Heavy-Metals-Induced Plant Stress

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What is ‘Heavy Metal’ ?

A **heavy metal** is a member of a loosely defined subset of elements that exhibit metallic properties. Many different definitions have been proposed—some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity. The term *heavy metal* has been called a "misinterpretation" due to the contradictory definitions and its lack of a coherent scientific basis

Terminology

Heavy Metals (HMs)

Potentially Toxic Elements (PTEs)

Biologically Labile Elements (BLEs)

The term heavy metals has been vaguely applied to a group of physically miscellaneous and chemically heterogeneous elements, at times being biologically essential or environmentally significant inorganic contaminants, in most of the published literature without any established authoritative or coherent scientific basis of reference. Although Potentially Toxic Elements (PTEs) as an alternative for popularly known heavy metals, describes their toxic nature in terms of concentration fluctuations, exposure limits and speciation varieties for a given exposed organism, yet it is poorly elucidating potential hazard classification qualitatively from species to species on an ecosystem-scale. This has led to a controversy in the categorization of large range of unrelated metal (loid)s with specific mode of action relevant to their speciation and the organism concerned. The aim of describing a comprehensive element-specific identification, characterisation and quantification exposure-toxicity model in context of key factors like geo-chemical speciation, bio-availability or fate and effect is unrealistic unless a proper and scientifically recommended categorization of differently behaving divergent class of elements is achieved. Hence, an appropriate nomenclatural prospect is required to rectify the inconsistency for which I suggest the term Biologically Labile Elements (BLEs) or simply Bio-labile elements for its biological, chemical, environmental and toxicological relevance as discussed in this paper.

Bhat and Kahn (2011)

Periodic Table of the Elements

14	28.09
Si	
Silicon	

atomic number — atomic weight — symbol: — name

black solid
blue liquid
red gas
white synthetically prepared
most stable isotope

- alkali metals
- alkaline earth metals
- transitional metals
- other metals
- nonmetals
- noble gases

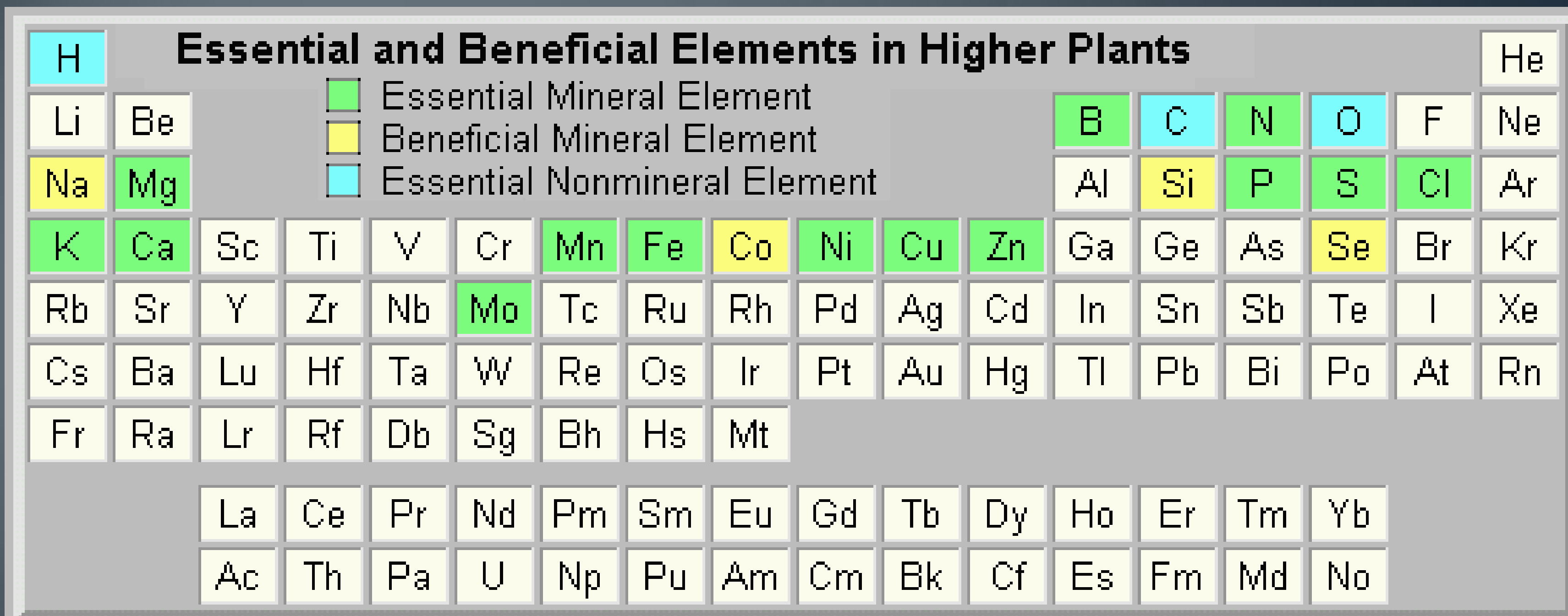
1 H Hydrogen 1.01																	2 He Helium 4.003
3 Li Lithium 6.94	4 Be Beryllium 9.01											5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.18
11 Na Sodium 22.99	12 Mg Magnesium 24.31											13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.90	23 V Vanadium 50.94	24 Cr Chromium 51.996	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.70	29 Cu Copper 63.55	30 Zn Zinc 65.37	31 Ga Gallium 69.72	32 Ge Germanium 72.59	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 83.80
37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.40	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.69	51 Sb Antimony 121.75	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.30
55 Cs Cesium 132.91	56 Ba Barium 137.33	57 La Lanthanum 138.91	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.85	75 Re Rhenium 186.21	76 Os Osmium 190.20	77 Ir Iridium 192.22	78 Pt Platinum 195.09	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.37	82 Pb Lead 207.19	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium 226.03	89 Ac Actinium 227.03	104 Rf Rutherfordium (261)	105 Ha Hahnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 (271)	111 (272)	112 (277)	(113)	114 (285)	(115)	116 (289)	(117)	118 (293)

58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.40	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.97
90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium 237.05	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (260)	102 No Nobelium (259)	103 Lr Lawrencium (262)

Metals – essensial and not essensial

- Certain trace metals or metalloids that are essential (Cu, Mn, Zn, or Ni)
- or not essential (e.g. Cd, Pb, Hg, Se, Al, As) at amounts that would be extremely toxic to plants

