Chapter 17 The Responses of Salt-Affected Plants to Cadmium

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Abstract Salinisation and contamination by trace elements are expected to be some of the most critical environmental and sustainability issues in the forthcoming era of global warming and human population growth. Agro-ecosystems could be increasingly influenced by salinity, given that exploitation of saline pedo/hydroresources (>20 mM in water or soil saturation extract) will have to increase across many irrigated as well as rain-fed areas, despite poor yield and low food stuff quality. Using experimental and computational (modelling) approaches it has been well established that one of crucial plant responses under salinity is increased Cd phytoextraction. In salt-affected rhizosphere environments excessive concentrations of dissolved ions can impact Cd biogeochemistry through complexation and/or competition reactions with inorganic and organic ligands. For ecologically relevant conditions (e.g. Cd-contaminated and organically-depleted salinised soil) it was estimated that under low salinity (<30 mM) free Cd²⁺ ion predominates across a wide range of pHs (3.5–9), whereas in moderate-to-strong salinity (135–270 mM) Cd-chloro/sulphate complexes prevail (mostly comprising Cd-Cls). Although Cd-Cl interactions are still under intensive investigation and not fully understood, complexation is likely to be one of the main mechanisms for increasing Cd transfer to plants from the salt-affected rhizosphere. Also, there is evidence that Cd uptake by plants is underpinned by additive effects of salt and Cd stresses. Great efforts have been made in elucidating Cd biochemistry after uptake, (re)translocation and its deposition in plants differing in salt/metal tolerance; it is highly likely that the role of Cd-Cl complexation in plants is of negligible importance vs. that in the rhizosphere. Sharing similar or the same routes for crossing plant membranes with essential elements (Zn, Cu, Fe, Ca), Cd-organo complexes (with S, O and N radicals) relatively easily reach transpirational tissues via the xylem, and thereafter the depositing tissues dominantly via the phloem. Genetic engineering is a promising strategy

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in (1) increasing plant resistance to excessive soil salinity, and (2) producing genotypes for enhanced phytoremediation of areas overloaded by metals. However, under ecologically-relevant conditions (e.g. rhizosphere soil with poor metal-buffering capacity) Cd soil-plant transfer can be enhanced by soil salinity, simultaneously interfering with nutrient (Cu, Zn, Fe) extraction. So, if salinity resistance (as a multi-gene trait) is closely associated with gene loci responsible for Cd extraction, care needs to be taken that genetically improved (e.g. salt-resistant) genotypes do not impair crops foodstuff safety/security via increased Cd accumulation and/or micronutrient deficiency.

Keywords Salinity • Metal contamination • Cd complexation • Cd soil-plant transfer

Introduction

Salinity is the most widespread abiotic constraint to higher plants, affecting metabolism of cultured and/or native vegetation on~1 billion hectares of Earth's surface. Naturally- (sea water intrusion, groundwater fluctuation) and/or anthropogenically induced (unsustainable agricultural management practices, excessive groundwater withdrawal) environmental salinisation processes in the era of climate change and global warming may be especially pronounced and unpredictable. Recently, WMO (World Meteorological Organisation) confirmed that the last decade (2000–2009) was recorded as the warmest, and some of the recent years (e.g. 2009) are among the warmest for the past 160 years, i.e. since the beginning of official meteorological measurements in 1850 (WMO 2009). Under such conditions of global warming, salinity is expected to induce more severe phytoeffects, principally to cultivated glycophytes (crop food production), but also in long-term, exacerbate a certain interrelations (soil buffering potential to retain contaminants, provoke further soil degradation, decrease the quality of hydro-resources, reduce biodiversity etc.) in terrestrial ecosystems.

In the short-term, salinity impairs crop production and food/feed quality as a consequence of a wide range of physiological disorders known as salt stress effects (Zhu 2001; Chinnusamy et al. 2005; Zhang et al. 2012). In the long-term, particularly under specific geological (parent rock material), pedological (lower hydraulic permeability, excessive soil alkalinity and sodicity), atmospheric (high evapotranspiration demands, low precipitation) and/or hydrospheric (shallow ground water level) surroundings, salinity leads to permanent land degradation, i.e. desertification (Ondrasek et al. 2011). Topsoil crusting and salt crystallisation, dispersion of secondary clay minerals (soil aggregates), subsoil sodicity and/or toxicity of specific elements (boron, aluminium, chloride) are some of the most important long-term salinity impacts on the pedosphere.

Salt-affected areas are often situated on land used for agriculture or industrial purposes. For instance, a large part of some marine estuaries, such as Nile (Egypt) (Rashad and Dultz 2007), Murray-Darling (Australia) (Biggs et al. 2010), Ebro

(Spain) (Romani et al. 2011), Neretva (Croatia) (Romic et al. 2012), developed on floodplains (alluvial soils) and used for agriculture over a long time, are subject to salinisation. Large infrastructural projects (power generation, water flow regulation, irrigation) may substantially change the hydrology of an area (e.g. decrease downstream water refreshing) and exacerbate salinisation. In the modern era, estuarine ecosystems have been shown to be some of the most vulnerable regarding environmental protection and food safety and security. Due to their naturally low topsoil fertility (e.g. light sandy soils usually with <1% organic matter) or human-induced activities (e.g. emission of industrial/municipal effluents, intensive cultivation) aimed at retaining or even improving agricultural production, alluvial soils may gradually become overloaded by various (in)organic substances, i.e. potential contaminants. Estuarine environment thus may (1) represent an important sink for hazardous materials as a result of fluvial deposition of potentially-contaminated sediment material, and (2) become more susceptible to salinisation as a consequence of altered fresh water hydrology (river/aquifer level decreasing) and global warming (sea level rising).

Contamination of biosphere by trace elements (TEs) is expected to be one of the most critical environmental and sustainability issues of this century. Among TEs, cadmium (Cd) and its biogeochemical interactions are frequently elaborated regarding soil (rhizosphere) ecology and transfer to higher plants, i.e. into the food chain (McLaughlin and Singh 1999 and references therein; Adriano et al. 2004). Summarising the most of soil-, nutrient solution- and plant-based studies yields a several key statements for Cd: (1) its rhizosphere biogeochemistry is highly pH-dependent; (2) it is relatively easily bioavailable, especially from acidic environments; (3) it has a substantial potential for complexation/chemosorption with inorganic (salts) and organic ligands; (4) it does not any known essential biological function in plants (animals/humans), although shares some uptake/translocation mechanisms with particular essential elements; (5) it is preferentially accumulated in underground plant tissues; (6) it enters the human/animal food chain via food/ feed consumption; and (7) it is toxic to a wide range of organisms, including plants and humans.

