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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 allotments and industrial areas in the southern part of Madrid (Spain). Several slag and soil samples were collected in an area of 10 km^2 and characterized by different conventional (XRD and XRF) and no so common methods (ESEM, thermoluminescence and EDS-WDS). The analysis reveal the presence of: (i) important amounts of Fe (43%), Mg (26%), Cr (1.1%), Mn (4.6%), S (6.5%) in the form of Fe-rich slag phases (wüstite, magnetite...), Si and Ca-rich phases (larnite, ghelenite...), Cr (chromite), Mn (bustamite) and graphite, (ii) traces of some other contaminants such as Cr (7700 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 areas 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 movilization of these elements have to be performed to determine the possibility of severe human health risks. This sort of study can 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 direct or indirect risks to human beings, since they produce toxic effects such as neurological, hepatic, cancer or renal upsets. It is well-known that, for instance, high levels of: (i) cobalt could act inhibiting the growth of plants (Chatterjee and Chatterjee 2000) and could harm lungs and heart (ATSDR 2004); (ii) lead could induce damage in nervous system or kidneys (ATSDR 2007); 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 1992); however, there is few information about vanadium contamination (Mochizuki et al. 1999).

Nowadays, the Spanish authorities do a strict regulation to establish controls of metal concentration on the

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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 iron ore in two stages. In the first one, coal is used to remove oxygen from the ore and to melt it, a process that produces large amounts of wüstite (FeO), which 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 km^2 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$_\alpha$ 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 performed using EDS-WDS (30kV; work distance 10 mm) in large samples, i.e., up to 5×5cm^2. The WDS analyses were performed on well-polished samples covered 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 $^{90}Sr/^{90}Y$ 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 Terciary 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 and small amounts of dolomite and chert. The claystone compositions are mainly smectite-illite and illite, with less than 15% in kaolinite for both formations. Concerning the Quaternary river-banks and valley-filled materials, they are composed by many different gravel types with minor quantities of sands and slime. The valley-filled sediment levels covering the top of the river-banks, with 1 to 5 m in depth, are composed by gross to medium sized sands (Fig. 1a). The sand is mainly formed by quartz with very small parts of granitoid, chert, sepiolite and limestone. A quarry is close to the studied area for extracting quartz-rich sands. The sampled area (10 km^2) holds important amounts of steel and iron slag samples, which are usually employed to pave 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 mudstone, and covered by a 60 cm-layer of slag dumps.

STEEL-SLAGS CHARACTERIZATION

All collected samples, located at 30 cm depth from the surface, exhibit a high level of porosity regardless the size of the piece (Fig. 2). This property is especially interesting for local farmers who use this material in the farmlands since it can host amounts of water that are very useful during drought periods. Such behavior is also observed in some areas of Canary Islands where local farmers employ fragments of lava (also high porosity materials) for similar purposes. At a glance, one can guess a very different composition of the specimens because of (i) the color (from deep black to greyish), (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 (powder method), and most of the samples are a mixture of several phases. The list of the identified phases with the corresponding stequiometric composition and the ICDD (International Centre for Diffraction Data) XRD reference cards are shown in Table I. This analysis shows, on one hand, plenty of uncommon mineral phases such as Si and Ca-rich phases (larnite, ghelenite, pseudowollastonite), and graphite indicating a synthetic origin (from the factory) and, on the other hand, the presence of high

