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ASSESSING SOIL CONTAMINATION AND TEMPORAL TRENDS OF HEAVY METAL CONTENTS IN GREENHOUSES ON SEMIARID LAND

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ABSTRACT

Information about the behaviour and temporal evolution of heavy metals in agricultural soils is limited, particularly about greenhouse soils on semiarid lands, which is non-existent. Western Almería (Southern Spain) is a semiarid land where some 30,000 ha are occupied by greenhouses with high productivity. As these greenhouses are fundamental to the socio-economic development of this area, they should be maintained

and well-conserved. However, there are indications that long-term intensive agriculture with considerable agrochemicals use can deteriorate soil quality, which in turn, would reduce productivity and food quality. This study was conducted to investigate soil contamination and the temporal trends of heavy metal concentrations in greenhouse soils of western Almería. Contamination level, availability and sources of metals were evaluated by the extractable fraction percentage, by indices zinc equivalent, geo-accumulation, enrichment factor and pollution load, and by a correlation analysis between soil properties and metal contents. The results showed that the total contents of Cd, Cu, Ni and Pb, and the available concentration of Cd, Cu, Pb, and Zn, were significantly higher than background levels. Temporal patterns indicated that these elements accumulate in greenhouse soils. After more than 20 years of intensive agriculture, the available concentration of elements, and contamination, had clearly increased.

KEYWORDS: intensive agriculture impact; contamination indices; Trace elements; heavy metal-enriched; Agrochemicals.

INTRODUCTION

Soil heavy metal (HM) pollution are related to different sources of pollution, such as such as mining (Mirzaei *et al*., 2014; Odumo *et al*., 2014; Rodríguez-Martín *et al*., 2014; Sakizadeh *et al*., 2015), industry and energy production (Gutiérrez *et al*., 2016; Rodríguez Martín & Nanos, 2016; Hou *et al*., 2017), which results in very high concentrations in the soil. However, the contamination by HMs takes greater importance in cultivated soils, although the contents in soils are smaller than in industrial soils (Shao

et al., 2016; Tianlik *et al*., 2016). Soil is one of the most important reservoirs of HMs and one of the principal routes of metals uptake in crops. High-intensity cropping can increase the HM concentration in soil and water, which could affect the content of HM in plants (Li *et al*., 2017; Zhang *et al*., 2017). It can potentially affect human health; metals such as Pb and Cd can enter soil via the food chain, exceed normal limits, and have harmful effects (Roy & McDonald, 2015).

The intensification of certain agricultural practices, the continued or excessive use of fertilizers and pesticides, as well as machinery, all increase HM contents in agricultural soils (Ramos-Miras *et al*., 2011; Long *et al*., 2013; Ding *et al*., 2017; Khaledian *et al*., 2017). Several studies have revealed that greenhouse intensive-production practices increase the accumulation of trace metals in soils, particularly Cd, Cu, Hg and Zn, which has been related with agrochemical inputs (Gil *et al.,* 2010; Ramos-Miras *et al.,* 2012; Rodríguez-Martín *et al*., 2013).Others have shown evidences about the behaviour of HM over time (Álvarez-Ayuso *et al*., 2008; Kochem-Mallmann *et al*., 2012; Long *et al*., 2013; Ordoñez *et al*., 2015; Chen *et al*., 2016), but information on this topic in greenhouse soils (GS) is scarce and no other information except for Ramos-Miras *et al*. (2012) on Hg have been found about GS in semiarid lands in the Mediterranean region.

The western Almería region is a very important semiarid land of South Spain from both socio-economic and agricultural viewpoints. The zone is intensively cultivated, but not industrialised. Agriculture is based on greenhouses, wherein soils have been vastly altered by the intense agricultural practices to which they are submitted. The average yearly consumption of fertilisers in western Almería is about 2,200 kg ha^{-1}, and can even reach 3,400 kg ha^{-1} for some crops, while the yearly consumption of pesticides is about 150 kg or 150 L per ha (Gil *et al*., 2004; Plaza-Bolaños *et al*., 2012) and there is evidence

that this intense agricultural activity is having a very strong impact on soils and on the environment (Plaza-Bolaños *et al*., 2012).

For these reasons, this work aimed to: (i) determine soil properties, total contents and the extractable concentrations with EDTA of Cd, Co, Cu, Fe, Ni, Pb Zn, in 71 GS from a traditionally Mediterranean agricultural area of semiarid land (western Almeria, South Spain); (ii) assess soil contamination; (iii) establish relationships between metal contents and soil properties; (iv) assess temporal trends after three periods (<10, 10-20 and >20 years) of intensive cultivation. The results were compared with the background levels obtained for soils in the same area. Different indices have been used to assess soil pollution. Some provide a simple, comparative means for assessing the level of heavy metal pollution in soils. Indices proposed by Andreu & Boluda (1995), Ramos-Miras *et al*. (2011) and Tamim *et al*. (2016), among others. Thus, metal available fraction percentage (A), zinc-equivalent (ZnEq), geo-accumulation index (Igeo), enrichment factor (EF), contamination factor (CF), and the pollution load index (PLI) were used as methods to assess soil contamination.

MATERIALS AND METHODS

Study Area and Sampling

The study area (330 km^2 in a coastal lying area with about 30 000 ha occupied by greenhouses) is located to the southeast of Spain (Figure 1). The predominant crops in the area are fruits and vegetables: pepper, tomato, zucchini, cucumber, melon, eggplant, and watermelon. The soil of most greenhouses could be classified as Technosols (IUSS Working Group WRB 2015) and could be described as an artificially layered soil, with commonly three layers over the natural substrate (Figure 2): sand layer (10-15 cm),

organic matter layer (manure, 5-10 cm), and a clay layer (CL), brought in origin from quarries, and commonly known as "tierra de cañada" (25-50 cm). Clay layer is important because is involved in water storage, nutrient retention, contaminant fixing, on which fertilizers were supplied to the GS, and, therefore, where toxic elements could be accumulated. For these reasons, CL was sampled and analysed. Its features are: calcareous nature, colluvium-alluvium origin, red to reddish brown, loam to clayed.

