

# Metal contamination of agricultural soils amended with biosolids (sewage sludge) at a ceramic production area in NE Spain: A 10-year resampling period

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## Abstract

Heavy metals in ecosystems affect human health through the web chain. Castellon Province is home to the largest ceramic production hub in Spain, with 94% of the country's total production. Agricultural soils in the vicinity of the ceramic hub were reported to contain potentially toxic elements (Pb, Cr, Ni and Cd) in 2008 and have since been subject to repeated amendment with biosolids (sewage sludge). The sample sites were revisited in 2019, and the chemical distribution of these metals reassessed. The distribution of heavy chemical forms was analysed using a sequential extraction protocol that fractionates these four heavy metals into five phases. The incorporation of biosolids for the past 10 years has changed the chemistry of the soil, leading to increased levels of some hazardous elements. The carbonate-sorbed, residual and reducible phases were dominant. From the point of view of compliance with regulations, levels of Cd remained elevated and have increased over the 10-year period.

## KEYWORDS

biosolids amended soils, ceramic cluster, environmental pollution control, heavy metals, sequential extraction, Spain

## 1 | INTRODUCTION

Keeping heavy metals under control is an important objective when evaluating the risk of contamination (Vicente et al., 2014). Metal pollution of the soils raises concern about the possible risk for public health, and the presence of trace elements of natural (Arikibe & Prasad, 2020; Galán et al., 2008; Tume et al., 2008) or human origin (Arikibe & Prasad, 2020; Bech et al., 2008) in soils is recognized as a potential source of human exposure (Davis et al., 2009; Şehribanoğlu et al., 2020). Because of determining health and environmental factors, the processes of water treatment and purification have spread the world, especially in those countries where the growing shortage of water resources

has made purification an obligatory process (Jordán et al., 2017). A type of mud sludge called 'biosolids' is generated in water treatment processes. These are heterogeneous solid materials whose composition is determined by the origin of the effluent to be treated and by the technology used (Jordán et al., 2009). Spain, with a census of 47 million inhabitants, produces about four million tonnes year<sup>-1</sup> of sewage sludge. Between 65% and 75% of the sludge can be used for agricultural purposes (Jordán et al., 2009) after being composted. There are three main groups of destinations for this type of waste: being sent to a dump or poured in the sea, being used for amended soil purposes or incinerated following the EU regulations (Jordán et al., 2009). The composition of the sewage sludge depends on the origin of the wastewater and on

the physical and chemical treatments carried out. The treated effluent will condition the presence of hazardous components or toxic agents. Sludge from ceramic areas usually has higher contents of Cr, Cd and Ni (Jordán et al., 2009). The use of biosolids in agriculture has important benefits: firstly, costs are quite low soils cultivated close to the water treatment plant. And secondly, N, P, K and organic matter can be recycled, by improving the properties of the soil and reducing the fertilizer costs (Eid et al., 2019). Jing et al. (2019) conclude that maize plants performed better on soil receiving biosolids compared with soil receiving a similar quantity of N, P and K in mineral fertilizers. A better appraisal of the availability for plants of P provided by biosolids is crucial to alleviate the environmental impact from the current excessive incorporation of P in soils that have to withstand high livestock densities (Jing et al., 2019). In fact, in Mediterranean soils rich in CaCO<sub>3</sub> with low quantities of Fe, biosolids may supply Fe, Cu and Zn while reducing the use of chemical fertilizers (Hue, 1995; Jordán et al., 2009; Kim et al., 2007; McGrath et al., 2000). Biosolids applied to agricultural land can behave very differently to inorganic fertilizers in terms of their effects on soil P and N sorption dynamics and soil P availability (reducing the risk of eutrophication) because of the extensive stabilization at wastewater treatment plants to make them safe to use (Withers et al., 2016). However, the use of biosolids as fertilizer could cause issues because of the soil becoming contaminated with heavy metals, and waters with nitrates and phosphates passing through soil horizons and deep geological strata until reaching aquifers (Almendro-Candel et al., 2002; Jordán et al., 2017). In recent years, the role of metals and their importance in biological systems have become quite evident (Arikibe & Prasad, 2020). Metals play dual roles, as essential micronutrients at low concentrations and then switching to toxic agents as concentrations increase (Şehribanoğlu et al., 2020). Biosolids used caused a progressive decrease of the pH of the soil without increasing metal movement down the profile (Masindi & Muedi, 2018). Thus, a decrease in pH can affect the bioavailability of heavy metals (Lundy et al., 2017). As the concentrations and bioavailability of heavy metals increase, they can cause environmental degradation and pose serious risks to the ecosystems (Arikibe & Prasad, 2020) and health. The dietary intake of foods containing high levels of heavy metals could lead to health risks, especially for children (Luo et al., 2017).

In the last 40 years, many papers addressing the partition of metals through the profile of biosolid-amended soils have shown that there is a relatively small downward movement of metals in the short term (Al-Solaimi, 1987; Camobreco et al., 1996; Campos et al., 2019; Gebhardt et al., 1988; McGrath, 1987; McLaren et al., 2004; Richards et al., 1998; Tóth et al., 2016). Williams et al. (1987) found that Fe, Ni, Zn and Cd tend to remain in the sewage sludge incorporation zone for a period of nine years. After applying biosolids to

the grassland surface, Davis et al. (1988) discovered that Zn, Cr, Cu, Pb, Ni and Cd were moving towards the top 10 cm of the profile. Fiskell et al. (1984) found that most of the heavy metals were limited to the first 7 cm of the surface in forest soils. However, there are some authors such as Juste and Solda (1977) or Legret et al. (1988), who found a higher movement of heavy metals. In these studies, on soils that had been repeatedly amended with sewage sludge, Ni moved from the topsoil to depths of 40–60 cm, Cd to depths of 60–80 cm and Pb to depths of 20–40 cm. However, the Cr remained on the surface. Campos et al. (2019) found a similar behaviour for Ni and Cr. Tóth et al. (2016) carried out a detailed analysis of the heavy content in agricultural topsoils of the European Union (EU). The analysis covers the main potentially toxic elements (As, Cd, Cr, Cu, Hg, Pb, Zn, Sb, Co and Ni). These authors estimated that 6.24% or 137,000 km<sup>2</sup> of agricultural lands in the EU need local assessment and eventual remediation action (Marmo, 2003) and suggested the establishment of harmonized screening values for soil contamination in the EU.

The contamination of soils by heavy metals is related to their retention capacity, mainly regarding specific parameters (texture, mineralogy, organic matter content), which affects the chemical properties of the metal and soil particle surfaces (Moral et al., 2005). Heavy metals may be precipitated or coprecipitated as oxides, hydroxides, sulphides or carbonates, or be retained by soil components (Adamo et al., 1996; Masindi & Muedi, 2018).

Several authors focus their studies on trace metal content in agricultural or natural soils (Chang et al., 1992; Tóth et al., 2016). Soil properties are also a determining factor for the bioavailability of heavy metals for plants. The adsorption-desorption mechanisms, the precipitation reactions and the availability of heavy metals in the soil solution play an important role (Arikibe & Prasad, 2020; Fotovat et al., 1997).

The partition of metals among soil components can be determined by a sequential extraction protocol (Singh et al., 1998; Tessier et al., 1979). Research on how pollutants are distributed among various chemical forms allows for better knowledge of the processes of retention and release involved in soil remediation mechanisms (Cabral & Lefebvre, 1998).

In Castellon Province, the expansion of agriculture across hillsides with sharp slopes increases grazing, deforestation and wildfires (Jordán et al., 1998). Furthermore, soils can be polluted and adversely impacted by anthropogenic activities: heavy metals (mainly from the ceramic industry), fats, lubricants (mainly from agriculture devices), ceramic raw material extraction treatments, etc. (Jordán et al., 1998; Jordán et al., 2009). In addition to all these sources of pollution, PM10 and PM2.5 particles are also emitted, mainly because of ceramic activities, and are deposited on soils (Vicente et al., 2014). For example, the mean atmospheric

deposition rate for Cd is around  $2 \text{ g ha year}^{-1}$  (Alloway, 1999). Soil Cd pollution is attributable to many sources, among which the ceramic industry is an important contributor. Their relationship has been explored in this and other studies. Nicholson et al. (1999) calculated the air deposition of other metals such as Ni on soils. High contents of hazardous elements in water, soils and plants are of great concern because of the possible impact on the food chain (Tume et al., 2008). For example, while essential trace metals are necessary for human nutrition, trace elements like Pb and Cd, may reach the food chain and pose health risks (Micó et al., 2006).