Salinisation of soil environment may substantially change Cd biogeochemistry and consequently its dynamics in the soil-plant-human continuum. For instance, by adding one of the most used agro-chemicals such as phosphatic fertilizers (e.g. diammonium phosphate, potassium dihydrogen orthophosphate) and liming salts (e.g. calcium carbonates, calcium hydroxides) can increase soil Cd adsorption, i.e. reduce its phytoavailability and/or phytotoxicity (Basta et al. 2001; Bolan et al. 2003a, b). In contrast, NaCl as the widespread salt in the nature can improve Cd mobilization by the formation of soluble inorganic chloride complexes (see Sect. 3.2.1) and thus enhance Cd phytoaccumulation, i.e. food/feed contamination. In the alkaline sodic soils Cd mobility and uptake can be enhanced due to facilitated organo-complexation with certain DOC (dissolved organic carbon) fractions (Harter and Naidu 1995). Using artificial seawater (15 g salts/L), Lores and Pennock (1998) obtained 100% desorption of Cd from dissolved organic complexes at relatively low DOC concentration (10 mg humic acid/L). Therefore, it is of great importance to elucidate Cd interactions under different salinity given that some outcomes could be highly important for improving management strategies to minimise Cd contamination and achieve food safety and security.

Plant Responses to Increased Environmental Salinity

Increased sodicity (Na) and chloride (Cl) concentration are two the most naturally widespread and intensively studied environmental types of salinity affecting plant populations worldwide. Unfortunately, in agricultural food/feed production those salinities are often accompanied by numerous environmental constrains such as: (1) water-logging or water scarcity, (2) high evapotranspirational demands, (3) shallow groundwater salinity, (4) soil acidity/alkalinity, (5) soil organic matter depletion, (6) ion toxicity (B, Al), (7) increased exchangeable sodium percentage (ESP) and/or sodium adsorption ratio (SAR), and (8) disturbed soil structure (Ondrasek et al. 2011). Complex interrelations among these variables make it almost impossible to detect which constraint is the major limitation factor in plant growth (e.g. Dang et al. 2008); hence, land management of salt-affected areas is exceedingly complicated with usually high cost-to-benefit ratio for grown crops.

In a majority of cultivated plant species, the important economic responses to increased environmental salinity (e.g. a decline in yield quality/quantity) occur even at relatively low salinity in either (1) soil (e.g. threshold salinity of ~10 mM reduced bean and onion yield by ~20%) (Chinnusamy et al. 2005) or (2) irrigation water (e.g. sprinkler irrigation with~10 and~30 mM salinised solution reduced watermelon yield by 50 and 100%, respectively, of the yield achieved with drip irrigation using the same salt concentrations) (Romic et al. 2008).

Many other plant metabolic functions (e.g. root/leaf membrane selectivity, photosynthesis, transpiration) (e.g. Grattan and Grieve 1999) usually are seriously compromised under excessive salinity. Moreover, using a variety of experimental approaches and many plant genotypes, it has been well established that one of crucial plant responses to increased salinity could be reduced ion selectivity resulting in enhanced Cd phytoextraction (see Sect. 3.2.1).

Cadmium in the Pedosphere

Origin of Soil Cadmium

Under natural pedosphere conditions, native soil Cd mostly has geogenic origin. Some of the most Cd-enriched natural materials are sedimentary rocks (e.g. phosphorites up to 980 and marine shales up to 219 mg Cd/kg) and sulphide minerals (e.g. sphalerite up to 50,000 and metacinnabar up to 117,000 mg Cd/kg) (Krishnamurti et al. 2005). These minerals are fairly rare in the surface lithosphere, which is the main reason for Cd naturally occurring in trace amounts, usually at several tenths of mg per kg of dry soil. Generally, soils with <0.5 mg Cd/kg (Zovko and Romic 2011), i.e. soil solution with <0.3 μ M (Sanitá di Toppi and Gabbrielli 1999) can be considered as non-contaminated, whereas in contaminated environment Cd concentrations may be several magnitudes higher.

The main contributors of high Cd emission to environment during recent past have been industry, urbanisation and agriculture. Given certain physical properties of Cd (melting point 321°C), during the ore smelting and emissions from metallurgic plants, Cd relatively easily reaches atmosphere and can cause long-distance environmental contamination. From the anthropogenic Cd emission annually (~30 million kg), about 8 million kg (27%) is emitted to the atmosphere mostly as a consequence of ore smelting and related heavy industry (metallurgic) activities, whereas a dominant portion (74%) of Cd emission (~22 million kg) is deposited/applied to pedosphere, mostly as industrial wastes/by-products (9.5 million kg), urban wastes/ effluents (4.4 million kg) and agricultural wastes/fertilisers (2.4 million kg) (adopted from Sanitá di Toppi and Gabbrielli 1999).

On salt-affected soils, which are usually deficient in phytonutrients and/or organic matter, a common practice for improving crop production is application of mineral (inorganic) and organic fertilisers/amendments. As mentioned above, sedimentary phosphorus-(P) and Cd-enriched minerals like phosphorites, as a main raw material for P fertilisers, are some of the most ubiquitous sources of Cd contamination in modern agricultural production. An application of P fertilisers may be totally avoided (extensive pastures), but on the other side additions of >500 kg/ha (double cropping in intensive horticulture) (Romic et al. 2008) may in a long-term increase soil Cd from 0.3 up to>4 g/ha annually (e.g. Singh 1994). This is in a line with recent findings by Romic et al. (2012) who in the horticultural topsoils observed high association of bioavailable P and total Cd content probably due to overuse of mineral P fertilisers.

Most soil organic amendments from industrial/urban (biosolids, composts) or agricultural (slurries, manures) sectors used for improving soil productivity are usually enriched (contaminated) by Cd even more than P-fertilisers. Allochthonous soil Cd, irrespective of whether it enters the pedosphere via previously mentioned antropogenic activities or natural processes (precipitation, flooding), is firstly deposited in the surface horizons and thereafter is transferred by soil management practices (e.g. ploughing, discing) into the rhizosphere zone of cultivated crops. However, even on such a relatively small scale (rhizosphere vs. bulk soil, soil solution vs. particulate soil), certain soil properties can be markedly different, thus variably affecting Cd chemical forms/distribution, i.e. its environmental biogeochemistry (Ondrasek and Rengel 2012).

Out of the total soil Cd content, in most pedospheres and climates, almost negligible Cd portion (<1%) (e.g. Christensen and Huang 1999) is bioavailable. However, this fact does not diminish ecological importance of Cd highlighted in recent reviews by Kabata-Pendias (2004) and Clemens (2006).

Chemical Speciation of Cd in Salinized Environment

According to Florence (1982), chemical speciation of Cd would be a function of concentrations of its various chemical forms (species) that together make up the total Cd concentration (Cd_{TOT}) in a given sample. However, mobility, bioavailability and thus toxicity of Cd in soil media in most cases cannot be related only to Cd_{TOT}. Particular forms in the Cd_{TOT} pool differ in their physico-chemical properties, from the readily available to the highly unavailable, and thus have varied environmental impacts. Accordingly, Cd_{TOT} content comprises three main physico-chemical Cd forms: (1) dissolved in soil solution (the most bioavailable and potentially the most toxic), (2) adsorbed onto soil in/organic particles (less bioavailable but still potentially toxic), and (3) Cd precipitates (inactive, i.e. non-toxic).