Seventy-one GS samples were selected to study soils. To obtain true reference values (control soils, CS samples), eleven quarry samples were collected too as control soil samples (CS). This quarries soils have similar edaphic characteristics and all the GS studied were build up with these similar sediments. The background level is calculated as the mean value of these eleven CS. Figure 1 illustrates the location of the 82 sampling points. Random subsampling was carried out at each site to obtain five subsamples, which were mixed and homogenised to form a single compound sample, which was analysed.

Compound samples were then grouped according to their cropping age as follows: 24 samples from GS used for less than 10 years (GS1), 29 GS used for 10-20 years (GS2), and 18 samples from GS used for more than 20 years (GS3).

Analytical Methods

All the samples were air-dried, sieved with a 2-mm grid sieve and stored in hermetically sealed polyethylene bags until analysed. Standard soil analyses were carried out according to the methods referenced by Gil *et al*. (2004), Ramos-Miras *et al*. (2011) and Rodríguez-Martín *et al*. (2013). Three soil granulometric fractions (sand, silt, clay) were determined by the pipette method. Soil pH was measured in a 1:5 (soil/distilled water) extract. Soil organic matter (SOM) was analysed by the Walkley–Black method and

carbonate concentration by gas volumetric method. Available P was established following the Olsen method. Determination of HM total content was performed using hydrofluoric and nitric acid digestion in a microwave oven Milestone 1200 (Milestone Inc, CT USA) following the EPA 3052 procedure reported by Kingston & Walter (1995) using a sample of 0.5 g. A reference material was used (BCR-141, calcareous loamy soil, sample no. 00051; BCR, Brussels, Belgium) to assess the method's accuracy. EDTA-extractable content was carried out by the Quevauviller *et al.* (1994) procedure, which estimates the available fraction for plants in calcareous soils (Ramos-Miras *et al.*, 2011; Zeng *et al.*, 2011). Five grams of soil were extracted with 50 mL of EDTA 0.05 M, pH=7.

The metal concentrations in digested and EDTA extracts were measured in atomic absorption spectrophotometer equipment GBC-906AA (GBC, Hampshire, IL, USA). Matrix interferences were checked by standard addition techniques; no matrix interferences were observed for Cd, Co, Cu, Fe, Ni, Pb and Zn. The blank sample and the certified reference material were extracted and analysed with each batch of 15 samples. Good recoveries were obtained: 96% Cd, 103% Co, 92% Cu, 97% Fe, 94% Ni, 110% Pb and 102% Zn. Three replicates were analysed per sample to check the accuracy of the results. The determined analytical variations were lower than 10% for all the metals. The limit of quantification (LOQ) ranged between 0.07 (Cd) and 32 mg kg^{-1} (Fe). All the analysed metals were above the LOQ. The concentrations of elements are presented as mg kg^{-1} dry matter.

Quantification of Soil Contamination

The metal available fraction percentage (A), the zinc-equivalent (ZnEq), geo-accumulation index (Igeo), enrichment factor (EF), contamination factor (CF) and the pollution load index (PLI) were used as methods to assess GS contamination.

Following Andreu & Boluda (1995), Gimeno-García *et al.* (1996), Gil *et al*. (2004), and Ramos-Miras *et al*. (2011), A and ZnEq indices were calculated and applied to provide a basis to compare the potential HM mobility and toxicity in soils in accordance with Expressions (1) and (2):

$$A = (MA/MT) \times 100 \quad (1)$$

where MA is the EDTA-extractable metal concentration, MT is the total metal content.

$$ZnEq = [Zn] + 2 \times [Cu + 8 \times [Ni] \quad (2)$$

where [Zn], [Cu], [Ni] are the respective total concentrations of metals in soils.

Igeo, EF, CF, and PLI to CS and GS were calculated and interpreted according to Müller (1969), Bloundi *et al*. (2009), Zhang *et al.* (2009) and Tamin *et al*. (2016). In our study, we used the metal abundances of the CS soils, as the background data, and iron, as the commonest reference element. Expressions (3), (4), (5) and (6) were used respectively in each case:

$$Igeo = \mathrm{Log}_2 [C_{GS} / (1.5 \times C_{CS})] \quad (3)$$

$$EF = (C_{GS} / C_{CS}) / (Fe_{GS} / Fe_{CS}) \quad (4)$$

$$CF = C_{GS} / C_{CS} \quad (5)$$

$$PLI = (CF1 \times CF2 \times CF3 \times \ldots\ldots\ldots\ldots \times CF_n)^{1/n} \quad (6)$$

Where C_{GS} is the metal content in the tested soil (GS), C_{CS} is the metal concentration in the control soils (CS, background level), Fe_{GS} and Fe_{CS} are the iron concentrations in the GS and the CS, respectively, CF_1 to CF_n represent the contamination factors for the

specific toxic metals, and n is the total number of considered contamination factors; in our case n=6 (excludes Fe).

Statistical Analyses

All the statistical analyses were performed using the SPSS 15.0 software. The results showed a mean value, ranges (MIN-MAX), standard deviation (SD) and Spearman's correlation analysis. Mann-Whitney U test and Kruskall-Wallis test, followed by Scheffe´s post-host test, were used to test for any significant differences in the HM between the CS and the considered GS. The confidence interval for the Student's *t*-test was calculated at $\alpha = 0.05$.

