




Engineering plants for heavy metal stress tolerance

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Received: 10 January 2018 / Accepted: 16 April 2018 / Published online: 25 April 2018
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Abstract

Plants are continuously exposed to abiotic environmental pressures. One of principal abiotic stress factors is heavy metal (HM), which as edaphic contaminants is noteworthy environmental hazard posing great negative impact on overall plants' growth, metabolism and hence economic crop productivity and sustainability. During plants' exposure to elevated HM stress, plants suffer from oxidative stress leading to changes in processes at molecular, biochemical, morpho-physiological and at whole levels. In high HM-contaminated soils, it is essential for plants to generate specific, appropriate protective/defensive mechanisms to nullify the toxic effects of these pollutants, for the normal growth and development. Plants are equipped with efficient strategies which enable them to uptake and accumulate the HMs in various parts or phytoremediate them into non-toxic forms from contaminated soils. Recent advancement in different disciplines of biosciences, such as genetic engineering, plant stress physiology, plant nutrition, transgenics, have aided us in the identification and characterization of compounds, transcription factors, gene products, exogenous phytoprotectants and segments of DNA which involve signal transduction cascades and stress-inducible proteins involved in HM detoxification and tolerance, however, underpinning various strategies for engineered heavy metal plant-stress tolerance is a topic of burning issue which remain least discussed. Taking into consideration several recent literature, the present paper (a) sheds light on the responses and impacts of various HMs to an array of plants' physiological and cellular processes, (b) shows role of various underlying mechanisms behind tolerance or detoxification against specific metal/metalloid, and finally, (c) briefly highlights the possibility of obtaining transgenic improved HM stress tolerant crop plants which could clear the desks for engineering HM stress tolerance in plants for developing improved HM tolerant crop plants and challenging the heavy metal-induced threats to sustainable agricultural system and for qualitative and quantitative improvements in economic yield of crop plants.

Keywords Heavy metal stress tolerance · Metabolic engineering · Physiological and cellular changes · Transgenics · Crop improvement

1 Introduction

From the past few decades, we have seen an increase in modern agricultural practices, anthropogenic activities and rapid industrialization, urbanization and burning of fossils

fuels which have altogether orchestrated the threshold level of various heavy metals (HMs) in the plant–soil, aquatic environments, thereby causing negative impacts to the living forms (Piscopo et al. 2016; Förstner and Wittmann 2012; Sohail et al. 2016; Shahid et al. 2017). Vast tracts of land

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areas under cultivation have been contaminated as a result of elevated HMs presence due to the unlimited, continuous and excessive chemicals usage in agriculture for crop production (chemical manures, pesticides, fertilizers, weedicides, and herbicides), military operations, besides urban and rural municipal solid waste, metalliferous mines, energy and fuel production, mining, mismanagement of agribusiness wastewater, power transmission and industrial effluents also results in HM release (Boparai et al. 2011; Lionetto et al. 2016; Lajayer et al. 2017; Bardiya-Bhurat et al. 2017). Although there are many HMs occurring naturally in the biosphere at a particular region, however, the situation gets from bad to worse due to their release in excess amounts into the soil environment as a result of prevalence of natural calamities and/or increased anthropogenic activities (Wuana and Okieimen 2011). When released into the environment, they may occur as free cations (such as Zn^{2+}), cations bound to organics (such as Cu^{2+}) and oxyanions (such as MoO_4^{2-}) and radioactive isotopes (such as ^{238}U , ^{137}Cs , ^{239}Pt , ^{90}Sr) (Hossain et al. 2012). The accumulation of the metals in water environments over time can result in severe diseases to human beings such as cancer, liver damage, lungs congestion, kidney failure and reproductive system dysfunctioning (Shaban et al. 2018). In plants, many HMs such as Ni, Zn, Cu, Fe, Co, B and Mn are considered as biometals as they form constituents of a range of important enzymes/proteins synthesis, therefore, they are essential for basic and optimal plant metabolism and development, however, the too much concentration of essential as well as and non-essential HMs in the plant–soil continuum lead to generation of toxicity symptoms and dysfunctioning/inhibition of various normal plant processes—ranging from molecular, morphological, physiological and at whole plant level (Shahzada et al. 2018; Shahid et al. 2016; Ali et al. 2013). Both macro- and micro-mineral nutrients play an exemplified and profound role in numerous plant processes, i.e. respiration, photosynthesis, chlorophyll biosynthesis, DNA synthesis, pollen tube germination, protein stabilization and modifications, translocation processes, redox reactions in semi autonomous organelles (chloroplast and the mitochondrion), metabolism of sugars, metabolites, enzyme regulation and fixation and assimilation of nitrogen and sulphur (Nagajyoti et al. 2010; Singh et al. 2016; Wuana and Okieimen 2011). The 53 elements of d block in the periodic table, having atomic density greater than 5 g/cm^{-3} , are defined as HMs. However, elements such as Cd, Cr, Pb, Al and Hg although have no precise and defined role to play in plant cell metabolism, are also considered as very toxic even in low concentrations. Consequently, other elements such as Fe, Cu, Zn, Mo, and Ni are regarded as essential HMs (Arif et al. 2016). During the era of flowering plant evolution, only 19 elements; macronutrients, viz. C, Ca, Mg, O, H, S, N, P and K, and micronutrients, viz. B, Cu, Zn, Mn, Fe, Mo, Ni, Co, and Cl were utilised by

