Chapter 11
Impact of Heavy Metals on Non-food Herbaceous Crops and Prophylactic Role of Si

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11.1 Introduction

Since several decades, various anthropogenic activities have negatively affected the environment. Heavy metals are one of the key factors that constitute an important health problem. Mining activities, metallurgical and petrochemical industries, fertilizers and pesticides are increasing the dissemination and mobilization of heavy metals. Worldwide, approximately 22 millions ha of land have been estimated to be contaminated by heavy metals and toxic metalloids such as arsenic (Nsanganwimana et al. 2014). An important proportion of these contaminated sites is not suitable and even prohibited for cultivating food crops. Cultivation of crops devoted to biomaterial and bioenergy production may thus constitute an attractive alternative (Fernando et al. 2015). This implies that biomass production is not compromised by heavy metals from

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a quantitative point of view and that the properties of the harvested biomass remain compatible with the requirements of industry from a qualitative point of view.

Phytomanagement of contaminated sites appears as a challenging task, since heavy metals may affect plant growth and development in several ways. Toxic elements such as Cd, Pb, Ni or Hg, as well as an excess of essential elements like Zn and Cu may indeed induce a wide range of morphological changes associated with growth inhibition. Heavy metals compromise absorption of essential elements and may induce nitrogen, phosphorous and iron deficiencies (Jalmi et al. 2018). Plant water status is directly affected by heavy metals in relation to an impact on stomatal properties, or root hydraulic conductivity (Rucińska-Sobkowiak 2016). Toxic elements impair photosynthesis by reducing chlorophyll and carotenoid content, altering the stability of light harvesting complexes and photosystems, affecting carbon assimilation by limiting CO_2 diffusion, or by acting on RuBisCO and other enzymes involved in the Calvin cycle (Chandra and Kang 2016). The production of reactive oxygen species (ROS) is an unavoidable consequence of aerobic metabolism, but oxidative stress is drastically increased by heavy metals, which strongly hasten the generation of free radicals (Fryzova et al. 2017).

Some plant systems are regulated by metals, such as enzyme reactions, photosystem and symbiotic microbial associations (Emamverdian et al. 2015). Metals such as Cu, Zn, Mn, Ni and Fe are considered fundamental plant micronutrients in natural growth processes when present in low concentrations. An excess of metals or of heavy metals (such as Cd), can trigger processes leading to irreparable damages in plants (Seneviratne et al. 2017). For instance, Cd is one of the most common heavy metals derived from anthropogenic activities. Cd is very dangerous for plants because of its toxicity at low concentration and high solubility in water. Cd accumulation is more evident in roots compared to that in leaves, and this accumulation in plant structures was extensively reported to cause stress effects related to plant growth (Okem et al. 2015). Metals are used in nanotechnology applications: for instance, nanomaterials are used agriculture as nanofertilizers and nanopesticides (Prasad et al. 2017). This technological progress is making an inevitable release of nanoscale particles into the environment (Hossain et al. 2015). Therefore, we believe it is necessary to briefly mention here the reported negative impact observed for metal nanoparticles (NPs) on plants. In this sense, the scientific community draws attention to these nanocomponents and discusses that these may cause phytotoxic effects in plants, with a particular emphasis on metal-based nanoparticles (Nowack and Bucheli. 2007). The effects of metal NPs were tested on different model species, such as algae and higher plants. Several works reported significant oxidative stress in algae (Jiang et al. 2012) and deleterious effects on the root length in rice (Boonyanitipong et al. 2011). Moreover, other negative effects were observed in seed germination, photosynthetic performance index and DNA (Stampoulis et al. 2009; Atha et al. 2012; Shaw et al. 2014). NPs also stimulate plant secondary metabolism via production of reactive oxygen species (ROS) (Marslin et al. 2017).

Concerning nanomaterials, Cd-based nanoparticles like Cd sulphide (CdS) nanodots and nanorods are used in electronic, optical as well as biological applications. Their negative effect has been reported for eukaryotic cells, as well as for

organs in mice (Liu et al. 2014). The effects of Cd-based nanomaterials in plants seems to be linked to the concentration, since it was reported that CdO NPs at low concentration increased amino acid production in barley, without affecting photosynthesis (Vecerova et al. 2016).