RESULTS AND DISCUSSION

Soil characteristics and metal concentrations, together as the main descriptive statistics for the CL of GS in western Almería, are listed in Tables I and II. In general, the GS had a high clay content, slightly basic, moderate fertility (lower SOM and CEC), were highly calcareous with some salinity problems, which is in accordance with that previously reported by Gil *et al*. (2004).

Total and Available Metal Contents in Soils

Table II summarises the main descriptive statistics related to the total and available metal contents in both the CS (background values) and GS. Table II also includes the background levels obtained by Gil *et al*. (2004), Sierra *et al*. (2007) and Ramos-Miras *et al.* (2011), and the baselines proposed for Almería soils by Aguilar *et al*. (2005). Our background levels were like those obtained by Gil *et al*. (2004) and Ramos-Miras *et al.* (2011) and all, except Zn, were lower than the baseline values proposed by Aguilar *et al*. (2005) for soils in Almería. The levels in GS of Cd, Cu, Pb and Ni were significantly

higher than the CS, while the levels of Zn and Co were similar among CS and GS. When comparing the mean total concentration values, they were generally 1.5 to 2.0-fold higher CS than GS. The levels obtained for the GS were higher than those described by Rodríguez-Martín *et al*. (2009) for the whole Spanish territory, and higher than those described for farming soil (Andreu & Boluda, 1995; Gimeno-García *et al*., 1996), while the CS were lower than the background levels proposed for Almería (Sierra *et al*., 2007) and Andalusia (Aguilar *et al*., 2005), except for Cd and Zn levels, which were higher in the CS. The concentrations of the HM in the CS were significantly lower than in the GS, except for Zn and Co, which were similar (Table IIA). The origin of these two elements could be endogenous; this fact explained that the levels of Zn and Co were similar in both GS and CS (Magrisso *et al*., 2009).

Our results revealed a significant increase in the available concentrations of Cd, Cu, Pb, Ni and Zn in GS compared to the CS, which were 3-, 8-, 4-, 2-and 5-fold higher, respectively (Table II). The available levels were in the same order as or higher than, those reported for Spanish agricultural soils (Andreu & Boluda, 1995; Gimeno-García *et al*., 1996; Ramos-Miras *et al*., 2011), and were similar to those previously described by Ramos-Miras *et al*. (2011).

Table IIB provides the extractable fraction percentage values for the studied elements and confirms increased availability (A), where Cd, Pb, Zn and Cu are 1.6-, 3-, 6-and 6-fold higher in the GS compared to the CS, respectively. The available fraction percentage (A) is an indicator of its comparative mobility (Boluda *et al*., 1993; Ramos-Miras *et al.,* 2011) and is an appropriate indicator for recent soil pollution history (Massas *et al*., 2009). The A values are: Cd, 11.0-62.0; Co, 3.8-25.0; Cu, 4.0-79.5; Ni, 0.8-12.0; Pb, 10.6-81.5; Zn, 1.1-20.2. The order of available fraction percentage among

the analysed samples was: Cd >Pb> Cu >> Co >Zn> Ni. This result indicated that the most toxic elements were also the most mobile ones, and also revealed that except for Co and Ni, they were significantly higher in the GS than in the CS. Moreover, the value of these indices for the GS were in the same order as those described by several authors for Mediterranean farm soils, whereas the CS gave lower values, save Co and Ni (Andreu & Boluda, 1995; Ramos-Miras *et al*., 2011). According to Tarvainen & Kallio (2002), levels of the available fraction index below 5% indicate non-contaminated soils. Our results revealed that all save Co, the mean A values in the GS were over 5%, which was very possibly due to the excessive use of agrochemicals, the irrigation system and its high frequency.

The above described facts suggest that intensive agriculture which greenhouses undergo favoured the accumulation and availability of HM in soils, which has been previously described by Gil *et al*. (2004), Ramos-Miras *et al*. (2011) and Rodríguez-Martín *et al*. (2013). Long *et al*. (2013) assessed the spatial-temporal variations of HM in farmland soils in Shanghai (China) to find that Cd, Zn and Hg contributed the most pollution. Recently, Zhang *et al*. (2017) found that Cd, Cu, Hg and Zn had clearly accumulated in GS in southwest China, which favours their enrichment in vegetable crops due to high-intensity cropping and management practices. Li *et al*. (2017) found that greenhouse cultivation greatly enhanced the bioconcentration of most metals from soil to plant roots.

Assessing Soil Contamination

The concentrations of Cd, Cu and Pb exceed our background levels. The highs concentrations of Cd and Cu may be due to abusive use of fertilizers; the high Pb contents observed in GS must be similarly related to the greenhouse activities carried

out by means of farming machinery and emissions deriving from burning fuel within a confined area (Rodríguez Martín *et al*., 2013). Moreover, when using the mean CS value criterion plus twice the standard deviation as a reference level, 66 GS (93%) exceeded this value for CdT, as did 47 GS (66%) for CuT, while three (4%) and 60 (85%) GS respectively exceeded these values when using the baselines proposed by Aguilar *et al.* (2005) and the criterion of Sierra *et al.* (2007). This demonstrates the importance of using the obtained geochemical levels, within the same area, to more suitably assess contamination status in soil.

Indices ZnEq, Igeo, EF and PLI (Tables III and IV) confirmed the potential risk of contamination. The Igeo, EF and PLI values were higher for Cd, Cu, and Pb. Major differences were found when comparing the values obtained from the total (T) concentration or the available fraction (E: EDTA-extractable content), and the indices gave higher values when the available concentration is employed to calculate them. According to ZnEq-T only 35% of the GS (25 samples) have toxicity problems, however ZnEq-E showed that 97% of the GS (69 samples) may have toxicity problems (Table IV).

Based on previously adopted criteria (Tamim *et al.,* 2016) and on the available concentration for Igeo calculations, when total concentration was applied, 56% GS were considered practically uncontaminated (Class 0) and 44% were uncontaminated to moderately contaminated (Class 1).