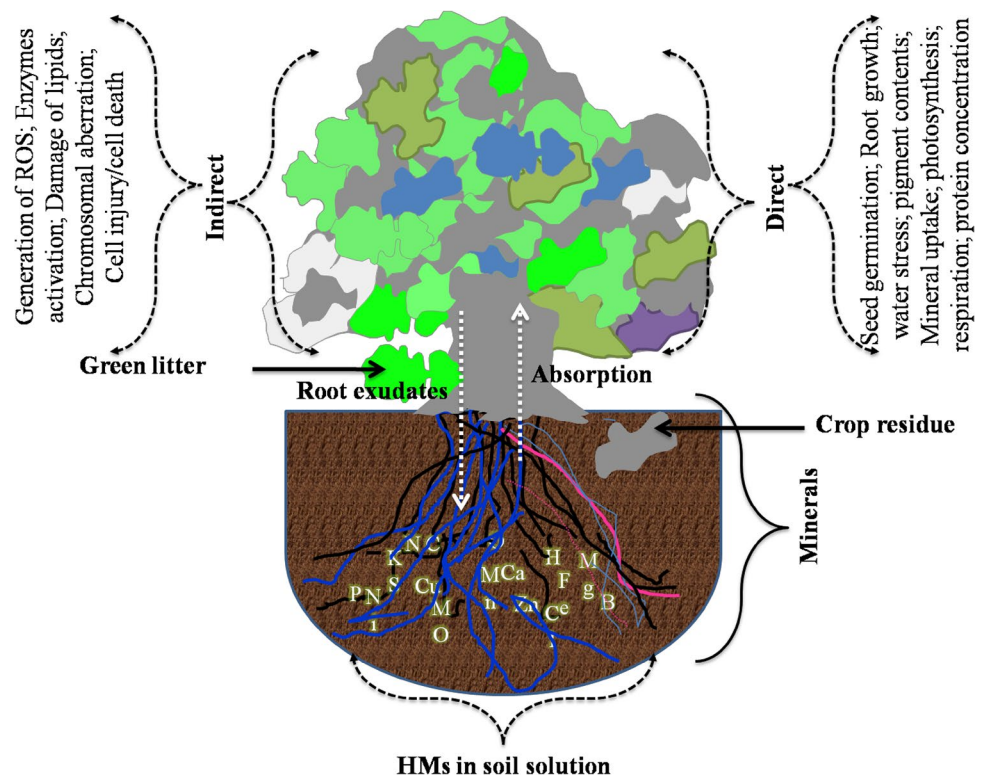
plants for performing their normal growth and development (Ernst 2006). In addition to this, later on silicon, lanthanum, and titanium were also considered as beneficial elements, and reported to be involved in vital activities in some crop plants (Epstein 1999; Zhang et al. 2017; García-Jiménez et al. 2017; Lyu et al. 2017).

Toxic effects of HMs on plants are generally the same which mostly include growth inhibition, low biomass production and accumulation, chlorosis, altered water and mineral nutrients' balance, which ultimately lead to plant senescence. Nevertheless, besides the impacts of HMs on plants, they are regarded as a great threat to human welfare because of their long retention in the environment (Bardiya-Bhurat et al. 2017; Mitra 2015). Plants inhabiting high HM-contaminated soils are called as metallophytes and they accumulate higher amounts of HMs mostly in above ground parts, and metallophytes are further classified as facultative metallophytes which have capacity to flourish well on both metal/metalloid contaminated and non-contaminated habitats and obligate metallophytes which inhabit only metal-challenged environments (Pollard et al. 2014; Hermann and Aneta 2017). Nevertheless, plants growing in HM-contaminated soils accumulate higher amounts of HMs, resulting their entry in food chain that act as major routes for entry of HMs into living beings, the result of which is the manifestation of several diseases (Ashrafzadeh et al. 2017; Shahid et al. 2015; Lajayer et al. 2017). This problem may accelerate further, if sufficient protective measures are not taken (Murtaza et al. 2014). Therefore, devising broad strategies in this broad area to decrease the penetrance of HMs in various crop plants via soil and to reduce the risk of their contamination is need of the hour. Hence, an action to remediate polluted soils is required on the basis of soil contaminants, crop specific and with respect to changing climatic conditions. The main aim of the present addendum is thus to explore the various effects of HMs on plants and the underlying resistance mechanisms that may prove beneficial for the use of plants to clean up and phytoremediate excess metal/metalloid from the environment.

2 Plant responses to HM stress

Plants, being sessile organisms cannot move to more favourable places to escape the adverse effects of HM toxicity. Exposure of the plants to toxic levels of HMs triggers a wide range of molecular, biochemical, and physiological processes (Sofa et al. 2013) (Fig. 1); and plants to cope with the negative impacts of toxicity develop and/or adopt a series of strategies (Hayat et al. 2012). The initial response of the plants to various stresses, including HM accumulation in the soils involve perception of stress stimuli, signal transduction and transmission of amplified signal (mitogen-activated

Fig. 1 Showing direct and indirect toxic effects posed by heavy metal stress on diverse plant processes which possibly results in reduced crop production. Figure shows how various plant nutrients including biometals are absorbed from rhizosphere. After absorption and translocation in various plant tissues, elevated concentrations of biometals impose various direct and indirect effects which are described in text. For detailed discussion of direct and indirect effects, readers are requested to please go through the text



proteins, viz. SIMKK, SIMK, SAMK, MMK3, and MMK2) into cell and acceleration of the cell machinery to bring about comparative changes in cascades of physiological, biochemical and molecular activities. It is perhaps difficult to gauge the induced changes in signal transduction pathways after plants' exposure to HM stress (Hossain et al. 2011). However, it may prove fruitful to our knowledge of understanding to study the changes in signal transduction pathways that happen after plants are exposed to metal/metalloid stress through the early plant responses to HMs' stress by analysing the transcriptomic, proteomic and metabolomic changes (Tamás et al. 2010) (Fig. 1).

