

Article

Environmental Risk from Organic Residues

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Abstract: Soil nutrient imbalance is a global threat to food security and ecosystem sustainability but adding organic residues or constructing anthropogenic soils and technosols can optimize it. However, FAO considers organic residues not “risk-free”, mainly due to their heavy metal content. Despite the fact that applying pruning residues to soil is a worldwide fertilization practice, its potential heavy metal risk has been poorly studied. This work characterizes Cu, Zn, Cd, Cr, Ni and Pb elemental composition concentration and their solubility content in almond tree pruning, commercial peat substrate, hay straw, olive tree pruning, pomegranate peel, pine needle, date palm leaf pruning, sewage sludge compost and vine pruning. Furthermore, we compare the legal frameworks governing heavy metal content in agricultural substrates to heavy metal concentration in each residue. Results show that commercial peat substrate is the only one among those studied that surpasses the threshold value for Cr in agricultural substrates. All pruning residues met the heavy metal threshold value; hence, their application to soil involves minimal soil toxicity. Moreover, the solubility index of heavy metals and the maximum quantity of each residue are crucial to discerning a heavy metal-free organic fertilization plan.

Keywords: soluble heavy metal; ecosystem services; circular economy; Sustainable Development Goals



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1. Introduction

Consequences for crops, human health and ecosystems due to improper use of inorganic fertilizers have been widely debated. However, an efficient supply of nutrients to the soil is increasingly necessary since soil nutrient imbalance is a global threat to food security and ecosystem sustainability [1]. To optimize soil nutrient cycles and solve functional problems, the Food and Agriculture Organization (FAO) of the United Nations (UN) [2] and other authors [3–5] propose adding organic residues or constructing technosols [6–8], in line with sustainable agriculture, circular economy strategy and Sustainable Development Goals (SDGs) [9–11]. At the same time, the European Green Deal (EGD) aims towards carbon neutrality until 2050, with midterm goals of at least 55% decrease in greenhouse gas emissions by 2030. EGD enables European countries and, by extension, citizens to benefit from sustainable practices toward green transition [12]. In this regard, the European Commission proposed innovative objectives linked directly and indirectly with EGD (i.e., European climate Law, Farm to Fork strategy) in order to establish cutting-edge research and innovation in order to preserve the natural environment and ensure, among others, sustainable soil management [13,14]. In addition, applying organic residues synchronized with crop nutritional requirements can be key to its yield due to the rapid supply of soluble nutrients [15–18].

FAO defines organic fertilizer as “one derived from living organisms, such as manure, green manure, compost and crop residues, and municipal wastes” [19]. Although organic fertilizers’ benefits are unquestionable (improve physical properties, microbial activity,

nutrient supply, biodiversity and ecosystem services provision and CO₂ storage, among others) [5,9,17,18,20–22], according to FAO [23], they are not “risk-free” either, and is mainly associated with the material that it is made of, such as excreted matter or industrial process waste. Consequently, aspects to keep in mind are heavy metal concentration, polluting substances (microplastics, chemical substances, pharmaceutical products and other emerging contaminants), salt concentration and the presence of pathogenic microorganisms [24–26]. Although a priori crop residues are the ones with the lowest risk of toxicity or pathogenicity, this work focuses on dangers that are not so obviously related to crop residues’ nutrient content and transfer. Both the lack and excess of nutrients in soils pose problems for public health (i.e., malnutrition, human diseases), for the development of crops (i.e., food insecurity) and for ecosystem sustainability [23,27,28].

Plants need nutrients for their development. Depending on the amount of nutrients required by plants, they are categorized as macronutrients (N, P, K, Ca, Mg and S) or micronutrients (Fe, Mn, B, Mo, Cu, Zn and Cl) and are considered essential in completing the stages of the plant life cycle. Na, Si, Co and V are essential for some plants. In addition, plants uptake from the soil solution; other elements are not essential (Cd, Cr, Ni, Pb, Hg, As, Li, Rb, Al, Se, etc.) if they are in available forms [23,29]. However, when concentrations of these elements in the soil are unbalanced due to excess or deficiency, they can lead to plant toxicity or malnutrition, respectively. Deficiency-yield-toxicity margins of the elements depend mainly on the type of element, plant species, soil physical–chemical properties and climatic conditions [28,30]. In general, plants have better tolerance for macronutrient excess than micronutrients, where the limits between yield and loss are closer [29].