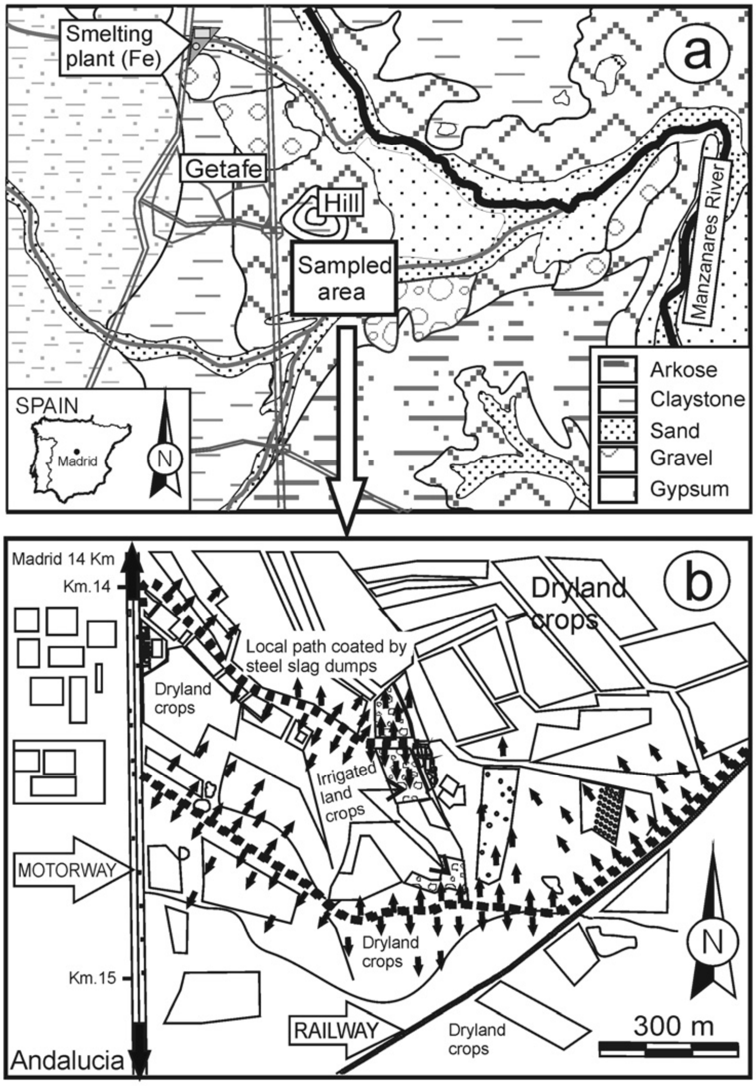

Fig. 1 – (a) Geological sketch of the studied and sampled area. (b) Location map of the area affected by the presence of steel-slag dumps.

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 discriminate meteorites from steel slag. TL is a method based on the emission of light from a solid sample (insulator 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 mineralogical composition, allow us to speculate about the origin of the sample; however, some TL tests have been