3 HM-induced cellular changes

3.1 Effects on the cell division cycle and the cell division exponent

Cell division is one of the important metabolic processes in plants' life cycle that gets affected by various abiotic pressures including HMs. Each HM is having different types of adverse effect on the rate of cell division and elongation in plant. For instance, Cd toxicity affects cell division of root tips in beans (He et al. 2012b), however, Zn, Cd, and Pb application on bean plants showed that the duration of cell division was extended under low concentrations of 0.01, 1.0, and 10 ppm of Cd, Pb, and Zn, respectively; while the rate of

cell division was shortened but the cell cycle was extended by increasing the concentration of HMs (Azevedo and Rodriguez 2012). In an in vitro culture of *Rauvolfia tetraphylla*, Shahid et al. (2016) observed that Cd dose caused a gradual decrease in shoot regeneration. A suppression in mitotic activity by high dose of HM in pea plants was reported by Fusconi et al. (2006). HM such as Cd appears to be a known and one of the main targets to cytoskeleton microtubule (MT). Cd at the concentrations of 85–170 μM distorts the structure and function of the MT in the root cells of *Glycine max* (Gzyl et al. 2015). The root growth in soybean plants was thus diminished accompanied by a reduction in mitotic activity and disturbed MT arrays which also includes randomization in the arrangement of the cortical MT, distorted mitotic arrays and completed depolymerisation of the MT. Furthermore, Cd had significant impact on gene expression patterns and subsequently on post-translational modification of tubulin unit, which is responsible for impairment of MT cytoskeleton's structure and functioning in root cells of soybean plants (Gzyl et al. 2015).

3.2 Effects on the form of chromosomes

The toxic effect of HMs in plant genome severely affects the process of DNA replication and chromosomes as well as inducing chromosomal aberrations and abnormalities (Niture et al. 2014). For example, barley grains treated with Cd showed distorted nucleolus, DNA damage, chromosomal

fragmentation, aberration and liquefaction as a result of Cd interference with nucleic acids (Qin et al. 2015). Aslam et al. (2014) showed the genotoxic effects induced by HM in capsicum plants using random amplified polymorphic DNA (RAPD) technique. They reported a higher degree of polymorphism in DNA bands of Cd-exposed capsicum plants and concluded that Cd caused chromosomal abnormalities and mutations such as multivalent formations, chromosome stitching, bridging and laggard formation at anaphase I stage of cell division. Ghiani et al. (2014) reported DNA damage in *Trifolium repens* (L.) plants exposed to combined HM stress. Nevertheless, there are numerous proteins which can annul the metal-induced oxidative stress. One such protein is Dps proteins which is an efficient detoxification and DNA-protecting protein in response to iron-induced oxidative stress (Chiancone 2008).

4 Physiological impacts of HMs on plants

4.1 Effects of HMs on plant growth

HM-contaminated soil is the primary route of entry of metals into the plant tissues (DalCorso et al. 2013). The most common physiological impact of HM stress to plants is growth retardation (Huang and Wang 2010). In model plants, such as *Arabidopsis thaliana*, plant-receiving HM stress showed a decrease of 40% root growth as compared with wild type no stress plants (Abozeid et al. 2017). There are noticed changes in leaf morphology and anatomy and in various physiological processes, rates of photosynthesis, transpiration and respiration, which brings about changes in gross plants' metabolism, and hence results in less biomass production (Maksimović et al. 2012). Transpiration and uptake and translocation of mineral nutrients between different parts of a plant are also severely affected by HM toxicity (Ying et al. 2010). The nutrient and water uptake by roots of plants gets impaired under HM stress, due to reduction in rate of cell division (Hu et al. 2013). The cumulative effect of these changes affects normal functioning of roots and leaves, which in turn affects various plant developmental processes including chlorophyll biosynthesis, seed formation, pollen dispersal, flowering and embryogenesis. HM toxicity also affects plants multi-dimensionally causing phytotoxicity which is followed by leaf chlorosis, molting, dieback, destructions of PSII pigments, stunted plant growth, decline in yield, wilting, restricted mineral nutrient uptake and reducing nitrogen fixing ability in legume plants (Chen et al. 2012). Under HM pollution, yields of important agricultural crop are reduced and deleterious effects of HM on human and animal health can be observed through food chain contamination and transmission (Park et al. 2011). Non-essential HM such as Cd is considered as very toxic

to plants even in low doses causing enzyme inhibition and saturation of Calvin–Benson cycle which results in loss of photosynthesis, thereby reducing photosynthetic potential. It limits enzymes/protein activities by reacting and saturating the thiol group and active sites on enzymes and formation of mercaptide (Cailliatte et al. 2009). It also orchestrate the generation of many reactive oxygen species (ROS), including hydrogen peroxide, superoxides, which are strong oxidants, causing oxidation to bilayered lipid membranes and biopolymers (Hood and Skaar, 2012). It has been reported that high accumulations of copper (Cu) not only reduces the plant biomass by causing chlorosis, but also interferes with the electron transport chain system by saturating the plastocyanin protein pigment of photosynthesis (Wang et al. 2013). Elevated concentrations of micronutrient such as Ni is responsible for many physiological disorders in plants manifested in the form of chlorosis and necrosis, photosynthetic capacity inhibition, reduction in enzyme activities of N, S and concomitant increase in oxidative stress biomarkers (Yadav 2010; Khan et al. 2016a). Plants grown on Ni-challenged habitats showed an imbalance in nutrient assimilation rate and exhibited disorders in membrane functions due to malfunction of H-ATPase activity and lipid composition of the plasma membranes (He et al. 2012a).

