

SOIL CONTAMINATION AT THE DUMP-FIELD OF ABANDONED Cu-DEPOSIT LIBIOLA, ITALY

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Abstract: In the past centuries significant and now closed Libiola copper deposit in Liguria (Northern Italy) can be considered one of the most important mining areas of the Apennine Peninsula. The environmental risk is caused by the character of the dump matter, whose average pH is 4.03 and whose shows a high proportion of sulphidic sulphur (in average 0.30 %) in comparison with sulphate sulphur (in average of 0.10 %), so it has still great potential to create acidity and release potentially to the country components (soil, water, atmosphere, and biota) potentially toxic elements. The average concentrations of these elements are: Fe 16.37 %, Cu 3.753, Ni 771, Pb 35, As 12, and Cd 1.5 mg·kg⁻¹. To characterize the mineralogical composition of the dump matter was used X-ray diffraction analyses. The risk is increased by the absence of carbonates, which could neutralize the acidity. On the other hand, the soil colloids have negative surface charge which facilitates the sorption of metals released into the solution and thus cause their partial immobilization. This article also presents the potential distribution of main potentially toxic elements, processed as an interpolation model in GIS.

Keywords: dump-field, technosol, contamination, distribution, environmental risk

1. INTRODUCTION

The ore field Libiola, situated on steep slopes of the Gromolo valley was in the past the most important Cu-mine in the Liguria district. It was exploited since the Copper/Bronze Age, mining activity is documented at the end of the 4th millennium BC (Maggi & Pearce, 2005) and later in the 17th century, as well as from 1864 to 1961. The large open-scale quarry operations in the fifties and sixties of 20th century overlapped part of the ancient mining localities and substantially changed the country relief (Kienlin & Pearce, 2008).

The mineralization is formed on the western boundary of the Valgraveglia ophiolite complex, in

noth-east direction from Sestri Levante. More than 1.5 Mt of Cu-ore was between 1864 and 1961 exploited (Galli, 1996). The sulfide mineralization forms massive lenses at the top parts of a huge pillow-basalt dome (Ferrario & Garuti, 1980). These basalts underlain and locally overthrust by serpentinite and gabbro bodies (Garuti et al., 2008). The second type of sulphide mineralization is the serpentinite hosted low-grade one, connected with shear zones. According to Bertolani (1952) it was formed by syntectonic remobilization of original magmatic sulfides.

The ore mineralization of quartz-calcite veins (with chlorite) consists most of all of pyrite and chalcopryrite, accompanied by less represented

sphalerite and pyrrhotite (Marescotti et al., 2007; Garuti et al., 2008; Di Lisi et al., 2020; Andr    et al., 2021).

The aim of the presented article is describe the geochemical characteristics of the dump matter and visualize the spatial distribution of the selected PTEs.

Two types of mine waters were distinguished within the studied area. The first one is represented by red acid waters (pH 2.4 - 2.8), and the second type by neutral waters (pH 7.0 - 7.5) of blue colour, which is caused by precipitated phases. Also, a mixture of these two specific types of mining waters is present (Marini et al., 2003).

The studied dump-field (Figures 1-3) is localized on a steep slope without vegetation above Gromolo creek and topped by a quarry at the top of the hill. At the central part, there are several natural outcrops of the underlying rock complex. The aim of the article is to characterize the dump field's technosol contamination and present its spatial distribution using GIS tools.

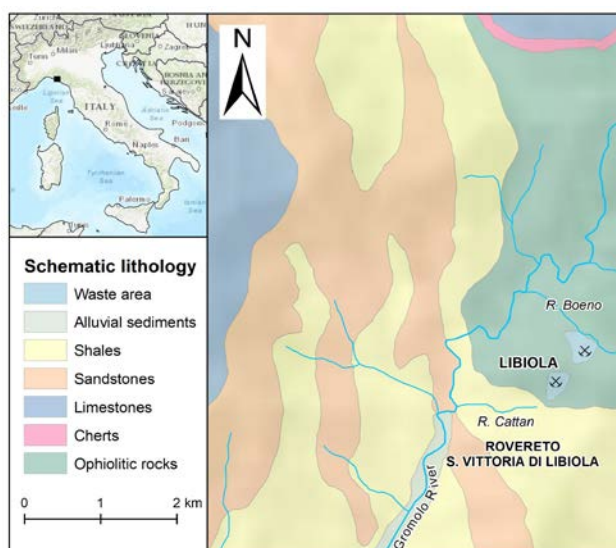


Figure 1. Geological map of the studied area of the Libiola ore deposit according to Dinelli et al. (2001).



Figure 2. The dump-field at Libiola Cu-deposit.

2. MATERIAL AND METHODS

The technosol is very shallow, only several centimeters deep on the slope. The depth overreaching 1 m is only at the foot of the dump-hill. The sampling was realized in regular grid network (50x50 m) with respect to the terrain conditions. Each sample by homogenization of 10 smaller samples weighing 500 g was created. All of them were dried at laboratory temperature to minimize loss of volatile elements and both rinse and paste pH/Eh was determined according to Sobek et al. (1978) from distilled water and 1M KCl lixivium, using pH-metre EUTECH Instruments device. The obtained data was calculated for standard hydrogen electrode.

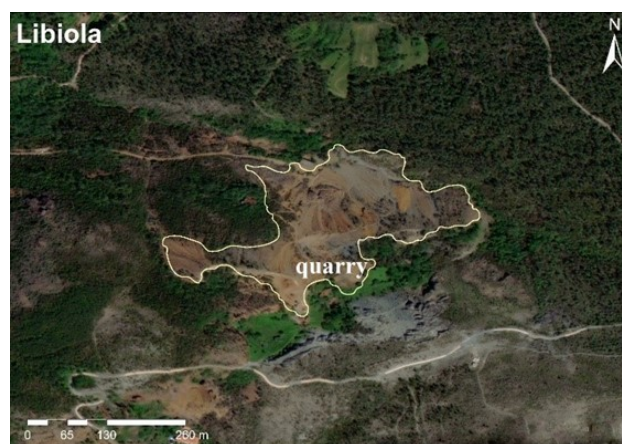


Figure 3. The area of the mining area of the Cu-deposit Libiola with the border of the dump-field.

