sustainability

MDPI

Article

Trace Metal Content and Availability of Essential Metals in Agricultural Soils of Alicante (Spain)

Jose Navarro-Pedreño [1,*], María Belén Almendro-Candel [1], Ignacio Gómez Lucas [1], Manuel M. Jordán Vidal [1], Jaume Bech Borras [2] and Antonis A. Zorpas [3]

[1] Department of Agrochemistry and Environment, Miguel Hernández University of Elche (UMH), Av. de la Universidad s/n. Edificio Alcudia, 03202 Elche, Spain; mb.almendro@umh.es (M.B.A.-C.); ignacio.gomez@umh.es (I.G.L.); manuel.jordan@umh.es (M.M.J.V.)

[2] Soil Science Laboratory, Faculty of Biology, University of Barcelona, 08028 Barcelona, Spain; jaumebechborras@gmail.com

[3] Laboratory of Chemical Engineering and Engineering Sustainability, Faculty of Pure and Applied Sciences, Environmental Conservation and Management Open University of Cyprus, P.O. Box 12794, 2252 Latsia, Cyprus; antonis.zorpas@ouc.ac.cy or antoniszorpas@yahoo.com

* Correspondence: jonavar@umh.es; Tel.: +34-966-658-417

Received: 17 October 2018; Accepted: 29 November 2018; Published: 1 December 2018

Abstract: This article analysed the presence of trace metals (essential elements and pollutants) and soil properties in rural abandoned soils of a Mediterranean region. The soil properties determined were texture, pH, equivalent calcium carbonate, soil organic matter, availability of micronutrients (Fe, Mn, Cu, and Zn), and acid microwave digestion extraction to measure the trace metals considered as main pollutants (Cu, Zn, Cd, Cr, Ni, and Pb). Descriptive statistics and correlations were used to determine the relations among these parameters. pH, soil organic carbon (SOC), and clay were the main properties that controlled the availability of essential metals. pH was the main factor related to these metals in these calcareous soils. However, SOC, which can be incremented by adding organic fertilizers for soil rehabilitation as a sustainable practice, played an important role. Mean values of the metal composition in soils (Cu, Zn, Cd, Cr, Ni, and Pb) obtained in this study were similar to values reported for other areas in the Mediterranean basin.

Keywords: essential metals; Mediterranean agriculture; organic matter; pH; soil quality; trace metals

1. Introduction

Agriculture has been practiced for a long time in Mediterranean regions. Intensive agriculture and irrigation have been developed in the inner valleys between ranges and coastal areas. In mountainous areas and piedmonts, dry farming was the main type of cultivation for centuries, and soils were fertilized using organic amendments (i.e., manure). Nowadays, these regions are suffering from the abandonment of these traditional activities and the consequent soil degradation [1].

European policy has the aim of improving and maintaining sustainable agriculture and recovering the landscapes of mountain regions. Therefore, checking the soils to provide information about the soil quality status and developing correct environmental policy is important [2].

It is well known that soil quality is usually associated to the organic matter content in the soils. Concerning the physical properties and the soil organic carbon, organic matter amendments (an indicator that belongs to the environmental and economic pillar of sustainability) can increase water holding capacity, soil porosity, water infiltration, and percolation while decreasing soil crusting and bulk density [3–5]. Nowadays, the use of organic wastes as a source of soil organic matter has increased in Europe towards a circular economy [6]. A major assessable effect of the repeated application of organic wastes in soils (such as compost, biosolids, olive mill waste, etc.) is the optimization of the porosity of the soils, and, at the same time, the reduction in bulk density [7,8]. By improving soil properties, the soil efficiency could be incremented, which provides direct results in product safety and yield, and maintains agricultural job positions and the landscape.

However, other parameters should be considered besides only the physical properties—for instance, the presence of metals (both as pollutants and/or micronutrients). The natural concentrations of metals in soils tend to remain low depending on the geological parent material composition [9,10]. Anthropogenic inputs, including excessive use of agrochemicals and manure, in agricultural soils contribute to an increase of the content of some toxic heavy metals (such as Pb, Ni, Cr, and Zn) [11–14]. Although inorganic and organic fertilizers are necessary for agriculture, providing adequate nutrients and ensuring successful harvests, an enrichment of soils with Cu, Zn, and Cd has been reported when these materials are used during long-term repeated additions [15–18]. After the abandonment of agricultural fertilization, trace metals can remain in the soil. Heavy metal (HM) contamination and accumulation is a serious problem around the world due to the potential threat to food safety and its detrimental effects on human and animal health [19]. In recent years, there has been increasing ecological and global public health concern associated with environmental contamination by these metals [20,21].

Soils, by definition, are a part of the pillar of sustainability (economic, environmental, and social). The effort by the European Union in creating an information system on the Land Use/Cover Area frame Survey (LUCAS), a survey that provides harmonised and comparable statistics on land use and land cover across the whole of EU territory, is considerable. LUCAS Topsoil is the most comprehensive harmonised soil database for the EU, as it has 13 categories of physical and chemical properties, analysis of 12 heavy metals, and a visible and near infrared spectral library [21].

In fact, if soils receive pressure from outside sources, this may negatively and positively affect the sustainability on a horizontal level. In general, according to several researchers, heavy metals (trace metal elements according to Pourret, 2018 [22]) could affect soil sustainability [23–25]. For example, according to Tóth et al. (2016) [24], the presence of trace metals in soils may affect food safety as they enter the food chain. Moreover, soils receive pressure at the EU level and these pressures pose danger to the services that healthy soils provide; however, there is no common EU policy on soil protection [26].