4.2 Effects of HMs on photosynthesis

The fast increasing human population requires a concomitant increase in net plant productivity. The natural plant productivity under the influence of metal/metalloid contamination and the current available techniques, it would be quite impossible to achieve this task. Photosynthesis is a principal driver of life on the Earth, involving the transformation of energy from sunlight into the biosphere zone and simultaneously releasing molecular oxygen from water (Foyer et al. 2017). Among non-biotic stresses, HM stress reduces productivity of plants and alters plant ecosystems' functions; hence affects the photosynthesis and plant productivity (Picorel et al. 2017). HM pollution has inhibitory effects on photosynthetic and respiratory activities of plants (Volland et al. 2012). Although certain biometals such as Fe, Cu, Zn, Ni, Co, and Mo are essential plant nutrients and are required for optimum photosynthesis and a large number of enzymes as cofactors (Kováčik et al. 2010), but their elevated dose retards all the vital activities of plants. Photosynthesis is an important anabolic oxidation–reduction process responsible for providing energy and biomass accumulation and requires a consistent and uninterrupted and normal working of various cell components. The major components of light-scavenging pigment system (chlorophyll and carotenoids) are saturated in the presence of metal/metalloid stress (Kuzminov et al. 2013) and disruption in their functions occurs due to block of electron flow in energy

transfer reactions in light-harvesting antennae. Metal/metalloid stress also affects pigment proteins associated in two phases of photosynthesis, such as plastoquinones, plastocyanins, cytochrome b6f complex, D1 and D2 proteins of PSII, RUBISCO activity, thereby affecting the normal functioning of both light and carbon reactions of photosynthesis (Ceppi et al. 2012; Masood et al. 2012). Higher levels of metalloid/metal toxicity (As, Cd, Mn, Zn and Ni) affect electron passage system on the acceptor side of photosystem II (PS II), thereby inhibiting rate of electron flow between photosystem PS (II) and PS (I) due to toxicity of their ions to membrane lipids (Wu et al. 2012).

4.3 Effects of HMs on chlorophyll

Photosynthetic machinery is very sensitive to changes in cellular redox homeostasis affected by metal/metalloid stress. The thylakoid membranes constitute a well-organized system containing chlorophyll and protein complexes (Kraner and Colville, 2011), which function to couple photolysis of water molecules with electron transport system, thereby make available reducing powers such as adenosine triphosphate (ATP) and nicotinamide adenine dinucleotide phosphate (NADPH) for the carbon phases of photosynthesis. The chlorophyll molecules and photosystem complexes (PSI) and (PSII) are present in segregated manner in the chloroplast membranes in mega and super complexes forms (Dekker and Boekema, 2005; Taiz and Zeiger, 2010). HMs' contamination severely affects the functioning of the photosynthetic apparatus (Shahid et al. 2014a). Several research undertaken had shown that Pb, Cd, Cu, and Zn affect the rate of photosynthesis significantly (Burzyński and Kłobus 2004; Khan et al. 2010). Pb stress brings about distorted chloroplast ultra structure, decrease chlorophyll biosynthesis, non-coupling in electron transport system and decrease in activities of enzymes of Calvin cycle (Verma and Dubey 2003). In a hydroponic study conducted on *Tagetes erecta* plants, Bardiya-Bhurat et al. (2017) found that the increasing concentration of Ni and Pb caused a marked decreased in chlorophyll content. Under metal/metalloid toxicity, marked changes were observed in the absorption peaks of the chlorophyll fluorescence spectra. Less fluorescence re-absorption was detected in plants contaminated with Cd stress, which indicates that the chlorophyll fluorescence parameters are sensitive in detecting changes in the PSII under Cd exposure (Marques and Nascimento 2013). Bioaccumulation of Cd in tomato plants poses negative impacts on PSII photochemistry but increased energy flashes per reaction centre (Singh et al. 2017). Cd stress also decreased chlorophyll fluorescence parameters differently in two mustard cultivars showing differential Cd stress tolerance (Per et al. 2016a). Photo inhibition and oxidation as a result of damage to photosynthetic apparatus may either be short-term and reversible, or

long-term and irreversible (Kono and Terashima, 2014). Pigment contents in photosynthesis also get reduced by high metal presence (Cambrollé et al. 2011). However, low photosynthetic potential may result from adversity of excess metals which decrease chlorophyll biosynthesis or accelerate its degradation (Marques and Nascimento 2013). HM contamination caused a significant decrease in chlorophyll content and caused disruptions in the structure and function of photosynthetic apparatus, decreasing mesophyll thickness and stomatal density (Per et al. 2016b; Tang et al. 2013).

4.4 Effect of HM stress on nutrient uptake

HM toxicity significantly affects rate of nutrient uptake, translocation and assimilation processes in plants (Gopal and Rizvi, 2008). The endogenous concentration of essential ions such as S, K, Mg^{2+} , Zn^{2+} , Ca^{2+} , Fe^{2+} and Mn^{2+} in plant roots and shoots system also gets reduced by the presence of biometals (Chatterjee et al. 2004; Lopez et al. 2006; Ahmad et al. 2016). Exposure to Pb stress reduced significantly the nitrate content, nitrate reductase activity and amino acid content in *B. Pekinensis* (Matecka et al. 2008). Cd is known to modify the structural, physiological, and biochemical processes in crops in soil–plant interaction (Feng et al. 2010) by hindering the uptake and translocation rate and usage of mineral nutrients (Asgher et al. 2015; Nazar et al. 2012). Cd, a non-essential heavy metal for plants, is readily absorbed by plant roots and gets accumulated in various vegetative plant parts, thereby deteriorating quantity and quality as well as the yield of important crop plants (Mahmood et al. 2006) by restricting the absorbance and distribution rate of important macro/micro-mineral nutrient elements (Rizwan et al. 2016; Sandalio et al. 2001) and the processes such as respiration and photosynthesis (Lu et al. 2012). Furthermore, Cd also causes stomatal closure, hence, inhibits gaseous exchange, water uptake and its transportation (Kang et al. 2010; Per et al. 2016b). Inside the plants, it slows down the photosynthesis by reducing the activity of Calvin–Benson cycle enzymes, thus, reduces the metabolism of triose phosphates, and hence of sugars (Mittler and Blumwald, 2010).