The key effects of Cd and, more generally, heavy metals, are chiefly related to the generation of reactive oxygen species (ROS) in high concentrations. Consequently, the cell reacts by producing secondary metabolites (e.g. polyphenols, flavonoids, terpenes and anthocyanins) which scavenge ROS (Sharma et al. 2012). Scientific reports have shown an increased secondary metabolism in plants stressed by Cd or heavy metals as a protective mechanism maintaining the integrity of cellular components (nucleic acids, proteins) and membranes (Ramakrishna and Ravishankar 2011). Several studies have analysed the phenylpropanoid pathway in response to heavy metal stress and reported an increase in products derived from this biochemical pathway (Pham et al. 2017; Lajayer et al. 2017; Ashraf et al. 2018). Results highlighted an overproduction of phenolic acids and a decreased synthesis of flavonoids in metal-stressed plants (Babula et al. 2015). The gene expression analysis confirms these evidences and shows an overexpression of *PAL* (phenylalanine ammonia lyase) in plants subjected to stress by heavy metals (Zhang and Liu 2015). PAL plays a key role in phenolic compound formation; indeed, it is the first rate-limiting enzyme in the phenylpropanoid pathway and thereby it plays an important role in the formation of the precursors needed for the biosynthesis of the different classes of aromatic molecules (Valifard et al. 2015). Notably, also genes involved in PAL formation were overexpressed in plants exposed to heavy metals, compared to the control (Finger-Teixeira et al. 2010). Generally, the gene encoding enzymes of the phenylpropanoid pathway are used as markers of (a)biotic stress in plants (Pawlak-Sprada et al. 2011).

Besides heavy metal absorption, translocation of pollutants to the aerial parts and their distribution among shoot organs are of paramount importance for the putative use of plant biomass as a source of biomaterial for building purposes or energy production.

Numerous studies correlate silicic acid ($Si(OH)_4$) uptake with enhanced tolerance of plants to various biotic (Guerriero et al. 2018b) and abiotic stress, including heavy metal toxicity (Imtiaz et al. 2016), but the mechanisms of silicon (Si) function still remain elusive. In grasses, silicified tissues may reach up to 10% of the total dry weight, but silicification processes are poorly documented and a comprehensive approach is still lacking (Annenkov et al. 2017).

We believe it is interesting to mention here the role of the metalloid silicon (Si) which alleviates the toxic effects caused by heavy metal stress in plants. Differently to micronutrients, Si is considered quasi-essential. Indeed, it is not an essential element for the life cycle of plants (Liang et al. 2015); nevertheless, it is useful when supplied in the form of orthosilicic acid $Si(OH)_4$, for example, the response to (a)biotic stresses (Guntzer et al. 2012; Balakhnina and Borkowska 2013). For example, it was demonstrated that Si nanoparticles (NPs) induced an increase in plant antioxidant enzymatic defence: peroxidase (POD), catalase (CAT), superoxide dismutase (SOD) as well as glutathione reductase (GR) and reduced glutathione (GSH) were

found in higher abundance as compared to control plants (Bu et al. 2016). Si also decreases lipid peroxidation and helps preserve membrane integrity (Sattar et al. 2017). Data in the literature showed an increase in phenolic acids and flavonoids that was correlated to higher plant resistance against (a) biotic stress factors (Shetty et al. 2011). Besides the impact on plant secondary metabolism, Si is known to affect plant cell wall properties by precipitating as amorphous opaline silica (SiO_2), thereby associating with wall components and creating a physical barrier to the invasion of pathogens, e.g. fungi (Guerriero et al. 2018b).

In roots of several plant species, silicification mainly occurs in the endodermis and enhances the function of this crucial cell layer as an apoplasmic barrier (Fleck et al. 2010; Lukačová et al. 2013). Quantifying the precise impact of root silicification process on heavy metal retention in the root system requires additional experimental approaches and such knowledge is essential to develop management practices for non-food crop production on contaminated soils. If Si contributes to restrict the upward movement of heavy metals, this may determine that the aerial fraction of the plant can be further valorized for energy or fibre production (Fernando et al. 2015). However, it has also been reported that $Si(OH)_4$ moves via the transpiration stream and deposits as biogenic silica (SiO_2) when water evaporates in the aerial parts (Trembath-Reichert et al. 2015). Recently, Kumar et al. (2017) demonstrated that, besides transpiration, still undetermined biological factors influence $Si(OH)_4$ polymerization in the cell wall. Since the cell wall also constitutes a major site of heavy metal deposits (Guerriero et al. 2016; Luyckx et al. 2017b), thus preventing them from entering the cytoplasm (Krzeslowska 2011), an interaction between Si and heavy metals cannot be ruled out which could have some impact on fibre differentiation or properties of the ligno-cellulosic biomass.

