

Critical Review

An Assessment of the Feasibility of Phytoextraction for the Stripping of Bioavailable Metals from Contaminated Soils

Javier Santa-Cruz,^a Brett Robinson,^b Yurii A. Krutyakov,^c Olga A. Shapoval,^d Patricia Peñaloza,^e Carolina Yáñez,^{f,*} and Alexander Neaman^{g,*}

^aEscuela de Ciencias Agrícolas y Veterinarias, Universidad Viña del Mar, Viña del Mar, Chile

^bSchool of Physical and Chemical Sciences, University of Canterbury, Christchurch, New Zealand

^cDepartment of Chemistry, Laboratory of Functional Materials for Agriculture, Lomonosov Moscow State University, Moscow, Russian Federation

^dPryanishnikov All-Russian Scientific Research Institute of Agrochemistry, Moscow, Russian Federation

^eEscuela de Agronomía, Pontificia Universidad Católica de Valparaíso, Quillota, Chile

^fInstituto de Biología, Pontificia Universidad Católica de Valparaíso, Valparaíso, Chile

^gDepartamento de Recursos Ambientales, Facultad de Ciencias Agronómicas, Universidad de Tarapacá, Arica, Chile

Abstract: Phytoextraction has been proposed in many papers as a low-cost method for remediating contaminated soil. However, if national regulation is based on total metal(loid) concentrations in soil, phytoextraction is generally infeasible because of the long time required for remediation. Assessing phytoextraction requires determination of the dynamic rate of metal removal from soil. Phytoextraction may be feasible if the main goal is to reduce the soluble fraction of the metal(loid) with the goal of reducing bioavailability. However, it has been reported that there is a large mass balance mismatch between the reduction of the soluble metal fraction in contaminated soil and metal uptake by plants. Several studies report that the decrease of soluble fraction of metals in soil is higher than can be accounted for by plant uptake. In other words, studies generally overestimate the feasibility of bioavailable contaminant stripping. Therefore, a more rigorous approach is advisable to ensure that papers on bioavailable contaminant stripping include relevant information on mass balances. Furthermore, to implement the concept of bioavailable contaminant stripping, regulations must distinguish between the bioavailable fraction and the total metal concentration in soil. *Environ Toxicol Chem* 2023;42:558–565. © 2022 SETAC

Keywords: Phytoextraction; metal; metalloid; remediation; phytoremediation; bioavailable contaminant stripping

PHYTOEXTRACTION: A LOW-COST METHOD FOR CLEANING UP CONTAMINATED SOILS?

Phytoextraction attempts to remove contaminants (e.g., metals; to simplify the discussion in the present study, the term *metals* also includes metalloids (e.g., arsenic and selenium); the term *heavy metal* is not recommended by the International Union of Pure and Applied Chemistry and will be avoided) from soil through uptake by roots and accumulation in harvestable plant parts. Many studies, starting with the work of Baker et al. (1994), have proposed phytoextraction as a low-cost method for cleaning up contaminated soils. However, phytoextraction is generally infeasible because of the excessive time required (Mertens et al., 2005; Neaman, Robinson, et al., 2020;

Robinson et al., 2015; Van Nevel et al., 2007). In the present study, the time frame required for soil cleanup will be referred to as the *duration of phytoextraction*.

The duration of phytoextraction is a function of the metal extraction rate, which is the biomass of the harvestable organs of the plant multiplied by the metal concentration in the biomass. The metal concentration in the biomass depends mostly on the following factors (Robinson et al., 2009): (1) root interaction with metals, (2) plant capacity for metal adsorption and accumulation in harvestable parts, and (3) bioavailability of soil metals. However, the rate of metal extraction is not constant because plant metal uptake decreases as the bioavailable fraction of metal in the soil decreases (Robinson et al., 2015). Furthermore, metal contaminants tend to accumulate to the depth of a few centimeters in the topsoil (e.g., 0–5 cm; Ulriksen et al., 2012) and thus do not interact with deeper plant roots unless the metals leach into deeper soil layers (Prudnikova et al., 2020).

Furthermore, plant species vary widely in their capacity to adsorb and accumulate metals in harvestable parts, with

* Address correspondence to carolina.yanez@pucv.cl or

alexander.neaman@gmail.com

Published online 30 December 2022 in Wiley Online Library

(wileyonlinelibrary.com).

DOI: 10.1002/etc.5554

hyperaccumulator species being particularly useful for these purposes (Ghazaryan et al., 2021). However, in most cases soils are contaminated by several metals, whereas hyperaccumulator species absorb high concentrations of a particular metal, with other metals remaining in the soil. For example, *Sauropus androgynus* (L.) Merr. proposed by Xia et al. (2013) efficiently absorbs zinc but not lead. Our calculations (Neaman, Robinson, et al., 2020), based on the results of that study (Xia et al., 2013), yielded a time horizon of no more than 25 years, or less than one human generation, to remediate contamination with zinc. However, the extraction of lead using the same species would take >1000 years.

Moreover, low metal solubility in soil, particularly in alkaline soils (Zhikharev et al., in press), can limit the plant metal accumulation in harvestable parts. The solubility of metals in the soil can be increased with chelating agents, that is, chemicals that form metal ion compounds in the soil solution (González et al., 2014). By increasing the solubility of metals in the soil, chelators may increase metal uptake by plants, thus reducing the duration of phytoextraction. However, any such chelator application inevitably causes groundwater contamination unless it is performed ex situ or in arid climates (Nowack et al., 2006). For this reason, the use of traditional chelators is not recommended for phytoextraction. Although biodegradable chelators, such as methylglycinodiacetic acid, can decrease metal leaching (González et al., 2014), they are expensive, and the time gain to complete a cleanup is unclear.

Practical phytoextraction research has recently come under the umbrella of phytomanagement, which includes nonfood crop production on contaminated soils to source biomass for various sectors of bioeconomy, such as bioenergy, timber, fiber, ecomaterials, green chemistry, and essential oils (Mench et al., 2018; Robinson et al., 2009). However, this has diminished the importance of metal phytoextraction for soil cleanup in favor of the pursuit of profit from contaminated land. For instance, Mench et al. (2018) discussed long-term phytoextraction as part of the phytomanagement and questioned its

time frames. Our calculations (Neaman, Robinson, et al., 2020), based on the results of that study (Mench et al., 2018), yielded a time horizon of approximately 9000 years, indicating that perhaps biomass production for monetary returns should not be associated with soil remediation at all.