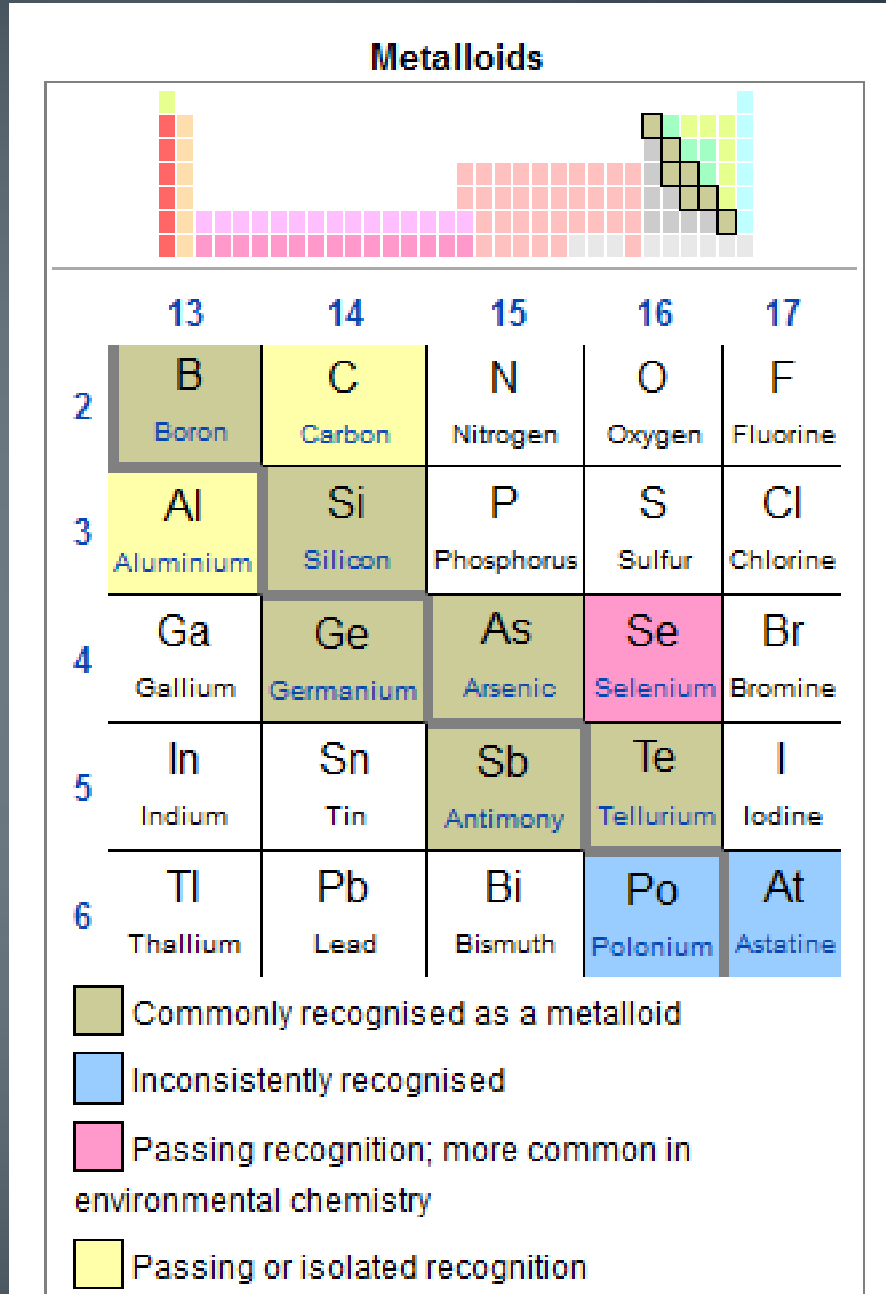
Barceló and Poschenrieder (2003)


Essential and Beneficial Elements in Higher Plants
Essential Mineral Element
Beneficial Mineral Element
Essential Nonmineral Element
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Lr Rf Db Sg Bh Hs Mt
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No

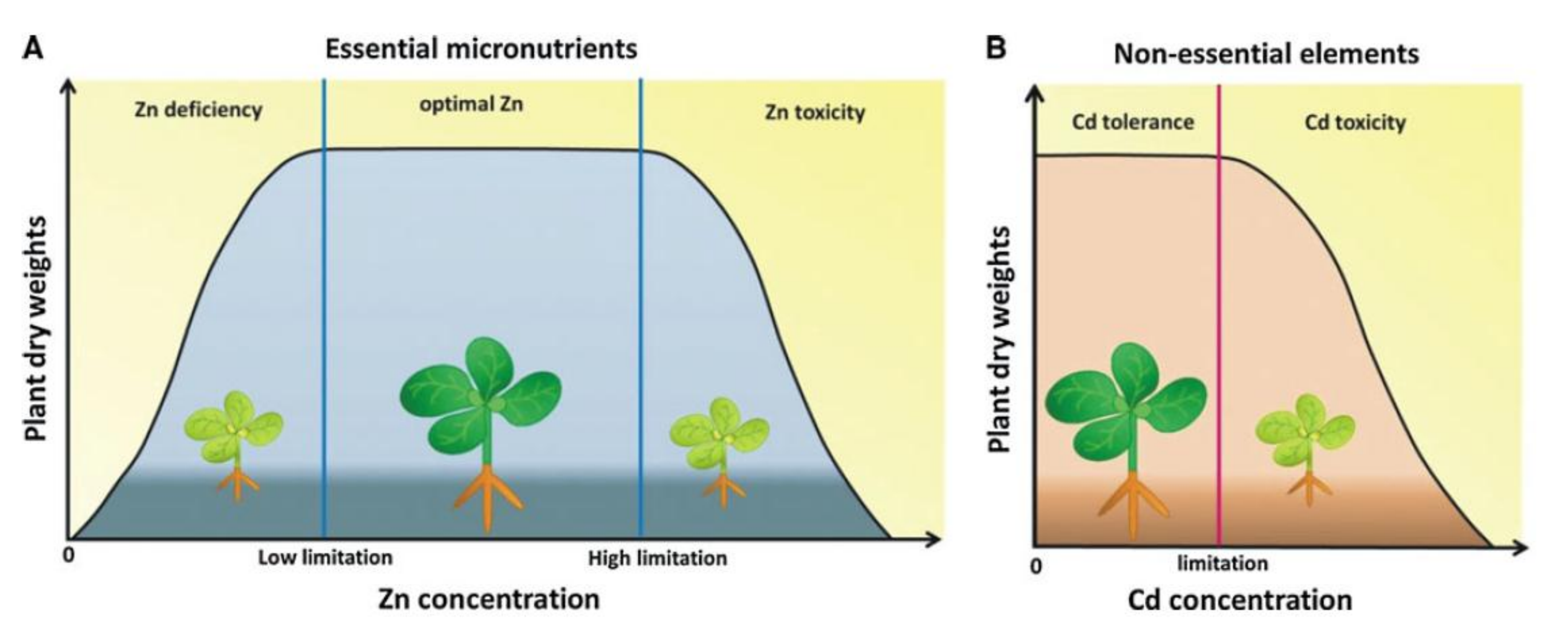
Terms

- *metalloid is an element intermediate in properties between the typical metals and nonmetals*
- *a ligand is an ion or molecule that binds to a central metal atom to form a coodination complex.*
- *Chelation describes a particular way that ions and molecules bind metal ions*

Barceló and Poschenrieder (2003)


Metalloids
13
14
15
16
17
2
3
4
5
6
B Boron
C Carbon
N Nitrogen
O Oxygen
F Fluorine
Al Aluminium
Si Silicon
P Phosphorus
S Sulfur
Cl Chlorine
Ga Gallium
Ge Germanium
As Arsenic
Se Selenium
Br Bromine
In Indium
Sn Tin
Sb Antimony
Te Tellurium
I Iodine
Tl Thallium
Pb Lead
Bi Bismuth
Po Polonium
At Astatine
Commonly recognised as a metalloid
Inconsistently recognised
Passing recognition; more common in environmental chemistry
Passing or isolated recognition

Essential or Toxic Element ?



