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Influence of accumulation of heaps of steel slag on the environment: determination of heavy metals content in the soils

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ABSTRACT

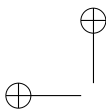
The presence of high level of heavy metals involves a human healthy risk that could induce chronic diseases. This work reports on the metal contamination due to heaps of steel-slag accumulated during more than 40 years in allotment and industrial areas in the southern part of Madrid (Spain). Several slag and soil samples were collected in an area of 10 km² and characterized by different conventional (XRD and XRF) and not so common methods (ESEM, thermoluminescence and EDS-WDS). The analysis reveal the presence of: (i) important amounts of Fe (43%), Mg (26%), Si (1.1%), Mn (4.6%), S (6.5%) in the form of Fe-rich slag phases (wüstite, magnetite...), Si and Ca-rich phases (larnite, gehlenite...), Cr (chromite), Mn (bustamite) and graphite, (ii) traces of some other contaminants such as Cr (77 ppm), Zn (3500 ppm), Ba (3000 ppm), Pb (700 ppm) or Cu (500 ppm) on pathway soil samples that come from the steel slag, and (iii) Co (13 ppm), Pb (78 ppm) and V (54 ppm) in farmland soil samples. Although the existing heavy metals content is not appropriate for the current use, the extremely high metal contamination of the surrounding area is more worrying. The properties of the soil farmlands (pH circa 7, 13% of clay, mainly illite, and 1-4% of organic matter content) show suitable conditions for the retention of cationic metals, but further studies on the mobilization of these elements have to be performed to determine the possibility of severe human health risks. This sort of study could provide useful information for the politicians regarding the appropriate use of the territory to prevent possible health hazard for the population.

Key words: EDS, ESEM, metal contamination, steel slag, TL, XRD, XRF.

INTRODUCTION

The production of iron and steel yields important amounts of slag as by-products, which is one of the main sources of metal environmental pollution. Long time ago, the industrial activities were characterized by a lack of pollution control involving a potential release not only represented by hazardous chemicals (organic, organometallics or inorganic compounds), but also by metals into the environment. There is concern all over the world as the accumulation of metals increases the

due toxic effects such as neurological, hepatic, or renal upsets. It is well-known that, for instance, levels of: (i) cobalt could act inhibiting the growth of plants (Chatterjee and Chatterjee 2000) and could damage the lungs and heart (ATSDR 2004); (ii) lead could cause damage in nervous system or kidneys (ATSDR 2004) depending on the pH, the solubility and bioaccessibility of lead from soils can change (Ren et al. 2006); (iii) vanadium could produce lung irritation, coughing, wheezing, chest pain, runny nose and a sore throat (ATSDR 2004); however, there is few information about vanadium



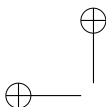
soil to improve the environmental quality, and, thereby, decrease the risk on the population. Based partially on the CLEA (Contaminate Land Exposure Assessment) model employed in England and Wales (Environment Agency 2002), the local authorities in Madrid (Spain) standardized the levels of soil contaminants assuming three different scenes depending on the land use: industrial, urban and others (e.g. agricultural crops) (Comunidad de Madrid 2006). Of course, it should be necessary to take into account many other aspects, such as the form of the elements (with mobile forms or not), the type of soil (with clay minerals) and the concentration of humus (Palm 1994, Grytsyuk et al. 2006). One of the main challenges required from the local authorities or policy makers concerning the metal contamination is to define new methodologies that are faster, simpler, more reliable and cheaper, which look for different and sensitive analytical techniques to discriminate, among others, (i) geogenic and anthropogenic origin of metal concentration, (ii) biological interactions including oxidation-reduction processes, (iii) phase complexation, (iv) precipitation, (v) dissolution, etc. In addition to the conventional methods commonly employed for sample characterization (X-ray diffraction, XRD, scanning electron microscope, SEM, Inductively Coupled Plasma Mass Spectrometry, ICP-MS, or X-ray fluorescence, XRF), there are some others techniques that could contribute especially to single-particle characterization, namely: environmental scanning electron microscope (ESEM), thermoluminescence (TL) or energy-dispersion, and wavelength-dispersive spectrometry (EDS-WDS), depending on the nature of different soil constituents. All of them show pros and cons, but all together offer an excellent sample characterization since the deficiency of one technique can be covered by some of the others (Gunst et al. 2000).

