



Ecological risk assessment of mercury and chromium in greenhouse soils

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Abstract Very little information is available about Hg and Cr evolution in greenhouse soils. This paper presents the results of determining Hg and Cr in greenhouse soils in a semi-arid region in the southern Iberian Peninsula (Almería, Spain), and assessing the enrichment level and the Potential Ecological Risk Index (PERI) according to crop age. Hakanson's approach was used to evaluate the PERI. To investigate the behaviour of Hg and Cr in greenhouse soils over time, samples were grouped into values in soils for blocks according to crop age: 0 years, 5–10 years, 10–20 years, more than 20 years. The results showed that 74% of GS exceeded the obtained background level ($37.1 \mu\text{g kg}^{-1}$) for Hg, with 43% (48.9 mg kg^{-1}) for Cr. Temporal patterns indicated

that these elements are accumulating in greenhouse soils and this trend was very significant for Hg. After more than 20 intensive crop-farming years, concentrations and the PERI had clearly increased. Although the ecological risk was moderate, our observations suggest that the farming practices performed in the last 35 years have allowed these metals to accumulate. In fact, the 15% of the studied soils presented a considerable potential risk and were the soils that had been used longer.

Keywords Heavy metals · Intensive agriculture · Poniente Almeriense · Soil contamination

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Introduction

Heavy metals (HM) have become a focal point given the threat they pose for the natural environment and human health due to their toxicity and persistence because they do not degrade in the environment and tend to bioaccumulate. The presence of these elements in greenhouse soils (GS) has been described to have been influenced by the natural concentration and dynamics of soil and by human activity, whose concentration can significantly rise (Rodríguez-Martín et al. 2013; Gil et al. 2018; Jia et al. 2019). As they persist in the environment, more interest has been recently shown in the presence of HM in farmlands, as indicated by the more than 4000 scientific articles published on this theme in the last 10 years (Scopus). This GS contamination is particularly interesting as it may enter the food chain and affect consumer health (Jones et al. 2012). Nuñez et al. (2017) found a relation between HM contents in soil and death from tumours in the digestive tract in Spain. Moreover, the presence of large quantities of HMs in soil can make them less productive and can lower the percentage of seed germination by as much as 30% (El-Alam et al. 2018).

The Poniente Almeriense area in southeast Spain is a very important zone from the agricultural and socio-economic viewpoints. There, agriculture is based mainly on building greenhouses whose soils have been considerably altered by intensive agriculture practices. Artificial soil is used in many greenhouses in Almería (Technosols, Gil et al. 2018) because the soil in the study area presents low fertility (Ramos-Miras et al. 2002) and is formed by three layers in this order: sand, organic matter and imported clay. The clay layer employed to build the GS in Poniente Almeriense comes from local quarries (Ramos-Miras et al. 2002; Gil et al. 2004, 2010, 2018; Ramos-Miras et al. 2011, 2012).

Mercury (Hg) accumulation in soil can come from two sources of contamination: natural, owing to meteorisation of rocks; and anthropogenic, from emissions released by human activities (industrial, urban and some farming practices, like applying sludge) that increase Hg contents in air, water and soil (Sánchez-Báscos et al. 2017). Therefore, Hg can be absorbed by vegetables and affect the Hg concentration in horticultural products (Gil et al. 2010;

Ramos-Miras et al. 2012). Hg does not abound in nature, and its mean concentration in the Earth's crust is about $50 \mu\text{g kg}^{-1}$ (Rodríguez-Martín et al. 2009). Gil et al. (2010) determined the background concentration, standard levels and reference value for calcareous soils in the Mediterranean Region as being $25.1 \mu\text{g kg}^{-1}$, $9.8\text{--}64.3 \mu\text{g kg}^{-1}$ and $64.3 \mu\text{g kg}^{-1}$, respectively. Soil represents the biggest Hg deposit in terrestrial ecosystems and is the largest source of contamination for the food chain and aquatic systems. Given its potential toxicity, Hg is the object of many bibliographic references in the literature. However, no study conducted in Spain was found about the potential ecological risk for Hg in GS. Conversely, chromium (Cr) is very abundant in the Earth's crust, with a mean global content in soil estimated at 60mg kg^{-1} (Kabata-Pendias 2011) and is considered the seventh most abundant element in the earth's crust (Shanker et al. 2005). Although the presence of Cr in soil is closely related with the original material (Hseu et al. 2018), its environmental impact can be significant, mainly as Cr(VI) as it is transferred to waters (Nielsen et al. 2014). Its toxicity symptoms in vegetables are manifested by stunted root growth, smaller biomass, chlorosis and photosynthetic damage. Eventually, plants die (Vernay et al. 2007), because, in some cases, its toxicity is more marked than lead (Pb) toxicity (Singh et al. 2015).

The Potential Ecological Risk Index (PERI), established by Hakanson (1980), has been widely used to evaluate contamination (e.g. Li et al. 2014; Yuan et al. 2014; Ke et al. 2017; Yang et al. 2017; Rastmanesh et al. 2018; Wieczorek et al. 2018), as opposed to other indices [I_{geo} , extractable fraction, enrichment factor (EF), etc.], which can be employed to evaluate the potential risk associated with the simultaneous presence of different HMs in an environment because the toxic effect of HM is enhanced by the combined input of several of these elements in the environment (Wang and Fowler 2008). This work presents the results of a study that evaluated PERI for both Hg and Cr in GS of Almería (Spain). Its objectives were to: (1) establish the background and reference levels of both Hg and Cr for these soils; (2) evaluate the degree of enrichment and the PERI; and (3) analyse the possible temporary trend.