Chemical speciation as well as chemisorption (adsorption) and complexation of Cd with particular inorganic (chlorides, carbonates, Al/Fe/Mn hydroxides and organic (low-/high-molecular weight) ligands in soil environment can be detected, i.e. predicted (modelled) by appropriate analytical/computational procedures (Fig. 17.1). Formation of Cd precipitates (salts) is very rare in most naturally-occurring environmental conditions; however, it may be induced in controlled experiments and simulated by modelling. For instance, speciation-solubility geochemical modelling is a convenient concept for studying Cd (TEs) mobility and bioavailability, i.e. assessing a potential risk from metal conditions. Certain methods/techniques for controlled (e.g. rhizoboxes, soil columns, chelate-buffered nutrient solution cultures) or non-controlled field (e.g. lysimeters) conditions can be useful tools for quantifying Cd in the soil solution pool and its mobility to other surrounding interfaces, as well to plants (food) (Fig. 17.1).

The soil (rhizosphere) solution generally contains most of the readily bioavailable (dissolved) and potentially the most toxic Cd forms such as free ionic hydrated Cd²⁺. Consequently, the potential Cd toxicity is mostly related to specific Cd²⁺ concentrations and physico-chemical properties of aqueous soil media, particular pH as a soil master variable (e.g. Rengel 2002). Even though dispersed inorganic (e.g. metal hydroxioxides) and organic (e.g. humic acids) colloids cannot be technically considered soil solution constituents (Helmke 1999), their active interfaces (can be altered by sampling techniques and filtration) are highly relevant in biogeochemistry of the dissolved Cd pool (Fig. 17.1). In salt-affected environments, excessive concentrations of dissolved salts, particularly anions (Cl⁻, SO₄²⁻, HCO₃⁻) have a large influence on Cd chemical speciation through complexation (McLaughlin and Singh 1999). Also, presence of cationic metals (Na⁺, Mg²⁺, Ca²⁺) is important for (1) competition with in/organic rhizosphere matrix constituents (Ondrasek and Rengel 2012), thus increasing Cd solubility and mobility in the rhizosphere solution, and (2) possibly influencing pH reaction of the media (e.g. Lores and Pennock 1998).

The predominant salt forms in salinised agro-exploited natural resources (e.g. soils, water used for irrigation) are those of sodium (Na⁺), chloride (Cl⁻) and sulphate (SO₄²⁻) (Ondrasek et al. 2011), and they may influence Cd bioavailability in



Fig. 17.1 Some analytical and computational approaches for determination/evaluation of Cd chemical speciation under field as well as controlled-experiment conditions

the rhizosphere. In the next section, an emphasis will be on Cd biogeochemistry and Cd transfer into food/feed plants under salinity caused by Cl⁻, Na⁺ and SO₄²⁻. To create a supporting material for further discussion, a Cd "pre-screening modelling" (i.e. Cd speciation assessment) was performed for realistic salt-affected aqueous environments (e.g. soil solutions of salt-affected sandy soils, salinised channel waters, sea-intruded aquifers) over a wide range of pH levels. For instance, the modelled pH range 3.5–9.5 covers the most naturally-occurring conditions (e.g. Tipping 2005), whereas under strong acidity (pH < 3.5) or alkalinity (pH > 10.5) it is almost impossible to characterise in full the proton-affinity distribution because of a lack of reliable data (Kinniburgh et al. 1999). Inorganic speciation modelling in the Visual MINTEQ framework (Gustafsson 2006) was done using a default thermodynamic database and settings (e.g. Davies equation at 25°C), whereas organic complexation was performed by incorporated NICA-Donnan model (Kinniburgh et al. 1999) as one of the most advanced models for competitive Cd binding to dissolved high-molecular-weight organics (DOC) (Weng et al. 2001). Assumed constant concentrations of Cd (1 μ M) and DOC (1 mg/L) in all models correspond well to Cd-contaminated and organicallydepleted salinised soil environments.

Free Cd²⁺ pool was estimated from the modell to predominate in most of tested pHs but only under low salinity, whereas in moderate-to-strong salinity conditions the most prevalent pool was Cd-chloro-/sulphate complex (Cd-Cl/Cd-SO₄) (Fig. 17.2). Inorganic Cd-complexes mostly comprised CdCl⁺, CdCl₂(aq), Cd(SO₄)₂⁻² and CdSO₄(aq) species (data not shown), although concentration of Cd in the chloro-complex (vs. Cd-SO₄) was multi-fold higher (Fig. 17.2). In all three models, inorganically-complexed and free Cd²⁺ pools decreased with pH rising, contrary to organically-complexed pool (Cd-ORG) whose concentration positively responded to increasing pH, but predominated only under high alkalinity (pH>9.0) and low salinity (Fig. 17.2).

Cl-induced Salinity and Cd Soil (Rhizosphere) Solution-plant Transfer

Over the last several decades it has been well documented that Cl salinity may be of crucial importance for food/feed safety and security (quality) with respect to Cd (trace metals) contamination, because of Cl effects on Cd mobility (Fig. 17.2) and thus soil-plant transfer (Table 17.1). In a survey study with 124 paired topsoil and durum wheat grain samples collected under highly variable field conditions (e.g. pH 5.95–8.07; Cl²⁻1696 mg/kg; Cd_{DTPA} 0.064–0.155 mg/kg) Norvell et al. (2000) confirmed that Cd phytoaccumulation in grains (Cd_{grain}) was strongly positively correlated (P < 0.01) with water-extractable soil Cl (Cl_w). Although Cd-Cl interactions are still under intensive investigation and not fully understood, complexation is likely to be one of the main mechanisms for enhancing Cd uptake from Cl-affected rhizospheres and deposition in plant tissues (Table 17.1). Generally, it is accepted that cadmium free cationic form (Cd²⁺) is the most efficient in crossing the root



Fig. 17.2 Concentration distribution of Cd species in particular pools (uncomplexed cationic Cd²⁺; chloro-complexed Cd-Cl; sulphate-complexed Cd-SO₄ and organo-complexed Cd-ORG) modelled by Visual MINTEQ under different pHs and salinities (in mM): (**a**) low (Na⁺ 15, Cl⁻ 12, SO₄²⁻ 1.5), (**b**) moderate (Na⁺ 75, Cl⁻ 45, SO₄²⁻ 15) and (**c**) strong (Na⁺ 150, Cl⁻ 90, SO₄²⁻ 30). In all models, concentrations of Cd (1 μ M) and DOC (1 mg/L) were constant

membranes (Sect. 3.3). Most studies listed in Table 17.1 as well as others (Bingham et al. 1984; Boukhars and Rada 2000; Li et al. 1994; McLaughlin et al. 1994, 1997; Smolders and McLaughlin 1996a, b; Smolders et al. 1998; Weggler-Beaton et al. 2000; López-Chuken and Young 2005; López-Chuken et al. 2012) indicated possible root extraction of certain Cd forms from the Cd-Cl pool, although with low efficiency (in comparison with Cd^{2+}). Based on various experimental approaches (e.g. nutrient solution, soils) and a wide range of plant species (differing in salinity and Cd tolerance) and conditions (pH, Cl concentrations/length of exposure), it was suggested that certain Cd-Cl forms could be phytoavailable, i.e. enter roots (1) directly as a Cd-Cl-complex and/or (2) serving as a proxy form for facilitated diffusion to the root-binding sites, and afterwards dissociating and entering cells as uncomplexed Cd²⁺ (Cl⁻) (McLaughlin et al. 1994, 1997; Smolders and McLaughlin 1996a, b) (Fig. 17.3 in Sect. 3.3).

