CADMIUM IN CROP PRODUCTION

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Introduction

Cadmium is a heavy metal, present in varying amounts in phosphate fertilizer. Excess levels of cadmium in the human diet has been implicated in kidney disfunction and liver abnormalities, prompting the World Health Organization to propose a limit for the daily intake of cadmium in the human diet. Codex Alimentarus has proposed a limit of 0.1 and 0.3 ppm in durum wheat and flax. Some Canadian durum wheat and flax at times rises above the proposed limits. As durum wheat is used for the production of pasta, it can be a significant route of entry for Cd into the human diet. While flax is less likely to be a major part of the diet, consumption of flax seed and flax oil is increasing, based on the potential health benefits of flax. Therefore, reduction of Cd concentration in both flaxseed and durum is desirable.

Cadmium uptake by crops is influenced by crop genetics the concentration of Cd in the soil solution accessed by crop roots. Therefore, crop selection and crop management practices may be manipulated to reduce the Cd concentration in foodstuffs. The concentration of Cd present in durum wheat and flax can vary substantially depending on the combination of genetic, environment and management factors influencing the crop. Breeding programs have developed lines of both durum and flax with the potential to produce Cd concentrations below the proposed Codex limits, but even these cultivars produce higher than desirable Cd concentrations with some soil-environmental-management combinations.

Species and Cultivar Effects on Cadmium Accumulation

Cadmium accumulation and distribution in plants differ with species and among cultivars within a species. Cadmium concentration of plants grown in solution culture increased in the order: Oats, wheat<bean, pea, sunflower, cucumber<corn, mustard<radish, kale, rape<tomato, carrot, sorrel< lettuce (Petersson 1977). Leguminosae generally show low accumulation, Gramineae moderate accumulation and Cruciferae high accumulation of Cd (Kuboi et al. 1986).

Cadmium accumulation also varies among cultivars (Pettersson 1977). Growth chamber studies conducted at Brandon Research centre showed considerable differences between low- and high-Cd cultivars of durum wheat, across a number of fertilizer treatments (Table 1). Unpublished information from Agriculture and Agri-food Canada at Brandon, Winnipeg and Swift Current indicates substantial genetic variation in Cd concentration of durum grain, with the potential for release of cultivars selected for low Cd accumulation in the near future.

Table 1: Effect cultivar and P and Zn application on cadmium concentration in durum wheat, under growth chamber conditions (Grant, unpublished)

	Cd in grain (ppb)	
Treatment	Biodur	Medora
Control	41 c	157b
Reagent Grade MAP	68ab	219a
Commercial MAP	78a	219a
Reagent Grade MAP + Zn	41c	122b
Commercial MAP + Zn	58bc	169ab
MSE	79.6	463

The amount of Cd that enters the diet from a plant depends not only on the amount of Cd that the plant accumulates, but also on whether Cd accumulates in the portion of the plant that is consumed. Distribution of Cd in the plant differs depending on the plant species and growing conditions and may be related in part to Cd tolerance of the crop (Williams and David 1973, Mullins et al. 1986, Jackson and Alloway 1992, Choudhary et al. 1994, Pettersson 1977). Roots and old leaves may act as a barrier to the accumulation of Cd in younger plant parts. It is possible that accumulation of high levels of Cd in the root may limit the accumulation of Cd in edible above-ground portions of the plant. Differences in Cd concentration in the seed among durum isolines may relate to the amount of Cd retained in the root.

Factors Influencing Cd Accumulation in Crop Production

While genetic characteristics affect Cd concentration in crops, environmental conditions and management practices also play an important role. Uptake of Cd by the plant increases with increasing concentration of Cd in the soil solution and is influenced by the size and uptake characteristics of the plant root system (Mullins et al. 1986). Therefore, any factors which influence soil solution concentration of Cd or root growth are likely to impact upon the Cd accumulation in the crop.

The pH of the soil has a dominating effect on solution concentration of Cd, by influencing the form of Cd present in the soil solution and the distribution of Cd between the soil and the solute (Christensen 1984a, Eriksson 1990, Naidu et al. 1994). Increased sorption of Cd with increasing pH would reduce the solution concentration, reducing Cd available for plant uptake.