In this work, we evaluated the relation between soil properties and the availability of essential trace elements and the content of pollutants (trace metals) in abandoned agricultural soils in eastern Spain in an area northwest of the province of Alicante. Herein, we present a study of some selected soil properties to predict the mobility of metals due to future actions related to soil rehabilitation (e.g., adding organic amendments).

This area, situated in the Mediterranean basin, has been long cultivated with cereal, almonds, and olive trees, among others. It is a typical Mediterranean cultivated land representative of those located in inner regions, close to the seacoast, and surrounded by mountains. Nowadays, soils are being abandoned and degraded (i.e., soil erosion) because of poor agricultural and economic returns. The landscape is changing, and sustainable dry agriculture may be a great opportunity to rehabilitate the area based on the maintenance or to increment organic matter levels in the soils and improve soil quality. However, soil pollution will be a concern.

2. Materials and Methods

In this work, one hundred agricultural soil samples were taken from different abandoned cultivation plots in the northwest of the province of Alicante (Spain) and analysed to check their quality based on trace metal composition (potential harmful elements), micronutrient availability, and soil properties (texture, pH, organic matter, and calcium carbonate content). The parcels were located in an area that is 24 km^2 (Figure 1), corresponding to fluvial terraces, and one sample was taken from each plot, approximately equally distributed in the area (based on a regular grid of the parcels), equivalent to four/five samples taken per square kilometre. The climate is Mediterranean (Csa, Köppen-Geiger climate classification) with a mean annual temperature of 15 °C and average rainfall of 500 mm, and the altitude is about 600 m above sea level. This area is in the upper valley of the Vinalopó River, and limestone neogenic sediments, consisting of sands, gravels, ridges, silts, and clays, determine the lithology. Soils present in the area are predominantly calcaric Fluvisols [27].

Soil samples (arable layer, first 20 cm) were taken and analysed, determining soil characteristics: texture by the Bouyoucos method [28] indicating the proportion of size particles (sand, silt, clay); pH 1:2.5 *w*/*v* water extract [29]; equivalent calcium carbonate content (CO_3) using the Bernard calcimeter [30]; and soil organic carbon (SOC) by the Walkley–Black method [31]. The availability of essential metals (Cu, Fe, Mn, and Zn) were determined by extracting with DTPA, as it is a commonly used method to determine this property [32–34], and measured in the extract by atomic absorption spectrometry. The content of trace elements (Metal-T) that can be considered as environmental pollutants (Cd, Cr, Cu, Ni, Pb, and Zn) was measured in soil samples after microwave acid digestion with HNO_3-H_2O_2 [35,36], quantifying the concentration of metals by ICP-OES analysis.

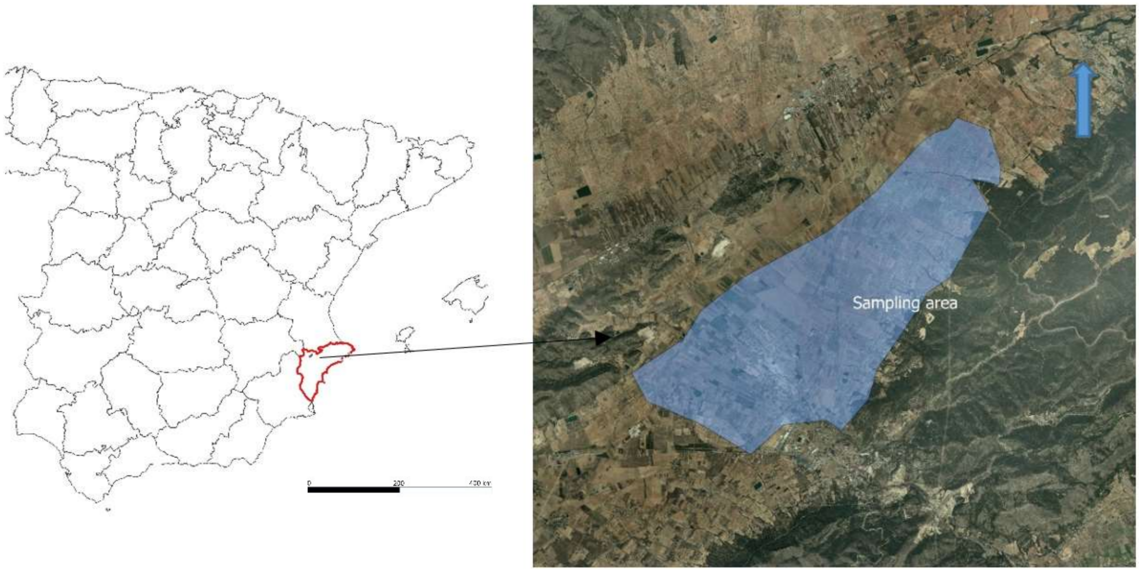

Figure 1. Location of the sampling area, northwest of the province of Alicante (eastern Spain).

Statistical analyses were performed using SPSS v. 24.0© software. Descriptive statistical parameters (mean, standard deviation) for soil data were calculated. Moreover, bivariate correlation (Pearson) analysis was applied among all the variables analysed; linear multiple regression analysis was used to learn the influence of soil properties on extractable and metal content in soils [37].