To assess the PTEs concentrations in soil, a dry sample was ground to fine powder. For the performance of microwave digestion (Ethos plus 2, MLS), 100 mg of powder was dissolved in a solution of nitric and hydrochloric acid (aqua regia) in a ratio of 1:3 according to Krachler et al. (2002). The elemental concentration was measured by mass spectrometry with inductively coupled plasma (ICP-MS), single quadropole (Agilent 7900, USA).

X-ray powder diffraction analysis were performed by a Bruker D8 Advance diffractometer (Earth Sciences Institute in Bansk   Bystrica) using CuK   radiation generated at 40 kV and 40 mA and Sol-X SDD detector. Experimental data were compared with the PDF2 database. The X-ray powder diffraction analysis was performed to identify the mineralogical composition of the technosol. Analyses were performed by a Bruker D8 Advance diffractometer (Earth Sciences Institute in Bansk   Bystrica) using CuK   radiation generated at 40 kV and 40 mA and position sensitive detector SSD 160. Experimental data were compared with the PDF2 database.

The Energy-dispersive micro X-ray fluorescence spectrometry (ED-XRF) analysis was performed using an M4 TORNADO (Bruker) spectrometer. Element distribution maps were obtained from the selected area within a polished grainy specimen. The excitation current 600 μ A at 50 kV of Rh anode was used. The analyses were carried out in a vacuum of 20 mbar, the distance between the two measurement points was 15 μ m, at a speed of 5 ms/pixel (spot size was 20 μ m). The SDD detector that collects the fluorescent signal has an active area of 30 mm² and a spectral resolution of 145 eV. Element concentrations were computed by the fundamental parameter method, concentrations were integrated across homogenous areas selected from elemental maps.

The values of the rH_2 factor, defined by (Richter & Hlušek, 2003) given by the formula: $rH_2 = Eh/30 + 2pH$, vary for well aerated soils in the range 28–34, and the not aerated soils are defined by values < 20.

The D_{pH} factor represents the value that can be obtained by subtraction of pH_{H_2O} from pH_{KCl} . A positive D_{pH} factor determines the presence of soil colloids with negative surface charge, while negative D_{pH} values indicate the presence of colloids with positive charge (McNeill, 1992).

2 g of well homogenized fine-grained samples (80 mesh) were wetted with a distilled H₂O and dissolved in H₂O-HF-HClO₄-HNO₃ mixture. The limpid solution was refilled by HCl to exact volume and analysed for Fe, Cu, Pb, Zn, As, Sb, Ni, Co, Cd, Sr, Bi, U, Th, Mn, Mo, Ag and Au, by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in Acme Laboratories (Vancouver, Canada) by Perkin-Elmer Elan 6000 device.

The sulphur content (total sulphur – S_{tot} , sulphidic sulphur – S_s and sulphate sulphur – SO_4) was measured in Ecologic Laboratories in Spišská Nová Ves by Inductively coupled plasma atomic emission spectroscopy (ICP-AES) in 0.5 g of sample. The carbon content (C_{tot} and C_{org}) was measured in the Geological Institute of the Slovak Academy of Sciences in Banská Bystrica by IR spectroscopy using a Ströhlein C-MAT 5500 device in 0.5 g of sample. The C_{inorg} was calculated as a difference of $C_{tot} - C_{org}$.

The Spearman rank correlation coefficients between couples $S_s/pH_{(H_2O)}$ as well as Cu and Ni /pH were calculated from all metal pairs in software application SPSS Statistics (version 19) provided by IBM. The correlations characterized by $p \leq 0.05$ values were considered as statistically significant.

In order to estimate the spread of contamination by selected elements, GIS tools were applied. The base-map and the boundaries of dump-

field were generated with respect to the original orthophoto documentations. Distribution was modelled in ArcGIS application (version 10.3.1), which is one of the most popular and universal software used by numerous experts. The models of contamination spread were generated separately for each element using the IDW interpolation method which uses the measured values surrounding the prediction locations.

3. RESULTS

At Libiola dump-field is the dump-matter very acidic, the pH_{H_2O} varies from 2.76 to 4.94 (\bar{x} 4.03) and the pH_{KCl} from 3.37 to 6.47 (\bar{x} 4.82). The reddish-brown colour of the sediments indicates oxic conditions (Eh_{H_2O} 12 – 146, \bar{x} 67.71; Eh_{KCl} 32.5 – 223.3, \bar{x} 128.8). The D_{pH} factor (McNeill, 1992) which fluctuates between -1.71 to 0.05 (\bar{x} -0.79; Table 1) indicates soil colloids with negative surface charge.

The values of rH_2 factor (Richter & Hlušek, 2003) 13.32 to 14.58 (\bar{x} 14.00; Table 1), are characteristic for not well aerated soils. The mineralogical composition of the technosol is as follows: the dominant minerals are phyllo-silicates (chlorite, chlorite-smectite and tri-smectite/ saponite; categorically are present also talc and minerals from the serpentinite group), quartz, plagioclase, magnetite, hematite, and goethite, as well as some not exactly defined micas (Figures 4-5).

Among potentially toxic elements (PTE) show the highest concentrations Fe (7.75 – 42 %), Cu (325 – 12,400 mg·kg⁻¹), Ni (9.1 – 1,115 mg·kg⁻¹), Pb (14 – 476 mg·kg⁻¹), Sr (8 – 53 mg·kg⁻¹), As (3 – 266 mg·kg⁻¹) and Cd (0.7 – 9.4 mg·kg⁻¹; Table 2).

The area of the dump-field is shown on Figure 1. The distribution of the main contaminants is presented on Figures 6 – 13. The highest Fe and Pb contents were detected on the northern border of the dump-field on the foot of the hill and in the open-scale quarry on the top of the landfill itself (Figures 6-7). The highest Cu contamination (Figure 8, as well as of the As and Zn is in the quarry (Figures 9-10). Chromium and nickel are concentrated mainly under the slope in the depression above Gromolo creek (Figures 11-12).