Increasing the cation exchange capacity (CEC) of the soil will also tend to increase Cd sorption and decrease the amount of Cd in the soil solution (Eriksson 1990). In studies in

Manitoba and Saskatchewan, plant Cd accumulation was higher on light-texture than heavy-textured soils, due to the lower sorptive capacity of the low CEC, light-textured soils (Selles et al. 1996; Grant et al. 1996).

Competing ions in the soil solution may displace Cd from the sorption sites in the soil and increase its concentration in the soil solution. Increasing soil solution concentrations of Zn, H, or Ca increased Cd desorption from the soil, increasing soil solution concentration of Cd (Christensen 1984b). Increases in ionic strength also increased concentration of Cd in the soil solution (Lorenz et al. 1994).

Chlorides may form mobile Cd complexes which could increase the mobility of Cd in a soil system (Smolders and McLaughlin 1996a,b) independent of its effects on ionic strength. The Cl complexes of Cd are negatively or neutrally charged and therefore reduce Cd sorption on cation exchange sites and may increase movement of Cd to and possibly into the root. Thus, under relatively high Cl concentrations, as may occur with some saline soils, the solubility of Cd may be increased substantially, but reduced sorption was also observed at Cl concentrations representative of those commonly found in soil solutions (Garcia-Miragaya and Page 1976).

Managing Agricultural Systems to Reduce Cd in Crops

As discussed previous, cadmium accumulation in crops is influenced by crop cultivar and by cadmium concentration in the soil solution. Therefore, crop selection and management practices can be manipulated to reduce Cd concentration in foodstuffs (Grant et al. 1998).

Genetic Selection

Genetic variation in Cd accumulation occurs not only among species, but also among cultivars within a species (Pettersson 1977). Therefore, genetic selection may be effective in reducing Cd content of crops. Breeding programs, enhanced by biotechnological input, are currently underway at Agriculture and Agri-food Canada in Swift Current and Morden to produce cultivars of durum and flax with low levels of Cd in the grain. In durum, low Cd lines have been identified and future cultivars released will be genetically low in Cd. Low Cd flax lines have also been identified and will be incorporated into the breeding program. Biotechnological techniques for gene transfer across species may also play a role in development of low Cd food crops (Wagner 1993).

Sludge and Manure Application

Increasing amounts of sewage sludge are being applied to agricultural lands. The Cd content of sewage sludge is highly variable, depending on the nature and volume of effluent discharged (Alloway 1990). Establishment and enforcement of limits for Cd application to soils in sludges is important to prevent the accumulation of excess levels of Cd in agricultural soils.

Manure application contributes to Cd accumulation in crops both through direct addition of Cd and mobilization of Cd already present in the soil. Farm yard manures contain, on average, 0.3 to 1.8 mg Cd g^{-1} dry weight (McGrath 1984, Kabata and Pendias 1984). Jones et al. (1992) reported that annual application of 35 t ha^{-1} of fresh manure since 1850 in trials at Rothamsted increased soil Cd compared to untreated or phosphate-treated plots. In addition, the high N and organic acids of the manure may lower soil pH and mobilize Cd already present in the soil. The organic acids may also provide binding sites for Cd^{2+}, which can be readily released into the soil solution. More stable organic complexes may also form as the manure decomposes, binding Cd and reducing its availability for plant uptake. Investigations are bing undertaken at Brandon Research Centre to investigate the role of manure application in reducing Cd uptake into plants.

Fertilizer Management

Phosphate fertilizers contain Cd in varying concentrations, reflecting the Cd content of the rock from which the fertilizer was derived (Williams and David 1973). Plants generally take up only 1-5% of the soluble Cd added to soils (Williams and David 1976). Therefore, over a number of years, the Cd can accumulate, increasing the Cd concentration in the soil (Table 2) (Williams and David 1973, 1976). The impact of this Cd addition will depend on the amount of Cd in the fertilizers and its relative contribution compared to native soil levels and other anthropogenic sources.

