LONG TERM APPLICATION OF DAIRY SLURRY REDUCES CD CONCENTRATION IN SUNFLOWER (*HELIANTHUS ANUUS* L.)

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1 INTRODUCTION

Cadmium (Cd) is a toxic trace element and movement of Cd into the food chain is a significant concern for human health (Meeus et al. 2002). The total Cd intake in humans is a function Cd concentration and quantity of food consumed, and the Cd consumption should not exceed 70 ug day^{-1}. The tendency to accumulate Cd in edible parts of plants varies among plant species (Grant et al. 1998). Food crops such as sunflower, durum wheat and rice are considered Cd accumulators and their Cd concentrations may exceed safe levels even when grown on uncontaminated soils. While sunflower is not a major component of human diets, its high Cd concentration may be of concern for diets rich in durum and rice, and may affect trade in this crop.

Uptake of Cd is influenced by soil conditions including available Cd, pH, cation exchange capacity, arbuscular mycorrhizal fungi, organic matter content and availability of competing ions (Grant et al. 1998). The Cd concentration in agricultural products may be reduced by reducing Cd inputs to soil and by reducing Cd uptake in crops through improvements of soil conditions and changes in agricultural management practices. For example, since commercial P fertilizers can be a significant source of Cd inputs to agricultural soils, avoiding excess P fertilization can reduce Cd inputs to soil. Livestock manures are typically high in P concentration and may substitute for mineral fertilizers, but the long term effects of manure application on Cd concentration in crops is not well understood. Manure may increase Cd through addition of N (Mitchell at al. 2000), effects on soil pH, and effects on other ions such as Zn which may affect Cd uptake in complex ways. Although manure contains some Cd and other heavy metals, at equivalent application rates of N or P, the amount of Cd input into soil with manure is usually less than with chemical fertilizer (Del-Castilho et al. 1993). However, recently Li et al. (2009) reported that application of swine manure increased the Cd concentration in rice above the National Standard for Hygiene in China while applications of both swine and cattle manure on the Canadian Prairies also lead to an increase in Cd concentration in wheat, which was attributed to lowering pH and increasing root mass (Lipoth and Schoenau 2007). This greenhouse study tested the hypothesis that long term use of dairy manure slurry rather than mineral fertilizers will lower Cd uptake by the Cd-accumulator, sunflower. The influence of additions of chemical fertilizers to the sunflower crop in the year of study was also investigated.

2 MATERIALS AND METHODS

This pot culture trial was conducted in the greenhouse in 2008 using soil collected (0-30 cm depth) from four replicated treatments of a 13-yr forage (*Festuca arundinacea* Schreb.) field experiment (12 yr of nutrient application) carried out in cool moist conditions in south-western BC, Canada (Bittman et al. 2007). The field treatments included: 1) Control, 2) dairy manure slurry applied at 400 kg total N ha^{-1} year^{-1} (Man400), 3) mineral fertilizers at 400 kg total N ha^{-1} year^{-1} with other chemical nutrients applied according to soil test (Fert400), and 4) dairy slurry at 800 kg total N ha^{-1} year^{-1}, (Man800). The annual rate of 400 kg total N ha^{-1} is typical but somewhat below maximum agronomic response for grass at this location (Bittman et al. 2007). The manure was obtained from typical intensive commercial dairy operations where cows are confined year-round in passively ventilated, free-stall barns with wood chip bedding. Diets consisted mostly (70%) of locally grown maize and perennial grasses with the remainder comprising of imported concentrates including minerals. Historical annual applications of P and K averaged approximately 6 and 92 kg ha^{-1} for Fert400; 56 and 350 kg ha^{-1} for Man400; and 105 and 700 kg ha^{-1} for Man800.

Each of the historical treatments received, in the greenhouse, various mineral fertilizer treatments: 1) control with no fertilizer additions, 2) 80 kg N ha^{-1} (N80); 3) 80 kg N ha^{-1} with other required nutrients (N80+Rec), and 4,5) two N rates (80 and 160 kg N ha^{-1}) with added recommended nutrients and Zn (N80+Rec+Zn and

160N+Rec+Zn, respectively). The N was applied as urea. The recommended fertilizers were: 175 kg K_2O ha^{-1} as potassium chloride, and 33 kg S ha^{-1} and 25 kg Mg ha^{-1} as magnesium sulphate; no P was required. Zinc EDTA (15%) was applied at 5 kg ha^{-1}.

The 4x4 factorial treatment combinations were arranged in a randomized complete block design with 4 blocks. In each pot (28-cm diameter), 12 sunflower seeds (Pioneer 63A70) were planted (28 April 2008) then gradually thinned to two. One of these plants was sampled at the 5- to 6-leaf-pair stage (30 May 2008) while the remaining plant was harvested at maturity (13 August 2008). Pots were initially watered weekly, but as the plants grew larger and the weather became warmer, watering frequency was increased to two or three times a week. Care was taken to not over water to minimize leaching from the pots. Cadmium in plants and grain (shells removed) was determined by transverse-heated graphite furnace atomic absorption spectrometry. The data was subjected to Analysis of Variance using a randomized complete block design with probability set at <0.05%.