In the literature, there are only a handful of studies concerning the role of Si alone in non-food herbaceous crops. We have schematically resumed the most interesting in Table 11.1.

11.2 Fibres and Sorption of Heavy Metals

Technologies such as chemical precipitation, flotation, ion exchange, electrolyte recovery and membrane separation are available for the removal of heavy metals from wastewater, but most of them are economically expensive and present high energy requirements. Adsorption is a process by which a solid adsorbent attracts a component in solution onto its surface, thus removing it from the liquid phase (Bediako et al. 2016). Numerous plant fibres have been used for this purpose and offer cheap and eco-friendly methods for effluent treatment.

According to Pejic et al. (2009), metal ions sorb mainly to carboxylic (primarily present in hemicelluloses, pectins and lignin), phenolic (lignin) and, to some extent, hydroxylic and carbonyl groups. Increased production of hemp fibres results in an increased amount of waste, namely short and entangled fibres that are not suitable for industrial processes. Pejic et al. (2009) efficiently used this material to remove

Table 11.1 Summary of the studies available on the role/effects of Si alone in non-food herbaceous crops

Species	Effect	Reference
Cotton (*Gossypium hirsutum* and *G. barbadense*)	High Si concentration during elongation phase. A peak was attained during secondary cell wall formation	Boylston et al. (1990)
Textile hemp (*Cannabis sativa*)	1 mM sodium metasilicate results in improved germination. Si protective effect on Cd-treated plants (10 and 20 μM) at both 0.5 and 2 mM of silicic acid	Luyckx et al. (2017b)
Flax (*Linum usitatissimum*)	Identification of aquaporin genes (no NIP2 genes). Quantification of Si resulted in 0.24% on a DW basis	Shivaraj et al. (2017)
Ramie (*Boehmeria nivea*)	Si (and Se) ameliorated Cd toxicity by increasing the content of glutathione; the decrease in antioxidant enzyme activities was reversed by Si	Tang et al. (2015)
Miscanthus and switchgrass (*Panicum virgatum*)	*M.* × *giganteus* showed the lowest Si levels (better combustion and use as biofuel crop). Warmer temperature and greater precipitation were correlated with higher Si levels in plant biomass	Woli et al. (2011)

Pb^{2+}, Cd^{2+} and Zn^{2+} ions from aqueous media and observed that the proportion of lignin and hemicelluloses impacts on sorption properties. Cerchiara et al. (2016) obtained similar results with fibres from *Spartium junceum*. Wang et al. (2016) used kapok fibres (natural fibres derived from the fruit of *Ceiba pentandra*) to remove both heavy metals and organic contaminants from aqueous stream. *Furcraea andina* (cabuya) produces a valuable fibre very efficient for the biosorption of Cu, Zn, Pb and Cd (Mayacela Rojas et al. 2017), while flax fibres are able to remove 97% of lead, 79% of copper and 74% of zinc from aqueous solution using batch-adsorption techniques (Abbar et al. 2017). Volatile pollutants like organoarsenicals may also be removed by fibres extracted from rabbitfoot grass (*Polypogon monspeliensis*; Ruppert et al. 2013).

The chemical transformation of the fibres may improve their efficiency for biosorption processes. The surface transformation of waste textile fibres by carboxymethylation introduces carboxyl binding sites, thereby allowing the fibres to retain a higher amount of Cd^{2+} (Bediako et al. 2016). Similarly, treatment of short hemp fibres with 0.7% $NaClO_2$ at the boiling temperature for 5 min improved their capacity to retain Pb^{2+}, Cd^{2+} and Zn^{2+} (Pejic et al. 2011). Carbonized hemp fibre exhibits a large sorption capacity linked to a well-developed internal pore structure, a large specific surface and the presence of a wide spectrum of surface functional groups (Vukcevic et al. 2014a, b).