Table 2: Cadmium (ppm) extracted by N hydrochloric acid from paired soil samples taken from fertilized field and adjacent unfertilized areas (Williams and David 1976)

Crop	Total P applied (kg ha^{-1})	Soil Cadmium Unfertilized Soil	 Cropped Soil	Metal retained in cultivated layer (% of applied)
Wheat	250	0.055	0.118	95
Pasture	185	0.024	0.085	94
Potatoes	1200	0.030	0.303	102
Tobacco	850	0.114	0.270	92
Celery	4000	0.033	0.342	83
Vegetables	900	0.016	0.076	53

Mortvedt (1987) reported no significant change in the Cd content of soils in long-term field studies in the United States. However, the Cd level of the fertilizer used in this trial was very low. Andersson and Hahlin (1981) observed in field studies conducted for 15 years, from 1963 to 1978, that the effects of Cd added in P fertilizer was small in relation to other causes of variation. Reducing the amount of Cd in phosphorus fertilizer is one method of reducing the long-term accumulation of Cd in the soil. Singh (1991)reported that the proposed maximum concentration of Cd in fertilizers for Norway was 100 mg kg^{-1} P from 1992 and 50 mg kg^{-1} P from 1995. To produce fertilizer P low in Cd, sources of rock may be selected that contain naturally lower levels of Cd, or Cd may be removed during the processing of the fertilizer. Either course of action will significantly increase the cost of the fertilizer and may restrict the amount of P fertilizer available for trade.

While Cd will logically increase in a soil when the amount that enters the system is greater than the removal, the effect on Cd accumulation by crops is less clear. In spite of an increase in Cd content of the soil with P application, the Cd contents of crops were not increased by long-term P fertilization (Andersson and Hahlin 1981, Baerug and Singh 1990, Singh 1993). In long-term field studies, Andersson and Siman (1991) reported that Cd concentrations in grain and seeds consistently increased with increasing P application, when the fertilizer contained 70 to 150 mg Cd per kg P. They attributed the increase to the Cd applied with the P fertilizer. However, increasing levels of P fertilizer were also accompanied by increasing levels of N and K fertilizer, confounding the interpretation of the data. Studies by Nicholson et al. (1994) showed that Cd concentrations in grasses grown on plots which had received P fertilizer since 1859 were higher than those on unfertilized sites, in the absence of lime. On the limed plots, the Cd levels of fertilized and unfertilized grasses were similar, indicating the importance of changes in soil pH caused by fertilizer additions.

The concentration of Cd in P fertilizer also appears to have little influence on Cd concentration of crops in the year of application (Table 3)(Sparrow et al. 1993a,b, McLaughlin et al. 1995). In growth chamber studies, Grant et al. (unpublished data) observed no difference in Cd concentration in durum grown with reagent grade MAP, containing trace levels of Cd and fertilizer grade MAP, containing 15 mg g^{-1} (Table 1). In contrast, He and Singh (1994a) reported higher Cd concentration in oat, ryegrass, carrot and spinach when high-Cd as compared to low-Cd fertilizers were applied.   Again, the immediate effect of Cd level in fertilizer will depend on its importance relative to other sources and influencing factors.

Table 3: Effect P fertilizer type and Cd content on cadmium concentrations in potato tubers at sites 1-3 (McLaughlin et al. 1995)

Site	SSP[a] Low[b]	SSP High	DAP Low	DAP High	MAP Low	MAP High
	Tuber Cd concentration (mg kg^{-1} FW)					
1	0.016	0.018	0.015	0.018	0.027	0.018
2	0.166	0.186	0.164	0.188	0.155	0.185
3	0.071	0.083	0.074	0.064	0.072	0.072

[a] SSP = single superphosphate, DAP = diammonium phosphate, MAP = monoammonium phosphate

[b] Low = <100 mg Cd kg^{-1} P, High = >300 mg Cd kg^{-1} P.