3 RESULTS AND DISCUSSION

Although the experimental site is not contaminated, the concentration of Cd in grain of sunflower from the Control soils, which had produced a grass crop with no nutrient application for 13 yr, were much higher than the 0.2 mg kg^{-1} generally considered to be safe for human consumption (Table 1). The grain Cd concentrations for the Control (with no Zn added in greenhouse) of 0.88-0.98 mg kg^{-1} are consistent with previous reports and confirm that sunflower is a Cd accumulator (Grant et al. 1998); less than 100g of grain would exceed allowable daily Cd intake. Historical applications of chemical fertilizers (Fert400) increased Cd concentration 18% ($P<0.05$) compared to Control, averaged across all greenhouse treatments. This can be attributed to the Cd contained in the P fertilizer applied in the field and to the lower pH in Fert400 (5.3) than control (5.5) caused by applications of ammonium nitrate (Grant et al 1998). There was little effect of Fert400 on sunflower yield (not shown) so Cd uptake in sunflower grains, averaged across greenhouse treatments, was significantly higher in Fert400 than Control treatments (Table 2). Both Man400 and Man800 greatly decreased the concentration of Cd compared to Fert400 and Control soils, and the Man800 treatment had significantly lower Cd concentrations than Man400 (Table 1). The sunflowers on the Man400 treatment took up significantly less Cd than the Fert400 treatment despite higher yield (Table 2). Similarly, Man800 treatments had higher yields but took up significantly less Cd than Man400 treatments. In the field, the Man800 rate with 2x the amount of applied Cd compared to Man400, increased grass yield by only about 20%, so it is likely that much more manure Cd remained in the Man800 soil. Although greatly lowering sunflower Cd concentrations, long term dairy manure did not reduce grain Cd concentration to the safe level.

TABLE 1 **Effect of historical field applications of fertilizers and dairy manure slurry and current applications of fertilizers on Cd concentration (mg kg-1) in sunflower grain at maturity**

	Historical Treatments				
Greenhouse treatments	Control	Fert400	Man400	Man800	Mean
N80	0.98b[1]	1.2a	0.67c	0.46ef	0.83A[2]
N80+Rec	0.88b	0.96b	0.70c	0.39fg	0.73B
N80+Rec +Zn	0.47ef	0.60cd	0.29gh	0.21hi	0.39C
N160+Rec +Zn	0.54de	0.66c	0.27hi	0.18i	0.41C
Mean	0.72B[3]	0.85A	0.48C	0.31D	

[1]values in any row or column followed by the same lower case letters are not significantly different at P<0.05
[2]values in column followed by the same upper case letters are not significantly different at P<0.05
[3]values in row followed by the same upper case letters are not significantly different at P<0.05

Averaged across historical treatments, applications of recommended nutrients (N80+Rec) decreased grain Cd concentrations and uptake significantly (Tables 1 and 2) but the effect was most apparent in Fert400, probably due to relatively low historical cation applications and high removal rates relative to Man and Control.

Addition of Zn (N80+Rec+Zn) had a significant effect across all historical treatments, reducing grain Cd concentrations and uptake by an average of 45%. In previous studies Zn application either increased or decreased Cd in plants, the difference attributed to contrasting effects in the soil, where Zn increases Cd availability, and in the plant where Zn reduces Cd uptake (Grant et al. 1998). Increasing N rate from 80 to 160 kg ha^{-1} increased yield by

13% but had little effect on Cd concentration or uptake, which contrasts with some reports that N increases Cd uptake. Application of Zn reduced Cd concentrations in sunflower to about 0.5 to 0.7 mg kg^{-1} on the Control and Fert400 soils, still much above the acceptable level. However, Zn application combined with historical manure reduced grain Cd to safe or near safe concentrations (<0.3 mg kg^{-1}).

TABLE 2 **Effect of historical applications of fertilizers and dairy manure and current applications of fertilizers on Cd uptake in sunflower grain (µg plant-1) at maturity (footnotes explained in Table 1)**

	Historical Treatments				
Greenhouse treatments	Control	Fert400	Man400	Man800	Mean
N80	10.03b	13.12a	8.42bcde	6.62efgh	9.54A
N80+Rec	9.37bc	9.57bc	9.16bcd	6.11fgh	8.55B
N80+Rec +Zn	5.10ghi	7.70cdef	3.36ij	3.26ij	4.86C
N160+Rec +Zn	6.95efg	7.47def	4.75hij	3.22j	5.60C
Mean	7.86B	9.47A	6.42C	4.80D	