The area here studied (Getafe), which is located in the southern part of Madrid (Spain) in the Manzanares River basin, is one of the most industrialized areas with more than 150 000 inhabitants. One can easily appreciate how the many pathways, in this flat area, are paved by tons of slag heaps coming from the Aristrain's iron and steel factory covering a surface of several ha. In the steel plants of Madrid, crude steel is produced from

relieves the phosphorous element. In the second step, oxygen and CaCO_3 are added to reduce the carbon content of the melt. This produces calcium silicates such as gehlenite, larnite and bredigite (Luxan et al. 2000), which help to remove the sulphur. During both stages, huge amounts of carbon dioxide are produced; as an example, the Japanese iron and steel industry accounts for approximately 15% of all Japan's greenhouse gas emissions (Gielen and Moriguchi 2002). The aim of the present work is to determine the effect of the presence of the aforementioned heaps of steel slag in a part of the district of Getafe environment. For such purpose, several slag and soil samples, selected from different areas, have been analysed by conventional mineralogical and geochemical methodology that provide information on the spread of contamination in the affected area. Thus, XRD, ESEM, XRF, TL and EDS-WDS have been performed to the sample characterization.

EXPERIMENTAL

Fifteen representative samples, among almost 200 collected, were selected in an area of about 10 km² including allotments and industrial suburbs in Villaverde-Getafe-Parla, in the southern part of Madrid (Spain) surrounding the Aristrain's iron and steel factory. All sampling locations were on ground with unrestricted access. The slag phases were characterized by X-ray powder diffraction using a Phillips PW1710/00 powder diffractometer with a CuK_α radiation source, equipped with a graphite monochromator. Patterns were obtained by step scanning from 2° to 64° (2θ in steps of 0.020°; 4 s per step) and compared with the XRD card files of the Joint Committee on Powder Diffraction Standards. Mineral identification was performed using X-powder software developed by Martin-Ramos (2004). Slag samples were also analyzed using a FEI QUANTA 200 ESEM operating under low vacuum conditions and equipped with both secondary electron and backscattering detectors. The microscope was equipped with two X-ray detectors (Oxford Analytical-Inca Instruments) that could be used simultaneously or in alternating mode. The average and single-spot chemical analysis of samples was per-



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with sputtered graphite, under high vacuum conditions (10^{-4} torr). WDS can detect elements at concentrations one order of magnitude lower than EDS can using the following standards: (C) Calcite, (Fe) Iron, (Ba) BaF_2 , (Mn) Manganese, (Cr) Chromium, (Cl) NaCl , (Na) Albite, (Si) Orthoclase, (Al) Orthoclase, (K) KBr , (Ti) Titanium, (Cu) Copper, (P) GaP , (Sn) Sn, (S) Pyrite and (Mg) periclase. TL measurements were achieved using an automated Risø TL system model TL DA-12 (Bøtter-Jensen and Duller 1992); this TL-reader is provided with an EMI 9635 QA photomultiplier, and the emission was observed through a blue filter (FIB002 of the Melles-Griot Company), in which the wavelength is peaked at 320-480 nm; FWHM is 80 ± 16 nm and peak transmittance (minimum) is 60%. It is also provided with a $^{90}\text{Sr}/^{90}\text{Y}$ source with a dose rate of 0.021 Gy s^{-1} calibrated against a ^{60}Co photon source in a secondary standards laboratory (Correcher and Delgado 1998). All TL measurements were made using a linear heating rate of 5 K/s from room temperature up to 773 K under N_2 atmosphere. Four aliquots of 5.0 ± 0.1 mg, each of the 15 steel slag samples were used for each measurement. The samples were carefully powdered with an agate pestle and mortar to avoid triboluminescence (Garcia-Guinea and Correcher 2000). Analysis of soil sample was carried out by X-Ray Fluorescence using a Philips PW1410 spectrometer with Sc-Mo tube (Si, Al, Ti, Fe, Mg, Mn, Ca, Na and K elements).

RESULTS AND DISCUSSION

GEOLOGICAL FRAME AND SAMPLING AREA

The studied area is situated in the Manzanares River basin where Tertiary age formations are incised by younger Quaternary age materials as river deposits. The lithologies of Tertiary materials are mainly composed by clay-rich levels with two different associations, gypsum and sandstone (Fig. 1a). The first formation is a thick level of brownish clays with intercalated beds of gypsum and gypsum-rich marls ranging from 0.5 to 1 m thickness and growing downwards. The second type of materials is a greenish clay level with micaceous sands

cerning the Quaternary river-banks and valley materials, they are composed by many different types with minor quantities of sands and silt. The valley-filled sediment levels covering the top of the banks, with 1 to 5 m in depth, are composed by fine to medium sized sands (Fig. 1a). The sand is formed by quartz with very small parts of gravel, chert, sepiolite and limestone. A quarry is close to the studied area for extracting quartz-rich sands. The studied area (10 km^2) holds important amounts of steel iron slag samples, which are usually employed as drainage pathways in local allotments and is consequently exposed to weathering by rainfall, wind and different types of vehicles. Nowadays, this area combines industrial and agricultural activities and the population is progressively increasing. Figure 1b depicts a sketch in which the irrigated and dry-farmed lands are quite close to the local path mainly formed by clays, gypsum and limestone, and covered by a 60 cm-layer of slag dump.