In interpreting results from Table 17.1, it is impossible to consider all variables and their influence to Cd phytoavailability. Soils (especially clayic, organic) usually have a complex matrix, composed of different organic (inorganic) metal sorbents that interact with Cd and decrease its concentration (activity) in the dissolved pool (Ondrasek et al. 2009a; Ondrasek et al. 2012). Similarly to some other metals (e.g. Cu), Cd has a strong potential for complexation with organic ligands (Romic et al. 2012). Also, a soil background and applied Cd concentrations varied considerably, from inorganic (e.g. CdCl₂, Cd(NO₃)₂, fertilisers) to organically-enriched sources (histosols, biosolids) (Table 17.1). Phytoavailability of applied Cd is generally higher from inorganic vs. organic sources, particularly under salinity (NaCl) (Weggler et al. 2004). For instance, biosolids and some other organically-enriched materials (ORG) (e.g. peats, composts) are frequently used for improving fertility of organic matter- and nutrient-depleted soils, although simultaneously may induce contamination by Cd (TEs). Due to a substantial portion of negatively-charged reactive interfaces, ORG substances strongly compete with Cl⁻ (SO₄²⁻) ligands in

When present, type of letters (small/capital) indicates inside of which groups treatments were compared. Treatments with the same letters are not significantly different. Approximate values (\sim) are taken from graphical presentation in cited references Table 17.1 Soil (rhizosphere) solution and plant responses to induced salinity and Cd contamination in nutrient solution (NS) or soil experiments.

	EXI	PERIMEN	TAL C	SNOILIGNO.				SOIL SOLUTION AND PLANT	RESPONSES
		N	Tedium (characteristics				Cd content	Biomass
				Salini	ty	Cd	In soil	In nlant tissue	Parameters
Plant spp. T.	ype Te	exture	Ηd	Type mM	duration	content mg/kg	solution µg/L		on dry or fresh weight (DW or FW) basis
1. Soil								Shoot	Shoot DW
Cereal We	ggler et al. 20	004						(% of total Cd in soil solution)	g/pot
Triticum aestivum cv. Halberd	i L. A	A sand	ç	0		0.12	n.d.	n.d.	1.32a
	A 95%	A sand	<i>c.</i> 0	27.4 NaCl	30	0.12	0.23	0.383	1.11a
	Alfi bid	sol+8% osolid		27.4 NaCl	days	0.72	1.6	0.444	1.10a
	Alfis bid	sol+16% osolid		27.4 NaCl	1	1.32	0.75	0.114	1.32a
2. Soil								Shoot	Shoot DW
Cereal Kh	oshgoftar et ;	al. 2004						mg/kg	g/plant
Triticum aestivum	ι L.		7.8	0			10a	0.90a	~15a
cv. Kusnan	Calc 54%	igypsids % clav		120 NaCl	35 davs	3.8	130b	1.27c	~11b
				120 NaNO ₃			20a	1.01b	~11b
3. Soil								Shoot	
Cereal Khe	oshgoftarmaı	nesh et al.	2006					mg/kg	
Triticum aestivum	، L.			0			*14a	**0.01a	
cvs. Kusnan, Kav Cross and Falat	AIF, Calc	igypsids	7.6		35 daue	3.2	5		
Triticum turgidum	1 L. TU	/0 CIA 9		180 NaCl	adaa		*960	dCU.U**	
cv. Durum				_					

4.	Soil							Grain		Grain yield	
Cereal	Ozkutlu e	t al. 2007						mg/kg		g/plant	
Triticum tur,	gidum L.			0	140			~2,8A		3.5A	1
CV. Dalcall-2	000			167 NaCl ^x	secolids	1.27	1	~3,8B		3.2A	
				0				0.05a		2.52a	1
		Clayic	8.1	167 NaCl ^y +8.8 CdCl2	140		I	0.55c		2.79a	
				167 NaCl ^y +8.8 CdSO4	seconds	0.27		0.34b		2.40a	1
				167 NaCl ^y +8.8Cd(NO ₃) ₂			1	0.49bc		2.57a	1
5. Vegetables	Soil McLaughl	lin et al. 1998b						Shoot nmol/g	Total uptake nmol/pot	Shoot DW g/plant	
Beta vulgari,	sL.cv.			0			2.61a	~11.6A	18.2A	~0.187A	
	זומוונ	Alfisol	r v	$120 \text{ Na}_2 \text{SO}_4$	19	0.31	7.9c	~20.84B	12.6B	~0.079B	
		81% sand	0.4.	0	days	extractable)	2.63a	~12.5a	18.2a	~0.181a	
				120 NaNO ₃			5.0b	~16.22a	7.3b	$\sim 0.061b$	
6. Vegetables	Soil Ondrasek	et al. 2009a, 200	960					Leaves mg/kg	Pulp mg/kg	Yield kg/plant	
Cucumis me. Dawn	lo L. cvEarl	y		0	50 1(60-73.)	5.4^{3n}	18.4 ³ⁿ	10a	¹ (0.4a)	¹ (3.72a)	
				60 NaCl	days			15b	$^{1}(0.4a)$	$^{1}(1.94b)$	
		Histosol >90% OM	5.7					Leaves mg/kg	Hypocotyls mg/kg	Yield g/m2	
Raphanus sa.	tivus L. var.			0	34	u2 €	77 A ³ⁿ	27.5A	6.4A	659A	
sauvus, cv. 1	arzan			60 NaCl	days	0.7	7 .77	33.1B	5.9A	426B	
7. Vegetables	Soil Oporto et	al. 2009						Root uptake flux pmol/cm ² h	Shoot mg/kg	Shoot DW mg/plant	
Spinacia ole.	racea L. cv.	Viking		0				~0.1a	~9a	448	
			6.7	120 NaCl	18 davs	0.4		~0.6b	~55b	160	
				120 NaNO ₃	Ì			~0.2a	~25c	114	
										(continued	