Silicon dioxide treatment of jute fibres also modified their properties and even reinforced them for producing structural composites with better environmental performances (Rahman et al. 2017). Treatments of fibres with Si-containing compounds, such as silane, during industrial processing of harvested fibres, modify their structural properties, suggesting that Si-treatments during fibre development in plants may induce new interesting properties for their use in sorption processes (Luyckx et al. 2017a) (Fig. 11.1). Silica precipitating in the bast fibre cell walls may improve the

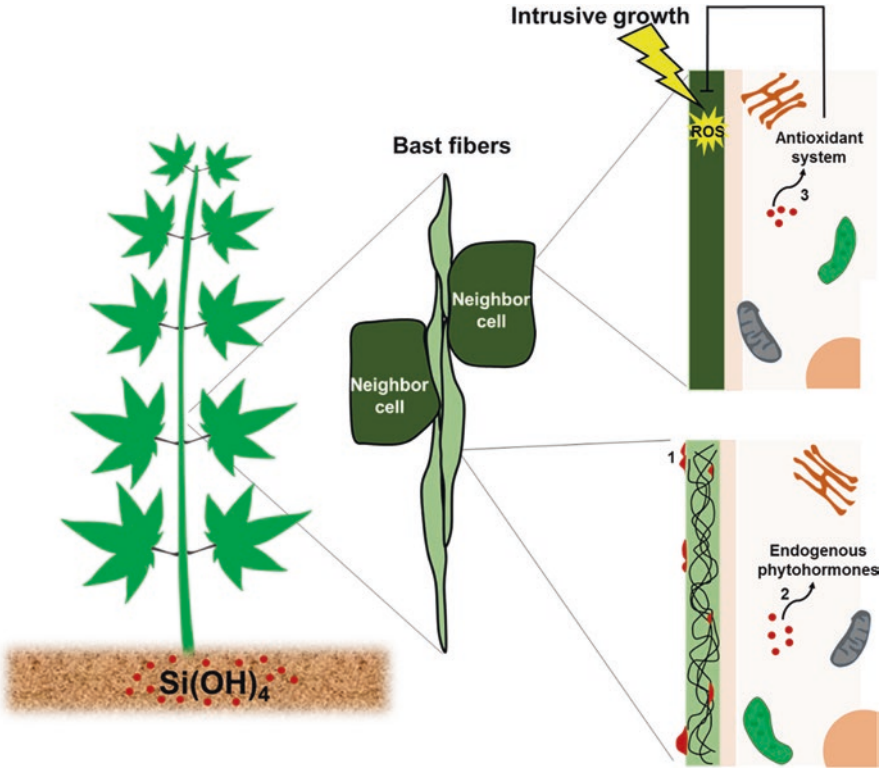

Fig. 11.1 Effects of Si on fibre crops (textile hemp is represented in the picture). Silica (in red) in the cell walls of bast fibres (1) contributes to improve the mechanical properties of the fibres; Si (red dots) can have an effect on the synthesis of endogenous phytohormones, resulting in improved growth (2). Si in the cells neighbouring intrusively growing bast fibres stimulates secondary metabolism and the formation of antioxidant molecules scavenging the reactive oxygen species (ROS) formed in the apoplast, due to the invasion of the middle lamellas (3)

mechanical properties of the fibres and Si can have an influence on the endogenous phytohormones, thereby impacting growth. Additionally, Si is known to boost plant secondary metabolites, which can scavenge the apoplastic ROS produced in the cell walls of adjacent cells during the invasion of their middle lamellas.

11.3 Impact of Heavy Metals on Crops Used for Building and Construction

Urbanization emanating from rapid population growth in developing countries and new technical needs in industrial regions have put pressure on the demand for adapted building materials. Biomaterials may constitute, in numerous cases, a suitable option offering a source of renewable material and interesting rheological

properties (Moroz et al. 2014). The presence of metals in self-compacted concrete may influence numerous parameters conditioning the structural performance, such as maximum ductility, tensile strength and durability (Hassan et al. 2010; Cattaneo et al. 2012). However, the presence of heavy metals, especially zinc and lead, in bioconcretes may represent risk of dispersal and adapted coating needs to be applied to prevent runoff from porous material (Harada and Yanbe 2018). It may also be hypothesized that the presence of Si could indirectly influence the longitudinal reinforcement ratio, the shear span-to-depth ratio and the maximum size of the coarse aggregate (Muñoz et al. 2014; Aruny et al. 2017). Besides a direct influence of heavy metals and Si on the physical properties of the biomaterial, an indirect influence may also result from their influence on cell wall formation and fibre development (Fig. 11.1).

Hodson et al. (2005) showed that the variability in Si over plant species is mainly explained by genetic variation. Bamboo species are widely used for industrial purposes and are considered as Si accumulators with Si concentrations ranging from 3 to 400 mg g^{-1} SiO_2 (DM) (Ding et al. 2008). Bamboos are frequently found in volcanic soils containing easily weatherable silicate minerals in relation to poorly crystalline minerals and low-polymerized aluminosilicates (Basile-Doelsch et al. 2005). Collin et al. (2012) reported significant differences in Si, Cu and Zn contents between bamboo species, particularly between monopodial and sympodial species. No correlation between Cu, Zn and Si was found in stems and leaves and in natural conditions, the Si and trace metal behaviour in bamboos seems to be independent. Using a hydroponic system, Collin et al. (2013) increased Cu concentration up to 1.5 μM and unexpectedly showed that even under these toxic conditions, bamboo growth did not depend on Si level and that absorption of Cu by bamboo plants was not altered by Si supplementation.