STEEL-SLAGS CHARACTERIZATION

All collected samples, located at 30 cm depth from the surface, exhibit a high level of porosity regardless of the size of the piece (Fig. 2). This property is especially interesting for local farmers who use this material in their farmlands since it can host amounts of water that is very useful during drought periods. Such behavior has also been observed in some areas of Canary Islands where local farmers employ fragments of lava (also highly porous materials) for similar purposes. At a glance, one can guess a very different composition of the slag because of (i) the color (from deep black to grey), (ii) the texture (glassy with several drop-shaped inclusions), (iii) the size of pore and (iv) the density that differs considerably from sample to sample. The mineralogical composition was determined by XRD (X-ray diffraction method), and most of the samples are a mixture of several phases. The list of the identified phases with their corresponding stoichiometric composition and the corresponding (International Centre for Diffraction Data) XRD reference cards are shown in Table I. This analysis shows, on one hand, plenty of uncommon mineral phases

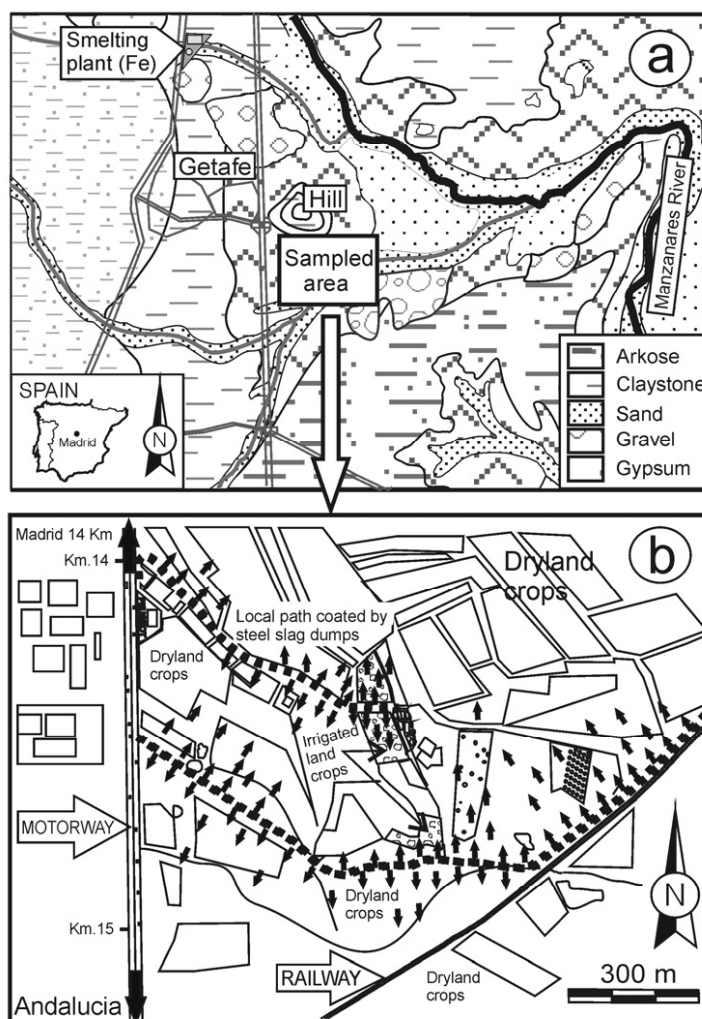


Fig. 1 – (a) Geological sketch of the studied and sampled area. (b) Location map of the area affected by the presence of steel-slag dumps.

concentration of metal contaminants such as Fe (43%), Mg (26%), Cr (1.1%), Mn (till 4.6%), in the form of Fe-rich slag phases (wüstite, magnetite, goethite...), Cr (chromite), and Mn (bustamite), with an important content of S (6.5%).

These steel slag materials could create confusion among beginners that have been catalogued as meteorites or ‘pseudometeorites’ due to their external aspect. Nevertheless, possible doubts about this fact can be clarified by the TL technique that arises as a good possibility to

lator or semiconductor) when it is heated after being irradiated by some kind of radiation such as X-rays, gamma rays, beam of electrons, cosmic rays, etc. (McKeever 1985). During the heating, the TL signal is detected by a photomultiplier tube and recorded as a function of the temperature or wavelength. The resulting curve is called a TL curve or glow curve; the luminescent intensity and the shape of this glow curve are functions of radiation dose and heating rate. The presence of a huge amount of samples, close to the iron smelting factory, and the min-