Lin and Aarts (2012)

Related Terms

- ✓ Metallophytes = plants that can colonize metal-contaminated soils.
- ✓ Metalliferous habitats = metal-contaminated soils.
- ✓ Hyperaccumulator = natural adaptation mechanism to metalliferous habitats.

Barceló and Poschenrieder (2003)

Source and Problems

- ✓ Heavy metals (HMs), added to the soil largely through diverse anthropogenic activities, constitute one of the major environmental contaminants that restrict plant productivity.
- ✓ Their non-biodegradability results in prolonged persistence in the environment.
- ✓ If heavy metals are allowed to accumulate in crop plants, toxic metals pose a threat to human and animal health.

Solution

Phytoremediation, a sustainable and inexpensive technology based on the removal of pollutants* from the environment by plants, is becoming an increasingly important objective in plant research.

*) including HMs

Gohre and Paszkowski (2006)

Phytoremediation as a Solution

- ✓ Phytoremediation has recently emerged as a new, cost-effective, and environment-friendly alternative.

Barceló and Poschenrieder (2003)

Method of Phytoremediation

- ✓Phytoremediation can be done by utilizing [a] ‘hyperaccumulator’ plants with or without [b] arbuscular mycorrhiza symbioses.

Hyperaccumulator Plants

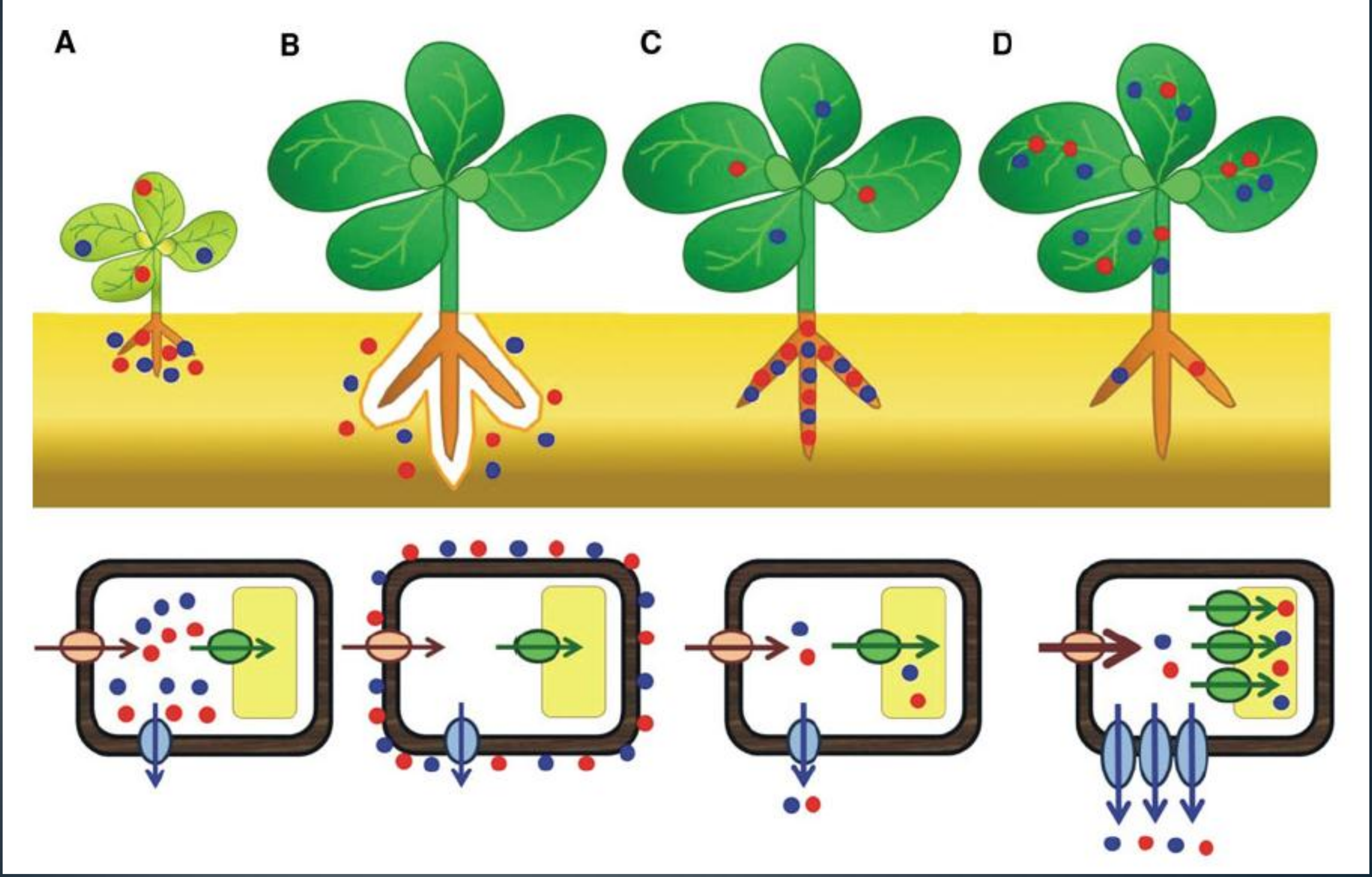
The term hyperaccumulator describes plants that have ability to grow on metalliferous soils and to accumulate extraordinarily high amounts of heavy metals in the aerial organs, far in excess of the levels found in the majority of species, without suffering phytotoxic effects.

Rascioa and Navari-Izzo (2011)

Three basic hallmarks distinguish of hyperaccumulators

1. strongly enhanced rate of heavy metal uptake,
2. faster root-to-shoot translocation, and
3. greater ability to detoxify and sequester heavy metals in leaves.

Rascioa and Navari-Izzo (2011)



Lin and Aarts (2012)

Remediation or Mining ?

Metal accumulating species can be used for phytoremediation (removal of contaminant from soils) or phytomining (growing plants to harvest the metals)

Rascioa and Navari-Izzo (2011)

What is arbuscular mycorrhiza ?

An arbuscular mycorrhiza is a type of mycorrhiza in which the fungus penetrates the cortical cells of the roots of a vascular plant.

Advantage of Using Mycorrhiza

Arbuscular mycorrhizal (AM) fungi provide an attractive system to advance plant-based environmental clean-up. During symbiotic interaction the hyphal network functionally extends the root system of their hosts. Thus, plants in symbiosis with AM fungi have the potential to take up HM from an enlarged soil volume.

Gohre and Paszkowski (2006)

Advantage of Using Indigenous Strains

The use of adapted indigenous fungal strains that are more suitable for phytostabilization and extraction purposes than laboratory strains.