The cumulative contamination given by the sum of all PTEs is presented on Figure 13. The highest correlation factor r was confirmed for metal pairs Co/Mn (0.79), As/Ag (0.67), Fe/Mo (0.67), Fe/Ag (0.61), Pb/As (0.76) and Pb/Sr (0.66), Mo/Ag (0.78), Zn/Cd (0.67), Zn/As (0.60) and Zn/Sr (0.65); correlation between two most risk metals Cu/Ni is very low (0.18).

This high degree of correlation corresponds to element pairs that migrate during weathering the close geochemical properties of the bound-ed (Polański & Smulikowski, 1978; Aiello et al., 2021).

Table 1. Characteristic of the technosol from Libiola dump-field.

Sample	pH _(H2O)	Eh _(H2O)	pH _(KCl)	Eh _(KCl)	rH ₂	D _{pH}
1	2.76	242.6	3.98	178.9	13.61	-1.22
2	3.16	238.2	3.37	212.3	14.26	-0.21
3	3.78	173.9	4.78	130.3	13.36	-1.00
4	3.34	221.5	4.04	170.1	14.06	-0.70
5	4.04	170.9	4.97	122.3	13.78	-0.93
6	3.92	185.6	4.58	139.2	14.03	-0.66
7	3.62	182.3	4.87	130.1	13.32	-1.25
8	3.52	214.8	4.69	136.1	14.20	-1.17
9	3.92	169.7	5.25	110.7	13.50	-1.33
10	4.18	173.3	5.53	91.1	14.14	-1.35
11	3.78	181.3	4.20	167.5	13.60	-0.42
12	3.94	186.7	5.41	97.5	14.10	-1.47
13	3.65	193.7	4.74	134.7	13.76	-1.09
14	3.27	223.6	3.76	188.7	13.99	-0.49
15	3.41	203.1	4.52	153.1	13.59	-1.11
16	3.46	213.1	4.70	135.3	14.02	-1.24
17	3.03	226.6	3.78	190.8	13.61	-0.75
18	4.26	175.5	5.16	106.5	14.37	-0.90
19	4.10	161.5	5.81	68.7	13.58	-1.71
20	4.95	135.5	5.39	94.6	14.42	-0.44
21	5.13	100.3	5.59	95.2	13.60	-0.46
22	5.56	103.9	6.35	37.7	14.58	-0.79
23	5.29	99.6	6.47	32.5	13.90	-1.18
24	5.16	110.4	6.23	48.5	14.00	-1.07
25	4.88	128.5	5.67	65.7	14.04	-0.79
26	4.25	171.1	5.17	106.1	14.20	-0.92
27	4.17	165.2	5.09	106.9	13.85	-0.92
28	3.76	204.1	4.18	161.8	14.32	-0.42
29	3.93	167.9	4.95	118.6	13.46	-1.02
30	3.06	239.7	3.74	186.5	14.11	-0.68
31	3.97	168.4	4.77	134.4	13.55	-0.80
32	4.58	158.4	4.53	141.8	14.44	0.05
33	4.30	154.2	5.25	109.8	13.74	-0.95
34	4.38	156.4	6.06	61.1	13.97	-1.68
35	4.21	164.7	5.34	80.8	13.91	-1.13
36	3.35	215.4	3.83	184.9	13.88	-0.48
37	4.06	173.5	4.80	131.5	13.90	-0.74
38	2.99	240.9	3.96	177.3	14.01	-0.97
39	3.31	210.6	4.07	176.4	13.64	-0.76
40	3.35	214.9	4.25	160.7	13.86	-0.90
41	4.28	152.5	5.22	108.3	13.64	-0.94
42	4.24	166.5	4.76	126.3	14.03	-0.52
43	4.38	152.4	4.68	140.1	13.84	-0.30
44	4.49	148.5	4.96	119.4	13.93	-0.47
45	3.26	216.5	3.84	188.3	13.74	-0.58
46	4.11	172.1	4.15	165.1	13.96	-0.04
47	4.81	128.3	4.87	129.3	13.90	-0.06
48	5.15	113.6	4.41	151.2	14.09	0.74
49	4.94	120.6	5.29	105.7	13.90	-0.35
\bar{x}	4.03	175.4	4.82	128.8	14.00	-0.79

Explanations: Sb, Bi, U, Th and Au were below the detection limit.

Table 2. ICP-MS analyses of technogenosol from dump-field Libiola (concentrations of PTEs, which exceed the limit for soil, given by the Italian Legislativo Decree No. 152/06 are highlighted by bold).

