17

Cadmium and Zinc

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17.1 Introduction

Cadmium (Cd) is well known for causing adverse health effects in subsistence rice farmers in Asia, and as a subject of food-chain concern, but is seldom important as a cause of phytotoxicity in the field. On the other hand, zinc (Zn) is commonly both a deficient and phytotoxic element in soils, the latter due to industrial contamination. And Zn is associated with significant food-chain deficiency concerns, but not food-chain toxicity risk. In nearly all cases, soil Cd contamination occurs with 200-fold higher Zn contamination. Because these elements are usually co-contaminants, have similar properties in soils and plants, and are readily absorbed and translocated to plant shoots, Cd and Zn should be considered together. Further, their uptake and transport to plant shoots are competitive, therefore both elements need to be considered together to understand either Cd or Zn in detail. Thus the focus of this chapter is potential food-chain transfer of soil Cd risks, and remediation of Zn phytotoxicity. The interaction of soil Zn limiting Cd risk to food-chains is very important in understanding why rice has caused essentially all Cd disease attributed to soil Cd.

17.2 Geogenic Occurrence and Sources of Soil Contamination

What are normal levels of Cd and Zn in soils? Surveys of topsoil trace elements have been conducted in many countries. When agricultural soils are sampled, the slow accumulations
Table 17.1 Concentrations of Cd and Zn in agricultural soils of the United Kingdom and United States

<table>
<thead>
<tr>
<th></th>
<th>Cd (mg kg⁻¹)</th>
<th>Zn (mg kg⁻¹)</th>
<th>Number</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median</td>
<td></td>
<td>Median</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>&lt;0.2–40.9</td>
<td>82</td>
<td>5–3648</td>
<td>5665</td>
</tr>
<tr>
<td>0.20</td>
<td>&lt;0.005–2.0</td>
<td>53.</td>
<td>1.5–264</td>
<td>3045</td>
</tr>
<tr>
<td>0.20</td>
<td>&lt;0.1–5.2</td>
<td>56.</td>
<td>8–377</td>
<td>254</td>
</tr>
</tbody>
</table>

of Cd and Zn from agricultural amendments are included in the result. And soil contamination may be included in the set of samples, so the high end concentrations are due to contamination. But the median soil concentrations are representative of background concentrations of metals in surface soils. Table 17.1 shows the results of surveys in the United States and United Kingdom [1–3].

The most important sources of soil Zn and Cd contamination are anthropogenic with ore-like mixtures of Zn and Cd (mine wastes, smelter emissions). Most soils with ore-like Cd+Zn contamination have about 200-fold higher Zn than Cd (Cd:Zn = 0.005); this is the average ratio in Zn ores around the globe, with some variation (0.002–0.04). Huge land areas have become Zn/Cd co-contaminated from Zn, Pb, Cu, and Ag ores from dispersal of mine wastes or smelter emissions in many countries, and the contamination is persistent. Examples include the many locations in Japan, China, Korea, and Thailand where mine waste-contaminated rice soils have caused human Cd disease [4–7]. Zinc mine and smelter waste contamination of soils have been reported in many countries; large areas with historic mine waste contamination in Somerset [8] and Wales [9] were reported in the United Kingdom, and the Palmerton, Pennsylvania [10–12] and Bunker Hill, Idaho [13,14] Zn smelters are famous for denuded mountains where vegetation was killed and could not regrow due to Zn phytotoxicity. At the most contaminated locations, surface soils near smelters exceed 4% Zn, and deposits of pyrite–rich Zn-Pb mine wastes are over 1% Zn and pH < 4 with no living plants [15].

A few sources of geogenic Cd enrichment without 200-fold Zn contamination of soils have been identified. The high Cd:Zn ratio of these soils makes them much higher potential Cd risk to humans. In California, USA, marine shale parent soils caused Cd enrichment without much Zn enrichment, which allows the soil Cd to be much more mobile in crops [16–18]. Alum shale in Norway was also geochemically enriched in Cd [19]. Another unusual geogenic Cd enrichment case occurs in Jamaica where several ‘Parishes’ have soils with up to 200 mg Cd kg⁻¹ in calcareous soils with bauxitic parent materials [20]. Garrett et al. [21] did an extensive analysis of the source of the Jamaica Cd enrichment and were able to trace it back to marine phosphorite, similar to other marine shale Cd enrichment cases. Many phosphate ore deposits have surface soils with substantial Cd and Cd:Zn enrichment.

Besides the ore-like Zn + Cd and phosphorite-Cd enrichment of soils, other important anthropogenic sources of high Cd or Zn contamination include Cd plating wastes (and indirectly through biosolids) (Cd:Zn ≈ 0.05–0.10); Cd-Ni battery production wastes (and indirectly through biosolids) (Cd:Zn > 1.0) [22]; Cd pigment production and use (and indirectly through biosolids) (Cd:Zn > 1.0) [23]; Cd plastic stabilizer production
(Cd:Zn > 1.0) [24]; Cu-Cd alloy production emissions (Cd:Zn ~ 0.3) [25,26]; steel production emissions (Cd:Zn < 0.01); phosphate fertilizers (Cd:Zn ~ 0.13) [27]; phosphogypsum (Cd:Zn ~ 0.5) [28]; galvanized steel use (Cd:Zn << 0.01) [29]; by-product limestone from Zn-Pb mine wastes (Cd:Zn ~ 0.01) [30]; Zn in hazardous steel mill fume wastes applied as limestone [31]; by-product Zn fertilizers (Cd:Zn << 0.01) [32,33]; orchard Zn fungicide sprays [34]; and rubber products (Cd:Zn << 0.01) (contain 1–2% Zn but only about 0.2–5 mg Cd kg⁻¹ because purified ZnO is used in rubber manufacturing) used in potting media or soils contaminated by burned rubber [35,36]. In previous years, biosolids from industrialized countries contained as high as 3400 mg Cd kg⁻¹, and as high as 49 000 mg Zn kg⁻¹ [37]. But in more recent decades, industrial pretreatment and regulation of biosolids use on land yielded extensive improvement in biosolids quality. Modern biosolids had a median Cd of 2 mg kg⁻¹ dry weight (DW), and the 90th centile was only 4 mg Cd mg⁻¹ DW, and Zn in the order of 500–1500 mg kg⁻¹ [38].

As noted above, when biosolids came under intense research starting about 1970, it was found that many biosolids were highly contaminated by industrial discharges in some cities (for example, [39]). Cd and Zn plating wastes, Cd-Ni battery manufacturing wastes, Cd-pigment production or use wastes, among others, caused biosolids to exceed 1000 mg Cd kg⁻¹ and 10 000 mg Zn kg⁻¹ at some cities. These levels are far above the levels achieved by the year 2000 after enforcement of industrial pretreatment programs. As noted in Stehouwer et al. [38], pretreatment allowed production of biosolids with low levels of Cd and Zn in essentially all cities if they wanted to achieve agricultural utilization of their biosolids. With the establishment of regulations for use of biosolids on land, cities learned of the need to produce biosolids with low levels of metals such as Cd and Zn.

Unfortunately, the legacy of already applied contaminated biosolids has not been dealt with in the United States or other countries except in research. In the early 1970s, we found more than 1000 mg Cd kg⁻¹ DW and high Cd:Zn ratio in some biosolids from three Pennsylvania cities where metal plating and Cd pigment users discharged Cd into wastewater [39]. In crop uptake tests grown on farmers' fields and matched control soils, Chaney and Hornick (in [40]) found remarkable Cd accumulation by representative crops when they were grown on strongly acidic soils that had been amended with the highly Cd-contaminated biosolids (Table 17.2). Thus, the Cd in the historically applied biosolids remains plant available long after application and some remedy is needed for these legacy contaminated sites. In the case of the city with Cd-pigment waste contamination, the city was able to sue the source of the Cd and obtain funds to raise all the treated fields to pH 7 or above [41], lowering risks from the applied Cd. But because of the high Cd:Zn of these biosolids, that cannot be considered a final remediation. Development of these soils for home sites has been prohibited because of the high soil Cd and Cd:Zn levels.