High levels of metals in soils increase their uptake by plants. This fact depends not only on metal content in soils, but also on physical, chemical and mineralogical parameters such as soil pH or clay mineral and organic matter content (Navarro Pedreño et al., 1997; Navarro-Pedreño et al., 2018).

The present study is a concise review of the distribution of selected heavy metals in biosolid-amended soils from the ceramic cluster of Castellon and also aims to link the metal distribution patterns to the components of the soil. The main goals of this paper were (a) to assert the total content and chemical partitioning of four heavy metals in agricultural soils repeatedly amended with biosolids, (b) to determine the mineralogical composition of the soils and clay fraction and (c) to compare the results obtained over a period of 10 years (2008–2019).

## 2 | MATERIAL AND METHODS

### 2.1 | Study area

The area under study is located by the coast (NE, Spain). This zone is based on Quaternary lithologies formed by sediments of rivers and estuaries from the inland massifs (*Maestrazgo* Range and *Sierra de Espadán* Range). The Mijares River is the main source of sediments (Jordán et al., 2009; Vicente et al., 2014). The main lithological materials are limestone, sand, gravel, conglomerates, marl and clay. Castellon is located in the Quaternary and the main lithologies are silts, clays and sands (Vicente et al., 2014). The materials around Alcora are, mainly, limestone, marl, sand, clay and gravel. Onda is surrounded by Quaternary and Triassic lithology. The main materials around Onda are red clays in the Quaternary, and conglomerates, limestone, dolomites, marl and limestone in the Triassic (Vicente et al., 2014).

The climate is characterized by mild summers and high average temperatures in the winter. Rainfall does not usually surpass  $550 \text{ mm year}^{-1}$ . In dry farming, the predominant crops are cereals, vines, almond trees and olives. The

orchard crop that has enormous potential in the area is the orange.

### 2.2 | Selected soils and biosolid composition

Two sampling campaigns were carried out, one in spring 2008 (third week of March) and the other in spring 2019 (first week of April). Five surface soils (0–15 cm) that were polluted as a result of agricultural activities were used in this experiment (Jordán et al., 2009). The diversity of physicochemical properties, specially carbonate content and pH, was the selection criteria of amended soils (Table 1). The soils were classified as calcareous (Soil 2–5) and non-calcareous (Soil 1). Figure 1 shows the location of the sampling sites. Soil 1 is a biosolid-amended soil sampled in the Alcora area. Almond trees are the predominant cultivations. Soils 2–4 are soils modified with sewage sludge that have been irrigated with polluted water in an experimental plot. The cultivation in this experimental plot is orange trees. Soil 5 comes from a disposal site in the Onda area. The selected soil classification (FAO/UNESCO, 1998) is as follows:

*Fluvisols* (Soils 1–4): Typical Mediterranean soils, widely represented in the studied area, found in valley bottoms and flood plains. These occupy the terraces of the river courses from the inland areas to the coast and the coastal plains. These soils are well drained and have a significant depth of horizons and variable texture (Antolín, 1998).

*Calcisol* (Soil 5): These types of soils are characterized by horizons with enrichment of calcium carbonate, favoured by semi-arid conditions. In these soils, percolation and carbonate accumulation are linked to geomorphic processes (Antolín, 1998).

All soils were sampled and crushed, sieved (2 mm), mixed and stored. The physical and chemical properties of the soils were analysed following standard methods (Haltar et al., 2010). The pH was measured in soil suspended in deionized water, at a proportion of 1:2.5 (m/V). EC was measured using 1:5 soil:water extract. The  $\text{CaCO}_3$  equivalent was determined with a Bernard calcimeter. Rhoades method was used for determining the CEC. The determination of soil organic carbon was based on the Walkley–Black chromic acid wet oxidation method. The determination of the content of different metals was carried out following microwave digestion using  $\text{HNO}_3$ . Metals were analysed by ICP-MS (Krishnamurti et al., 1994; Pérez, 2001).

The addition of biosolids to soil is not devoid of environmental risks or drawbacks resulting from the possible presence of organic compounds that are hard to degrade, hazardous metals, microorganisms, an excess of

**TABLE 1** Chemical and physical properties of the selected biosolid-mended soils (2008/2019)

Properties	Non-calcareous soil		Calcareous soils			F-ANOVA
	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	
pH (1/2.5)	6.51/ <b>6.71</b>	8.05/ <b>8.10</b>	8.15/ <b>8.41</b>	7.95/ <b>8.10</b>	7.80/ <b>8.00</b>	*
EC (1:5)/dS m <sup>-1</sup>	0.40/ <b>0.65</b>	0.75/ <b>0.87</b>	0.60/ <b>0.79</b>	1.00/ <b>1.20</b>	1.47/ <b>1.87</b>	*
Sand/%	60.0/ <b>62.0</b>	18.0/ <b>18.5</b>	17.5/ <b>17.0</b>	18.0/ <b>18.0</b>	33.5/ <b>35</b>	n.s.
Silt/%	23.0/ <b>22.0</b>	68.5/ <b>69.0</b>	70.0/ <b>70.5</b>	73.0/ <b>72.5</b>	62.5/ <b>60</b>	n.s.
Clay/%	17.0/ <b>16.0</b>	13.5/ <b>12.5</b>	12.5/ <b>12.5</b>	9.0/ <b>9.5</b>	4.0/ <b>5.0</b>	n.s.
Total CaCO <sub>3</sub> /%	3.4/ <b>3.3</b>	52.0/ <b>53.0</b>	50.5/ <b>51.5</b>	48.9/ <b>49.9</b>	36.8/ <b>40.0</b>	*
Active CaCO <sub>3</sub> /%	1.8/ <b>2.0</b>	17.5/ <b>17.9</b>	15.7/ <b>16.2</b>	15.8/ <b>16.4</b>	13.5/ <b>14.7</b>	*
Organic C/%	0.50/ <b>0.70</b>	2.08/ <b>2.15</b>	1.99/ <b>2.1</b>	2.54/ <b>2.9</b>	1.10/ <b>1.50</b>	**
CEC/mol <sub>c</sub> kg <sup>-1</sup>	0.15/ <b>0.20</b>	0.30/ <b>0.6</b>	0.32/ <b>0.55</b>	0.33/ <b>0.58</b>	0.26/ <b>0.32</b>	***
Total Fe/mg kg <sup>-1</sup>	11 10 <sup>3</sup> / <b>12 10<sup>3</sup></b>	14 10 <sup>3</sup> / <b>15 10<sup>3</sup></b>	11 10 <sup>3</sup> / <b>12 10<sup>3</sup></b>	13 10 <sup>3</sup> / <b>14 10<sup>3</sup></b>	10 10 <sup>3</sup> / <b>11 10<sup>3</sup></b>	***
Total Mn/mg kg <sup>-1</sup>	466/ <b>502</b>	345/ <b>398</b>	340/ <b>359</b>	471/ <b>510</b>	372/ <b>401</b>	**
Total Cu/mg kg <sup>-1</sup>	15.5/ <b>16.2</b>	66.0/ <b>62.7</b>	35.1/ <b>36.9</b>	50.1/ <b>52.7</b>	20.2/ <b>26.3</b>	*
Total Zn/mg kg <sup>-1</sup>	26.0/ <b>27.1</b>	260/ <b>272</b>	95.0/ <b>99.2</b>	140/ <b>153</b>	105/ <b>112</b>	*
Total Cd/mg kg <sup>-1</sup>	6.0/ <b>7.8</b>	79/ <b>82</b>	102/ <b>134</b>	205/ <b>234</b>	4.5/ <b>6.0</b>	***
Total Ni/mg kg <sup>-1</sup>	7.5/ <b>9.0</b>	36.5/ <b>46.4</b>	38.2/ <b>42.6</b>	52.2/ <b>55.3</b>	30.5/ <b>35.6</b>	**
Total Cr/mg kg <sup>-1</sup>	17.9/ <b>20.8</b>	29.7/ <b>32.0</b>	32.1/ <b>42.2</b>	35.8/ <b>45.6</b>	24.8/ <b>30.3</b>	***
Total Pb/mg kg <sup>-1</sup>	28.0/ <b>27.8</b>	229/ <b>224</b>	32.0/ <b>30.0</b>	35.0/ <b>29.6</b>	27.0/ <b>33.0</b>	**

Note: Legend: 2008/2019 (bold); \*, \*\*, \*\*\* indicate significance at levels of p=0.05, 0.01 and 0.001 respectively; ns: not significant).