BIOAVAILABLE CONTAMINANT STRIPPING

Metal bioavailability is a function of metal solubility and the properties of the receptor organism. Other things being equal, reducing the soluble fraction of the metal will reduce the bioavailable fraction (Lillo-Robles et al., 2020; Robinson et al., 2009). However, if in the process the solubility of a nontarget element is also reduced, then changes in the physiology of the receptor organism, for example, up-regulation of transporter genes, can actually increase bioavailability (Cao et al., 2019).

Bioavailable contaminant stripping refers to the removal of the soluble metal fractions from contaminated soil (Hamon & McLaughlin, 1999), rather than significantly reducing the total metal concentration. If stripping the bioavailable fraction is the primary goal, phytoextraction may be feasible because of the shorter time requirements. For example, Mench et al. (2018) found that the rate for stripping bioavailable copper was in the range of 2.6%–9% per annum. Thus, it would be possible to reduce the exchangeable (and potentially bioavailable) copper concentration in soil by half in 5–20 years. This time frame is clearly more feasible than the time frame required to reduce the total soil copper concentration by half (~9000 years).

The mechanism of bioavailable contaminant stripping becomes clear after considering the quantity, intensity, and capacity factors that govern soil metal availability to plants (Figure 1). The *quantity* factor refers to the total metal concentration in the soil, whereas the *intensity* factor refers to the metal concentration in the soil solution and metals bound to soil colloids, that is, the metal fraction immediately available to

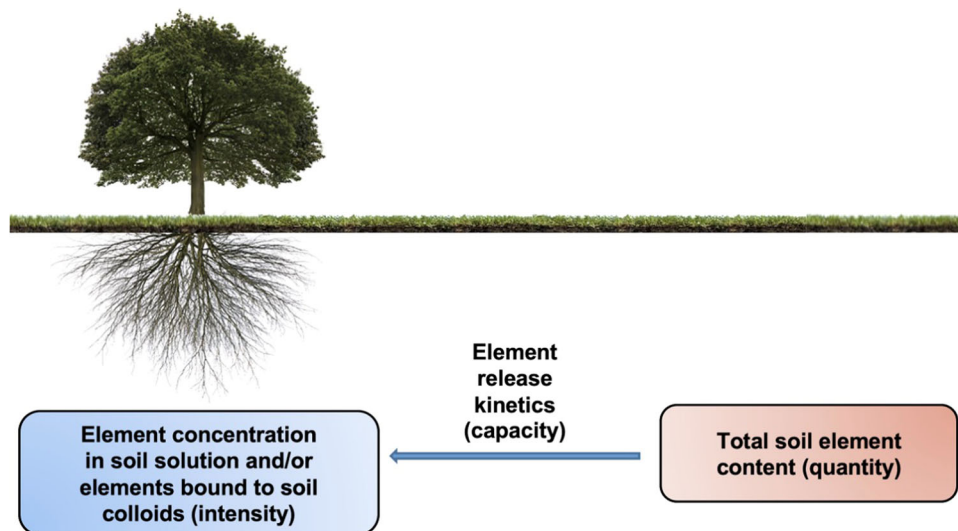


FIGURE 1: Intensity, quantity, and capacity factors of soil element bioavailability (adapted from Marschner, 1993).

the roots at a given point in time. In turn, the *capacity factor* is the release rate of the element, that is, the soil buffering capacity to supply metal ions from the solid phase to the soil solution. These factors govern nutrient phytoavailability in soils, as discussed in many previous studies (Marschner, 2012; Shirvani et al., 2005; Taiwo et al., 2010). The uptake of an element by plants depends not only on the concentration (intensity) of the element in the soil solution but also on the total amount (quantity) of the element in the soil and the dynamics (capacity) of element supply.

Some authors proposed that the same factors that govern nutrient phytoavailability in soils also apply to metal phytoavailability (Echevarria et al., 1998; Prudnikova et al., 2020; Song et al., 2004). For instance, in the study of Sauvé et al. (1996), the plant tissues accumulated an average of 2000 times the amount of copper dissolved in solution. This is only possible if the copper concentration in the soil solution is buffered by desorption/dissolution mechanisms (Sauvé, 2002). Thus, bioavailable contaminant stripping is only feasible when the elemental supply dynamics are slow enough to allow the reduction of the soluble metal fraction in the soil.

However, the capacity, that is, the rate of replenishment of the soluble element, may change over time because of changes in the soil's physicochemical properties, such as acidification, which may lead to a rapid increase in bioavailable metal. For instance, a single application of lime was sufficient for sustainable revegetation of industrially contaminated areas under the semiarid climatic conditions of central Chile, that is, not requiring

repeated lime applications (Neaman & Yáñez, 2021). However, studies conducted on the Kola Peninsula in the Russian Federation, that is, under conditions of high rainfall, have shown that a single application of lime is not sufficient for sustainable revegetation in industrially contaminated areas around copper–nickel smelters (Koptsik et al., 2016), requiring periodic applications of lime to maintain phytostabilization effects.

Table 1 summarizes some of the more promising bioavailable contaminant stripping greenhouse experiments and field trials that show successful stripping in repeated long-term experiments (three or more growth periods). However, it is unclear whether the soluble metal fraction in the contaminated soil was reduced by plant uptake. Some studies have reported huge mass balance discrepancies (up to 98%!) between the reduction of the soluble metal fraction in the soil and plant uptake (Table 2). Unfortunately, many studies do not perform mass balance calculations, and those that do (see Li, Wu, Luo, & Christie, 2014; Table 2) do not discuss the possible causes of such discrepancies (Table 3). Such causes may include contaminant volatilization (e.g., selenium), water surface runoff, leaching that causes the loss of soluble metal fraction (Table 3), and metal entrapment on plant surfaces (Cary et al., 1994; Yan et al., 2022). On the input side, metal influx from the atmosphere may increase metal concentration in soil. Mass balance discrepancies may be exacerbated by spatial variability in metal concentrations. Mass balances that include the total, rather than the soluble fraction, may prove to be more robust because heterogeneity in the bioavailable fraction that are caused by

TABLE 1: Promising bioavailable contaminant stripping greenhouse and field trials