By-product Zn fertilizers were listed above as a source of Cd contamination. Several experimental studies of Cd uptake by indicator crops on soils amended with the steel mill fume waste-derived Zn fertilizers showed that Cd accumulation was not important [32,33]. This appears to be a consequence of the Cd:Zn ratio of the fume wastes, much lower than 0.01 because recycled steel had relatively higher Zn content than Cd. In a recent study by Kuo et al. [42], varied rates were applied over time and the additional Zn with each increment caused lower slopes for Cd uptake by lettuce.

Another class of deliberate contamination of ZnSO₄ fertilizer and feed ingredients occurred starting in 1998. In this case, a commercial ZnSO₄ seller certified that their
Table 17.2 Composition of Swiss chard (Beta vulgaris var. cicla) and oat (Avena sativa L.) grown in 1977 on long-term biosolids utilization farms and matched control soils at six cities in the north-eastern United States (Chaney and Hornick in [40]). Cities are identified by numbers; C = control field; S = biosolids amended field; U = unlimed; L = limed; H = at near neutral pH as managed by farmer. Soil pH as measured in May 1977. Chard leaves harvested by July 1977. Soil pH is 1:1 soil:water mixture, by volume, after 1 hour. Biosolids were applied to Hagerstown silt loam soil from 1962 to 1975 at city 4; to Lansdale sandy loam from 1967 to 1973 at city 9; to Readington silt loam from 1967 to 1974 at city 13; to Lansdale loam from 1967 to 1975 at city 1; on Genesee silt loam from 1960 to 1976 at city 19; and on Hagerstown silt loam from 1960 to 1971 at city 39. Biosolids sampled during the experiment contained 22.1 mg Cd kg⁻¹ DW and 1720 mg Zn kg⁻¹ DW at city 4; 169 mg Cd kg⁻¹ DW and 5050 mg Zn kg⁻¹ DW at city 9; 683 mg Cd kg⁻¹ DW and 6430 mg Zn kg⁻¹ DW at city 13; 100 mg Cd kg⁻¹ DW and 3450 mg Zn kg⁻¹ DW at city 1; 6.6 mg Cd kg⁻¹ DW and 1430 mg Zn kg⁻¹ DW at city 19; and 95 mg Cd kg⁻¹ DW and 2460 mg Zn kg⁻¹ DW at city 39.

<table>
<thead>
<tr>
<th>City</th>
<th>Soil total metals (mg kg⁻¹ dry soil)</th>
<th>Soil pH</th>
<th>Metals in chard leaves (mg kg⁻¹ dry weight)</th>
<th>Metals in oat grain (mg kg⁻¹ dry weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn</td>
<td>Cd</td>
<td>Zn</td>
<td>Cd</td>
</tr>
<tr>
<td>4C</td>
<td>73.1</td>
<td>0.22</td>
<td>5.4</td>
<td>179.1</td>
</tr>
<tr>
<td>4C-L</td>
<td>63.0</td>
<td>0.16</td>
<td>6.4</td>
<td>49.3</td>
</tr>
<tr>
<td>4S</td>
<td>156.</td>
<td>0.98</td>
<td>4.9</td>
<td>800.</td>
</tr>
<tr>
<td>4S-L</td>
<td>154.</td>
<td>0.94</td>
<td>6.0</td>
<td>105.</td>
</tr>
<tr>
<td>9C</td>
<td>52.9</td>
<td>0.18</td>
<td>4.9</td>
<td>189.</td>
</tr>
<tr>
<td>9C-L</td>
<td>50.6</td>
<td>0.15</td>
<td>6.4</td>
<td>51.7</td>
</tr>
<tr>
<td>9S</td>
<td>82.4</td>
<td>1.06</td>
<td>4.9</td>
<td>1230.</td>
</tr>
<tr>
<td>9S-L</td>
<td>91.0</td>
<td>2.10</td>
<td>6.3</td>
<td>65.6</td>
</tr>
<tr>
<td>13C</td>
<td>58.6</td>
<td>0.10</td>
<td>5.3</td>
<td>183.</td>
</tr>
<tr>
<td>13C-L</td>
<td>60.7</td>
<td>0.10</td>
<td>6.1</td>
<td>50.3</td>
</tr>
<tr>
<td>13S</td>
<td>146.</td>
<td>9.10</td>
<td>5.5</td>
<td>823.</td>
</tr>
<tr>
<td>13S-L</td>
<td>129.</td>
<td>7.02</td>
<td>6.2</td>
<td>90.</td>
</tr>
<tr>
<td>1C</td>
<td>53.3</td>
<td>0.07</td>
<td>5.9</td>
<td>63.4</td>
</tr>
<tr>
<td>1C-L</td>
<td>52.5</td>
<td>0.07</td>
<td>6.3</td>
<td>52.0</td>
</tr>
<tr>
<td>1S</td>
<td>146.</td>
<td>3.26</td>
<td>5.5</td>
<td>896.</td>
</tr>
<tr>
<td>1S-L</td>
<td>212.</td>
<td>4.50</td>
<td>6.2</td>
<td>212.</td>
</tr>
<tr>
<td>1H</td>
<td>150.</td>
<td>2.54</td>
<td>6.6</td>
<td>109.</td>
</tr>
<tr>
<td>19CH</td>
<td>51.8</td>
<td>0.09</td>
<td>6.1</td>
<td>99.4</td>
</tr>
<tr>
<td>19SH</td>
<td>156.</td>
<td>0.41</td>
<td>5.9</td>
<td>40.6</td>
</tr>
<tr>
<td>39CH</td>
<td>56.3</td>
<td>0.05</td>
<td>5.6</td>
<td>31.6</td>
</tr>
<tr>
<td>39SH</td>
<td>60.2</td>
<td>12.7</td>
<td>6.7</td>
<td>162.</td>
</tr>
</tbody>
</table>


The product contained low Cd, but they had mixed very high levels of Cd wastes into the product. Table 17.3 shows the analysis of five samples of the product received in Seattle, WA, USA and analyzed by the Washington Department of Agriculture, compared with normal ZnSO₄ fertilizer products. Because Washington State had established limits on Cd
Table 17.3  Cd and Zn concentration and Cd:Zn ratio of Cd-contaminated Zn-fertilizer product delivered to north-western United States/Canada

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cd (mg kg$^{-1}$ DW)</th>
<th>Zn (mg kg$^{-1}$ DW)</th>
<th>Cd:Zn (g g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>China-Zn-1</td>
<td>46 400</td>
<td>345 000</td>
<td>0.135</td>
</tr>
<tr>
<td>China-Zn-2</td>
<td>72 800</td>
<td>313 000</td>
<td>0.233</td>
</tr>
<tr>
<td>China-Zn-4</td>
<td>215 000</td>
<td>216 000</td>
<td>0.995</td>
</tr>
<tr>
<td>China-Zn-5</td>
<td>199 000</td>
<td>230 000</td>
<td>0.865</td>
</tr>
<tr>
<td>Cenes$^{a}$ ZnSO$_4$</td>
<td>7.1</td>
<td>320 000</td>
<td>0.000 022</td>
</tr>
<tr>
<td>Blue-Min$^{b}$</td>
<td>49.0</td>
<td>420 000</td>
<td>0.000 127</td>
</tr>
</tbody>
</table>

$^{a}$ Zn fertilizer grade product.
$^{b}$ By-product Zn-fertilizer.

Data provided by Washington State Department of Agriculture.

levels in Zn fertilizer products, they could prohibit importation or sale of the product. In subsequent years, similar episodes of sale of highly Cd contaminated ZnSO$_4$ were identified in the European Union (EU), Australia, South Africa, and Kenya. The product had been used as Zn fertilizer, or as Zn feed additive and the livestock manure was spread on farmland before the contamination was identified. These Cd contamination episodes are also legacy situations where the high Cd:Zn ratio of the applied materials promotes uptake by plants, and the high uptake and potential risk will persist.

Zinc-fungicide orchard spray caused accumulation of Zn in acidic light-textured soils, which caused Zn phytotoxicity to subsequent crops [34]. Farmers limed soils to prevent this adverse effect of the accumulated Zn. Later, partly because of the higher soil pH, and partly because of Zn inhibition of Ni uptake by plants, Ni deficiency was observed in pecan trees growing on old orchard soils in Georgia, USA [43]. This Zn-contaminated soil-induced Ni deficiency is a new mechanism for adverse effects of accumulated soil Zn.

