Europ. J. Agronomy 53 (2014) 56–66

Contents lists available at ScienceDirect

European Journal of Agronomy

journal homepage: www.elsevier.com/locate/eja

Long-term phytomanagement of metal-contaminated land with field crops: Integrated remediation and biofortification

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ARTICLE INFO

Article history:
Received 21 October 2013
Received in revised form
19 November 2013
Accepted 20 November 2013

Keywords:
Agronomic practice
Biofortification
Crop species
Metal contamination
Phytoremediation
Soil root colonisation

ABSTRACT

Several studies on the phytomanagement of mixed-metal-contaminated land were carried out over a period of 10 years in an agricultural soil at Carpiano (Milan, Italy) and in pyrite waste at Torviscosa (Udine, Italy), in order to investigate the practicability of using various field crops for this purpose. Here we demonstrate that seed germination and initial growth are never critical steps under high levels of Cd or Cr, whereas poor plant productivity limits metal removal rates from contaminated waste. Phytoextraction alone was rarely an efficient remediation technology and, if the process was not chemically assisted, only Zn and Mn were accumulated above-ground in considerable amounts. A maximum of 8 kg ha^{-1} of metals with rapeseed and only 0.33 kg ha^{-1} with fodder radish were removed from soil. Cultivation of metal-contaminated land did provide some limited opportunity for natural biofortification of crops with Zn and Cu, with no apparent risk of toxic metals in the seeds of only a few crops. Improvements in tissue metal rates achieved with auxins, humic acids or chelators were largely detrimental to biomass yield. We conclude that the efficient use of crop species in phytoremediation requires the achievement of high productivity by appropriate agricultural management involving tillage, fertilisation and perhaps also capping or dilution with clean soil. The considerable metal stock in roots suggests exploring the effectiveness of long-term stabilisation, particularly in non-tillage systems.

1. Introduction

Trace elements usually occur at low concentrations in both soils and living organisms, but they play an important biological role as essential micro-nutrients and environmental contaminants. The presence of heavy metals in soils has been rapidly increasing worldwide in the last few years, mainly due to human activities. In the EU, the number of contaminated sites is currently estimated at approximately 250,000, and is predicted to increase by 50% within the next 20 years (European Environment Agency, 2011). The most common contamination sources are industry and trade, as well as waste treatment and disposal. According to national reports from the EU, heavy metals are the most frequent contaminants (∼37% of cases), and similar statistics may be retrieved worldwide.

Within this framework, there is interest in studying the response of food crops to metal pollution, in order to ascertain whether they can be cultivated safely, or whether they may become a suitable mild decontamination tool. Phytomanagement of metal-contaminated land describes the manipulation of soil–plant systems in order to affect metal fluxes in the environment, with the goals of remediating contaminated soils (Ernst, 2005; Lasat, 2002), recovering valuable elements and metal-based nanoparticles (Barbaroux et al., 2012; Rico et al., 2011), and increasing micro-nutrient concentrations in food (White and Broadley, 2009). Successful phytomanagement would require cheap remediation or fortification technologies and the production of high-value plant biomass products, including food and feed, bioenergy and timber production. Phytoextraction of trace elements through the above-ground biomass of higher plants started to be reported in the literature around the 1990s (e.g., Raskin et al., 1994), after the discovery of hyperaccumulator plants. Currently, much attention is focused on biomass species, including field crops, and there is a need to study their specific behaviour in order to define proper agronomic management for suitable cultivation in mixed-metal-contaminated sites. *Brassicaceae*, *Poaceae*, *Fabaceae* and *Asteraceae* species have been tested for their suitability for phytoremediation over the last 10 years, and *Brassica juncea* L. Czern. (Indian mustard), *Helianthus annuus* L. (sunflower), *Brassica napus* L. var. *oleifera* D.C. (rapeseed) and *Zea mays* L. (maize) are the most frequently cited in the literature (Vamerali et al., 2010). However, great

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http://dx.doi.org/10.1016/j.eja.2013.11.008

Table 1
EU limits (when available) for plant foods and common metal concentrations in unpolluted soils (total) and crop species. Y/N: essential/non-essential metal for plants, respectively. *Note*: legal limits based on fresh weight.

