Geochemical Baseline Concentrations of Available Heavy Metals in Mediterranean Agricultural Soils: A Case Study in calcareous soils of Southwest Iberian Peninsula

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Abstract— The characterization of the content and sources of trace metals in soils is an instrument in many programs of environmental protection, including the establishment of regional-level standards to detect sites affected by contamination. The objectives of the present study were to study the available levels of Cd, Cr, Cu, Ni, Pb, and Zn in surface horizons of agricultural calcareous soils in a typical European Mediterranean region, to establish the geochemical baseline concentration (GBC), background level (BL), and reference value (RV) of each of these metals, and to investigate their possible correlations with soil properties. To establish the GBC and RV values we used the "standard threshold method". Topsoil samples (0-20 cm) were collected from 630 sites, and extracted with DTPA to determine their available heavy metal concentrations. The measured total and available concentrations were lower than or close to those reported by other researchers for agricultural soils. The GBC values established were: 0.04 to 0.90 mg kg 1, 0.70 to 2.50 mg kg 1, 0.10 to 6.30 mg kg 1, 0.30 to 7.90 mg kg 1, 0.29 to 4.50 mg kg 1, and 0.18 to 2.50 mg kg 1 for Cd, Cr, Cu, Ni, Pb, and Zn, respectively. Soil properties were found to be correlated with the available heavy metal content, suggesting that the enhanced of mobility of heavy metals are related to anthropic activities. Available GBC determination is a tool that can provide insight into the risk of trace element contamination and transfer to other environmental compartment.

Keywords— available heavy metals, Mediterranean agricultural soils, DTPA, geochemical baseline concentrations, reference values.

I. Introduction

THE Mediterranean region has been subject to intense anthropic pressure for millennia, resulting in a vulnerable and often fragile ecosystem [1]. Livestock and crop farming are the main human activities in the area [2]. The excessive use of fertilizers in the region has, in general, led to soil acidification, problems of soil degradation, and a major proportion of contaminant trace metals [3, 4]. Moreover, in the European Mediterranean region, cropping intensity is often inconsistent with the soil's natural potential, with 26% of the soils used for farming being in fact unsuitable for that purpose [5]. The concentration of heavy metals in agricultural soils is related mainly with the parent material of the area [6], although there are few studies on availavilty and movility of the heavy metals in agricultural soils.

The characterization of the content and sources of heavy metals in soils is a key element in many programs of environmental protection, including the establishment of regional-level quality standards to detect sites affected by contamination [7, 8].

The accumulation of heavy metals in the soil is considered to be a serious risk at the environmental level [9]. Published results on the levels of heavy metals in soils been based on indirect estimation, small-scale studies, or poorly defined time periods, but often represent the only information available for extensive territories. Also, they are not only hard to extrapolate, but seem unlikely to provide any reliable picture of long-term trends that might be applicable to any large agricultural area under commercial management. For this reason, the present large scale field study represents a major research contribution to determining and quantifying the impact of agriculture on soil available heavy metal content under Mediterranean conditions.

It is widely accepted that determining the total content of heavy metals in a soil is neither sufficient to understand their relative mobility and ecological availability as contaminants nor particularly useful as a tool to estimate potential risks. The toxicity of metals for plants and animals including humans depends not only on their total concentrations, but also on their mobility and reactivity with other components of the

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ecosystem [10, 11]. The "bioavailable fraction" is the fraction of the total contaminant in the interstitial water and soil particles that is available to the receptor organism [12]. However, there is still very little direct measurement data or predictions of the available fraction of metals in soils. In Portugal and Spain for instance, there is hardly any information at all on available heavy metals in agricultural soils, and this lack of information is reflected in poorly informed legislation which does not take soil characteristics into account [13, 14].

The initial soil pH and the ability of plant roots to change the pH have been found to be the principal predictors of the exchange of heavy metals, and therefore of their bioavailability [15]. It is generally accepted that anthropogenic heavy metal contamination exists mainly in the form of reactive species on the soil surface, and the concepts of "bioavailability" and "bio-accessibility" were introduced to express the actual effect of the concentration of a contaminant on organisms in the ecosystem [12, 16, 17, 18].