Livestock manures also contain Cd and Zn (Table 17.4) [44] and, because high cumulative quantities of manure are applied on agricultural land, it can be the most important source of soil enrichment over time. Several research groups have attempted to model

Table 17.4  Zn and Cd levels in livestock manures

<table>
<thead>
<tr>
<th>Species</th>
<th>Zn (mg kg$^{-1}$ dry matter)</th>
<th>Cd (mg kg$^{-1}$ dry matter)</th>
<th>Cd:Zn (g g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Range</td>
<td>Mean</td>
</tr>
<tr>
<td>Dairy cattle FYM$^a$</td>
<td>153</td>
<td>99–238</td>
<td>0.38</td>
</tr>
<tr>
<td>Dairy cattle Slurry</td>
<td>209</td>
<td>&lt;5–727</td>
<td>0.33</td>
</tr>
<tr>
<td>Beef cattle FYM</td>
<td>81</td>
<td>41–274</td>
<td>0.13</td>
</tr>
<tr>
<td>Beef cattle slurry</td>
<td>133</td>
<td>68–235</td>
<td>0.26</td>
</tr>
<tr>
<td>Pig FYM</td>
<td>431</td>
<td>206–716</td>
<td>0.37</td>
</tr>
<tr>
<td>Pig slurry</td>
<td>575</td>
<td>&lt;5–2500</td>
<td>0.30</td>
</tr>
<tr>
<td>Broiler/turkey litter</td>
<td>378</td>
<td>208–473</td>
<td>0.42</td>
</tr>
<tr>
<td>Layer manure</td>
<td>459</td>
<td>350–632</td>
<td>1.06</td>
</tr>
</tbody>
</table>

$^a$ FYM, farmyard manure.

Adapted from Nicholson, F.A.; Chambers, B.J.; Williams, J.R.; Unwin, R.I., Heavy metal contents of livestock feeds and animal manures in England and Wales; Bioresource Technol. 1999, 70, 21–31 [44].
### Table 17.5 Metal accumulation in soils of England and Wales from different sources

<table>
<thead>
<tr>
<th>Source</th>
<th>Zn (Mg y⁻¹)</th>
<th>Cd (Mg y⁻¹)</th>
<th>Cu (Mg y⁻¹)</th>
<th>Cd:Zn (g g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosol deposition</td>
<td>2457</td>
<td>21.</td>
<td>631</td>
<td>0.0085</td>
</tr>
<tr>
<td>Livestock manure</td>
<td>1858</td>
<td>4.2</td>
<td>643</td>
<td>0.0022</td>
</tr>
<tr>
<td>Biosolids</td>
<td>385</td>
<td>1.6</td>
<td>271</td>
<td>0.0042</td>
</tr>
<tr>
<td>Phosphate fertilizers</td>
<td>213</td>
<td>10.0</td>
<td>30</td>
<td>0.047</td>
</tr>
</tbody>
</table>


Long-term additions of Cd, Zn, Cu, and P in soils, considering atmospheric inputs, fertilizer inputs, biosolids/compost inputs, and manure inputs. Table 17.5 shows an inventory of average Cd and Zn additions to the soils of England and Wales based on studies by Nicholson et al. [45]. Livestock manure was the most important agricultural source of added Zn, while phosphate fertilizers were more important than manure, which was more important than biosolids as a source of added Cd. Atmospheric deposition was larger than the usual soil amendments. It is not clear how much of the measured atmospheric deposition resulted from suspended soil/dust, which should be considered recycled soil rather than input unless the loss by wind erosion is also measured. Manures are important sources because of both the importation of feedstuffs from off farm and the supplementation of diets with Zn and Cu salts. Both swine and poultry diets are often greatly enriched in Zn and Cu to promote growth, and local utilization of the manure enriches soil Zn and Cu levels. Many nations regulate the levels of Zn and Cu in pre-mixed feeds, but not in locally mixed feeds.

Manure is a significant source of Cd addition but because Zn is usually added at much higher rates, the Cd:Zn of manures are usually quite low, <0.002 (Table 17.4). The plant uptake of manure-applied Cd was examined by Jones and Johnston [46] on long-term plots at Rothamsted Experimental Station in the United Kingdom. In that case, plant uptake from aerosol-deposited plus fertilizer Cd and Zn was compared with plots amended annually with livestock manure, which added considerably more Cd and Zn to the soils. Interestingly, over time plant uptake of Cd declined on the manure plots but increased on the aerosol deposition plus fertilizer plots. Repeated application of manure raised soil pH, while the pH of the control plot soils fell over time.

Another kind of inventory considers the multiple sources of fertilizer nutrients and likelihood of application on particular farms. For example, livestock farms produce manure rich in N and P, so they would not need to purchase P-fertilizers or accept biosolids as a P-fertilizer source. Table 17.6 shows this assessment of Cd application from significant sources to soils of Sundgau Canton of Switzerland [47]. Again, manure was the most important Cd source among normal amendments, but atmospheric deposition was still larger. And among farm types, livestock farms accumulated Cd faster than others.

An assessment of potential additions of various potentially toxic elements including Cd and Zn was recently conducted for Canada. The approach was different from the two discussed above, but considered the same sources. Both manure (Zn, Cu) and P-fertilizers (Cd) were important sources of Zn and Cd enrichment, and livestock farms received the most important additions of Zn and Cd [48].
Table 17.6  Estimated Cd accumulation in soils of Sundgau Canton from different sources, and for different farm types

<table>
<thead>
<tr>
<th>Fluxes</th>
<th>Arable farming</th>
<th>Dairy and mixed</th>
<th>Animal husbandry</th>
<th>Whole region</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input fluxes (g ha⁻¹ y⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manure</td>
<td>&lt;0.1</td>
<td>0.7</td>
<td>8.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Biosolids</td>
<td>0.4</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Commercial fertilizers</td>
<td>0.6</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>Deposition</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Output fluxes (g ha⁻¹ y⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crop removal</td>
<td>0.6</td>
<td>1.9</td>
<td>0.6</td>
<td>1.4</td>
</tr>
<tr>
<td>Leaching</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Net flux (g ha⁻¹ y⁻¹)</td>
<td>2.3</td>
<td>0.8</td>
<td>9.1</td>
<td>1.4</td>
</tr>
</tbody>
</table>


17.3  Chemical Behavior in Soils

The chemical form of Cd and Zn in soils is important because added soluble metals react over time to less phytoavailable forms in soils. Further, because rice has comprised such an important source of human Cd risk, the chemistry of Cd in flooded (anaerobic; reduced) soils is especially important. In general, both elements co-occur in sphalerite as a solid solution of ZnS. When sphalerite is mixed in aerobic soil, the sulfide is oxidized by microbes and soluble Zn and Cd are released to react with the soil [49]. At least temporarily some ZnS and CdS are present in the mine waste-contaminated soil [50]. In flooded soils, several changes occur sequentially that affect the phytoavailability of Zn and Cd [51]. As reduction of soil chemicals increases over time, soil pH rises and CdS has been shown to be formed [52] by using X-ray absorption spectroscopy (XAS). And upon drainage of the flooded soil, pH falls and CdS is oxidized rapidly. The oxidation of CdS and drop in pH greatly increase soil Cd phytoavailability [51,53], allowing little adverse effect of Zn on rice yields but for grain to contain high Cd levels at harvest. In the same reduced soils, Zn does not appear to form sphalerite [54]. Fields are normally drained at rice flowering to maximize yields and prepare the fields for harvest. An important management method to reduce rice Cd accumulation is to keep the field flooded until grain maturity, but growers seldom want to use this method because of reduced yield and inconvenience at harvest. Rainfall during the grain filling period can slow soil oxidation and reduce Cd accumulation in rice [55], causing variation in grain Cd from year to year. Because of the flooding management, most rice roots are restricted to the near surface soil [51], which promotes Cd uptake after drainage.