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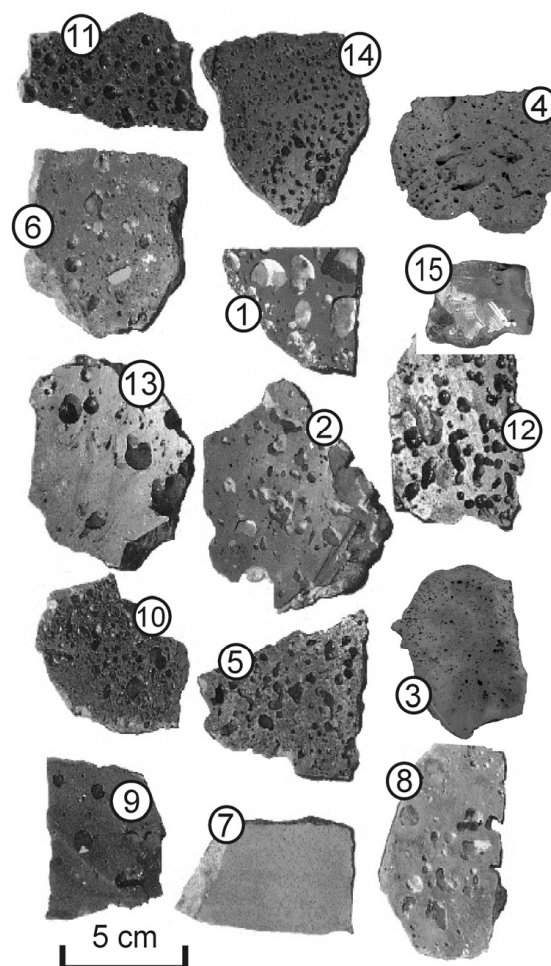


Fig. 2 – Fifteen of the more representative steel slags samples, selected among 200 specimens, from different places of Villaverde-Getafe-Parla in an area of 10 km² in the southern part of Madrid.

carried out to distinguish geogenic from anthropogenic origin of the samples. The meteorites that come from the main asteroid belts placed between Jupiter and Mars have usually been exposed to high levels of radiation (cosmic rays) and the presence inside of such meteorites of cosmogenic radioisotopes for a long time. This fact concerns the samples that arrive at the Earth's surface possessing a very intense TL signal regardless of their composition.

In Figure 3, 14 collected samples and one cata-

(between Getafe and Villaverde villages), and considered by Dr. Martínez-Frías to be a possible meteorite or even more, a pseudo-meteorite (Martínez-Frías and Martínez-Frías et al. 1999, 2004). All of the collected samples tested (four replicates each) exhibit a very low TL intensity, never higher than 200a.u. Although sample number 1 is four times brighter than the rest (to 800 a.u.), the TL emission of this sample can be considered almost negligible when compared to the natural TL of other terrestrial and particularly extraterrestrial samples (Correcher et al. 2007). This bigger intensity is probably due to the several analyses that have been made in different North American laboratories considering not only short irradiations during the studies of the samples over the last ten years, but also the associated cosmic rays at airport controls during the journeys among the laboratories. The conclusion after the TL study of the 15 samples exhibit a very low TL emission because of the last heating (usually known as ‘zeroing’) of the samples were made only a short time ago (less than 50 years) and never compared with geological times.

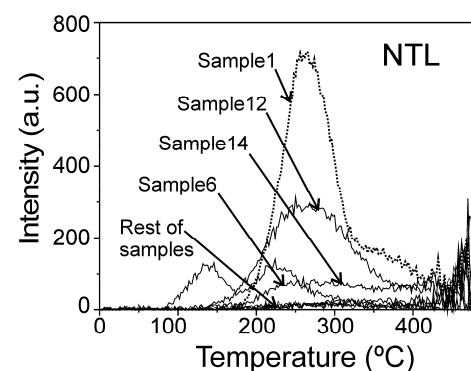


Fig. 3 – Thermoluminescence glow curves of slag materials; very low emission signals in all cases.

Some of selected ESEM images obtained from two of the slags (number 2 and 10) are respectively shown in Figures 4a and b. As illustrated in Figure 4a, the core corresponds to a grain of leftover magnesia, i.e., a magnesite refractory phase surrounded by a thin internal rim composed of a mixture of MgCO₃ and CaO. The matrix contains little amounts of calcium-

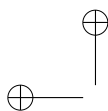


TABLE I
Quantitative analyses of slag phases (in percentage) by X-ray diffraction (powder method) including (i) the list of the detected phases in the analyzed steel slag, (ii) the ICDD (International Centre for Diffraction Data) card file for XRD and (iii) the stequiometric formula.

