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1   **Earth walls as repositories of background levels of soil metal**  
2   **contaminants.**

3

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12

13   **Running title:** background levels of PTE in crude earth walls

14   **Abbreviations:**

15   PTE: potentially toxic elements

16   CEC: cation exchange capacity

17   EF: enrichment factor

18   FAAS: flame atomic absorption spectrometry

19   FP: open field soil profile

20   WP: wood soil profile

21

22   **Keywords:** background concentration, crude earth wall, Italy, potentially toxic elements

23   **Abstract**

24   Data about the background concentration of potentially toxic elements in soils is  
25   indispensable for establishing legislative limits, risk thresholds and, in general, assess the  
26   intensity of the pollution. Crude earth buildings are diffuse in the Mediterranean area and  
27   may be used as archives for original concentration of various metals. The building  
28   technique uses local soil which is mixed with water, let dry in formworks and covered with  
29   plaster. This has protected the soil material from external additions. The aim of this work  
30   was to evaluate the crude earth walls as repositories of the original concentration of some  
31   metals. Six crude earth walls were investigated in a location in north-western Italy. Their  
32   concentration in Cd, Cu, Cr, Ni, Pb and Zn were measured and compared with those of

33 surrounding soil profiles. Also, the results were compared with those of the Province.  
34 Organic carbon and pH seem to confirm the different evolution of the soils in the field with  
35 respect to that in the wall while iron oxides were not useful in discriminating the samples.  
36 Cadmium and Pb appeared to be the most reliable for the evaluation of the accumulated  
37 contamination evaluated while Cr and Ni are influenced by the lithogenic substratum.

38

39 **Introduction**

40 Very often anthropic activities result in the accumulation of potentially toxic elements  
41 (PTE) in soils ( Alloway, 1995; Ajmone-Marsan and Biasioli, 2010).

42 These inputs may affect the biosphere and the hydrosphere very intensively and therefore  
43 the environment quality and the human health. Industrial and other related anthropic  
44 activities intensified since the second half of 20<sup>th</sup> century, and caused a significant addition  
45 of PTE to the lithogenic background content (e.g. Chen et al., 2012; Costa et al., 2012;  
46 Eyles et al., 2013). The concentration of PTE in soil consists therefore of a natural pedo-  
47 geochemical fraction and an anthropogenic fraction. This latter fraction makes often  
48 difficult to quantify the natural background concentrations of soil inorganic contaminants,  
49 especially when diffuse contamination is evaluated on large areas (Reimann and Garrett,  
50 2005). Still, the knowledge of a contaminant background value is necessary for the  
51 assessment of the intensity of pollution and for the setting of regulatory levels.

52 In a study in the city of Agra, India, it was possible to trace the pollution by analyzing  
53 bricks of different ages that contained the original metals plus those added to the soil by  
54 industrial activities (Shrivastav et al., 1998). Similarly, the pre-industrial revolution  
55 pollution was defined relative to present day contamination by analyzing 800-year-old slag  
56 heaps produced by medieval metallurgical activities (Baron et al., 2006). In Ferrara (Italy),  
57 the composition of mediaeval and renaissance bricks was traced back to the sediments used

58 to manufacture them by using of a variety of analytical techniques (Bianchini et al., 2006).  
59 A study was conducted on soils of burial mounds to assess metal contamination over the  
60 last 3300 years and to conclude that cultivated soils were significantly enriched with  
61 respect to Cd, Pb, Zn and Cu and that forest soils were enriched with Pb (Elberling et al.,  
62 2010). More recently, the impact of human settlement was evaluated in Canada and  
63 revealed an abrupt increase of metal concentrations in soils after 1840 (Eyles et al., 2013).  
64 The construction of buildings with crude earth has been employed for centuries in the  
65 Mediterranean area and is still in use in various parts of the world. In the Piemonte region,  
66 in northwestern Italy, this technique has been used in the last centuries for residential and  
67 farm buildings (Maritano Comoglio and Pagliolico, 2008; Mattone, 2010). The soil  
68 material was usually mixed with water, lightly compressed, and let dry in wooden  
69 formworks to build the walls directly in their final location (Fig. 1). In both cases the soil  
70 material was collected *in situ* to minimize transport costs. The roof cover, as well some  
71 added plaster or external thin brick walls, have protected the soil material from major  
72 chemical changes and contaminant additions thus preserving a potential archival material  
73 for contamination studies.

