Introduction

Certain soils in Salinas Valley, CA, are Cd mineralized from parent shale which has Cd from phosphorites (Burau, 1983; Holmgren et al., 1993). Both residual soils and alluvial soils with contribution from the shale parent materials contain high Cd but not high Zn because of the source. Many of the very high Cd residual soils have high slopes and are not used for vegetable production. But some alluvial soils with higher contribution from the shale parent materials contain high levels of Cd. It was learned in the early 1970s that such soils caused high uptake of Cd by leafy vegetables (especially spinach and Romaine lettuce) and some other crops (Burau, 1983). The Cd-mineralized soils extend from the Malibu Canyon area (Lund et al., 1981) thru Ventura County and Monterey County (Wolnik et al., 1981; Chen et al., 2009), into Santa Cruz County (Golling, 1983).

Burau (1983) and Hatch et al. (1988) reported that contrary to findings from other Cd uptake research, when they added limestone to raise the pH of these Cd-mineralized soils, the amendment did not statistically reduce Cd accumulation by leafy vegetables. These findings were very different from many other researchers (Logan and Chaney, 1983; Chaney et al., 1999) who studied Zn-smelter or mine waste contaminated or biosolids-amended soils with Cd:Zn ratios more like geogenic soil Cd:Zn levels (1 Cd:200 Zn).

Studies of soils with high Cd:Zn ratio due to application of a highly Cd enriched biosolids also found that liming could increase lettuce Cd perhaps due to lime-induced Zn deficiency, and found that Zn fertilization inhibited Cd uptake by leafy vegetables from such limed soils with high Cd:Zn ratio (Chaney et al., 2006). Thus we hypothesized that adding Zn fertilizers to the Lockwood soil may yield lower crop Cd levels. It could be important to growers to be able to produce these crops with lower Cd because leafy vegetables grown on the Cd mineralized soils can exceed international (CODEX) proposed limits for Cd in foods. The proposed CODEX limit for Cd in vegetables is 0.05 mg kg^{-1} fresh weight; because lettuce and spinach are about 5% dry weight, the CODEX Cd limit is essentially 4 mg Cd kg^{-1} dry lettuce leaves.

Lettuce, spinach and other vegetables were sampled from Cd mineralized soils in Salinas Valley and the known Cd-accumulating crops exceeded CODEX Cd limits on higher Cd soils (Wolnik et al., 1981; Chen et al., 2009). Some remedy is needed to limit production of such high Cd lettuce in grower=s fields. Three experiments were undertaken to test application of limestone plus Zn fertilizer to inhibit Cd accumulation by spinach and lettuce.

Experimental

Lockwood shaly loam was collected from southwestern Salinas Valley for pot tests. The soil was mixed well, sieved < 4 mm, and weighed into drained plastic pots. Each pot contained 1.8 kg of the air dry Lockwood soil. The soil contained 5.3 mg Cd and 56 mg Zn kg^{-1} dry weight extracted by hot HNO_3, and was initially pH 7. In Experiment 1, Zn was applied at 0, 5, 25, 50, 75 and 100 mg Zn kg^{-1} to decrease the Cd:Zn ratio and inhibit Cd uptake if possible. The soils were simultaneously made calcareous by addition of a mixture of reagent grade powdered $CaCO_3$ (90%) and $MgCO_3$ (10% of alkalinity) to reach pH 7.5-8.0. In Experiment 2, 0, 100, 250, and 500 mg Zn kg^{-1} were applied to the soil and all were made calcareous. A mixture of $ZnCO_3$ and $ZnSO_4$

was added to prevent acidification of the soil due to Zn displacement of protons from the exchange surfaces of the soil. In Experiment 3, the basal Lockwood soil was adjusted to various pH levels by addition of limestone or dilute nitric acid, and soluble salts were leached from the soil. All pots were fertilized with appropriate levels of N, P and K for pot culture of Romaine lettuce. All treatments were grown in four replications.

>Parris Island= Romaine lettuce was grown to maturity, yield measured, and dry leaves prepared for analysis (basal leaves not normally consumed were not included in the leaf sample). Dried leaves were ground, mixed well, dry ashed overnight at 550°C, the ash dissolved with acid, and the concentrations of nutrients and Cd analyzed by inductively coupled plasma emission spectrometry with internal standard (Y). Results were analyzed statistically using SAS.