Reference	TS	Metal	MB	Species	Metal pool	Method	Growth period							
							0	1st	3rd	7th				
Li, Wu, Hu, et al. (2014), Li et al. (2016)	Pot	Zn	x	<i>Sedum plumbizincicola</i>	Total (mg kg ⁻¹)	HCl-HNO ₃	476	NA	300 ^a	229				
					Extractable (μg kg ⁻¹)	1 M NH ₄ OAc	51,500 ^a	NA	8500 ^a	1030 ^a				
						0.01 M CaCl ₂	62,700	NA	12600	3990				
					Soluble (μg L ⁻¹)	0.05 EDTA	60,400	NA	15600	6590				
						Porewater	15,900	NA	450	160				
					Shoot (mg kg ⁻¹)	C _{DGT}	4950 ^a	NA	350 ^a	100 ^a				
						HNO ₃ -HClO ₄	—	11,600 ^a	5800 ^a	2900 ^a				
					Pot	Cd	x	<i>Sedum plumbizincicola</i>	Total (mg kg ⁻¹)	HCl-HNO ₃	8.7	NA	1.9 ^a	0.9
									Extractable (μg kg ⁻¹)	1 M NH ₄ OAc	5100 ^a	NA	730 ^a	120 ^a
									Soluble (μg L ⁻¹)	0.01 M CaCl ₂	2230	NA	338	88
										0.05 EDTA	2300	NA	258	86
	Lessl and Ma (2013)	Field ^a	As	x	<i>Pteris vittata</i>	Total (mg kg ⁻¹)	HNO ₃ -H ₂ O ₂	129	120 ^a	98 ^a	78			
						Extractable (μg kg ⁻¹)	0.05 M (NH ₄) ₂ SO ₄	3570	4200 ^a	2700 ^a	800 ^a			
						Shoot (mg kg ⁻¹)	HNO ₃ -H ₂ O ₂	—	3480	2627	1949			
								0	1st	3rd	4th			
Rees et al. (2020)	Field	Cd	√	<i>Noccaea caerulescens</i>	Total (mg kg ⁻¹)	HF-HClO ₄	17	10	8.8	8.8				
					Extractable (μg kg ⁻¹)	0.01 M CaCl ₂	311	95	64	51				
					Shoot (mg kg ⁻¹)	HNO ₃ -H ₂ O ₂	—	3057	852	435				

^aEstimate based on illustrations. Raised beds filled with contaminated soil.

Growth period 0: initial concentration.

DGT = diffusive gradients in thin films; MB = mass balance; NA = not available; TS = trial scale; x = studies not showing mass balance; √ = studies showing mass balance.

TABLE 2: Mass balance discrepancies after repeated long-term phytoextraction trials (three or more growth periods)

Reference	Metal	Species	MD	PU	D (%)
Greenhouse trials (mg pot ⁻¹)					
Bañuelos et al. (1997)	Se	<i>Brassica napus</i>	188	107	43
		<i>Festuca arundinacea</i>	84	7.0 ^a	92
Li, Wu, Luo, & Christie (2014)	Cd	<i>Sedum plumbizincicola</i>	0.5–5.6	0.6–4.8	–6.7 to 15
	Zn	<i>Sedum plumbizincicola</i>	743–917 ^a	661–480 ^a	11–48
Field trials (kg ha ⁻¹)					
Kertulis-Tartar (2005)	As	<i>Pteris vittata</i>	114	26	78
Niazi et al. (2012)	As	<i>Pityrogramma calomelanos</i>	1230	25	98
		<i>Pteris vittata</i>	404	9.7	98
Deng et al. (2016)	Cd	<i>Sedum plumbizincicola</i>	3.6–5.6	3.6–5.5	–0.6 to 2.0
		<i>Sedum plumbizincicola</i> intercropped with <i>Zea mays</i>	6.7	4.1	39
Zhou et al. (2018)	Cd	<i>Sedum plumbizincicola</i>	3.0	1.3	56
Rees et al. (2020)	Cd	<i>Noccaea caerulea</i>	27–24	23–19	15–21
Deng et al. (2016)	Zn	<i>Sedum plumbizincicola</i>	886–1135	290–198	67–83
		<i>Sedum plumbizincicola</i> intercropped with <i>Zea mays</i>	1238	208	83
Zhou et al. (2018)	Zn	<i>Sedum plumbizincicola</i>	55	10	81
Rees et al. (2020)	Zn	<i>Noccaea caerulea</i>	116–244	118–160	–1.7 to 34

^aEstimate based on illustrations.

A negative discrepancy means that plant uptake is greater than the decrease in soluble fraction of metals in soil. Conversely, a positive discrepancy means that plant uptake is less than the decrease in the soluble fraction of metals in soil.

D = discrepancy, understood as the percentage of decrease in soluble fraction of metals in soil that cannot be explained by plant uptake: $D = [(MD - PU) \times 100]/MD$; MD = decrease of soluble fraction of metals in soil; PU = plant uptake.

rhizosphere processes will be less important (Robinson et al., 2009).

ENVIRONMENTAL REGULATIONS

Bioavailable contaminant stripping is not recognized as a soil remediation technology in countries where only the total metal concentration in soil is used as a legal standard. Therefore, it is unlikely that this method will be used

unless the environmental regulations are amended to recognize bioavailability instead of the total metal concentration. Nevertheless, some recent guidelines have incorporated bioavailability concepts in ecological risk assessment (Organisation for Economic Co-operation and Development, 2017). Thus, accounting for metal bioavailability in soils can possibly allow acceptance of bioavailability contaminant stripping in environmental regulations.

Some national regulatory values for bioavailable metal fractions in soil are summarized in Table 4. Furthermore,

TABLE 3: Summary of possible causes of the discrepancies listed in Table 2

Reference	Metal	Species	Listed causes
Greenhouse trials			
Bañuelos et al. (1997)	Se	<i>Brassica napus</i>	Volatilization
		<i>Festuca arundinacea</i>	Volatilization
Li, Wu, Luo, & Christie (2014)	Cd	<i>Sedum plumbizincicola</i>	Not discussed
	Zn	<i>Sedum plumbizincicola</i>	Not discussed
Field trials			
Kertulis-Tartar (2005)	As	<i>Pteris vittata</i>	Spatial variability
Niazi et al. (2012)	As	<i>Pityrogramma calomelanos</i>	Spatial variability
		<i>Pteris vittata</i>	Spatial variability
Deng et al. (2016)	Cd	<i>Sedum plumbizincicola</i>	Spatial variability, surface runoff, leaching, atmospheric fallout
		<i>Sedum plumbizincicola</i> ^a	Spatial variability, surface runoff, leaching, atmospheric fallout
Zhou et al. (2018)	Cd	<i>Sedum plumbizincicola</i>	Surface runoff or leaching
Rees et al. (2020)	Cd	<i>Noccaea caerulea</i>	Leaching
Deng et al. (2016)	Zn	<i>Sedum plumbizincicola</i>	Spatial variability, surface runoff, leaching, atmospheric fallout
		<i>Sedum plumbizincicola</i> ^a	Spatial variability, surface runoff, leaching, atmospheric fallout
Zhou et al. (2018)	Zn	<i>Sedum plumbizincicola</i>	Surface runoff or leaching
Rees et al. (2020)	Zn	<i>Noccaea caerulea</i>	Leaching

^aIntercropped with *Zea mays*.