Sample	Fe %	Cu	Pb	Zn	As	Ni	Co	Cd	Sr	Mn	Mo	Ag
	mg·kg ⁻¹											
1	18.89	2860	28	286	10	352	47	0.8	15	446	9	4.2
2	17.63	2699	22	304	10	580	61	0.7	19	633	6	3.2
3	16.39	2394	29	265	9	429	53	1.1	25	708	4	2.7
4	10.63	1699	14	512	9	967	123	0.9	67	1481	<2	0.8
5	11.34	3181	<5	136	<5	1508	117	<0.4	6	724	4	1.8
6	17.97	3951	14	344	10	697	79	1.1	9	521	9	3.5
7	16.24	3774	16	299	7	777	81	0.9	9	569	8	3.8
8	15.40	3814	17	337	6	742	83	1.4	9	582	8	4.4
9	18.15	3971	52	347	7	449	75	1.5	16	991	8	2.4
10	17.34	4407	14	270	5	715	88	1.3	9	590	10	3.1
11	18.07	4299	13	273	5	671	83	1.2	8	570	10	3.2
12	20.16	5243	17	261	5	484	83	1.4	11	579	12	3.1
13	19.85	5724	10	234	<5	464	82	0.8	9	520	11	3.2
14	20.70	5250	21	227	<5	421	85	0.8	8	511	12	3.3
15	11.24	3773	7	166	<5	1216	97	1.0	8	728	5	1.7
16	16.67	6867	<5	122	<5	629	91	0.5	8	578	7	1.4
17	15.33	4483	<5	214	<5	786	110	1.0	10	723	8	1.9
18	16.31	4304	7	305	<5	575	93	1.5	11	652	8	2.6
19	13.96	3952	9	222	<5	851	96	1.6	9	653	7	2.2
20	13.12	2660	7	389	<5	1057	131	1.8	9	996	3	1.1
21	12.64	2301	30	206	<5	1110	99	0.9	17	994	5	1.6
22	11.45	499	15	119	<5	2855	189	<0.4	16	1818	<2	0.6
23	11.40	112	10	103	<5	3455	216	<0.4	20	2127	<2	<0.5
24	11.91	140	7	102	<5	3684	231	<0.4	19	2065	<2	<0.5
25	20.39	2864	192	308	18	382	45	0.9	27	517	11	5.3
26	14.84	2529	60	400	9	503	75	2.5	36	1168	5	1.7
27	12.82	2622	39	507	8	778	119	2.4	42	1724	<2	1.3
28	14.97	2322	30	430	11	669	89	2.4	37	1411	4	2.0
29	15.77	3348	20	397	10	465	67	2.2	21	706	6	3.4
30	19.15	3511	22	278	15	358	68	1.1	20	545	11	3.9
31	20.29	3726	34	271	18	481	63	1.0	37	568	14	4.9
32	15.94	5043	16	474	8	217	118	0.6	37	916	3	1.7
33	17.48	5911	15	327	6	165	185	2.6	39	1790	<2	0.8
34	18.43	5835	23	255	10	204	439	<0.4	31	2519	<2	0.9
35	17.91	4218	36	495	13	257	81	1.0	44	770	6	2.6
36	19.12	3237	26	245	14	334	55	0.8	18	474	12	4.0
37	18.18	2855	25	247	14	287	54	0.8	27	572	9	3.1
38	18.84	2646	19	259	14	224	41	<0.4	16	376	9	3.7
39	18.73	5355	34	315	19	1117	122	1.2	27	860	13	5.8
40	14.20	2632	26	480	12	1109	139	1.4	53	1599	3	2.3
41	15.32	5118	36	661	18	572	82	4.0	22	694	5	5.0
42	15.80	4640	24	445	9	874	111	2.5	26	1161	4	3.4
43	16.73	2691	35	328	15	254	50	1.8	26	597	6	3.8
44	21.57	2515	31	516	20	426	50	0.7	23	564	7	5.7
45	18.77	3860	164	555	32	500	41	1.8	40	473	18	9.5
46	18.00	8363	47	669	14	548	77	2.7	43	641	5	2.8
47	15.22	3581	183	382	16	585	66	2.3	41	568	9	3.5
48	16.36	5410	61	502	12	366	76	3.7	38	689	5	2.6
49	14.70	6732	38	608	23	653	154	3.6	33	1439	29	6.9
\bar{x}	16.37	3753	35	335	12	771	101	1.5	23	900	8	3.1

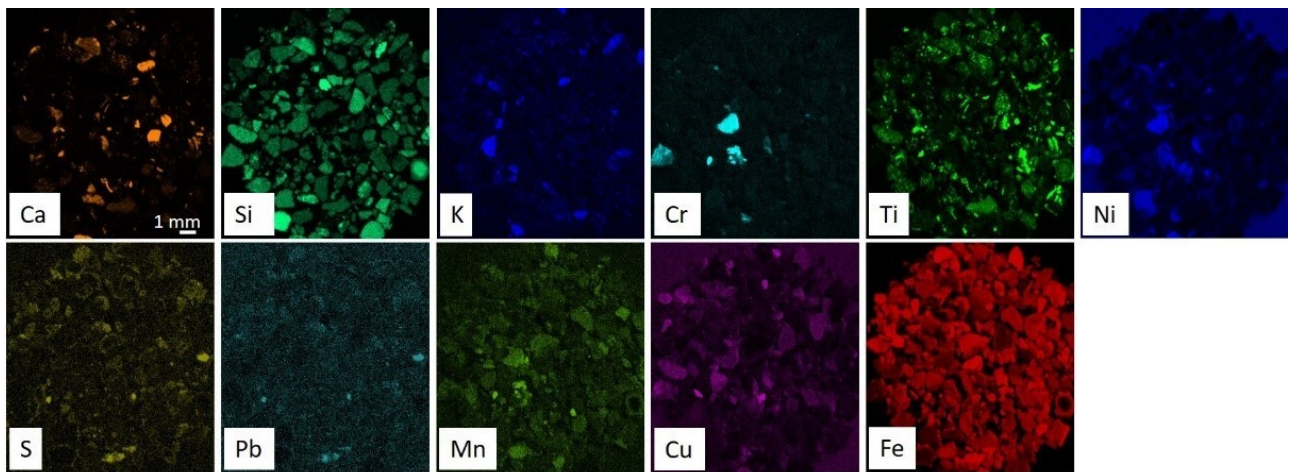


Figure 4. Representative spectrum of Energy-dispersive micro X-ray fluorescence spectrometry (ED-XRF) analysis with lines corresponding to measured elements.