Results

In Experiment 1, addition of $ZnSO_4$ fertilizer strongly decreased Cd in leaves of Romaine lettuce grown on the limed Lockwood soil (Figure 1). With each increment of added Zn, lettuce leaf Cd declined. In the 0 Zn treatment, foliar Zn was present at a level which indicates Zn deficiency, and adequate Zn for normal growth was not present until 20 mg Zn kg^{-1} had been applied. Addition of 100 mg Zn kg^{-1} lowered lettuce Cd to below 4 mg Cd kg^{-1} dry leaves, the CODEX limit calculated on dry weight basis.

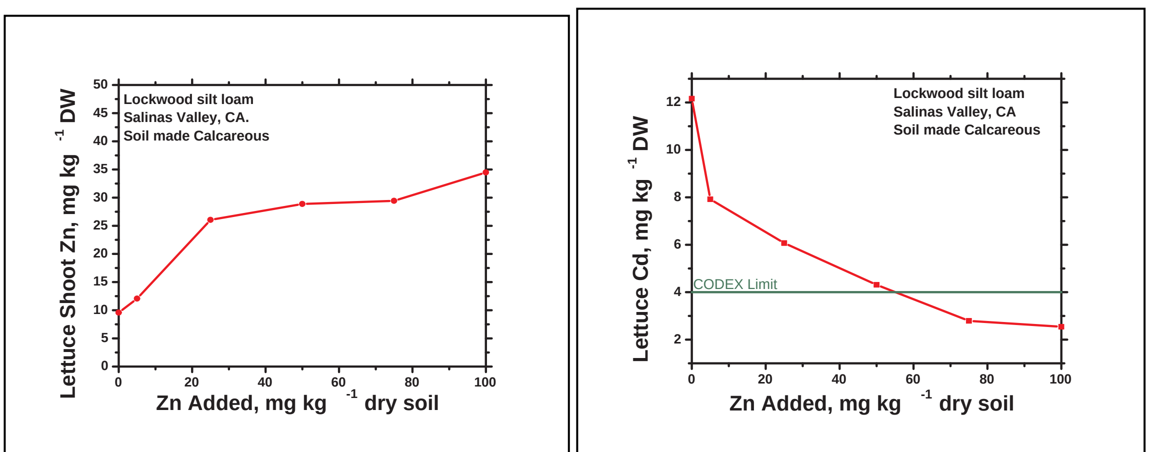

Figure 1 A and B. Effect of Zn fertilizer addition to limed Lockwood soil on Zn and Cd accumulation by Romaine lettuce.

In Experiment 2, adding 100 mg Zn kg^{-1} again reduced foliar Cd to levels below the CODEX proposed limit, but adding higher Zn levels caused a significant increase in foliar Cd (Table 1). Much higher foliar Zn levels were reached with the higher Zn fertilizer rates.

Table 1. Effect of added Zn fertilizer on Cd, Zn, Mn and Cu levels in Romaine lettuce (Experiment 2).

Zn treatment	Leaf Zn	Leaf Cd	Leaf Cu	Leaf Mn
$mg\ kg^{-1}$	-------------------- $mg\ kg^{-1}$ dry weight	--------------------		
0	14.4 b'	13.2 a	3.2 a	39.3 a
100	43.0 b	2.0 d	2.6 b	16.4 c
250	177. a	6.3 b	2.7 ab	23.1 b
500	196. a	3.9 c	2.5 b	24.4 b

'Means in a column followed by the same letter are not significantly different according to the Waller-Duncan K-ratio t test ($P<0.05$).

In experiment 3, the soil was adjusted to a range of pH to evaluate the potential for soil acidification to cause increase in lettuce Cd, and to evaluate the simple effect of liming the soil on lettuce accumulation of Cd (Table 2). As might be expected, soil acidification caused a significant increase in lettuce Cd, Zn and Mn, reaching levels of Cd which clearly exceed CODEX proposed limits. Making the soil calcareous did cause a significant increase in lettuce Cd similar to the report of Burau (1983).

Table 2. Effect of soil pH adjustment on Cd and other element accumulation by Romaine lettuce grown in Lockwood soil; geometric means for Cd, Zn and Mn. The pH of the "as is pH" Lockwood soil at harvest was 7.08 (Experiment 3).