TABLE 4: Country-specific regulations on thresholds for bioavailable metal fractions in soil

Country	Method	Unit	Metal					
			As	Cd	Cu	Ni	Pb	Zn
Czech Republic ^a	1 M NH ₄ NO ₃ , SSR 1/2.5	mg kg ⁻¹	1.0	0.04/0.1ⁱ	1.0	1.0	1.5	20
Germany ^b	1 M NH ₄ NO ₃ , SSR 1/2.5	mg kg ⁻¹	0.4	0.04/0.1ⁱ	1.0	1.5	0.1	2.0
Slovakia ^c	1 M NH ₄ NO ₃ , SSR 1/2.5	mg kg ⁻¹	0.4	0.1	1.0	1.5	0.1	2.0
Switzerland ^d	0.1 M NaNO ₃ , SSR 1/2.5	mg L ⁻¹	n.s.	0.02/0.1	0.7/4.0	n.s.	n.s.	5.0
	Salt-exchangeable mean	mg kg ⁻¹	0.6 ± 0.3	0.1 ± 0.0	1.0 ± 0.0	1.3 ± 0.3	0.6 ± 0.8	8.0 ± 10
		mg L ⁻¹	n.s.	0.02	0.7	n.s.	n.s.	5.0
Mexico ^e	Water, SSR 1/20	mg L ⁻¹	0.5	0.1	n.s.	1.1	0.5	n.s.
Japan ^f	Water, SSR 1/10	mg L ⁻¹	0.01	0.01	n.s.	n.s.	0.01	n.s.
	Water-soluble mean	mg L ⁻¹	0.3 ± 0.3	0.1 ± 0.1	n.s.	1.1	0.3 ± 0.3	n.s.
Australia (Tasmania) ^g	0.1 M CH ₃ COOH, SSR 1/20	mg L ⁻¹	5.0	0.5	100	8.0	5.0	250
Australia (Victoria) ^h	0.1 M CH ₃ COOH, SSR 1/20	mg L ⁻¹	2.8	0.8	800	8.0	4.0	1200
	Acid-extractable mean	mg L ⁻¹	3.9 ± 1.6	0.7 ± 0.2	450 ± 495	8.0 ± 0.0	4.5 ± 0.7	725 ± 672

^aThresholds for agricultural soils (Ministry of the Environment of the Czech Republic, 2016).^bThresholds for agricultural soils (German Federal Government, 2020).^cThresholds for agricultural soils (National Council of the Slovak Republic, 2004).^dThresholds for agricultural and residential soils with >15% humus (Swiss Federal Council, 2016).^eThresholds for soils when there is no potentially exposed human population (Secretaría de Medio Ambiente y Recursos Naturales, 2007).^fThresholds for soils with potentially harmful effects on human health (Government of Japan, 2002).^gThresholds of soils for landfill disposal (Environment Protection Authority of Tasmania, 2010).^hThresholds of soils for landfill disposal (Environment Protection Authority of Victoria, 2009).ⁱOnly for soils with pH (CaCl₂) >6.5. A threshold of 0.04 mg kg⁻¹ must be applied to light-texture soils (up to 20% of <0.01-mm fine particles); otherwise, the threshold is 0.1 mg kg⁻¹.^jA threshold of 0.04 mg kg⁻¹ must be applied to lands used for the cultivation of bread wheat or strongly cadmium-accumulating vegetables (species not detailed); otherwise, the threshold is 0.1 mg kg⁻¹.

Nonbold values indicate trigger thresholds (a.k.a. prevention thresholds), understood as pollution limits at which site-specific risk assessments must be conducted. Bold values indicate intervention thresholds (a.k.a. action, cleanup, remediation, or indication thresholds), understood as values when a risk exists and it is considered necessary or advisable to address it. Mean values were calculated using the most conservative option within the range specified in the standard.

n.s. = not specified; SSR = soil/solution ratio.

bioavailable metal fractions are established in different ways in different countries based on salt-exchangeable, water-soluble, or acid-extractable fractions. Another challenge is that the unit of measurement is not standardized among countries (mg kg⁻¹ or mg L⁻¹), making direct comparisons impossible. Finally, there is no single extraction that mimics the bioavailable fraction for several metals and soil organisms. Therefore, developing a consistent international legal

framework based on extractable metals has a long way to go, if it is possible at all.

It should be noted that ecotoxicological studies of soil metal toxicity are usually based on metal-spiked soils, that is, uncontaminated soils that have been progressively enriched with metals in the form of soluble salts in a laboratory setting. This approach is complicated by the difficulty of extrapolating laboratory results to actual soils exposed to decades of

TABLE 5: Summary of effective concentrations for plants, invertebrates, and microorganisms (Lillo-Robles et al., 2020; Santa-Cruz, Peñaloza, et al., 2021)

		Plants			Invertebrates		Microorganisms
Metal	Unit	EC10	EC25	EC50	EC10	EC50	EC50
Salt-exchangeable							
Cu	mg kg ⁻¹	0.6	0.9	20 ± 26	—	—	—
	mg L ⁻¹	0.2	0.4	0.5 ± 0.1	—	—	—
Ni	mg kg ⁻¹	—	9.3 ± 6.3	—	—	—	—
Pb	mg kg ⁻¹	—	—	—	3.0 ± 3.7	35 ± 26	—
Zn	mg kg ⁻¹	—	—	236 ± 129	—	—	—
	mg L ⁻¹	—	—	2.4	—	—	6.0 ± 4.9
Water-soluble							
Cu	mg L ⁻¹	0.3	—	0.5 ± 0.2	—	—	—
Pb	mg kg ⁻¹	—	—	—	1.0 ± 1.3	3.2 ± 1.8	—
	mg L ⁻¹	—	—	—	34 ± 56	25 ± 37	—
Acid/chelate-extractable							
Cu	mg kg ⁻¹	—	—	930	—	—	139
Ni	mg kg ⁻¹	—	465	607	—	—	—
Zn	mg kg ⁻¹	—	—	3798	—	—	—

Only real soils exposed to long-term contamination are included, and metal-spiked soils are excluded because of their limited use in environmental assessment and soil quality decision-making. Likewise, only studies showing the impact of a single pollutant on biological responses were considered.