74 The aim of this work was to evaluate the potential of crude earth walls to function as  
75 archive of uncontaminated soil material that could be used as background levels of PTE  
76 contamination. Concentration of metals in crude earth walls is compared with surrounding  
77 cultivated soils, a forest soil and the overall data for the Province.

## 78 **Materials and methods**

### 79 **Study area**

80 The area is located in and around the small town of Spinetta Marengo (44°54'N; 8°37'E,  
81 100 m asl; Province of Alessandria, Italy). The soils of the area were formed on the  
82 quaternary alluvial deposits of the Tanaro and Bormida River, but were preserved from

83 recent flooding events (1926, 1970, 1996, 1998) (Fig. 2). In this area, nowadays crossed by  
84 intense vehicular traffic, various chemical industrial plants are active since 1930 (Fig. 3).

85 In the town some ancient buildings are located with walls made entirely with crude earth,  
86 dug *in situ*. As these crude earth walls were already mapped in 1878, these soil materials  
87 can be useful to estimate the contamination of the area in the last century.

88 Data for the soils of the Province of Alessandria were used for comparison. These were  
89 obtained by the Regional Agency for the Protection of the Environment in a survey of  
90 diffuse contamination at the Regional scale. The validated database provides for the  
91 general properties of 63 soil samples and the metals for 115 samples. The analytical  
92 methods used were the same as described below.

93 ***Crude earth walls***

94 Samples were taken from 6 different buildings (Fig. 3). Each sample was taken from the  
95 wall inner part in order to avoid any contamination from the plaster or the brick cover. A  
96 minimum of 10 cm layer was removed from the surface before sampling about 3 kg of the  
97 soil material.

98 ***Soil profiles***

99 A profile was dug under a wood established and maintained since Napoleon age (circa  
100 1820). This profile would represent a soil that has not been affected by anthropic activities  
101 except for airborne contamination. Another profile, distant about 500 m from the first, was  
102 dug in a field crop (wheat) to represent the typical agricultural soil of the area.

103 The field crop soil profile (FP) was 80 cm deep and samples were taken every 20 cm. In  
104 the wood soil profile (WP) three samples were taken at 0-5 cm (WP2), 5-20 cm (WP3) and  
105 20-40 cm (WP4) depth. A sample was also taken from the litter (WP1, 0.5-0 cm).

106    ***Analytical methods***

107    Samples were air-dried, gently crushed (to <2 mm particle size) and sieved with a plastic  
108    sieve to prevent metal contamination (ISO 11464). A portion of each sample was further  
109    ground to <0.15 mm for *aqua regia* (HCl/HNO<sub>3</sub>, 3:1 solution) digestion (ISO 11466).  
110    Particle size distribution was determined by sedimentation and sieving (ISO 11277). The  
111    pH was determined in water at 1:5 soil:solution ratio (ISO 10390), electrical conductivity  
112    in a H<sub>2</sub>O solution, 1:5 soil:solution ratio (ISO 11265), organic carbon by elemental  
113    analyser (ISO 10694). An internal reference material was used to ensure that the two  
114    methods gave comparable results. Cation exchange capacity (CSC) was determined with  
115    BaCl<sub>2</sub> at pH 8.1 (ISO 13536) the exchangeable cations were measured via FAAS.  
116    Carbonates were measured using a volumetric method (ISO 10693).

117    Cadmium, Cu, Cr, Ni, Pb and Zn concentration was analysed in the *aqua regia* extracts by  
118    FAAS. Results were accepted when the coefficient of variation of duplicates was within  
119    5%. A blank and the Certified Reference Material 141 R (Community Bureau of  
120    Reference, Geel, Belgium) were included in each batch of analyses for quality control of  
121    metal measurements. Results were considered satisfactory when within a range of ± 10%  
122    of the certified value.