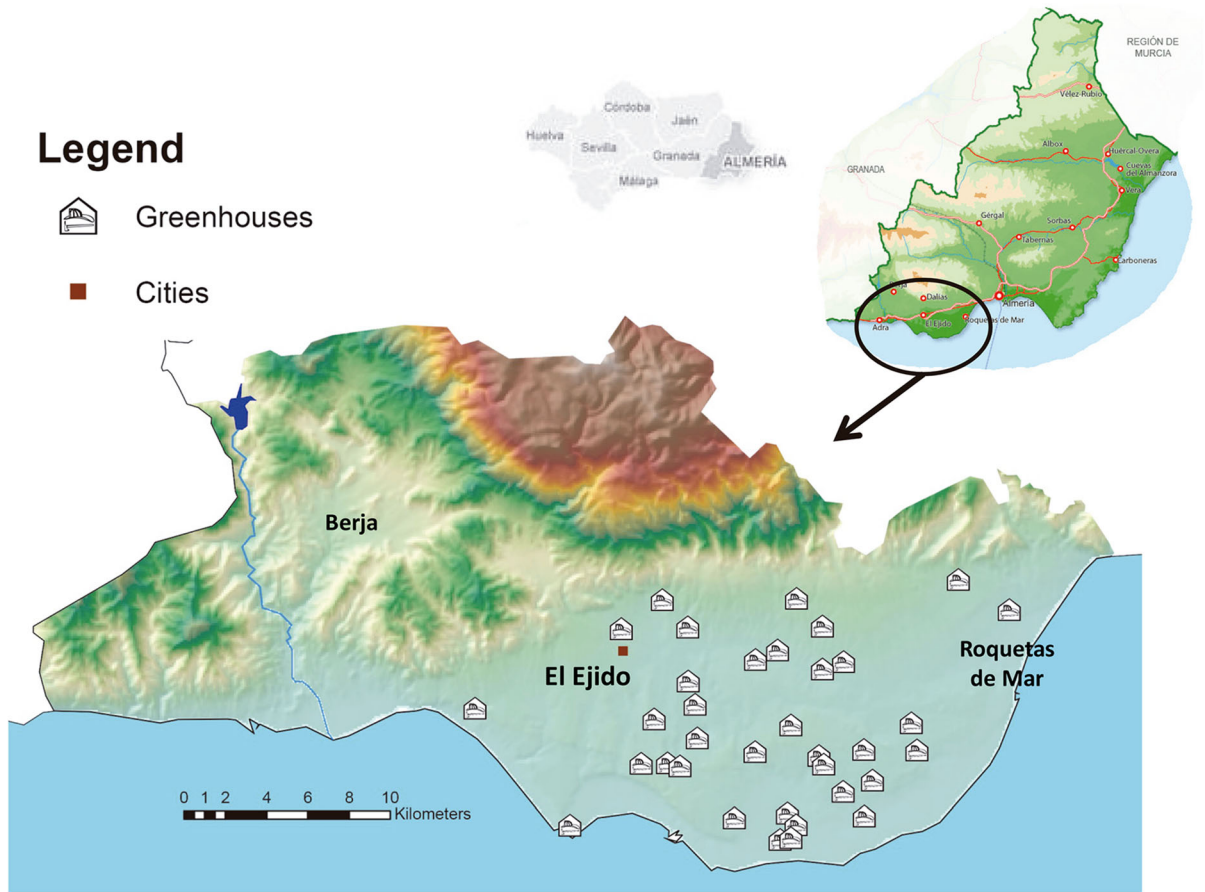


Fig. 1 Study area and location of sampling points

Materials and methods

Thirty-five soil samples were collected that corresponded to the clay layer (10–30 cm) in each greenhouse (Fig. 1). In all the greenhouses, five points were taken to obtain compound samples. Furthermore, seven samples were taken from the quarries (quarry samples; CS) from which the material was taken to prepare the clay layer with which to construct GS (Gil et al. 2018). All the samples were air-dried, homogenised and sieved (2 mm). An aliquot of the sample was ground in an agate mortar before being stored in polyethylene bags to determine both Hg and Cr. Standard soil analyses were carried out following the methods referenced by Roca-Pérez et al. (2002), Gil et al. (2004, 2018), Ramos-Miras et al. (2011), Rodríguez-Martín et al. (2013). Three soil granulometric fractions (sand, silt and clay) were determined by the pipette method. Soil pH was measured in a 1:2.5

(soil/distilled water) extract. Electrical conductivity (ECs) was determined in the soil saturation extract. Soil organic matter (SOM) was analysed by the Walkley–Black method, and carbonate concentration by the gas volumetric method. Cation exchange capacity was established by the NaCH₃COO/NH₄.CH₃COO method. Available phosphorous (P) was analysed following the Olsen method, and N total by the Kjeldahl method. The Zn equivalent contamination index (ZnEq) was calculated according to Expression (1) (Chumbley 1971; Gil et al. 2004, 2010).

$$\text{ZnEq} = [\text{Zn}] + 2[\text{Cu}] + 8[\text{Ni}] \tag{1}$$

The Hg concentration was directly determined in the samples previously ground in an agate mortar by thermal decomposition, amalgamation and atomic absorption spectrophotometry (Campisano et al. 2017) in a DMA-80 Milestone Srl direct analyser.