3. Results

Table 1 shows the descriptive statistics of soil properties and trace elements of the one hundred soil samples.

The texture of the soils varies between sandy-loam and clay-loam, which may depend on the relative position of the soils close to the Vinalopó River, which crosses through the centre of the area from NW to SE. These soils are calcareous soils, with an important content of equivalent calcium carbonate (33%) and the pH of all of the samples was basic (mean value, 8.6).

The abandoned agricultural soils have low SOC contents and extractable micronutrients, which can be associated to degradation processes (e.g., reduction of the input or organic matter and oxidation of SOC, precipitation of metal-carbonates, losses of nutrients by run-off or leaching, among others). Fe was the major micronutrient extracted, followed by Mn, Cu, and Zn. The relative contents of the available microelements, expressed as individual percentages of all of them extracted with DTPA, were Fe (37.6%), Mn (35.1%), Cu (16.9%), and Zn (10.4%).

Table 1. Statistical summary of soil properties (mean and SD: standard deviation).

Descriptive Statistics	Sand (%)	Clay (%)	Silt (%)	pH	CO_3 (%)	SOC (%)
Mean	56	23	21	8.6	33	0.65
SD	18	13	8	0.2	15	0.29
	Fe-DTPA (mg/kg)	**Mn-DTPA (mg/kg)**	**Cu-DTPA (mg/kg)**	**Zn-DTPA (mg/kg)**		
Mean	2.1	2.0	1.0	0.6		
SD	1.3	1.1	0.7	0.6		
	Cd-T (mg/kg)	**Ni-T (mg/kg)**	**Pb-T (mg/kg)**	**Cr-T (mg/kg)**	**Cu-T (mg/kg)**	**Zn-T (mg/kg)**
Mean	0.21	13	10	16	10	21
SD	0.07	6	3	7	4	9

The mean values of the metal composition determined by acid microwave digestion (Cd, Cr, Cu, Ni, Pb, and Zn) of the soils followed this decreasing order: Zn > Cr > Ni > Pb ≈ Cu > Cd (Table 1). The relative content of each element, considering a pool of all of them, was Zn (30.5%), Cr (22.5%), Ni (18.3%), Pb and Cu (14.2%), and Cd (0.3%). These soils had a very low concentration of Cd, which is positive considering its high potential toxicity [38]. The concentrations of these metals for the area studied are in accordance with the values given for total concentration in topsoil in the GEMAS (Geochemical Mapping of Agricultural and Grazing Land Soil, http://www.eurogeosurveys.org/projects/gemas/) project, although the scale and detail of sampling of GEMAS and this study were different. We compared the values obtained in this study with the limits given in GEMAS for the area where the soils are located (Table 2).

Table 2. Comparison between mean values of M-T in topsoil of this study and those given in GEMAS (interval of the geochemical baseline of maps in: http://www.eurogeosurveys.org/projects/gemas/).

	Cd-T (mg/kg)	Ni-T (mg/kg)	Pb-T (mg/kg)	Cr-T (mg/kg)	Cu-T (mg/kg)	Zn-T (mg/kg)
Mean	0.21	13	10	16	10	21
GEMAS interval	0.140–0.200	11–18	18–23	33–41	8.66–12.9	18–27

The main differences can be observed for Cr and Pb, where the values in this area are under the values given in GEMAS. The extraction method employed to determine the composition (nitric acid digestion in microwave) might be responsible in part. However, the scarcity of sources of pollution (industry and transport) for both trace metals in the area may be another important factor to consider.

In general, for all the parameters considered, low standard deviation values were obtained, especially for total composition of trace metals. This may indicate that the metal concentrations are closely related to the geochemical composition of the parent material of the soils (quaternary sediments) [36]. For instance, the high Ni, Cd, and Cr mean values in agricultural soils in Thiva have been ascribed to local parent materials enriched with these specific metals [39]. Mean levels of the total metal concentrations obtained in this study are similar to the corresponding values reported by other authors in Mediterranean environments, as indicated in Table 3 [39–44].

In comparison with the Canadian, Dutch, and Spanish guideline values for these pollutants in agricultural soils (Table 4), concentrations of all metals analysed are always lower than the threshold value established.

The bivariate correlations (Pearson's R) among all the parameters were determined among the soil characteristics (Appendix A). Negative correlations between pH and Fe-DTPA, Mn-DTPA, and Cu-DTPA were observed. Consequently, an increase of the pH of these soils, i.e., applying a basic amendment, could diminish the availability of these micronutrients for plants. There is also a positive correlation between Cu-T and Cu-DTPA. The concentration of pollutants of these soils, for most of the metals analysed, was related positively or negatively with clay, silt, pH, $CaCO_3$ equivalent (CO_3), and SOC.

Table 3. Mean metal concentrations (mg/kg dw) determined in agricultural soils of various Mediterranean areas.