Among micronutrients, although Cu and Zn are heavy metals (HMs), both are essential micronutrients for human and animal nourishment. Moreover, other HMs, such as Cd, Cr and Pb, are essential too [30] but only at very low concentrations to avoid ecosystem contamination and food chain accumulation [28], as Cd and Pb are the most toxic elements to the human body [27]. Knowing the HM concentration that plants uptake from soil solution and store in edible parts is vital for human health, as well as knowing the HM concentration in non-edible tissues that can be applied to soil, as when HM concentration is high, a loop of contamination can be initiated. Moreover, HMs affect soil microorganisms, which hinders organic waste decomposition [28].

HM presence in agricultural soil, due to anthropogenic causes, may be related to inorganic fertilizers or waste application [30]. In the European Union, even though the amount of agricultural land affected is not very high, it is estimated that 137,000 km² (6.24%) of agricultural land has an HM concentration above the guideline values [31]. Following the FAO’s recommendation [2,23], we provide an analysis of some nutrients and HM legal threshold concentrations, depending on the crop residue applied to the soil. Currently, we do not have a legal framework on a European level for the formulation and use of anthropogenic man-made soils and technosols that sets technical and safety criteria for crops, the environment and human health [32].

Characterization and monitoring of residue mixtures are important, as well as the soil to which they are applied, since there may be an enhancement or a reduction in adverse effects, as in the case of metal mobilization and leaching [8]. Therefore, this work analyzes Cu, Zn, Cd, Cr, Ni and Pb elemental composition concentration in organic residues and their solubility content that may pose a risk after soil application, as HM can cause great concern [33]. In addition, the legal framework related to HM content in agricultural substrates is compared to the heavy metal concentration in each residue. Furthermore, this research calculates from what number of applications organic residues can entail a potential HM risk.

2. Materials and Methods

2.1. Selected Residues

Based on its availability (proximity to consider circular economy and zero waste strategy) and potentiality to be part of technosols (considering man-made and transformed soils), the following organic residues were selected:

- Almond tree pruning (AP).
- Commercial brown peat (CP).
- Hay straw (HS).
- Olive tree (*Olea europaea* L.) pruning (OP).
- Pomegranate (*Punica granatum* L.) peel (PG).
- Pine (*Pinus halepensis*) needle fall (PN).
- Date palm (*Phoenix dactylifera* L.) leaf pruning (PP).
- Sewage sludge compost (SC).
- Vine (*Vitis vinifera*) pruning (VP).

Pruning and harvesting residues (AP, HS, OP, PG, PN, PP and VP) were collected from agricultural areas close to Elche (Alicante, Spain). SC was processed and obtained from Aspe Wastewater Treatment Plant (Alicante, Spain). PP was subjected to an initial shredding after pruning and PN was collected directly from the ground surface in a nearby *Pinus halepensis* forest area.

2.2. Residue Characterization and Methods

All residues were subjected to conditioning processes consisting of air drying at room temperature inside a greenhouse (reaching temperatures over 40 °C), shredded and sieved (2 mm).

HM elemental composition (Cu, Zn, Cd, Cr, Ni and Pb) was determined by atomic absorption spectrometer (AAS) (Thermo Scientific, iCE 3000 Series AA Spectrometer, Waltham, MA, USA) after acid digestion (69% nitric acid + H₂O₂) of samples (0.2 g) in a microwave [34]. AAS is calibrated before use by testing the absorbance with solutions of quantitative certificated standards. AAS detection limits are Cu, 0.04; Zn, 0.01; Cd, 0.005; Cr, 0.02; Ni, 0.01 and Pb, 0.02 mg L⁻¹. Cr is evaluated as total Cr content.

HM aqueous extraction (1:10 *w/v*) of each residue was obtained by using 100 mL deionized water added to 10 g of residue and shaking for 2 h. After filtering, HM soluble content was measured by using AAS (Thermo Scientific, iCE 3000 Series AA Spectrometer).

Additionally, HM solubility index (I_{HM}) was calculated as the percentage of HM extracted in aqueous solution with respect to elemental composition in each residue, both expressed in dry weight basis, according to Equation (1) [35]:

$$I_{HM} = (W_{HM}/C_{HM}) \times 100 \quad (1)$$

where

I_{HM} : heavy metal;

W_{HM} : water extractable heavy metal average content;

C_{HM} : heavy metal average concentration in elemental composition.