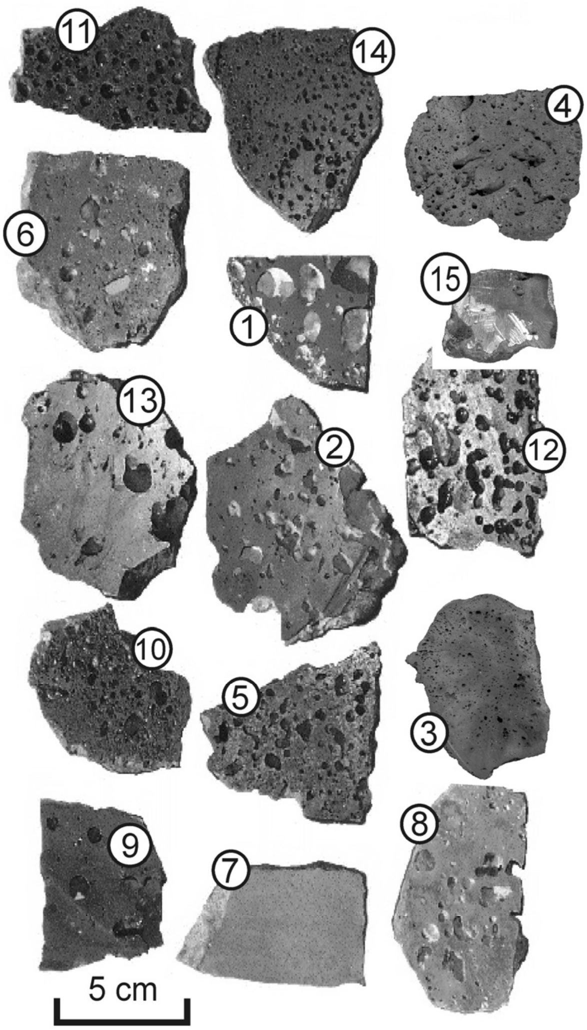

Fig. 2 – Fifteen of the more representative steel slags samples, selected among 200 specimens, from different places of Villaverde-Getafe-Parla in an area of 10 km^2 in the southern part of Madrid.

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 catalogued 'pseudometeorite' TL spectra are shown. This last sample is identified as the fragment that hit a car in 1994 at 17 km from Madrid in the Andalusia Motorway (between Getafe and Villaverde villages), and considered by Dr. Martínez-Frías to be a possible meteorite or even more, a pseudo-meteorite (Martínez-Frías 1998, 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 the sample number 1 is four times brighter than the rest (up 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 concerning not only short irradiations during the studies of the samples over the last ten years, but also the assorted X-rays at airport controls during the journeys among the laboratories. The conclusion after the TL study is that the 15 samples exhibit a very low TL emission because 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.

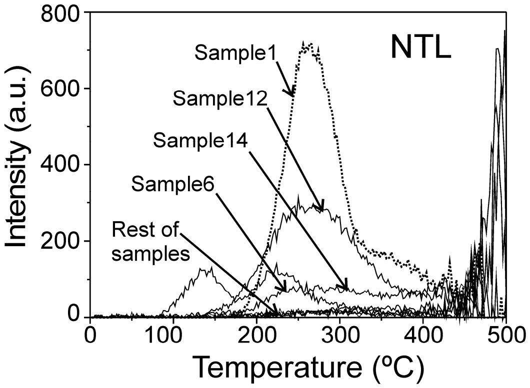

Fig. 3 – Thermoluminescence glow curves of slag materials; note the low emission signals in all cases.

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 $MgCO_3$, i.e., a magnesite refractory phase surrounded by an external rim composed of a mixture of $MgCO_3$ and FeO. The matrix contains little amounts of calcium-iron silicates, calcium-iron carbonates and iron carbonates undetected by XRD. It is interesting to note the presence of sparkling inclusions of $BaCO_3$-$BaSO_4$. Both types

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_2SiO_4	29-371	18	4							15		30				
Gehlenite	$Ca_2Al_2SiO_7$	35-755	25		40	58	25				5			75			
Chromite	$FeO.(Cr,Al)_2O_3$	34-140	10	8								25			15		
Magnetite	$FeO.Fe_2O_3$	19-629			25							5					
Kirschteinite	$CaFeSiO_4$	34-98		22		39	20							25	30		
Monticellite	$CaMgSiO_4$	35-590													35		
Akaganeite	β-FeOOH	34-1266					5										
Bredigite	$Ca_7Mg(SiO_4)_4$	36-399							95								
Bustamite	$(Mn,Ca)_3Si_3O_9$	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	$Al_2O_3.SiO_2$	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 $MgCO_3$ and $BaCO_3$ can be explained by the use of dirty natural limes ($CaCO_3$ with $CaMg(CO_3)_2$ or dolomite with barite veins ($BaSO_4$), 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 (Fe_2O_3) 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 metals (i.e., barium, copper and tin) have been also detected by EDS-WDS; however, the concentration levels seem not to be very significant to speculate with subsequent higher levels of contamination in soil samples. The oxygen:iron ratio suggests that the above crystals are composed of hematite (Fe_2O_3) with accessory mayenite ($Ca_{12}Al_{14}O_{33}$). 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 of dirty lime, which was revealed by the presence of abundant magnesium-calcium silicates in the iron slag. The existence of aluminium in the slag can be explained

