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Review

Heavy metals and metalloids: Sources, risks and strategies to reduce their accumulation in horticultural crops

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ABSTRACT

Food production in areas contaminated with heavy metals is associated with health risks because of their adverse effects on food safety and marketability, and on crop growth and yield quality. The present review focuses on sources and risks of heavy metals, mainly in cultivated fields in various regions, and strategies to reduce their accumulation in horticultural crops. The following heavy metals are discussed: arsenic (As), boron (B), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), mercury (Hg), molybdenum (Mo), nickel (Ni), strontium (Sr), tin (Sn), titanium (Ti), vanadium (V) and zinc (Zn). Heavy metal sources in the environment can originate from natural and anthropogenic activities. Their main natural enrichment in soils stems from parent-material weathering. However, in coastal areas, precipitation of sea spray may enrich soil with B. In contrast, the main anthropogenic sources of heavy metals in cultivated areas are irrigation with treated sewage water, application of residual biosolids, and atmospheric pollution. Plants absorb heavy metals predominantly through roots and, to a lesser extent, through leaves. Leaf uptake can occur through the stomata, cuticular cracks, ectodesmata, and aqueous pores. Heavy metal uptake may lead to their accumulation in vegetables and fruit trees, and their consequent introduction into the food chain, which is recognized as one of the major pathways for human exposure to them. This exposure can result in retardation, several types of cancer, kidney damage, endocrine disruption, and immunological and neurological effects. High concentrations of heavy metals can also affect the growth and yield of many crops: Zn and Cd decrease plant metabolic activity and induce oxidative damage; Cu generates oxidative stress and reactive oxygen species; Hg can induce visible injury and physiological disorders; Cr affects photosynthesis in terms of CO_2 fixation, electron transport, photophosphorylation and enzyme activities; Pb induces plant abnormal morphology; Ni spoils the nutrient balance, resulting in disorders of cell membrane functions; Fe causes free radical production that irreversibly impairs cell structure and damages membranes, DNA and proteins; As causes leaf necrosis and wilting, followed by root discoloration and retardation of shoot growth. Therefore, international organizations, such as the US EPA and EU bodies, are working on regulating the maximum allowable levels of food pollutants. A number of direct (mycorrhiza, transgenic plants and grafting) approaches can be deployed to overcome problems of heavy metal contamination in horticulture.

1. Introduction

"Heavy metals" is a general collective term that applies to the group of metals and metalloids with atomic density greater than $4\,g\,cm^{-3}$ (Hawkes,1997). Most are toxic to humans, even at low concentrations (Lenntech Water Treatment and Air Purification, 2004). The heavy metals that are discussed in the present review are arsenic (As), boron (B), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), mercury (Hg), molybdenum (Mo), nickel (Ni), strontium (Sr), tin (Sn), titanium (Ti), vanadium (V) and zinc (Zn). The heavy metals can be divided into two main groups: (i) elements, such as B, Cu, Fe, Mo, Ni, and Zn, which are essential for plant growth, but become toxic to animals and plants when their concentrations exceed certain threshold levels. For some of these elements, the margin between recommended and toxic concentrations is quite narrow; (ii) elements, such as As, Cd, Hg, and Pb, which are not essential for plants or animals.

Sources of heavy metals in soils are: weathering of soil minerals, land application of treated wastewater (TWW), sewage sludge and fertilizers, and industrial activities (Gupta et al., 2010). Heavy metals

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not only lead to soil contamination, but also affect food production, quality and safety (Muchuweti et al., 2006). Some heavy metals are toxic to plants at very low concentrations, whereas others may accumulate in plant tissues to relatively high levels with no visible symptoms or reduction in yield (Verkleij et al., 2009).

Plants growing in heavy metal-polluted sites may exhibit altered metabolism, and physiological and biochemical processes that result in growth reduction, lower biomass production and metal accumulation (Nagajyoti et al., 2010). Humans exposed to high levels of heavy metals may suffer from various diseases, such as: cancers, cardiovascular problems, depression, hematic, gastrointestinal and renal failure, osteoporosis, and tubular and glomerular dysfunctions (ATSDR, 2005; European Food Safety Authority, 2012; Fewtrell et al., 2003; Steenland and Boffetta, 2000; Vogtmann et al., 2013; WHO, 2010). Infants, children, and adolescents are particularly susceptible to heavy metal poisoning, resulting in developmental challenges and low intelligence quotients (Dapul and Laraque, 2014; Ernhart et al., 1987, 1988; Schwartz, 1994).

To prevent human consumption of food poisoned by heavy metals, most countries have regulations for maximum levels (MLs) of toxic elements. ng g^{-1}.

The present review focuses on the sources and risks of heavy metals, mainly in cultivated fields in various regions, and strategies to reduce their accumulation in horticultural crops.