(-							_				
			0				~10A		~700A		150	
			120 NaCl		10.5		~10A		$\sim 2000 \mathrm{B}$		13	
			120 NaNO ₃				~10A		$\sim 1000 \mathrm{B}$		41	
8. Soil			-				Root	Steam	Leaf		Root le	ngth
Legume Helal et al. 1999								g/gµ		DW g/plant	densi cm/]	£.,1
Leucaena leucocephala L. Sano	dy		² Control			24a	3.96a	2.17a	0.38a	47a	141;	T
73% s	and	7.9	² Control +	134 days	0.76	35b	3.75a	2.04a	0.89b	57b	1281	
SN _c 6			10 NaCl		ľ	27	Ina	l plant bio	mass	ΕW	DW	Lenath
Submersed spp. Fritioff et al. 2	2005				βη	L,		μg/g		g/L	g/L	cm
Elodea canadensis L.			0					269a		8.7a	0.45a	78.5a
			0.5 NaCl					244b		8.7a	0.44a	78.8a
			5.0 NaCl	16				212c		8.3a	0.41a	78.2a
Potamogeton natans Michx.		5.0	0	hours	112	4		151A		11.7A	1.35A	
			0.5 NaCl	SIDUL		1		100B		11.7A	1.39A	
			5.0 NaCl					63C		10.3A	1.19A	
10. NS							Root	-	Leaf	Root DV	V Shoo	ot DW
Cereal Mühling and Läuchl	i 2003						g/FW		μМ		g/pot	
Triticum aestivum L. cv. Chinese Sl	pring		1 NaCl	ç	0		0		0a	~5.8a	Ŷ	32a
	-	6.0	1 NaCl	s weeks	22.5 (2	weeks)	~440a		23ab	~5.0a	2	20b
			75 NaCl		1124 (1	week)	~490a		33b	~4.1a	2	[3b
11. NS							Root		Shoot	Root DV	V Shoe	ot DW
Vegetables Smolders and Mclau	ghlin 19	96a					1	oer kg DW	1		mg	
Beta vulgaris L., cv. Fordhook Gi	ant		0.01 NaCl				$\sim 250 \text{ mg}^{4n}$		$^{-33} \text{ mg}^{4n}$	7.0	ŝ	2.4
unbuilerea			120 NaCI	:			~115 mg		$\sim 1 / mg^{-1}$	2.5	ń ı	2.0
NTA-buffered		6.1	0.01	Π.	5.	, ,	~100 mg^		~10 mg^"	5.0	5	1.6
		;	120 NaCl	days			~115 mg		~15 mg	5.2	5	1.4
FGTA-buffered			0.01			1	~240 µg		~60 µg	11.1	6	2.5
POINT-PIIN			120 NaCl				~310 µg		~60 µg	12.6	10	6.6
12. NS						1	Root		Shoot	Root DV	V Shoe	ot DW
Vegetables McLaughlin et al. 19	98a							mmol/kg			g/pot	
Beta vulgaris L., cv. Fordhook Gia	int	- L Y	$8 Na_2 SO_4$	11	2		~1.4a		~0.16a	~0.20a	2	.8a
		0.1	$58 Na_2SO_4$	days			~1.6a		~0.15a	~0.19a	~]	.9a

 Table 17.1 (continued)

Mean value of four bread and one durum wheat genotypes

Salinity treatment was applied (nearly after 80 and 110 days of growth) by immersion of leaf to NaCl solution "Mean effect of NaCl salinity on shoot Cd concentration in four bread and one durum wheat genotypes

Salinity and Cd treatment were applied (nearly after 80 and 110 days of growth) by immersion of leaf to NaCI- and Cd-containing solution Fruit harvesting was obtained in between 60 and 73 days of salinity treatment and values in brackets are referred to that period

 $^2\!\mathrm{Control}$ had an average molar ratio: Na 3.1, Cl 4.6, Mg 1, Ca 1.2, K 1.4, SO $_4$ 1.4

³Values are refereed for 20°C ²ⁿMean values of two replicates

³ⁿMean values of three Cd treatments

⁴ⁿMean values of four replicates

complexing positively-charged Cd forms, and therefore affect Cd availability and phytoextraction (Ondrasek and Rengel 2012). Bolan et al. (2003c) indicated that the addition of ORG (biosolid compost) to soil decreased the concentration of the soluble/exchangeable Cd pool at the expense of the Cd-ORG pool. As a consequence, the same authors observed decreased Cd phytoaccumulation (i.e. alleviation of Cd phytotoxicity) by ORG addition. Similar results were reported by others (e.g. Shuman et al. 2002; Pinto et al. 2004) and are mostly due to the formation of poorly phytoextractable Cd forms in the Cd-ORG pool.

However, ORG application (up to 18% of biosolids) to sandy soil (Weggler et al. 2004) and increasing Cl salinity in predominantly (>90%) ORG soil (Ondrasek et al. 2009a) resulted in (1) increased Cd (Cd-Cls) concentration in soil solutions, (2) enhanced Cd phytoaccumulation in wheat shoots or muskmelon leaves (Table 17.1), and (3) closer correlation of Cd concentration in wheat shoots with CdCl⁺ than with Cd²⁺. Both studies indicated that even in the presence of relatively high ORG content, Cd-Cl complexation was of crucial importance for the soil-plant Cd transfer.

Norvell et al. (2000) obtained a curvilinear relationship among Cd_{grain} and soil Cl, with an increased rate of Cd phytoaccumulation being most pronounced at marginal Cl concentrations (~10 mM) and relatively low Cd concentration in the topsoil (Cd_{DTPA} ranged from 0.064 to 0.155 mg/kg). Though specific mechanisms responsible for Cd acquisition under low Cl_w salinity from uncontaminated soil are still unclear, possible influence of particular pedosphere and/or plant variables was tested. Fig. 17.2a (low Cl salinity/Cd) shows that one of possible explanation could be Cd biogeochemistry in the soil solution pool, whereby in the pH range ~6–8 (similar to Norvell et al. 2000), the most bioavailable Cd²⁺ and thereafter Cd-Cl forms predominated. However, in study by Norvell et al. (2000), topsoils (0–15 cm) were quite enriched with dissolved ORGs (i.e. forming poorly available Cd-ORG pool), given that organic C was ~20–40 g/kg. Another explanation for better Cd than CdCl uptake by plants at relatively low soil background concentration was suggested by Oporto et al. (2009), whereby Cd-Cl-complexation was of negligible importance for plant uptake under higher Cd supply.