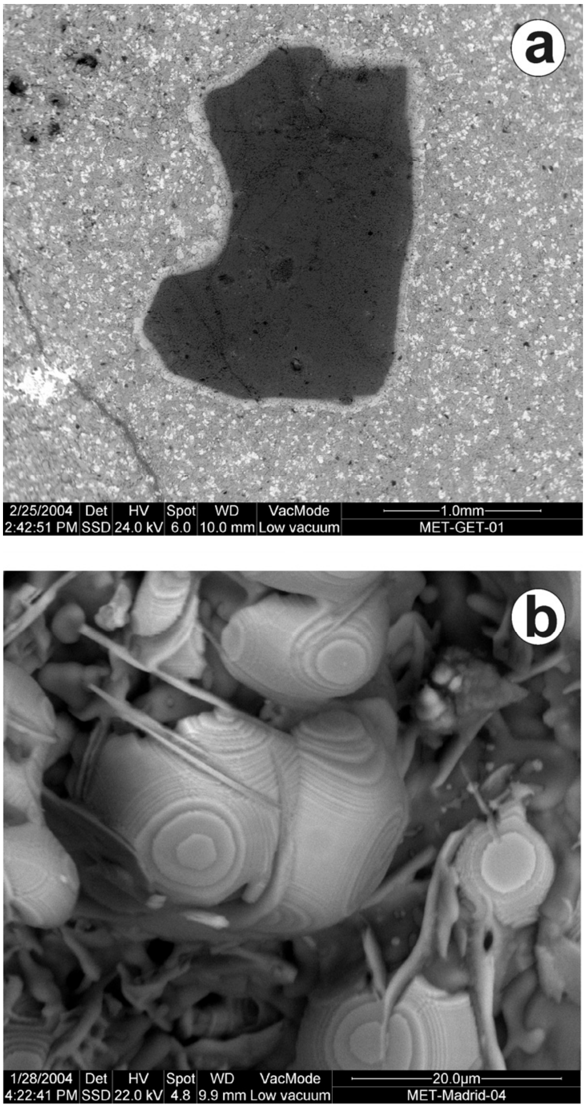

Fig. 4 – Selected images from the ESEM analyses: (a) Magnesite ($MgCO_3$) grain and (b) Hematite (Fe_2O_3) spherical crystals; note the hexagonal shapes along the *c* axis.

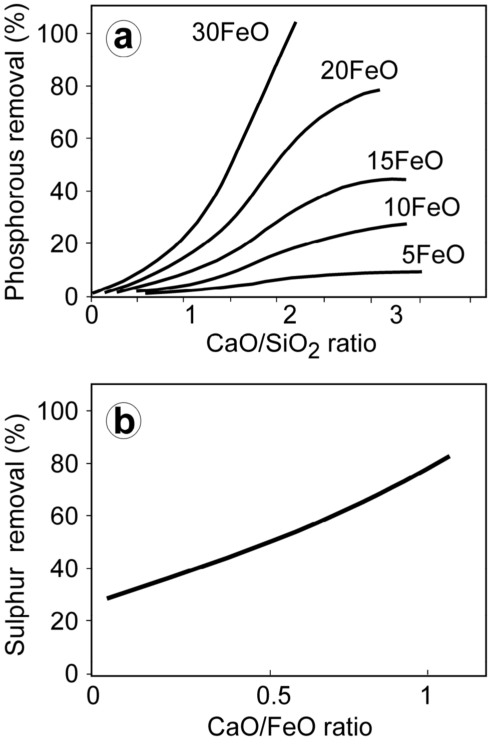

Fig. 5 – (a) Evolution of the Phosphor release depending on the CaO/SiO_2 ratio. It explains the great abundance of wüstite in the Getafe slag heaps: large amounts of it were produced in the manufacturing process to induce greater dephosphorylation of the iron. (b) Sulphur removal *versus* CaO/FeO ratio.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

by the use of clay or feldspar raw materials in the second manufacturing stage; these materials generate unstable mayenite oxide ($Ca_{12}Al_{14}O_{33}$).