EC10/EC25/EC50, 10%, 25%, and 50% effect concentrations, respectively.

contamination. Specifically, the toxicity of metals is higher in metal-spiked versus anthropogenically contaminated soils (Neaman, Selles, et al., 2020; Santa-Cruz, Vasenev, et al., 2021). This is because metal toxicity depends on, among other factors, the residence time of the metals in the soil (McBride & Cai, 2016; Zeng et al., 2017).

In our summary in Table 5, only real soils exposed to long-term contamination are included, and metal-spiked soils are omitted. The source of a metal contamination might be a confounding factor determining metal toxicity. For example, Hamels et al. (2014) reported a high 50% effect concentration (EC50) value (36 000 mg kg⁻¹) for total zinc at La Calamine site (Belgium) contaminated with mine tailings containing smithsonite (ZnCO₃; Van Damme et al., 2010). In contrast, EC50 values for total zinc at sites polluted by zinc smelters were an order of magnitude lower (up to ~7000 mg kg⁻¹). This difference can be explained by the low solubility of ZnCO₃ (Grigorita et al., 2020). Therefore, the source of metal contamination profoundly affects metal toxicity, and this may prevent the direct comparison between thresholds based on extractable metal concentrations reported in Table 4 and the toxicity data reported in Table 5.

In Table 5, we grouped the reported values for salt-exchangeable, water-soluble, or acid-extractable fractions and expressions in either mg kg⁻¹ or mg L⁻¹. Soils with contrasting properties can result in differences in these values. Rooney et al. (2006) reported that soil properties profoundly affected the toxicity of metals in metal-spiked soils. However, soils with contrasting properties fit well on a dose–response curve in our studies on nonspiked soils that had been exposed to decades of contamination (Mondaca et al., 2017; Verdejo et al., 2016). Salt-exchangeable, water-soluble, and acid-extractable fractions reflect the differences in soil properties (McBride et al., 1997; Mondaca et al., 2015); thus, soil properties are not expected to be confounding factors in determining the metal toxicity thresholds summarized in Table 5.

Nevertheless, there are other confounding factors that do not allow direct comparison between thresholds based on extractable metal concentrations reported in Table 4 and the toxicity data reported in Table 5. For instance, according to the biotic ligand model, not only the concentration of the metals themselves but also the concentration of competing ions for binding at the biotic ligand affects the uptake and toxicity of metals (Smolders et al., 2009; Stuckey et al., 2021). Therefore, ecotoxicity thresholds based on a single extractable metal concentration do not indicate bioavailability in contrasting conditions.

For this reason, in some countries, national regulations on soil contamination have evolved toward assessing risk to biota and/or human health (Hou et al., 2017; Ministère de la transition écologique et solidaire, 2017; Reinikainen et al., 2016) and away from threshold values for total or partial concentrations of metals in soil. Hence, site-specific risk assessments, for example, using vegetables, may be feasible (Lizardi et al., 2020; Yang et al., 2022). However, setting threshold values may be necessarily conservative to protect against worst-case scenarios, for example, metal exposure to

humans via the ingestion of dust or soil, where the total concentration, rather than the phytoavailable fraction, is the greatest determiner of risk (Petrucelli et al., 2020).

CONCLUSIONS AND FUTURE RESEARCH NEEDS

Unlike phytoextraction for soil cleansing, phytoextraction with the aim of reducing the bioavailable fraction of metals in contaminated soil is at least feasible in principle. However, it is unclear whether the reduction of the soluble metal fraction in contaminated soil can be achieved through plant uptake because studies report large mass balance discrepancies (up to 98%) between the reduction of soluble metal fraction and plant uptake. Thus, we encourage a stricter approach to studies on bioavailable contaminant stripping that should include relevant information on mass balances. Similarly, broader experimental designs would be advisable to overcome the spatial variability of metal concentrations in soil. Furthermore, the use of advanced instruments (e.g., lysimeters) is essential to monitor metal leaching from soil (Rees et al., 2020) and/or atmospheric metal inputs.

Successful application of bioavailable contaminant stripping is impossible without environmental regulations that are based on the bioavailable fraction of soil metals rather than total metal concentration. Studies on phytoextraction would be more useful if they provided sufficient information on metal phytoextraction rates expressed, for instance, in grams of extracted metal per hectare per year. Metal phytoextraction rates, in turn, will allow estimation of the time necessary to achieve the target bioavailable concentrations of metals specified by environmental regulations.

Author Contributions Statement—**Javier Santa-Cruz**: Data curation; Formal analysis; Investigation. **Brett Robinson**: Writing—review & editing. **Yurii A. Krutyakov**, **Olga Shapoval**: Conceptualization; Validation. **Patricia Peñaloza**: Project administration; Resources. **Carolina Yáñez**: Conceptualization; Project administration; Writing—original draft. **Alexander Neaman**: Conceptualization; Methodology; Supervision; Writing—original draft; Writing—review & editing.

Data Availability Statement—This is a review article. No data were generated.

REFERENCES

- Baker, A. J. M., McGrath, S. P., Sidoli, C. M. D., & Reeves, R. D. (1994). The possibility of in situ heavy metal decontamination of polluted soils using crops of metal-accumulating plants. *Resources, Conservation and Recycling*, 11, 41–49.
- Bañuelos, G. S., Ajwa, H. A., Mackey, B., Wu, L., Cook, C., Akohoue, S., & Zambrozski, S. (1997). Evaluation of different plant species used for phytoremediation of high soil selenium. *Journal of Environmental Quality*, 26, 639–646. <https://doi.org/10.2134/jeq1997.00472425002600030008x>
- Cao, Y., Feng, H. Y., Sun, D., Xu, G. H., Rathinasabapathi, B., Chen, Y. S., & Ma, L. N. Q. (2019). Heterologous expression of *Pteris vittata* phosphate transporter PvPht1;3 enhances arsenic translocation to and