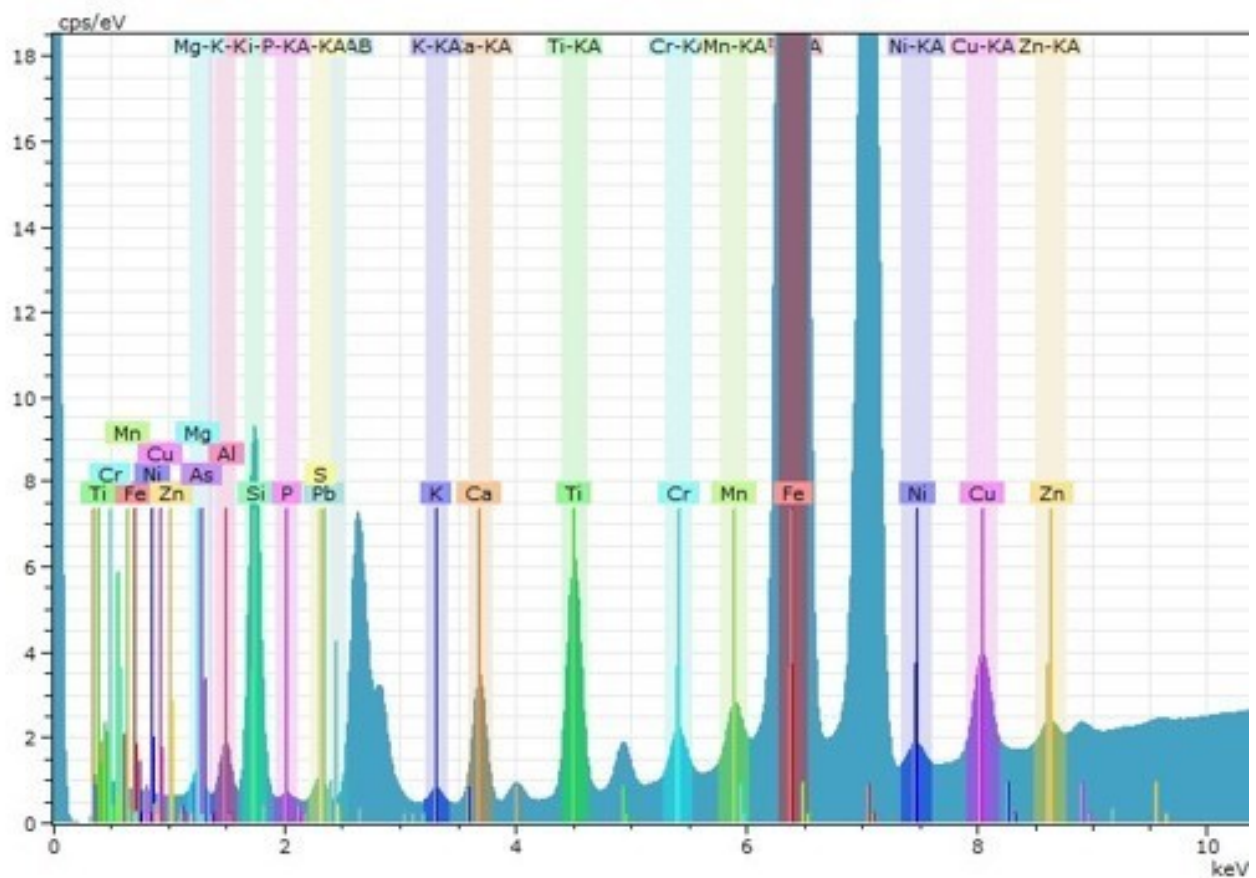


Figure 5. Representative spectrum of Energy-dispersive micro X-ray fluorescence spectrometry (ED-XRF) analysis with lines corresponding to measured elements .

As a consequence of the not well aerated technosol matter, the Eh–pH diagram for the Fe–S–H₂O system (Osseso-Asare et al., 1984; Figure 14) shows the presence of not oxidized (or only slightly oxidized) iron in Fe²⁺ form.

Application of pH-Eh diagram according to Ryu et al. (2002) show that the substantial proportion of As belongs to the stability field As₂S₃ (Figures 16), it means that it is present in the high toxic As³⁺ form. It is caused by the low degree of the technosol aeration (rH₂ 20;

Table 1). Also the higher content of sulphidic sulphur (S_s) in comparison to sulphate sulphur (S_{SO4}) presented in Table 3 explain the low degree of the As oxidation.

The studied technosols samples contain 0.07 – 2.22 % of S_{tot}. (Table 3). In the dump-field matter sulphidic sulphur (S_s in average 0.35 %) prevalence on sulphate sulphur (S_{SO4} 0.10 %) was recognized, thus the dump matter still contain a great portion of not oxidized primary sulphidic minerals.

The correlation between sulphidic sulphur S_s

content and pH ($r = -0.46$) show moderate (weak) of dependence between the content of sulfides and relationship. These data indicates a certain degree their ability to produce acidity.

Table 3. Sulphur and carbon analyses of technosol from dump-field Libiola.

Sample	S _{tot.}	S _{SO4}	S _s	C _{tot.}	C _{org.}	C _{inorg}
	%					
1	2.22	0.38	0.93	0.47	0.46	0.01
2	0.10	0.07	0.03	1.39	1.34	0.05
3	0.12	0.06	0.06	4.15	4.11	0.04
4	0.30	0.00	0.29	1.60	1.59	0.01
5	0.12	0.06	0.06	0.75	0.74	0.01
6	0.12	0.00	0.11	0.38	0.36	0.02
7	1.19	0.28	0.95	0.27	0.26	0.01
8	1.21	0.18	0.89	0.47	0.46	0.01
9	0.09	0.06	0.03	0.49	0.47	0.02
10	0.08	0.05	0.03	0.77	0.73	0.04
11	0.11	0.08	0.03	1.00	0.99	0.01
12	1.14	0.30	0.84	0.65	0.54	0.11
13	1.09	0.22	0.87	0.29	0.27	0.02
14	1.10	0.16	0.94	0.51	0.50	0.01
15	1.15	0.22	0.93	0.34	0.32	0.02
16	1.25	0.32	0.93	0.44	0.42	0.02
17	0.10	0.00	0.10	0.18	0.16	0.02
18	0.09	0.03	0.06	1.29	1.25	0.04
19	0.12	0.05	0.07	3.13	3.12	0.01
20	0.12	0.08	0.04	0.85	0.83	0.02
21	0.12	0.06	0.06	0.39	0.37	0.02
22	0.07	0.02	0.05	0.40	0.38	0.02
23	0.06	0.01	0.05	0.37	0.34	0.03
24	0.05	0.02	0.03	0.28	0.28	0.00
25	0.10	0.03	0.07	0.55	0.50	0.05
26	0.08	0.03	0.05	0.29	0.26	0.03
27	0.09	0.04	0.05	0.28	0.24	0.04
28	1.23	0.19	1.04	0.38	0.34	0.04
29	0.07	0.04	0.03	1.02	0.98	0.04
30	1.15	0.30	0.84	0.66	0.53	0.03
31	1.24	0.27	0.97	0.51	0.49	0.02
32	0.13	0.05	0.08	2.39	2.35	0.04
33	0.12	0.04	0.08	1.12	1.11	0.01
34	0.30	0.03	0.27	0.00	0.00	0.00
35	0.10	0.05	0.05	0.11	0.09	0.02
36	0.07	0.02	0.05	0.00	0.00	0.00
37	1.10	0.18	0.92	0.45	0.42	0.03
38	1.09	0.23	0.86	0.19	0.17	0.02
39	0.99	0.11	0.88	0.50	0.46	0.04
40	0.35	0.06	0.29	0.34	0.31	0.03
41	0.78	0.11	0.67	0.24	0.22	0.02
42	0.12	0.02	0.10	0.14	0.11	0.03
43	0.09	0.04	0.05	0.99	0.95	0.04
44	0.13	0.05	0.08	0.13	0.12	0.01
45	0.14	0.04	0.10	0.65	0.64	0.02
46	0.09	0.06	0.03	0.07	0.04	0.03
47	0.14	0.10	0.04	0.22	0.19	0.03
48	0.09	0.02	0.07	0.29	0.28	0.01
49	1.00	0.11	0.89	0.41	0.39	0.02
\bar{x}	0.45	0.10	0.35	0.67	0.64	0.02