4.5 Activity of enzymes

Most of the effects of HM toxicity on the enzyme activity are inhibitory (Wang et al. 2014). Cd has been shown to reduce the activity of nitrate reductase in *Lepidium sativum* (Gill et al. 2012). In *Brassica juncea* plants, Cd has been shown to negatively affect the activity of ribulose-1,5-bisphosphate carboxylase/oxygenase activity which is main carbon dioxide acceptor in C_3 plants, thereby affecting the net photosynthetic rate (Khan et al. 2016b; Per et al. 2016c). Mobin and Khan (2007) reported reductions in carbonic anhydrase activity (CA) in mustard plants subjected to Cd stress. Singh

et al. (2008) using increased doses of Cd in blackgram reported significant reductions in CA activity. In *Triticum aestivum* plants, nitrate reductase (NR) activity showed a significant decrease on exposing plants to Cd stress (Khan et al. 2015). In the tonoplast of wheat plants, the ATPase and PPase activity showed a decreasing trend rapidly under aluminium (Al) stress (Harb et al. 2010). Essential HMs such as nickel and zinc at elevated concentrations have significantly diminished the activity of NR in mustard plants (Khan and Khan, 2014). Similar concomitant decrease of NR and CA activity against varied doses of cobalt and aluminium stresses in chickpea and mung bean plants have been worked out by Ali (2014, 2017).

4.6 Water relation

HM contamination can alter the water relation in plants (De Vries et al. 2013), causing severe dehydration by restricting the movement of water both via apoplastic and symplastic route from roots to shoot part of plants (Hussain et al. 2013). The toxic effects of HMs have been dissected in multiple processes such as stomatal behaviour, movement and uptake of water through symplast or apoplast (Mombo et al. 2016). Balance between transpiration rate and water uptake greatly determines water status in plants. Many studies have shown that HM such as Ni can decrease the water content, transpiration rate, stomatal conductance, internal carbon dioxide concentrations, water-use efficiency and net photosynthesis in plants (Moosavi et al. 2012; Khan and Khan, 2014). In

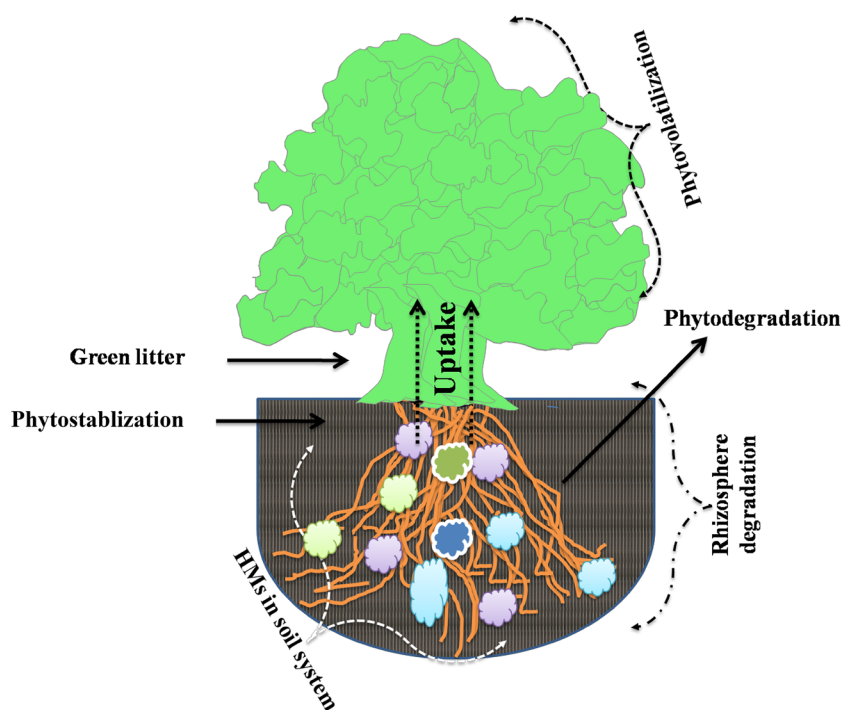
sand culture experiment, 4-day-old seedlings of *T. aestivum* were exposed to 10 mM Ni stress and a reduction in leaf water potential, transpiration rate, stomatal conductance and total moisture content was observed (Yusuf et al. 2011).

The toxic impacts of Ni^{2+} ions can reduce the mean leaf area of plants (Mou et al. 2011; Khan et al. 2016a). A significant percent reduction in leaf area of wheat and mustard plants was detected under the Ni stress conditions (Siddiqui et al. 2013; Khan et al. 2016a). Similar type of reduction also happened in *Brassica oleracea* plants due to application of Ni in the form of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (Nadeem et al. 2012). The main toxic impact of HM toxicity is also the reduced transpiration rate and closing of the stomatal aperture (Per et al. 2016b; Pierart et al. 2015). However, abscisic acid (ABA), a plant growth regulator which causes stomatal closing, gets increased in *P. vulgaris* plants under Ni stress conditions (Sharma et al. 2012).

5 Potential mechanisms involved behind detoxification and tolerance to specific metal/metalloids

During the course of evolution, plants have adapted compatible strategies for nullifying the induced responses of metal/metalloid toxicity in the environment (Fig. 2). Some of these strategies have been briefly discussed in the following sections.