__Table 4: Response of Cd concentration in the grain of Medora and Sceptre durum wheat to N, P and Zn fertilization on a clay loam and silty clay soil, from 1991 to 1993. (Grant and Bailey 1998)

	Clay Loam		Silty Clay			
	Medora	Sceptre	Medora			Sceptre
	(1991-93)		1991	1992	1993	1991-93
	(μg kg^{-1})					
1. Control	57	45	55	122	73	71
2. Zinc	44	46	60	118	59	66
3. N Band	76	67	80	134	65	98
4. N Broadcast	60	68	79	165	74	99
5. P Band[a]	96	79	52	119	91	89
6. P-N Band Apart[b]	92	95	74	181	73	112
7. P-N Dual Band	82	77	94	163	65	100
8. P-N Dual Band + Zn	69	72	74	139	78	98
9. P Band N Broad	97	86	122	150	77	120
10. P Broad N Band	70	72	95	153	59	103
11. P Broad N Band + Zn	58	64	79	142	75	98
12. High P Broad N Band	84	69	103	160	79	107
SE	14.6	12.8	9.01	11.07	7.06	11.32
N vs no N (1,5 vs 3,4,6,7,8)[c]	ns[d]	0.049	<0.001	<0.001	0.064	<0.001
P vs no P (1,3,4 vs 5,6,7,9,10,12)	0.020	0.018	0.016	0.090	ns	0.035
Zn vs no Zn (1,7,10 vs 2,8,11)	0.074	ns	ns	ns	ns	ns
High P vs Low P (11 vs 12)	0.031	ns	0.064	ns	ns	ns
P Band vs Broad (6,7,8 vs 10,11)	0.064	ns	ns	ns	ns	ns
N Band vs Broad (3,6,7 vs 4,9)	ns	ns	ns	ns	ns	ns
N vs P (3,4, vs 5)	0.008	ns	0.021	0.032	0.035	0.021
N+P vs P (5 vs 6,7,9,10,12)	ns	ns	<0.001	0.002	0.030	0.010
N+P vs N (3,4 vs 6,7,9,10,12)	ns	ns	0.011	0.067	ns	ns

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[a] Rate of P fertilizer is 22 kg P ha^{-1}, except for treatment 12, where the rate is 44 kg P ha^{-1}

[b] N Band = N banded 7.5 cm deep in the soil; Broad=broadcast and incorporated; P Band= P side-banded 2.5 cm below and 2.5 cm to the side of the seed-row; P-N Dual Band = P and N banded together 7.5 cm deep in the soil; P-N Band Apart = N banded 7.5 cm deep in the soil and P side-banded 2.5 cm below and 2.5 cm to the side of the seed-row.

[c] Numbers in parentheses indicate treatment numbers included in contrast.

[d] ns indicates that the treatments being contrasted do not differ at the 10% level of significance

Phosphorus fertilizer may also influence Cd availability through its effects on soil pH, ionic strength and plant growth. Levi-Minzi and Petruzzelli (1984) reported that MAP decreased soil pH and the amount of Cd adsorbed by two soils, while diammonium phosphate (DAP) led to precipitation of the Cd, increasing the quantity fixed. In contrast, McLaughlin et al. (1995) found little effect of P source on the concentration of Cd in potato tubers. Kaushik et al. (1993) reported that increasing applications of KH_2PO_4 increased water-soluble plus exchangeable Cd, while decreasing the carbonate, organic and crystalline Fe oxide fractions, thereby increasing the availability of Cd for plant uptake. Thus, it may be possible to select specific P carriers, that are plant available in terms of P, but have limited effects on the availability of Cd for plant growth.

Placement of P fertilizer may influence Cd accumulation in crops. Sparrow et al. (1992, 1993b), using triple superphosphate, observed that Cd content of potato tubers was increased to a greater extent with banded as compared to broadcast P application. Grant and Bailey (1998) observed higher Cd accumulation in durum wheat and flax with banded as compared to broadcast applications of MAP, where P was deficient for crop production (Table 4). Unfortunately, P availability and yield increase generally tend to follow the same pattern, being greater with banded as compared to broadcast application, so broadcasting the fertilizer is not a reasonable practice to reduce Cd accumulation. Although banded P application may lead to higher Cd accumulation in the crop in the year of application as compared to broadcast application of an equivalent amount of fertilizer, banding generally reduces the amount of fertilizer addition required to optimize crop production, leading to lower long-term accumulation of Cd in the soil.