Even if heavy metal content was not reduced by Si, some authors consider that the formation of heavy metal silicate compounds in the cytoplasm may be responsible for alleviation of heavy metal toxicities (Neumann and zur Nieden 2001). In bamboo, Collin et al. (2014) showed that both Cu(I) and Cu(II) accumulated depending on the plant parts and that high Cu sequestration occurred through Cu binding to amino and carboxy ligands in the roots, and through complexation with inorganic sulphur ligands in the stems and in the leaves. Si supplementation decreased Cu-induced damages and acted on Cu speciation in the leaves. Nevertheless, a synchrotron approach used by these authors clearly demonstrated that there was no substantial co-deposition of Cu and Si and that no Cu inclusion in silicate was observed.

Hemp (*Cannabis sativa* L.) is a thermophilic crop able to drain soil from poisonous substances and heavy metals. It contains about 23% of fibres and is an interesting material for insulation and concrete production. Linger et al. (2005) showed that hemp is tolerant to Cd and that up to 800 mg Cd Kg^{-1} DW had no major effect on hemp growth, although high Cd content in the leaves had detrimental effects on chlorophyll synthesis, water splitting apparatus and energy distribution in PSII. According to Meers et al. (2005), heavy metal accumulation in hemp remains too low for phytoextraction purposes, but the use of chelating agents such as EDTA or biodegradable EDDS (ethylene diamine tetraacetate) may strongly improve the

use of this plant to clean up contaminated soils. Kos and Lestan (2004) confirmed that the use of chelators increased more than ten times the total amount of Pb, Zn and Cd extracted by hemp growing on a polymetallic-contaminated substrate, but an important percentage of the mobilized heavy metals were lost by uncontrolled leaching of the pollutant before absorption by the plant.

Arru et al. (2004) used an X-ray microanalysis to investigate the localization of Cu in *C. sativa* and found that this element accumulated preferentially in the upper leaf epidermal cell and in the abaxial trichomes, but the primary bast fibres were not involved in copper accumulation. Linger et al. (2002) tested the fibre quality by measuring the pure fibre content in the stems, and the fibre properties after mechanical separation such as fibre fineness and strength from hemp growing on heavy metal-contaminated soils. They concluded that there is no evidence of fibre damage due to heavy metal contamination and that hemp seems to be best suited for soils with a moderate heavy metal content due to its phytoextraction potential. The arbuscular mycorrhizal fungus *Glomus mosseae* significantly enhances the translocation of Cd, Ni and Cr(VI) from the root to the shoot (Citterio et al. 2005).

Piotrowska-Cyplik and Czarnecki (2003) confirmed the efficiency of fibrous hemp for heavy-metal phytotextraction from sewage sludge, but Löser et al. (2002) reported that the seedling stage is extremely sensitive to polluted river sediments and that this could be due to the concomitant presence of unidentified organic pollutants. Ahmad et al. (2015b) identified the genes coding for glutathione-disulphide reductase and phospholipase D as stress-responsive genes in hemp exposed to high soil concentration of Cu, Ni and Cd. More examples concerning the response of hemp to heavy metals are provided in the Sect. 11.5.

11.4 Impact of Heavy Metals on Energy Crops

Several crops are cultivated as sources of energy and used for production of biofuels, bioethanol or material for combustion. Besides willow and poplar, temperate grasses such as *Miscanthus* spp. and *Pennisetum purpureum* are promising species for bioenergy production, while other crops, such as jatropha, rapeseed, soybean or cotton are used for biodiesel production. Since these plants are used for non-food purposes, they may appear as an attractive alternative for cultivation of lands which are excluded from food production, such as moderately contaminated substrates. Nevertheless, there is a risk of pollutant dissemination that needs to be carefully considered. This risk is probably limited for biodiesel production because seeds are commonly used for this purpose and most angiosperms drastically limit heavy metal accumulation in these crucial structures. In contrast, the risk for heavy metal dispersal is by far higher when vegetative parts are used for combustion at high temperatures, but there is still a lack of reliable data regarding the quantification of this risk. According to Werle et al. (2017), the gasification process is more suitable than combustion because it gives the possibility of controlling the fate of extracted heavy metals and prevents the emission of heavy metal oxides.