In aerobic soils, it is clear that added soluble Zn reacts to form adsorbed and occluded species with lower phytoavailability. When Zn fertilizers are applied, even to acidic soils, the Zn becomes less phytoavailable over time [56–58]. When the labile pool of Zn in soils was assessed, the labile fraction varied among soils with generally lower lability in alkaline soils than in acidic soils [59]. More recent studies using XAS have shown
that Zn–Al layered double hydroxides (LDH) can be formed from Zn added to soils, and that this form becomes more stable over time by additional reactions with aluminosilicates [60–62]. Roberts et al. [63] and Scheinost et al. [64] used EXAFS (extended X-ray absorption fine structure) spectroscopy to examine forms of Zn in a highly contaminated soil from Palmetton, PA, USA that contained 6200 mg Zn kg$^{-1}$, had a pH value of 3.2 and was rich in organic matter. They found 2/3 franklinite ($\text{ZnFe}_2\text{O}_4$) and 1/3 sphalerite ($\text{ZnS}$), along with some Zn adsorbed on Fe and Mn oxides. These minerals could have been present in wind-blown ore particles which contaminated the area. More samples of highly Zn-contaminated soils need to be characterized by XAS to determine the kinds of Zn species which can form after Zn reacts with soils, especially in contaminated soils made calcareous to prevent adverse Zn effects.

Cadmium’s reactions in soils are substantially different from those of Zn. Although several groups have tested for formation of LDH compounds from Cd, none have found this reaction to occur [62]. Instead, most Cd remains in the labile pool over time. This is especially evident in soils amended with biosolids, where more than 90% of added Cd remained labile over 25 years after the biosolids had been land-applied [65]. Cadmium in phosphate-amended soils may be slowly transformed to nonlabile forms, but the process is slow and incomplete [66]. Mine waste-contaminated soils may have a lower fraction of labile Cd because CdS persisted in the soil, or because the Cd was occluded in other mineral [50].

### 17.4 Plant Accumulation of Soil Cadmium and Zinc

Plant uptakes of Cd and Zn are affected by soil properties, plant species and cultivar, fertilizers, agronomic management, and properties of the metal source. So many factors can affect crop Cd and Zn accumulation in particular cases that only the key factors are discussed here. More information can be found in reviews of soil and plant factors that may affect accumulation of Cd in edible crop tissues [67–70]. Because soil Cd remains in the labile pool in Cd-enriched soils, the Cd remains phytovailable: no method to transform soil Cd into low phytovailable forms has been identified although soil management can reduce uptake such as by raising soil pH.

Membrane transporters are now understood to absorb Cd and Zn from soil solution. The primary uptake uses transporters of the ZIP family cloned from *Arabidopsis* [71], and other types of transporters are believed to move Cd and Zn into the xylem, into leaf cells, and into vacuoles. Two membrane transporters for uptake of soil solution Zn have been cloned from *Arabidopsis thaliana* L. [72]. The OsZIP1 protein is a high-affinity Zn transporter with $K_m = 16.3 \, \mu\text{M}$, which is much higher than found in soil solutions of fertile soils [73]. The HMT4 protein was shown to control Zn transfer into the xylem of *Arabidopsis halleri*, a Zn hyperaccumulator species [74].

In other studies, Cohen et al. [75] reported that the ferrous transporter of dicot roots also transported Zn, Cd, Cu, and Mn. Subsequently, they reported studies at activities of these other ions more like those in soil solutions and noted that the IRT1 ferrous transporter was likely only important for Fe uptake, not for Cd or Zn [76]. Thus, Cd$^{2+}$ and Zn$^{2+}$ ions are believed to be accumulated across the root plasma membrane by a specific permease or transport protein. The study of Hart et al. [77] showed that Zn and Cd uptake were mutually
inhibitory when practical concentrations were examined; Zn$^{2+}$ is usually at much higher activity in soil solution than is Cd$^{2+}$. Transport from roots to shoots varies widely among plant species [78], and also among cultivars within species (see below).

Major soil and plant factors which influence Cd and Zn accumulation include (i) plant species and cultivar; (ii) soil Cd and Zn phytoavailability and Cd:Zn ratio; (iii) soil pH; (iv) soil sorption surfaces including organic matter, and amorphous Fe and Mn oxides; (v) chloride; (vi) fertilizer N and P; and (vii) crop rotation or preceding crop. The role of plant species and cultivar variation in Cd accumulation is discussed by Grant et al. [79] and will not be addressed in detail here. All species which have been tested have been found to have substantial genetic variation in Cd accumulation. Breeding programs have been conducted for durum wheat and sunflower to obtain lower Cd levels in grain/kernels [80,81] with good success. In durum wheat, the key difference between lower- and higher-Cd genotypes was translocation from root to shoots [82]. But breeding for lower Cd is expensive and competes with normal breeding goals such as yield, disease resistance, and so on. Many groups are attempting to breed lower-Cd rice cultivars (for example, [53,83]), but this is unlikely to be fully successful unless contaminated soils are kept flooded to lower soil Cd phytoavailability to rice [79].

The soil Cd and Zn concentrations and Cd:Zn ratio of the Cd source is one key factor. The lower the Cd and Cd:Zn ratio, the less likely that increased bioavailable Cd will accumulate in crops. Zn and Cd are affected similarly by soil properties in many ways, and Zn inhibits Cd uptake by roots and transport to shoots [77,84]. For some crops, Zn inhibits Cd transfer to grain or other storage tissues [85]. Chaney et al. [85] also illustrated the strong effect of Cd:Zn ratio on maximum Cd concentrations which can be reached in lettuce shoots (Table 17.7): when shoot Zn exceeded 400–500 mg kg$^{-1}$ dry leaves, plants became chlorotic and had reduced yield. Studies of lettuce grown on Zn-smelter-contaminated garden soils showed the very strong reductions in yield if highly Cd+-Zn contaminated soils were acidic [37]. When no edible crop yield is produced, humans are not at risk from the soil Cd. The strong impact of Cd:Zn ratio of land-applied biosolids in subsequent Cd uptake if the soil becomes acidified is illustrated in Table 17.2.

Soil pH is usually considered a central factor in Cd accumulation; more acidic soils bind Cd less strongly, allowing more Cd uptake [86,67]. A few rare cases have been reported where increasing pH did not reduce crop Cd concentration [87]. Soils on one farm where a high-Cd and high-Cd:Zn biosolids had been applied before regulations were developed caused lettuce to accumulate very high Cd concentrations whether acidic or calcareous (Table 17.8) [23]. The high Cd:Zn ratio apparently induced a Zn deficiency stress that caused the lettuce to keep trying to take up Zn, but the plant accumulated more Cd because Zn activity was so low in the calcareous soil. Actual Zn deficiency has been repeatedly observed to cause higher Cd accumulation by plants [68,88].

Chloride was identified as very important in Cd uptake from neutral pH soils [89]. High soil chloride causes formation of CdCl$^+$ complex that is soluble in soil solution. The mechanism by which this complex is absorbed has not been determined, but high chloride caused high crop Cd accumulation even from alkaline soils [89–91]. A study by Smolders and McLaughlin [92] tested the role of Cd$^{2+}$ activity versus chloride in Cd uptake by using a chelating resin to buffer Cd$^{2+}$ activity; added chloride caused more Cd to be dissolved in the resin-buffered nutrient solution, and more Cd to be absorbed by the plant even though Cd$^{2+}$ activity was tightly controlled. For soils irrigated with
### Table 17.7  Interactions of Cd and Zn in uptake by lettuce grown on acidic soil: Cd and Zn in lettuce shoots in relation to Cd:Zn ratio and Zn phytotoxicity response to the treatments [86]. A shows the metal additions and Cd:Zn ratio of the added Cd and Zn; B shows the leaf Cd, and C, shows the leaf Zn [85]. Bold type denotes nonphytotoxic Zn; low Cd:Zn ratio = edible crop

<table>
<thead>
<tr>
<th>Added soil Cd (mg kg⁻¹)</th>
<th>Added soil Zn (mg kg⁻¹)</th>
<th>Cd:Zn of added metals</th>
<th>Cd (mg Cd kg⁻¹ dry leaves)</th>
<th>Zn (mg Zn kg⁻¹ dry leaves)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td></td>
<td>&lt;0.001</td>
<td>1.15</td>
<td>30</td>
</tr>
<tr>
<td>0.75</td>
<td></td>
<td>&gt;0.10b</td>
<td>8.14b</td>
<td>31.5</td>
</tr>
<tr>
<td>1.50</td>
<td></td>
<td>&gt;0.10b</td>
<td>4.21b</td>
<td>31.5</td>
</tr>
<tr>
<td>3.00</td>
<td></td>
<td>&gt;0.10b</td>
<td>7.75b</td>
<td>31.5</td>
</tr>
</tbody>
</table>

Note: Cd:Zn < 0.001 limit of recommended biosolids.

Zn phytotoxicity caused yield reduction >35%.