The EF index related the geochemical origin of the element, its mobilisation and the anthropogenic nature of its abundance (Tamim *et al*., 2016). The highest EF values were the same as in the previous case for available metals: for CuE (EF = 8.0), PbE (EF=4.7), ZnE (EF=4.5) and CdE (EF=3.4). Five GS groups were established according

to degree of modification: non-modification (10%), minor modification (24%), moderate modification (30%), severe modification (32%) and very severe modification (4%). A higher EF value than the unit meant that the element was anthropogenic in nature (Tamim *et al.,* 2016). When total concentration was used, 14 GS obtained an EF ≤ 1, while only two GS obtained this same value using the available concentration. For EF-E, 23 GS presented severe modification, whereas no GS was classified as such when total concentration was used. With PLI, the difference was not so large as PLI-T and PLI-E suggested that 97% and 100% of GS respectively presented progressive deterioration.

All these results confirmed that the total concentration of an element or using a single index was not sufficiently reliable to properly assess soil pollution. Differences were found in interpretations depending on the adopted criterion. In any case, all these results confirmed that a large proportion of GSs in the study area could have soils that present adverse effects. The potential risk contemplated jointly by Cd, Cu and Pb was confirmed by the indices employed herein to generally assess soil pollution status, which agrees with several other authors (Bloundi *et al.*, 2009; Zhang *et al.*, 2009; Tamim *et al.*, 2016; Zhang *et al.*, 2017), and demonstrates their effectiveness.

Assessing Relationship with Soil Parameters

Table V showed the correlation analyses to determine the extent of the relationship between the parameters investigated. SOM and carbonate contents are the main properties that show a higher affinity to HM. Different authors have demonstrated the affinity of SOM to distinct HM in soils (Gil *et al*., 2004; Rodríguez *et al*., 2006; Tume *et al*., 2006; Massas *et al*., 2010; Roca-Pérez *et al*., 2010; Businelli *et al*., 2011; among others). Our results confirmed the role that soil carbonates play in retaining HM, just as

several authors have already reported (Businelli *et al*., 2011). One noteworthy aspect was the correlations obtained between available phosphorus and Cd, Cu, Ni Pb, Zn and ZnEq as this fact was related to the use of fertilisers in the agrosystem, which could be due to presence of HM in phosphorous fertilisers (Gimeno-García *et al.*, 1996; Gil *et al*., 2004). Moreover, the relation between HM could indicate that these elements in the GS could share a common origin that could be related with anthropic activity (Gil *et al*., 2004).The positive and highly significant correlations found between MT and MA were logical this fact has been associated with an enriched exogenous origin, which diminished the retention force between the HM and soil colloids that favoured the mobility of HM, which could pass to other environmental compartments (Tarvainen & Kallio, 2002; Massas *et al*., 2010; Ramos-Miras *et al*., 2011).

Temporal Trends of Heavy Metals in GS

No historic data about the concentration of HM in the GS are available. Using the background levels obtained in this study, and based on knowledge about the cropping ages of the GS, we could establish temporal distribution patterns for the studied elements. Figure 3 shows the changes in the temporal trends of HM. The total contents in HM showed a significant increase for the Cd, Cu, Pb and Ni contents in GS compared to the CS, while no variations were observed for Co and Zn (Figure 3A). The same behaviour pattern was observed for available concentration, but in this case Zn also presented major variations between the contemplated soil groups (Figure 3B). This fact revealed that progressive enrichment and the availability of Cd, Cu, Pb and Zn increased in the GS with cropping age. This scenario confirmed that soil management and the use of agrochemicals was the main source of HM (Molina *et al*., 2009; Uprety *et al*., 2009; Zaccone *et al*., 2010; Gonçalves *et al*., 2011). In the case of Cd, the main source would

be phosphorus fertilisers (Gimeno-García *et al*, 1996). It has also been observed that nitrogen fertilisers favour Cd accumulation in plants (Wångstrand *et al*., 2007). Regarding Cu, apart from it being present in agrochemicals, the irrigation waters of the greenhouses in Almería are continuously treated with copper salts (SO_4Cu) for biocide purposes (Casas *et al*., 2011), which contributes to soil enrichment. For ZnT and CoT, no accumulation was observed, thus the original matter must be the main source for soils (Magrisso *et al*., 2009).

The increase observed in the available concentrations of Cd, Cu, Ni, Pb and Zn (Figure 3B), especially for GS2 and GS3, could be related with the fact that HM added to soil exogenously favours the mobility of HM (Massas *et al*., 2009; Ghaderi *et al*., 2012). This might represent an important health risk (Zhang *et al*. 2017; Roy & McDonald 2015).

Regarding the contamination indices, a significant increase in ZnEq, Igeo, EF and PLI was observed (Figure 4), which was also observed with HM as indices ZnEq, Igeo, EF and PLI showed the same behaviour patterns. Thus, cultivation led to rapidly increasing index values in the first years after setting up greenhouses (GS1, 0-10 years). After 20 years of cultivation, all the index values exceeded those of the background values (CS-soils), except for CoT, CoE and ZnT.

In relation to temporal trends, some studies have specifically shown that the concentrations of Hg, Cd, Cu and Zn tend to rise in GS with cropping ages (Ramos-Miras *et al.*, 2012; Chen *et al.*, 2016). Li *et al*. (2009) observed temporal distribution patterns for Cd, Cr, Cu, Ni, Pb and Zn in soil layers at 0-20 cm, following exponential regression equations, caused by sewage irrigation after more than one century. Long *et al.* (2013) assessed the spatial-temporal variations of HM in farmland soils of Shanghai (China) and

found that Cd, Zn and Hg contributed the most pollution. When use of fertilisers was reduced, among other human activities, the impact of agricultural activities on the temporal variation of farmland soil quality weakened. Although some studies have shown that the reduced application of nutrients and pesticides reduces metal contamination in soil (Narimanidze & Brückner, 1999). Using fewer fertilisers has been reported to relieve the impact of agriculture on temporal farmland soil quality variation (Long *et al*., 2013). This work demonstrates for the first time the HM concentration trend in GS in a semiarid area, and warns about the risks that stem from intensive agriculture.