2.3. Statistical Analysis

Descriptive statistics were used to calculate mean and standard deviation for each individual analysis of residues (five repetitions per each one). Analysis of variance (ANOVA) and Tukey's multiple comparisons test were performed to compare the mean value of HM content by using SPSS Statistics (v.26).

3. Results and Discussion

3.1. Elemental Composition

Table 1 provides the total content of Cu, Zn, Cd, Cr, Ni and Pb results in organic residue elemental composition (dry matter).

Table 1. HM elemental composition, average content (Ave.) and standard deviation (Std.) of each residue.

Residue	Cu (mg kg ⁻¹)		Zn (mg kg ⁻¹)		Cd (mg kg ⁻¹)		Cr (mg kg ⁻¹)		Ni (mg kg ⁻¹)		Pb (mg kg ⁻¹)	
	Ave.	Std.	Ave.	Std.	Ave.	Std.	Ave.	Std.	Ave.	Std.	Ave.	Std.
AP	4.0 a	0.3	4.6 a	1.7	nd	-	nd	-	nd	-	nd	-
CP	11.2	1.4	5.3 ab	0.7	0.629	0.005	2.8	0.4	nd	-	nd	-
HS	3.6 a	0.1	31.3	3.7	nd	-	nd	-	nd	-	nd	-
OP	4.9 a	0.3	12.4 c	0.6	nd	-	nd	-	nd	-	nd	-
PG	5.3 a	0.2	110.8	2.0	nd	-	nd	-	nd	-	nd	-
PN	7.0 a	0.8	11.4 bc	1.0	nd	-	nd	-	nd	-	nd	-
PP	3.8 a	0.4	15.7 cd	0.9	nd	-	nd	-	nd	-	nd	-
SC	79.7	14.6	249.5	8.4	0.686	0.108	26.4	0.7	6.2	0.5	10.8	1.9
VP	8.2 a	1.3	19.4 d	1.5	nd	-	nd	-	nd	-	nd	-
F ¹	100.4 ***		2474 ***									

¹ F values followed by *** indicate significant differences at $p = 0.001$. By columns, mean values with letters in common (a, b, c, d) are statistically equal to $p = 0.05$. nd: under detection limit.-: not calculated.

As expected, SC is the residue with the highest concentration of those studied HM (Table 1). The most striking result to emerge from our data (Table 1) is that Cd and Cr presence has been detected in CP, which is provided as a gardening substrate. Nevertheless, no organic pruning or harvesting residues studied (AP, HS, OP, PG, PN, PP and VP) achieve Cd, Cr, Ni or Pb concentrations above the equipment detection limit. Consequently, they can be used as an essential micronutrient source (Cu, Zn) if their legal threshold concentration is not exceeded and thus does not pose a threat to soil toxicity.

Cu concentration in SC (79.7 mg kg⁻¹) is higher among the other residues (Table 1). CP includes 11.2 mg kg⁻¹ of Cu elemental composition, which is similar data to pruning residue although a bit higher, as Cu concentration in pruning residue is between 3.6 and 8.2 mg kg⁻¹.

Regarding Zn elemental composition, SC achieves the highest concentration (Table 1). Curiously, PG has the second-highest Zn content compared with the other pruning residues. Woody or more lignified residues have a lower Zn concentration, between 4.6 and 31.3 mg kg⁻¹. These findings suggest that all studied residues (except for AP) can provide more Zn than the commercial peat studied (CP). SC and CP have similar Cd concentrations (0.686 and 0.625 mg kg⁻¹, respectively). However, there are high levels of Cr in SC (26.4 mg kg⁻¹) than in CP (2.8 mg kg⁻¹). SC is the only waste that provides Ni and Pb.