The effect of treatments was apparent on Cd uptake and concentrations in whole sunflower plants sampled at the 5- to 6-leaf-pair stage (Tables 3 and 4). Averaged across greenhouse fertilizer treatments, Fert400 increased Cd concentrations compared to Control, while manure treatments decreased Cd concentrations compared to Control with Man800 significantly lower that Man400. A similar pattern was apparent for Cd uptake; Fert400 increased and manure treatments decreased whole plant Cd uptake. Manure rates had similar effects on Cd uptake indicating that the lowered concentration in the Man800 plots may have been caused by dilution due to better growth. There was evidence that application of N (0 vs. 80 kg ha^{-1} and 80 vs. 160 kg ha^{-1}) to the sunflower increased Cd concentrations and Cd uptake in the plants. The higher Cd concentration in the higher yielding crop indicates that the difference was not caused by dilution. The effect of N on Cd was not apparent in the mature grain. The additions of both recommended fertilizers and Zn to the sunflowers also lowered Cd concentrations in the young plants. The effect of the recommended fertilizers could have been due to dilution or to the direct effect the ions added on Cd uptake but Zn application decreased Cd uptake as well as concentration, eliminating dilution as a factor. The effect of addition of fertilizers to sunflower was not as great as the effect of historical treatments which produced a 4-fold difference between Fert400 and Man800. The greenhouse fertilizer treatments generally had little effect on Cd concentrations of sunflower plants grown on either Man treatment but did affect concentrations in the higher-Cd containing Fert400 and Control treatments.

TABLE 3 **Effect of historical applications of fertilizers and dairy manure and current applications of fertilizers on Cd concentration (mg kg-1) in sunflower at 5-leaf pair stage (footnotes explained in Table 1)**

	Historical Treatments				
Greenhouse treatments	**Control**	**Fert400**	**Man400**	**Man800**	**Mean**
N0	0.71de[1]	0.91b	0.34gh	0.26hij	0.55B[2]
N80	0.79cd	1.09a	0.34gh	0.23ij	0.61A
N80+Rec	0.57f	0.86bc	0.28hi	0.24hij	0.49C
N80+Rec +Zn	0.40g	0.68e	0.21ij	0.18j	0.37D
N160+Rec +Zn	0.51f	0.86bc	0.29hi	0.19j	0.47C
Mean	0.59B[3]	0.88A	0.29C	0.22D	

Lower Cd uptake and concentrations in the high-yielding sunflower grown on historically manured soils relative to unfertilized Control cannot be attributed to lower Cd loadings or to dilution. The low crop Cd on manured soils may be attributed to higher pH (Man, 5.8-5.9; Fert, 5.3; Control, 5.5) and to the addition of large amounts of organic matter which may adsorb Cd (Grant et al 1998). The lower Cd concentration in manured soils may also be attributed to large nutrient loadings and high concentrations of soil extractable Zn, K, Ca, and Mg (data not shown). The effects of these ions vary because of contradictory effects on soil availability and uptake, but the lower Cd from direct applications to sunflower of Zn and recommended nutrients (K, Mg and S) suggests a role for these ions in the manured soils. Recent reports of manure raising Cd concentrations have tested pig manure which has lower K concentrations and organic matter than cattle manure (Li et al. 2009) or tested soils with higher pH than in our study (Lipoth and Schoenau 2007). More work is needed to understand the long term effects of dairy manure on Cd concentration.

TABLE 4 **Effect of historical applications of fertilizers and dairy manure and current applications of fertilizers on Cd uptake by sunflower (µg plant-1) at 5-leaf pair stage (footnotes explained in Table 1)**

	Historical Treatments				
Greenhouse treatments	**Control**	**Fert400**	**Man400**	**Man800**	**Mean**
N0	3.6efg[1]	4.1def	1.9j	1.9j	2.8C[2]
N80	5.2bc	4.8bcd	3.2fgh	2.2ij	3.9B
N80+Rec	5.5ab	6.5a	2.9ghi	2.5hij	4.3A
N80+Rec +Zn	3.2fgh	4.5cde	2.0ij	1.8j	2.9C
N160+Rec +Zn	4.3cde	6.3a	2.5hij	2.4hij	4.0AB
Mean	4.4B[3]	5.3A	2.5C	2.2C	

4 CONCLUSIONS

Lower Cd concentration in grains of sunflowers gown on historically manured compared to fertilized soils supports the hypothesis that dairy manure may be a safer long term source of P than mineral fertilizers where Cd accumulation is a concern, and suggests that soils with a long term history of manure application may be useful for growing Cd accumulating crops including staples such as durum wheat and rice. While sunflower is not generally consumed in large quantities, it may contribute meaningfully to diets already high in Cd. With continued applications of mineral fertilizers, Cd concentration in soils is likely to increase, especially as cleaner phosphate reserves are preferentially depleted. On dairy farms, Cd is the toxic trace element at greatest risk of accumulation (Li et al. 2005). Recycling manure as source of P on dairy farms and limiting fertilizer P usage will lower Cd loadings on soils.

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