The geochemical baseline concentration (GBC) and background level (BL) of different heavy metals in soils have been studied in various Mediterranean countries [8, 14, 19, 20, 21, 22, 23]. It is widely accepted that the BL and GBC were the best approach to establish the levels of non-contaminated soils. Different approaches have been taken to establishing the GBC of trace elements in Mediterranean soils [8, 14, 24, 25, 26]. Most have centred on the total heavy metal content without considering the bioavailability of the different elements involved [27], even though, according to Baldantoni *et al*. [28], bioavailability constitutes the best indicator of the potential impact of these contaminants.

The present study is aimed at contributing to improved information on available heavy metals in Mediterranean agricultural soils in particular, it being important to bear in mind that there is only limited data available on available heavy metals in Mediterranean soils in general. Given this context, the specific objectives were: (i) to study the levels of available heavy metals in typical agricultural soils of a Mediterranean region; (ii) to establish the available GBC of these metals.

II. MATERIAL AND METHODS

A. Study area and sampling

The study area is located within the administrative townships of Elvas and Campo Maior, at the confluence of the Rivers Caia and Guadiana, near the Portuguese-Spanish border (Figure 1). A total of 630 sites were selected in the "Caia Irrigation Perimeter". At each sample site, 10 topsoil (0–20 cm) subsamples were collected at random and merged to give a composite sample of roughly 2 kg. Later all samples were air dried, crushed and sieved to < 2 mm, and stored.

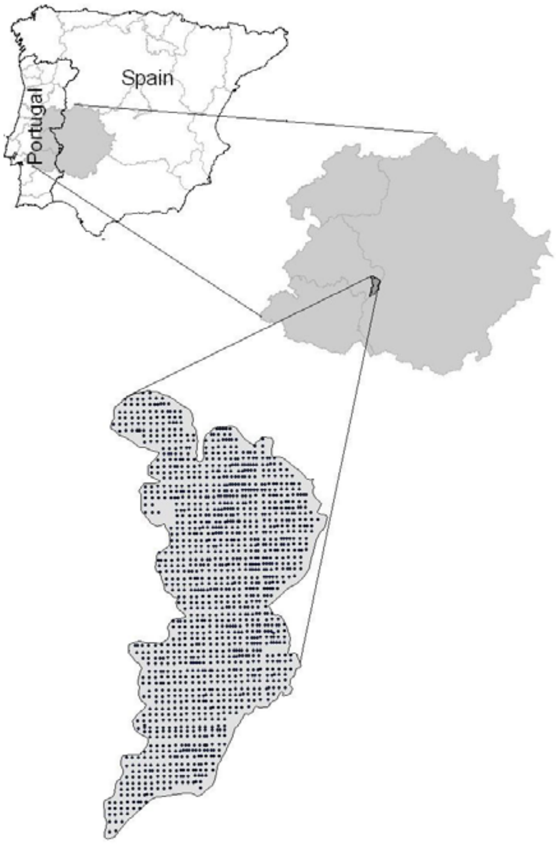

Figure 1 - Localization map of the area studied

The geology of this area consists essentially of Cambrian and Silurian formations, with some small eruptive zones associated with hyper-alkaline and alkaline rocks [29]. The average annual rainfall is approximately 483 mm, most of which coincides with the coolest temperatures from October to March. The maximum average monthly temperature corresponds to July with 24.7°C and the minimum to January with 8.8°C. The Mediterranean region is characterized by its hot dry summers and cool wet winters. The most important crops are: maize (Zea mays) for feed-grain production with almost half of the cultivated area (49%), wheat (Triticum aestivum) (17%), sunflower (Helianthus annuus) (7%), tomato (Lycopersicum esculento) (6%), and olive (Olea europea) (4%).

B. Analytical methods

The physical and chemical soil analyses were carried out following Roca-Pérez [30] and were determinated for each individual soil (data not show). The available heavy metals were determined by the method described by Lindsay and Norvell [31] (extraction with DTPA + CaCl2 + triethanolamine). According to Hooda and Alloway [32]; Soriano-Disla *et al*. [33] and Hao *et al*. [34], DTPA extraction is the most efficient method of extracting heavy metals from soils, independently of the soil's properties, and hence can be an effective way to assess the availability of heavy metals to plants. We considered this farction as biavailable heavy metals.