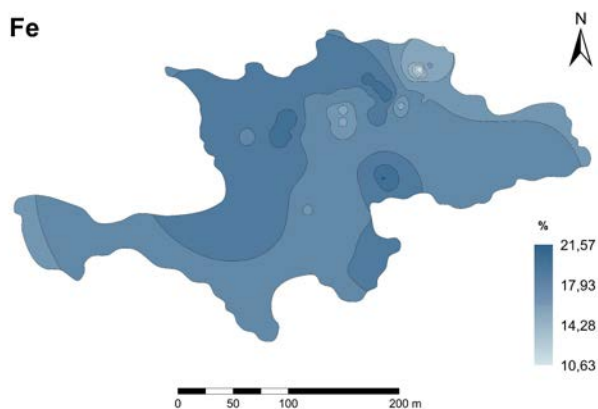


Figure 6. Distribution of Fe at the Libiola dump-field.

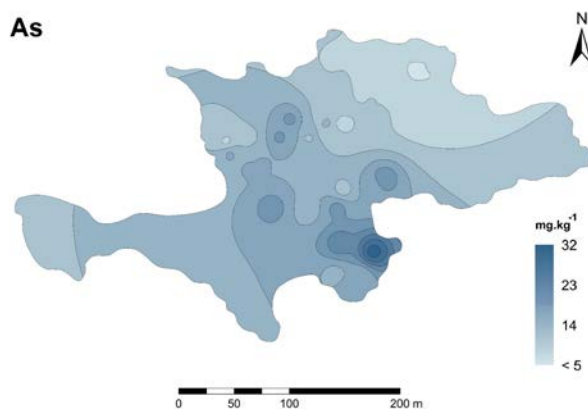


Figure 9. Distribution of As at the Libiola dump-field.

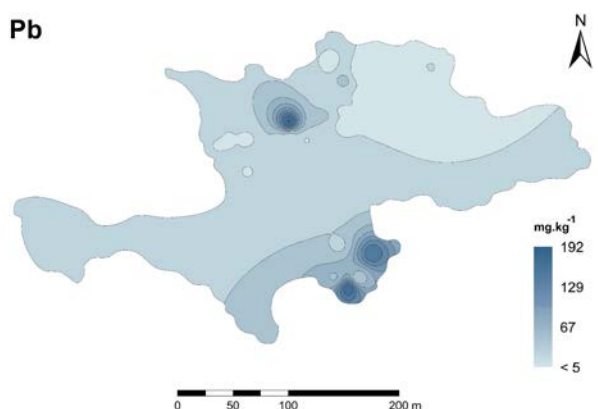


Figure 7. Distribution of Pb at the Libiola dump-field.

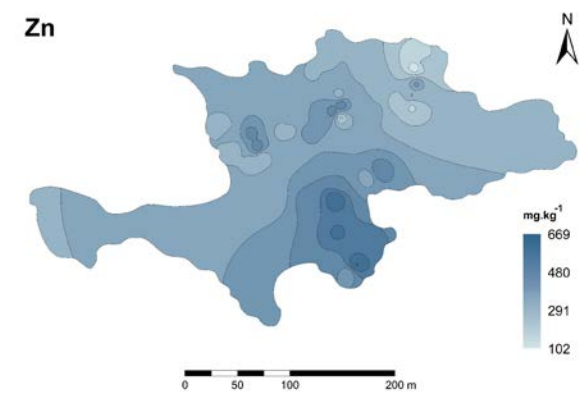


Figure 10. Distribution of Zn at the Libiola dump-field.

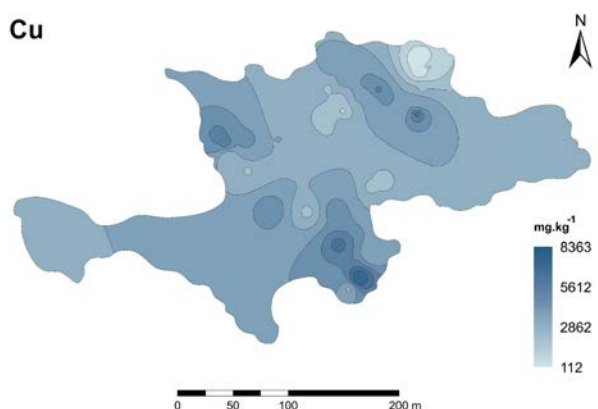


Figure 8. Distribution of Cu at the Libiola dump-field.

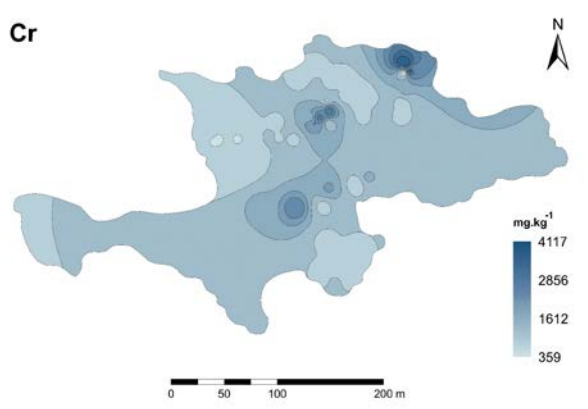


Figure 11. Distribution of Cr at the Libiola dump-field.