Mediterranean Area	Cd	Ni	Pb	Cr	Cu	Zn	Reference
Almería (Spain)	0.4	26.9	25.6	29.6	25.7	65.7	Rodríguez et al. (2013)
Alicante (Spain)	0.34	20.9	22.8	26.5	22.5	52.8	Micó et al. (2006)
Murcia (Spain)	0.22	13.5	48.9	17.6	11	18.4	Acosta et al. (2011)
Castellón (Spain)	0.33	19.3	55.8	33.3	36.6	78.5	Peris et al. (2008)
Piemonte (Italy)	-	83.2	16.1	46.2	58.3	62.7	Facchinelli et al. (2001)
Zagreb (Croatia)	0.66	49.5	25.9	-	20.8	77.9	Romic and Romic (2003)
Thiva (Greece)	32.0	1521.0	24.0	277.0	-	67.0	Antibachi et al. (2012)
Peloponnese (Greece)	0.54	146.8	19.7	83.1	74.7	74.9	Kelepertzis (2014)

Table 4. Reference values for contaminated soils in national regulations.

Regulation	Cd-T	Ni-T	Pb-T	Cr-T	Cu-T	Zn-T	Reference
Canadian regulation	1.4	50.0	70.0	64.0	63.0	200.0	CCME (2007)
Dutch regulation [1]	0.8	35.0	85.0	100.0	36.0	140.0	VROM (2000)
Dutch regulation [2]	12.0	210.0	530.0	380.0	190.0	720.0	VROM (2000)
Spanish regulation [3]	3.0	112.0	300.0	150.0	210.0	450.0	RD1310/90 (1990)

[1] Dutch target value, [2] Dutch intervention value, [3] for soil pH > 7, nowadays the limits depend on each Spanish autonomous community based on RD 9/2005 and their own regulations [45].

After analysing the results of bivariate correlations, a multiple correlation analysis was carried out between each of the metals (micronutrients extracted with DTPA and metal concentration after acid microwave digestion Metal-T) and the characteristics of the soils. The results of the Pearson test give significant differences, especially for soil pH.

Most of the trace elements analysed, available essential metals or concentration of pollutants, are correlated with the soil pH. The sorption/desorption reactions of metal(loid)s on/from soil sorbents are influenced by pH, the nature of soil components, and the presence and concentrations of cations and inorganic anions. In general, low pH can favour metal mobility, affecting variable charge of the surfaces, whereas metal cations are fixed more easily at high pH [46]. Moreover, a high pH favours the precipitation of metal-carbonates [47].

Table 5 shows the equations obtained, and the coefficients R and F. pH, SOC, clay, and CO_3 were closely related to the content of pollutants (extracted by acid microwave digestion). The most significant values (R and F) were obtained for the multiple regressions obtained for Ni-T and Zn-T. However, Ni-T was associated to Clay and Zn-T was to SOC as secondary important factors in these multiple regression tests, after which the pH was the most important for both metals.

Table 5. Multiple regression equations between micronutrients (metal-DTPA) and metal content (Metal-T, extraction with HNO_3-H_2O_2), and soil properties.

Equation	R value	F value
Fe-DTPA = −1.64 pH − 0.04 Clay + 17.0	0.429	10.90 ***
Mn-DTPA = −1.55 pH + 15.2	0.325	11.60 ***
Cu-DTPA = −0.62 pH + 6.30	0.220	04.97 *
Zn-DTPA = 0.30 pH − 0.09 Clay − 0.08 Silt − 1.61	0.336	04.08 *
Cd-T = 0.05 SOC − 0.02 pH − 0.001 CO_3 + 0.304	0.337	04.09 *
Ni-T = −8.10 pH + 0.22 Clay + 0.06 CO_3 + 0.03 Silt + 74.47	0.714	24.60 ***
Cu-T = −4.30 pH + 2.37 SOC + 0.09 Clay + 43.20	0.511	11.33 ***
Zn-T = −2.99 pH + 2.87 SOC + 0.43 Clay − 0.07 Silt + 32.69	0.709	24.00 ***
Cr-T = −3.13 pH + 0.22 Clay + 0.19 CO_3 − 0.11 Silt + 33.65	0.553	10.44 ***
Pb-T = 4.12 SOC − 0.09 CO_3 + 0.07 Clay + 8.52	0.576	15.87 ***

* and *** indicate a significance level at p = 0.05, 0.01, and 0.001, respectively.

4. Discussion

In these calcareous soils, it is important to notice that the pH seemed to be the most important factor controlling micronutrient availability, although the chemical form of the metal in the soil is also important for understanding the metal uptake by plants [48]. Negative correlation coefficients with the pH were found for Fe, Mn, and Cu (DTPA extraction), but it was positive for Zn. However, as several researchers report, it is important to consider the influences of other soil properties, such as the case of Zn [49,50]. In this work, clay and silt were related, as multiple regression analysis showed, along with Zn.

The scarcity of organic matter may be, in part, responsible for the great pH influence, because its content seems to be low enough to have poor influence (associated to the abandonment of traditional agricultural practices without the addition of organic inputs).

The SOC of these soils can be incremented, adding organic amendments, which is a sustainable practice based on traditional agriculture. The addition of organic amendments may improve the physical, chemical, and biological properties of soil [51]. However, it should be taken into account that soil organic carbon can control the metal content and availability, and this strategy can move pollutants with environmental risk.

High levels of metals in soils increase their uptake by plants, which depends not only on metal content in soils but also is determined by the soil pH value, organic matter, and clay contents, and is influenced by fertilization and the use of pesticides [21,52]. Micó et al. (2006) [41] found, using 54 samples of agricultural soils throughout the province of Alicante (surface of 5816 km^2), a significant correlation between lithogenic metals and some soil properties, such as soil organic matter, clay content, and carbonates. This previous work is very relevant and is centred on finding the baseline of soil metal concentration. Starting from this point, the present study paid attention to the next step, i.e. what would happen if we considered soils for restoration and change the soil properties.