Total heavy metals were determined following the method described in EPA 3052 [14]. The concentrations of Cd, Cr, Cu, Ni, Pb, and Zn (total and available) were determined by ICP-OES (IRIS INTREPID II XDL THERMO). Measurements were made in triplicate for each sample to check the precision of the results. To assess both the quality of the methods applied and the assay by atomic absorption spectroscopy, a check was made for matrix interferences using standard addition techniques. No such interferences were observed for the determination of the metals studied. In other hand 30 samples were re-analysed and a paired t-test realized, the results indicated no significant differences in the values [35].The concentrations of available Cd, Cr, Cu, Ni, Pb, and Zn are indicated as mg kg 1 dry matter. The limit of detection of the method was 0.01 mg kg 1.

The Zn Equivalent Indices (ZnEqT for total heavy metals and ZnEqB for available heavy metals) were used to compare the potential heavy metal toxicity in these soils [8, 13, 14, 36]. They both were calculated as:

$$ZnEq = [Zn] + 2[Cu] + 8[Ni]$$

where [Zn], [Cu], and [Ni] are the respective soil concentrations of the metal (total and available for ZnEqT and ZnEqB, respectively).

C. Statistical analyses

All statistical analyses were performed using the SPSS version 15.0 software package, calculating the arithmetic mean (AM), range (MINV-MAXV), standard deviation (SD), and geometric mean (GM) as descriptive statistics.

D. Baseline concentrations

To establish the GBC and BL values, the soil sample population was segregated into non-contaminated and contaminated soils on the basis of probability plots applying the "standard threshold method" described by Fleischhauer and Korte [37] and used by several authors.

Following this method a log-normal distribution was assumed, and Q-Q plots were drawn. From these plots the overlap corresponding to different population can be determined from slope changes of the plots. The tipping points formed by the superposition of the two populations were identified as data endpoints of the raw data for which the resulting population has a skewness nearest to zero and hence the populations can be segregated (contaminated and non-contaminated soils). The reference value (RV) was taken as the upper limit of the GBC, and was used to determine whether a soil might be contaminated or not [35]. The identification of a specific type of soil as contaminated means that the total contaminant content is higher than would normally be expected in non-contaminated areas [26]. The RV values were used to evaluate the soils' contamination and quality.

III. RESULTS AND DISCUSSION

The main soil characteristics are listed in Table 1. The commonest soil groups in the study area are Fluvisols (42.7%), Luvisols (21.7%), Calcisols (16.1%), Cambisols (6.1%), Vertisols (1.8%), and Regosols (0.6%), as is usual in Mediterranean ecosystems [29]. In general, these are medium-loam and clay-loam soils with a pH close to 7, slightly calcareous, and low levels of soil organic matter (SOM, 1.54%) and total nitrogen (N, 0.1%).

Table 1: Mean values, standard deviation, and ranges for general descriptive parameters of Caia soils (n=630)

	SOM (%)	**N** (%)	**Soil Carbonates** (%)	**pH**	**CEC** cmol$_c$kg^{-1}	**CE$_{25}$** dS cm^{-1}	**P$_2$O$_5$** (mg/100g)	**K$_2$O** (mg/100g)
MINV	0.2	0.03	0.1	4.5	3.8	0.01	4.0	18
AM	1.5	0.10	5.5	6.9	15.8	0.11	197	220
MAXV	4.4	0.31	16.4	8.9	71.5	1.00	5920	3268
STD	0.6	0.04	4.2	1.1	10.2	0.11	413	185
GM	1.4	0.09	3.6	6.9	13.5	0.09	120	186

MINV—minimum value.
AM—mean.
MAXV—maximum value.
STD—standard deviation.
GM—geometric mean

They have intermediate levels of cation exchange capacity (CEC, 15.8 cmolc kg 1), with calcium as the principal exchangeable cation, and a degree of saturation of exchangeable cations of 70%. Their levels of available phosphorus and potassium (P2O5 and K2O, respectively) are high, indicating intensive use of soil fertilizers which is thus suggestive that farming may be incorporating pollutants into the soils [38, 39]. Their saturated soil-paste electrical conductivity is low (EC25, 0.11 dS cm 1), indicating that these soils have no salinity problems.