Gohre and Paszkowski (2006)

3 Mechanisms of HM Toxicity

1. Direct interaction with proteins due to their affinities for thioyl-, histidyl- and carboxyl-groups, causing the metals to target structural, catalytic and transport sites of the cell;
2. Stimulated generation of reactive oxygen species (ROS) that modify the antioxidant defence and elicit oxidative stress; and
3. Displacement of essential cations from specific binding sites, causing functions to collapse. For example, Cd^{2+} replaces Ca^{2+} in the photosystem II reaction centre, causing the inhibition of PSII photoactivation

Sharma and Dietz (2008)

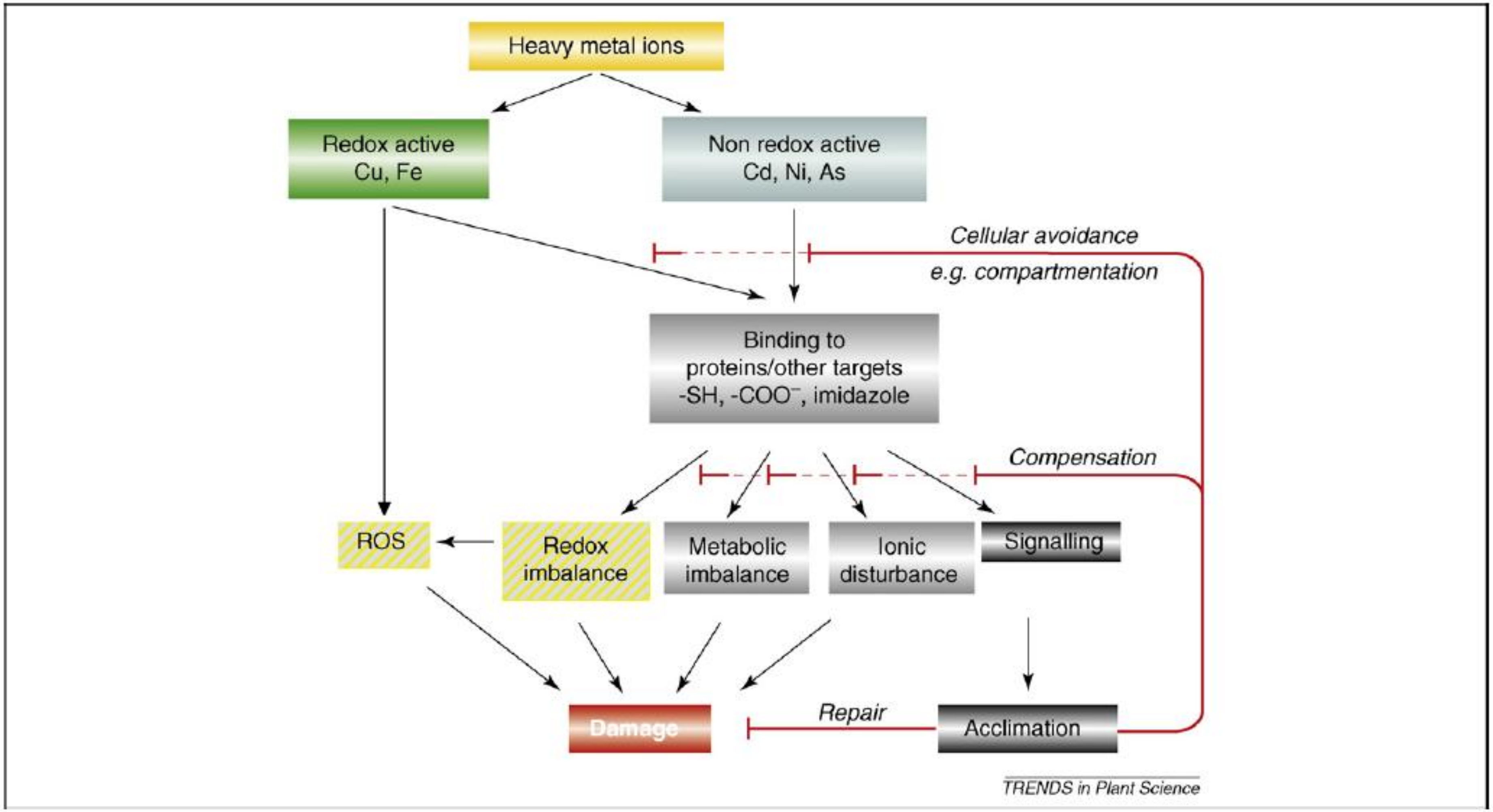


Figure 1. Principal mechanisms of heavy metal (HM)-induced damage development in sensitive plants and points of interaction and counteraction during acclimation in tolerant plants. Redox-active HMs directly elicit reactive oxygen species (ROS) generation. As a general property, HMs bind to and interfere with targets or compete for binding sites (-SH represents thiols, -COO represents carboxylic acids and imidazole represents histidyl residues), thereby altering target protein functions, which in turn causes changes in cell metabolism or triggers signalling events that can lead to acclimation. Activation of acclimation responses causes feedback loops with various sites of HM action, leading to, for example, the repair of damaged macromolecules, strengthening of the antioxidant defence system and lowering of HM concentrations in plasmatic compartments.

Sharma and Dietz (2008)