Although the pH is in fact more important in this case, as statistical results indicated, the variation of pH and a possible decrease of this by applying organic amendments, may favour the mobilization of pollutants in these calcareous soils. The choice of a particular amendment is often problematic and the soil characteristics may be considered before its application [53].

It is important to check the availability of micronutrients and the effects on trace metal composition to ensure soil quality. On the one hand, it was observed that pH is the factor that most affects the availability of micronutrients analysed. On the other hand, trace metals are related to clay and SOC, and less with the equivalent calcium carbonate (CO_3). However, great retention of Cr, Cu, Ni, Zn, and Cd in calcaric Fluvisols has been reported [54]. In this sense, the effect of pH may be associated to the relation between soil pH and the presence of carbonates.

In general, the correlations obtained were higher between the soil properties and the metal concentration extracted by acid microwave digestion than those obtained for the essential metals extracted with DTPA. This result should be considered for agriculture or soil rehabilitation purposes. In fact, pollutants present in the soils can be mobilized and be available for plants, but with environmental consequences if inadequate fertilization is applied. These are the two faces of the same situation: availability of micronutrients versus mobility and environmental pollution.

Determining which is the main factors controlling the bioavailability of metals is important for future soil rehabilitation and landscape recovery, whether they come from bedrock or from anthropogenic inputs. Nunes et al. (2014) [55], in a work done with Mediterranean soils located in the west of Spain, suggested that the enhanced mobility of heavy metals is related to anthropic activities. Agriculture has a great influence due to the inputs of micronutrients/pollutants with fertilization and the effect on soil properties. These effects could be the same when restoring soils. At policy level, managing heavy metal balances in the environmental framework requires well-defined soil protection policies with a specific focus on agricultural soils [21].

In some cases, a combination of both factors, bedrock composition and the influence of anthropic activities, should be considered. Mainly, the presence of metals needs to be determined in the soils before adding organic amendments. Along these lines, the GEMAS project can be considered a good tool before soil rehabilitation.

5. Conclusions

Soil is a key factor of sustainability and landscape, and soil quality is in fact one of the major considerations that should be considered before land restoration. In this case, the results of this study provide data about trace metal levels in calcareous soils of a Mediterranean area that can help to improve the strategies for land rehabilitation. The most important soil properties related to metal content should be considered. Many land restoration techniques involve the addition of organic matter to the soils and this can pose a risk if this modifies soil conditions (i.e., pH) and, as a consequence, the availability and mobility of trace metals.

Our results indicate that soil pH influences the available forms of essential metals (DTPA extraction). Moreover, trace metals were positively correlated with SOC and clay, and negatively correlated with the pH values of soils.

The mean values of the metal composition in soils (Cd, Cr, Cu, Ni, Pb, and Zn) obtained in this study were similar to values reported for other areas in the Mediterranean basin [36], and these results may be extended to other calcareous soils. Their total content in soil seems to be determined by the bedrock composition.

The soil quality of this area is associated to a low metal content, and this facilitates the possibility of adding manure or other organic fertilizers to improve soil quality without increasing the mobility of pollutants (i.e., by leaching to underground waters). The amendments can increment the soil organic matter content, which may positively affect physical properties, carbon sequestration by soils, help develop sustainable agriculture or forestry activity, recover the landscape, and promote compliance with the strategic objectives of the European Union's environmental policy. Rain-fed agriculture could be recovered, improving soil quality.

These actions are focused on the strategies for sustainable development. However, the type of organic matter and the effects on trace elemental composition should be considered before to avoid the mobilization of metals, for food safety [24], and to maintain micronutrient availability.

Author Contributions: Conceptualization and methodology: J.N.-P., M.B.A.-C. and I.G.L.; software and validation: I.G.L. and A.A.Z.; formal analysis and data curation: J.N.-P., M.B.A.-C. and I.G.L.; writing—original draft preparation: J.N.-P. and A.A.Z.; writing—review and editing: J.N.-P. and M.B.A.-C.; supervision: M.M.J.V. and J.B.B.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1.

Propertie	Sand	Clay	Silt	pH	CO_3	SOC	Fe (1)	Mn (1)	Cu (1)	Zn (1)	Cd (2)	Ni (2)	Pb (2)	Cr (2)	Cu (2)	Zn (2)
Sand	1	−0.922 **	−0.747 **	0.284 **	−0.281 **	−0.120	0.309 **	0.103	0.106	0.315 **	−0.031	−0.628 **	−0.190	−0.423 **	−0.279 **	−0.615 **
Clay		1	0.432 **	−0.185	0.077	−0.029	−0.307 **	−0.150	−0.039	−0.285 **	−0.064	0.592 **	0.262 **	0.402 **	0.345 **	0.632 **
Silt			1	−0.345 **	0.522 **	0.330 **	−0.193	0.016	−0.181	−0.246 *	0.182	0.448 **	−0.007	0.296 **	0.058	0.347 **
pH				1	−0.225 *	−0.445 **	−0.237 *	−0.325 **	−0.220 *	0.201 *	−0.198 *	−0.466 **	−0.140	−0.225 *	−0.401 **	−0.31 **
CO_3					1	0.153	−0.005	−0.076	−0.021	−0.113	0.241 *	0.282 **	−0.341 **	0.389 **	−0.028	0.106
SOC						1	0.041	0.120	0.017	0.050	0.263 **	0.106	0.294 **	0.227 *	0.288 **	0.292 **
Fe (1)							1	0.690 **	0.480 **	0.206 *	0.134	0.164	−0.013	−0.142	0.060	−0.221 *
Mn (1)								1	0.493 **	0.028	0.191	0.334 **	0.131	0.035	0.168	−0.012
Cu (1)									1	0.196	−0.070	0.208 *	0.193	0.074	0.452 **	0.077
Zn (1)										1	−0.172	−0.208 *	−0.020	−0.234 *	−0.148	−0.154
Cd (2)											1	0.146	−0.130	0.434 **	0.106	0.059
Ni (2)												1	0.317 **	0.544 **	0.473 **	0.637 **
Pb (2)													1	0.310 **	0.516 **	0.442 **
Cr (2)														1	0.376 **	0.535 **
Cu (2)															1	0.642 **
Zn (2)																1