The limit of detection (LOD) was $1.0 \mu\text{g kg}^{-1}$. Two reference materials were used to study the method's exactness: BCR 141R and NIST 2709. The obtained recovery values were $95.1\% \pm 3.1\%$ and $101.0\% \pm 4.0\%$, respectively. Cr and total iron (Fe) was determined by acid digestion using nitric acid and hydrofluoric acid in a Milestone 1200 microwave oven (Milestone Inc, CT, USA) (Campisano et al. 2017). The digested product was prepared to 20 ml with milli-Q water, and Cr was quantified by GBC-906 AA atomic absorption spectrophotometer equipment (GBC, Hampshire, IL, USA). The LOD was 0.5 mg kg^{-1} . A reference material was used, namely BCR 141R, and recovery was $98.0\% \pm 2.0\%$. All the analyses were carried out in triplicate. The results are expressed as mg kg^{-1} over dry matter.

To establish the background levels (BL) and the reference levels (RV), the Cr and Hg concentrations were analysed in the CS, since they do not present pollution of anthropic origin. The theoretical normal distribution criterion was followed (Dudka et al. 1995; Chen et al. 1999; Gil et al. 2002, 2010). Thus, the BL was the geometric mean (GM), while the RV was considered the upper geochemical baseline concentration (GBC) level, calculated as $\text{GM} \times \text{GD}^2$, where GD is the geometric standard deviation (Chen et al. 1999; Gil et al. 2010). Hakanson's approach (1980) was used to evaluate the contamination or enrichment factor (C_f) and the PERI (Er^i), and has been applied by different authors (e.g. Ke et al. 2017; Yang et al. 2017; Rastmanesh et al. 2018; Wiczorek et al. 2018). Compared with other methods, this includes the response factor to the toxicity of a given substance and can be employed to evaluate the risk of the combined contamination for several elements that are potentially hazardous for ecosystems. A given metal's Er^i is calculated by Expressions (2) and (3):

$$C_f = C_{0-1}/C \quad (2)$$

$$\text{Er}^i = \text{Tr}^i \times C_f \quad (3)$$

where Er^i is the PERI for the studied metals, Tr^i is the biological toxicity factor (for Hg = 40 and Cr = 2; Yuan et al. 2014), C_f is the contamination or enrichment factor for the studied metals, C_{0-1} is the background concentration of both Hg and Cr obtained with CS (in $\mu\text{g kg}^{-1}$), and C_i is the concentration of each HM studied for the soil to be evaluated (in $\mu\text{g kg}^{-1}$).

If C_f is > 1 , enrichment exists.

If $\text{Er}^i < 40$, the risk is low; 40–80, moderate; 80–160, considerable; 160–320, high; ≥ 320 , very high.

To evaluate the total risk caused by metals, the PERI is used. It is calculated with Expression (4).

$$\text{PERI} = \sum_{i=1}^n \text{Er}^i \quad (4)$$

If $\text{PERI} < 150$, the risk is low, 150–300 moderate, 300–600 considerable and ≥ 600 high.

To evaluate the temporal trend, soil samples were grouped according to crop age, which meant that four groups were considered: CS, which corresponded to the sediments brought from local quarries, and employed to determine the BL (7 samples); GS1, GS that were younger than a crop age of 10 years (11 samples); GS2, GS with crop ages of 10–20 years (12 samples); GS3, GS with crop ages of more than 20 years (12 samples), which follows the methodology put forward by Gil et al. (2018). The statistical analysis was done using the SPSS 22.0 software package (SPSS Inc., Chicago, Illinois, USA). All the employed statistical methods were performed with a 95% confidence interval ($p < 0.05$).

Results and discussion

Soil properties and metal contents

The soil properties and the main descriptive statistics for the GS in western Almería are listed in Table 1. In general terms, soils contained moderate to high clay contents ($163.6\text{--}570.5 \text{ g kg}^{-1}$), low SOM ($4.1\text{--}29.8 \text{ g kg}^{-1}$) and N ($0.4\text{--}2.3 \text{ g kg}^{-1}$) contents, and had a low cation exchange capacity (CEC, $3.3\text{--}19.6 \text{ cmol}_c \text{ kg}^{-1}$), which agree with the clay and SOM contents. These soils are very calcareous, with a mean equivalent calcium carbonate content of 328.6 g kg^{-1} , which corresponds to its basic pH (7.8–8.9), and with moderate salinity and EC values between 0.8 and 4.4 dS m^{-1} in the saturation extract. Similar results have been reported by Gil et al. (2004) in GS in the same area. Likewise, high assimilable phosphorus levels were obtained (a mean of 126.4 g kg^{-1}), which would be related with the widespread use of agrochemicals owing to the farming

Table 1 Soil properties of the greenhouse soils (GS) in western Almería (Spain) (GS, $n = 35$)