123    The total amount of pedogenic Fe oxides was estimated by a dithionite-citrate-bicarbonate  
124    (DCB) extraction (Mehra and Jackson, 1958) at room temperature for 16h. As a control, in  
125    order to measure the iron release from the silicate matrix, an extraction without dithionite  
126    was carried out (CB). The amorphous or poorly crystalline Fe oxide fraction was estimated  
127    by NH<sub>4</sub>-oxalate extraction (OX) (Schwertmann, 1964).

128    ***Calculation of the Enrichment Factor***

129    Assuming that all contaminants originate from diffuse sources and are deposited on the soil  
130    surface, the intensity of contamination can be evaluated by calculating the Enrichment

131 Factor (EF) which is obtained by dividing the concentration of a contaminant in the  
132 uppermost layer of a soil by its concentration in a deep layer which is supposed to have the  
133 same parent material and not to have been reached by contamination (Facchinelli et al.,  
134 2001, Boruvka et al. 2005; Fabietti et al., 2010; Biasioli et al., 2012). An EF>>1 indicates a  
135 surface enrichment of contaminants. In this study the crude earth material were taken as  
136 reference.

137

## 138 **Results and discussion**

### 139 ***Soil and earth walls properties***

140 In the soil material used in the buildings, the soil particle-size distribution of the <2 mm  
141 fraction is silty loam, in line with the local soils and with soils of the Province (Table 1).

142 Variations are observed in the superficial layers of the forest soil where aggregation of clay  
143 particles by organic matter might have resulted in a coarser texture.

144 The pH reveals some differences between the wall and the surrounding soils: the crude  
145 earth in the wall might have retained some carbonates as the pH is above neutrality (except  
146 for Wall 7) while in the soils of the cultivated profile and more so in the forest soil the  
147 carbonates appear to have leached out of the soil and the pH is below neutrality in the  
148 surface horizon. Organic matter content provides another indication that the soil used to  
149 manufacture the walls have been preserved from anthropic influence. The earth in the walls  
150 contains an average of 0.45% of organic carbon while cultivation has brought this content  
151 to 1.22% on the average which is in line with the mean content in the soils of the Province  
152 (1.14%). In the forest soil, where the absence of disturbance has allowed for organic matter  
153 accumulation, the content of carbon raised up to 4.6% in the first mineral layer. The cation  
154 exchange capacity follows the distribution of the main exchanger, clay and organic matter.

155 The soils of the Province show a high CSC but the range of values spans from 6.4 to 40.4  
156 cmol<sub>+/kg</sub> the latter being observed in a clayey soil.

157 ***Iron oxides***

158 Iron oxides have been used as indicators of time of soil formation in the region (Arduino et  
159 al., 1986; Ajmone-Marsan et al., 1988) and a preliminary investigation (Boero and Leone,  
160 1998) had shown that the geological and dynamical settings of the area could be described  
161 with the help of iron oxide mineralogy. Fe<sub>DCB</sub> would represent the total pedogenic iron  
162 oxides while Fe<sub>ox</sub> the amorphous or poorly crystalline Fe oxide fraction. Little differences  
163 were observed in the content of Fe extractable with oxalate or DCB (Table 2). The ratio of  
164 Fe<sub>ox</sub> with respect to the average Fe<sub>DCB</sub> is 14, 18 and 17% in the crude earth wall, in the FP  
165 and WP profile, respectively.