Bold values correspond to results from soils sampled in 2009.

nutrients and the mobility of ions or potentially contaminating substances (Almendro-Candel et al., 2002; Bech et al., 2008; Jordán et al., 2017). In 2018, the average composition of biosolids from 10 wastewater treatment plants located around the ceramic hub were analysed showing different composition in nutrients and heavy metals: organic C (25%–30%), N (3%–6.8%), P (0.26%–0.78%), K (0.05%–0.1%), Ca (0.05%–0.15%), Mg (0.09%–0.18%), Fe (6,165–59,855 mg kg<sup>-1</sup>), Cu (110–512 mg kg<sup>-1</sup>), Cd (10–2,010 mg kg<sup>-1</sup>), Ni (9–52 mg kg<sup>-1</sup>), Pb (23–303 mg kg<sup>-1</sup>), Zn (355–2,100 mg kg<sup>-1</sup>), Hg (1–3.5 mg kg<sup>-1</sup>) and Cr (20–1,039 mg kg<sup>-1</sup>). It was not possible to obtain proven information about the origin, doses and application periods of these biosolids from the local farmers.

### 2.3 | Mineralogical analysis

Soils were treated with a HOAc-NaOAc buffer (pH 5.0) to remove carbonates and with H<sub>2</sub>O<sub>2</sub> to remove organic matter. Furthermore, the clay fraction was separated by sedimentation (Gee & Bauder, 1986). The mineralogical analysis of whole samples of soil and clay fractions was carried out by X-ray diffraction (XRD) of oriented aggregate (normal, treated with ethylene glycol for 24 hr and heated to 550°C for 2 hr) following the protocols described in Kahle and Jahn (2002), using a Siemens D5000 with

Bragg-Bretano geometry with CuK $\alpha$  radiation (40 kV, 30 mA). Samples were analysed using the Siemens automatic software DIFFRACT-AT.

### 2.4 | Sequential extraction procedure

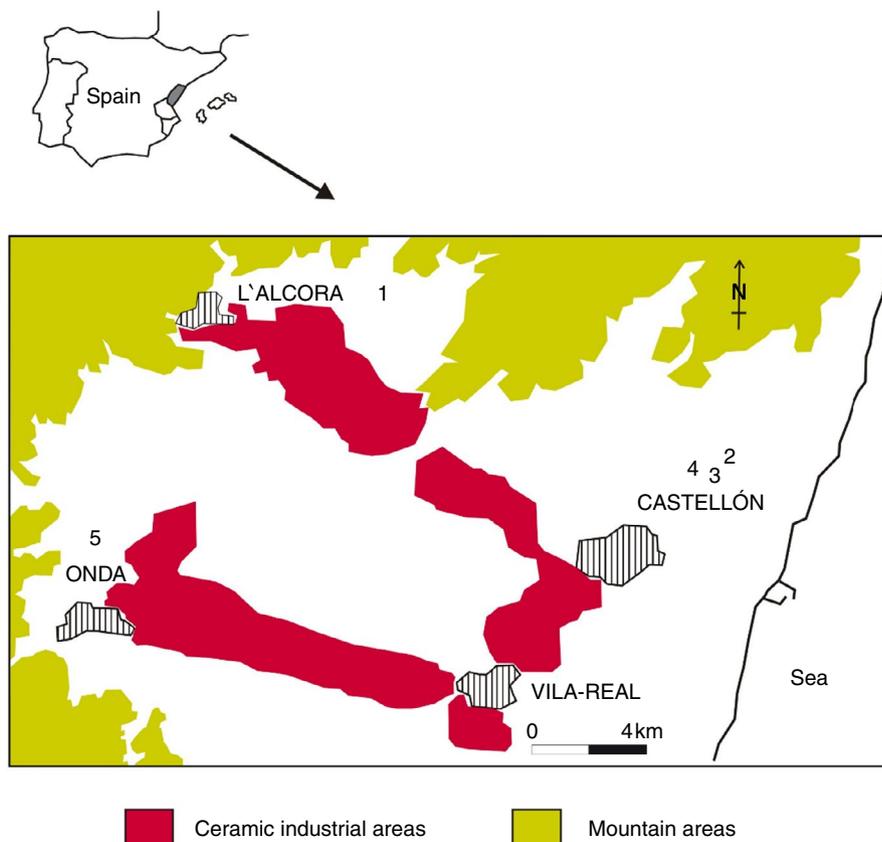
The analytical methodology was adapted from procedures developed by Shuman (1982); Shuman (1985); Beckett (1989) and Ahnstrom and Parker (1999). The entire analytical protocol is described in Moral et al. (2005); Jordán et al. (2009). Triplicate portions of 4 g were weighed in 100-ml polycarbonate centrifuge tubes and extracted sequentially as follows:

F1: Soluble-exchangeable phase: Each sample was reacted with 30 ml of 0.1 M SrCl<sub>2</sub> in a shaker (3,600 rpm) for 2 hr at 20°C.

F2: Sorbed-carbonate bound: the residue was treated with 60 ml of 1.0 M NaOAc pH 5.0 and shaken for 5 hr at 20°C. This extraction was performed several times until  $\Delta$ pH < 0.1 in the supernatant.

F3: Oxidizable phase: the residue was mixed with 10 ml of 5% NaOCl at pH 8.5 and reacted in a bath of water (90°C) for 30 min. This procedure was repeated four times in order to maximize oxidation of the organic matter.

**FIGURE 1** Location of the sampling sites (Jordán et al., 2009) [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



F4: Reducible phase: the residue was mixed with 40 ml of 0.2 M oxalic acid + 0.2 M ammonium oxalate + 0.1 M ascorbic acid adjusted to pH 3 with  $\text{NH}_4\text{OH}$  in a bath of water ( $90^\circ\text{C}$ ) for 30 min. This procedure was repeated four times.

F5: Residual phase: the residue was oven-dried, pulverized and mixed. Duplicate 0.400 g subsamples were digested by microwave digestion with 20 ml  $\text{HNO}_3$ .

Extracts and solutions were acidified using  $\text{HNO}_3$  (1%). ICP-MS determinations were carried out with matrix-matched standards. The recovery values of the elements were quantified, and the relative standard deviations were calculated. The solvents and the reagents used in the analysis were considered in determining the detection limits of Cd, Ni, Cr and Pb. The equation proposed by Skoog and Leary (1991) was used ( $X_c = \bar{x}_{\text{blank}} + 3S_{\text{blank}}$ ).

The ANOVA test was used to assess the statistical significance of the results obtained for the two sampling periods (indicating significance at levels of  $p = .05$ ,  $.01$  and  $.001$ , respectively; ns: not significant). Correlation coefficients between the extractable contents of Cr, Cd, Pb and Ni and some chemical and physical properties of the studied biosolid-amended soils were calculated. All correlations have been carried out using Spearman's coefficient (Dodge, 2010).

### 3 | RESULTS

Table 1 shows the main physicochemical properties of studied soils. A wide range of properties of these soils are discussed below. The organic C content ranged from 0.50% to 2.54% in the 2008 sampling and 0.70%–2.90% in the 2019 sampling which represents a significant increase ( $p = .01$ ) in a short period of time. Electrical conductivity ranged from 0.40 to  $1.47 \text{ dS m}^{-1}$  in the 2008 sampling and 0.65– $1.87 \text{ dS m}^{-1}$  in 2019, which is a slight increase ( $p = .05$ ). The pH values, which experienced a slight increase ( $p = .05$ ), are linked to the presence or absence of  $\text{CaCO}_3$ . Total Cd content ranged from 6 to  $205 \text{ mg kg}^{-1}$  in the 2008 samplings and 7.8 to  $234 \text{ mg kg}^{-1}$  in 2019 which is a significant increase ( $p = .001$ ). Total Ni content is between 7.5 and  $52.2 \text{ mg kg}^{-1}$  in the 2008 sampling and 9.0– $55.3$  in 2019 which is a significant increase ( $p = .01$ ). Total Cr content ranged from 17.9 to  $35.8 \text{ mg kg}^{-1}$  in the 2008 sampling and 20.8– $45.6$  in 2019 which is a significant increase ( $p = .001$ ). Total Pd content ranged from 28 to  $229 \text{ mg kg}^{-1}$  in the 2008 samplings and 27.9 to  $224 \text{ mg kg}^{-1}$  in 2019 indicating a significant decrease ( $p = .01$ ).