	Clay (g kg^{-1}) ($< 0.002 \text{ mm}$)	SOM (g kg^{-1})	N (g kg^{-1})	CEC ($\text{cmol}_c \text{ kg}^{-1}$)	pHw	CaCO ₃ (g kg^{-1})	ECs (dS m^{-1} 25 °C)	P (mg kg^{-1})	Fe (g kg^{-1})	Zn Eq (mg kg^{-1})
GS1	242.6	12.8	0.9	12.5	8.8	513.4	0.8	74.5	5.4	784.6
GS2	337.0	13.6	1.0	4.2	8.5	324.2	1.5	154.4	4.7	629.0
GS3	339.8	4.3	1.0	7.1	8.2	360.1	2.4	55.2	3.0	530.3
GS4	275.9	6.8	1.2	5.4	8.3	382.9	2.0	24.9	4.2	355.4
GS5	431.0	8.8	1.0	7.1	8.1	398.2	1.2	118.1	3.2	850.9
GS6	292.9	8.3	0.9	4.6	8.0	150.4	3.6	89.8	4.6	654.5
GS7	299.7	18.6	0.8	3.3	8.2	150.0	2.5	124.1	9.3	538.5
GS8	334.0	10.6	0.9	6.2	8.3	534.7	2.8	45.9	3.1	338.5
GS9	163.6	14.0	0.9	14.2	8.2	110.7	1.4	87.8	14.0	663.0
GS10	570.5	7.4	0.9	12.1	8.4	395.4	2.1	54.7	3.3	569.7
GS11	377.6	14.7	1.5	7.5	8.5	390.7	2.2	113.2	5.9	459.4
GS12	470.8	10.5	0.8	3.5	8.6	398.6	1.3	114.0	4.1	621.1
GS13	258.3	10.9	0.7	7.5	8.7	339.2	1.6	71.0	7.8	439.1
GS14	382.7	29.8	0.7	8.3	8.1	326.0	1.5	579.8	4.0	627.6
GS15	277.8	11.2	0.7	3.3	8.7	400.7	1.4	164.1	3.4	639.9
GS16	322.9	4.1	2.3	14.2	8.9	217.8	1.5	79.2	10.0	352.0
GS17	299.7	15.7	0.8	7.5	8.0	450.4	3.8	349.1	4.1	461.9
GS18	282.6	11.4	0.6	12.9	8.2	15.2	3.4	189.5	9.4	518.1
GS19	226.7	5.2	0.6	5.8	8.3	409.7	1.9	125.8	5.0	548.5
GS20	401.0	7.8	0.6	19.6	8.2	416.7	0.8	39.3	3.1	686.5
GS21	432.1	4.9	0.9	4.9	8.4	528.0	1.0	27.7	4.8	464.2
GS22	227.2	7.8	0.6	14.2	8.4	649.9	1.1	46.6	2.8	639.2
GS23	201.4	13.4	0.9	8.0	8.3	55.5	0.9	42.0	20.1	567.2
GS24	260.8	12.1	0.9	17.9	8.4	251.5	1.8	175.2	6.3	387.9
GS25	299.7	15.7	0.8	7.5	8.0	450.4	3.8	349.1	4.1	461.9
GS26	318.4	16.2	0.8	6.3	8.4	324.6	1.9	269.9	7.0	434.0
GS27	372.0	12.9	1.0	5.8	8.9	316.8	2.1	180.2	4.9	511.5
GS28	480.2	11.4	0.9	5.8	8.4	396.8	1.6	26.5	2.6	617.1
GS29	245.8	23.3	0.8	9.6	8.0	454.7	4.4	85.5	4.3	701.6
GS30	317.4	21.6	0.7	4.9	7.8	292.0	3.9	175.7	5.5	560.8
GS31	337.0	17.8	0.4	3.6	7.9	189.6	1.9	63.4	9.6	625.8
GS32	457.2	8.4	0.7	4.9	8.2	431.2	1.3	77.3	4.2	594.0
GS33	308.7	9.5	0.4	4.0	8.1	378.9	1.5	140.0	4.9	725.7
GS34	357.8	12.0	1.0	7.9	7.8	71.5	3.0	46.6	17.0	461.6
GS35	178.7	16.8	0.7	8.3	8.5	25.0	1.8	63.4	4.5	266.3
MINV	163.6	4.1	0.4	3.3	7.8	15.2	0.8	24.9	2.6	266.3
AM	325.2	12.3	0.9	8.0	8.3	328.6	2.0	126.4	6.1	551.1
MAXV	570.5	29.8	2.3	19.6	8.9	649.9	4.4	579.8	20.1	850.9
STD	89.9	5.6	0.3	4.2	0.3	154.0	1.0	113.3	4.0	131.1
GM	313.3	11.1	0.8	7.1	8.3	263.7	1.8	94.4	5.3	534.8

SOM soil organic matter, N total nitrogen, CEC cation exchange capacity, EC electric conductivity, P available phosphorous, Fe total soil iron, ZnEq zinc equivalent index, MINV minimum value, AM mean value, MAXV maximum value, STD standard deviation, GM geometric mean

Table 2 Levels and statistics of Hg and Cr in the studied soils from western Almería (Spain)