- accumulation in tobacco shoots. *Environmental Science & Technology*, 53, 10636–10644. <https://doi.org/10.1021/acs.est.9b02082>
- Cary, E. E., Grunes, D. L., Dallyn, S. L., Pearson, G. A., Peck, N. H., & Hulme, R. S. (1994). Plant Fe, Al and Cr concentrations in vegetables as influenced by soil inclusion. *Journal of Food Quality*, 17, 467–476. <https://doi.org/10.1111/j.1745-4557.1994.tb00167.x>
- Deng, L., Li, Z., Wang, J., Liu, H. Y., Li, N., Wu, L. H., Hu, P. J., Luo, Y. M., & Christie, P. (2016). Long-term field phytoextraction of zinc/cadmium contaminated soil by *Sedum plumbizincicola* under different agronomic strategies. *International Journal of Phytoremediation*, 18, 134–140. <https://doi.org/10.1080/15226514.2015.1058328>
- Echevarria, G., Morel, J. L., Fardeau, J. C., & Leclerc-Cessac, E. (1998). Assessment of phytoavailability of nickel in soils. *Journal of Environmental Quality*, 27, 1064–1070. <https://doi.org/10.2134/jeq1998.00472425002700050011x>
- Environment Protection Authority of Tasmania. (2010). *Environmental management and pollution control (waste management) regulations 2000. Classification and management of contaminated soil for disposal*.
- Environment Protection Authority of Victoria. (2009). *Industrial waste resource guidelines. Soil hazard categorization and management (IWRG621)*.
- German Federal Government. (2020). *Bundes-bodenschutz und altlastenverordnung (BBodSchV)*.
- Ghazaryan, K. A., Movsesyan, H. S., Minkina, T. M., Nevidomskaya, D. G., & Rajput, V. D. (2021). Phytoremediation of copper-contaminated soil by *Artemisia absinthium*: Comparative effect of chelating agents. *Environmental Geochemistry and Health*, 44, 1203–1215. <https://doi.org/10.1007/s10653-021-01151-2>
- González, I., Neaman, A., Cortés, A., & Rubio, P. (2014). Effect of compost and biodegradable chelate addition on phytoextraction of copper by *Oenothera pinnatifida* grown in Cu-contaminated acid soils. *Chemosphere*, 95, 111–115.
- Government of Japan. (2002). *Soil contamination countermeasures act (53/2002)*.
- Grigorita, G., Neaman, A., Brykova, R., Brykov, V. A., Morev, D. V., Ginocchio, R., Paltseva, A. A., Vidal, K., Navarro-Villarroel, C., & Dovletyarova, E. A. (2020). Use of zinc carbonate spiking to obtain phytotoxicity thresholds comparable to those in field-collected soils. *Environmental Toxicology and Chemistry*, 39, 1790–1796. <http://doi.org/10.1002/etc.4809>
- Hamels, F., Malevé, J., Sonnet, P., Kleja, D. B., & Smolders, E. (2014). Phytotoxicity of trace metals in spiked and field-contaminated soils: Linking soil-extractable metals with toxicity. *Environmental Toxicology and Chemistry*, 33, 2479–2487. <https://doi.org/10.1002/etc.2693>
- Hamon, R. E., & McLaughlin, M. J. (1999). Use of the hyperaccumulator *Thlaspi caerulescens* for bioavailable contaminant stripping. In W. W. Wenzel, D. C. Adriano, B. Alloway, H. Doner, C. Keller, N. W. Lepp, M. Mench, R. Naidu, & G. M. Pierzynski (Eds.), *5th International conference on the biogeochemistry of trace elements* (pp. 908–909). International Society for Trace Element Research.
- Hou, D. Y., Qi, S. Q., Zhao, B., Rigby, M., & O'Connor, D. (2017). Incorporating life cycle assessment with health risk assessment to select the “greenest” cleanup level for Pb contaminated soil. *Journal of Cleaner Production*, 162, 1157–1168. <https://doi.org/10.1016/j.jclepro.2017.06.135>
- Kertulis-Tartar, G. M. (2005). *Arsenic hyperaccumulation by L. and its potential for phytoremediation of arsenic-contaminated soils Pteris vittata* [Unpublished doctoral dissertation]. University of Florida.
- Koptsik, G. N., Koptsik, S. V., & Smirnova, I. E. (2016). Alternative technologies for remediation of technogenic barrens in the Kola Subarctic. *Eurasian Soil Science*, 49, 1294–1309. <https://doi.org/10.1134/s1064229316090088>
- Lessl, J. T., & Ma, L. Q. (2013). Sparingly-soluble phosphate rock induced significant plant growth and arsenic uptake by *Pteris vittata* from three contaminated soils. *Environmental Science & Technology*, 47, 5311–5318. <https://doi.org/10.1021/es400892a>
- Li, Z., Jia, M. Y., Wu, L. H., Christie, P., & Luo, Y. M. (2016). Changes in metal availability, desorption kinetics and speciation in contaminated soils during repeated phytoextraction with the Zn/Cd hyperaccumulator *Sedum plumbizincicola*. *Environmental Pollution*, 209, 123–131. <https://doi.org/10.1016/j.envpol.2015.11.015>
- Li, Z., Wu, L. H., Hu, P. J., Luo, Y. M., Zhang, H., & Christie, P. (2014). Repeated phytoextraction of four metal-contaminated soils using the cadmium/zinc hyperaccumulator *Sedum plumbizincicola*. *Environmental Pollution*, 189, 176–183. <https://doi.org/10.1016/j.envpol.2014.02.034>