### Table 17.8  Effect of adding limestone, Zn, or peat plus Zn to pH 6.2 soil which contained 6.8 mg Cd kg⁻¹ and 89 mg Zn kg⁻¹; a Cd-rich, high-Cd:Zn biosolids was applied for many years. Zn deficiency was induced by liming in the presence of high soil Cd levels, causing higher shoot Cd concentration than the unlimed treatment

<table>
<thead>
<tr>
<th>Treatments</th>
<th>pH</th>
<th>Yield (g per pot)</th>
<th>Lettuce CD (mg kg⁻¹)</th>
<th>Lettuce Zn (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>5.6</td>
<td>5.9 c</td>
<td>14.3 b</td>
<td>12.8 e</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>7.5</td>
<td>1.6 d</td>
<td>19.5 a</td>
<td>9.9 f</td>
</tr>
<tr>
<td>CaCO₃ + Zn</td>
<td>7.4</td>
<td>6.8 abc</td>
<td>1.9 g</td>
<td>53.7 c</td>
</tr>
<tr>
<td>CaCO₃ + peat</td>
<td>7.3</td>
<td>1.2 e</td>
<td>12.0 bc</td>
<td>9.3 f</td>
</tr>
<tr>
<td>CaCO₃ + peat + Zn</td>
<td>7.3</td>
<td>7.9 ab</td>
<td>2.2 f</td>
<td>62.8 b</td>
</tr>
</tbody>
</table>

Note:Means followed by the same letter are not significantly different (P < 0.05) according to the Waller–Duncan K-ratio test.

Adapted from R.L. Chaney et al., Zn deficiency promotes Cd accumulation by lettuce from biosolids amended soils with high Cd:Zn ratio, J. Residual Sci. Technol, 2006, 68–75 [23].
high-chloride waters, or soils with geogenic chloride. Cd is increased in crops as much as 10-fold compared with similar soils with basal chloride. Interestingly, increasing soil chloride does not increase crop Zn, so the increased Cd in crops may have higher bioavailability to animals that ingest the crops. One possible mechanism adding to the effect of chloride on Cd uptake may be induced Zn-deficiency; Khoshgoftarmanesh et al. [93] found that chloride reduced Zn activity and uptake by wheat, and that adding Zn fertilizer in this case significantly reduced wheat Cd. Because chloride is an essential element, and applied to reduce disease incidence, tests have been conducted with fertilizer levels of chloride application [94]; fertilizer chloride rates had little effect on crop Cd.

The role of Cd in P-fertilizers in soil and crop Cd concentrations is a complicated picture. As noted above, regular small additions of Cd in P-fertilizers may accumulate in soil, but uptake is usually little affected except by the quite high Cd phosphates such as those from Nara [27]. In many studies the form of N-fertilizer applied has greater effect on crop Cd than the amount of Cd in the P-fertilizer applied [96]. The recent work of Huang et al. [95] evaluated repeated applications of P-fertilizers over five crops of lettuce and found low additivity of the applied Cd on crop Cd. It appears that P reaction with Fe oxides may increase the selective adsorption of Cd, thereby reducing Cd phytoavailability. As noted above, studies of long-term fertilizer plots with low-Cd phosphates has shown little or no affect of long-term repeated applications of P-fertilizers on Cd accumulated in staple grains (for example, [97]). European Union regulations have encouraged production of phosphates with lower Cd levels [98].

One aspect of Cd in crops has been difficult to explain, the effect of previous crops (crop rotation) on Cd uptake by the current crop. Oliver et al. [99] found that previous legume crops caused higher Cd uptake by wheat than did previous cereal crops. Grant et al. [68] noted some evidence of a similar effect of a previous Cd-accumulating crop such as flax or sunflower on Cd in wheat grain. Khoshgoftarmanesh and Chaney [100] found that when sunflower stover was removed from the field, the following crop of wheat had lower grain Cd than following wheat. None of the expected factors (pH, organic matter, etc.) seems to explain these results.

Another complication is soil moisture in the tillage depth where applied Cd accumulates. If active roots are not present in the topsoil during grain filling, properties of the topsoil (pH, Zn) may have little effect on grain Cd accumulation [68,88]. Further, chloride in the subsurface soil can move up during dry conditions and have large impact on plant Cd accumulation.

### 17.5 Risk Implications for Cadmium in Soil Amendments

**Biosolids, Composts, and Manures**

As noted above, rice and tobacco soils are unique in their potential to transfer soil Cd to humans when soils contain ore-like Zn+Cd enrichment. Today most soil amendments (manure, compost, biosolids) in the European Union, North America, and Australasia have favorable Cd:Zn ratios to limit Cd transfer and bioavailability. Biosolids have received much attention regarding Cd risk, but readers should recognize that the apparent risks of Cd in biosolids came from experiments that used biosolids that are no longer produced or
permitted under national regulatory systems. Industrial pretreatment and reduced use of Cd in products had greatly improved biosolids quality at nearly every treatment works [38].

Subsequent research on Cd applied in biosolids has shown that when high-quality (low Cd and low Cd:Zn ratio) biosolids were applied, crop Cd was only marginally increased and Zn came along with the Cd so that bioavailable Cd in leafy vegetables was not increased [101,102]. Over 20 years after field plots were established, Cd uptake by lettuce was not increased over time for biosolids with lower Cd levels even though added organic matter was largely biodegraded [103]. Research by Hettiarachchi et al. [104] and Kukier et al. [65] showed that the presence of Fe and Mn oxides and phosphates in applied biosolids had increased the specific Cd adsorption capacity of the inorganic fraction of biosolids-amended soils, which substantially lowered the phytoavailability of soil Cd (see Figure 17.1) (see also Basta et al. [105]).

Many sources of error have been identified in testing potential Cd uptake by crops, from using Cd salts without the matrix of a soil amendment, to using greenhouse pots which restrain all roots to the contaminated soil depth (see [27]). Because of the strong adsorption of Cd and other metals by the matrix of biosolids, especially those which contain Fe oxides from Fe added to remove phosphate during wastewater treatment, and the low bioavailability of Cd in plants when Cd:Zn ratio is similar to geogenic, there is no longer any basis to predict increase in human Cd risk due to land-application of biosolids, composts, or

**Figure 17.1** Effect of historic biosolids application on the phytoavailability of applied Cd salts to Romaine lettuce (Lactuca sativa var. longitila). Soils were collected from long term biosolids amended and control soils from plots established in 1976 on Christiana fine sandy loam. Soils with all treatments were amended with Cd salt and adjusted to pH 6.5 in 0.01 M Ca(NO₃)₂ before growing 'Parris Island' Romaine lettuce to maturity; Cd in the heat-treated biosolids was 13.4 mg Cd kg⁻¹, and in the composted biosolids, 7.2 mg Cd kg⁻¹ (Modified from Kukier, U.; Chaney, R.L.; Ryan, J.L.; Daniels, W.L.; Dowdy, R.H.; Granato, T.C., Phytoavailability of cadmium in long-term biosolids amended soils' J. Environ. Qual. 2010 [65].)
livestock manure except for rice or tobacco soils. An examination of the literature shows that biosolids caused high crop Cd only when they had high Cd and Cd:Zn ratio, and soils were strongly acidic [37,106].

**Crops with Unusually High Normal Cadmium Concentrations**

We have described above how rice and tobacco can transfer soil Cd into humans to cause health risks. No other crops have been implicated in human Cd disease. Some foods naturally contain comparatively high Cd levels (for example, sunflower kernels, flax, poppy seeds, durum wheat, chocolate [107–110]) (Figure 17.2), but only small amounts of these are consumed daily. The Cd in these crops appear to have low bioavailability as evidenced by a one-year sunflower kernel consumption trial with human volunteers who showed no increase in blood Cd despite doubling of Cd intake [111]. This result was similar to that of Vahter et al. [112] who sampled nonsmoking young Swedish women, some of whom ingested shellfish, which tripled their Cd intakes, compared with women not consuming shellfish in their diets. Shellfish significantly increased daily Cd intakes, but this did not cause increased blood Cd. The shellfish also supplied high levels of bioavailable Zn and Fe that lowered the absorption of diet Cd compared to non-shellfish-containing diets. Therefore, the mere fact that a diet contains elevated levels of Cd does not mean that humans will absorb higher amounts of Cd with concomitant adverse effects on health. Fox et al. [113] stressed that estimates of food-Cd risks should be based on intakes of Cd similar to those of human diets, not the massive levels often studied. Fox et al. [113] illustrated trace element deficiency interactions in Cd absorption and used

![Figure 17.2](image)
‘nutritional’ rather than ‘toxicological’ approaches to the study of dietary Cd risk. The
nutritional perspective seems even more important after our recent research showing that
Fe-Zn-Ca ‘marginal’ diets can cause a large increase in diet Cd bioavailability [114].
Indeed, despite many papers showing a possible role of metallothionein in intestinal Cd
metabolism, when Reeves et al. [115] used metallothionein-null mice and the nutritional
approach for testing, they found no effect of the metallothionein genes on uptake or
retention of Cd, or on the large effect of Fe-Zn-Ca marginal deficiency on Cd retention.
A fuller discussion of the complexity of dietary Cd bioavailability is reported by Reeves
and Chaney [114].