Pearson correlations R (p = 0.05) among soil properties determined. (1): DTPA; (2): Total content; *, **, and ***: significance level at p = 0.05, 0.01, and 0.001.

References

1. Rey Benayas, J.M.; Martins, A.; Nicolau, J.M.; Schulz, J.J. Abandonment of agricultural land: An overview of drivers and consequences. *CAB Rev.* **2007**, *2*, 1–14. [CrossRef]
2. Marques, M.J.; Jimenez-Ballesta, R.; Álvarez, A.; Bienes, R. Spanish Research on Soil Damage. *Sci. Total Environ.* **2007**, *378*, 1–4. [CrossRef]
3. Celik, I.; Ortas, I.; Kilic, S. Effects of compost, mycorrhiza, manure and fertilizer on some physical properties of a Chromoxerert soil. *Soil Tillage Res.* **2004**, *78*, 59–67. [CrossRef]
4. Herencia, J.F.; García-Galavís, P.A.; Maqueda, C. Long-term effect of organic and mineral fertilization on soil physical properties under greenhouse and outdoor management practices. *Pedosphere* **2011**, *21*, 443–453. [CrossRef]
5. Li, Z.; Schneider, R.L.; Morreale, S.J.; Xie, Y.; Li, C.; Li, J. Woody organic amendments for retaining soil water, improving soil properties and enhancing plant growth in desertified soils of Ningxia, China. *Geoderma* **2018**, *310*, 143–152. [CrossRef]
6. Lee, P.; Sims, E.; Bertham, O.; Symington, H.; Bell, N.; Pfaltzgraff, L.; Sjögren, P.; Wilts, H.; O'Brien, M.; Benke, J. Towards a Circular Economy—Waste Management in the EU. Available online: http://www.europarl.europa.eu/RegData/etudes/STUD/2017/581913/EPRS_STU%282017%29581913_EN.pdf (accessed on 1 December 2018).
7. Martin, M.P.; Seen, D.L.; Boulonne, L.; Jolivet, C.; Nair, K.M.; Bourgeon, G.; Arrouays, D. Optimizing pedotransfer functions for estimating soil bulk density using boosted regression trees. *Soil Sci. Soc. Am. J.* **2009**, *73*, 485–493. [CrossRef]
8. Schjønning, P.; Thomsen, I.K. Shallow tillage effects on soil properties for temperate-region hard-setting soils. *Soil Tillage Res.* **2013**, *132*, 12–20. [CrossRef]
9. Shan, Y.; Tysklind, M.; Hao, F.; Ouyang, W.; Chen, S.; Lin, C. Identification of sources of heavy metals in agricultural soils using multivariate analysis and GIS. *J. Soil Sediments* **2013**, *13*, 720–729. [CrossRef]
10. Jiménez, R.; Navarro Pedreño, J. Introducción a la contaminación de suelos. In *Introducción a la Contaminación de Suelos*; Jiménez, R., Ed.; Ediciones Mundiprensa: Madrid, Spain, 2017; pp. 1–21. ISBN 978-84-8476-789-3.
11. Nicholson, F.A.; Smith, S.R.; Alloway, B.J.; Carlton-Smith, C.; Chambers, B.J. An inventory of heavy metals inputs to agricultural soils in England and Wales. *Sci. Total Environ.* **2003**, *311*, 205–219. [CrossRef]
12. Hani, A.; Pazira, E. Heavy metals assessment and identification of their sources in agricultural soils of Southern Tehran, Iran. *Environ. Monit. Assess.* **2011**, *176*, 677–691. [CrossRef]
13. Lu, A.; Wang, J.; Qin, X.; Wang, K.; Han, P.; Zhang, S. Multivariate and geostatistical analyses of the spatial distribution and origin of heavy metals in the agricultural soils in Shunyi, Beijing, China. *Sci. Total Environ.* **2012**, *425*, 66–74. [CrossRef]
14. Romic, D.; Romic, M.; Zovko, M.; Bakic, H.; Ondrasek, G. Trace metals in the coastal soils developed from estuarine floodplain sediments in the Croatian Mediterranean region. *Environ. Geochem. Health* **2018**, *34*, 399–416. [CrossRef] [PubMed]
15. Peris, M.; Recatalá, L.; Micó, C.; Sánchez, R.; Sánchez, J. Increasing the knowledge of heavy metal contents and sources in agricultural soils of the European Mediterranean region. *Water Air Soil Pollut.* **2008**, *192*, 25–37. [CrossRef]
16. Franco-Uria, A.; López-Mateo, C.; Roca, E.; Fernández-Marcos, M.L. Source identification of heavy metals in pastureland by multivariate analysis in NW Spain. *J. Hazard. Mater.* **2009**, *165*, 1008–1015. [CrossRef] [PubMed]
17. Maas, S.; Scheifler, R.; Benslama, M.; Crini, N.; Lucot, E.; Brahmia, Z.; Benyacoub, S.; Giraudoux, P. Spatial distribution of heavy metal concentrations in urban, suburban and agricultural soils in a Mediterranean city of Algeria. *Environ. Pollut.* **2010**, *158*, 2294–2301. [CrossRef] [PubMed]
18. Acosta, J.A.; Faz, A.; Martínez-Martínez, S.; Arocena, J.M. Enrichment of metals in soils subjected to different land uses in a typical Mediterranean environment (Murcia city, southeast Spain). *Appl. Geochem.* **2011**, *26*, 405–414. [CrossRef]
19. Hu, B.; Jia, X.; Hu, J.; Xu, D.; Xia, F.; Li, Y. Assessment of heavy metal pollution and health risks in the soil-plant-human system in the Yangtze River Delta, China. *Int. J. Environ. Res. Public Health* **2017**, *14*, 1042. [CrossRef]