Although SC is at the top of the HM concentration in Table 1, data are much lower than those detected by consulted references. Milik et al. [36] and Alonso et al. [37] obtained Cd (1.16 mg kg⁻¹), Ni (53.85 mg kg⁻¹), Pb (23.92 mg kg⁻¹), Cd (2.69 mg kg⁻¹), Cr (53.9 mg kg⁻¹), Ni (28.4 mg kg⁻¹) and Pb (108 mg kg⁻¹), respectively. However, the data obtained (Table 1) for Cr (26.4 mg kg⁻¹) are higher than the one achieved by Milik et al., Cr (15.32 mg kg⁻¹) [36]. It is worth mentioning that there are raised levels of HM in SC from several European countries, compared to Table 1 values [36]. For instance, SC values obtained for Cu vary from 1467.13 to 237.5 mg kg⁻¹; Zn from 7026.66 to 620.5 mg kg⁻¹; Cd from 36.81 to 1.5 mg kg⁻¹; Cr from 210.35 to 38.4 mg kg⁻¹; Ni from 214.29 to 19.3 mg kg⁻¹ and Pb from 221.5 to 48.2 mg kg⁻¹. The presence of HM in wastewater fluctuates as it is closely linked to the amount and type of industrial activity developed in each city. Therefore, for this type of waste, where HM elemental composition is highly variable, characterization of each batch is needed.

The presence of HM in peat bogs has been studied before. Sypalov et al. [38] considered that HM concentration varies depending on the depth at which each peat sample was taken, while the concentration ranges from Cu, 0.98–3.92 mg kg⁻¹; Zn, 3.89–23.8 mg kg⁻¹; Cd,

35.3–125 $\mu\text{g kg}^{-1}$; Cr, 0.18–1.89 mg kg^{-1} ; Ni, 0.46–1.9 mg kg^{-1} and Pb, 0.59–10.2 mg kg^{-1} . Similar research reached even higher values of HM in peat, as 333, 8.8 and 245 mg kg^{-1} for Zn, Cd and Pb, respectively [39], thus explaining the presence of HP in CP (Table 1).

References related to HM elemental composition content in pruning residue are scarce. Musa Ozcan et al. [40] analyzed the presence of HM in pomegranate peel. HM concentration in PN can vary on the strength of spice type: Cu, 0.705–1.48; Zn, 6.45–22.2; Cd, 0.021–0.091; Ni, 0.144–0.351 and Pb, 0.172–0.147 mg kg^{-1} [41] and of needle age too: Cu, 3.7–11.2; Zn, 18.6–59.2; Cd, 0.1–2.5 and Ni, 3.5–17.1 mg kg^{-1} [42]. Al-Busaidi et al. [43] obtained HM in PP elemental composition: Cu, 0.001; Zn, 6.5–12.92; Cd, 0.001; Ni, 9.93–10.19 and Pb, 0.001 mg L^{-1} .

3.2. Soluble Elements and Solubility Index

HM water extractable content is shown in Table 2 (dry matter).

Table 2. HM water extractable average content (Ave.) and standard deviation (Std.) of each residue.

Residue	Cu (mg kg^{-1})		Zn (mg kg^{-1})		Cd (mg kg^{-1})		Cr (mg kg^{-1})		Ni (mg kg^{-1})		Pb (mg kg^{-1})	
	Ave.	Std.	Ave.	Std.	Ave.	Std.	Ave.	Std.	Ave.	Std.	Ave.	Std.
AP	0.240 ab	0.020	4.2 ab	0.3	nd	-	nd	-	nd	-	nd	-
CP	0.091 a	0.009	4.3 ab	0.3	nd	-	nd	-	nd	-	nd	-
HS	1.024 de	0.267	7.8 d	1.9	nd	-	nd	-	nd	-	nd	-
OP	1.144 e	0.187	5.6 bc	0.6	nd	-	nd	-	nd	-	nd	-
PG	1.797	0.329	13.9	1.0	nd	-	nd	-	nd	-	nd	-
PN	0.437 b	0.046	4.7 ab	0.4	nd	-	nd	-	nd	-	nd	-
PP	0.819 cd	0.105	10.5	0.6	nd	-	nd	-	nd	-	nd	-
SC	0.522 bc	0.051	4.0 a	0.2	nd	-	nd	-	nd	-	0.38	0.25
VP	1.116 de	0.103	6.7 cd	0.5	nd	-	nd	-	nd	-	nd	-
F ¹	45.0 ***		89.6 ***									

¹ F values followed by *** indicate significant differences at $p = 0.001$. By columns, mean values with letters in common (a, b, c, d, e) are statistically equal to $p = 0.05$. nd: under the detection limit. -: not calculated.