By employing the technique of diffusive gradients in thin-films (DGT; in which a Chelex resin induces a diffusive flux of Cd^{2+} from a labile complexes such as dissolved Cd-Cls and/or sorbed forms on soil solids) (see Zhang and Davison 1995, 2001), fluxes of Cd (in soil/soil solution) were quantified together with root Cd uptake and shoot Cd concentration at variable Cl (0–120 mM) and Cd supply (0.4–10.5 mg/kg). They observed that (1) rising Cl salinity significantly increased shoot Cd at all soil Cd levels, but it was relatively more pronounced at the low (background) than at high soil Cd, (2) Cd uptake flux into root increased significantly (>5-fold) due to addition of Cl at the lowest (but not at the highest) soil Cd concentration (Table 17.1), whereas DGT fluxes increased to the same extent but at all Cd levels. Correlation between the fluxes measured based on DGT and fluxes calculated based on root uptake at the background soil Cd suggested that at low Cd supply Cd phytoextraction was controlled (limited) by diffusion of Cd²⁺ and its replenishment from labile (e.g. Cd-Cl) pools (e.g. Oporto et al. 2009). This is in a

line with recent observations by López-Chuken et al. (2012), whereby CdCl⁺ complexes appeared to saturate root sorption sites even at low activities and, therefore, CdCl⁺ activities greater than this saturation level do not cause any increase in Cd phytoextraction. With high concentration of Cd in the contaminated rhizosphere environment, the kinetics of other Cd-borne forms should also be considered, given that precipitation-dissolution reactions may significantly control element speciation (e.g. Khoshgoftar et al. 2004) and thus uptake.

With respect to possible genotypic influence on the Cd-Cl interaction, it is well known that durum is more effective in Cd_{grain} accumulation than bread wheat (Norvell et al. 2000). Increasing Cl-salinity exacerbated Cd accumulation in durum wheat shoots more than in four bread wheat cultivars (Khoshgoftarmanesh et al. 2006). More recently, Ozkutlu et al. (2007) confirmed that even short (<2.5 min) foliar application of Cl may be important for soil Cd extraction and/or Cd (re) mobilisation in durum wheat, i.e. Cd_{erain} deposition. In experiment 1, where soil was spiked with 1.0 mg Cd kg (i.e. with a background concentration totally contained 1.27 mg Cd/kg) they observed increases in Cd $_{\rm grain}$ concentrations by up to 41% with 167 mM Cl foilar application (vs. H₂O treatment). In experiment 2 (with unspiked soil) foliar application of Cd-contaminated solution (8.8 mM with different Cd salts) significantly enhanced Cd_{grain} concentration but it was even more pronounced (~45% in case with CdCl₂) by applying of Cl salinity (Table 17.1). Above studies suggesting that durum (vs. bread wheat) genotypes could be more effective, not only in Cd root extraction, but also in Cd root-shoot (i.e. leaf-fruit) translocation under exposure to Cl salinity.

Although in many studies (Table 17.1), Cd phytoaccumulation positively correlates with salinity, there are certain exceptions. Fritioff et al. (2005) detected that accumulation of Cd in submergent spp. (*Elodea canadensis* L. and *Potamogeton natans* Michx.) significantly decreased with NaCl, without any influence of salinity on growth (Table 17.1). However, they used relatively low NaCl (up to 5 mM), corresponding well to the modelled situation in Fig. 17.2a where the proportion of Cd²⁺ appeared to increase with increasing salinity.

Na-induced Salinity

Na is the most frequent causative agents of naturally-induced soil alkalinity and is accompanied with salinity induced by Cl. As a consequence, similar to Cl, Na might also correlate well with phytoextracted Cd, although it seems unlikely to play any significant role in enhancing Cd uptake (e.g. Smolders et al. 1998; Mühling and Läuchli 2003); such relationships are attributed mostly to multi-colinearity with Cl (Norvell et al. 2000). Indirectly, it is possible that excessive Na⁺ substantially impacts Cd biogeochemistry in the rhizosphere via (1) competition with Cd cationic free/complexed species for (in)organic exchange interfaces, root transport mechanisms, and thereafter (re)translocation/deposition in the plant (Sect. 3.3), (2) deprotonation from (in)organic soil matrix (e.g. humics) and thus acidification of surrounded (unbuffered) solution (e.g. Lores and Pennock 1998), and/or (3) induced



Fig. 17.3 A conceptual representation of root uptake and translocation of Cd and characterisation of transport systems principally for plants with aerial fruiting bodies (adopted from references cited in the text). *Chemical composition of xylem/phloem sap in wild tobacco (*Nicotiana glauca* Grah.) (Hocking 1980), **Cd concentration in xylem/phloem sap collected during 3 stages [1st (at 10th), 2nd (at 14th) and 3rd (at the early grain-filling) stage] from rice (*Oryza sativa* L.) grown in flooded-soil containing 1.55 mg Cd/kg (extracted with 0.1 M HCl). **Fe and **Zn concentration represent their average concentration obtained during 3 stages (Yoneyama et al. 2010). ***Cd concentration in xylem sap of Indian mustard (*Brassica juncea* L.) exposed to 0.6 µg/mL Cd for 10 h or 7 days (in parenthesis) (Salt et al. 1995), ****Cd concentration in phloem sap of rice (*Oryza sativa* L.) treated with a nutrient solution containing 10 µM Cd for 2 days (Tanaka et al. 2007)

osmotic effects in the rhizosphere solution (e.g. water stress, Na toxicity, disruption of integrity/selectivity of root plasma membrane and the plant homeostasis) (reviewed by Tester and Davenport 2003; Munns and Tester 2008). Na⁺ may become harmful for many plants if its cytosolic concentration exceeds 10 mM (e.g. Munns and Tester 2008). This is relatively easily achievable in natural saline environments, causing common plant responses to Na-toxicity such as growth inhibition (Table 17.1) and in extreme cases early senescence and plant mortality (e.g. Romic et al. 2008).

When associated with anions other than Cl-, Na salts may induce relatively moderate plant (environmental) responses. An addition of NaNO₃ can be sevenfold less effective than NaCl in increasing Cd_{TOT} content (Table 17.1) and without influence on Cd^{2+} and $CdCl^+$ concentrations in soil solution (Khoshgoftar et al. 2004). In comparison to non-salinised control, NaNO3 salinity did not increase concentration of soil Cd_{ror}, as in case of NaCl, but it significantly reduced wheat growth/yield, and marginally (but significantly at P < 0.05) improved shoot Cd accumulation (Table 17.1). Similarly, the relative increase in Cd_{TOT} in soil solution was fivefold at 120 mM NaNO, and 20-fold at 120 mM NaCl, which was attributed to formation of Cd-Cls (Oporto et al. 2009). The twofold greater Cd accumulation in shoots was obtained with NaCl than NaNO, application at the same molar rates (Table 17.1), probably as a result of the reduced plant yield at increasing ionic strength (Oporto et al. 2009). Both salinity types imposed similar negative effects on shoot yield at low but not at high Cd supply, where NaCl depressed the yield more severely (12fold) than NaNO₂ (4-fold) compared to non-salinised control (Table 17.1), probably due to additive NaCl/Cd toxicities, i.e. stresses (Sect. 3.3).