	Hg ($\mu\text{g kg}^{-1}$)	STD (Hg)	Cr (mg kg^{-1})	STD (Cr)
Panel A				
CS1	32.2	2.4	49.8	4.6
CS2	48.2	2.8	42.8	6.7
CS3	37.3	1.5	55.9	2.1
CS4	35.0	2.1	49.4	3.2
CS5	42.9	1.4	49.2	9.6
CS6	37.9	0.3	47.3	12.3
CS7	31.8	1.2	48.8	1.4
MINV	31.8		42.8	
AM	37.5 ^a		49.0 ^a	
MAXV	48.2		55.9	
STD	5.9		3.8	
GM	37.1		48.9	
GD	1.2		1.1	
Panel B				
GS1	75.6	1.0	107.4	3.7
GS2	72.8	3.7	33.1	1.0
GS3	63.1	1.1	36.6	3.5
GS4	32.3	2.8	128.7	5.85
GS5	29.3	3.9	42.0	2.8
GS6	54.4	3.2	136.1	4.1
GS7	35.6	2.6	70.6	2.3
GS8	28.2	3.3	47.1	4.9
GS9	37.0	4.7	52.3	3.2
GS10	21.0	0.7	65.6	3.4
GS11	54.3	2.3	41.3	5.4
GS12	85.1	9.7	41.4	3.4
GS13	53.6	7.5	31.6	3.9
GS14	65.0	0.6	42.8	1.9
GS15	54.0	2.5	35.8	0.2
GS16	68.9	6.2	69.07	2.6
GS17	233.3	0.8	48.1	2.2
GS18	27.5	3.1	32.1	3.9
GS19	60.6	3.9	34.5	6.3
GS20	38.8	5.7	210.8	14.2
GS21	163.0	9.6	114.1	4.6
GS22	37.7	1.8	45.3	4.9
GS23	37.4	2.9	33.8	11.9
GS24	94.6	1.6	63.3	1.2
GS25	60.2	5.5	50.9	2.5
GS26	43.7	2.9	43.5	5.6
GS77	32.6	2.4	170.4	0.8
GS28	148.8	4.1	37.0	6.7

Table 2 continued

	Hg ($\mu\text{g kg}^{-1}$)	STD (Hg)	Cr (mg kg^{-1})	STD (Cr)
GS29	114.2	7.1	42.3	1.2
GS30	45.8	0.1	38.2	1.2
GS31	73.7	0.1	360.7	4.1
GS32	22.6	0.6	47.8	5.1
GS33	67.2	1.7	76.9	3.5
GS34	65.5	1.2	46.9	4.1
GS35	64.7	1.0	143.2	11.9
MINV	21.0		31.6	
AM	64.6 ^b		74.9 ^a	
MAXV	233.3		360.7	
STD	43.4		66.3	
GM	55.1		59.8	
GD	1.7		1.8	

MINV minimum value, AM mean value, MAXV maximum value, STD standard deviation, GM geometric mean, GD geometric deviation

The different letters on the means denote significant differences ($p < 0.05$)

practice they are submitted to (Ramos-Miras et al. 2002). The Fe concentrations ranged between 2.6 and 20.1 g kg^{-1} , which fall within the range of the geochemical baseline concentrations established by Roca-Perez et al. (2010) for natural (non-anthropised) soils in the Mediterranean Region (1.7–124.5 g kg^{-1}). Finally, the concentrations of other HM like Cd, Cu, Ni, Pb and Zn were high in many greenhouses. This finding is reflected by the ZnEq contamination index values (266.3–850.9 mg kg^{-1}), which suggests that these soils are submitted to a HM accumulation process in relation to intensive agricultural use (Gil et al. 2004, 2018).

The Hg and Cr contents in all the analysed soils are found in Table 2. The Hg content in CS was ranged from 31.8 to 48.2 $\mu\text{g kg}^{-1}$, with a mean value of 37.5 $\mu\text{g kg}^{-1}$. This content in the GS ranged between 21.0 $\mu\text{g kg}^{-1}$ and 233.3 $\mu\text{g kg}^{-1}$, with a mean value of 64.6 $\mu\text{g kg}^{-1}$. The Hg concentration in GS was of the same order of magnitude as those observed by other authors in Spanish farm soils (Higueras et al. 2006; Rodríguez-Martín et al. 2009; Gil et al. 2010). Generally speaking, 300 $\mu\text{g kg}^{-1}$ is considered the threshold soil value from which plants may present toxicity symptoms (Rodríguez-Martín et al. 2009). No

GS exceeded this limit in the present study. The Cr concentrations in the CS went from 42.8 to 55.9 mg kg⁻¹, and from 31.6 to 360.7 mg kg⁻¹ for GS, with a mean value of 74.9 mg kg⁻¹. These values exceed those reported by Rodríguez-Martín et al. (2013) in farm soils, but fall within the range of data described by Roca-Perez et al. (2010) in soils from the Mediterranean Arc. In Italian soils, Di Giuseppe et al. (2014) found that high Cr contents in Italian soils were related with its presence in the parent material.

Using the CS data, the BL and RV for our soils were established, with 37.1 µg kg⁻¹ and 49.4 µg kg⁻¹, respectively, for Hg. These values were, respectively, 48.9 mg kg⁻¹ and 59.2 mg kg⁻¹ for Cr. In a study conducted in calcareous soils in the Mediterranean Region, Gil et al. (2010) established a BL of 25.1 µg kg⁻¹ and GBC went from 9.8 to 64.3 µg kg⁻¹ for Hg. Roca-Perez et al. (2010) conducted a similar study and established GBC from 5 to 217 mg kg⁻¹ and an RV of 217 mg kg⁻¹ for Cr. These minor differences are logical and may be due to the variability of the analysed soils. Indeed, we believe that our values were suitable for being used as reference values to evaluate contamination in the GS of Almería. For Hg, 74.3% of the GS (26 greenhouses) exceeded the BL, while 60.0% (21 greenhouses) exceeded the RV. For Cr, 60.0% of the GS (21 greenhouses) exceeded the BL, whereas 37.1% (13 greenhouses) exceeded the RV. Based on these results, we can state that a large number of GS analysed herein had abnormally high Hg and Cr concentrations, which suggests that a contamination process exists. In order to evaluate the degree of the significance of these differences, a Mann–Whitney *U* test was carried out with the sediments from local quarries (CS) and with the GS. The results showed significant differences (95%) between CS and GS for Hg, but none for Cr (Table 2).