Curiously, in SC and CP, the Cd, Cr Ni and Pb water extractable content are below equipment detection limits, compared to elemental composition values (Table 1), except for Pb in SC (0.38 mg kg^{-1}). These findings suggest that, in general, Cu and Zn are the most soluble elements among the studied metals. Scaling soluble Cu results from highest concentration to lowest, the order revealed is PG > OP > VP > HS > PP > SC > PN > AP > CP. In such a way, all studied residues provide more Cu in a short time than CP, and PG can release the most quantity (1.797 mg kg^{-1}). Related to Zn water extractable content (Table 2), the list of studied residues scaled from the highest to lowest are PG > PP > HS > VP > OP > PN > CP > AP > SC. PG has the highest concentration of soluble Cu and Zn. Nevertheless, CP and SC are at the bottom, SC, due to the loss of soluble elements during the composting process [35,44].

It is important to be aware of the presence of rapidly soluble HM because, with the first rain or irrigation, they would be released into the soil solution, so the HM solubility index (I_{HM}) is calculated (Table 3).

It can be seen from the data in Table 3 that Zn and Cu are the metals with the highest solubility index, with certain peculiarities associated with residue origin and composition. Zn achieves the highest rates of solubility in most of the residues. AP involves 90% of Zn solubility, and the list from top to bottom is AP > CP > PP > OP > PN > VP > HS > PG > SC. Although AP and CP have a low concentration of Zn in their elemental composition (Table 1), most of Zn is in a soluble form (between 90 and 82%, respectively) (Table 3). However, PP is the second residue related to the concentration of soluble Zn (Table 2) and PP has the third place for solubility index (67%).

Residues with higher I_{Cu} are PG > HS > OP > PP > VP > PN > AP > CP > SC. Notwithstanding, SC is the residue with the lowest I_{Cu} and I_{Zn} , and is the only one that

has I_{Pb} (4%). Accordingly, although SC is the residue with the highest concentration of Cu and Zn in its elemental composition (Table 1), its low I_{Cu} and I_{Zn} show that SC can have an optimum performance as a long-term nutrient source. None of the pruning residue, nor CP, have I_{Cd} , I_{Cr} , I_{Ni} and I_{Pb} . So, in addition to its high I_{Cu} and I_{Zn} , pruning residues can rapidly release Cu and Zn to nourish crops.

Table 3. Solubility index (%) of each metal (I_{HM}).

Residue	I_{Cu}	I_{Zn}	I_{Cd}	I_{Cr}	I_{Ni}	I_{Pb}
AP	6	90	-	-	-	-
CP	1	82	-	-	-	-
HS	29	25	-	-	-	-
OP	23	45	-	-	-	-
PG	34	13	-	-	-	-
PN	6	42	-	-	-	-
PP	21	67	-	-	-	-
SC	1	2	-	-	-	4
VP	14	35	-	-	-	-

-: not calculated.

Although the bibliography on the subject is scarce and focuses mainly on SC, Milik et al. [36] considered Ni and Cd in SC as the most easily movable elements. However, other references obtain high rates of exchangeable Ni and Zn among the elements studied in this article [37]. Even so, Alonso et al. [37] concluded that the rapidly soluble HM percentage in SC is low, at only 7%.

3.3. Potential Toxicity

The presence of soluble HM can be a short-term harmful potential indicator. However, HM total concentration is needed to ensure crops, environment and human safety since they can become bioavailable over time. Although there is no Cd, Cr, Ni or Pb concentration in the elemental composition of pruning residues (above equipment detection limit) (Table 1), this paper checks whether its Cu and Zn content fulfill legal requirements, as well as whether Cu, Zn, Cd, Cr, Ni and Pb concentrations in SC and CP, can entail a certain risk.

Regulations taken as reference include Council Directive 86/278/EEC [45] related to environmental protection, and in particular soil protection, when sewage sludge is used in agriculture. It was transposed into Spanish law by the Real Decreto 1310/1990 [46]. For the rest of the analyzed residues, we investigated the Spanish Real Decreto 865/2010 [47] regarding crop substrates. Regulation EU 2019/1009 [48] lays down rules on fertilizing and amending products, establishing HM content that cannot be exceeded depending on type and use (Table 4).