Phases		ICDD*	Sample number														
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Wüstite	FeO	6-615	47	51	35		50			85		60	50		20		
Larnite	Ca ₂ SiO ₄	29-371	18	4							15		30				
Gehlenite	Ca ₂ Al ₂ SiO ₇	35-755	25		40	58	25				5			75			
Chromite	FeO.(Cr,Al) ₂ O ₃	34-140	10	8								25			15		
Magnetite	FeO.Fe ₂ O ₃	19-629			25							5					
Kirschsteinite	CaFeSiO ₄	34-98		22		39	20							25	30		
Monticellite	CaMgSiO ₄	35-590					5								35		
Akaganeite	β-FeOOH	34-1266															
Bredigite	Ca ₇ Mg(SiO ₄) ₄	36-399							95								
Bustamite	(Mn,Ca) ₃ Si ₃ O ₉	26-1066						100									
Graphite	C	25-284							5								
Mayenite	Ca ₁₂ Al ₁₄ O ₃₃	9-413		12						15	80	10	15				
Quartz	SiO ₂	33-1161														3	
Calcite	CaCO ₃	5-586														2	10
Sillimanite	Al ₂ O ₃ .SiO ₂	38-471															90
Magnesite	MgCO ₃	80-870		3									5				
Goethite	α-FeOOH	29-713				3											
Pseudo-wollastonite	CaSiO ₃	31-300														95	

of neo-formed inclusions of MgCO₃ and BaCO₃ can be explained by the use of dirty natural limes (CaCO₃ with CaMg(CO₃)₂ or dolomite with barite veins (BaSO₄), typical of Palaeozoic limestones). In addition, the presence of 1% copper and 1% chromium could be better explained as coming from electrical wires or scrap chromium steel. Some neo-formed hematite (Fe₂O₃) spheres with hexagonal crystal shapes are recognizable within some slag samples, as micrometer scale grains (Fig. 4b that corresponds to the slag 10). The compositions of the number 2 slag corresponding to white core, colourless rim, external rim, brown matrix, white and dark areas in the matrix and sparkling inclusions are shown in Table II. These analyses indicate that the maximum relative content of iron is mainly located in the matrix and in the external rim of the slag, which could help this metal to diffuse in a more suitable way from the slag to the environment. Average and single-spot analyses were plotted successively from the white core to the encircling matrix. In general, dark areas in the samples can be linked in the presence of high relative concentrations of Fe. Some amounts of toxic

sequent higher levels of contamination in soil samples. The oxygen:iron ratio suggests that the above crystals are composed of hematite (Fe₂O₃) with accessory mayenite (Ca₁₂Al₁₄O₃₃). The list of stable phases at room temperature (Table I) shows that the sample had passed through the two classic stages of steel production (Parais 1978). In the first step, large amounts of carbon are added; in this piece of slag, some amounts of graphite and wüstite (FeO) could be found. The latter is unstable under normal environmental conditions and appears as a white, oxidised crust. This carbon is usually added to raw material to remove oxygen from ores and to melt them. As observed in Figure 5a, one can appreciate the presence of large amounts of wüstite in the slag number 2 that were produced during the manufacturing process to induce a strong iron dephosphorylation usually from 0.2% up to 0.01%. Similarly, Figure 5b explains the great abundance of calcium-iron silicates in this slag, since large amounts of limestone are added to bring about greater desulphurisation during the second manufacturing step. In this second step, oxygen was used to decrease the carbon content in the melt by the addition



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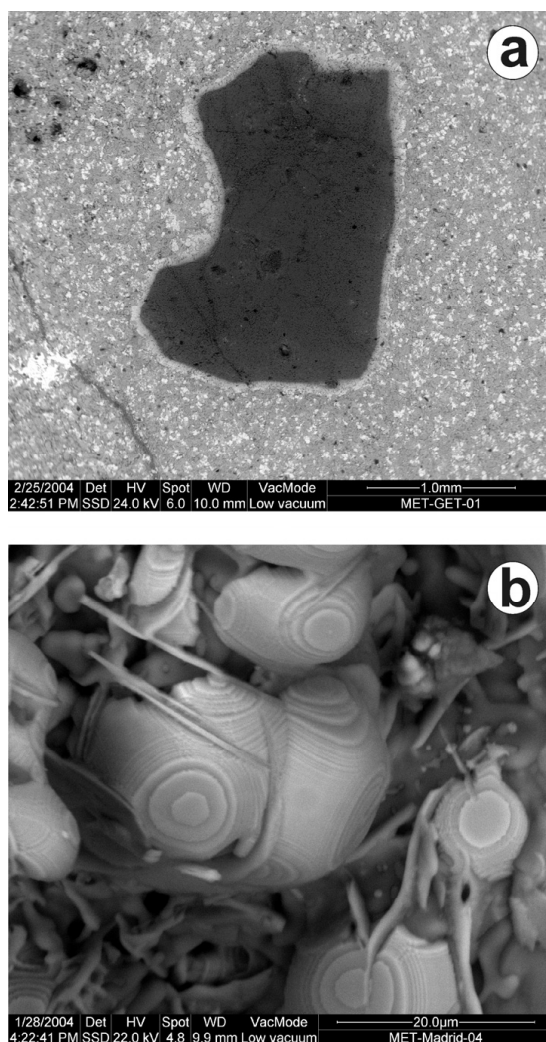


Fig. 4 – Selected images from the ESEM analyses: (a) Magnesite (MgCO_3) grain and (b) Hematite (Fe_2O_3) spherical crystals; note the hexagonal shapes along the c axis.

by the use of clay or feldspar raw materials in the second manufacturing stage; these materials generate unstable mayenite oxide ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$).