The total concentrations for the heavy metals in these soils based on the 30 representative top soils of the study area were (mg kg 1): ranges, Cd <d.l.–0.7; Cr 10.8-89, Cu 9.5–489, Ni 5.2-48.6, Pb 7.7–41.9; and Zn 10.1–65.6; mean values ± SD, 0.6 ± 0.1, 48.4 ± 25.5, 16.7 ± 9.1, 23.6 ± 13.6, 19.1 ± 8.9, 29.6 ± 15.1 (mg kg 1) for Cd, Cr, Cu, Ni, Pb, and Zn, respectively (Table 2). According to these data therefore, the order of the heavy metals' total content was Cr>Zn>Ni>Pb>Cu>>Cd. In general, in all the soils these levels are low compared with literature values for Mediterranean agricultural soils [40, 41, 42]. The ZnEqT values (252 ± 135 mg kg 1) were also lower than Gil *et al.* [8] obtained in Mediterranean greenhouse soils, and the present study's heavy metal total concentrations do not surpass the RV established by Inácio *et al.* [20] in Portuguese soils or the GBC values of natural soils in the Mediterranean region established by Roca-Pérez *et al.* [22].

Table 2: Total concentrations (mg kg^{-1} dry soil) of trace elements in soil samples (n=30) from Caia area.

	Cd	Cr	Cu	Ni	Pb	Zn	Zn EqT
MINV	<d.l.	10.8	5.4	5.2	7.7	10.1	63
AM	0.6	48.4	16.7	23.6	19.1	29.6	252
MAXV	0.7	89.0	45.0	48.6	41.9	65.6	506
STD	0.1	25.5	9.1	13.6	8.9	15.1	135
GM	0.6	41.1	14.6	19.6	17.1	25.9	214

<d.l. below detection limit
ZnEqT—Zinc equivalent of total heavy metals

Table 3 presents the mean concentrations of available Cd, Cr, Cu, Pb, Ni, and Zn in the soils, with the corresponding values of the standard deviation, range, and geometric mean.

Table 3: Available concentrations (mg kg^{-1} dry soil) of trace elements in soil samples (n=630) from Caia area with associated statistical parameters.

	Cd	Cr	Cu	Ni	Pb	Zn	Zn EqB
MINV	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0.3
AM	0.24	0.85	1.23	1.95	3.16	0.64	19.4
MAXV	1.10	3.30	10.00	6.60	13.00	5.00	130
STD	0.23	0.79	1.15	1.30	2.33	0.58	14.5
GM	0.15	0.50	0.86	1.48	2.25	0.51	14.3

<d.l. below detection limit
Zn EqB—Zinc equivalent of bioavailable heavy metals

The available concentrations of these potentially toxic elements averaged over the 630 representative surface soil samples were (mg kg 1 dry wt, mean ± SD): Cd 0.24 ± 0.23; Cr 0.85 ± 0.79; Cu, 1.23 ± 1.15; Ni, 1.95 ± 1.30; Pb 3.16 ± 2.33, and Zn 0.64 ± 0.58. According to these data, the order of the available content of the metals was Pb>Ni>Cu>Cr>Zn>Cd. The content of the most available heavy metal in this kind of soil, Pb, is known to be essentially anthropogenic [19].

The availability data for Cr, Cu, Pb, and Zn are lower than or close to those reported by different workers in the literature considering the same extractant (Table 4), but the data for Pb are perceptibly higher than those reported by Antolin *et al.* [43] and Buccolieri *et al.* [44]. The only work that determine available Cd is Antolin *et al.* [43] and their data are lower than we found in the study area.

Although the levels of available heavy metals vary greatly among different Mediterranean soils, the order of their concentrations in the present study are similar to those found by other workers, implying that the processes operating are similar. The levels of ZnEqB found are lower than those reported by Ramos-Miras *et al.* [36], in greenhouse soils (44.6 ± 43.5 mg kg 1), although they use other extracting agent. This is indicative of the present soils being free of relevant contamination or large scale mobilization of the heavy metals analysed as might have been caused by farming activities, despite the large amounts of fertilizers (available phosphorous and potassium) detected in them.