	Essential	Concentration limits in food[a] (mg kg^{-1} FW)	Unpolluted soils		Crops
			Most frequent concentration[b] (mg kg^{-1} DW)	Concentration range[b] (mg kg^{-1} DW)	Concentration range[b] (mg kg^{-1} DW)
As	N	–	6	0.1–40	0.1–5
Cd	N	0.050[c]–0.20[d]	0.06	0.01–0.7	0.2–0.8
Cr	N	–	100	5–3000	0.2–1
Pb	N	0.10[e]–0.20[f]–0.30[g]	10	2–200	0.1–20
Cu	Y	–	20	2–100	4–15
Ni	Y	–	40	10–1000	1
Zn	Y	–	50	10–300	15–200

[a] Commission Regulation (EC) No. 1881/2006 of 19 December 2006, setting maximum levels for certain contaminants in foodstuffs.
[b] Aspetti et al. (2002).
[c] Vegetables and fruit (excluding leaf vegetables, fresh herbs, fungi, stem vegetables, pine nuts, root vegetables and potatoes).
[d] Bran, germ, wheat and rice, soybean, leaf vegetables, fresh herbs, cultivated fungi and celeriac.
[e] Vegetables (excluding *Brassica* vegetables, leaf vegetables, fresh herbs and fungi; for potatoes, maximum level applies to peeled potatoes) and fruit (excluding berries and small fruit).
[f] Cereals and legumes.
[g] *Brassica* vegetables, leaf vegetables and cultivated fungi.

concern is caused by increasing concentrations of metals entering the food chain, especially non-essential ones. In uncontaminated soils, crops may accumulate toxic elements at concentrations ranging between 0.1 (As, Pb) and 20 (Pb) mg kg^{-1} DW, whereas higher values are found for essential minerals, e.g., up to 200 mg kg^{-1} DW for Zn (Table 1) (Aspetti et al., 2002).

Within this framework, several aspects of contaminated land and phytomanagement have been studied, as regards: (i) plant responses to metal pollution (i.e., germination, shoot and root growth), (ii) efficiency of enhancing phytoextraction/biofortification tools (e.g., tillage, fertilisation, humic acids, auxins and chelators), and (iii) possible related environmental risks. We aimed at understanding how the land can be safely and productively used for agricultural crops and whether phytotechnologies can offer suitable solutions to contamination problems. A summary of results is presented, with particular reference to agronomic management in two real-life contaminated sites in Italy.

2. Materials and methods

Over a 10-year period of research of metal-contaminated land, starting from 1998, various crop species have been subjected to a wide range of experiments. A list of trials is presented in Table 2.

2.1. Germination tests and hydroponic cultivation under Cd and Cr

In preliminary trials carried out during 1998–1999, the effects of Cd and Cr on seed germination were evaluated in six *Brassicaceae* species in growth chambers, seeds being placed in a 10%-diluted

Table 2
List of trials.

Year	Site	Contaminants	Focus/treatments	Plant species
1998–1999	Laboratory (Petri dishes)	Cd, Cr	Germination Inter- and intraspecific variability	6 *Brassicaceae* (26 accessions)
2000–2001	Laboratory (hydroponics)	Cd, Cr	Early growth Inter- and intraspecific variability	6 *Brassicaceae*
2002	Carpiano (pots)	Cd	Species comparisons	17 crops
2002	Carpiano (pots)	Cd, Cr, Cu, Pb, Zn	Soil capping Species comparisons	4 *Brassicaceae*
2003	Carpiano (pots)	Cd, Cr, Cu, Pb, Zn	Soil capping Intraspecific variability	Fodder radish (6 varieties)
2003	Carpiano (field)	Cd, Cr, Cu, Pb, Zn	Species comparisons	5 crops
2005	Torviscosa (field)	As, Cd, Cr, Cu, Pb, Zn	Soil managements Species comparisons	4 crops
2006	Torviscosa (pots)	As, Cd, Co, Cu, Pb, Zn	Humic acids (doses and application methods)	Fodder radish
2007	Torviscosa (pots)	As, Cd, Co, Cu, Pb, Zn	IBA (doses and application methods)	Fodder radish
2008	Torviscosa (pots)	As, Cd, Co, Cu, Pb, Zn	EDDS (doses and application times)	Fodder radish Ethiopian mustard