CONCLUSIONS

A true trend pattern for temporal accumulation of Cd, Cu and Pb is demonstrate for the GS of Western Almería (Spain), which is associated with the intensive agriculture practices. In addition to metal accumulation, increasing the available concentration implies enhanced Cd, Cu, Pb, Zn and Ni mobility. The values of the pollution indices (ZnEq, Igeo, EF and PLI) employed in this work reveal the same behaviour pattern, which confirms the above-indicated aspects. Thus, they are good tools to assess soil contamination and to address monitoring studies.

The disproportionate volume of agrochemical substances constantly used in GS is linked to increase of HMs. All the above indications suggest that this situation could reduce soil quality in the long term, and could affect the crop yields and nutritional quality of the obtained vegetables. This study also demonstrates the importance of soil monitoring and assessment in the subjected GS to find the possible problems caused by intensive agriculture practices and to prevent pollution risks. Soil organic matter, soil carbonates and greenhouse management can help reduce the mobility and

bioavailability of these metals in the GS. Sustainable management practices (e.g., use of quality compost instead of manure amendments) should be assessed and monitoring studies should continue in the future. The Cd, Cu, Ni, Pb and Zn inputs in the GS should also be controlled to minimise pollution effects and to maintain soil quality. Therefore, future studies about plant uptake and ecological risk assessments should be conducted

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564 Table I. Main descriptive parameters for GS soils (n=71)

	Clay (%)	SOM (%)	CEC ($cmol_c\ kg^{-1}$)	pH	ESP (%)	EC (dSm^{-1})	P_2O_5 (mg $100\ g^{-1}$)	$CaCO_3$ (%)
MIN	13.6	0.3	4.6	7.6	1.0	0.7	4.9	5.6
MEAN	32.7	1.0	9.9	8.3	12.0	2.0	25.3	31.6
MAX	57.1	3.0	15.5	8.9	40.0	5.2	79.3	64.9
STD	9.15	0.5	6.6	0.3	6.0	1.0	20.6	15.3

SOM, soil organic matter; CEC, cationic exchange capacity; ESP, exchangeable sodium percentage; EC, electric conductivity; P_2O_5, available phosphorus; MIN, minimum value; MEAN, mean value; MAX, maximum value; STD, standard deviation.

565

Table II. Main descriptive statistics for metals in CS (n = 11), and GS (n = 71), mg kg^{-1} dry weight. Panel A: total content (T), and available content (A) Panel B: available fraction percentage. Different letter indicates statistically significant differences ($p < 0.05$) after Mann–Whitney U test

A

	CS				GS					
	MIN	MEAN	MAX	STD	MIN	MEAN	MAX	STD	C	BA
CdT	0.46	0.63[a]	0.80	0.10	0.71	1.27[b]	1.89	0.27	0.6[*]	0.3
CdA	0.11	0.13[a]	0.16	0.02	0.15	0.41[b]	0.80	0.12	0.4[***]	Na
CuT	9.9	16.4[a]	27.1	5.7	9.5	28.7[b]	67.1	9.7	21.2[**]	47.2
CuA	0.2	0.8[a]	1.2	0.3	0.9	6.8[b]	41.9	7.4	9.5[***]	Na
PbT	15.3	49.3[a]	74.2	20.4	18.0	75.4[b]	404.9	52.1	46.2[*]	93.9
PbA	1.2	6.0[a]	12.2	3.8	5.8	24.3[b]	171.4	25.5	26.3[***]	Na
ZnT	60.1	158.5[a]	213.4	58.1	63.4	156.6[a]	374.7	72.2	135.7[**]	129
ZnA	0.2	2.1[a]	4.4	1.4	1.6	11.5[b]	53.8	9.4	11.8[***]	Na
NiT	17.6	26.5[a]	37.7	6.2	19.7	39.6[b]	53.6	8.1	23.4[*]	70.9
NiA	0.1	0.8[a]	1.4	0.5	0.4	1.7[b]	3.5	0.5	1.7[***]	Na
CoT	9.8	14.4[a]	18.1	3.0	12.1	17.1[a]	23.3	2.3	13.7[**]	26.7
CoA	0.2	1.0[a]	2.6	1.0	0.6	1.6[a]	4.6	0.7	1.7[***]	Na

B

	CS				GS			
	MIN	MEAN	MAX	STD	MIN	MEAN	MAX	STD
Cd	15.7	20.8[a]	25.8	3.9	11.0	33.7[b]	62.0	11.7
Cu	2.2	3.9[a]	5.2	1.1	4.0	21.9[b]	79.5	15.7
Pb	7.6	10.4[a]	16.5	10.8	10.0	30.5[b]	81.5	10.8
Zn	0.3	1.3[a]	2.5	0.8	1.1	7.6[b]	20.2	4.8
Ni	1.9	3.2[a]	5.0	2.2	0.8	4.6[a]	12.0	2.0
Co	1.4	8.2[a]	22.7	8.5	3.8	9.5[a]	25.0	4.0

MIN, minimum value; MEAN, mean value; MAX, maximum value; STD, standard deviation. C, comparison with background levels by Gil *et al.* (2004) [*], Sierra *et al.* (2007)[**] and Ramos-Miras *et al.* (2011)[***]; BA, baselines proposed for Almería by Aguilar *et al.* (2005); Na, not available..

