI shows effects on the soils with the greatest intensity in the sediments of the live-bed channel in the upper section of the Grande River in the lower section of the Renegadero River and throughout the entire Campana River.

The results obtained from the study of the sediments of the Grande riverbed show that this old mining basin has been highly affected especially because the waste generated was accumulated without any preventive measures after abandonment requiring competent administrations to take remediation measures.

Heavy metals have a significant presence in the area studied, resulting in highly contaminated sediments according to data obtained in this work, similar other work was carried out in other mining basins around the world such as that of the Environment Agency in England [5]. This contamination was transported several kilometres away from the pollutant sources and is guaranteed to contribute heavy metals to the human water supply reservoir damage the ecosystem and lead to a deteriorated ecological state.

Finally note that an old mining basin was analysed in its entirety that until now had not been studied. Considering the results obtained this is a significantly contaminated area that until now had gone unnoticed by the regional environmental agency.

Author Contributions: Conceptualization, R.M., J.M. and M.C.H., Investigation, R.M., J.M. and J.R., Software, R.M., Formal analysis, R.M. and M.J.C.-S., Writing—original draft, R.M., Writing and review, R.M., J.M., M.C.H., J.R. and M.J.C.-S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors thank the CEACTEMA (University of Jaén) for the partial financing of this work.

Conflicts of Interest: The authors declare no conflict of interest.

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