A multivariate principal component analysis (PCA) was carried out to identify the possible origin/s of the anomalies observed for Hg and Cr in these soils. This analysis is a very powerful tool to separate different sources of contaminants entering the environment as it facilitates their interpretation (e.g. Micó et al. 2006; Yuan et al. 2014; Rodríguez-Martín et al. 2013; Lv 2019). The PCA results for our soils are presented in Table 3. Three principal components were drawn with eigenvalues > 1, which explained 75.6% of variance. The first component explained 38.7% of variance and

Table 3 Loading corresponding to the three principal components (PCs) for the greenhouse soils (GS) in the study area

	PC1	PC2	PC3
SOM	0.164	0.722	0.306
pH	- 0.371	- 0.423	- 0.452
CaCO ₃	- 0.856	- 0.080	0.147
Fe	0.923	- 0.014	- 0.077
Hg	- 0.142	0.870	- 0.173
Cr	0.924	0.030	0.113
ZnEq	- 0.198	0.005	0.894
Eigenvalues	2.709	1.582	1.005
Total variance (%)	38.7	22.6	14.4
Cumulative variance (%)	38.7	61.3	75.7

Extraction method: principal component analysis with varimax rotation

was associated with the mineral component of soils by encompassing Fe, CaCO₃ and Cr, which indicated that most of the Cr present in soils had an autochthonous origin. In fact, Cr in soils is absorbed specifically by the oxides of Fe and Mn (Adriano 2001) and is related with having a mainly lithological origin (Lv 2019), while the inversely proportional relation with the content in carbonates suggests that Cr may be also immobilised by this component that is so readily present in these soils. The second component grouped SOM and Hg, and explained 22.6% of variance, which would be related with Hg entering the environment and its accumulation. Different authors have shown the affinity of Hg with SOM (Tack et al. 2005; Higuera et al. 2006; Rodríguez et al. 2008; Gil et al. 2010), which is thus immobilised, but not transferred, to other environmental compartments (Jing et al. 2007). The continuous use of manure of different origins in GS could be one of the sources of contamination, along with the excessive use of agrochemicals. The third component explained 14.4% of variance and was represented by ZnEq (Cu, Ni and Zn). This indicates the exogenous origin of HM in these soils, which is related with the contamination process formerly described in this area and in such soils (Ramos-Miras et al. 2011; Rodríguez-Martín et al. 2013; Gil et al. 2018).

Temporal Hg and Cr trends in GS

As no historic data are available about Cr and Hg contents in these soils, by following the procedure of

Table 4 Summary of the heavy metal concentrations and statistics in the analysed soils ($n = 42$) grouped as crop age

	MINV	AM	MAXV	STD
Hg ($\mu\text{g kg}^{-1}$)				
CS (7)	31.8	37.5 ^a	48.2	5.9
GS1 (11)	21.0	34.5 ^a	53.3	9.6
GS2 (12)	32.6	58.4 ^{ab}	85.1	15.1
GS3 (12)	45.8	99.8 ^b	233.3	55.8
Cr (mg kg^{-1})				
CS (7)	39.5	47.5 ^a	55.9	3.8
GS1 (11)	32.1	56.5 ^a	128.6	28.1
GS2 (12)	31.6	70.5 ^a	210.8	57.6
GS3 (12)	33.1	94.5 ^a	360.7	92.5

CS, control soils; GS, greenhouse soils; GS1, crop age from 0 to 10 years; GS2, crop age from 10 to 20 years; GS3, crop age of more than 20 years. The number of analysed samples is shown in brackets. *MINV* minimum value, *AM* mean value, *MAXV* maximum value, *STD* standard deviation. Different letters indicate significant differences ($p < 0.05$)

Gil et al. (2018), the CS values and the crop age of GS were used to investigate the behaviour patterns of these elements through out the production time. Data were evaluated by comparing the mean values obtained for the greenhouse groups, as indicated in the “Materials and methods” section using the Kruskal–Wallis test, followed by post hoc Tukey tests. When comparing the mean Hg and Cr values in the soils for the GS groups (GS1, GS2, GS3) with the BL (CS) (Table 4), the Hg concentration significantly increased beyond a crop age of 20 years ($37.5 \mu\text{g kg}^{-1}$ for CS vs. $99.8 \mu\text{g kg}^{-1}$ in GS3). This fact agrees with the previous results of Ramos-Miras et al. (2012), who associated this with greenhouse farming activities. The same trend was found for Cr, but it was not statistically significant. Here, the entry of Cr in soil due to anthropic activity was considered less influential than that owing to natural sources and edaphic dynamics. This has also been observed by other authors (ex. Facchinelli et al. 2001). The observed Hg accumulation might be related with GS management, and specifically with the continuous use of agrochemicals, because this area presents no atmospheric contamination and very little industrial activity. These facts agree with the observations made by former works conducted in the same area (Rodríguez-Martín et al. 2009; Gil et al. 2010, 2018).