- Li, Z., Wu, L. H., Luo, Y. M., & Christie, P. (2014). Dynamics of plant metal uptake and metal changes in whole soil and soil particle fractions during repeated phytoextraction. *Plant and Soil*, 374, 857–869. <https://doi.org/10.1007/s11104-013-1927-2>
- Lillo-Robles, F., Tapia-Gatica, J., Díaz-Sieffer, P., Moya, H., Celis-Diez, J. L., Santa Cruz, J., Ginocchio, R., Sauvé, S., Brykov, V. A., & Neaman, A. (2020). Which soil Cu pool governs phytotoxicity in field-collected soils contaminated by copper smelting activities in central Chile. *Chemosphere*, 242, Article 125176. <https://doi.org/10.1016/j.chemosphere.2019.125176>
- Lizardi, N., Aguilar, M., Bravo, M., Fedorova, T. A., & Neaman, A. (2020). Human health risk assessment from the consumption of vegetables grown near a copper smelter in central Chile. *Journal of Soil Science and Plant Nutrition*, 20, 1472–1479. <https://doi.org/10.1007/s42729-020-00226-w>
- Marschner, H. (1993). Zinc uptake from soils. In A. D. Robson (Ed.), *Zinc in soils and plants* (pp. 59–77). Kluwer Academic.
- Marschner, P. (2012). *Marschner's mineral nutrition of higher plants* (3rd ed.). Academic.
- McBride, M. B., & Cai, M. F. (2016). Copper and zinc aging in soils for a decade: Changes in metal extractability and phytotoxicity. *Environmental Chemistry*, 13, 160–167. <https://doi.org/10.1071/en15057>
- McBride, M., Sauvé, S., & Hendershot, W. (1997). Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *European Journal of Soil Science*, 48, 337–346. <https://doi.org/10.1111/j.1365-2389.1997.tb00554.x>
- Mench, M. J., Dellise, M., Bes, C. M., Marchand, L., Kolbas, A., Coustumer, P. L., & Oustrière, N. (2018). Phytomanagement and remediation of Cu-contaminated soils by high yielding crops at a former wood preservation site: Sunflower biomass and ionome. *Frontiers in Ecology and Evolution*, 6, Article 123.
- Mertens, J., Luyssaert, S., & Verheyen, K. (2005). Use and abuse of trace metal concentrations in plant tissue for biomonitoring and phytoextraction. *Environmental Pollution*, 138, 1–4. <https://doi.org/10.1016/j.envpol.2005.01.002>
- Ministère de la transition écologique et solidaire. (2017). *French national methodology for managing contaminated land*. http://circulaire.legifrance.gouv.fr/pdf/2017/04/cir_42093.pdf
- Ministry of the Environment of the Czech Republic. (2016). *Vyhláška o stanovění podrobností ochrany kvality zemědělské půdy a o změně vyhlášky č. 13/1994 Sb., kterou se upravují některé podrobnosti ochrany zemědělského půdního fondu* (Vyhláška č. 153/2016 Sb).
- Mondaca, P., Catrin, J., Verdejo, J., Sauvé, S., & Neaman, A. (2017). Advances on the determination of thresholds of Cu phytotoxicity in field-contaminated soils in central Chile. *Environmental Pollution*, 223, 146–152. <https://doi.org/10.1016/j.envpol.2016.12.076>
- Mondaca, P., Neaman, A., Sauvé, S., Salgado, E., & Bravo, M. (2015). Solubility, partitioning and activity of copper in contaminated soils in a semiarid zone. *Journal of Plant Nutrition and Soil Science*, 178, 452–459. <https://doi.org/10.1002/jpln.201400349>
- National Council of the Slovak Republic. (2004). *Zákon o ochrane a využívaní poľnohospodárskej pôdy a o zmene zákona č. 245/2003 Z. z. o integrovanej prevencii a kontrole znečisťovania životného prostredia a o zmene a doplnení niektorých zákonov* (Zbierka zákonov č. 220/2004).
- Neaman, A., Robinson, B., Minkina, T. M., Vidal, K., Mench, M., Krutyakov, Y. A., & Shapoval, O. V. (2020). Feasibility of metal(loid) phytoextraction from polluted soils: The need for greater scrutiny. *Environmental Toxicology and Chemistry*, 39, 1469–1471. <https://doi.org/10.1002/etc.4787>
- Neaman, A., Selles, I., Martínez, C. E., & Dovletyarova, E. A. (2020). Analyzing soil metal toxicity: Spiked or field-contaminated soils? *Environmental Toxicology and Chemistry*, 39, 513–514. <https://doi.org/10.1002/etc.4654>
- Neaman, A., & Yáñez, C. (2021). Phytoremediation of soils contaminated by copper smelting in Chile: Results of a decade of research. *Eurasian Soil Science*, 54, 1992–1999. <https://doi.org/10.1134/S1064229321120085>
- Niazi, N. K., Singh, B., Van Zwieten, L., & Kachenko, A. G. (2012). Phytoremediation of an arsenic-contaminated site using *Pteris vittata* L. and *Pityrogramma calomelanos* var. *austroamericana*: A long-term study. *Environmental Science and Pollution Research*, 19, 3506–3515. <https://doi.org/10.1007/s11356-012-0910-4>
- Nowack, B., Schulin, R., & Robinson, B. H. (2006). Critical assessment of chelant-enhanced metal phytoextraction. *Environmental Science & Technology*, 40, 5225–5232. <https://doi.org/10.1021/es0604919>