166 In general the ratio of crystalline Fe oxides to the total Fe (Fe<sub>DCB</sub>-Fe<sub>o</sub>)/Fe<sub>t</sub> gives an  
167 indication of the progress of pedogenesis and is usually lower in younger soils due to the  
168 short time of exposure to soil forming factors. Contrary to what expected, the crude earth  
169 wall show an average value of 51% while the FP samples average 40% and the WP layers  
170 33%. If the parent material is homogeneous, as it is expected in such a small area (Boero  
171 and Leone, 1998), the lower values of the profiles could be related to the role of organic  
172 matter, which in general hinders Fe oxides crystallisation (Schwertmann, 1988) but also  
173 may dissolve the Fe oxides by complexation. Under this hypothesis , this indicates that  
174 along a time span of hundreds of years iron oxides would not follow the general trend of an  
175 increase of crystallinity but would rather depend on short range soil evolution, i.e.  
176 accumulation of organic matter. An intense agriculture cultivation over 100 years or forest  
177 growth over 180 years could have diminished, via complexation/reduction the pedogenic  
178 evolution of Fe oxides.

179 **Potentially toxic elements**

180 **Copper**

181 In Italy Cu has been widely used both in the metallurgic industry and in agriculture as a  
182 fungicide during the last 120 years. It is now widely recognized as an anthropic metal  
183 contaminant. The average content of Cu in crude earth walls is 26.5 mg/kg (Table 4). The  
184 average total Cu in the FP profile is 59.0 mg/kg and is 67.5 mg/kg in the WP profile. In  
185 terms of Enrichment Factor of the first mineral horizon in the two soil profile, calculated  
186 on the content of the wall soil, the FP soil would have an average  $EF_{Cu}$  of 2.0 and 2.8 for  
187 FP and WP respectively. This would confirm that there has been a considerable deposition  
188 of contaminants in the last 120 years that more than doubled the soil Cu content. This  
189 appears to be even worse in the forest soil which was left undisturbed for nearly two  
190 centuries. If the EF is calculated over the arable soils of the entire Province (n=107), the  
191 value is 1.49. Similar results, EF above 1.5 for Cu, were obtained in a study [18] of the  
192 soils of the entire Piemonte Region which includes the Province of Alessandria described  
193 here.

194 **Zinc**

195 A distribution similar to Cu is observed for Zn. Zinc is a component of a variety of tools  
196 and is used in agriculture *e.g.* in the molecule of the pesticide mancozeb. The mean Zn  
197 concentration in crude earth wall is 78.5 mg/kg (Table 3), whereas it is 92.0 and 100.2  
198 mg/kg in FP and WP profiles respectively. The average EF is therefore 1.1 for the FP  
199 profile and 1.6 for WP. Contrary to what expected, however, the EF for the soils of the  
200 Province is below 1. This can be due to a different distribution of Zn in the lithological  
201 substrate. This confirms the limited possibility of extension of background values at scales  
202 larger than the local one (Reimann and Garrett, 2005). Evidently the Zn distribution in the

203 area allows the use of the background value obtained from crude earth walls only at a local  
204 scale.

205 In the FP profile the similarity between the two layers is probably due to the dilution effect  
206 of ploughing while in the WP profile the Zn content tends to diminish with depth,  
207 indicating a likely accumulation in the surface litter.

208 **Cadmium**

209 Cadmium in the walls is always below the detection limit but the average concentration in  
210 the FP and WP profiles is 1.9 and 3.8 mg/kg, respectively. It clearly appears that Cd is  
211 totally of anthropic origin. The arable soils of the Province have an average Cd content of  
212 0.8 mg/kg. Cadmium entered in the industrial production around 1930 and arrives to the  
213 soil through the use of P fertilizers (McLaughlin et al., 1996). In this case the metal  
214 appears to work well as an index of anthropic pollution.

215 **Lead**

216 Although its use as an antiknock additive in gasoline has been ruled out in Italy since 2002,  
217 previous depositions have built up in the soils and the soils sampled here are close to high  
218 traffic roads. Total Pb is on the average 24, 51 and 59 mg/kg in the crude earth wall, FP  
219 and WP profiles respectively. The highest values are observed in the surface layers of the  
220 undisturbed forest profile indicating that most of the accumulation was through  
221 atmospheric deposition. The EF for Pb is in fact very high for all soils, up to 3.3 in the  
222 upper mineral layer of the WP profile. The EF is lower in the cultivated profile due  
223 probably to the dilution effects of soil labouring. Comparison with soils of the Province is  
224 not useful in this case as their EF is around 1. This might be due to the absence of a  
225 specific source of pollution, a road, a city close to the sampling points of the province  
226 survey.