SO₄-Induced Salinity

Sulphate is a relatively abundant anion in agro-exploited pedo/hydrosphere resources affected by salinity (Rhoades et al. 1999). In such circumstances, and in sufficient magnitude of Cd^{2+} pool, Cd-sulphate complexes were common, although orders of magnitude less abundant (Fig. 17.2) and less stable compared to Cd-Cls (cf. Norvell et al. 2000). The Cd-sulphate complexes might also influence Cd chemistry in the rhizosphere (e.g. McLaughlin et al. 1998b). From negatively-charged $Cd(SO_4)_2^{-2}$ to neutral CdSO⁴ complexes, these complexes can enhance soil-plant Cd transport by either (1) diffusive transport of $CdSO_4^0$ through the lipophilic plasma membrane bilayers as shown for HgCl⁰ by Gutknecht (1981), and suggested for H₂BO species by Welch (1995) and recently in durum wheat leaf epiderms for CdCl₂⁰ by Ozkutlu et al. (2007), or (2) through facilitated diffusive transport of charged $Cd-SO_4$ complexes to absorption sites at the root interface as suggested above for Cd-Cl (Fig. 17.3). In support of the first assumption, McLaughlin at al. (1998a) did not observe better plant uptake of Cd by increasing dissolved calcium (Ca) concentration in solution to compensate for $CaSO_4$ complexation, confirming that $CdSO_4^{0}$ could be phytoextracted as efficiently as Cd^{2+} . Direct crossing of negative Cd-SO₄ forms across the plasma membrane via channel/transport proteins seems less likely given possible size restriction of their ionic radii (see discussion by Smolders and McLaughlin 1996a).

Compared to studies focused on Cd-Cl interactions and their plant responses, those including Cd-SO₄ are rare and less instructive. Cd-SO₄ complexation in nutrient solutions (up to 58 mM SO₄) has been shown as having an insignificant effect on Cd phytoextraction (McLaughlin et al. 1998a), whereas in approximately double SO₄-concentrated soil solution, Cd shoot deposition increased marginally but significantly (P<0.05) (McLaughlin et al. 1998b). Comparing some other studies that used low Cl salinity and other crop species (Table 17.1), and also earlier similar

approaches and conditions (e.g. salinity duration, chemical environment in the rhizosphere) with the same tested plant species (Smolders and McLaughlin 1996a; Smolders et al. 1998), obviously a substantially lower effects of Cd-SO₄ complexation may be expected in Cd transfer to crops than in Cd-Cl complexation. Norvell and associates (2000) also obtained (1) highly positive correlation among concentrations of Cd_{grain} and water-extractable sulphates (SO_{4w}) (Pearson correlation coefficient was even higher then with Cl_w), and (2) explained high variability (around 60%) in Cd_{grain} by attributing such a relationship mostly to SO₄²⁻ association (i.e. multi-colinearity) with Cl, rather than to direct causality.

Soil-Plant Transfer of Cd from Saline Environment

As one of the most soluble and bioavailable trace metals in the rhizosphere, and due to low selectivity for root extraction in majority of plant species, Cd relatively easily overcomes the soil-plant barriers. Although concentration as well as distribution of Cd decreases with the upstream transpirational flow (hence, it is higher in belowground than aboveground plant parts, Table 17.1, Fig. 17.3), consumption of crops produced in Cd-enriched environment is the principal route of Cd "intoxication" for humans. Relatively enhanced soil-plant transfer of Cd and its biotoxicity are main causes for strictly defined acceptable limits of Cd intake from foodstuff (e.g. 1 μ g Cd per kg body weight per day) (WHO 1992). In Australia and New Zealand for example, Cd is recognised as the most common trace metal reaching the food chain through animal transfer in pastoral agriculture (Bolan et al. 2003a). Also, for the same populations consumption of crop foodstuffs represents predominant route (>80%) in total daily Cd intake of ~9 µg, with >60% originating from potatoes $(\sim 4.3 \ \mu g)$ and wheat $(\sim 1.5 \ \mu g)$ consumption (Ondrasek and Rengel 2012), whereas \sim 50% of the total Cd intake by Japanese comes from white rice (Yoneyama et al. 2010). A similar situation could be expected across other Cd-noncontaminated areas worldwide, given that potatoes, wheat and rice are among the top five agricultural crop commodities in the world (FAO 2009). In irrigated potato production, but under highly contaminated (e.g. Cd in soil up to 80 mg/kg and in irrigated water up to 240 µg/L) and salinised conditions [e.g. in soil solution (mM) 107 Cl⁻, 90 Na⁺ and 42 SO₄²⁻], it was estimated that daily Cd intake from potato consumption could reach ~100 µg (Oporto et al. 2007).

Similarly to other metals, the Cd species most capable of entering root is soluble Cd²⁺, though under certain conditions Cd uptake is better explained by the activity of the Cd-Cl complexes than Cd²⁺ (López-Chuken et al. 2012). Evidence on Cd-complexes being extracted by plant root is relatively scarce and based mostly on assumptions. Besides, in the presence of Cd-Cl (Table 17.1), increased Cd uptake was confirmed under increasing concentrations of low- (Chiang et al. 2011) and high-molecular-weight organic acid (L/HMWOA) ligands (Evangelou et al. 2004; Bandiera et al. 2009). Undoubtedly, metal complexation with dissolved ligands would enhance Cd desorption from the (in)organic solid interfaces in the rhizosphere, and improve the transfer of Cd complexes into plants, although complete

mechanisms are not fully explained. Also, Cd-Cl⁺ complexes (vs. Cd^{2+}) are less strongly sorbed onto rhizosphere interfaces, and thus formation of Cl-complexes tends to shift Cd from solid to dissolved phase, thereby enhancing its solubility/ mobility (López-Chuken et al. 2012). The most logical explanations of Cd uptake from the rhizosphere would rely on well characterised Cd²⁺ and CdCl⁺ forms (Fig. 17.3).