Harvest pH	Leaf Zn	Leaf Cd	Leaf Cu	Leaf Mn
5.25 e'	29.6 a	16.2 a	2.4 b	724. a
5.39 de	24.4 ab	12.3 bc	2.1 b	437. b
5.55 d	24.9 ab	11.1 c	2.2 b	79.4 c
6.58 c	27.9 ab	6.54 d	2.2 b	28.3 e
7.08 b	22.7 b	7.50 d	3.1 a	22.7 e
7.92 a	14.1 c	13.1 c	3.2 b	39.1 d

'Means in a column followed by the same letter are not significantly different according to the Waller-Duncan K-ratio t test ($P<0.05$).

Discussion

The natural high Cd and Cd:Zn of Lockwood soil promote Cd phytoavailability to leafy vegetable crops such as spinach, Romaine lettuce, endive and some other crops (Burau, 1983). For many years, growers were advised to produce grapes on these soils because of the very low Cd accumulation in grapes. But in recent years, economics encouraged return to leafy vegetable production and some high Cd lettuce was produced (e.g., Chen et al., 2009). Within the USA, no Cd limits for crops have been established by the US Food and Drug Administration, but export crops may have Cd limits imposed. Failure to deal with the natural high Cd crops produced on Cd-mineralized soil series of CA could threaten markets for these crops.

We hypothesized that the low soil Zn failed to inhibit Cd uptake or translocation as effectively as seen on normal soils with 1 Cd per 200 Zn (the geogenic ratio). Liming the high Cd:Zn ratio soils may induce Zn deficiency in the crop, thereby inducing the plant to up-regulate root Zn transport proteins to try to obtain more soil Zn. Because the Zn transport proteins also accumulate Cd (Hart et al., 2002), higher Cd could be accumulated due to the lime-induced Zn deficiency stress. Alternatively, low soil solution Zn^{2+} activity would provide low competition with Cd^{2+} for uptake by the root Zn-transporters. Previous research showed that Zn fertilization of high Cd:Zn ratio biosolids amended soils could inhibit uptake of Cd by Romaine lettuce and spinach (Chaney et al., 2006), so we tested Zn fertilizers plus limestone on the Lockwood soil. An initial test with unlimed soil and spinach showed that Zn could reduce spinach Cd, but not to low enough levels to comply with CODEX standards. In addition, after the spinach crop, soil pH was only 6.5 so higher pH would be expected to reduce Cd uptake.

The soil was then limed to calcareous pH and Romaine lettuce was grown to maturity. The combination of high pH and 100 kg Zn fertilizer kg^{-1} caused a highly significant reduction in lettuce Cd concentration, and lowered Cd to below the CODEX proposed limit for vegetable crops. In Experiment 2, to our surprise, adding more Zn increased lettuce Cd somewhat, perhaps because of Zn competition for binding sites within the roots. Further, adjusting the basal soil to a range of pH showed that both acidification and liming could cause increased Cd accumulation by Romaine lettuce compared to the “as is” pH of the soil.

Another possible benefit of applying the Zn fertilizer would be prevention of high bioavailable Cd crops if the soil were allowed to become acidified. As pH declines, Zn uptake increases and if Zn exceeds about 400 mg kg^{-1} dry lettuce, crop yield is reduced. In tests of growing Romaine lettuce on Zn-smelter contaminated soils in Pennsylvania, Baker and Bowers (1988) found that if lettuce Cd exceeded levels acceptable for garden foods, Zn phytotoxicity substantially reduced lettuce yield (see graphical results in Chaney and Ryan, 1994). In soils with normal Cd:Zn ratios, Zn phytotoxicity serves as another protection against excessive dietary Cd intakes from garden foods. In addition, higher Zn in the crop can inhibit absorption of Cd in the intestine, lowering potential Cd risks (Reeves and Chaney, 2008; Chaney et al., 2004).

Alternatively to liming plus Zn fertilizer, phytoextraction might be used to remove soil Cd and limit Cd uptake by crops. However, this may not be as cost effective as Zn fertilization plus liming. Growers are unlikely to do anything about Cd in these soils unless markets demand lower Cd levels in crops grown and marketed in the US. Continued use of acidifying N fertilizers and irrigation will lower soil pH and potentially increase Cd uptake, but liming is not effective enough in reducing lettuce Cd accumulation unless Zn fertilizer is applied with the limestone used to raise soil pH. Further research is needed to characterize the interactions between Zn and Cd in uptake and translocation within accumulator crops such as lettuce and spinach.

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