227 **Nickel and chromium**

228 While the Ni average concentration in the crude earth wall is 71.5 mg/kg, in the FP and  
229 WP it is 212 and 247 mg/kg, respectively (Table 3). In the cultivated soils we have  
230 therefore a high increase of concentration with respect to crude earth with a mean of EF is  
231 3.0 in FP and 3.2 in WP. This could be due to the anthropic activities, as confirmed by the  
232 average EF of arable soils of the Province which is 1.05. However, as the concentration  
233 and the EF within the profile tend to remain constant with depth, a lithogenic source should  
234 also be taken in account because of the occurrence of some serpentinitic components in the  
235 parent material (Ajmone-Marsan et al., 2008).

236 Similar results were obtained for Cr as the two metals are present in the same minerals.  
237 The total Cr in wall crude earth is 76.0 mg/kg on average; in FP and WP this concentration  
238 is 175 and 191 mg/kg respectively. Again the EF (average 2.3 for FP and 2.5 for WP)  
239 indicates some contamination but the increasing concentration towards deeper horizons  
240 suggests a strong lithogenic contribution.

241

## 242 **Conclusions**

243 The soil material (crude earth) that was used for manufacturing the walls appears to have  
244 been protected from metal pollution during the last 120 years. It is therefore useful to  
245 define background concentrations of several metals although a more extensive survey of  
246 contamination of the soils in the area is necessary to validate the data. A comparison with a  
247 cultivated soil profile, an undisturbed forest soil profile and the results of a contamination  
248 survey in the larger area indicated that post-industrial metal contamination can be  
249 appreciated by calculating the Enrichment Factor. Among the metals Cd and Pb appeared  
250 to be the most reliably evaluated while Cr and Ni seemed to be influenced by the lithogenic  
251 substratum. These data contribute to the general picture of soil contamination in the region  
252 and may help in the establishment of thresholds for environmental risk assessment

253

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258

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332 Figure Captions

333 Figure 1: partially disrupted earth walls showing the plaster cover

334 Figure 2: Location of the study area

335 Figure 3: Location of the soil profiles (WP and FP) and soil-walls in Spinetta Marengo

336

Table 1:

General properties of the crude earth walls, soil profiles (FP and WP) and the Province territory

<b>Sample</b>	<b>Depth</b>	<b>pH</b>	<b>pH</b>	<b>C org<sup>a</sup></b>	<b>CEC<sup>b</sup></b>	<b>sand</b>	<b>silt</b>	<b>clay</b>
	cm	H <sub>2</sub> O	KCl	%	cmol <sub>+</sub> /kg	%		
wall 1		7.5	7.4	0.43	9.0	48	40	12
wall 2		7.6	7.6	0.43	6.2	31	54	15
wall 5		7.4	7.3	0.39	15.1	45	37	18
wall 7		6.4	6.0	0.57	9.0	47	44	10
wall 8		7.4	7.3	0.43	4.5	48	39	13
wall 9		7.3	7.2	0.47	11.8	38	40	23
FP1	0-20	6.4	5.3	1.30	11.4	32	52	16
FP2	20-40	7.1	6.3	1.14	11.4	34	49	17
FP3	40-60	7.3	5.7	0.77	18.5	28	32	40
FP4	60-80	8.1	7.0	0.67	18.4	30	31	39
WP1	0.5-0	6.6	6.0	6.85	7.4	46	48	6
WP2	0-5	6.8	5.9	4.60	25.4	40	51	10
WP3	5-20	6.7	5.6	1.93	16.8	34	51	15
WP4	20-40	6.2	4.8	1.52	20.2	29	45	27
<b>Province of Alessandria</b>								
Mean	0-15	7.1	6.1	1.14	23.6	41	42	17
Median		7.7	6.7	0.91	23.1	34	44	16
St. Dev.		1.16	1.39	0.70	8.01	19	14	10
C.V %		16	23	61	33.9	46	32	60
max		8.7	7.9	3.83	40.4	83	80	45
min		4.9	3.7	0.33	6.4	9	14	3
n		63	49	50	63	63	63	63