Table III. Contamination indexes

INDEX	ELEMENT	MIN	MEAN	MAX	STD
ZnEq	(Zn, Cu, Ni) T	266	531	851	116
	(Zn, Cu, Ni) E	14	38	111	20
Igeo	Cd T	-0.4	0.4	1,0	0.3
	Cd E	-0.4	1.0	2.0	0.5
	Co T	-0.8	-0.3	0.1	0.2
	Co E	-0.9	0.5	2.1	0.6
	Cu T	-1.2	0.3	1.6	0.5
	Cu E	-0.2	2.3	5.4	1.1
	Ni T	-1.0	0.0	0.5	0.3
	Ni E	-1.1	0.8	2.0	0.5
	Pb T	-1.9	-0.1	2.6	0.7
	Pb E	-0.4	1.3	4.5	0.9
	Zn T	-1.8	-0.7	0.7	0.6
	Zn E	-1,0	1.5	4.1	1,0
	MULT EL T	-1.1	-0.1	0.5	0.3
	MULT EL E	0.5	1.2	2.2	0.4
EF	Cd T	0.9	2.2	5.1	0.9
	Cd E	0.2	3.4	14.9	2.7
	Co T	0.6	1.3	2.4	0.5
	Co E	0.1	2.3	10.1	1.8
	Cu T	0.5	2.2	5.3	1.0
	Cu E	1.1	8.0	38.0	7.0
	Ni T	0.4	1.7	3.4	0.7
	Ni E	0.5	2.8	10.9	2.0
	Pb T	0.3	1.9	16.7	2.0
	Pb E	0.3	4.7	38.5	5.5
	Zn T	0.2	1.2	3.7	0.8
	Zn E	0.2	4.5	18.0	3.2
	MULT EL T	0.6	1.8	5.5	0.8
	MULT EL E	0.5	4.3	12.3	2.5
PLI	Cd T	1.1	2.0	3.0	0.4
	Cd E	1.1	3.2	6.1	0.9
	Co T	0.8	1.2	1.6	0.2
	Co E	0.8	2.3	6.6	1.0
	Cu T	0.6	2,0	4.6	0.7
	Cu E	1.3	10.1	62.6	10.4
	Ni T	0.8	1.5	2.1	0.3
	Ni E	0.7	2.8	5.9	0.9
	Pb T	0.4	1.7	8.9	1.1
	Pb E	1.1	4.8	33.6	5.0
	Zn T	0.4	1.0	2.5	0.5
	Zn E	0.7	5.2	24.5	4.3
	MULT EL T	0.7	1.5	2.2	0.3
	MULT EL E	2.1	3.7	7.1	1.1

MIN, minimum value; MEAN, mean value; MAX, maximum value; STD, standard deviation.

Table IV. Results after soil contamination indices interpretation (n, numbers of GS affected; %, percentage of GS affected)

		Total Metal (T)		Extractable Metal (E)	
INDEX	Interpretation	n	%	n	%
ZnEq[a]	No contaminated soil	46	65	2	3
	Soil with toxicity problems	25	35	69	97
Igeo	Class 0 (practically uncontaminated)	40	56	0	0
	Class 1 (uncontaminated to moderately contaminated)	31	44	24	34
	Class 2 (moderately contaminated)	0	0	45	63
	Class 3 (moderately to heavily contaminated)	0	0	2	3
EF	Non modification (< 1.5)	28	40	7	10
	Minor modification (1.5 - 3.0)	40	56	17	24
	Moderate modification (3.0 -5.0)	2	4	21	30
	Severe modification (5.0 - 10)	0	0	23	32
	Very severe modification (> 10)	0	0	3	4
PLI	No deterioration (PLI ≤ 1)	3	4	0	0
	Progressive deterioration (PLI > 1)	68	96	71	100

[a]ZnEq-T: no contaminated soil (ZnEq-T ≤ 580), soil toxicity (ZnEq-T > 580); ZnEq-E: no contaminated soil (ZnEq-E ≤ 17), soil toxicity (ZnEq-E > 17). Reference value calculated as background level + 2 x STDt.

Table V. Correlation coefficients among elemental concentrations and soil properties in GS (n = 71)

	Clay	SOM	CEC	ESP	pH	P_2O_5	$CaCO_3$	CdT	CdE
Clay	1								
SOM	n.s.	1							
CEC	0.421(**)	n.s.	1						
ESP	0.304(**)	n.s.	n.s.	1					
pH	n.s.	n.s.	n.s.	n.s.	1				
P_2O_5	n.s.	0.576(**)	n.s.	-0.301(**)	n.s.	1			
$CaCO_3$	0.299(**)	n.s.	n.s.	n.s.	n.s.	n.s.	1		
CdT	n.s.	0.449(**)	n.s.	-0.408(**)	n.s.	0.458(**)	0.250(*)	1	
CdE	n.s.	0.386(**)	n.s.	n.s.	n.s.	n.s.	0.435(**)	0.363(**)	1
CuT	n.s.	0.313(**)	n.s.	n.s.	n.s.	0.441(**)	0.228(*)	0.484(**)	0.323(**)
CuE	-0.317(**)	0.475(**)	n.s.	-0.242(*)	-0.261(*)	0.357(**)	n.s.	0.413(**)	0.320(**)
PbT	0.398(**)	n.s.	n.s.	n.s.	n.s.	n.s.	0.556(**)	0.283(**)	0.318(**)
PbE	n.s.	0.444(**)	n.s.	n.s.	n.s.	0.352(**)	0.512(**)	0.395(**)	0.471(**)
ZnT	0.450(**)	n.s.	0.303(**)	n.s.	n.s.	n.s.	0.462(**)	n.s.	0.345(**)
ZnE	n.s.	0.509(**)	n.s.	n.s.	n.s.	0.467(**)	0.271(*)	0.474(**)	0.564(**)
NiT	n.s.	0.297(**)	0.321(**)	-0.226(*)	n.s.	0.431(**)	n.s.	0.489(**)	n.s.
NiE	n.s.	0.351(**)	-0.313(**)	n.s.	n.s.	n.s.	n.s.	n.s.	0.237(*)
CoT	0.323(**)	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.239(*)	n.s.
CoE	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
ZnEq	0.293(*)	0.277(*)	0.322(**)	n.s.	n.s.	0.342(**)	0.259(*)	0.471(**)	0.378(**)