Table 4. Threshold value (mg kg^{-1} dry matter) for metals in substrates, amendments and fertilizers used in agriculture.

Substance	C.D. 86/278/EEC [45] and R.D. 1310/1990 [46]		R.D 865/2010 [47]	EU 2019/1009 [48]
	Soil pH < 7	Soil pH > 7		
Cu	1000	1750	70	200 (GM)/300 (OF, L, SI)/600 (OMF) *
Zn	2500	4000	200	500 (GM)/800 (OF, L, SI)/1500 (OMF) *
Cd	20	40	0.7	1.5 (GM, OF)/2 (L, SI)/3-60 ¹ (OMF) *
Cr	1000	1500	70	2
Ni	300	400	25	50 (GM, OF, SI, OMF)/90 (L) *
Pb	750	1200	45	120

* GM: growing medium. OF: organic fertilizer. L: liming material. SI: organic and inorganic soil improver. OMF: organo-mineral fertilizer. ¹ Related to phosphorus content.

Comparing data of elemental composition HM total content (Table 1) with respect to the threshold value (Table 4), SC complies with Council Directive 86/278/EEC [45] and with Real Decreto 1310/1990 [46]. In the same way, pruning residues AP, HS, OP, PG, PN, PP and VP met permissible limits according to Real Decreto 865/2010 [47] and EU 2019/1009 [48]. On the contrary, Cr elemental composition concentration (Table 1) in CP (2.8 mg kg^{-1}) exceeds EU 2019/1009 [48] threshold. Furthermore, Cd elemental composition in CP (0.629 mg kg^{-1}) is close to the maximum extent (0.7 mg kg^{-1}) permitted by applicable law Real Decreto 865/2010 [47]. Cd is a metal with high toxicity, mobility and bioavailability, so the interest is focused on soil and plant health. These characteristics are self-evident in the most restrictive threshold value in current law compared with the other HM (Table 4).

None of the water-extractable HM content (Table 2) supposes a non-compliance of the threshold value for metals in substrates, amendments and fertilizers used in agriculture (Table 4).

Another key aspect to consider is prior HM concentration in agricultural soils where pruning residues will be applied. Table 5 presents the HM concentration threshold in agricultural soils that cannot be exceeded to set organic residues. SC application is controlled by Council Directive 86/278/EEC [45] and Real Decreto 1310/1990 [46]. In addition, Table 5 provides international HM concentration limits considered by the UN Environment Programme (UNEP) for agricultural land [31,49], chosen by the wide range of legal approaches in each European country.

Table 5. Threshold value (mg kg^{-1} dry matter) for metals in agricultural soil.

Substance	C.D. 86/278/EEC [45] and R.D. 1310/1990 [46]		UNEP [49]		
	Soil pH < 7	Soil pH > 7	Threshold Value ¹	Lower Guide Value ¹	Higher Guide Value ¹
Cu	50	140/210 *	100	150	200
Zn	150	300/450 *	200	250	400
Cd	1	3	1	10	20
Cr	100	150	100	200	300
Ni	30	75/112 *	50	100	150
Pb	50	300	60	200	750

* 140, 300 and 75 mg kg^{-1} are limits defined by C.D 86/278/EEC; 210, 450 and 112 mg kg^{-1} by R.D 1310/1990.

¹ "Threshold value is equally applicable for all sites, and it indicates the need for further assessment of the area. If guideline value is exceeded, the area has a contamination level that presents ecological or health risks. Different guideline values are set for industrial and transport areas (higher guideline value) and for all other land uses, such as agriculture areas (lower guideline value)".

If HM concentrations in the soil do not exceed the threshold in Table 5, it will depend on the quantity and frequency of each residue application. As a preliminary approach, SC is the only residue with HM concentration in its elemental composition (Table 1) that surpasses the Table 5 threshold value. Cu and Zn elemental composition concentrations in SC (79.7 and 249.5 mg kg^{-1} , respectively) rise above threshold data for acidic soils [45]. Acidification of soils increases the solubility of HM and their absorption by plants [36]. Furthermore, Zn elemental composition in SC (249.5 mg kg^{-1}) is higher than the threshold value stipulated by UNEP (200 mg kg^{-1}) [49]. To conclude, due to the HM concentration variability of SC (stated before) and Cu and Zn elemental composition concentration surpassing the Table 5 threshold, SC is the residue that can involve potential soil toxicity.