Fig. 2 An overview of plant defence mechanisms against heavy metal(s) toxicity. Figure showing various phytoremediation-based mechanisms evolved by plants in response to heavy metal stress



5.1 Restriction of uptake and transport of HMs

Uptake and transport of HMs by plants involve root sensing, interception, entry and their transport to the aerial shoot systems (Pauget et al. 2012). Based on the type of ions being absorbed, the entry of HM ions into the plant occurs either through symplast or apoplast pathway (Radić et al. 2010). Most of the HM ions make their entry inside plant system by an energy-mediated manner via specialised metal-ion carriers, pumps or channels (Schreck et al. 2011). The plant could restrict HM uptake either by precipitating or by complexing metals in the rhizospheric zone (Shahid et al. 2013). Plants employ process of HMs' precipitation either by increasing rhizospheric pH or expelling ions as phosphates (Shahid et al. 2014b). In addition, in rice plants, Noctor et al. (2012) has reported Fe plaque formation as a possible underlying mechanism for excluding toxic ions.

5.2 Cellular exclusion of HMs

Cellular exclusion of ions is considered as a useful adaptive strategy for metal/metalloid tolerance in plant systems (Soudek et al. 2014). Large fractions/portions of HMs ions are found to be in the plant roots apoplastic space (Uzu et al. 2011a) and many metal transporter proteins have been found to be involved in the cellular exclusion of metal ions from apoplastic or symplastic space or vice versa (Uzu et al. 2011b).

5.3 HM complexation at the cell wall–plasma membrane interface

The cell wall–plasma membrane (CWPM) interface represents not only apoplastic mechanical barrier, but also a flexible structure involved in stress sensing, perception and signalling for the metal/metalloid stress. The CWPs engaged in response to various abiotic stresses, have been extensively recognised and characterised among different crop plants. Under various stress conditions, the main (CWPM) include phospholipases, the salt overly sensitive kinases (SOS), transcription factors, C-repeat binding factor, dehydration sensitive element-binding proteins, mitogen-activated protein kinases and phosphatases, and abscisic acid-responsive-binding factors (Ihsan et al. 2017; Dar et al. 2017). There are known CW proteins which form covalent bonds and undergo glycosylation with HMs; some of them are proline-rich proteins (PRPs), expansins, proline-rich extensin-like proteins (PRExts), formin-like proteins and hydroxyproline-rich *O*-glycoproteins (HRGPs) (Suzuki et al. 2015). The cell wall–plasma membrane interface is believed to be the potential site of HM tolerance as it accumulates large fractions of HMs (Wu et al. 2010). Pectins play a well role in ions induced formation of cell wall surface charge. In plants such

as *Pastinaca sativa* and *Apium graveolens*, Szatanik-Kloc et al. (2017) reported that the CWPM are jointly involved in ion exchange and surface characteristics of plants. Recently Barzegargolchini et al. (2017) have discovered the role of two potential genes, namely LAC4 and PER64 which increased their activity and brings about an increase in cell wall thickness of roots of *Aeluropus* plants in response to abiotic stress. Plasma membrane is also involved in sequestration and transport of HM ions by secondary messenger-dependent proton-ATPase (Liu et al. 2015). Plasma membrane is also involved in the exclusion of critical mineral nutrient (K^+) from *Agrostis capillaris* roots (Wainwright and Woolhouse, 1977). Some plants decrease metal concentration by employing the avoidance mechanisms such as accumulation in root cells via modifications of cell wall polysaccharides (Li et al. 2016) or organic acid anions exudation from the tops of root cells (Chen and Liao 2016).

5.4 Complexation of HMs and the role of heavy metal transporter proteins in compartmentalization within vacuoles

Once metal toxicity is recognised inside the plant cells, they adapt various anatomical and physiological strategies for performing proper optimum growth and development (Wannaz et al. 2012; Sitko et al. 2017). Transporting metal/metalloid ions out of the cell or sequestering them inside the plant organelles, thereby removing them from the cytoplasm or from other cellular environments through the active involvement of sensitive and essential metabolic activities is one such strategy (Xiong et al. 2014). Various plant cell organelles are involved in meta/metalloid ions' sequestration but the homeostatic role of vacuole in conferring HM stress tolerance is well established (Bashir et al. 2016). The central vacuole, therefore, represents a suitable storage bucket/reservoir for excessively accumulated metal pollutants. There are proton pumps located in the tonoplast, namely proton ATPase- (VATPase) and pyrophosphate (VPPase) which are involved in accelerating most solutes across vacuoles (Yan et al. 2010) through channels and transporters (Socha and Guerinot 2014). Although few HM transporter proteins have been well characterised, the molecular location and specificity of these transporter proteins in plants is still lacking. Some of the identified include iron-regulated transporter (IRT)-like protein ZIP family, zinc-regulated transporter (ZRT), P-type metal ATPases, mitochondrial ABC transporter, ATP-binding cassette (ABC), cation diffusion facilitator (CDF), natural resistance resistance-associated macrophage protein (NRAMP), pleiotropic drug resistance (PDR), CAX transporter involving Ca^{2+} , multidrug resistance-associated protein (MRP), copper transporter (COPT) and yellow strip-like (YSL) transporter (Dimkpa et al. 2015; Taiz and Zeiger 2010). There is a profound role of plant

vacuoles as main reservoirs of HMs (Xiao and Chye 2011). A mechanism of cellular detoxification of HMs is described diagrammatically in Fig. 3.

6 Transgenic plants and HM stress tolerance

Scientific know-how of the basic processes of metal transport, hoarding and forbearance in both plants and other organisms have led to the development of various strategies for the alteration of these traits in transgenic plants for increasing the strength of plants to phytoremediate more and more HM from the contaminating environment (Stolpe et al. 2017). Emerging fields of biotechnology and genetic engineering are considered as most important tools for identification and better understanding of several key steps at the molecular level to improve plant tolerance particularly HM toxicity (Dixit et al. 2015; Mosa et al. 2016).