Miscanthus biomass offers a wide range of end products depending on the transformation processes involving physical and non-chemical transformation or thermomechanical transformation. Several data are available for short-term hydroponic experiments, but field data regarding the behaviour of this perennial woody rhizomatous grass growing on contaminated sites remains scarce. The effects of heavy metals on the whole plant widely differ among *Miscanthus* species (Nsanganwimana et al. 2014). Guo et al. (2016) used a transcriptomic approach to compare two *Miscanthus* species differing in their phytoextraction potential and identified 681 differentially expressed genes in plants exposed to Cd. Genes upregulated under Cd stress are predominantly involved in metabolic pathways (including the biosynthesis of secondary metabolites) and transport of metal ions. Real-time PCR revealed strong differences between species for genes involved in Cd uptake from root and transfer from root to shoot.

The most common *Miscanthus* × *giganteus* generally performs well in soils contaminated by industrial activities. Nevertheless, Pavel et al. (2014) consider that the photosynthetic system of *Miscanthus* is especially sensitive to excess of heavy metals, but most data dealing with heavy metal and *Miscanthus* consider the putative interest of this species for phytoremediation rather than the impact of pollutant on the plant physiology. Pelfrêne et al. (2015) elegantly demonstrated that *M.* × *giganteus* is suitable for phytostabilization and strongly reduces oral bioaccessibility for Cd, Pb and Zn compared to soil without culture. The addition of arbuscular mycorrhizal fungus increased heavy metal accumulation in *M.* × *giganteus* (Nsanganwimana et al. 2015). *M.* × *giganteus* is able to remove high amounts of heavy metals when the soil is amended with contaminated municipal sewage sludge (Antonkiewicz et al. 2016). According to these authors, the decrease in biomass yield did not necessarily impair the efficiency of phytoextraction if it is compensated by an increase in heavy metal concentration in the aerial parts.

However, Korzeniowska and Stanislawaska-Glubiak (2015) reported that *M.* × *giganteus* was less efficient than *Spartina pectinata* for heavy metal removal from contaminated soils and also had a lower phytostabilization potential. Besides *Miscanthus*, giant reed (*Arundo donax*; Barbosa et al. 2015), common reed (*Phragmites australis*; Cubars et al. 2015), reed canary grass (*Phalaris arundinacea*; Antonkiewicz et al. 2016) and *Sida hermaphrodita* (Kocoǹ and Jurga 2017) are other energy crops suitable for phytoremediation.

Si may have a critical role in the biomass combustion process and causes a number of serious problems to power plants through slagging, corrosion and fouling. Hence, besides its beneficial biological effect, Si can negatively impact the thermoconversion of biomass energy. *M.* × *giganteus* and switchgrass (*Panicum virgatum*) contain high concentrations in Si which usually depend more on genotype and climatic conditions than on the soil type (Woli et al. 2011). *Miscanthus* biomass is also commonly used to produce biochar via slow pyrolysis at high temperature. Biochar from *Miscanthus* has been tested for Cu sorption (Shim et al. 2015). According to Houben et al. (2014), *Miscanthus* accumulates Si in the form of readily-soluble phytolith and these authors showed that the biochar produced from *Miscanthus* should be considered as a potential source of bio-available Si inducing positive

effects in the field. Amorphous structures of phytolith disappear at high temperatures and biomass should accordingly be pyrolized below 600 °C.

The cell wall quality is essential for plant biomass conversion to biofuels and is influenced by genotype and environmental conditions (da Costa et al. 2014). The precise impact of Si and heavy metals on cell wall properties in *Miscanthus* and other energy crops still needs to be precisely analysed.

11.5 Impact of Heavy Metals on Crops Used in the Textile Industry

Heavy metals negatively impact plant biomass production and hence productivity, by affecting fundamental physiological processes, namely photosynthesis, through, e.g. irreversible ultrastructural damages to chloroplasts (reviewed in Parrotta et al. 2015).

In this section, the impact of heavy metals on crops used in the textile industry will be discussed. The focus will be principally on cotton, given the availability of many studies on this crop, as well as bast fibre-producing plants (flax, ramie, hemp and stinging nettle).

Several studies are available on the heavy metal response of cotton, an economically relevant crop, which does not enter the food chain and produces an important biomass (Chen et al. 2015).