Enrichment factor and ecological risk

Many contamination indices that can be used to evaluate contamination by HM are described in the literature, and the principles which they are based on considerably differ (Zhuang et al. 2016). Most of these indices do not contemplate the repercussions that HM have on human health or other life forms (Yuan et al. 2014). Conversely, apart from Hakanson’s potential ecological risk (1980) (Er^i) contemplating enrichment factor (C_f), it also considers the potential health risk by incorporating the biological toxicity factor (Tr^i). This work calculated C_f and Er^i (data not shown) in the studied soils. The C_f values for Hg ranged between 0.5 and 6.2, with mean values of 1.7, while those for Cr went from 0.7 to 7.6, with a mean value of 1.6. These values were similar for both these metals, which means that soils have been modified at different levels. The Er^{Hg} value ranged between 18.1 and 249, while the Er^{Cr} value went from 1.3 to 15.2. When Hakanson’s criterion was applied to Hg, 50% of the studied soils presented a moderate potential risk, 15% a considerable potential risk and 5% a high potential risk. Several authors (e.g. Duodu et al. 2016) have found that Hg is one of the HMs that poses a higher potential ecological risk for soils. Campos et al. (2018) have observed a strong correlation between Hg contents in soils and plants, and how this metal transfers from soils to vegetables, which is not influenced by edaphic characteristics, but by contaminating load. The situation differed with Cr because Er^{Cr} was below 40 in all the analysed GS, which indicates that the potential ecological risk was very low. Ke et al. (2017) evaluated the ecological risk for HM on the surface of sediments from the Liaohe River, a protected area in China, and obtained values of the same order of magnitude for Cr, but they did not exceed the threshold value of 40 in any case.

With the obtained data, the PERI was also calculated. To do so, the Hg and Cr data were jointly employed. The results showed that 8% of GS presented a considerable risk (a PERI between 80 and 160). The mean obtained value was 70, which implies a moderate risk, where Hg was the element that contributed more to this index value (about 90%). When the data of Gil et al. (2004), Ramos-Miras et al. (2011) and Rodríguez-Martín et al. (2013) were employed, it was possible to extend this index value to HM Cd, Cu, Ni, Pb and Zn, and to Hg and Cr. In this

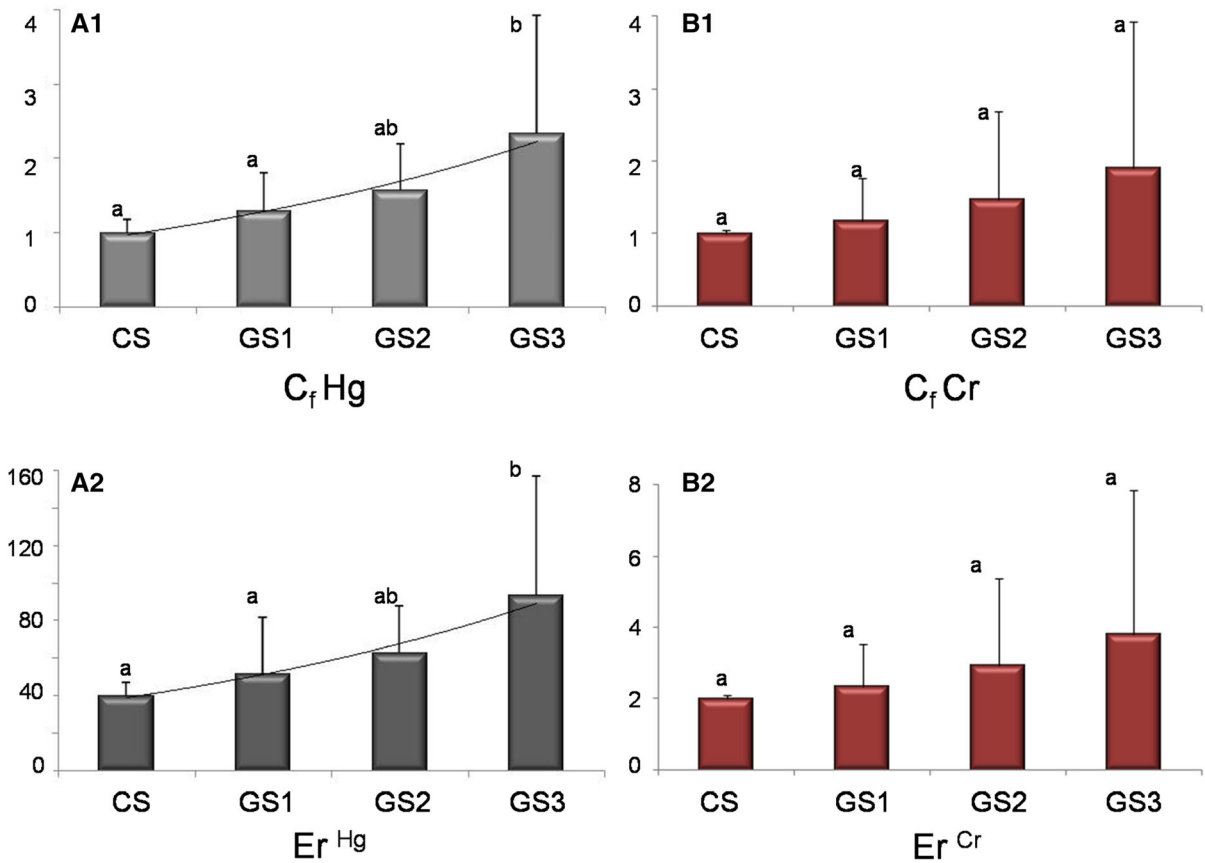


Fig. 2 Temporal trends of the C_f index (**A1**) and the Er^i index (**B1**) for the Hg, and C_f index (**A2**) and the Er^i index (**B1**) for Cr in the greenhouse soils of western Almería (mean \pm standard deviation). A different letter indicates statistically significant

differences ($p < 0.05$) after the post hoc Tukey test. CS, Control soils; GS1, < 10 years of crop age; GS2, 10–20 years of crop age; GS3, > 20 years of crop age

case, the mean value of this index was 157, which implies a moderate risk. These results confirmed that set out in the previous section.