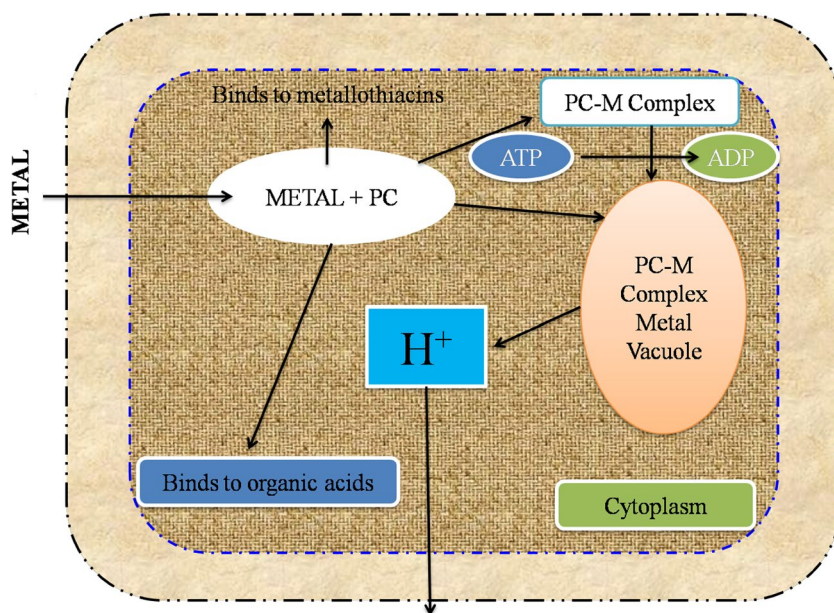
Overexpression of identified genes and the encoded polypeptide accountable for HM uptake, translocation, and sequestration may allow for the production of plants that can be successfully exploited for phytoremediation purpose. Increased tolerance to HM stresses by overexpressing metal-binding peptides—phytochelatin and metallothionein genes had been widely reported in plants (Xu et al. 2011).

Plants are equipped with different mechanisms for HM detoxification, one among which is the production of phytochelatin (PCs). In plants, PCs act as defensive mechanisms not only against metal-related stresses but also in retaliation to other abiotic stresses such as salinity and heat stress (Gautam and Agrawal 2017). PCs have been reported to be used as biomarkers for the early detection of HM stress in plants. *A. thaliana phytochelatin synthase (AtPCS1)* and wheat

(*Triticum aestivum* L.) *phytochelatin synthase (TaPCS1)* were amongst the first plant phytochelatin genes that were identified and extricated successfully (Bohra et al. 2015). Transgenic *Arabidopsis* plants were established with much better HM accumulation capacity than wild-type *Arabidopsis* as a result of expressing synthetic phytochelatin (ECs). Overexpression of arsenic-phytochelatin synthase 1 (*AsPCS1*) and yeast cadmium factor 1 (*YCF1*) (isolated from garlic and baking yeast) in *A. thaliana* resulted in an increased tolerance to Cd and As and also increased its ability to gather the metals to a greater extent (Pramanick et al. 2017). Overexpression of wheat PCS1 (*TaPCS1*) in tobacco plants leads to an increased accumulation of Cd and other HMs in leaves (Thakur et al. 2016). Transgenic tobacco plants overexpressing *TaPCS1* could accumulate more than 100 times biomass on HM-contaminated soils than the wild-type hyperaccumulator plants (Shahid et al. 2012). More and more research and investigations into this area has led to the identification of various PCS genes in distinct plant species such as *B. Juncea (BjPCS1)* and rice (*O. Sativa* L.) (*OsPCS1*) (Arévalo-Gardini et al. 2017).

In plants, metallothioneins (MTs) are cysteine-rich ligand metabolites that are involved in annulling toxicity of HMs through cellular sequestration, balancing intracellular metal ions, and metal transport accommodation in plants (Jan and Parray, 2016; Lionetto et al. 2016). Expression of *Elsholtzia hai chowensis* metallothionein type 1 (*EhMT1*) in tobacco plants not only led to an increase in the tolerance of transgenic tobacco to Cu toxicity, but also decreased the production of strong oxidant hydrogen peroxide and improved peroxidase activity (POD) in roots, thereby leading to an increase in the ability of plants to cope with oxidative stress (Hou et al. 2017). *TaMT3*, a metallothionein type 3 from

Fig. 3 Various schematic mechanisms behind cellular tolerance/detoxification of metal/metalloids inside plant systems



Tamarix androssowii, engineered into tobacco resulted in increased tolerance to Cd stress through significant increases of SOD functionality, which raised the ability of ROS cleaning up in transgenic plant (Ashraf et al. 2017). *OSMT1e-p*, a type 1 MT obtained from a salt-tolerant rice genotype (*O. sativa* L. cv. Pokkali) induced tolerance to Cu and Zn toxicity when ectopically expressed in transgenic tobacco (Soda et al. 2016). Ectopic expression of *BjMT2*, a metallothionein type 2 from *B. juncea*, in *A. thaliana* enhanced Cu and Cd tolerance at the plant seedling stage (Soda et al. 2016). Various representative studies involving role of transgenics in conferring heavy metal/metalloid stress tolerance have been given in Table 1.