Table 2 summarizes the mineral constituents of each soil. Quartz was the major component for Soil 1. Quartz and calcite were the major components for calcareous soils (2–5). At a semi-quantitative level, the mineralogical composition

	High	Moderate	Little	Traces		
Soil 1	Qtz	–	Il-M, K, Goe, H	–	Ch	–
Soil 2	Cc	Qtz	Il-M	F, Do	Ch	Ka
Soil 3	Cc	Qtz	Il-M	Do	Ch	Ka
Soil 4	Cc	Qtz	Il-M	F, Do	Ch	Ka
Soil 5	Qtz, Cc	–	Do, Il-M	F	Ch	Ka

Abbreviations: Cc, calcite; Ch, chlorite; Do, dolomite; F, feldspar; Goe, goethite; H, haematite; Il-M: illite-muscovite; Ka, kaolinite; Qtz: quartz.

of calcareous soils (Soils 2–5) was similar, with the presence of quartz, calcite, dolomite, illite and traces of chlorite and kaolinite. The mineralogy of Soil 1 was different (Table 2). A high content of quartz was found in these soils. The main difference was the presence of goethite and haematite along with a mixture of several clay mineral phases (illite-muscovite, kaolinite and chlorite). In the mineralogical composition of the clay fraction of the soils, the association of kaolinite, illite and chlorite, and small quantities of other minerals (calcite, quartz, feldspar, dolomite and haematite) was found (McLaren et al., 1998).

The sequential extraction procedure describes the affinity of the selected metals with soil matrix constituents (McBride et al., 2003). Table 3 shows a comparison between recovery and the total concentrations obtained with a microwave digestion. Figures 2–5 summarized the results for the sequential extraction of analysed heavy metals, as contents and percentages of the total metal in each fraction.

For Soil 1, the majority of the Cd was recovered in the reducible (4.7–5.9 mg kg<sup>-1</sup>) and oxidizable (0.9–1.5 mg kg<sup>-1</sup>) fractions (Figure 2). Cadmium was recovered mainly in the sorbed-carbonate (52.7, 83.2, 172 and 0.8 mg kg<sup>-1</sup> in the 2008 sampling and 53.7, 99.2, 219 and 1.4 mg kg<sup>-1</sup> in the 2019 sampling) and residual fractions (9.2, 9.7, 20 and 3 mg kg<sup>-1</sup> in the 2008 sampling and 10.4, 18.7, 10.1 and

4.1 mg kg<sup>-1</sup> in the 2019 sampling) for Soils 2, 3, 4 and 5. The percentages of Cd sorbed-carbonate fraction represent approximately 80% of the total Cd. For Soil 5, sewage sludge was the origin of sorbed-carbonate Cd (>19%). The main percentage of Cd in Soil 5 was found in the residual fraction (>68%).

Nickel was recovered mainly in the residual (3.4, 15.5, 15.3, 18.7 and 13 mg kg<sup>-1</sup> in the 2008 sapling and 4.4, 20.5, 20.3, 19.7 and 16 mg kg<sup>-1</sup> in the 2019 sampling) and reducible fractions (0.8, 10.2, 17.2, 10 and 10.3 mg kg<sup>-1</sup> in the 2008 sampling and 0.8, 12.5, 21.2, 11 and 12.3 mg kg<sup>-1</sup> in the 2019 sampling) of the soils. Calcareous soils show a different behaviour.

The residual fraction was the main Cr fraction in the calcareous soils (23.5, 25.7, 26.9 and 19.1 mg kg<sup>-1</sup> in the 2008 sampling and 25.4, 36.7, 38.9 and 22.3 mg kg<sup>-1</sup> in the 2019 sampling) and in Soil 1 (9 and 10 mg kg<sup>-1</sup> for 2008 and 2009 samplings, respectively). In Soil 1, around 50% of Cd was present in the residual fraction. However, in calcareous soils this percentage was higher than 75%.

In the calcareous soils studied, the main fraction for Pb (62%–90%) was the residual phase (185.5, 21.9, 20.7, 21.2 mg kg<sup>-1</sup> for the 2008 sampling and 189, 20.9, 16.6 and 26.8 mg kg<sup>-1</sup> for the 2019 sampling). The distribution of Pb in calcareous soils followed this sequence: F5 > F2 > F3. In

TABLE 2 Mineralogy of the soils

Metal	Soil number					DL µg ml <sup>-1</sup>
	1	2	3	4	5	
Sampling 2008						
Cd	93 ± 1	89 ± 3	96 ± 3	99 ± 3	94 ± 8	0.17
Ni	101 ± 5	94 ± 4	105 ± 7	96 ± 3	95 ± 5	0.35
Cr	90 ± 6	99 ± 3	108 ± 3	110 ± 5	99 ± 3	0.20
Pb	91 ± 7	90 ± 2	98 ± 3	91 ± 3	98 ± 3	0.14
Sampling 2019						
Cd	95 ± 3	88 ± 3	97 ± 3	99 ± 3	97 ± 8	0.14
Ni	102 ± 5	95 ± 4	109 ± 7	96 ± 3	95 ± 5	0.29
Cr	92 ± 6	99 ± 3	107 ± 3	112 ± 5	98 ± 3	0.18
Pb	93 ± 7	90 ± 2	97 ± 3	92 ± 3	98 ± 3	0.17

TABLE 3 Extraction efficiency of metals. Recovery and detection limits (DL)

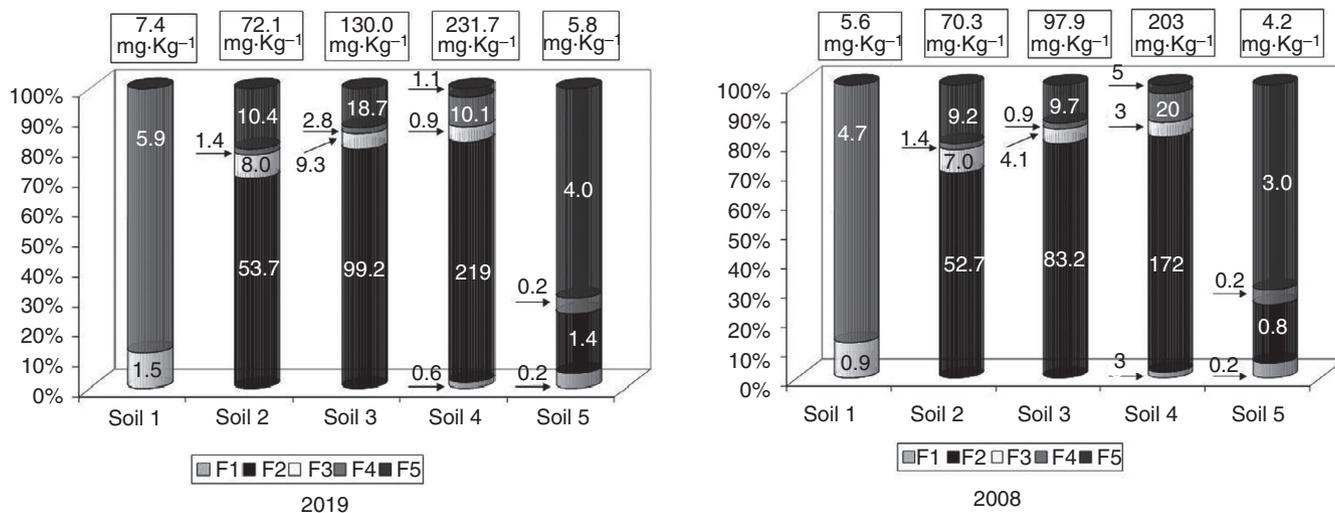


FIGURE 2 Distribution of total recovered Cd (%) in a set of five sewage sludge-amended soils