Nitrogen fertilizers can increase Cd concentration in plants, although the fertilizer does not contain significant levels of Cd (Table 4) (Andersson 1976, Grant et al. 1996, Grant and Bailey 1998, Oliver et al. 1993). The increased Cd with N application may be due to increases in osmotic strength of the soil solution, ion exchange reactions or soil acidification. In growth chamber studies, application of nitrogen fertilizer led to large increases in both conductance and Cd concentration of the soil solution (Mitchell 1997). Tissue and grain concentration of Cd also increased with increasing nitrogen fertilization rate. Fertilizers in general may increase Cd uptake by plants by improving plant growth, rooting intensity and mass flow.

The effect of N application on Cd accumulation tends to be greater in sand than in clay soils (Eriksson 1990, Grant et al. 1996). Sands have a lower CEC and a lower average soil water content than the clay, which results in higher Cd concentration in the soil solution and a higher Cd uptake by the plant. Effect of N fertilization may differ with the N source. In pH-buffered nutrient solution culture, plants grown with NH_4 solutions had higher Cd concentration in both shoots and roots than plants grown with NO_3 solutions (Florijn et al. 1992). Cadmium levels in the shoots of plants grown with both N-sources were highly correlated with Cd concentrations in the solution. Fertilizers with high NH_4^+ content depressed soil pH and increased the plant uptake of Cd (Eriksson 1990, Willaert and Verloo 1992). In contrast, Brown (1997) reported that fertilizer N sources increased Cd concentration of durum wheat in growth chamber studies in the order

$Ca(NO_3)_2$=urea>$(NH_4)_2SO_4$. McLaughlin (personal communication) reported similar results. The initial pH of the soil and its buffering capacity may play an important role in influencing the effects of fertilizer source on Cd availability.

Placement of N may influence Cd concentration, since the high concentration of N in a fertilizer band could impact on solubility of Cd. Dual banding of N and P fertilizers could also influence mobility of Cd present in the P fertilizer. In growth chamber studies, Brown (1997) reported lower concentrations of Cd in durum when urea fertilizer was banded as compared to mixed thoroughly with the soil. However, field studies showed no consistent effect of placement of urea fertilizer on Cd concentration of durum wheat (Table 4) (Grant and Bailey 1998, Brown 1997).

Potassium fertilizers may influence Cd content of plants. Sparrow et al. (1994) reported that application of KCl promoted higher Cd content of potato tubers than application of an equivalent amount of K_2SO_4, although McLaughlin et al. (1995) showed no difference between the two sources in similar studies with potatoes. Grant et al. (1996) reported that KCl application increased the Cd concentration of barley grain. The increased uptake of Cd with KCl application is likely a result of increased Cd complex formation in the presence of Cl, which would result in decreased Cd sorption and greater Cd availability for crop uptake. The Cd-Cl complexation may also enhance Cd movement to and into the root (Smolders and McLaughlin 1996a,b)

Zinc applications can increase (Williams and David 1976) or decrease (Choudhary et al. 1994, Grant and Bailey 1997) Cd accumulation in crops. Zinc and Cd are chemically similar and may compete for binding sites in the soil system and for uptake sites in the plant. Although Zn is not a strong competitor with Cd for binding sites in soils, increasing soil solution concentrations of Zn increased Cd desorption from the soil, increasing concentration of Cd in the soil solution (Christenson 1984a,b). Competition between Zn and Cd for uptake and translocation by the plant may reduce accumulation of Cd. McKenna et al. (1993) observed in solution culture that Zn decreased the accumulation of Cd in young leaves but not in old leaves. Zn appeared to interfere with the translocation of Cd from roots to young leaves by favouring Cd retention in roots, but at a higher Zn content in the solution, Zn might have further interfered with Cd uptake by the roots. In studies conducted by Grant and Bailey (1997) Cd concentration in flaxseed decreased with increasing concentration of Zn in the seed, whether the increase was due to application of Zn fertilizer, changing P fertility management or changes in soil levels of Zn (Figure 1). Due to the varying mechanisms where Cd and Zn may compete, the ultimate effect on Zn additions to a plant-soil system may vary depending on relative Cd and Zn concentrations, soil properties and plant characteristics. This is illustrated in studies by Moraghan (1993) who observed in greenhouse trials that Zn application reduced seed Cd of flax where Cd was not applied, but increased seed Cd where Cd was applied.