7 Conclusions and future prospects

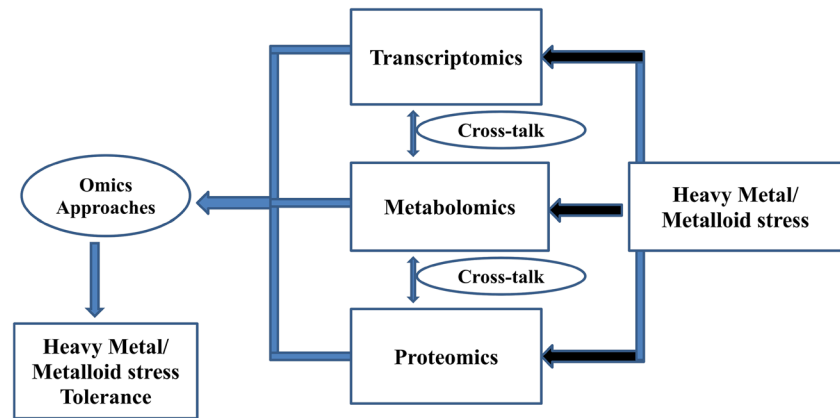
Almost 3.1 billion people live in rural areas and out of this population, ~2.5 billion people earn their livelihood from traditional agricultural practices, which contributes ~30% to economy because agriculture contribute major share to gross domestic products (Yang et al. 2011). Nevertheless, the world population is also estimated to rise to ~10 billion by the middle of the twenty-first century and drastic as well as serious food and energy crisis are most likely to be witnessed (Zeng et al. 2011). In this scenario, the situation is likely to get worse due to manifold increase in anthropogenic activities that caused unwanted and untoward changes in the natural environment such as soil, air, and water contamination (Nabulo et al. 2010). These situations (increasing population cum pollution) are posing an everlasting and increasing burden on natural endowments to enhance food production and consequently food security. Hence, there

are serious demands for engineering diverse crop varieties that stand healthy, adaptive and resistant to various abiotic stresses particularly heavy metal(s) (Syvertsen and Garcia-Sanchez 2014). In disparity to biotic stresses, which mostly relies under monogenic traits, abiotic stress tolerance mechanisms are genetically labyrinthine and intricate processes and multi-genic in nature, involving an array of components of signalling transduction pathways, and thus, more difficult to engineer. Real progress for plant-engineering stress tolerance procedures for HM tolerance therefore depend on the gene(s) expression and their product(s), which regulate signalling pathways or are involved in the synthesis of transcription factors that endow engineered heavy metal/metalloid stress tolerance (Singh et al. 2015). The present collected literature provides new insights in dynamics of metal/metalloid stress response, acclimation and recovery after stress treatment of various plant processes for developing engineered heavy metal/metalloid transgenic plants with elevated stress tolerance to other abiotic stresses as well as orchestrated crop productivity in decades to come. Up-regulation or the overexpression of genes has resulted into enhanced tolerance of plants to metal stress. Therefore, identifying the genes reported to regulate HM homeostasis, detoxification and exclusion can benefit sustainable agriculture. Further, by identifying plant promoters, signal transduction pathways, and transcription factors involved in HM stress tolerance can enlighten the molecular mechanisms behind HM stress resistance in plants. The same knowledge may prove beneficial in translating information to facultative metallophytes as well. Recently, several efforts were made for engineered heavy metal/metalloid stress tolerance through genetic concocting with moderate success. However, owing to genetically complex nature of heavy

Table 1 Showing various transgenic plants obtained by the modification of underlying genes/proteins involved

Gene	Plant	Effect	References
<i>AtPCS1</i>	Arabidopsis	Cd tolerance and accumulation	Soda et al. (2016)
<i>AtPCS1/CePCS1</i>	Tobacco	As tolerance and accumulation	Gielen et al. (2017)
<i>CdPCS1</i>	Tobacco	Accumulation of As and Cd	Das et al. (2017)
<i>NnPCS1</i>	Arabidopsis	Accumulation of Cd	De Araújo et al. (2017)
<i>TaPCS1</i>	Poplar	Accumulation of Pb and Zn	Gong et al. (2017)
<i>PtPCS1</i>	Poplar	Zn accumulation	Chen et al. (2017)
<i>TaPCS1</i>	Rice	Cd hypersensitivity	Mayerová et al. (2017)
<i>TcPCS1</i>	Tobacco	Accumulation of Cd	Zou et al. (2017)
<i>CAT1</i> and <i>CAT2</i>	Arabidopsis	Low level of H ₂ O ₂ and enhanced stress tolerance	González-Guerrero et al. (2016)
<i>DHAR/GR/GST</i>	Tobacco	Enhanced metal tolerance overexpression due to redox homeostasis of ascorbate and glutathione pool	Quintela-Sabarís et al. (2017)
<i>GST</i>	Tobacco	Enhanced Cd tolerance vis-a-vis no Cd accumulation, high activity of antioxidant enzymes	Zanella et al. (2016)
<i>Sulfite oxidase (SO)</i>	Tobacco	High tolerance against S as a result of efficient H ₂ O ₂ scavenging by CAT	Sharma et al. (2016)
<i>TcPCS1</i>	Tobacco	Engineered Cd tolerance due to decrease in malondialdehyde content and elevated activities of antioxidant enzymes	Clemens and Ma (2016)

Fig. 4 Coordinated approaches in engineering heavy metal stress tolerance in plants



metal/metalloid stress tolerance mechanisms and dissemination of this information from lab to field trials make it difficult to achieve. In addition, genetic transformation of heavy metal/metalloid stress-responsive metabolites, genes (particularly TFs) and proteins have yielded promising results, but still their complete genetic intricacies need to be exploited in much greater detail (Márquez-García et al. 2013). Future research based on unravelling major insights into the role and regulating engineered heavy metal stress tolerance can show promising results. Therefore, a well-coordinated omics-based approaches, viz. transcriptomics, metabolomics, proteomics and their crosstalk with respect to improved plant heavy metal/metalloid stress tolerance as well as to other non-biotic environmental pressures can provide new insights in economically important crop plants (Fig. 4).

Acknowledgements Abbu Zaid is thankful to Aligarh Muslim University, Aligarh and UGC-New Delhi India for financial assistance in the form of research fellowship No. BTM-2015-04-GH-7403. SHW gratefully acknowledges the grant for Raman Post-Doctoral Fellowship from University Grants Commission, New Delhi, India. KZM appreciates the funding source by SERB ECRA grant 2016/000025.

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