17.6 Plant Uptake of Cadmium and Zinc in Relation to
Food-Chain Cadmium Risk

When soils are strongly acidic, both Cd and Zn are more soluble and are taken up more readily by plants. Both elements are relatively easily translocated to plant shoots, so food-chain risks and benefits need to be considered. At some combination of acidic pH and nearly all Zn+Cd co-contamination, Zn becomes phytotoxic but Cd remains far below phytotoxic concentration because of the Cd:Zn ratio present in the soil. This is illustrated by Table 17.7 which reports the concentration of Cd and Zn in Romaine lettuce (Lactuca
sativa L. var. rotundifolium) shoots when the plants were grown on pH 5.5 soil
with factorial additions of salt Zn and Cd at different Cd:Zn ratios [85]. At some rate of
Zn application, lettuce accumulated more than 400 mg Zn kg$^{-1}$ DW and had 35 % yield reduction or greater. And at some rate of Cd application, the Cd:Zn ratio was higher than geogenic ratios such that Cd uptake to shoots was high enough that the lettuce should not be used as food (a CODEX limit for Cd in lettuce was proposed at 0.05 mg Cd kg$^{-1}$ fresh weight which would be equal to 4 mg Cd kg$^{-1}$ dry weight; see [134]). But when the Cd:Zn ratio was in the range of geogenic contamination, Zn phytotoxicity occurred before excessive Cd accumulation occurred in lettuce shoots.

In addition, when a food accumulates high levels of Zn along with increased levels of Cd in plant shoots such as lettuce or spinach (Spinacia oleracea L.), the much higher Zn inhibits absorption of Cd in the animal that ingests the crop [101,102,116,117]. Thus at the usual geogenic ratio of Cd and Zn, even crops (except rice and tobacco) with relatively high ability to accumulate Cd do not comprise risk to animals because Zn is also present. In addition, tests of Cd accumulation by lettuce grown on smelter-contaminated soils showed that whenever Zn reached levels near 500 mg kg$^{-1}$ DW, yield was strongly reduced; and that this phytotoxicity of Zn limited the potential yield of garden crops and hence risk from home garden soils. The raw data of Baker and Bowers [118] were presented graphically by Chaney and Ryan [37]; the strong Zn phytotoxicity protection against any food-chain Cd risk is evident.

Potential phytotoxicity from Cd or Zn raises the issue of Cd and Zn speciation in plant tissues. Ordinarily Zn$^{2+}$ in cytoplasm is mostly complexed with organic and amino acids. Grill et al. [119] discovered that when cell cultures were fed toxic levels of Cd, they accumulated a new form of Cd chelated with ‘phytochelatins’. Phytochelatins are derivatives of glutathione with additional γ-glutamyl-cysteine residues attached to make a more
selective Cd chelator. After much research on phytochelatins, it became evident that they were only formed under conditions of severe Cd phytotoxicity and have little relevance to normal plant metabolism of accumulated Cd or Zn [120,121]. Even when phytochelatins are produced in roots, only a small fraction of total Cd is present as phytochelatins [121]. Other research indicates that the presence of Cd drains reaction products from the glutathione metabolism system rather than inducing biosynthesis at the genetic level [122]. When Romaine lettuce was grown to contain basal or food-type levels of Cd, the Cd was not present as phytochelatins [123].

On the other hand, rice soils have been contaminated by geogenic Zn+Cd and caused human Cd disease without Zn phytotoxicity at many locations. From the locations in Japan where environmental Cd disease was discovered [4,124], it is clear that rice has a very different ability to accumulate soil Cd and Zn than found in other crops. It was found that rice grown at Tohyama, Jinzu Valley, Japan, had a large increase in grain Cd but no increase in grain Zn even though the soil was contaminated by Zn mine wastes which gave about 10 mg Cd kg⁻¹ and 1000 mg Zn kg⁻¹ soil [125]. The cause of environmental Cd disease in Japan was discovered by a soil scientist, Dr. Jun Kobayashi, who had a spectrograph and could measure Cd in water, soil, rice and human tissue samples, and who had experience with mine contamination of rice soils [4]. Dr. Kobayashi worked with the local medical doctor, Dr. Hagino, to identify the cause of bone disease and an epidemiologist at the Prefecture Medical School worked with them to test for specific effects of Cd and confirmed the Cd disease [126–128]. About 80% of farm families more than 50 years old experienced the proximal renal tubular dysfunction that is the first adverse effect of excessive dietary Cd intakes. At Tohyama, about 300 women and one man also suffered itai-itai disease (osteomalacia) with repeated bone fractures. Cadmium-induced bone disease is rarely induced by dietary Cd, but was also found at one location in China [129].

Since the original finding at Tohyama, Japan, more than 50 other locations in Japan have been found to have been contaminated by mine or smelter emissions and produced rice with excessive grain Cd [130]. Then locations were discovered in China [6] where rice and tobacco contributed to human Cd disease. Locations with excessive Cd in rice grain have also been discovered in Korea and Thailand [7] and are suspected in other locations. The case in Thailand illustrates the relationships between normal Zn mining and human risk when rice is the main local crop. Subsistence farmers consume the rice grain they produce on local soils. If those soils become contaminated by dispersal of mine or smelter emissions or industrially contaminated sewage, excessive Cd in rice grain is unavoidable.

J. Scott Angle and Rufus L. Chaney (unpublished) sought a location in Asia that had not been examined previously where the need to remediate risks from rice Cd may support development of commercial Cd phytoextraction. We had developed and patented Cd phytoextraction using southern France populations of Thlaspi caerulescens J.&C. Presl. (alpine pennycress) and wanted to test its use in rice fields [131–133]. We looked at other nations where rice was a common crop and where Zn ores were mined and/or smelted; and where western patents were respected. Mae Sot, Thailand, was identified and we cooperated with the Thai Ministry of Agriculture to design an evaluation of soil and crop contamination. Those results were first reported in detail by Simmons et al. [7], who show the same relationship found in Japan. In this case, soil Zn was as high as 7000 mg kg⁻¹ and Cd as high as 200 mg kg⁻¹, remarkable levels. As shown in Figure 17.3, even with the extremely high soil Zn levels, rice grain Zn was not increased, while rice grain Cd
was increased to extreme levels in all fields irrigated with the water supply contaminated by mine discharge. Simmons et al. [134] reported more details on the patterns of contamination across irrigation networks; fields were arranged on terraced hillsides with water entering the highest field and moving sequentially through lower fields until discharged. Because much of the contamination was from suspended solids, the highest contamination was deposited near the entrance of the highest field; soil Cd and Zn concentrations fell strongly in fields lower in the landscape because the suspended solids were deposited in fields above. Unfortunately, grain Cd is not a simple linear function of soil Cd, so even fields with only moderate Cd contamination produce rice with Cd level higher than allowed to be used as food (0.4 mg Cd kg$^{-1}$ rice grain set by the Codex Alimentarius Commission in 2006 [135]. Finally, examination of the older residents who consumed the rice grown at Mae Sot showed renal tubular dysfunction was prevalent in the population [136].