- Organisation for Economic Co-operation and Development. (2017). *Guidance on the incorporation of bioavailability concepts for assessing the chemical ecological risk and/or environmental threshold values of metals and inorganic metal compounds*.
- Petruzzelli, G., Pedron, F., & Rosellini, I. (2020). Bioavailability and bioaccessibility in soil: A short review and a case study. *AIMS Environmental Science*, 7, 208–225. <https://doi.org/10.3934/envirosci.2020013>
- Prudnikova, E. V., Neaman, A., Terekhova, V. A., Karpukhin, M. M., Vorobeichik, E. L., Smorkalov, I. A., Dovletyarova, E. A., Navarro-Villarreal, C., Ginocchio, R., & Peñaloza, P. (2020). Root elongation method for the quality assessment of metal-polluted soils: Whole soil or soil-water extract? *Journal of Soil Science and Plant Nutrition*, 20, 2294–2303. <https://doi.org/10.1007/s42729-020-00295-x>
- Rees, F., Sterckeman, T., & Morel, J. L. (2020). Biochar-assisted phytoextraction of Cd and Zn by *Nocca caerulea* on a contaminated soil: A four-year lysimeter study. *Science of the Total Environment*, 707, Article 135654. <https://doi.org/10.1016/j.scitotenv.2019.135654>
- Reinikainen, J., Sorvari, J., & Tikkanen, S. (2016). Finnish policy approach and measures for the promotion of sustainability in contaminated land management. *Journal of Environmental Management*, 184, 108–119. <https://doi.org/10.1016/j.jenvman.2016.08.046>
- Robinson, B. H., Anderson, C. W. N., & Dickinson, N. M. (2015). Phytoextraction: Where's the action? *Journal of Geochemical Exploration*, 151, 34–40. <https://doi.org/10.1016/j.gexplo.2015.01.001>
- Robinson, B. H., Bañuelos, G., Conesa, H. M., Evangelou, M. W., & Schulin, R. (2009). The phytomanagement of trace elements in soil. *Critical Reviews in Plant Sciences*, 28, 240–266.
- Rooney, C. P., Zhao, F. J., & McGrath, S. P. (2006). Soil factors controlling the expression of copper toxicity to plants in a wide range of European soils. *Environmental Toxicology and Chemistry*, 25, 726–732. <https://doi.org/10.1897/04-602r.1>
- Santa-Cruz, J., Peñaloza, P., Korneykova, M. V., & Neaman, A. (2021). Thresholds of metal and metalloid toxicity in field-collected anthropogenically contaminated soils: A review. *Geography, Environment, Sustainability*, 14, 6–21. <https://doi.org/10.24057/2071-9388-2021-023>
- Santa-Cruz, J., Vasenev, I. I., Gaete, H., Peñaloza, P., Krutyakov, Y. A., & Neaman, A. (2021). Metal ecotoxicity studies with spiked versus field-contaminated soils: Literature review, methodological shortcomings and research priorities. *Russian Journal of Ecology*, 52, 479–485. <https://doi.org/10.1134/S1067413621060126>
- Sauvé, S. (2002). Speciation of metals in soils. In H. E. Allen (Ed.), *Bioavailability of metals in terrestrial ecosystems: Importance of partitioning for bioavailability to invertebrates, microbes, and plants* (pp. 7–37). Society of Environmental Toxicology and Chemistry.
- Sauvé, S., Cook, N., Hendershot, W. H., & McBride, M. B. (1996). Linking plant tissue concentrations and soil copper pools in urban contaminated soils. *Environmental Pollution*, 94, 153–157. [https://doi.org/10.1016/S0269-7491\(96\)00081-4](https://doi.org/10.1016/S0269-7491(96)00081-4)
- Secretaría de Medio Ambiente y Recursos Naturales. (2007, March 2). Norma Oficial Mexicana NOM-147-SEMARNAT/SSA1-2004 que establece criterios para determinar las concentraciones de remediación de suelos contaminados por arsénico, bario, berilio, cadmio, cromo hexavalente, mercurio, níquel, plata, plomo, selenio, talio y/o vanadio. *Diario Oficial*.
- Shirvani, M., Shariatmadari, H., & Kalbasi, M. (2005). Phosphorus buffering capacity indices as related to soil properties and plant uptake. *Journal of Plant Nutrition*, 28, 537–550. <https://doi.org/10.1081/pln-200049235>
- Smolders, E., Oorts, K., van Sprang, P., Schoeters, I., Janssen, C. R., McGrath, S. P., & McLaughlin, M. J. (2009). Toxicity of trace metals in soil as affected by soil type and aging after contamination: Using calibrated bioavailability models to set ecological soil standards. *Environmental Toxicology and Chemistry*, 28, 1633–1642. <https://doi.org/10.1897/08-592.1>
- Song, J., Zhao, F.-J., Luo, Y.-M., McGrath, S. P., & Zhang, H. (2004). Copper uptake by *Elsholtzia splendens* and *Silene vulgaris* and assessment of copper phytoavailability in contaminated soils. *Environmental Pollution*, 128, 307–315. <https://doi.org/10.1016/j.envpol.2003.09.019>
- Stuckey, J. W., Neaman, A., Verdejo, J., Navarro-Villarreal, C., Peñaloza, P., & Dovletyarova, E. A. (2021). Zinc alleviates copper toxicity to lettuce and oat in copper contaminated soils. *Journal of Soil Science and Plant Nutrition*, 21, 1229–1235. <https://doi.org/10.1007/s42729-021-00435-x>
- Swiss Federal Council. (2016). *Verordnung über belastungen des bodens* (SR 814.12).
- Taiwo, A. A., Adetunji, M. T., Azeez, J. O., & Bamgbose, T. (2010). Potassium supplying capacity of some tropical Alfisols in southwest Nigeria as measured by intensity, quantity and capacity factors. *Nutrient Cycling in Agroecosystems*, 86, 341–355. <https://doi.org/10.1007/s10705-009-9296-1>
- Ulriksen, C., Ginocchio, R., Mench, M., & Neaman, A. (2012). Lime and compost promote plant re-colonization of metal-polluted, acidic soils. *International Journal of Phytoremediation*, 14, 820–833.
- Van Damme, A., Degryse, F., Smolders, E., Sarret, G., Dewit, J., Swennen, R., & Manceau, A. (2010). Zinc speciation in mining and smelter contaminated overbank sediments by EXAFS spectroscopy. *Geochimica et Cosmochimica Acta*, 74, 3707–3720. <https://doi.org/10.1016/j.gca.2010.03.032>
- Van Nevel, L., Mertens, J., Oorts, K., & Verheyen, K. (2007). Phytoextraction of metals from soils: How far from practice? *Environmental Pollution*, 150, 34–40. <https://doi.org/10.1016/j.envpol.2007.05.024>
- Verdejo, J., Ginocchio, R., Sauvé, S., Mondaca, P., & Neaman, A. (2016). Thresholds of copper toxicity to lettuce in field-collected agricultural soils exposed to copper mining activities in Chile. *Journal of Soil Science and Plant Nutrition*, 16, 154–158. <https://doi.org/10.4067/S0718-95162016005000011>
- Xia, B. C., Shen, S. L., & Xue, F. (2013). Phytoextraction of heavy metals from highly contaminated soils using *Suaeda androgynus*. *Soil & Sediment Contamination*, 22, 631–640. <https://doi.org/10.1080/15320383.2013.756452>
- Yan, X. X., An, J., Yin, Y. C., Gao, C. C., Wang, B. Y., & Wei, S. H. (2022). Heavy metals uptake and translocation of typical wetland plants and their ecological effects on the coastal soil of a contaminated bay in northeast China. *Science of the Total Environment*, 803, Article 149871. <https://doi.org/10.1016/j.scitotenv.2021.149871>
- Yang, Y., Li, Y. L., Wang, T. Q., Chen, W. P., Wang, M. E., & Dai, Y. T. (2022). Derivation of human health risk-based thresholds for lead in soils promote the production of safer wheat and rice. *Ecotoxicology and Environmental Safety*, 230, Article 113131. <https://doi.org/10.1016/j.ecoenv.2021.113131>
- Zeng, S. Q., Li, J. M., Wei, D. P., & Ma, Y. B. (2017). A new model integrating short- and long-term aging of copper added to soils. *PLOS ONE*, 12, Article e0182944. <https://doi.org/10.1371/journal.pone.0182944>
- Zhikharev, A. P., Sahakyan, L., Tepanosyan, G., Vidal, K., & Alexander Neaman, A. (in press). *Metal phytotoxicity thresholds in copper smelter-contaminated soils*. Idesia.
- Zhou, T., Zhu, D., Wu, L. H., Xing, W. Q., Luo, Y. M., & Christie, P. (2018). Repeated phytoextraction of metal contaminated calcareous soil by hyperaccumulator *Sedum plumbizincicola*. *International Journal of Phytoremediation*, 20, 1243–1249. <https://doi.org/10.1080/15226514.2016.1156641>