	CuT	CuE	PbT	PbE	ZnT	ZnE	NiT	NiE	CoE	CoE
CuT	1									
CuE	0.590(**)	1								
PbT	0.372(**)	n.s.	1							
PbE	0.263(*)	0.276(*)	0.769(**)	1						
ZnT	0.368(**)	n.s.	0.649(**)	0.413(**)	1					
ZnE	0.652(**)	0.689(**)	0.320(**)	0.540(**)	0.333(**)	1				
NiT	0.572(**)	0.248(*)	0.311(**)	0.316(**)	n.s.	0.263(*)	1			
NiE	n.s.	0.386(**)	n.s.	n.s.	n.s.	n.s.	0.240(*)	1		
CoT	0.300(**)	n.s.	n.s.	n.s.	n.s.	n.s.	0.484(**)	n.s.	1	
CoE	n.s.	n.s.	n.s.	n.s.	-0.312(**)	n.s.	n.s.	n.s.	n.s.	1
EqZn	0.747(**)	n.s.	0.581(**)	0.460(**)	0.660(**)	0.471(**)	0.798(**)	n.s.	0.333(**)	n.s.

SOM, soil organic matter; CEC, cation exchange capacity; ESP, exchangeable sodium percentage; -T, concentration of total metal; -E, concentration of available metal; EqZn, Zn equivalent. Significant levels: *p < 0.05 and **p < 0.01; n=71; n.s. not significant.

585

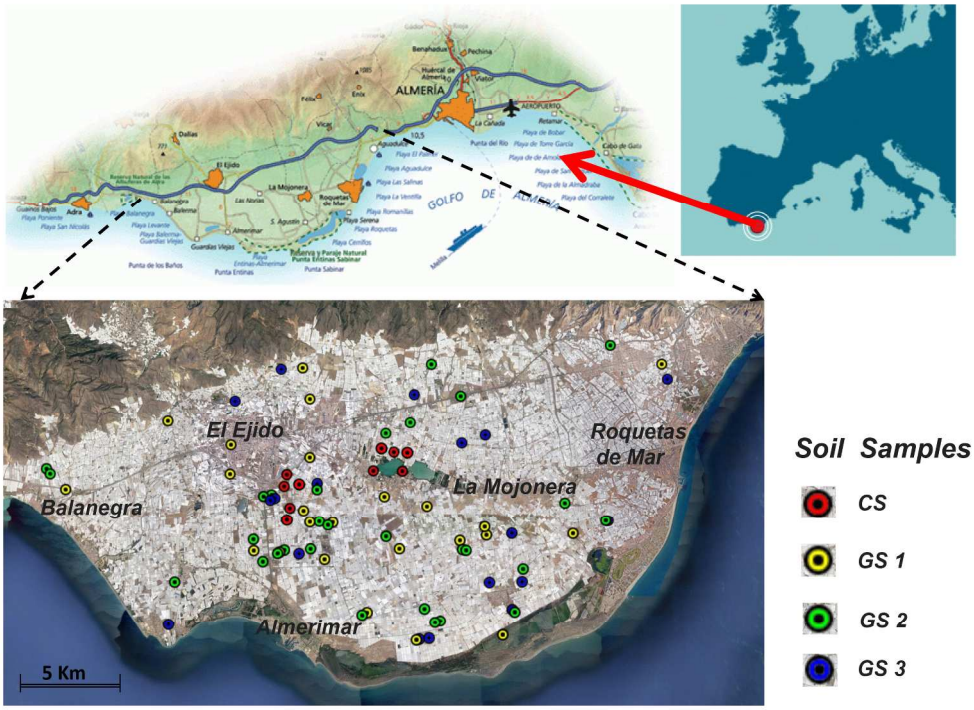

Figure 1. Location of area and for sampling soil points.

233x170mm (300 x 300 DPI)

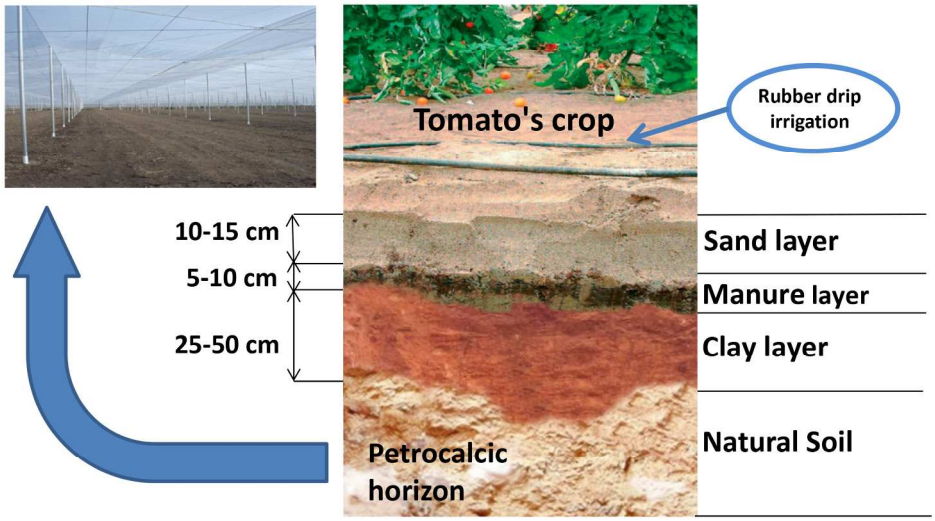

Figure 2. Schematic representation showing soil profile of greenhouse in Almería.