It is worth mentioning the difference between permissible limits established according to each regulation (Tables 4 and 5).

3.4. HM Contribution to Soil

This paper calculates HM contribution by applying $30,000 \text{ kg ha}^{-1}$ of each residue to soil (Table 6) from elemental composition and extractable content obtained in Tables 1 and 2. Table 6 illustrates that though high HM concentration can be available in the soil after SC

application, very low quantity is rapidly available in their soluble forms. Pruning residue contributes to most of the release of soluble metals (Cu and Zn).

Table 6. HM concentration added to soil by applying 30,000 kg ha⁻¹ of each residue (related to its elemental composition and aqueous extract content).

Residue	Elemental Composition (kg ha ⁻¹)						Aqueous Extract (kg ha ⁻¹)					
	Cu	Zn	Cd	Cr	Ni	Pb	Cu	Zn	Cd	Cr	Ni	Pb
AP	0.120	0.138	-	-	-	-	0.007	0.126	-	-	-	-
CP	0.336	0.159	0.019	0.085	-	-	0.003	0.129	-	-	-	-
HS	0.108	0.939	-	-	-	-	0.031	0.234	-	-	-	-
OP	0.147	0.372	-	-	-	-	0.034	0.168	-	-	-	-
PG	0.159	3.324	-	-	-	-	0.054	0.417	-	-	-	-
PN	0.210	0.342	-	-	-	-	0.013	0.141	-	-	-	-
PP	0.114	0.471	-	-	-	-	0.025	0.315	-	-	-	-
SC	2.391	7.485	0.021	0.793	0.186	0.323	0.016	0.120	-	-	-	0.011
VP	0.246	0.582	-	-	-	-	0.033	0.201	-	-	-	-

-: not calculated.

However, this paper estimates how many applications of 30,000 kg ha⁻¹ per year and residue in agricultural soil can be performed without surpassing the HM guideline value (Figures 1 and 2). Real Decreto 1310/1990 [46] is used as a reference, although this law has to do with SC application. Real Decreto 1310/1990 [46] HM threshold values are Cu: 12; Zn: 30; Cd: 0.15; Cr: 3; Ni: 3; Pb: 15 kg ha⁻¹ year.

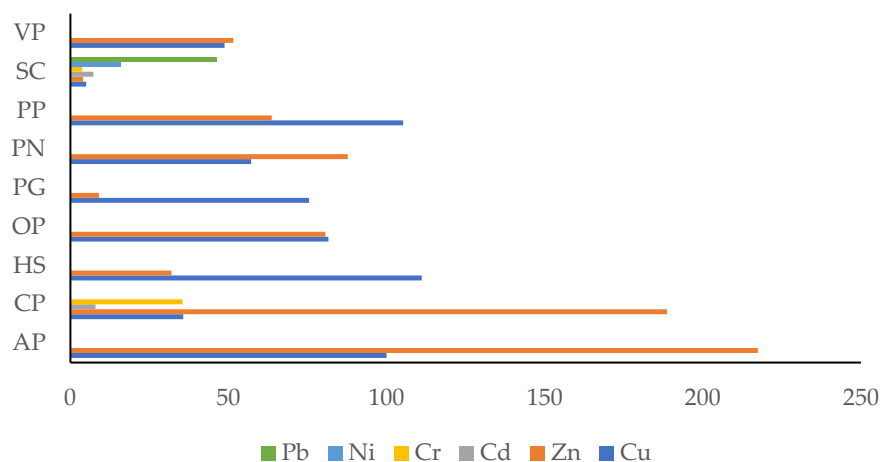


Figure 1. How many applications of 30,000 kg ha⁻¹ per year and residue are needed to exceed HM threshold stipulated by Real Decreto 1310/1990 [46], relying on elemental composition content.

As expected, HM elemental composition concentration is the limiting factor (Figure 1). SC is the residue that can exceed Zn and Cr thresholds with four applications, Cu threshold with five applications, Cd threshold with seven applications and Ni with 16 applications per year. CP showed non-compliance with the Cd threshold after eight applications per year. All pruning residues do not surpass Real Decreto 1310/1990 [46] HM permissible levels after monthly application over a one-year period. In fact, except for PG, where Zn can be exceeded after nine applications per year, the rest of the pruning residues needed between 32 and 217 applications per year to surpass HM critical levels. Related to soluble HM concentration (Figure 2), the HM threshold value (only for three elements) is exceeded by applying between 72 applications of PG and 4396 applications of CP.