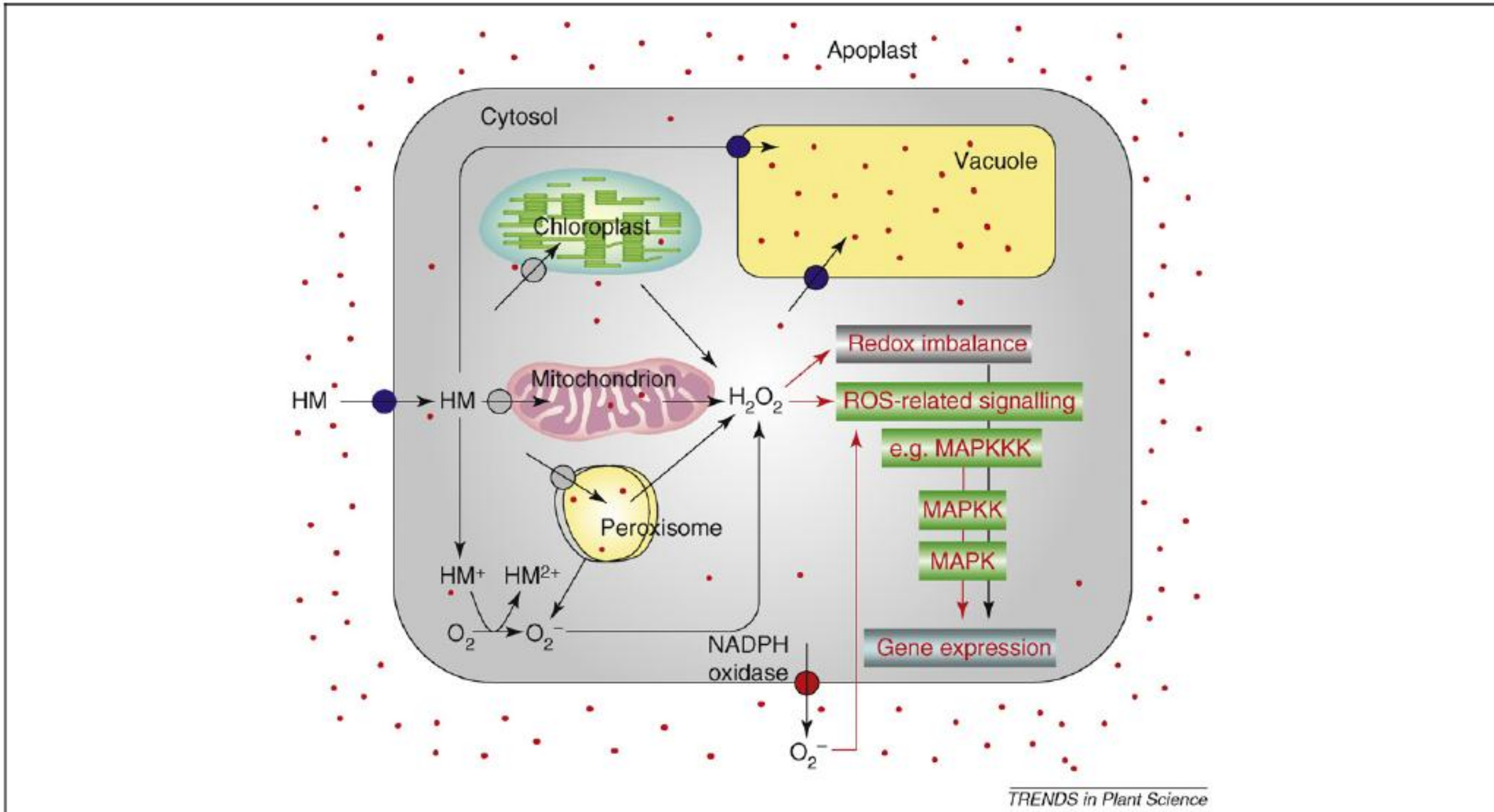
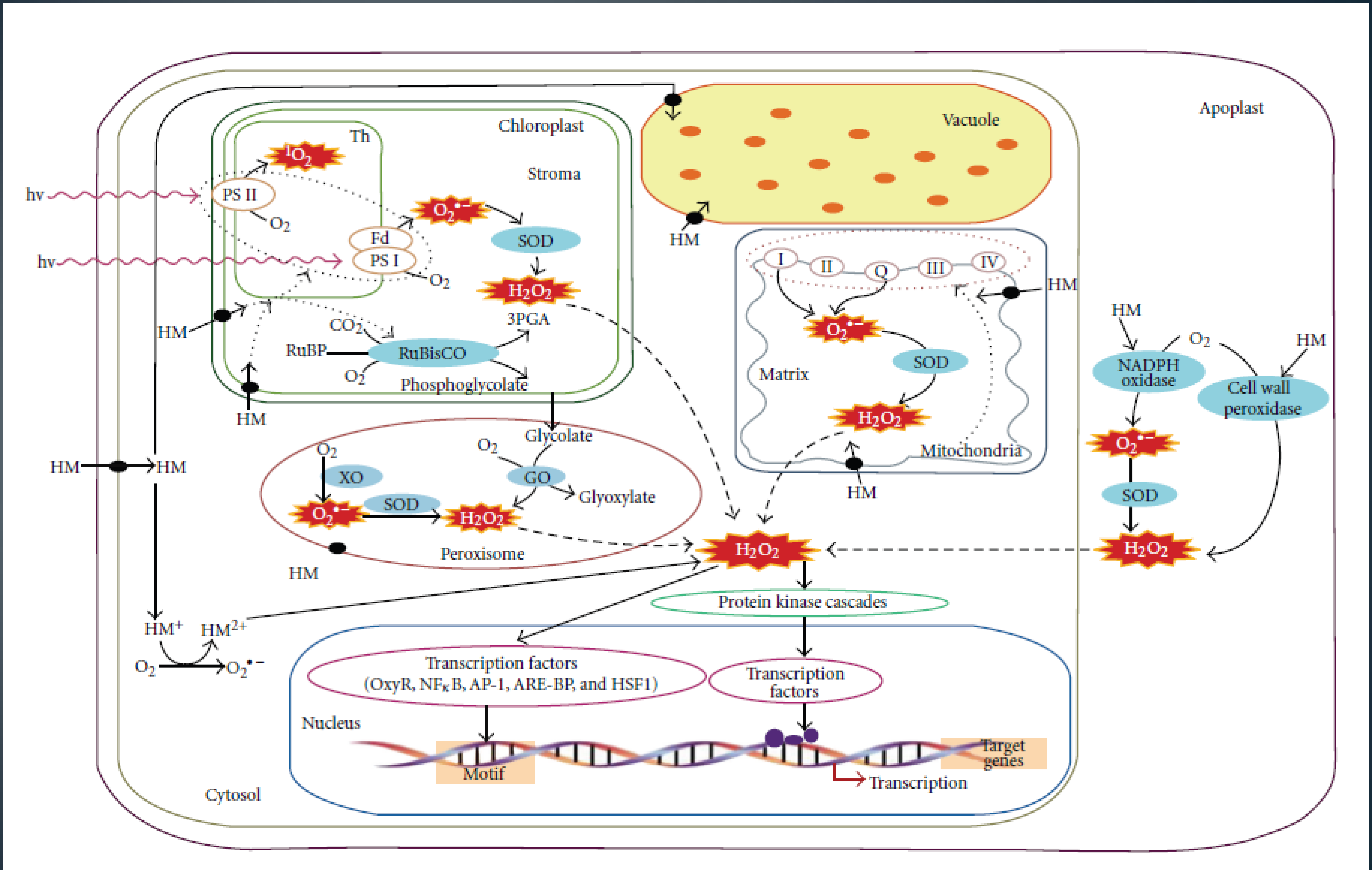


Figure 2. Pathways of heavy metal (HM)-dependent ROS generation. HM uptake by transporters and distribution to organelles is followed by ROS generation, stimulated either by HM redox activity or by HM effects on metabolism in a subcellular site-specific manner. HM-dependent activation of plasma-membrane-localized NADPH oxidase also contributes to the release of ROS. Excess ROS causes redox imbalances and disturbances in signalling processes (such as the MAPK pathways) that inhibit plant growth and might cause cell damage. Red dots symbolize the distribution of HM in the cell and apoplast.

Sharma and Dietz (2008)



Hossain, Piyatida, da Silva, and Fujita (2012)

Some Recent Findings

- cellular redox imbalances leading to oxidative stress and metal toxicity in plants
- indirect metal effect of cellular disregulation and progressive secondary damage development
- recent experiments revealed a clear relationship between metal stress and redox homeostasis and antioxidant capacity.
- salicylic acid have established a link between the degree of plant tolerance to metals and the level of antioxidants.

Sharma and Dietz (2008)

Influence of Organic Ligands

- Pb behavior in the soil-plant system and its phytotoxicity is greatly influenced by chemical speciation.
- Organic ligands are capable to modify Pb speciation by forming organo-metallic complexes of varying stability, bioavailability and toxicity.
- Efficiency of organic ligands to modify Pb behavior and impact greatly depends on their metal binding capacity.
- This binding capacity, in turn, depends on molecular structure, amount and type of functional groups of organic ligands.