As the composition of the slags involves a high content of heavy metals, the recycling of steel slags is of great interest for both the conservation of natural mineral resources and the decrease of metal contamination. Currently, modern or modernized steelmaking factories,

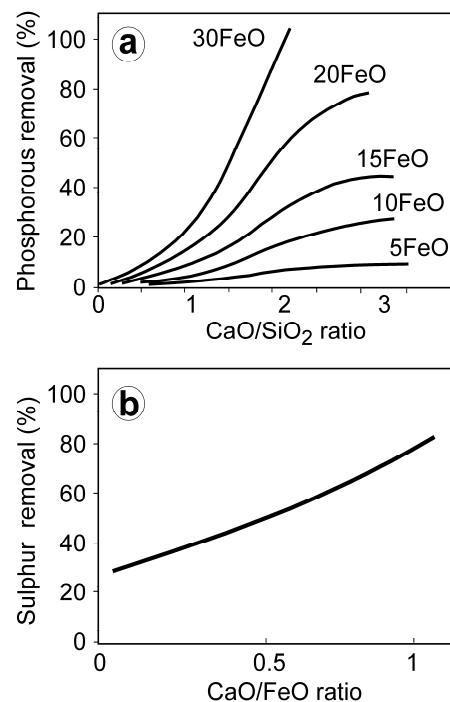


Fig. 5 – (a) Evolution of the Phosphorus release depending on the CaO/SiO_2 ratio. It explains the great abundance of wüstite in Getafe slag heaps: large amounts of it were produced in the manufacturing process to induce greater dephosphorylation of the iron. (b) Evolution of the Sulphur removal *versus* CaO/FeO ratio. It makes clear the abundance of calcium-iron silicates: large amounts of them were produced in the manufacturing process to induce greater desulphurisation during the second manufacturing stage.

products are discarded at controlled recycling centers to prevent the transfer of heavy metals to the environment.

CHEMICAL ANALYSIS OF SOILS

The concentration of heavy metals was measured at different points of pathways close to the irrigated lands (Table III) and five sites inside the farmland (Table IV). The first ones were collected about 0.5 m from the surface, and the soil farmland sample was taken at about 0.3 m depth from the surface and away from the main pathways.

As observed, there is a high homogeneity in the distribution of the metals in the soil samples, probably



TABLE II
Chemical analyses performed in the ESEM by EDS on the slag sample number 2
(shown in Fig. 4).

	white core	colorless rim	external rim	brown matrix	white areas matrix	dark areas in matrix	sparkling inclusion in matrix
C	13.90	14.61	8.72	2.24	6.64	8.77	7.84
Na	0.00	0.00	0.00	0.55	0.00	0.00	0.00
Mg	26.44	19.95	7.25	0.39	2.32	0.50	0.28
Al	0.40	0.73	1.16	3.07	2.12	1.01	1.75
Si	0.67	1.72	1.86	15.93	2.89	1.42	3.28
S	0.00	0.14	0.00	0.00	0.00	0.42	6.54
P	0.00	0.00	0.00	0.69	0.00	0.00	0.00
Cl	0.20	0.23	0.16	0.29	0.00	0.20	0.00
K	0.13	0.20	0.10	1.60	0.00	0.09	0.00
Ca	0.96	2.01	2.62	22.42	4.41	2.04	5.45
Ti	0.00	0.00	0.00	0.41	0.00	0.00	0.00
Cr	0.00	0.00	1.11	0.19	0.98	0.12	0.00
Mn	0.00	0.33	3.69	0.99	4.58	0.81	0.64
Fe	1.05	3.50	30.72	7.65	37.41	43.33	6.14
Ba	0.00	0.00	0.00	0.00	0.00	0.00	33.65
Cu	0.00	0.00	0.00	0.00	0.00	1.23	0.00
Sn	0.00	0.00	0.00	2.59	0.00	0.00	0.00
O	56.25	56.59	42.61	41.00	38.66	40.06	34.41

TABLE III
Chemical analysis performed by XRF of eight different soil samples of pathways close
to the irrigated land crops. Where L.I. means Lost due to the Ignition.