The correlation between pH and two most risk metal content show that Cu/pH ($r = -0.19$) Cu migrate in acid conditions much more better as Ni ($r = 0.43$). This finding is supported also by week correlation between Cu and Ni ($r = 0.18$).

Copper in technosol in pH/Eh plot according to Fairthorne et al. (1997) belongs predominantly to the stability field Cu^{2+} and only a very small part of the samples tends to the Cu (Fe_2O_3) field (Figure 15).

The total carbon content is with respect to the

character of the bedrocks (ultrabasic rocks) very low (in average 0.67 %) and the substantial part of this content depends on the concentration of the organic carbon (in average 0.64 %).

4. DISCUSSION

Several authors published basic descriptions of the PTEs contamination at Libiola dump field (Dinelli, et al., 1998; Marescotti et al., 2012; Buccheri

et al., 2014, 2019; Andráš et al., 2021) but first contour maps of selected compounds and elements (Fe_2O_3 , MgO , Cr_2O_3 , Cu, Ni), net acid-producing potential, and several selected minerals (sulphides, goethite, silicates) were published only by

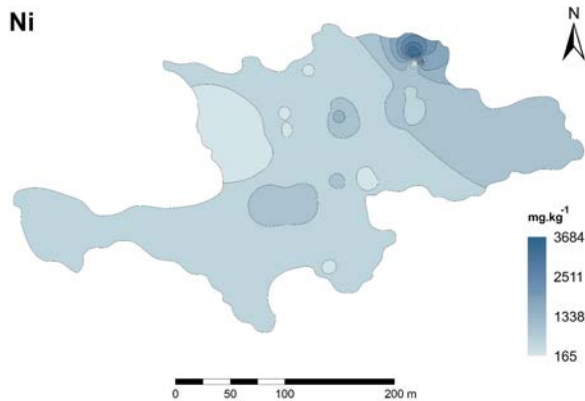


Figure 12. Distribution of Ni at the Libiola dump-field.

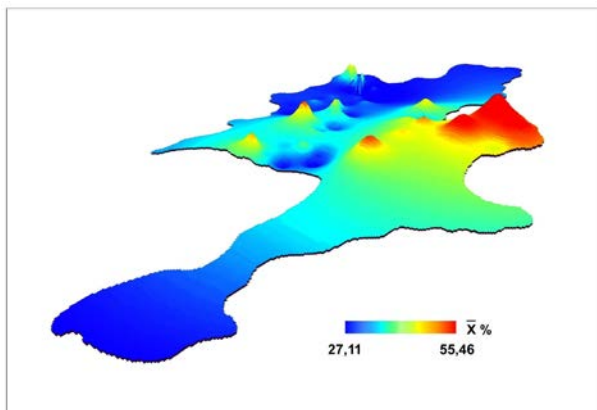


Figure 13. Cumulative distribution of all PTEs at the Libiola dump-field.

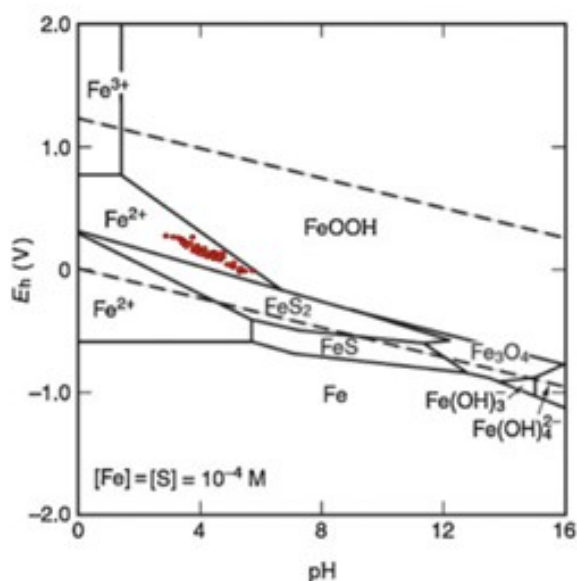


Figure 14. Eh-pH stability diagram for Fe-S- H_2O system at 25°C (Osseo-Asare et al., 1984).

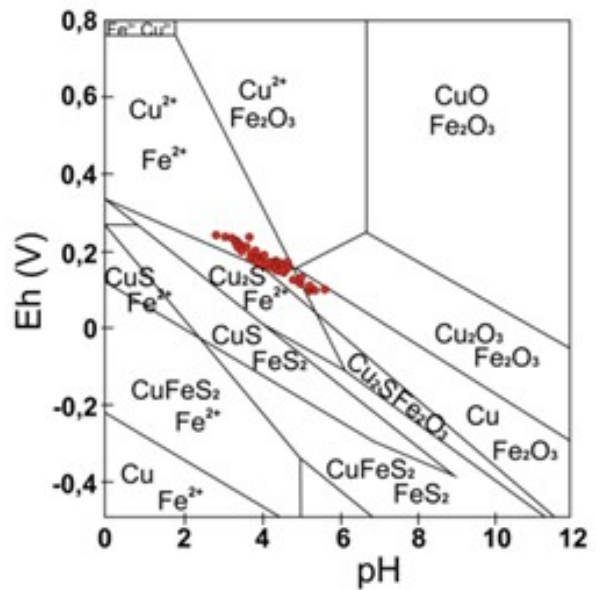


Figure 15. Eh-pH stability diagram for the Cu-Fe-S- H_2O system (Fairthorne et al., 1997).

(Marescotti et al., 2012, 2015). Our findings mostly correspond with data published in this work.

The PTEs distribution depends on the content of the individual metals in the bedrocks and by their migration, which is controlled by weathering, oxidation, geochemical properties of PTEs, by their solubility, influenced mainly by activity of acid drainage water, as well as by sorption capacity of the secondary minerals (e.g. clay minerals, Fe-hydroxides, described by (Marescotti et al., 2012) and by great erosion process on the steeply deeping slope (mostly without any vegetation cover) of the hill above the Gromolo creek.