A. Assessment of soil contamination

Soils constitute a complicated and heterogeneous system [45], so that simple monitoring of their heavy metal concentrations is insufficient guarantee of their environmental quality. Their trace element contents vary widely, so that it is inappropriate to use universal background concentrations as a criterion since the native concentrations of metals in a specific soil may exceed any given listed ranges. It is therefore important to determine the values of the GBC and RV concentrations locally [8, 14, 36, 46, 47]. To estimate the GBC values, the "standard threshold method" was applied [37]. The Q-Q plots are shown in Figure 2. Low values deviate from linearity because they were beneath the detection limit, and were hence assigned the detection limit value as proposed by Tack *et al.* [35]. The threshold was chosen as the point at which the slope of the Q-Q plot changes. Values beneath the threshold point denote the GBC (0.91, 2.52, 6.33, 7,32, 4.60, 2.53 threshold point of Cd, Cr, Cu, Ni, Pb and Zn, respectively) . The resulting GBC ranges were (in mg kg 1): 0.04 to 0.90, 0.70 to 2.50, 0.10 to 6.30, 0.30 to 7.30, 0.29 to 4.50, and 0.18 to 2.50 for Cd, Cr, Cu, Ni, Pb, and Zn, respectively. The BL estimated from non-contaminated soils were (in mg kg 1): 0.23, 0.72, 1.22, 2.00, 1.96, and 0.57 for Cd, Cr, Cu, Ni, Pb and Zn, respectively. The method of threshold points allows the differentiation of homogeneous populations using statistical criteria, assuming that populations with higher contents of heavy metals are subject to contamination processes.

Table 4: Available concentration of Cd, Cr, Cu, Ni, Pb and Zn, extracted with EDTA in different soils (mg kg^{-1}).

	In this work	Bucolieri et al., 2010	Masas et al., 2009	Gisbert et al., 2006	Ramos 2006	Antolin et al., 2005	Walker et al., 2003
Cd	0.24 ± 0.23	n.d.	n.d.	n.d.	n.d.	0.012-0.013	n.d.
Cr	0.85 ± 0.79	n.d.	1.5 ± 0.5	n.d.	n.d.	n.d.	n.d.
Cu	1.23 ± 1.15	5.40 ± 5.67	2.5 ± 1.2	0.9-8.8	15.3 ± 4.3	1.64-1.19	11.3
Ni	1.95 ±1.30	0.41 ± 0.32	1.3 ± 0.9	n.d	n.d.	n.d	n.d.
Pb	3.16 ± 2.33	2.09 ± 1.92	5.8 ± 3.2	22.1-179	n.d.	1.34-1.75	28.2-32.5
Zn	0.64 ± 0.58	3.67 ± 3.27	7.8 ± 9.7	10.5-7.7	2.2 ± 1.2	0.77-2.41	15.2-14.4