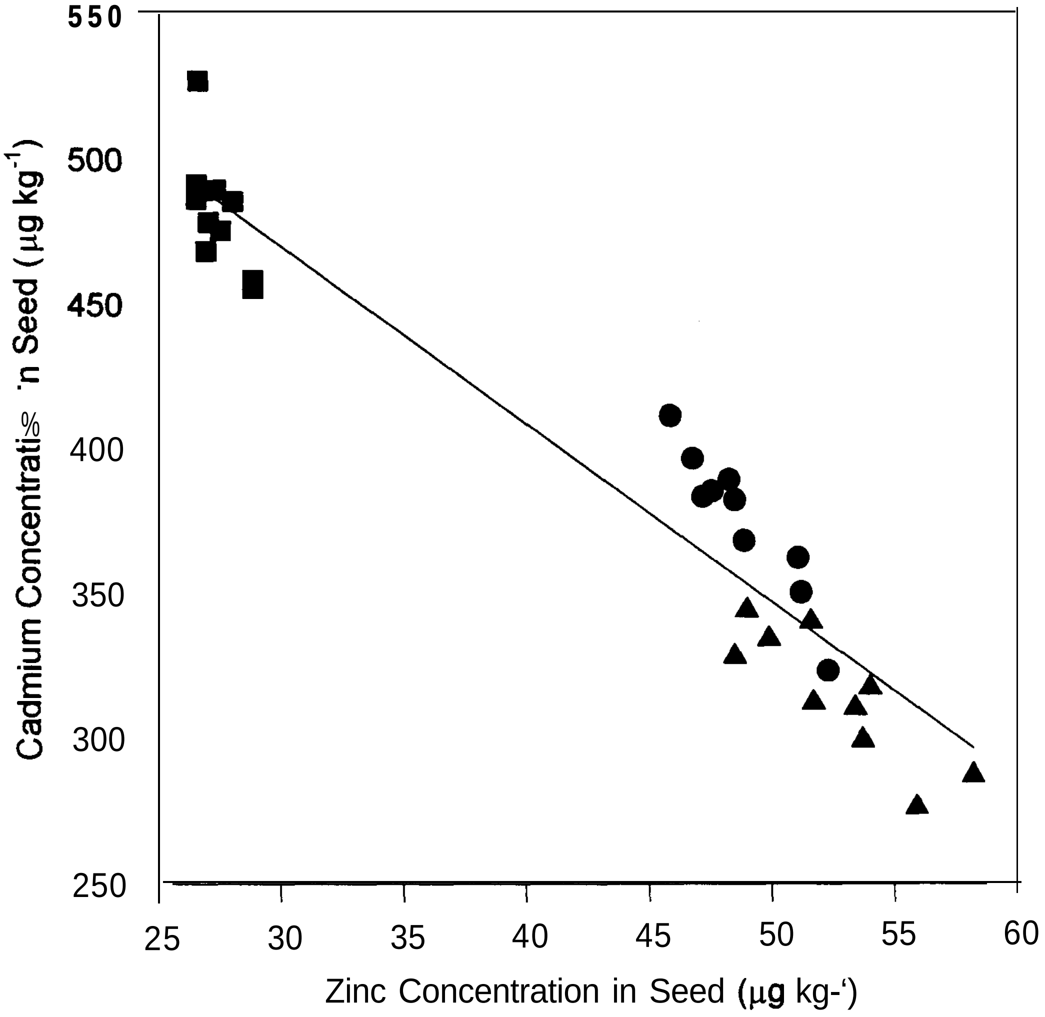

Figure 1: The relationship between cadmium and zinc concentration in the seed of Norlin flax over 10 P and Zn fertilizer treatment, on three soil types (average of three years' data) (Grant and Bailey 1997)

<u>Other Management Factors</u>

Other management factors may influence Cd concentration in crops. Oliver et al. (1993) observed that Cd concentration in wheat grain was higher when grown in rotation after lupins than after cereals. The increase in Cd concentration may be partially but not solely attributed to the acidifying effect of the legume mobilizing Cd for uptake by the subsequent crop. Biocyling of Cd accumulated in crop residues may also play a role. Andersson and

Siman (1991) observed in long-term field experiments that Cd values in crops tended to be higher where residues were returned to the soil. Therefore, high accumulator crops such as flax in a crop rotation may increase the Cd concentration in subsequent crops (Selles et al. 1996).