20. Tchounwou, P.B.; Yedjou, C.G.; Patlolla, A.K.; Sutton, D.J. Heavy metals toxicity and the environment. *EXS* **2012**, *101*, 133–164. [CrossRef]
21. Panagos, P.; Ballabia, C.; Lugato, E.; Jones, A.; Borrelli, P.; Scarpa, S.; Orgiazzi, A.; Montanarella, L. Potential sources of anthropogenic copper inputs to European agricultural soils. *Sustainability* **2018**, *10*, 2380. [CrossRef]
22. Pourret, O. On the necessity of banning the term "Heavy Metal" from the scientific literature. *Sustainability* **2018**, *10*, 2879. [CrossRef]
23. Zorpas, A.A. Heavy Metals Leachability Before, During and After Composting of Sewage Sludge with Natural Zeolite. *Desalination Water Treat.* **2009**, *8*, 256–262. [CrossRef]
24. Tóth, G.; Hermann, T.; Da Silva, M.R.; Montanarella, L. Heavy metals in agricultural soils of the European Union with implications for food safety. *Environ. Int.* **2016**, *88*, 299–309. [CrossRef] [PubMed]
25. Adagunodo, T.A.; Sunmonu, L.A.; Emetere, M.E. Heavy metals' data in soils for agricultural activities. *Data Brief* **2018**, *18*, 1847–1855. [CrossRef]
26. Glæsner, N.; Helming, K.; de Vries, W. Do Current European Policies Prevent Soil Threats and Support Soil Functions? *Sustainability* **2014**, *6*, 9538–9563. [CrossRef]
27. De la Torre, A.; Alías, L.J. *Suelos y Vegetación en el Alto Vinalopó*; Universidad de Alicante: Alicante, Spain, 1996; p. 263. ISBN 8479082712.
28. Gee, G.W.; Bauder, J.W. Particle-Size Analysis. In *Methods of Soil Analysis 1: Physical and Mineralogical Methods*, 2nd ed.; Campbell, G.S., Jackson, R.D., Mortland, M.M., Nielsen, D.R., Klute, A., Eds.; SSSA Book Series: Madison, WI, USA, 1986; pp. 383–411. ISBN 0-89118-088-5.
29. MAPA. *Métodos Oficiales de Análisis. Tomo III*; MAPA: Madrid, Spain, 1986; p. 532. ISBN 847479532X.
30. Hulseman, J. An inventory of marine carbonate materials. *J. Sediment. Petrol.* **1966**, *36*, 622–625.
31. Nelson, D.W.; Sommers, L.E. Total Carbon, Organic Carbon, and Organic Matter. In *Methods of Soil Analysis. Part 3. Chemical Methods*; Sparks, D.L., Page, L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnston, C.T., Sumner, M.E., Eds.; SSSA: Madison, WI, USA, 1996; pp. 961–1010. ISBN 978-0891188254.
32. Lindsay, W.L.; Norvell, W.A. Development of a DTPA Soil Test for Zinc, Iron, Manganese and Copper. *Soil Sci. Soc. Am. J.* **1978**, *42*, 421–428. [CrossRef]
33. Baldantoni, D.; Leone, A.; Iovieno, P.; Morra, L.; Zaccardelli, M.; Alfani, A. Total and available soil trace element concentrations in two Mediterranean agricultural systems treated with municipal waste compost or conventional mineral fertilizers. *Chemosphere* **2010**, *80*, 1006–1013. [CrossRef]
34. Iatrou, M.; Papadopoulos, A.; Papadopoulos, F.; Dichala, O.; Psoma, P.; Bountla, A. Determination of Soil-Available Micronutrients using the DTPA and Mehlich 3 Methods for Greek Soils Having Variable Amounts of Calcium Carbonate. *Commun. Soil Sci. Plant Anal.* **2015**, *46*, 1905–1912. [CrossRef]
35. Moral, R.; Navarro-Pedreño, J.; Gómez, I.; Mataix, J. Quantitative Analysis of Organic Residues: Effects of Samples Preparation in the Determination of Metal. *Commun. Soil Sci. Plant Anal.* **1996**, *27*, 753–761. [CrossRef]
36. Micó, C.; Peris, M.; Recatalá, L.; Sánchez, J. Baseline values for heavy metals in agricultural soils in a European Mediterranean region. *Sci. Total Environ.* **2007**, *378*, 13–17. [CrossRef]
37. Field, A. *Discovering Statistics with SPSS*, 3rd ed.; SAGE Publications Ltd.: London, UK, 2009; p. 821. ISBN 978-1847879073.
38. Moreno, J.L.; García, C.; Landi, L.; Falchini, L.; Pietramellara, G.; Nannipieri, P. The ecological dose value (ED50) for assessing Cd toxicity on ATP content and dehydrogenase and urease activities of soil. *Soil Biol. Biochem.* **2001**, *33*, 483–489. [CrossRef]
39. Antibachi, D.; Kelepertzis, E.; Kelepertis, A. Heavy metals in agricultural soils of the Mouriki-Thiva area and environmental impact implications. *Soil Sediment Contam.* **2012**, *21*, 434–450. [CrossRef]
40. Rodríguez, J.A.; Ramos-Miras, J.J.; Boluda, R.; Gil, C. Spatial relations of heavy metals in arable and greenhouse soils of a Mediterranean environment region (Spain). *Geoderma* **2013**, *200–201*, 180–188. [CrossRef]
41. Micó, C.; Recatalá, L.; Peris, M.; Sánchez, J. Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. *Chemosphere* **2006**, *65*, 863–872. [CrossRef] [PubMed]
42. Facchinelli, A.; Sacchi, E.; Mallen, L. Multivariate statistical and GIS-based approach to identify heavy metal sources in soils. *Environ. Pollut.* **2001**, *114*, 313–324. [CrossRef]