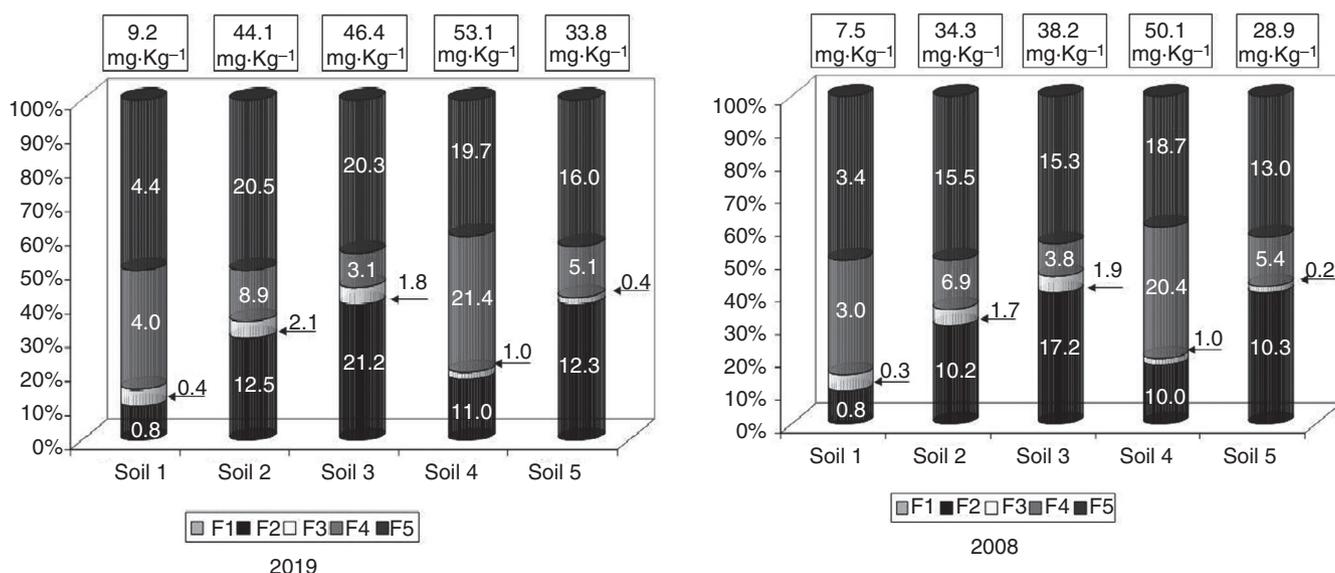


FIGURE 3 Distribution of total recovered Ni (%) in a set of five sewage sludge-amended soils

Soil 1, the amount of Pb in the residual and reducible phases (8–9 mg kg<sup>-1</sup>, 35%–40%) was similar.

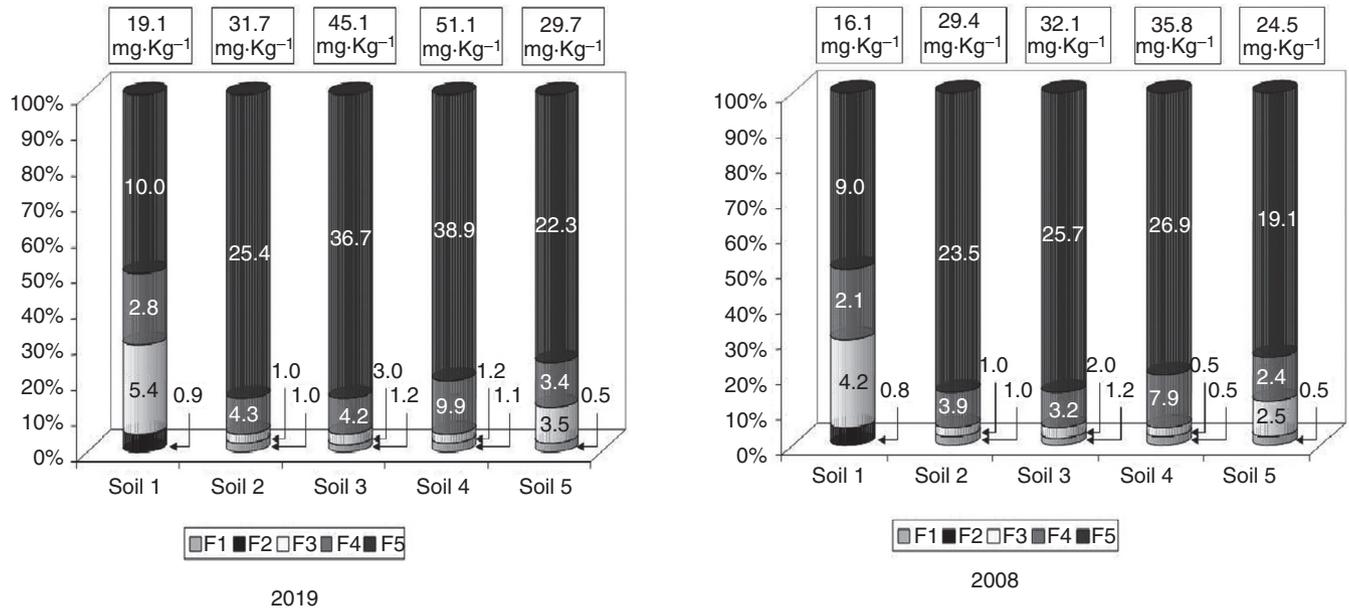
## 4 | DISCUSSION

### 4.1 | Total metal contents

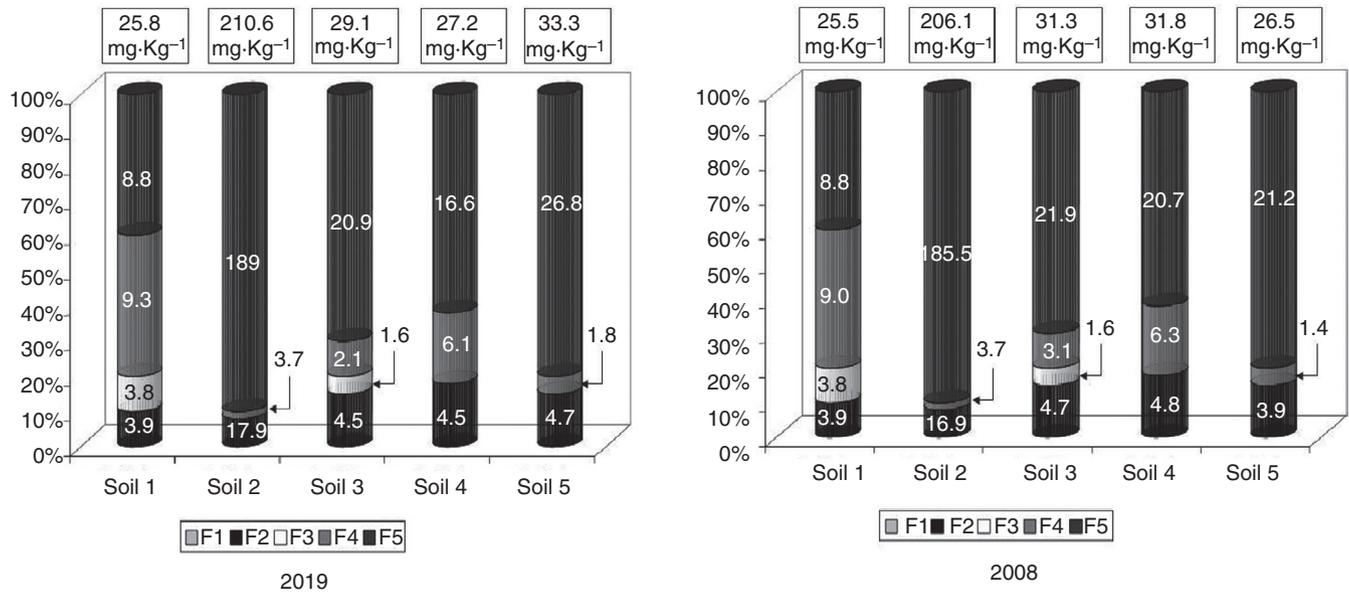
After a 10-year period between the two samples taken, there has been a significant increase in the total content of Cd, Ni and Cr (.001, .01 and .001 *p* values, respectively). However, the Pb contents have hardly changed and there has even been a slight decrease (*p* = .01). This behaviour of Pb can be explained by the limitation of the use of this metal in the ceramic frit and enamel industry (BOE, 2006), mainly in ceramic bodies for food or in contact with food. We also found an increase in electrical conductivity values (*p* = .05) as well

as the content of organic carbon (*p* = .01) and micronutrients (Fe, Mn, Cu and Zn), mainly Fe (*p* = .001). The repeated application of biosolids in the last 10 years has improved the organic C content in all soils, but unfortunately, it has also produced an increase in the total content of Cd, Ni and Cr, and an increase in EC.