Cotton grown on six different Cd treatments (from 0.26 to 20.26 mg kg^{-1}) showed that the plants could still develop and produce fibres in the highest Cd concentration (Chen et al. 2015). In the root, Cd was found associated to the secondary phloem and the periderm; however, the leaves were the preferential sites of accumulation when the concentration of Cd was <20.26 mg kg^{-1} (likely because of transpiration), with the heavy metal accumulating in the palisade cells. Chen and colleagues observed that the roots were instead the preferred accumulation site for Cd, when the concentration was the highest tested (20.26 mg kg^{-1}); Cd may complex with organic compounds in the roots, thereby restraining the translocation to the aerial parts.

In a study assessing the response of cotton to Zn toxicity (Anwaar et al. 2015), plants showed reduced fresh and dry weight of stems, leaves and roots, together with impairment of net photosynthetic rate, stomatal conductance, water use efficiency, chlorophyll and carotenoid contents. The addition of Si (as sodium metasilicate 1 mM), however, mitigated these adverse effects and, interestingly, hindered translocation from the roots to the shoots by creating a barrier to the apoplastic route (Anwaar et al. 2015). The barrier effect of Si is one of the mechanisms explaining the protective role of this metalloid against abiotic stresses in plants; this passive response (as opposed to the active one involving an effect on the plant metabolism and immunity) implies a silicification templating role of cell wall polysaccharides, which favour the precipitation of amorphous opaline silica (reviewed by Guerriero et al. 2016; Luyckx et al. 2017a). The still not fully understood role of Si in plant

physiology is complicated by the latent effect (e.g. at the gene expression level) in the absence of an exogenous stress. However, biochemical analyses coupled to multivariate statistics showed that the application of Si to unstressed cotton resulted in changes in the activities of antioxidant enzymes in the roots and leaves (guaiacol and ascorbate peroxidase, catalase); this means that Si is able to induce a new biochemical status in unstressed cotton plants.

Si protected cotton plants from Cd stress (1 and 5 μM) by improving physiological parameters (gas exchange, stomatal conductance and water use efficiency) and reducing oxidative stress (Farooq et al. 2013): notably, this study also recorded a decreased translocation from roots to shoots and the authors postulated Si-induced lignin deposition which may bind ions in the cell walls, and/or the Si-induced precipitation of toxic metal ions.

The cotton proteome is also altered in response to Cd exposure; a study assessing the proteome response after addition of Cd 500 μM revealed an induction of chitinases, methionine synthase, apoplastic anionic guaiacol peroxidase and a decreased accumulation of chaperones, stress- and seed storage-related proteins indicative of irreversible protein denaturation and membrane damage (Daud et al. 2015).

Reduced glutathione (GSH, 50 μM) was shown to improve the physiology and morphology of cotton leaves, either alone or when mixed with Cd (50 μM) (Daud et al. 2016); in particular, oxidative stress was alleviated, chlorophyll *a* fluorescence enhanced and ultrastructural aberrations decreased (namely thylakoid disruption, plasmolysed membranes).

Some studies are available on the response to Cd of bast fibre-producing plants. Among crops producing bast fibres, textile hemp certainly deserves importance, in the light of its multi-purpose applications (Andre et al. 2016). Hemp was reported to tolerate up to 27 mg/kg soil of Cd (Citterio et al. 2003) and, in response to the heavy metal, it accumulates phenolics in both roots and leaves (with however higher amounts in the leaves) (Ahmad et al. 2015a, b). The combination of Cd treatment with NPK application increased the heavy metal uptake, a finding which was related to the higher biomass yield favoured by the fertilizers (Ahmad et al. 2015a, b).

A study assessing the tolerance of industrial hemp to high levels of Cr(VI), Cd and Ni showed that most of the Cd and Ni was present in the roots and only a small amount was translocated to the shoot (Citterio et al. 2003); the uptake of Cr was instead very limited. The same study showed that 1 ha of hemp biomass is expected to extract a consistent amount of Cd and Ni (138–684 g for Cd and 105–285 for Ni, if considering the shoot only or the entire plant) and therefore hemp can help in the restoration of deeper soil portions thanks to its developed root system. The tolerance of hemp to heavy metals is likely linked to an increase in reduced glutathione and phytochelatins (among which a new one, called PC3, with longer release time from the HPLC column) (Citterio et al. 2003). These results have been confirmed by a later study (Shi and Cai 2009), where the potential of eight bioenergy crops to grow on Cd-polluted soils was evaluated; the results indeed indicated that hemp and the other fiber crop, flax, are excellent candidates for phytoremediation, as they accumulate large quantities of Cd in the roots, thereby contributing to Cd phytostabilization. The Cd sequestration/phytostabilization ability of hemp roots was further

reported in a study assessing Cd tolerance and bioaccumulation in 18 hemp accessions (Shi et al. 2012); among the different accessions, some (i.e. Yunma 1, 2, 3, 4, Qujing, Longxi, Lu'an, Xingtai and Shiyang) showed minimal root biomass reduction under heavy metal exposure and therefore represent interesting candidates for growth on Cd-polluted soils.