Due to many similarities between Cd and some divalent metal phytonutrients in physical (e.g. ionic radii in pm: Cd^{2+} 97, Ca^{2+} 99, Mn^{2+} 80, Fe^{2+} and Zn^{2+} 74) or chemical (e.g. redox-activity, Lewis acidity) properties, non-essential Cd would most probably enter roots via routes specific for similar essential elements. Cadmium uptake across the root cell plasma membrane was shown to occur via a concentration-dependent mechanism exhibiting saturable kinetics (Salt et al. 1995; Hart et al. 1998), with confirmed Cd-Zn; Cd-Mn and Cd-Cu competition (Hart et al. 2002; Salt et al. 1995) or Fe-Cd complementarity (Nakanishi et al. 2006). Cadmium uptake by plants could be facilitated under salt- (Na, Cl) (Ondrasek and Rengel 2012; Ondrasek et al. 2012) and/or Cd-stressed (e.g. Salt et al. 1995; López-Chuken and Young 2005; Ahmad et al. 2011) conditions. For instance, Mühling and Läuchli (2003) showed that a combined NaCl/Cd stress (vs. their separate influence) can enhance Cd phytoextraction, probably by exacerbating oxidative stress (i.e. production of O_{a} radicals and $H_{a}O_{a}$) which could increase plasma membrane permeability and/or inhibit activities of antioxidant enzymes involved in the oxidative defense mechanism (Ahmad et al. 2011). Also, Mühling and Läuchli (2003) highlighted that saltsensitive genotype exposed to salinity showed higher Cd accumulation than salt-resistant ones. Similarly, López-Chuken and Young (2005) confirmed Cl-enhanced uptake of Cd (at 100 mM NaCl) from highly contaminated soil (58 mg Cd/kg) by salt-tolerant genotypes (Brassica juncea G32192 and Zea mays hybrid W23/L317), with some seed not germinating probably due to salt and/or Cd toxicity. Both studies indicate large challenges faced by genetic engineering for improved food safety and security (e.g. Ahmad et al. 2012), especially if salinity tolerance (as multi-gene trait) is closely associated with gene loci responsible for Cd phytoextraction.

The likely Cd uptake routes from the rhizosphere are via channel (CP) and/or transport proteins (TP) (e.g. $Ca^{2+}CP$; $Zn^{2+}TP$; $Fe^{2+}TP$), and less probably via specific Cd²⁺CP or Cd²⁺TP embedded into the plasma membrane of root cells (Clemens 2006; Lee and An 2009; Yoneyama et al. 2010) (Fig. 17.3). It remains unclear whether Cd enters the roots as CdCl⁺ and is then translocated in the same form via the xylem to shoot (discussed in above sections).

To moderate high reactivity/toxicity of Cd²⁺ in the symplast caused by its strong complexation with cytosolic metabolites (e.g. organic acids, amino acids, peptides etc.; Kato et al. 2010 and refs therein), Cd must be immobilised. Salt et al. (1995) and recently Karlsson et al. (2005) confirmed by EXAFS (Extended X-ray Absorption Fine Structure) experiments that reduced organic S ligands could be involved in Cd complexation in the root tissues. After entering root cytoplasm, possible initial Cd complexation could be with glutathion (Gtn) to form Cd-Gtn complex as a precursor of Pht-Cd (Phytochelatin-Cd complex) (Fig. 17.3). Both Gtn and Pht are LMW cistein-enriched peptides involved in maintenance of low activity of

free forms of cytoplasmic metals. As a Pht-Cd complex, Cd can cross the tonoplast (via certain TPs) and create Phytochelatin-based HMW-Cd complexes in the vacuole (Salt and Rauser 1995); however, it remains unclear whether the same form can be loaded into the xylem. To some extent free cytosoilic Cd can be anti-ported into the vacuole (Salt and Wagner 1993) and sequestered to LMWOA-Cd compounds, whereas a fraction of Cd from the LMW vacuolar pool may be remobilised into the cytosol (over AtNramp3 proteins) and chelated with S-enriched ligands (Cd-S-L) (Fig. 17.3). The physiological mechanisms responsible for differential movement of Cd in roots and from roots to shoots (i.e. Cd xylem/phloem loading) still remain unclear (Hart et al. 2006; Yoneyama et al. 2010).

Due to slight acidity of the xylem sap (pH~6) (Fig. 17.3) there is a possibility that a large proportion of Cd is complexed. It is presumed that the same or similar transport and deposition routes (as in root) of Cd complexation occur in the aboveground tissues, as shown in tobacco cell leaves, where cytoplasmic Pht-Cd is directly transported to vacuole (Vögeli-Lange and Wagner 1990). Cadmium deposition could specifically be targeted to specific leaf cells such as trichomes, i.e. leaf hair/gland cells derived from specialized epidermal layer on the leaf or stem surfaces. Compared to concentration within leaves (without trichomes), Salt et al. (1995) observed a 43-fold greater accumulation of Cd in trichomes of Indian mustard leaves after 24-h exposure to 0.1 μ g Cd/ mL, explaining one of possible detoxification strategies in plants.

Under slightly basic conditions and prevalence of organic assimilates (e.g. S-, O-, N-rich compounds) that exist in the phloem sap, dominant Cd forms in the phloem could be those from Cd-ORG pool, but Cd-Cl complexation cannot be excluded because of Cl abundance (Fig. 17.3). During last decades, biochemistry of Cd transport in phloem was studied in potato tubers (Dunbar et al. 2003; Reid et al. 2003), peanuts seeds (Popelka et al. 1996), soybeans (Yada et al. 2004), wheat (Harris and Taylor 2001) and rice (Tanaka et al. 2007; Yoneyama et al. 2010); however, it is likely that Cd-Cl complexation inside the vascular system is less relevant than in the rhizosphere. Recently, Kato et al. (2010) reported that major Cd chelators in phloem rice sap are proteinous/S-rich (e.g. sulfhydryl) substances of ~13 kDa, which distinguishes it from similar metals (Fe, Zn, Cu, Mn, Ni, Co), probably complexed with other organics (e.g. nicotianamine, 2'-deoxymugineic acid, citrate and histidine). Although in both vascular systems (xylem and phloem) Cd has similar and relatively high mobility (Reid et al. 2003; Dunbar et al. 2003), and pose similar fluctuation pattern during vegetation period (from 10th leaf to early grain rice filling stage) in Cd concentration (Yoneyama et al. 2010), retranslocation and redistribution of Cd from leaves to fruits in cereals could predominantly (>90%) occur in phloem (Tanaka et al. 2007).

Conclusions and Future Perspective

It is expected that in the forthcoming era of global warming and human population growth agro-exploited resources could be dramatically impacted by salinity and metal contamination. During last decades a significant research effort with different genotypes has been devoted to elucidation of Cd biogeochemistry in the rhizosphere, its (re)translocation and deposition in plants. The importance of Cd complexation with inorganic salt ligands (particularly Cl) in the rhizosphere was established. Cadmium taken up is transported (notably in organo-complexed forms) to the transpirational tissues via the xylem, and thereafter to the depositing tissues dominantly via the phloem. Recently, genetic engineering combined with traditional breeding has been highlighted as a promising strategy for improving (1) agri-food production in saline environment, and (2) phytoremediation of metal-contaminated areas. Soil salinity can increase the soil-plant transfer of Cd under ecologicallyrelevant conditions (e.g. soils with poor metal-buffering capacity), but can also interfere with phytoextraction of nutrients (Zn, Cu, Fe). Thus, growing salt-resistant crops might impact food safety and security by exacerbating Cd accumulation and decreasing micronutrient content, especially if salinity tolerance (as a multi-gene trait) is closely associated with gene loci responsible for Cd phytoextraction.

Acknowledgments The author is grateful to Winthrop Professor Zed Rengel (University of Western Australia) for valuable discussion, comments and text improvement.

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