**Why Does Cadmium Comprise Such High Risk to Subsistence Rice Consumers?**

Rice is the only staple grain normally produced in flooded soils. Upon flooding, soil pH rises toward 7 and insoluble CdS is formed in flooded soils; both changes reduce Cd phytoavailability. But the growers usually drain their fields at flowering to improve yields. When the fields are drained, sulfides can be rapidly oxidized, as can the ammonium, ferrous, and manganous ions produced during flooding. This can cause a sharp decline in soil pH and increase in solubility of Cd and other metals. Because of the unusual properties of drained rice soils, and rice plants, little or no increase in rice grain Zn occurs (although Zn is increased in rice leaves), but Cd can be highly increased in rice grain [7,55]. This relative exclusion of soil Zn from rice grain was apparent in the first reports on the Jinzu Valley rice Cd poisoning case, and in research on rice grown in soils contaminated by mining wastes [55,125]. But the exclusion of Zn from grain on even highly Zn+Cd-contaminated rice soils was not appreciated until later research on contaminated Thai soils.
by Simmons et al. [7] (Figure 17.3). Interestingly, most soil testing is done on air-dried soils, and the extractable Cd and Zn levels do not give useful estimates of rice accumulation of Cd or Zn. However, when field-moist soil collected at grain maturity is tested immediately, extractable Cd is highly correlated with grain Cd [137].

In addition to the flooded-soil effect on phytoavailable Cd, the composition of rice grain promotes Cd absorption in animals. Rice grain is inherently low in Fe, Zn, and Ca concentrations, and milling of the grain [138] removes much of these elements in the brown rice. Interestingly, a much smaller fraction of Cd is removed during milling than of Zn and Fe [139,140]. Because Zn and Fe deficiency stress increase the absorption of dietary Cd, the natural composition of milled rice promotes Cd absorption by humans [114,141]. It has recently been discovered that most Cd enters the intestinal cells on the ferrous transporter (DMT1) in the duodenum [142,143]. Reeves and Chaney [144] found that a high fraction of diet Cd entered the duodenum and turned over in that tissue for many days; the longer retention in animals fed the Fe-Zn-marginal diets apparently caused 10-fold higher net absorption of diet Cd than found for animals with adequate Fe and Zn nutrition. In addition, higher dietary Zn can also inhibit Cd absorption by animals (for example, [116,145]).

These findings should influence decisions about tolerable Cd in diets and crops. Presently, Cd is considered to be equally bioavailable in all crops and at all crop Zn levels. But the marginal supply of Fe and Zn in polished rice grain is now recognized to compromise an international health problem due to practical Fe and Zn deficiency in subsistence rice consumers [146]. Further, higher plant Zn is known to reduce absorption of dietary Cd [116]. In addition, Cd in spinach was found to be half as bioavailable as Cd in lettuce or other foods [116,147]. This likely results from Cd co-precipitation with Ca-oxalate in the intestine. Other studies of diet Cd absorption by humans have shown that increased Cd ingestion in shellfish [112] or in sunflower kernels [111] did not cause higher blood or urine Cd. This is in strong contrast with rice diets [148].

Several northern European populations have been reported to possibly suffer adverse effect of dietary Cd at much lower dietary Cd, blood Cd, and urinary Cd [149,150] than other populations without identified adverse Cd effects [148]. These reports are not explicable in terms of known aspects of Cd metabolism, and remain debated among scientists. Ezaki et al. [151] reported tests on over 10,000 middle-aged nonsmoking Japanese women which strongly contradict the European results. Because of high rice consumption and somewhat high Cd levels in Japanese rice, these women consumed considerably more dietary Cd than the European subjects. Blood and urine Cd were higher for the Japanese women, but the renal dysfunction indicators revealed no case of adverse effects at least to 3 μg Cd l−1 urine. Compare this with claims of adverse effects at lower than 2.5 μg Cd l−1 in the Europeans. The difference in interpretation appears to be due to the ‘normal’ values used for comparisons of urine indicator proteins, and the Ikeda et al. team has provided a detailed examination of the control population normal values and how to express them [152].

Other crops
Although it is clear that geogenic Zn+Cd in rice soils can readily cause human Cd disease in subsistence farmers, other crop production systems with even higher geogenic Zn+Cd contamination have not been shown to cause such Cd disease. Smelters and mine wastes were also dispersed in western countries, and villages developed on the land such that
home gardens and some farm crops were produced on soils with very high Zn+Cd contamination. Examples include Shipham, UK [8,153–155], Palmetton, PA, USA [12,156], Stolberg, Germany [157,158], and France [159]. Kreis et al. [160] estimated increase in Cd ingestion from garden crops in the Kempenland, a smelter contaminated area of the Netherlands and Belgium, finding insufficient increase to cause individuals to exceed the allowable Cd intake. Full epidemiologic studies were conducted on persons who lived in the contaminated soil areas and similar villages without soil contamination. Thus garden foods did not cause human Cd disease even when grown on highly Zn+Cd-contaminated soils. One location in Belgium has been reported to have adverse Cd effects on human health, and crop uptake of Cd was measured [161], but as was discussed above, the Cd risk from crop exposure does not agree with the other studies [148,152].

Besides the studies of populations exposed to highly contaminated soils and crops, a population of oyster fishers in New Zealand was shown to consume large amount of oyster Cd, but no adverse effects on kidney or bone health were observed [162,163]. A similar outcome was observed for Swedish young women who consumed shellfish compared with those who did not consume shellfish; despite their consuming three times more Cd, blood and urine Cd levels were not different between the groups [112]. Oysters also accumulate high levels of Zn and Fe, which are important in inhibition of Cd absorption in humans. Thus the co-accumulated Zn was able to prevent adverse effects of high accumulation of Cd in oysters from Bluff, New Zealand. And consuming sunflower kernels which doubled daily Cd intake for one year had no effect on blood or urine Cd [111].

**Cadmium-Accumulating Crops**

As noted above, a few crops accumulate relatively more Cd in their edible tissues than do the major staple grains such as wheat. Sunflower kernels, flaxseed, poppy seed, and chocolate have substantially higher Cd than wheat or rice when grown on normal soils, and accumulate Cd effectively when soil Cd or chloride are high. Figure 17.2 shows the statistical distribution of Cd concentrations for major grains and some of these accumulating species. Figure 17.2 also shows the ‘richtwert’ limits for importing sunflower kernels and flax into Germany. Because the levels in these crops are not a result of growing them on contaminated soils, and the daily consumption of these crops is small, limits are higher than those for wheat.

Tobacco has exceptional ability to move soil Cd into human kidneys. Tobacco accumulates Cd from soils about as well as lettuce and spinach. Tobacco is a potentially adverse source of Cd when soils are contaminated [164]. Smoking transfers about 10% of tobacco Cd into mainstream smoke, and that Cd is effectively absorbed in the lung (about 40%; [165]) regardless of Fe-Zn-Ca nutritional status. In the study of Cai et al. [6], high tobacco Cd caused about half of the Cd absorption to result from tobacco and half from rice. The commercial market for tobacco products controls Cd concentration by not purchasing tobacco containing high Cd levels. Home-grown tobacco, produced on Cd-contaminated soils, may comprise as high a risk as home-grown rice in Asia. A recent paper reported that ‘illicit’ cigarettes are on average considerably higher in Cd than authentic major brand cigarettes, although likely not enough higher to comprise likelihood of causing tubular dysfunction in a lifetime [166]. But production of tobacco on contaminated soil, and smoking such home-grown tobacco can clearly comprise Cd risk to humans.
17.7 Food-Chain Zinc Issues

Zinc Deficiency

Many soils are deficient in phytoavailable Zn to support crop production, and Zn fertilizers are commonly applied for crops with high Zn demand or poor Zn uptake ability. Rice (Oryza sativa L.) and maize (Zea mays L.) are well known for being susceptible to Zn deficiency [167]. Most deficient soils are alkaline; high pH reduces Zn phytoavailability, and may hasten transformation of added soluble Zn into nonphytoavailable forms in the soil [57,58]. Even some strongly acidic soils can become Zn deficient over time as cropping removes Zn.

A more important Zn deficiency issue is the low concentration and low bioavailability of Zn in some staple food grains [168]. Because many grains contain high levels of phytate, and phytate reduces the bioavailability of dietary Zn, rice, maize, and some other food grains have been found to accumulate insufficient Zn to support human health. Perhaps one billion persons on Earth are Zn deficient [169]. Zn deficiency retards neurologic development and causes birth defects. The same grains are often Fe deficient for human health. The major international ‘Harvest-Plus’ project aims to improve the density of bioavailable Fe and Zn in staple grains [146]. These researchers have also reported that sowing seeds with higher Zn concentration can promote early growth of crops in low-Zn soils, and high enough Zn can substantially reduce yield reduction on deficient soils. One method to increase seed Zn to obtain this ‘primer’ effect is to spray the plants with soluble Zn-including detergent at flowering [170].