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, such as the Aristrain plant at Villaverde, do the recycle of slag, which reduces the manufacturing costs while being more environmental friendly. The final slag 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 in eight different points of pathways close to the irrigated farmlands (Table III) and five sites inside the farmlands (Table IV). The first ones were collected about 0.5m depth from the surface, and the soil farmland samples were taken at about 0.3 m depth from the surface and 10 m away from the main pathways.

As observed, there is a high homogeneity in the distribution of the metals in the soil samples, probably due to the presence of the slags in the studied area for more than 40 years. The results display that all the samples show different concentrations of Fe (up to 27.1%), Al

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_2O_3	7.05	6.94	6.77	6.86	6.32	6.55	6.41	6.72
Fe_2O_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_2O	0.86	0.58	0.54	0.66	0.55	0.6	0.58	0.68
K_2O	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_2O_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 lower than the recommended values. However, in some cases, the heavy metals concentration exceeds slightly the allowed limits described in the local regulation (Comunidad 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 soil samples from the boundaries among the farmlands, the concentration of all previous heavy metals (except Ni and Ba) exceeds the reference

TABLE IV
Comparison between the reference levels of heavy metals for the protection of human health in Madrid (Comunidad de Madrid 2006) 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 farmlands 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	Field 5
Cu	438	446	370	382	453	497	422	447	8000	800	80	20	17	7	52	23
Ni	154	160	124	136	200	191	160	187	15600	1560	405	14	17	12	18	13
Co	46	50	40	42	68	51	44	50	1500	150	15	11	13	9	11	10
Zn	3531	2507	2650	2950	2847	3144	3280	3514	100000	11700	1170	95	100	49	161	90
Pb	525	512	502	593	515	583	531	759	2700	270	75	59	32	27	78	52
Cr	7726	4500	4648	3123	5371	4169	3964	3410	2300	230	90	37	50	32	51	33
V	184	107	122	89	123	108	109	88	3700	370	37	38	54	29	51	32
Ba	3143	1615	2010	1257	1819	1732	1724	1543	100000	15200	4200	549	480	448	597	544

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 comparatives 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).

The soil beds developed onto the Manzanares riverbanks are of alluvial origin, relatively young, and with a poor pedological evolution. They show a differentiation in depth mainly due to the deposit of sediment (de Miguel et al. 2002). The samples collected have a pH value *circa* 7, a loamy-sand class textural (13% of clay, predominantly illite), and a percentage of organic matter that is characteristic of farmlands (1-4%). These properties show suitable conditions for the retention of cationic metals: i) for this pH, most of the soil constituents with variable electric charge are negatively charged, so having a high affinity for cations; and, furthermore, hydrolyzed metal species dominate instead of free hydrated forms involving those heavy metals and could be strongly adsorbed onto the solid surfaces. ii) Illite is not the clay with greater cation exchange capacity (CEC = 10-40 cmol$_c$/kg), but it is very important in the retention of pollutants by independent pH charges. iii) Organic matter is the component of the soil solid fraction with larger reactivity (CEC = 200 cmol$_c$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 metal species 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 against pest (anthropogenic input of Cd, Pb, Ni and Cr) and (iii) coal combustion. This preliminary study is only to determine the contaminant level of soils in the studied area.

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, ghelenite, 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 hazard for the population.

At present, it is not possible to estimate the number of ton slag heaps in the whole area; so, no plans 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 km^2 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, guelenita), 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 território e prevenção de riscos à saúde da população.

Palavras-chave: EDS, ESEM, contaminação por metais, escória de aço, TL, XRD, XRF.

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