The mean metal concentrations (mg kg<sup>-1</sup>) determined in agricultural soils from Castellon Province (NE Spain) were 0.33 for Cd, 19.3 for Ni, 33.3 for Cr and 55.8 for Pb (Peris et al., 2008). This paper is relevant in the studied area and it focuses on finding the baseline of soil metal concentration. In the case of Cd, the values found in Soils 1–5 exceed that value, even surpassing the reference values for contaminated soils in Spanish regulation (RD1310/90) set at 3.0 mg kg<sup>-1</sup> of Cd-T. In the case of Ni, only Soil 1 is below the average reference value in the region, whereas all other analysed soils exceeded this value. The maximum allowed value for Ni-T in Spanish



**FIGURE 4** Distribution of total recovered Cr (%) in a set of five sewage sludge-amended soils



**FIGURE 5** Distribution of total recovered Pb (%) in a set of five sewage sludge-amended soils

legislation is 112 mg kg<sup>-1</sup>. The five analysed soils have values that are well below this limit. As for Cr, Soils 3 and 4 exceed the average concentration value in the region. All soils have values well below the limit set for contaminated soils in Spanish regulation (150 mg kg<sup>-1</sup>). Total Pb values are also below the average of the Province of Castellon and far from the limit value of reference in Spanish regulation (300 mg kg<sup>-1</sup>). Therefore, from the point of view of compliance with regulations, we found concerning levels of Cd in the analysed soils. In addition, these values, far from diminishing, have increased over a period of 10 years. After 10 years, no significant changes in the mineralogical composition of the analysed soils are significant. Illite-muscovite is the main clay mineral in all soils.

## 4.2 | Metal partition

Mahler (1988) discovered that the Cd derived from sewage sludge was present mostly in the carbonate fraction. Soils 2–4 had a similar Cd distribution sequence. The differences in Cd adsorption were associated to the soil pH (Moral et al., 2005). Biosolid application reduces the soil pH and Cd adsorption, with lower values of soil pH (Lundy et al., 2017). Moral et al. (2005) and Masindi and Muedi (2018) explain this behaviour. Soils treated with sewage sludge reduce the amount of complexed Cd and increased the amount of exchangeable Cd. In Soil 1, most of the Cd is sheltered in the reducible phase (>79%) and then, in the oxidizable fraction

(>20%), most likely because of the presence of exogenous Cd pollution (biosolid application) along with the presence of goethite and haematite (Jordán et al., 2009). Exchangeable Cd pool rises with increasing organic matter in the soil. This fact was observed by other authors such as He and Singh (1993), Lamy et al. (1993), Ahumada et al. (2004) or Lundy et al. (2017). The increase in organic carbon (%), 10 years after the first sampling, can be associated with the increase in total Cd. This trend has also been observed in other more recent studies (Campos et al., 2019; Eid et al., 2019). However, the partition of Cd in the fractions has not changed. This is mainly because of the fact that the increase in the content of organic matter after the application of biosolids has not significantly affected the pH values. In fact, a slight increase is observed. This behaviour (buffer effect) is characteristic of Mediterranean calcareous soils (Peris et al., 2008). In the studied calcareous soils (2–5) amended with sewage sludge, a low percentage of Cd was found in the soluble-exchangeable (<10%). Chelation can increase the solubility of the metal at high pH values (Moral et al., 2005; Jordán et al., 2009 and Tóth et al., 2016). For biosolids rich in both Fe and Ca, and where Fe-rich biosolids were applied to calcareous soils, the negative influence of Fe on P lability appeared to be neutralized, possibly aided by the formation of hydroxides at high pH (Withers et al., 2016).

In Soils 2, 3 and 5, the Ni distribution sequence was F5 > F2 > F3. Only for Soil 4, F4 was higher than F5. This behaviour was tested in both 2008 and 2019 sampling periods. A significant percentage of Ni is present in the form of sorbed-carbonate (Jordán et al., 2009). A similar percentage of soluble-exchangeable Ni was observed for all soils (1–5). Narwal et al. (1999) found an interesting correlation between reducible and residual forms of Ni and the levels of Mn and Fe oxides in soils. Luo et al. (2017) concluded that sandy soils, rich in organic matter with a large Ni content, are unsuitable for the production of rice and legumes in Fujian Province, SE China. Many researchers observed that only the strong acids are able to fully extract Cr from soils (Ahumada et al., 2004; Karathanasis & Johnson, 2006). This fact confirms that Cr is tightly bound in the matrix (Jordán et al., 2009). The sequence of partition of Cr in calcareous soils (2–5) was F5 > F4 > F3. The chrome partition is different compared with the behaviour of Ni. The percentage of Cr sorbed on carbonate fraction was less than the soluble-exchangeable fraction (Jordán et al., 2009; Moral et al., 2005).

Lead is predominantly found in the residual fraction (Ahumada et al., 2004). Soils polluted with high contents of Pb showed an accumulation in the sorbed-carbonate fraction (Cabral & Lefebvre, 1998). However, in this study, the total content of Pb in soils is relatively low and a large proportion of Pb was found in the oxidizable phase (>10%). Even though the total content of Pb was higher in soils analysed in 2008, the Pb partition is quite similar in both sampling periods.

**TABLE 4** Correlation coefficients between the extractable contents of Cr, Cd, Pb and Ni and some chemical and physical properties of the studied biosolid-amended soils

	Cr	Cd	Pb	Ni
pH	-.261	-.165	-.325	-.056
EC	.354	-.234	-.314	-.027
CaCO <sub>3</sub>	-.245	.091	.409	-.213
CEC	<b>-.794</b>	<b>-.576</b>	-.323	-.696
Organic C	.495	.723	.567	.231
Clay	<b>-.536</b>	-.303	.015	-.197
Silt	-.433	-.137	.089	-.467
Sand	.526	.187	-.065	.309

Note: Significant correlation at the .05 level.

Bold values correspond to results from soils sampled in 2009.

### 4.3 | Metal recovery and correlations

In the extraction procedure, a good recovery percentage has been found for all the metals studied (Table 3). Soil pH changed with the incorporation of biosolids. The pH reduction is more pronounced where the amount of Fe in the biosolid is high (Withers et al., 2016). However, weak and negative correlations have been obtained between pH and the heavy metals studied (Table 4). At pH > 7, the metals were adsorbed and not available to plants. The results obtained differ from other published works. For example, Luo et al. (2017) found that Ni tended to rise with increasing clay and silt contents and, as a result, so did the CEC, with no strong correlations with other soil properties. This different behaviour is because Ca is the dominant cation in the exchange complex. The negative correlation coefficients obtained between heavy metals, the CEC and the percentage of clay fraction (Table 4) corroborate the dominance of the Ca cation in the exchange position.

Results showed different trends of metal partition among the different pools in biosolid-amended soils. This variability demonstrates that the values of total concentration of heavy metals in soils may not be appropriate as a useful indicator for toxicity or environmental risk in future studies at this ceramic hub.

## 5 | CONCLUSIONS

After a 10-year period between the two samples, there has been a significant increase in the total content of Cd, Ni and Cr. However, the Pb content has hardly changed and there has even been a slight decrease. The heavy metals in the studied set of soils were linked to carbonate, residual or reducible fractions and depended on the nature, mineralogy, pH and other soil properties. Cd is associated with

carbonate fractions. However, Ni, Cr and Pb are mainly associated with the residual phase. The variation of pH and a possible decrease of this property through the incorporation of biosolids can favour the mobilization of pollutants in Mediterranean calcareous soils. Thus, most importantly, the presence of hazardous metals in soils must be determined before adding biosolids. The authors recommend extending this study to other countries of the Mediterranean region of Europe.

## DATA AVAILABILITY STATEMENT

Data available on request from the authors.