2. Heavy metal sources in soil and irrigation water, and their bioavailability

Heavy metal sources in the environment can originate from natural and anthropogenic activities. The major anthropogenic sources are agriculture, industry, mining, transportation, fuel consumption, residual organic matter, and sewage water. The major natural sources of heavy metals are windblown dust, volcanogenic particles, forest wildfires, vegetation, and sea salt. Because the present review focuses on pollution of horticultural crops, mainly heavy metal sources in soils and irrigation water are addressed.

The total content ranges of major heavy metals in different rock types and typical, uncontaminated soils are presented in Table 1, where the processes of natural accumulation of heavy metals in arid and semiarid soils are taken from Ben-Hur's (1999) study. In that study, samples of 12 different soils types (Table 2), taken from the 0–90 cm layer at various uncontaminated sites in the Mediterranean coastal area (average annual rainfall > 400 mm) and desert (average annual rainfall < 400 mm) zones in Israel and their parent materials were discussed. The average total contents of selected heavy metals in those different soil samples as functions of their total content in the respective parent materials are presented in Fig. 1 for Mn, Cu, Co, and Zn, and in Fig. 2 for B. In general, higher Mn, Cu, Co, and Zn contents in the parent materials increased their contents in soils, significantly so for Mn, Cu, and Co. Most of the total contents of these heavy metals in the soils were above the 1:1 ratio line (Fig. 1), indicating their natural enrichment in the soils as a result of parent material weathering. For B (Fig. 2), however, a nonsignificant correlation was found between the total B contents in the parent materials and in the soils at $< 25\ \text{mg kg}^{-1}$ B in the parent materials (Fig. 2). In this range, the B contents in the soil samples, which were sampled mainly from the Mediterranean coastal area, were high above the 1:1 ratio line, indicating high B enrichment in those samples. For the other soil samples, the values of B content were distributed around the 1:1 ratio line. Ben-Hur (1999) suggested that B enrichment in soils from the Mediterranean coastal area is a result of precipitation of sea spray, which contains a high concentration of B (Goldberg, 1965), on the soil surface. In contrast, in soils from the desert zone, which is far from the Mediterranean Sea, the B content in the parent materials was the main source of B in the soils.

Table 2
Samples of different soil types and their parent materials, from various uncontaminated sites in the Mediterranean and desert zones in Israel (from Ben-Hur, 1999).

	Soil type	Parent material
	Mediterranean zone	
A	Terra rossa	Hard limestone
B	Mediterranean brown forest	Semi-hard limestone
C	Mountain rendzina	Chalk, marl
D	Basaltic brown	Basaltic rock
E	Brown-red sand	Calcareous sandstone
F	Brown-red degrading sand	Sand dunes
G	Vertisol	Old alluvium
I	Alluvial soil	Young alluvium
	Desert zone	
J	Raw loess	Sediments of desert dust
K	Raw loess-like	Sediments of desert dust
L	Desert dune sand	Desert sand
M	Reddish-yellow desert	Sandstone

Natural contamination by heavy metals of ground water can occur via the normal release of heavy metals from aquifer rocks, and their movement into the ground water. For example, natural, widespread groundwater contamination by As has been identified in India, Vietnam, Inner Mongolia, Greece, Hungary, USA, Ghana, Chile, Argentina, Thailand and Mexico (Chakraborti and Das, 1997; O'Neill, 1995; Smedley and Kinniburgh, 2002).

Many areas in the world, mainly arid and semiarid regions, are characterized by a long dry season and a short wet season, with crop production in these regions relying mainly on irrigation. However, conventional sources of good quality (fresh) water are scarce, mostly

Table 1
Range of total heavy metal concentrations in igneous and sedimentary rocks (Cannon et al., 1978) and in typical, uncontaminated soils and agricultural crops (Allaway, 1968).

Metals	Igneous and sedimentary rocks					Typical soils	Agricultural crops
	Basaltic igneous mg kg^{-1}	Granite igneous	Shales and clays	Black shales	Sandstone		
As	0.2–10	0.2–13.8	–	–	0.6–9.7	NR	NR
Cd	0.006–0.6	0.003–0.18	0.0–11	0.3 - > 8.4	–	0.01–0.7	0.2–0.8
Cr	40–600	2–90	30–590	26 – 1000	–	5 – 3000	0.2–1.0
Co	24–90	1–5	5–25	7–100	–	1–40	0.05–0.5
Cu	30–160	4–30	18–120	20–200	–	2–100	4–15
Pb	2–18	6–30	16–50	7–150	1 - > 31	2–200	0.1–10
Mo	0.9–7	1–6	–	1–300	–	0.2–5	1–100
Ni	45–410	2–20	20–250	10–500	–	0.0–5	1.0
Zn	48–240	5–140	18–180	34 – 1500	2–4	10–300	15–200
Fe						7000–55,000	–
Mn						100 – 4000	15–100

NR – not reported.