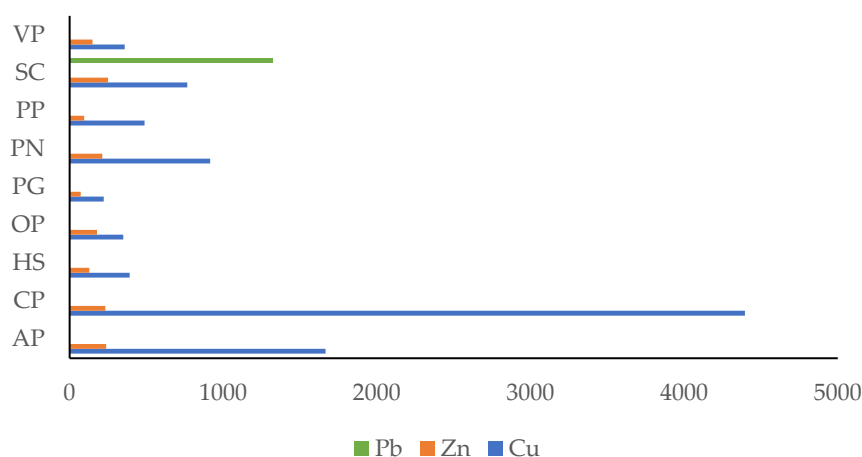


Figure 2. How many applications of 30,000 kg ha⁻¹ per year and residue are needed to exceed HM threshold stipulated by Real Decreto 1310/1990 [46], relying on aqueous extract content.

Several authors consider there to be a small risk of exceeding trace element toxicity limits by applying residues to soil [24,50,51], thus confirming these results. However, organic fertilizer from animal sources can entail a higher toxicity risk to soil and human health than organic fertilizer from plant residues [52–54]. The presence of HM in the elemental composition of pruning residues a priori does not involve a potential risk for soil or crops but depends on HM concentration, mobility, bioavailability and HM crop tolerance. Soil toxicity prevention is linked with food and water security (SDGs 2 and 6), pollution of marine (SDG 14) and terrestrial (SDG 15) environments due to land-based nutrients, as well as urban development (SDG 11) [55,56].

4. Conclusions

The application of pruning residues contributes to improving soil properties, ecosystem functioning, ecosystem services provision, food security and nutrition despite the fact that FAO urges the analysis of HM content in organic residues, which has been poorly studied, especially in relation to pruning residues.

Regarding the HM concentrations obtained, SC is the one with the highest content in the elemental composition. However, SC has very low HM solubility rates, so their availability must be tested in the long term. Although HM concentration in SC elemental composition met permissible limits for agricultural substrates, Cu and Zn content are above the HM concentration threshold in agricultural soils that cannot be exceeded to set organic residues. In addition, SC is the residue with more use constraints since an application of 30,000 kg ha⁻¹ can be made less than four times per year. CP has Cu, Zn, Cd and Cr in its elemental composition, which can be a matter of concern due to its use as a gardening substrate. Its I_{Cu} , I_{Cd} , I_{Cr} , I_{Ni} and I_{Pb} are very low or practically nonexistent; on the contrary, its I_{Zn} is 82%. Moreover, CP is the only residue among those studied that exceeds the threshold value for Cr in agricultural substrates.

None of the organic pruning or harvesting residues (AP, HS, OP, PG, PN, PP and VP) achieved Cd, Cr, Ni or Pb concentrations above the equipment detection limit. All pruning residues met HM threshold values; hence, their application to the soil does not involve any potential soil toxicity. Pruning residues can be an effective soil amendment and an invaluable source for short and long-term soil nutrition because of their high Cu and Zn solubility (between 6 and 34% and 13 and 90%, respectively) and because 30,000 kg ha⁻¹ can be applied to soil 31 to 216 times (except PG). These findings suggest that Cu and Zn are the most soluble elements among the studied metals. Due to the variability in residue origin, environmental conditions and adaptive mechanisms of each species, it would be useful to have a legal framework at the European level for the formulation and use of technosols that sets technical and safety criteria for crops.

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