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## REFERENCES

- Adamo, P. S., Dudka, S., Wilson, M. J., & McHardy, W. J. (1996). Chemical and mineralogical forms of Cu and Ni in contaminated soils from the Sudbury mining and smelting region, Canada. *Environmental Pollution*, *91*, 11–19.
- Ahnstrom, Z. S., & Parker, D. R. (1999). Development and assessment of a sequential extraction procedure for the fractionation of soil cadmium. *Soil Science Society of America Journal*, *63*, 1650–1658.
- Ahumada, I., Escudero, P., Carrasco, M. A., Castillo, G., Ascar, L., & Fuentes, E. (2004). Use of sequential extraction to assess the influence of sewage sludge amendment on metal mobility in Chilean soils. *Journal of Environmental Monitoring*, *6*, 327–334.
- Alloway, B. (1999). Atmospheric deposition of heavy metals onto agricultural land in England and Wales. In W. W. Wenzel, D. C. Adriano, B. Alloway, H. E. Doner, C. Keller, N. W. Lepp, M. Mench, R. Naidu, & G. M. Pierzynski (Eds.), *Fifth International Conference on the Biogeochemistry of Trace Metals*, 11–15 July 1999, Vienna, Austria, *1*: 414–415.
- Almendro, M. B., Navarro-Pedreno, J., Gomez Lucas, I., Jordan Vidal, M. M., Garcia Sanchez, E., & Mataix Solera, J. (2002). Movement of Fe, Mn, Cu and Zn in a sewage sludge-treated soil. In D. Almorza, C. A. Brebbia, D. Sales, & V. Popov (Eds.), *Waste management and the environment* (pp. 311–320). WIT Press.
- Al-Solaimi, S. G. (1987). Effect of sewage sludge-borne cadmium on crop production and on soil and plant composition. *Dissertation Abstracts International*, *47*(9), 3583B.
- Antolín, C. (1998). *El suelo como recurso natural en la Comunidad Valenciana*. Generalitat Valenciana.
- Arikibe, J. E., & Prasad, S. (2020). Determination and comparison of selected heavy metal concentrations in seawater and sediment samples in the coastal area of Suvas, Fiji. *Marine Pollution Bulletin*, *157*(2020), 111157.
- Bech, J., Tune, P., Sokolovska, M., Reverte, F., Sánchez, P., Longan, L., Puente, A., & Oliver, T. (2008). Pedogeochemical mapping of Cr, Ni, and Cu in soils of the Barcelona Province (Catalonia, Spain): Relationships with soil physico-chemical characteristics. *Journal of Geochemical Exploration*, *96*, 106–116.
- Beckett, P. H. T. (1989). The use of extractants in studies on trace metals in soils, sewage sludge and sludge-treated soils. *Advances in Soil Science*, *9*, 143–176.
- BOE (2006). *Royal Decree 8991/2006 of July 21*. Ministry of the Presidency, Government of Spain.
- Cabral, A. R., & Lefebvre, G. (1998). Use of sequential extraction in the study of heavy metal retention by silty soils. *Water, Air and Soil Pollution*, *102*, 329–344.
- Camobreco, V. J., Richards, B. K., Steenhuis, T. S., Peverly, J. H., & McBride, M. B. (1996). Movement of heavy metals through undisturbed and homogenized soil columns. *Soil Science*, *161*(11), 740–750. <https://doi.org/10.1097/00010694-199611000-00003>
- Campos, T., Chaer, G., dos Santos Leles, P., Silva, M., & Santos, F. (2019). Leaching of heavy metals in soils conditioned with biosolids from sewage sludge. *Floresta E Ambiente*, *26*(Spec No 1), e20180399. <https://doi.org/10.1590/2179-8087.039918>
- Chang, A. C., Granato, T. C., & Page, A. L. (1992). A methodology for establishing phytotoxicity criteria for Cr, Cu, Ni and Zn of municipal sewage sludge. *Journal of Environmental Quality*, *21*, 521–536.
- Davis, H. T., Aelion, C. M., McDermott, S., & Lawson, A. B. (2009). Identifying natural and anthropogenic sources of metals in urban and rural soils using GIS-Based data, PCA, and spatial interpolation. *Environmental Pollution*, *157*, 2378–2385. <https://doi.org/10.1016/j.envpol.2009.03.021>
- Davis, R. D., Carlton-Smith, C. H., Stark, J. H., & Campbell, J. A. (1988). Distribution of metals in grassland soils following surface applications of sewage sludge. *Environmental Pollution*, *49*, 99–115. [https://doi.org/10.1016/0269-7491\(88\)90243-6](https://doi.org/10.1016/0269-7491(88)90243-6)
- Dodge, Y. (2010). *The concise encyclopedia of statistics* (p. 508). Springer Verlag.
- Eid, E. M., Alrumman, S. A., El-Bebany, A. F., Fawy, K. F., Taher, M. A., El-Latif Hesham, A., El-Shaboury, G. A., & Ahmed, M. T. (2019). Evaluation of the potential of sewage sludge as a valuable fertilizer for wheat (*Triticum aestivum* L.) crops. *Environmental Science and Pollution Research International*, *26*, 392–401.
- FAO/UNESCO World Reference Base for Soil Resources (1998). *84 world soil resources reports*. International Society of Soil Science.
- Fiskell, J. G. A., Rebertus, R., Comeford, N. B., & Pritchett, W. L. (1984). Comparing soil test for a forested acid sandy soil topdressed with sewage effluent. *Soil Science Society of America Journal*, *48*, 1170–1174.
- Fotovat, A., Naidu, R., & Sumner, M. E. (1997). Soil ratio influences aqueous phase chemistry of indigenous copper and zinc in soils. *Australian Journal of Soil Research*, *35*, 687–710.
- Galán, E., Fernández-Caliani, J. C., Gonzalez, I., Aparicio, P., & Romero, A. (2008). Influence of geological setting on geochemical baselines of trace elements in soils. Application to soils of South-West Spain. *Journal of Geochemical Exploration*, *98*, 89–106. <https://doi.org/10.1016/j.gexplo.2008.01.001>
- Gebhardt, H., Grun, R., & Push, F. (1988). The accumulation of heavy metals in soils and crops through sewage sludge application. *Zeitschrift Für Pflanzenernährung Und Bodenkunde*, *151*, 307–310.
- Gee, G., & Bauder, J. W. (1986). Particle size analysis. In A. Klute (Ed.), *Particle-Size Analysis, Methods of Soil Analysis, Part I. Physical and Mineralogical Methods* (Agronomy Monograph no 9 (2nd ed.)). American Society of Agronomy-Soil Science Society of America.
- Haltar, B. I., Taimeh, A. Y., & Ziadat, F. M. (2010). Variation in soils chemical properties along toposequences in an arid region of the Levant. *Catena*, *83*(1), 34–45.