Figures 2 and 3 provide the results of these indices for GS1, GS2 and GS3. As shown, a directly proportional increase occurred in all cases with crop age which, save Cr (Fig. 2B1, B2), was statistically significant in all cases for greenhouse crop aged more than 20 years. After more than 20 years of intensive agriculture, the mean EF value went from 1.0 in CS to 2.4 in GS3 (Fig. 2A1), and the PERI increased from 38 in CS to 100 in GS3 (Fig. 2A2). The PERI for Hg and Cr rose from 42 in CS to 98 in GS3 (Fig. 3A), and from 87 in CS to 198 in GS3 for the set of HM (Fig. 3B). All this suggests that how GS are actually handled in Almería not only causes the enrichment of HM in soils, but also leads to the existence of a potential

ecological risk in many soils, which could pose a health risk.

Finally, like Yang et al. (2017), it was considered that using the PERI would provide a much broader and more rational evaluation of contamination compared to other indices, but its disadvantage is subjectivity owing to the biological toxicity factor (Tr^i). Given the area’s characteristics (semi-arid climate, moderate to strong westerly or easterly winds constantly blowing, little industrialisation) and its greenhouses (relatively closed agrosystems), the source of Hg contamination must be basically associated with farming practices, and specifically with excessive agrochemical use. In line with all this, some previous works have demonstrated the presence of HM in fertilisers and pesticides, which poses a contamination risk for soil (Gimeno-García et al. 1996). They have also evidenced contamination risks for Cd, Cu, Ni and Pb in GS from

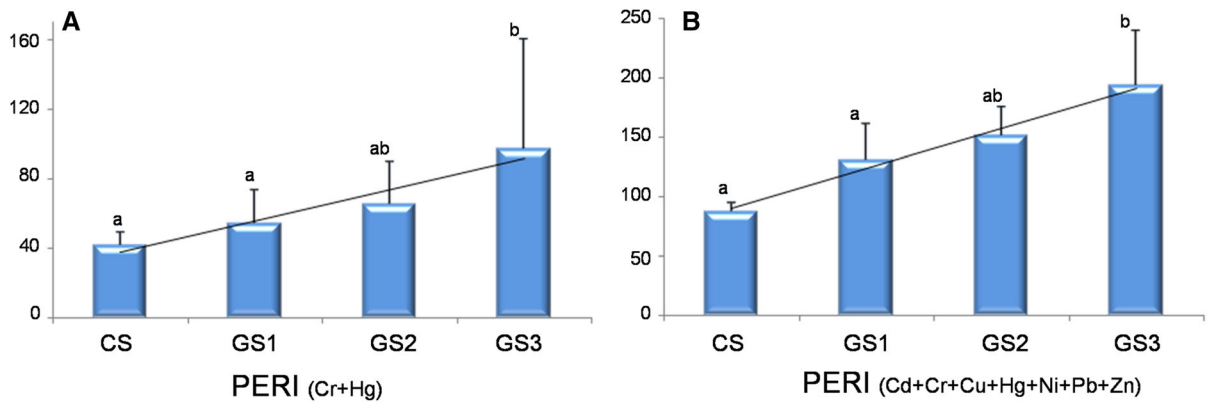


Fig. 3 Temporal trends of PERI (Hg + Cr) (a) and PERI (Cd + Cr + Hg + Ni + Pb + Zn) (b) in the greenhouse soils of western Almería (mean \pm standard deviation). A different letter indicates statistically significant differences ($p < 0.05$)

after the post hoc Tukey test. CS, Control soils; GS1, < 10 years of crop age; GS2, 10–20 years of crop age; GS3, > 20 years of crop age

Almeria, which have been associated with excessive agrochemical use as the main source of contamination by these elements (Ramos-Miras et al. 2002, 2011; Gil et al. 2004, 2018), to which Hg must be added given the results obtained herein.

Conclusions

Hg enrichment was found in GS from Poniente Almeriense, which was associated with agricultural practices. The results reveal that more than 60% of the studied soils exceed the obtained BL for GS. The Er^{Hg} value indicates that a moderate potential risk exists. Nonetheless, when studying the value of this index with crop age, a significant increase took place as values posed a considerable risk in the oldest GS. Although neither a significant risk nor a notable ecological risk was found for Cr, the PERI values obtained for Cr and Hg, and for all the HM, confirmed this trend.

For the first time, this study evidences the risk of Hg accumulation in the study area and proves the importance of conducting follow-up studies to evaluate risks and to correctly manage GS because, although the ecological risk was not high, many GS contained a Hg concentration that was much higher than the BL, especially in the oldest GS, with a considerable potential ecological risk (GS3 $Er^{Hg} = 100$). Further studies should be conducted in the future with more greenhouses to confirm the results

obtained herein. It will also be necessary to conduct studies into Hg absorption and accumulation in vegetables to evaluate the effects of contamination and to avoid health risks.

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