Shahid, Pinelli, and Dumat (2012)

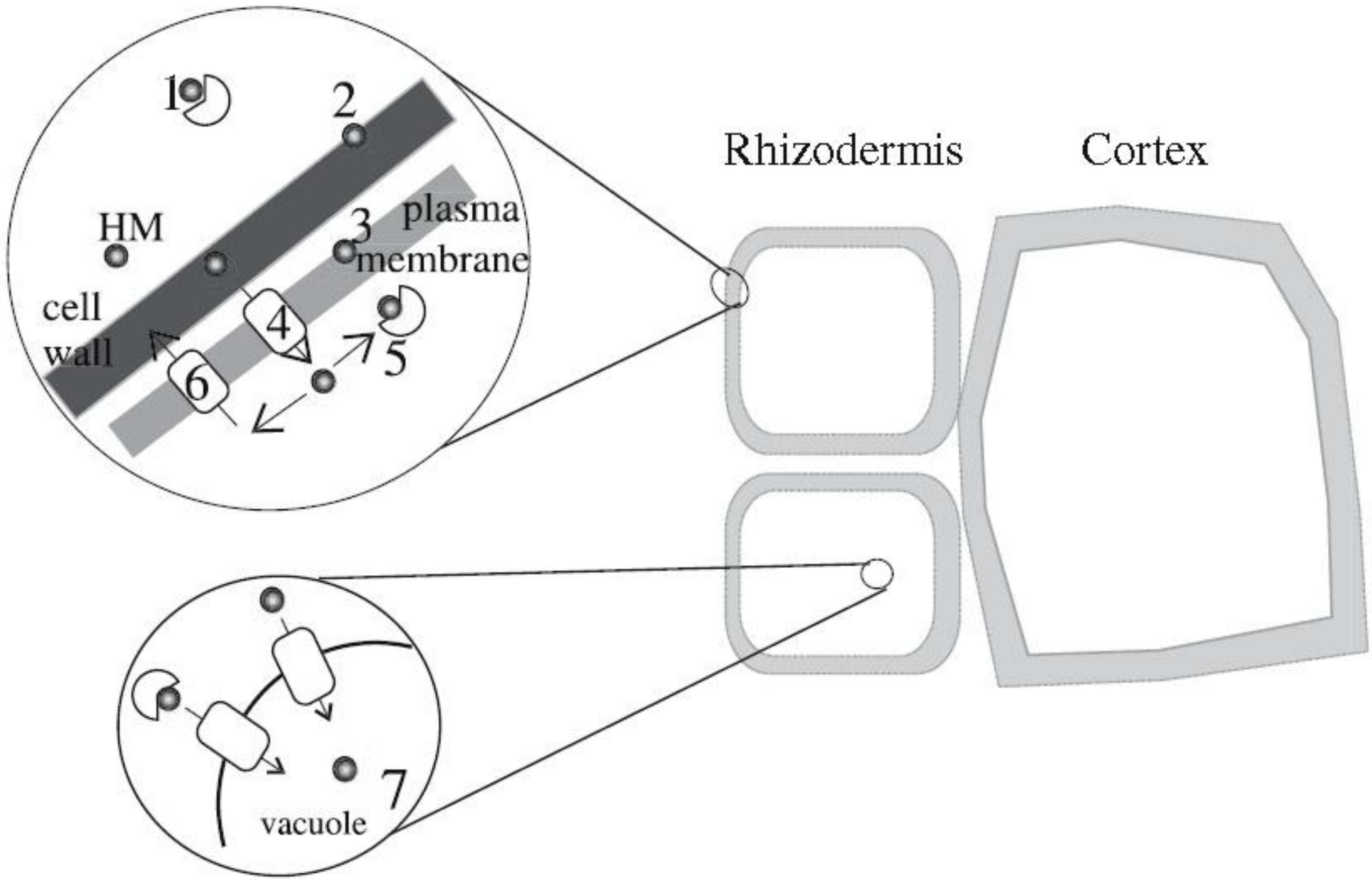
Detoxification Mechanisms

HM detoxification mechanisms of plants and fungi in arbuscular mycorrhiza symbioses:

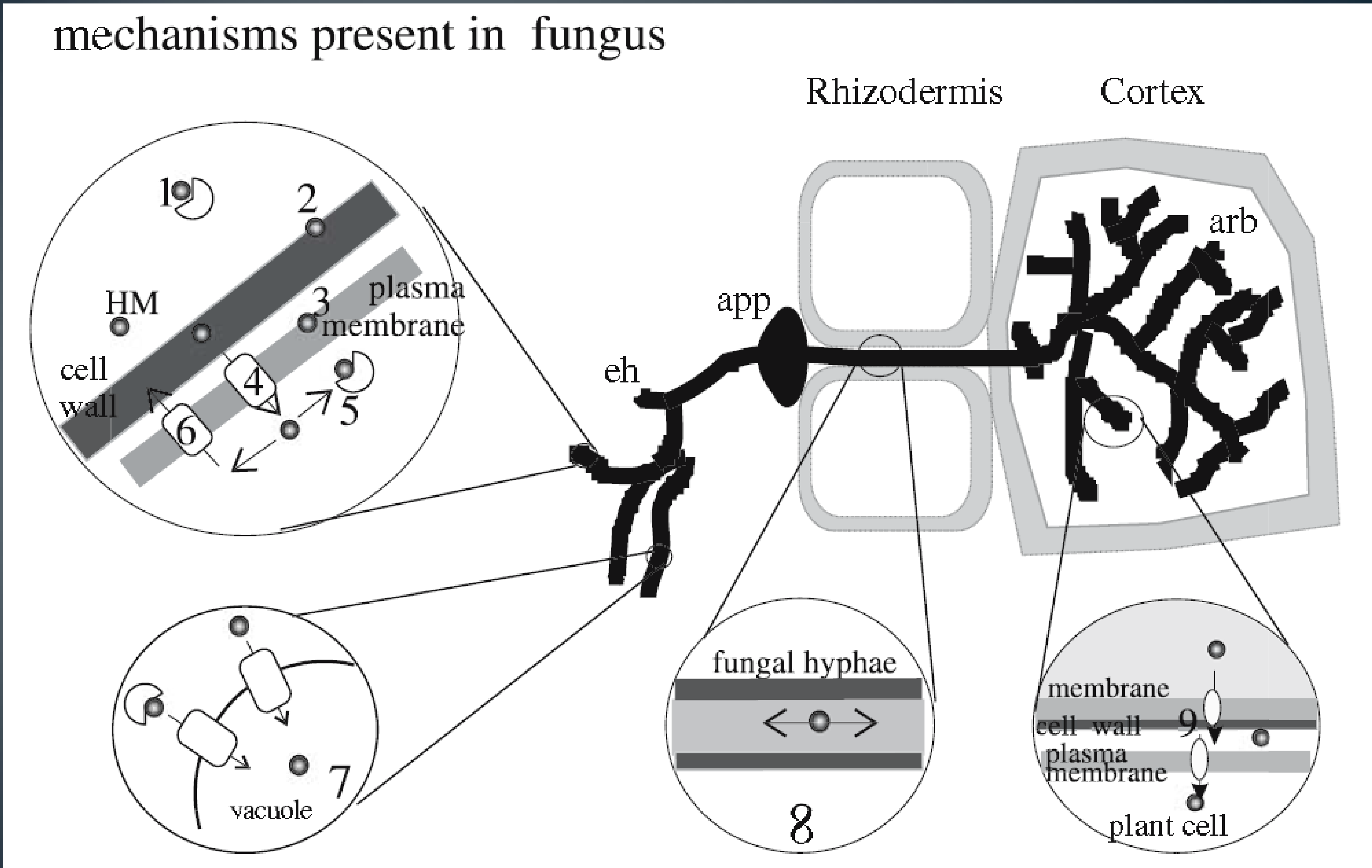
1. Chelating agents are secreted that bind metals in the soil, e.g. histidine and organic acids from the plant, glomalin from the fungus.
2. Binding of HM to cell wall components in plants and fungi.
3. The plasma membrane as a living, selective barrier in plants and fungi.
4. Specific and nonspecific metal transporters and pores in the plasma membrane of plants and fungi (active and passive import).
5. Chelates in the cytosol, e.g., metallothioneins (plants and fungi), organic acids, amino acids, and metal-specific chaperons.
6. Export via specific or nonspecific active or passive transport from plant or fungal cells.
7. Sequestration of HM in the vacuole of plant and fungal cells.
8. Transport of HM in the hyphae of the fungus.
9. In arbuscules, metal export from the fungus and import into plant cells via active or passive transport