Also the character of the soil solutions containing negative surface charge contribute to the PTEs immobilization. The equilibrium between the PTEs release from the technosol and of their adsorption processes during transport control the river pollution.

The pH data are identical with those of (Zotti et al., 2014). More authors studied the PTEs content in technosol at the Libiola deposit in a different context. Our results are comparable with those published by Dinelli et al. (1998) and Buscaroli et al., (2017), except Ni (244 – 455 $\text{mg}\cdot\text{kg}^{-1}$ vs. 165 – 3455 $\text{mg}\cdot\text{kg}^{-1}$ tab. 2. Zotti et al. (2014) presents comparable data for Cu content but lower data for the other metals. The highest mobility was observed in the case of PTEs, which are accumulated in the lower parts of the dump: Fe, Ni, Cr and Co. The generally very mobile Zn (Benvenuti et al., 1997, 2000; Lu et al., 2005) show the highest contents in the quarry on the top of the dump-hill. The rest of Zn was probably washed away along a steep slope into the Gromolo creek. This assumption is also confirmed by Zn

concentration data, which reach in the creek up to $2105 \text{ mg}\cdot\text{L}^{-1}$. Also, high concentrations of Cu and Ni (1057 and $44.78 \text{ mg}\cdot\text{L}^{-1}$) were in the creek drainage at the valley below the heap described (Singovszká et al., 2015; Buccheri et al., 2019; Buccheri & Andráš, 2022). These results document that the dump represents a significant source of metal pollution for the aquatic environment and confirm the link between geochemical conditions in technosol and surface water quality.

Italy has two different law limits for the content of PTEs given by the Italian Law Decree 152/2006 (Italiana, 2006) the first approving the Code on the Environment for industrial/ commercial use and the second one, more strict, for public and green areas. As the dump-field is several km away far from the village of Libiola, it is suitable to compare the PTEs contents with the law limits for industrial/commercial use.

The Cu content, except 3 samples, exceeds the limits allowed by law ($600 \text{ mg}\cdot\text{kg}^{-1}$). Pb contents exceed the stricter limits for residential and green areas only in three samples ($100 \text{ mg}\cdot\text{kg}^{-1}$). On the contrary, the Zn contents do not meet either of the limits (150 and $1,500 \text{ mg}\cdot\text{kg}^{-1}$), with exception of 4 samples that meet both. The Cd content in all samples respects the less strict standard ($15 \text{ mg}\cdot\text{kg}^{-1}$) and except for 11 samples which exceed the stricter standard ($2 \text{ mg}\cdot\text{kg}^{-1}$). Contents of Co don't exceed both the law limits (20 and $250 \text{ mg}\cdot\text{kg}^{-1}$). On the other hand, the Ni contents exceed the less strict limits ($500 \text{ mg}\cdot\text{kg}^{-1}$) in half of the samples. Except for one single sample, As contents don't exceed even the stricter standard (20 and $50 \text{ mg}\cdot\text{kg}^{-1}$). There are no limits established for the other studied elements in the Law Decree 152/2006.

The great part of the total sulphur content (0.45%) falls on the sulphidic sulphur (0.35%) and the sulphate sulphur forms only the rest (0.10%). It means that there is relatively great presence of undecomposed sulphides in the tailings which could possibly form increased acidic conditions, as a consequence of weathering processes.

The ultrabasic bedrocks at Libiola contain no carbonates, so therefore, the total carbon contents ($C_{\text{tot.}}$) are very low (in average 0.67%) and the substantial part of this carbon corresponds to the organic carbon ($\bar{x} = C_{\text{org.}} 0.64 \%$), whereas the inorganic carbon forms only the negligible part of the total carbon (0.02%). The lack of the carbonates significantly reduce the neutralization of the dump material and cause its high acidity, as described by Andráš et al. (2021) and others.

The GIS visualization of the contamination (Figs. 6–13) indicates, that the drainage water results first of all, the release of Ni and Zn to the environ-

ment, while the rest of the PTEs is less mobile and partly adsorbed by dump-material.

On the other hand, until the drainage water is rich in the inhabited area, its pH increase to value 6.91 and the contents of the PTEs are in comparison with the contents near the dump field generally ten times lower (Fe 5.1 , Cu 1057 , Pb 1.91 , Zn 2105 , As 7 , Sb 3.51 , Ni 44.78 , Co 16.06 , Cd $0.17 \text{ mg}\cdot\text{L}^{-1}$; Buccheri et al., 2014) and the environmental risk of such a water is relatively limited.

5. CONCLUSION

The main contaminants at the investigated dump-field are the following PTEs: Fe, Cu, Mn, Ni, Zn, Co, Pb and Sr. Only the Cu and Ni exceed substantially limits for soil, given by the Italian Legislativo Decree No. 152/06 (Italiana, 2006). The soil reaction is acid and the technogenous sediment/technosol is intensely oxidized and poorly aerated.

As sulphidic sulphur prevails in the technosol and carbonates absent, continuation of AMD/ARD formation is expected. The contrast between PTEs release and retention mechanisms underlines the high sensitivity of the system to changes in geochemical conditions. The relationship between increased sulfide content, the oxidation of which causes acidity, and low pH values has been confirmed. Higher acidity causes more significant Cu migration than Ni.

On the other hand, the negative charge of the soil solutions enables the immobilization of part of the metals released during the weathering process. Based on the obtained results, it is evident which parts of the dump field are most critical from the viewpoint of the individual PTEs' contamination.

The described environmental hazards correspond to the high PTEs contents (mainly of Cu and Ni) to the high toxicity of As^{3+} as well as to the weathering effectiveness and by the potential of the dump matter acidity production that could potentially intensify the release of the PTEs to the country elements. The risk is limited by the relatively great distance of the residential area (village Libiola).

These findings support the necessity of long-term monitoring and environmental risk assessment to minimize negative impacts on surface waters and soils in the Gromolo creek basin.

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