Element (%)	GE-1	GE-2	GE-3	GE-4	GE-5	GE-6	GE-7	GE-8
SiO ₂	31.64	34.1	30.64	37.37	28.91	31.67	30.14	31.07
Al ₂ O ₃	7.05	6.94	6.77	6.86	6.32	6.55	6.41	6.72
Fe ₂ O ₃ (total)	21.8	20.76	18.64	17.52	27.14	21.04	19.59	20.89
MnO	1.87	1.05	1.26	0.84	1.26	1.18	1.03	0.86
MgO	4.07	4.04	4.99	4.3	5.39	4.63	5.44	4.97
CaO	17.27	15.11	18.88	16	17.87	16.81	17.68	17.65
Na ₂ O	0.86	0.58	0.54	0.66	0.55	0.6	0.58	0.68
K ₂ O	1.66	1.95	1.57	2	1.45	1.83	1.69	1.92
TiO ₂	0.38	0.31	0.31	0.31	0.3	0.31	0.29	0.28
P ₂ O ₅	0.31	0.3	0.32	0.33	0.25	0.31	0.27	0.3
L.I.	13.1	14.86	16.07	13.81	10.55	15.06	16.87	14.66
Total	100.01	100	99.99	100	99.99	99.99	99.99	100

(up to 7.1%), Mn (up to 1.9%) and Cr (up to 7726 ppm), Zn (up to 3531 ppm), Ba (up to 3143 ppm), Pb (up to 759 ppm), Cu (ca. 500 ppm), etc, in pathway samples. The measurements performed on the soil samples of the farmlands were carried out in 5 different zones (Table IV). In general, the results exhibit heavy metals values

unidad de Madrid 2006). Thus, one can appreciate how the Co, Pb and V concentration in soil samples of farmlands with tomato crops goes over the limit of the Spanish recommendation value for human intake. These three metals, together with Cu, Ni, Zn, Cr and Ba, have to be controlled by the European Union (EU) (Covelo et al. 2007). In the case of farmlands for the production of



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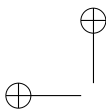
TABLE IV
Comparison between the reference levels of heavy metals for the protection of human health in Madrid (Comunidad de Madrid)
and the concentration of heavy metals in different soil samples.

Soil samples of pathways close to the irrigated farmlands Traces (mg/kg)									Reference level (mg/kg)			Soil samples from farmland Traces (mg/kg)			
Metal	GE-1	GE-2	GE-3	GE-4	GE-5	GE-6	GE-7	GE-8	Industrial Use	Urban Use	Other Uses	Field 1	Field 2	Field 3	Field 4
Cu	438	446	370	382	453	497	422	447	8000	800	80	20	17	7	52
Ni	154	160	124	136	200	191	160	187	15600	1560	405	14	17	12	18
Co	46	50	40	42	68	51	44	50	1500	150	15	11	13	9	11
Zn	3531	2507	2650	2950	2847	3144	3280	3514	100000	11700	1170	95	100	49	161
Pb	525	512	502	593	515	583	531	759	2700	270	75	59	32	27	78
Cr	7726	4500	4648	3123	5371	4169	3964	3410	2300	230	90	37	50	32	51
V	184	107	122	89	123	108	109	88	3700	370	37	38	54	29	51
Ba	3143	1615	2010	1257	1819	1732	1724	1543	100000	15200	4200	549	480	448	597

value for the protection of human health either for any land use (Cu, Co, Zn, Pb, Cr y V), such as urban use (Cr y Pb), or even industrial use (Cr). Some of these values (especially for Cr) are in somehow worrying, and further studies should be done to determine in which way metals appear in the soil and to what extent their concentration involves a risk to human health. With regard to the samples of the farmlands, the only heavy metals that are at a concentration higher than the one allowed by the actual law for agricultural land use (other uses) are Pb and V (samples 2 and 4). These comparative data are shown in Table IV. Such metals have been included in the Priority Pollutants List, which was created by the U.S. Environmental Protection Agency in 1993. Apart from the measurements of trace elements concentrations of these soils, there are some other properties to take into account: pH, textural class, and percentage organic matter. The behavior of different metals and the reactivity of the variable electric charge in soils depend on the pH (Bradl 2004). The textural class of the soil is a basic property because various processes of adsorption of metals are largely conditioned by phyllosilicate and metallic oxyhydroxides, which appear in the clay fraction. The presence of mobile forms of the elements in soils with high content of clay minerals is lower than in other types of soils (Palm 1994). Finally, the organic matter plays an important role in the heavy metal retention processes because of its high cation exchange capacity (Kalbitz and Wennrich 1998).

tion in depth mainly due to the deposit of sediments (Miguel et al. 2002). The samples collected have a value *circa* 7, a loamy-sand class textural (13% of sand, predominantly illite), and a percentage of organic matter that is characteristic of farmlands (1-4%). These conditions show suitable conditions for the retention of heavy metals: i) for this pH, most of the soil constituents with variable electric charge are negatively charged, so they have a high affinity for cations; and, furthermore, hydrolyzed metal species dominate instead of free hydrated metal ions involving those heavy metals and could be strongly sorbed onto the solid surfaces. ii) Illite is not the dominant clay with greater cation exchange capacity (CEC = 200 cmol_c/kg), but it is very important in the retention of heavy pollutants by independent pH charges. iii) Organic matter is the component of the soil solid fraction with high reactivity (CEC = 200 cmol_c/kg), and, so, this organic matter percentage in the superficial horizons contributes to heavy metals retention. When the pollutants are retained by the constituents of the soil, heavy metals do not cross to deep horizons and reach groundwater. However, it is necessary to know the bioavailability of metals in order to determine their toxicity since it warrants a concern not only for the quality of soil, but also (and potentially) for groundwater and surface water systems.