Milling grains is known to remove much of seed Zn, Fe, and phytate from cereal grains [138,171]. Whole grains which are not leavened carry high levels of phytate into diets, reducing dietary Zn bioavailability. Part of the goal of the ‘increase grain Zn bioavailability’ research program is to simultaneously reduce phytate, or to move more of the Zn into the embryo rather than the pericarp of cereal grains. Some success has been achieved in finding genetic sources of higher grain Zn [172,173]. ‘Biofortification’ was coined to express the concept of increasing the concentration and/or bioavailability of trace elements in staple foods.

Zinc Phytotoxicity Issues

Plant leaves accumulate about 400–500 mg Zn kg⁻¹ at the soil Zn addition which reduces yield significantly [174]. Several papers covered large numbers of species, showing about 500 mg Zn kg⁻¹ at 25 % yield reduction [175,176]. Other papers suggest that 290 mg Zn kg⁻¹ dry leaves is associated with reduced yields, but base that on the theoretical first point where yield would be decreased from control yields [177,178]. The method used by Beckett and Davis [177] was sand culture with complete nutrient solutions including FeEDTA. However, under the conditions of their experiments, Zn displaces Fe from the FeEDTA chelate [179], strongly reducing the phytoavailability of added Fe to grasses. Grasses use phytosiderophores to dissolve soil Fe, and actively accumulate Fe-phytosiderophore chelates into the young roots [180], and Zn can also inhibit Fe chelation by phytosiderophores [181]. Zn salt but not Zn-mugineic acid chelate inhibited Fe-mugineic acid uptake by barley [182]. It seems likely that the lower Zn phytotoxicity thresholds reported by Beckett and Davis [177] may have resulted from use of FeEDTA in their sand culture testing. In fundamental tests of Zn toxicity to plants, Pedler
et al. [183] tested the effect of various cations on the toxicity, finding that toxicity was substantially lowered by low levels of added Mg ion.

Most studies of Zn phytotoxicity have used addition of soluble Zn salts so that the added Zn could be presumed to be 100% phytoavailable at the time of addition. This method can cause significant artifacts in estimation of Zn phytotoxicity in soils because the addition causes a reduction in soil pH as the added Zn displaces sorbed protons from the soil solid phases [184,185]. The displaced protons cause soil pH to fall by 1–2 pH units depending on the exchange capacity of the soil and the initial soil pH. Thus many of the tests of Zn phytotoxicity are so confounded by pH lowering due to the Zn salt addition that the results should not be considered useful. In addition, the presence of the anion added with the Zn salt increases Ca\(^{2+}\) in soil solution, and increased Ca\(^{2+}\) can displace more Zn from adsorption sites. Only leaching and aging after Zn salt addition can allow the added salt-Zn to approach phytovailability levels found in field contaminated soils [186].

Estimation of toxicity to soil microbial process and soil organisms of Zn salts added to soils is increasingly recognized to be strongly affected by artifacts of pH shift, anion solubility, leaching, and aging. The organisms being studied are already present in the soil when the Zn salts are added to the soil, allowing exposures that are quite unrepresentative of soil equilibrium. And soil organisms can adapt to metals over time. McLaughlin and Smolders [187] found that soils with higher Zn levels tolerated higher Zn additions before toxicity was observed than soils with lower Zn levels and suggested a ‘metalloregion’ approach to setting soil Zn limits. Smolders et al. [188] studied field contaminated soils compared with Zn salt-amended paired control soils without and with leaching and aging and ‘concluded that there is a large discrepancy in microbial responses to elevated Zn between spiked soils and field-contaminated soils’. Smolders et al. [189] found the spiked soils were up to 100-fold more toxic (median factor 3.4) than corresponding field contaminated soils and confirmed that leaching and aging strongly reduced toxicity. Smolders et al. [189] extended this finding and suggest that ‘soil microbial processes are sensitively affected in soils that are freshly spiked with Zn salt but these effects are undetectable in the field’. It appears likely that Zn-sensitive plant species may be the most sensitive organism for excessive soil Zn (rather than soil microbial processes or soil fauna), and the same artifacts of spiking soils strongly affect Zn toxicity to higher plants.

Study of cultivar variation in tolerance of soil Zn has been reported for soybean [184,190]. Interestingly, variation in tolerance was a property of the scion, while uptake and translocation was a property of the rootstock [191]. Tolerance variation was great enough that one could breed for greater Zn tolerance, but this property has little value in normal agriculture. Another interpretation of these results is that the concentration of Zn which would be diagnostic of phytotoxicity varies among cultivars.

**Remediation of Zinc Phytotoxicity**

As noted by Chaney [174], Zn phytotoxicity is the most common practical metal toxicity resulting from soil contamination. This results partly from the frequency of Zn emissions and dispersal of Zn mine wastes, and partly because Zn is less strongly adsorbed by soils than are Pb and Cu. Especially when soils are acidic, Zn can achieve soluble Zn\(^{2+}\) levels which induce toxicity to sensitive plants. In acidic soils, Zn usually reduces root length and induces Fe deficiency chlorosis, but direct toxicity to leaf processes also limits growth.
Thus there is need for methods to remediate Zn phytotoxicity. In the author’s experience, every Zn phytotoxicity in the field has been alleviated by making soils calcareous if attention is paid to soil fertility needs of the remediated soils. Often the contaminated soils are barren and eroded, removing much of the stored soil organic matter, P, and N. Because P reacts with Fe oxides to increase specific Zn and Cd adsorption capacity of such soils, additions of P and Fe along with limestone and organic-N help achieve persistent remediation [192]. Organic matter improves soil structure and fertility so that application of organic amendments with limestone is beneficial. Even when soils exceed 10 000 mg Zn kg\(^{-1}\), remediation has been very effective [14,15,193–196].

Potential Zinc Toxicity to Animals Consuming High-Zinc Crops

Zinc is essential for animals, and active homeostasis of body Zn is observed [197]. When soluble Zn salts are mixed with practical diets, Zn toxicity to domestic livestock occurs at 300–1000 mg kg\(^{-1}\) dry diet [199]. Zinc toxicity appears to result from Zn-induced Cu deficiency [198,199–202]. Sheep are more sensitive to excessive dietary Zn if Cu in the feed is marginal to deficient [200]; as low as 300 mg Zn kg\(^{-1}\) diet induced Cu deficiency and lower gain rates in sheep fed diets low in bioavailable Cu. Unfortunately, the toxicity of intrinsic plant Zn to livestock has not been reported.

Forage crops comprise the worst case for evaluation of excess soil Zn. Under conditions of high soil Zn supply, grain and fruit contain lower Zn concentrations than leaves, and Zn toxicity from feed grains is very unlikely to occur. Research by Ott et al. [203], Campbell and Mills [200], L’Estrange [204], Bremer [201], and Bremer et al. [205] indicates that even crop uptake of Zn to leaves is very unlikely to cause Zn poisoning of cattle or sheep.

Although humans could consume appreciable amounts of high Zn leafy vegetables (acid soils; mild phytotoxicity), it is very unlikely that Zn toxicity would occur in humans in even this worst case. Many humans presently consume low or deficient amounts of Zn [169]; increased food Zn would be beneficial in many cases. Assuming lettuce accumulated 500 mg kg\(^{-1}\) dry weight, that is only 25 mg kg\(^{-1}\) fresh weight; consuming 50 g fresh lettuce would provide only 1.25 mg of the daily required 15 mg of Zn. Thus garden crops are very unlikely to comprise Zn risk to consumers.

Wildlife comprises a greater risk case than do domestic animals because wildlife could chronically consume Zn-phytotoxic foliage as most of their diet. It seems likely that high-Zn sludges and industrial wastes could cause adverse health effects (due to Zn-induced Cu deficiency) in wildlife such as that resulting from Zn smelters [202].

In summary, land application/treatment of sewage sludges and industrial wastes is very unlikely to cause Zn toxicity in domestic livestock or humans even under worst-case conditions. Wastes unusually high in Zn but low in Cu may cause Zn toxicity in animals if mismanaged.

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