- He, Q. B., & Singh, B. R. (1993). Effect of organic matter on the distribution, extractability and uptake of cadmium in soils. *Journal of Soil Science*, *44*, 641–650. <https://doi.org/10.1111/j.1365-2389.1993.tb02329.x>
- Hue, N. V. (1995). Sewage sludge (Chapter 6). In J. E. Rechcigl (Ed.), *Soil amendments and environmental quality* (pp. 199–247). CRC Lewis Publishers.
- Jing, J., Christensen, J. T., Sorensen, P., Christensen, B. T., & Rubaek, G. H. (2019). Long-term effects of animal manure and mineral fertilizers on phosphorous availability and silage maize growth. *Soil Use and Management*, *35*, 323–333.
- Jordán, M. M., García-Sánchez, E., Almendro-Candel, M. B., Pardo, F., Vicente, A. B., Sanfeliu, T., & Bech, J. (2017). Technosols designed for rehabilitation of mining activities using mine spoils and biosolids. Ion mobility and correlations using percolation columns. *Catena*, *148*, 74–80.
- Jordán, M. M., Mateu, J., & Boix, A. (1998). A Classification of sediment types based on statistical multivariate techniques. *Water, Air and Soil Pollution*, *107*, 91–104.
- Jordán, M. M., Montero, M. A., Pina, S., & García-Sánchez, E. (2009). Mineralogy and distribution of Cd, Ni, Cr, and Pb in biosolids-amended soils from Castellón province (NE Spain). *Soil Science*, *174*(1), 1–7.
- Juste, C., & Solda, P. (1977). Effets d'applications massives de boues de stations d'épuration urbaines en monoculture de maïs: Actions sur le rendement et la composition des plantes et sur quelques caractéristiques du sol. *Science Du Sol*, *3*, 147–155.
- Kahle, M., & Jahn, R. (2002). Review of XRD-based quantitative analysis of clay minerals in soils: The suitability of mineral intensity factors. *Geoderma*, *109*(3–4), 191–205.
- Karathanasis, A. D., & Johnson, D. M. C. (2006). Subsurface transport of Cd, Cr, and Mo mediated by biosolid colloids. *Science of the Total Environment*, *354*, 157–169. <https://doi.org/10.1016/j.scitotenv.2005.01.025>
- Kim, B., McBride, M. B., Richards, B. K., & Steenhuis, T. S. (2007). The long-term effect of sludge application on Cu, Zn and Mo behavior in soils and accumulation in soybean seeds. *Plant and Soil*, *299*, 227–236.
- Krishnamurti, G. S. R., Huang, P. M., Van Rees, K. L., Korak, L. M., & Rostead, P. W. (1994). Microwave digestion technique for the determination of total cadmium in soils. *Communications in Soil Science and Plant Analysis*, *25*, 615–625.
- Lamy, I., Bourgeois, S., & Bermond, A. (1993). Soil cadmium mobility as a consequence of biosolids disposal. *Journal of Environmental Quality*, *22*, 731–737.
- Legret, M., Divet, L., & Juste, C. (1988). Migration et spéciation des métaux lourds dans un sol soumis à des épandages de boues de station d'épuration à très forte charge en Cd et Ni. *Water Research*, *22*(8), 953–959.
- Lundy, L., Alves, I., Revitt, M., & Wildeboer, D. (2017). Metal water-sediment interactions and impacts on the ecosystem. *International Journal of Environmental Health Research*, *14*, 722–733.
- Luo, D., Zheng, H., Deleporte, P., Xie, T., Staunton, S., & Wang, G. (2017). Influence of soil properties on Ni accumulation in food crops and corresponding dietary health risk with a typical Chinese diet. *Soil Use and Management*, *33*(4), 653–662.
- Mahler, R. J. (1988). Cadmium sulphate application to sludge-amended soils: II. Extraction of Cd, Zn and Mn from solid phases. *Communications in Soil Science and Plant Analysis*, *56*, 1747–1770.
- Marmo, I. (2003). *Heavy metals in context of UE policies on soil and waste*. European Commission, DG Environment. [www.europa.eu.int](http://www.europa.eu.int)
- Masindi, V., & Muedi, K. L. (2018). Environmental contamination by heavy metals. In H. E. D. M. Saleh, & R. F. Aglan (Eds.), *Heavy metals* (pp. 115–133). In Tech.
- McBride, M. B., Nibarger, E. A., Richards, B. K., & Steenhuis, T. (2003). Trace metal accumulation by red clover grown on sewage sludge-amended soils and correlation to Mehlich 3 and calcium chloride-extractable metals. *Soil Science*, *168*, 29–38. <https://doi.org/10.1097/00010694-200301000-00004>
- McGrath, S. P. (1987). Long-term studies of metal transfers following application of biosolids. In P. J. Coughtrey, M. H. Martin, & M. H. Unsworth (Eds.), *Pollutant, transport and fate in ecosystems* (pp. 301–317). Blackwell Scientific Publications.
- McGrath, S. P., Zhao, F. J., Dunham, S. J., Crossland, A. R., & Coleman, K. (2000). Long-term changes in the extractability and bioavailability of zinc and cadmium after sludge application. *Journal of Environmental Quality*, *29*, 875–883. <https://doi.org/10.2134/jeq2000.00472425002900030025x>
- McLaren, R. G., Backes, C. R., Rate, A. W., & Swift, R. S. (1998). Cadmium and cobalt desorption kinetics from soil clays: Effect of sorption period. *Soil Science Society America Journal*, *62*, 332–337. <https://doi.org/10.2136/sssaj1998.03615995006200020006x>
- McLaren, R. G., Clucas, L. M., Taylor, M. D., & Hendry, T. (2004). Leaching of macronutrients and metals from undisturbed soils treated with metal-spiked sewage sludge. 2. Leaching of metals. *Australian Journal of Soil Research*, *42*(4), 459–471. <https://doi.org/10.1071/SR03168>
- Micó, C., Recalata, L., Peris, M., & Sánchez, J. (2006). Assessing heavy metal sources in agricultural soils of a European Mediterranean area by multivariate analysis. *Chemosphere*, *65*, 863–872.
- Moral, R., Gilkes, R. J., & Jordan, M. M. (2005). Distribution of heavy metals in calcareous and non-calcareous soils in Spain. *Water, Air, and Soil Pollution*, *162*, 127–142. <https://doi.org/10.1007/s11270-005-5997-5>
- Narwal, R. P., Singh, B. R., & Salbu, B. (1999). Association of cadmium, zinc, copper, and nickel with components in naturally heavy metal-rich soils studied by parallel and sequential extractions. *Communications in Soil Science and Plant Analysis*, *30*, 1209–1230. <https://doi.org/10.1080/00103629909370279>
- Navarro-Pedreño, J., Almendro-Candel, M. B., Gómez-Lucas, I., Jordán, M. M., Bech, J., & Zorpas, A. A. (2018). Trace metals content and availability of essential metals in agricultural soils of Alicante (Spain). *Sustainability*, *10*(4534), 1–11.
- Navarro-Pedreño, J., Gómez, I., Moral, R., Palacios, G., & Mataix, J. (1997). Heavy metals and plant nutrition and development. *Recent Research Developments in Phytochemistry*, *1*, 173–179.
- Nicholson, F. A., Alloway, B. J., & Carlton-Smith, C. (1999). Sources of heavy metals to agricultural soils in England and Wales. In W. Wenzel, D. C. Adriano, B. Alloway, H. E. Doner, C. Keller, N. W. Lepp, M. Mench, R. Naidu, & G. M. Pierzynski (Eds.), *Fifth International Conference on the Biogeochemistry of Trace Metals*, 11–15 July 1999, Vienna, Austria 1: pp. 264–265.
- Perez, B. (2001). Use of microwave single-extractions for metal fractionation in biosolids samples. *Analytica Chimica Acta*, *43*, 209–218.
- Peris, M., Recalata, L., Micó, C., Sánchez, R., & Sánchez, J. (2008). Increasing the knowledge of heavy metal contents and sources in agricultural soils of the European Mediterranean region. *Water, Air, and Soil Pollution*, *192*, 25–30.

- Richards, B. K., Steenhuis, T. S., Peverly, J. H., & McBride, M. B. (1998). Metal mobility at an old, heavily loaded sludge application site. *Environmental Pollution*, 99, 365–377. [https://doi.org/10.1016/S0269-7491\(98\)00011-6](https://doi.org/10.1016/S0269-7491(98)00011-6)
- Şehribanoğlu, S., Zorer, H., & Selçuk Zorer, Ö. (2020). Chemometric data analysis of gross radioactivity and heavy metal concentrations in soil and sediments of Bendimahi River, Turkey. *Journal of Radioanalytical and Nuclear Chemistry*, 326(1), 223–239. <https://doi.org/10.1007/s10967-020-07361-9>
- Shuman, L. M. (1982). Separating soil iron- and manganese-oxide fractions for microelement analysis. *Soil Science Society America Journal*, 46, 1099–1102. <https://doi.org/10.2136/sssaj1982.03615995004600050044x>
- Shuman, L. M. (1985). Fractionation method for soil microelements. *Soil Science*, 140, 11–22.
- Singh, S. P., Tack, F. M., & Verloo, M. G. (1998). Heavy metal fractionation and extractability in dredged sediment derived surface soils. *Water, Air and Soil Pollution*, 102, 313–328.
- Skoog, D. A., & Leary, J. J. (1991). *Principles of instrumental analysis* (4th ed., pp. 5–9). Saunders College Publishing.
- Tessier, A., Campbell, P. G. C., Muntau, H., & Griepick, B. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 51(7), 844–851.
- Tóth, G., Hermann, T., Da Silva, M. R., & Montanarella, L. (2016). Heavy metals in agricultural soils in European Union with implications for food safety. *Environmental International*, 88, 299–309.
- Tume, P., Bech, J., Tume, L., Bech, J., Reverter, F., Longan, L., & Cendoya, P. (2008). Concentrations and distributions of Ba, Cr, Sr, V, Al, and Fe in Torrelles soil profiles (Catalonia, Spain). *Journal of Geochemical Exploration*, 96, 94–105. <https://doi.org/10.1016/j.gexplo.2007.03.003>
- Vicente, A. B., Pardo, F., Sanfeliu, T., Casalta, S., & Bech, J. (2014). Assessment of PM10 and heavy metal concentration in a ceramic cluster (NE Spain) and the influence on nearby soils. *Journal of Geochemical Exploration*, 114, 320–327.
- Williams, D. E., Vlamis, J., Pukite, A. H., & Corey, J. E. (1987). Metal movement in sludge-amended soils: A nine-year study. *Soil Science*, 143, 124–131.
- Withers, P. J. A., Flynn, N. J., & Warren, G. P. (2016). Are stabilized biosolids a eutrophication risk? *Soil Use and Management*, 32, 138–148.

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