Studies are available in the literature concerning the response of ramie (*Boehmeria nivea* L. Gaud) to Cd. A transcriptomic analysis identified 155 Cd-responsive genes in ramie (whole plants) (Liu et al. 2015), belonging to suberin, wax and cutin biosynthetic pathways; additionally, this study also identified transcription factors of the families HD-ZIP, MYB, bHLH, and COL, as being regulated by Cd application. The experimental design is however limited as it does not allow a discrimination of the differential gene expression in specific plant organs/tissues, as whole plants were collected and processed. These results can however serve as guide for more specific molecular studies in the future. A subsequent study using Solexa high-throughput sequencing and focused on ramie roots, revealed 115 metabolic pathways involved in the response to Cd (She et al. 2015), with the major ones being glutathione (GSH) cysteine and methionine metabolic pathways. Under Cd stress (5 mg/L), both Si (1 mM) and Se (1 μM) decreased Cd concentration in plants (Tang et al. 2015). Indeed, Si and Se stimulated antioxidant enzymes, notably superoxide dismutase, guaiacol and ascorbate peroxidases and consequently decreased the hydrogen peroxide and malondialdehyde contents in the leaves. Like hemp, ramie shows sequestration of Cd at the root level (Tang et al. 2015); in a study assessing the tolerance to Cd, Pd and Zn of different ramie genotypes differing in the root phenotype (deep, middle, and shallow rooted), it was shown that deep-rooted genotypes are to be preferred for the remediation of poly-metallic polluted soils, because of the higher biomass production and higher tolerance to heavy metals (Yang et al. 2015).

Flax (cv. Hermes) was reported to be tolerant to Cd (Douchiche et al. 2012), and both roots and bottom parts of the stem (the shives) contained high levels of the heavy metal. Studies centred on the modification of the cell walls in flax hypocotyls (18 days old) subjected to Cd stress revealed changes in the structure of tangential walls where polysaccharide were deposited in an irregular manner (multilamellate « waves » within the inner cell wall domain) (Douchiche et al. 2010). These alterations were accompanied by major changes in pectin structure: a strong decrease in high methyl-esterified homogalacturonans was observed in the outer part of tangential cell walls, together with a decrease in low methyl-esterified homogalacturonans in the inner part. Interestingly, these modifications were not present in younger hypocotyls aged 10 days (Douchiche et al. 2011). However, in cell junctions of older hypocotyls, de-esterification of homogalacturonans was observed and this may lead to the formation of a gel with calcium ions (likely further cross-linked by peroxidases) which is necessary to maintain cohesion during Cd-induced expansion.

We believe it is interesting to mention the works related to stinging nettle (*Urtica dioica* L.) in this section dedicated to crops used for the textile industry, given the presence of silky and hypolignified bast fibres in its stem (Guerriero et al. 2017; Backes et al. 2018). Nettle is a multi-purpose crop that is also a source of secondary

metabolites of industrial interest (Guerriero et al. 2018a, b). It was shown previously that the nettle can be used more efficiently in phytoremediation by the use of biotechnology; transient expression using *Agrobacterium* is effective in nettle (Viktorova et al. 2017); however, future efforts should be devoted towards the establishment of a protocol for its stable transformation and regeneration. Nettle grown in the presence of Se (0–2–4 mg) accumulates it mainly in the roots, where phytochelatins also accumulate in higher concentrations (Krystofova et al. 2010). Likewise, nettle grown on Cd (0–0.045–0.090 mM) showed higher presence in the roots, where a lower accumulation of Fe, Zn, Mn and Cu was observed (Tarhan and Kavakcioglu, 2016). *U. dioica* grown on Cr (0–50–200–500 mg/L) was less capable of storing it in the stems as compared to the leaves, suggesting that in the bast fibres its occurrence should be lower than 1 mg/kg, i.e. the total amount found in whole stems (Shams et al. 2010).

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