<sup>a</sup>C org: organic carbon; <sup>b</sup>CEC: cation exchange capacity

Table 2: Iron forms<sup>\*</sup> in crude earth wall material and soil profiles (FP and WP)

Sample	Depth	Total	DCB <sup>a</sup>	CB <sup>b</sup>	Oxalate	DCB/ total	Oxalate/DCB
	Cm	%			%		
wall 1		2.14	1.25	0.02	0.18	57.7	14.9
wall 2		2.45	2.06	0.01	0.27	83.7	13.0
wall 5		3.28	1.79	0.01	0.23	54.3	12.8
wall 7		2.42	1.20	0.01	0.20	49.1	16.6
wall 8		2.56	1.24	0.01	0.21	47.9	16.7
wall 9		2.95	1.78	0.01	0.22	59.9	12.7
FP1	0-20	2.80	1.38	0.03	0.24	48.2	17.9
FP2	20-40	2.84	1.35	0.02	0.24	46.9	17.9
FP3	40-60	4.07	2.52	0.02	0.28	61.4	11.4
FP4	60-80	3.98	2.44	0.03	0.28	60.6	11.4
WP1	0.5-0	2.78	1.02	0.05	0.19	34.7	19.9
WP2	0-5	2.86	1.14	0.06	0.19	37.8	17.9
WP3	5-20	2.90	1.04	0.04	0.20	34.2	20.2
WP4	20-40	3.38	1.55	0.04	0.21	44.5	14.1

5 <sup>a</sup>DCB: dithionite-citrate-bicarbonate extractable; <sup>b</sup>CB: citrate-bicarbonate extractable

Table 3: Total PTE contents in crude earth walls, soil profiles (FP and WP) and the Province territory

<b>Sample</b>	<b>Depth</b>	<b>Cu</b>	<b>Zn</b>	<b>Cd</b>	<b>Pb</b>	<b>Cr</b>	<b>Ni</b>
	cm	mg/kg					
wall 1		30	84	<0.1	13	82	70
wall 2		31	69	<0.1	20	119	89
wall 5		21	96	<0.1	50	75	81
wall 7		27	72	<0.1	18	62	66
wall 8		23	65	<0.1	19	64	58
wall 9		27	85	<0.1	22	54	65
FP1	0-20	54	86	1.9	51	175	212
FP2	20-40	64	92	1.9	50	175	212
FP3	40-60	49	85	2.2	30	210	330
FP4	60-80	72	102	2.8	29	182	291
WP1	0.5-0	64	122	3.2	70	170	202
WP2	0-5	74	124	3.6	78	190	228
WP3	5-20	70	100	4.4	54	194	240
WP4	20-40	62	94	4.0	34	212	320
<b>Province of Alessandria</b>							
Mean	0-15	41	51	0.7	19	108	76
Median		29	48	0.8	18	84	63
St. Dev.		47.7	17.1	0.4	7.5	72.5	47.1
C.V.%		116	34	60	39	67	62
max		354	94	2	47	418	246
min		5	19	0	4	9	20
n		115	115	115	115	115	115

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Table 4: Average values of total Cu, Zn, Cd, Pb, Cr and Ni of wall samples and soil profile horizons; enrichment factor (EF) of the first mineral horizon of field profile ( $EF_{FP}$ ) and of wood profile ( $EF_{WP}$ ) with respect the average values in the wall samples.

Samples	Depth	Cu	Zn	Cd	Pb	Cr	Ni
	cm	mg/kg					
wall	-	26.5	78.5	<0.1	23.7	76.0	71.5
FP4	0-40	59.0	92.0	1.9	51	17.5	212
WP	0.5-0 and 0-40	67.5	100.2	3.8	59	191	247
$EF_{FP}$	-	2.0	1.0	>19	2.2	2.3	2.3
$EF_{WP}$	-	2.8	1.6	>36	3.3	2.5	3.2

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