Gohre and Paszkowski (2006)

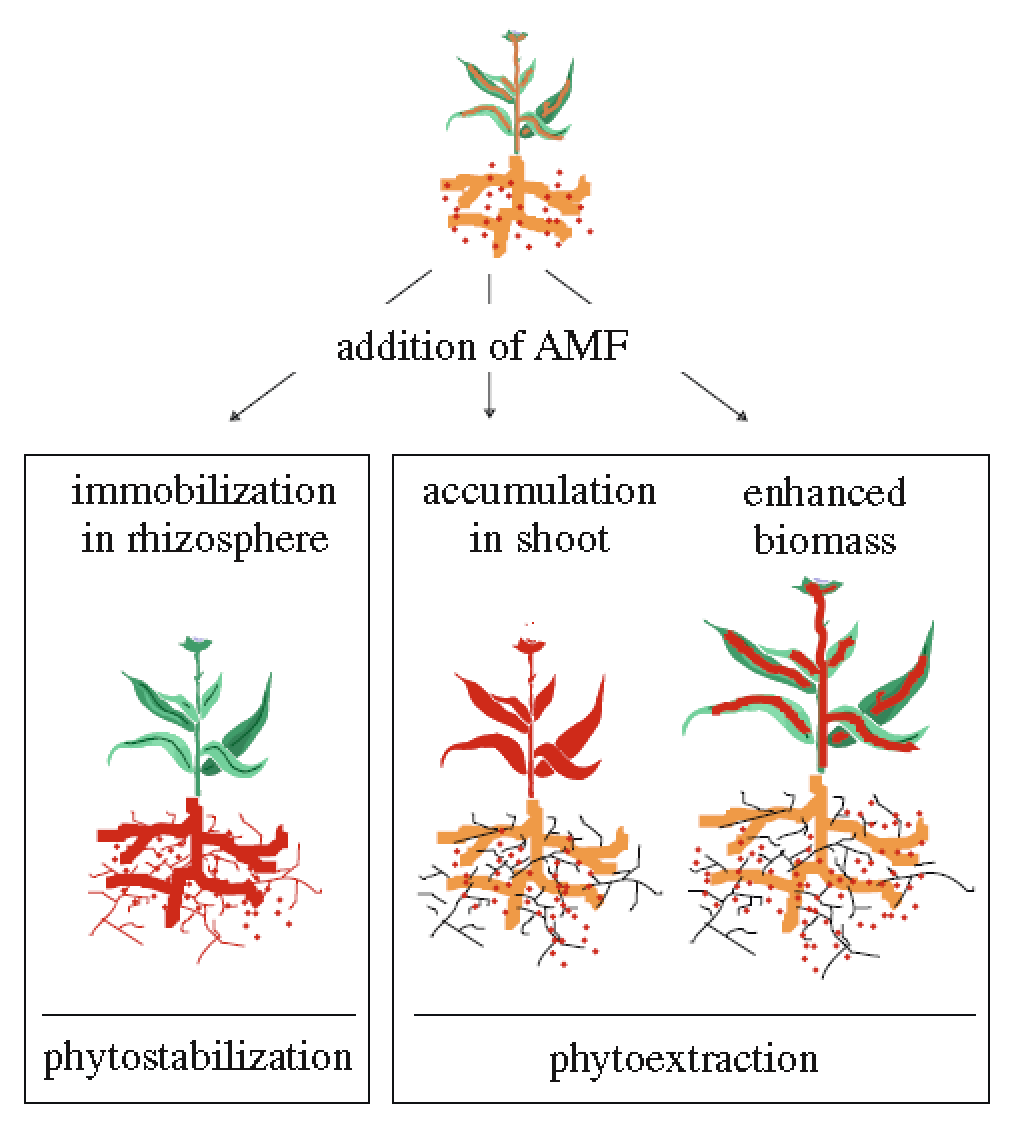
mechanisms present in the plant cell



Gohre and Paszkowski (2006)



Gohre and Paszkowski (2006)