43. Kelepertzis, E. Accumulation of heavy metals in agricultural soils of Mediterranean: Insights from Argolida basin, Peloponnese, Greece. *Geoderma* **2014**, *221–222*, 82–90. [CrossRef]
44. Romic, M.; Romic, D. Heavy metals distribution in agricultural topsoils in urban area. *Environ. Geol.* **2003**, *43*, 795–805. [CrossRef]
45. Jiménez Ballesta, R.; Navarro-Pedreño, J.; Gómez, I.; Almendro, M.B. Contaminación de suelos por metales pesados. In *Introducción a la Contaminación de Suelos*; Jiménez Ballesta, R., Ed.; Mundi-Prensa: Madrid, Spain, 2017; pp. 39–71. ISBN 978-84-8476-789-3.
46. Caporale, A.G.; Violante, A. Chemical processes affecting the mobility of heavy metals and metalloids in soil environments. *Curr. Pollut. Rep.* **2016**, *2*, 15–27. [CrossRef]
47. Rieuwerts, J.S.; Thorton, I.; Farago, M.E.; Ashmore, M.R. Factors influencing metal bioavailability in soils: Preliminary investigations for the development of a critical loads approach for metals. *Chem. Speciat. Bioavailab.* **1998**, *10*, 61–75. [CrossRef]
48. Cataldo, D.A.; Wildung, R.E. Soil and Plant Factors Influencing the Accumulation of Heavy Metals by Plants. *Environ. Health Perspect.* **1978**, *27*, 149–159. [CrossRef]
49. Sanders, J.R.; Adams, T. McM. The effects of pH and soil type on concentrations of zinc, copper and nickel extracted by calcium chloride from sewage sludge-treated soils. *Environ. Pollut.* **1987**, *43*, 219–228. [CrossRef]
50. Yuan, G.; Lavkulich, L.M. Sorption behavior of copper, zinc, and cadmium in response to simulated changes in soil properties. *Commun. Soil Sci. Plant Anal.* **1997**, *28*, 571–587. [CrossRef]
51. Soriano-Disla, J.M.; Gómez, I.; Navarro-Pedreño, J. The influence of soil properties on the mobility of metals following a single application of polluted sewage sludge to seventy agricultural topsoils: A laboratory column study. *Soil Sediment Control* **2011**, *20*, 961–976. [CrossRef]
52. Fytianos, K.; Katsianis, G.; Triantafyllou, P.; Zachariadis, G. Accumulation of heavy metals in vegetables grown in an industrial area in relation to soil. *Bull. Environ. Contam. Toxicol.* **2001**, *67*, 423–430. [CrossRef] [PubMed]
53. Hattab, N.; Motelica-Heino, M.; Faure, O.; Bouchardon, J.L. Effect of fresh and mature organic amendments on the phytoremediation of technosols contaminated with high concentrations of trace elements. *J. Environ. Manag.* **2015**, *159*, 37–47. [CrossRef] [PubMed]
54. Lafuente, A.L.; González, C.; Quintana, J.R.; Vázquez, A.; Romero, A. Mobility of heavy metals in poorly developed carbonate soils in the Mediterranean region. *Geoderma* **2008**, *145*, 238–244. [CrossRef]
55. Nunes, J.R.; Ramos-Miras, J.; López-Piñeiro, A.; Loures, L.; Gil, C.; Coelho, J.; Loures, A. Concentrations of available heavy metals in Mediterranean agricultural soils and their relation with some selected properties: A case study in typical Mediterranean soils. *Sustainability* **2014**, *6*, 9124–9138. [CrossRef]