203x123mm (300 x 300 DPI)

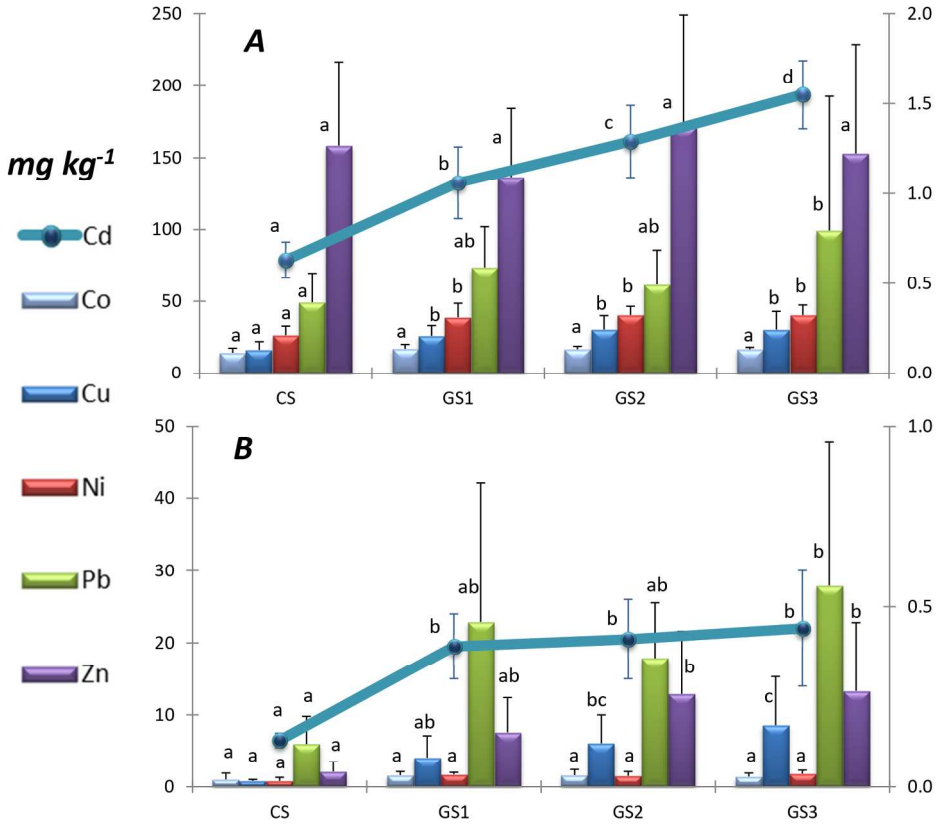

Figure 3. Temporal trends of heavy metal contents in greenhouse soils (GS) of western Almería, Spain (mean ± STD). A, total content; B, available content. CS, control soil (0 years); GS1, < 10 years; GS2, 10 to 20 years; GS3, > 20 years. Right scale is only for Cd values. Different letter indicates statistically significant differences ($p < 0.05$) after Krustall-Wallis and Scheffe's post-hoc tests.

180x157mm (300 x 300 DPI)

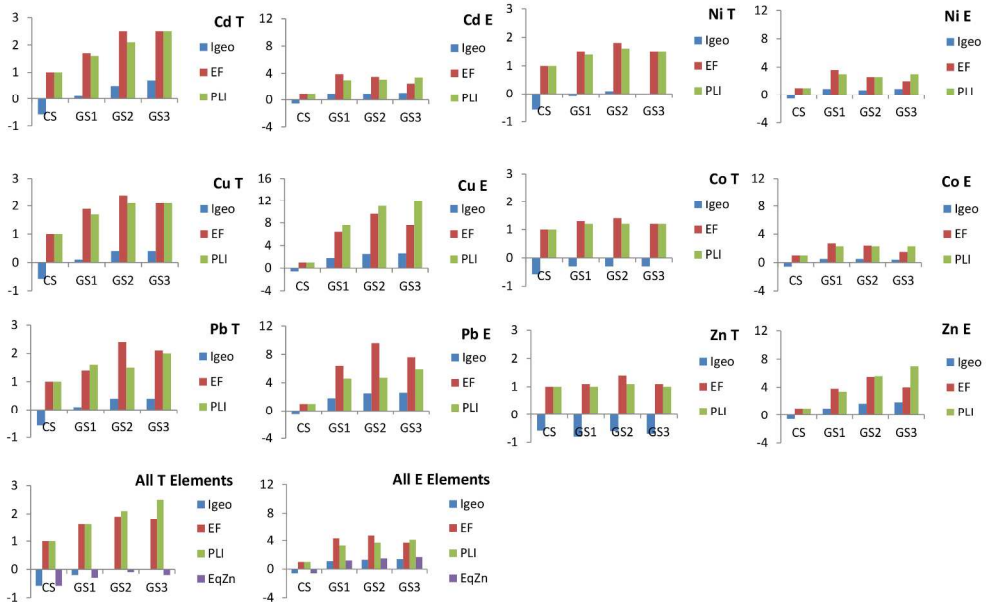

Figure 4. Temporal trends of contamination indices values. Igeo, geoaccumulation index; EF, enrichment factor; PLI, potential load index; ZnEq, zinc equivalent; T, total content; E, EDTA-extractable content; CS, control soils (0 years); GS1, < 10 years; GS2, 10 to 20 years; GS3, > 20 years.

255x162mm (300 x 300 DPI)