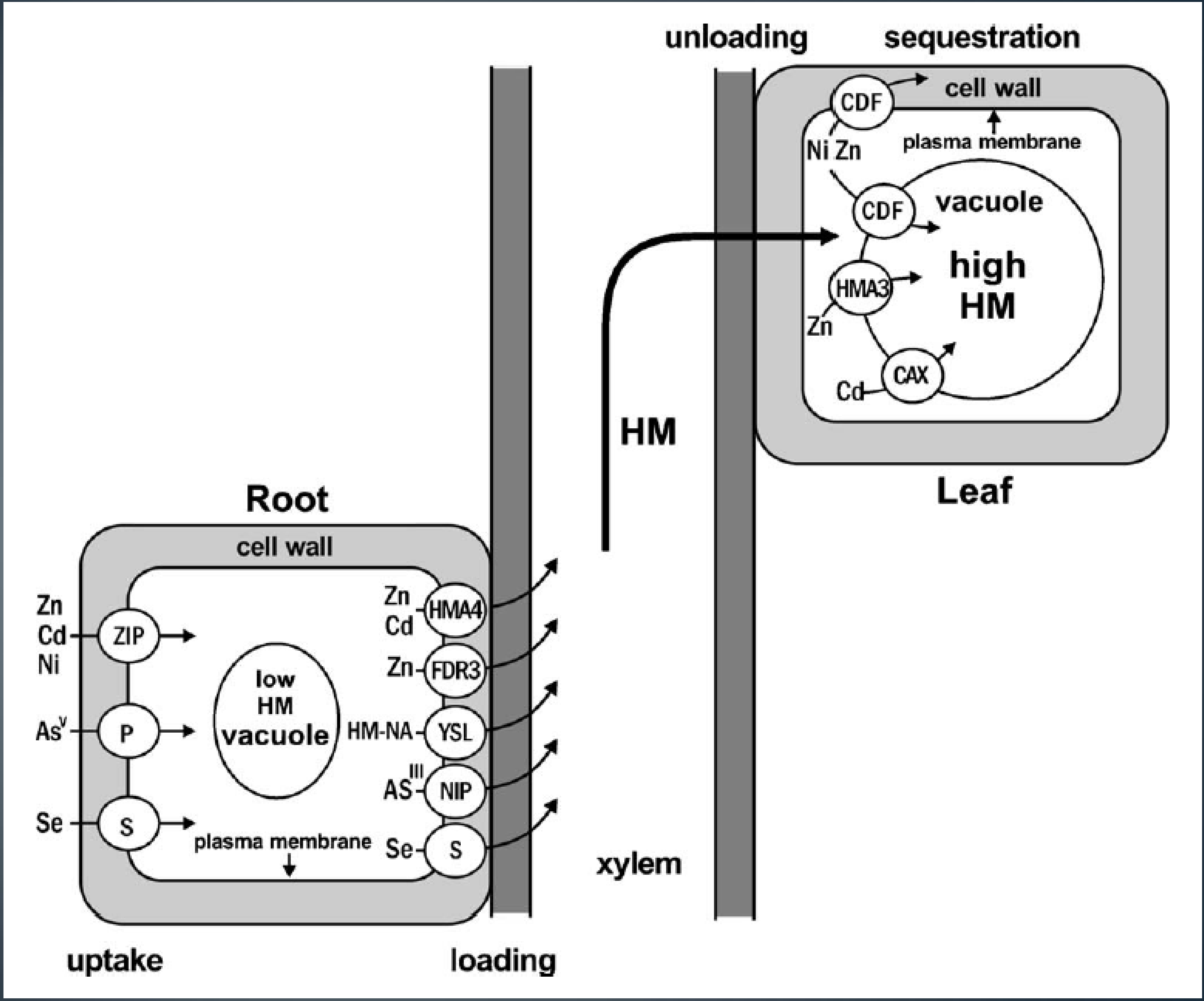


Gohre and Paszkowski (2006)

Notes

Contribution of AM fungi to phytoremediation of HM. Top: Non-mycorrhizal plant in HM-polluted soil. Left panel Improved stabilization of HM in soil upon mycorrhizal colonization; favored for phytostabilization. Right panel Enhanced uptake and transfer of HM to the shoot (left plant) and increased biomass of plants resulting from AM-fungi enhanced nutrition leading to increased removal of HM from soil (right plant); beneficial for phytoextraction. (red dots HM in the soil; orange or red plant or fungal parts: low and high concentrations of HM, respectively).

Gohre and Paszkowski (2006)

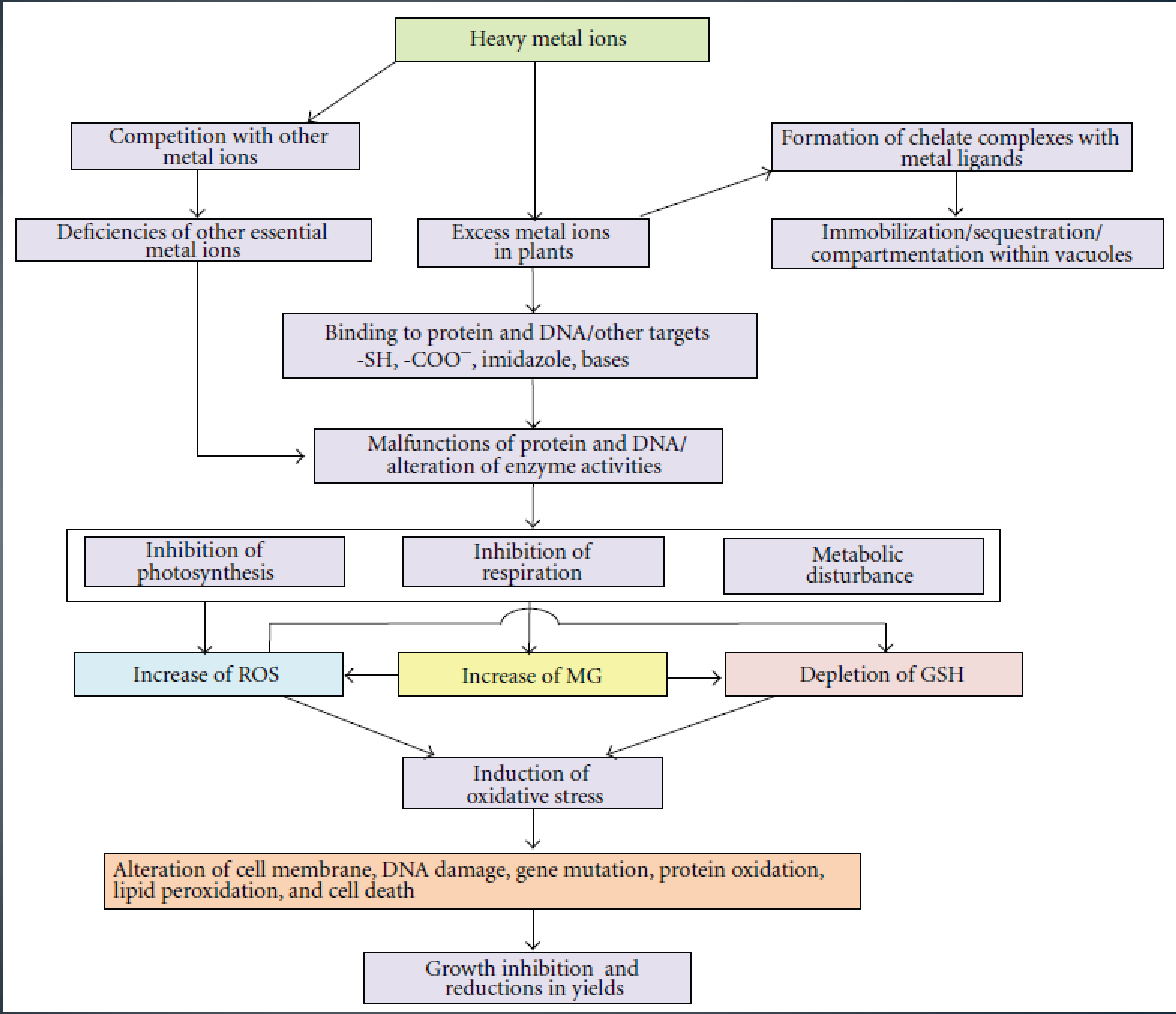


Rascioa and Navari-Izzo (2011)

Notes

A scheme showing transport systems constitutively overexpressed and/or with enhanced affinity to heavy metals, which are though to be involved in uptake, root-to shoot translocation and heavy metal sequestration traits of hyperaccumulator plants. (CAX = Cation Exchangers; CDF = Cation Diffusion Facilitators; FDR3 = a member of the Multidrug and Toxin Efflux family; HM= Heavy Metals; HMA= Heavy Metal transporting ATPases; NA= Nicotinamine; NIP = Nodulin 26-like Intrinsic Proteins; P = Phosphate transporters; S = Sulphate transporters; YSL = Yellow Strip 1-Like Proteins; ZIP = Zinc-regulated transporter Iron-regulated transporter Proteins).

Rascioa and Navari-Izzo (2011)



Hossain, Piyatida, da Silva, and Fujita (2012)

Notes

- A common consequence of HM toxicity is the excessive accumulation of reactive oxygen species (ROS) and methylglyoxal (MG), both of which can cause peroxidation of lipids, oxidation of protein, inactivation of enzymes, DNA damage and/or interact with other vital constituents of plant cells.
- Methylglyoxal (MG) = a cytotoxic compound.
- Glutathione (GSH) by itself and its metabolizing enzymes act additively and coordinately for efficient protection against ROS- and MG-induced damage in addition to detoxification, complexation, chelation and compartmentation of HMs.

Hossain, Piyatida, da Silva, and Fujita (2012)

http://benyaminlakitan.com