The distribution of pollutants in these soil samples has probably been influenced by several factors, among others: (i) weathered products of the slag (due to climatic conditions); (ii) the use of agrochemicals to fight pests.



Nevertheless, further work is necessary to determine how such pollutants are transferred to the crops (through the calculation of the transfer factor), the evolution of soil fertility, the content of organic matter and the distribution of heavy metals in the ploughing layer of soil to assess the environmental risk linked to contaminated soils.

CONCLUSIONS

This study, in which several pathways and farmlands soil samples from the southern part of Madrid (Spain) have been investigated, demonstrates the presence of a high concentration of metal contaminants coming from heaps of steel slag. Chemical analyses of the slags samples, which were produced in the manufacturing process by the Aristriain factory during more than 40 years, revealed the presence of heavy metals introduced by iron scraps: Fe (43%), Mg (26%), Cr (1.1%), Mn (till 4.6%), in the form of Fe-rich slag phases (wüstite, magnetite, goethite...), and Cr (chromite), Mn (bustamite), together with a 6.5% of S, Si and Ca-rich phases (larnite, ghehlenite, pseudowollastonite), and graphite. The XRF analyses performed on the farmlands soil samples demonstrate the presence of some of the heavy metals close to the threshold admitted by the local authorities for this use: Co (close to the limit, 15 ppm), Pb (over the limit in one of the analysed samples, 75 ppm) and V (some units over the allowed limit of 37 ppm). The pathways soil samples confirm important levels of Fe_2O_3 (about 20%), MgO (5%), MnO (0.8-2%) and traces of some other contaminants, such as Cr (up to 7726 ppm), Zn (up to 3531 ppm), Ba (up to 3143 ppm), Pb (up to 759 ppm) or Cu (up to 500 ppm). The Cr content exceeds the admitted limit for any possible use, whereas Pb and Cu, Co, Zn, and V go beyond the limits for urban and other uses (e.g. agricultural use), respectively. These values are worrying since they involve a risk to human health. Further studies have to be performed to determine the mobility of the heavy metal elements and establish their toxicity not only for the quality of soil, but also for ground water and surface water systems. This sort of studies can provide useful information for the politicians regarding the appropriate use of the territory to prevent possible health

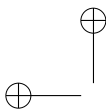
for remediation involving partial soil replacement in the whole affected area can be applied. Therefore, the study indicates that the multi-metal pollution in this area is of anthropogenic origin and the main source of metals is the slag. One of the solutions for this environmental pollution could be to employ these waste by-products in other fields, such as cement or ceramic industry, as raw material that could improve the quality of the final product.

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RESUMO

A presença de altos níveis de metais pesados envolve riscos à saúde humana e pode induzir doenças crônicas. Este trabalho relata a contaminação metálica causada por pilhas de escória siderúrgica acumulada durante mais de 40 anos em áreas industriais na parte sul de Madrid (Espanha). Amostras de escória e solo foram coletadas em uma área de 10 km² e caracterizada por diferentes métodos, convencionais (XRD, XRF) ou não (ESEM, termoluminescência e EDS-WDS). A análise revela a presença de: i) quantidades importantes de Fe (43%), Mg (26%), Cr (1,1%), Mn (4,6%), S (6,5%) formando várias fases ricas em Fe (wüstita, magnetita), Si e Ca (larnita, ghehlenita), Cr (cromita), Mn (bustamita) e grafite; (ii) traços de outros contaminantes, como Cr (7700 ppm), Zn (3500 ppm), Ba (3000 ppm), Pb (700 ppm) e Cu (500 ppm), no solo dos caminhos para as pilhas de resíduos e (iii) Co (13 ppm), Pb (78 ppm) e V (54 ppm) em amostras de solo agrícola. Embora os teores de metais pesados não sejam apropriados para uso corrente, a elevada contaminação de áreas adjacentes é mais preocupante. Os solos adjacentes (pH ca. 7, 13% de argila – principalmente ilita) e 1-4% de matéria orgânica mostram condições adequadas para a retenção de cátions, mas outros estudos deverão ser realizados para determinar a possibilidade de riscos à saúde humana. Este tipo de trabalho pode fornecer informação útil para gestores públicos, com relação ao uso do



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