Eriksson (1990) observed higher Cd uptake in oats grown in areas with higher precipitation. They suggested that high precipitation may result in higher wet deposition of Cd, which is taken up directly through the leaves or roots. They also suggested that higher water content of the soil could lead to higher mobility of Cd in soil or higher transport flux of Cd through the plant. The concept of increased transport flux of Cd through the plant resulting in higher accumulation of Cd is supported by growth chamber studies which showed that Cd concentration of radish increased with increasing mass flow (Lorenz et al. 1994). Field and growth chamber studies are currently being conducted at Brandon Research Station to more carefully evaluate the impact of precipitation and temperature on Cd accumulation in crops (Mitchell-unpublished data).

Changes in yield potential of crops may influence Cd concentration and uptake, through a range of effects. Healthy, more vigorous plants may have greater rooting and higher transpiration rates, increasing access to Cd in the soil. Root growth parameters and water influx rate were considered plant factors having the greatest effect on Cd uptake in the model proposed by Mullins et al. (1986). However, increased growth may lead to dilution of Cd in the tissue, through accumulation of higher levels of dry matter, resulting in lower Cd concentration. Williams and David (1976) reported that the relationships between concentration of Cd in soil and wheat grain were independent of yield. Wadge and Hutton (1986) reported that poor growth of barley was associated with reduced concentrations of Cd, but did not speculate as to the reason for the association. The balance of opposing influences will determine the ultimate effect on Cd levels.

Tillage may impact pH and nutrient stratification in the soil profile (Grant and Bailey 1994) which may influence availability of Cd for plant uptake. Although cultivation practices did not consistently influence Cd concentration in wheat in studies conducted by Oliver et al. (1993), there was a tendency towards higher concentrations of Cd in crops grown under direct drilling. The authors suggested that restricted rooting under no till could encourage uptake of Cd from the surface soil horizons, where concentration of Cd is higher that at lower soil depths. Preferential uptake of Cd from undisturbed acidified zones associate with lupin roots was also suggested as a possible reason for higher Cd uptake under no till (Oliver et al. 1993). Tillage effects were not consistent in studies conducted by Brown (1997), but Cd concentration in durum was significantly higher under conventional tillage as compared to zero tillage in some site years.

Conclusions

Cadmium is a naturally occurring heavy metal present in soils, but the concentration of Cd in soils can increase due to input from anthropogenic sources. Plant uptake of Cd at low soil solution levels is dependent on a system that is at least partially metabolically mediated and competitive with the uptake system for Zn. The amount of Cd accumulated and its distribution in the plant depends on the genetics of the plant, differing substantially with species and with cultivar within a species. The specific reasons for genetic differences are only now being investigated.

Cadmium will accumulate in the human body over time, therefore it is desirable to ensure that Cd levels in the diet are low. Concentration of Cd in the edible portions of plants can be influenced by genetic manipulation and by soil and crop management practices. Additions of N, P and KCl fertilizers and soil amendments such as pen manure, sewage sludge and legume residue have been shown to increase accumulation of Cd in crops. The increased accumulation of Cd by crops due to fertilizer applications may not be due to the presence of Cd in the fertilizer, but rather to the effects on ionic strength of the soil solution, pH, root growth, rhizosphere effects or transpiration. Applications of Zn fertilizer may increase or decrease Cd uptake by plants, depending on the levels of Cd and Zn in the soil and the relative importance of competition in soil sorption or plant uptake sites. Other factors such as tillage and residue management, crop rotation and environmental conditions may also impact on Cd accumulation by plants.

The problem of Cd accumulation in edible crops is complex. Plant breeding and practical agronomic practices can help to limit Cd availability to crops. Reduction of anthropogenic sources of Cd in the soil-plant system will also be necessary, to limit the long-term accumulation of Cd in agricultural soils.

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