MINV-MAXV
AM ± STD
n.d. not determined

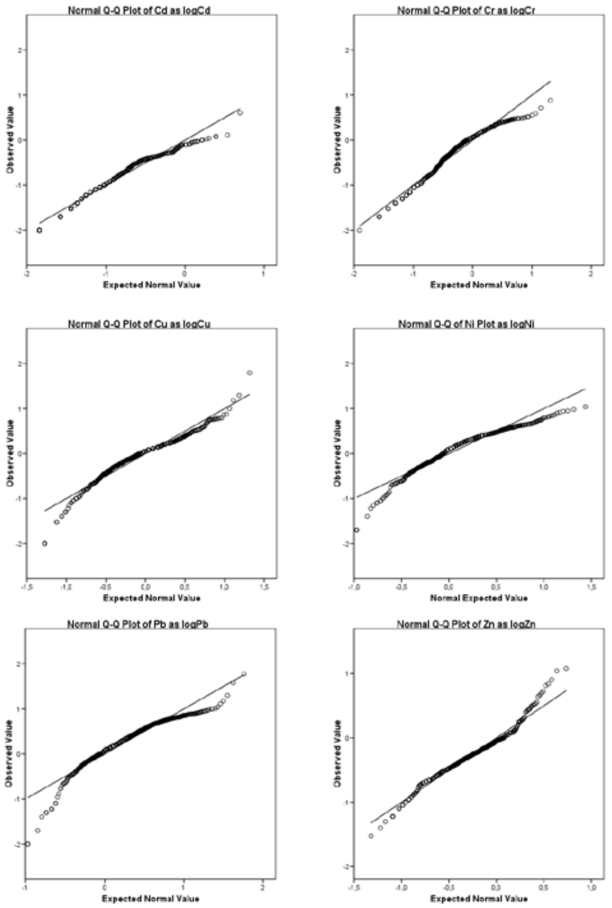

Figure 2 - Normal probability plot of bioavailable Cd, Cr, Cu, Pb, Ni and Zn contents as log[concentration

There are only two literature studies on the GBC of available heavy metals in soils – Tarvainen and Kallio [27] in natural soils in Finland, and Ramos-Miras *et al.* [36] in agricultural soils. They both used EDTA for extraction, however, so that it is difficult to compare their results with the present findings, even more so given that they did not analyse the same heavy metals. Nevertheless, the present results lie within the limits proposed by those authors.

The upper limit of the GBC could be used as the RV against which to assess soil contamination [26] find that this method is far more effective than others that have been put forward in the specialized literature. Using therefore the upper GBC values as the RVs of the available heavy metals (Cd 0.9; Cr 2.5; Cu 6.3; Ni 7.9; Pb 4.5; and Zn 2.50; all in mg kg 1) with which to determine whether or not a soil is contaminated, we found that 2% for Cd, 6% for Cr, 1% for Cu, 4.5% for Pb, 5% for Ni, and 4% for Zn of the samples were slightly contaminated.

In particular, only 6% of the sample soils had a higher available content of heavy metals than the RV limit (due mainly to Cr, Cu, Ni, and Pb). In sum, these results point to a minimal extension of soil contamination by available heavy metals. Using the 90% percentile value as reference to determine where a soil could be contaminated like Tack *et al.* [35] (Table 5). All of the heavy metals values for 90% percentile were lower than the RV proposed for these soils in this work, excepct for Pb, who value of 90% is higher than RV. This fact confirm that the contamination for available heavy metals was minimal except for Pb, who is one of the most mobile [36, 48].

Table 5: Estimated of baseline concentrations of Available heavy metals (mg kg^{-1} dry soil) based on percentile values of the data considered to be baseline values

Percentile	Cd	Cr	Cu	Pb	Ni	Zn
5%	0.01	0.05	0.14	0.24	0.35	0.14
25%	0.07	0.18	0.53	1.30	0.83	0.32
50%	0.16	0.55	1.00	2.50	1.70	0.50
75%	0.37	1.10	1.60	4.60	2.70	0.72
90%	0.50	1.70	2.37	6.10	3.56	1.00
95%	0.70	2.00	3.30	6.80	3.94	1.20
99%	0.92	2.30	5.70	7.70	4.40	1.90

IV. CONCLUSIONS

The concentrations of total and available heavy metals in these agricultural soils, which are typical of the Mediterranean region, were generally lower than or close to those reported in the literature for other agricultural areas. The GBCs of the available heavy metals were: 0.04 to 0.90 mg kg 1, 0.70 to 2.50 mg kg 1, 0.10 to 6.30 mg kg 1, 0.30 to 7.90 mg kg 1, 0.29 to 4.50 mg kg 1, and 0.18 to 2.50 mg kg 1, for Cd, Cr, Cu, Ni, Pb, and Zn, respectively. The threshold method is a good way to establish GBC values in an initially homogeneous population of soil. Only a small percentage of the 630 soils sampled had high available levels of heavy metals, so that there is no evidence for any extensive heavy metal contamination of these soils.

Given the potential risk to human health represented by available heavy metals, especial effort is called for to determine both the locations of contaminated soils and the sources of their contamination in order to be able to halt the contamination process and avoid larger areas being affected. We must emphasize that the present results are preliminary, and the findings will be more extensively studied in future work.

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