## Flue dusts as zinc fertilizers A. Lloyd Brown B. Richard G. Burau B. David R. Giger

A s pollution control becomes more and more important, many industrial plants must collect particulate matter from their stacks which would otherwise be distributed over the nearby landscape. Some of these materials, with or without further treatment, are being sold or potentially could be sold as micronutrient fertilizers, especially zinc fertilizer. The efficacy of these materials in comparison to zinc sulfate (ZnSO<sub>4</sub>), which is the most common zinc (Zn) fertilizer at the present time, was investigated.

## **Materials and methods**

The following materials were compared in a greenhouse pot experiment:

- Reagent grade ZnSO<sub>4</sub>. 7 H<sub>2</sub>O (22.7% Zn)
- Reagent grade zinc sulfide (ZnS) (67% Zn)
- Mine ore (FST)
- Granular sulfated flue dust (LC#1) from an electric-hearth furnace.
- Granular precipitator dust from a fertilizer plant (P.D.)

A partial analysis of three of these materials is shown in the table. The soil used in these greenhouse experiments was Balcom clay loam, a well-drained calcareous upland soil formed on calcareous sandstone. The pH of the soil was 7.5 and diethylene trianine pentaacetic acid (DTPA) extractable Zn was 0.22 ppm. It was known to be Zn deficient for Zn sensitive crops.

Six-inch clay pots with polyethylene liners were used in the greenhouse experiments, each pot containing 1600 g air-dry soil. Initial fertilizer applications to all pots were: 100 ppm nitrogen (N) as  $(NH_4)_2SO_4$ , 100 ppm phosphorus (P) as  $KH_2PO_4$ , and additionally 100 ppm N on a weekly schedule as  $NH_4NO_3$ . These fertilizers were added as solutions.

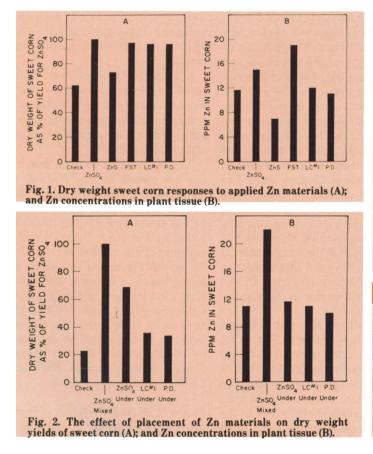
All Zn sources were applied at rates of 0, 1, 4, 16, and 64 ppm Zn.  $ZnSO_4$  was applied in solution; all other sources were applied as fine powders (50 to 100 mesh), or in the case of placement under the seed, they were applied as granular material. Treatments for Zn were in triplicate and pots were randomized on the greenhouse benches.

All fertilizer materials were applied to the soil surface in each pot, then the whole soil mass was dumped out on a sheet of heavy paper, mixed thoroughly, and returned to the pot. Pots were all planted to Golden Cross Bantam T51 sweet corn, 5 seeds per pot, later thinned to 3 plants per pot, and allowed to grow for about 7 weeks. Watering was as required using deionized water.

Tops were harvested by cutting plants about 1/2 inch above soil level, then they were dried in an oven at  $70^{\circ}$ C, weighed, ground in a Wiley-mill, and analyzed for Zn and Cadmium (Cd). Zn was determined by X-ray fluorescence and Cd by atomic absorption spectrophotometry following ashing of 3 g plant material with concentrated nitric acid (HNO<sub>3</sub>), and then separating and concentrating the heavy metals with dithizone. Lead (Pb) and manganese (Mn) were determined on one crop of sweet corn, both by X-ray fluorescence.

## **Results and discussion**

All sources except ZnS produced similar dry weight yields as shown in fig. 1A, when the various Zn sources were applied as powders and mixed throughout the soil. Results are expressed as percent



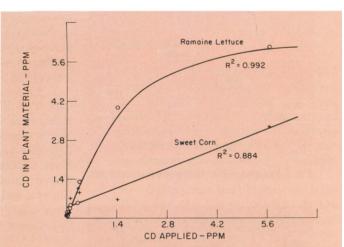


Fig. 3. The effect of soil incorporation of Cd contained in Zn sources on uptake of Cd by sweet corn and romaine lettuce.

Analytical Data for Three Zinc Sources			
Element	FST	LC#1	P.D.
		percent	
S	13.5	6.1	1.1
Р	<u> </u>	-	7.3
к	0.7	1.2	23.0
Mn	9.1	2.6	-
Fe	41.7	15.6	0.4
Zn	3.5	30.3	6.68
Pb	3.0	5.9	_
Cd	0.04	0.14	0.55
Cu	0.48	0.36	0.06

of the yield for ZnSO<sub>4</sub> which may be considered a standard. These values are for the O-Zn (check) and 4 ppm Zn rates only. The 4 ppm rate was found to be adequate, as yields were not increased above this level for the 16 and 64 ppm Zn rates. Note that ZnS caused a slight yield increase above the check (O-Zn) but was significantly below the other yields.

Another measure of the efficacy of Zn sources is to compare the Zn concentrations in the plants grown on the soils to which these sources were applied. This is indicative of relative availability of the sources to the plants. Concentration data are shown in fig. 1B. Obviously,  $ZnSO_4$  and FST produced plants with higher Zn concentrations than the check or other sources.

The reason for the higher Zn concentration due to FST is that on the basis of additional analyses, the actual rate of Zn application for this material was about 18 percent above the other materials. LC#1 and P.D. did not increase the Zn concentrations above the check, while ZnS actually depressed the Zn concentration. It is worth noting that the lower Zn concentrations for LC#1 and P.D. persisted for a romaine lettuce crop and another sweet corn crop grown in the same pots, but maximum yields were maintained.

In another greenhouse experiment, granular LC#1 and granular P.D. were compared to  $ZnSO_4$  in solution placed below the seed about <sup>3</sup>/<sub>4</sub> inch at rates of 0, 1, 4, 16, and 64 ppm Zn.  $ZnSO_4$  in solution was also mixed throughout the soil at all rates, to serve as a standard. N, P, and K (potassium) fertilizers were applied as described for the other experiment. Treatments were in triplicate. The dry weight yields and Zn concentrations are shown in fig. 2 for the 4 ppm rate only.

Placement of the sources has resulted in some yield increase, but much less than the  $ZnSO_4$  mixed with the soil. The Zn concentrations were unaffected by the application of these sources under the seed. Presumably there was not sufficient root contact with the relatively few Zn source particles under the seed to permit adequate absorption of Zn by corn roots.

Hence, from the standpoint of Zn availability, F S T LC#1, and P.D. would be considered useful Zn sources. Their effectiveness as Zn fertilizers will depend upon the crop, the method of application, and the particle size of the materials. If applied as large particles, the Zn availability may be decreased but this will depend upon the ease of particle disintegration and subsequent soil mixing. On the basis of Zn concentration data, LC#1 and P.D. appear to be slightly less available than either  $ZnSO_4$  or FST. This may be of minor consequence since all materials except ZnS were residually effective for three successive crops grown in the same pots.

The other important question in relation to the use of these and other similar Zn sources has to do with heavy metal contamination and, in particular, the Cd content. Cd is not known to be essential for plant or animal growth; but Cd is known to be highly toxic to humans and other animals. Furthermore, it tends to be an accumulative toxin. The fact that Cd as well as other heavy metals do not leach through or out of the soil means that they tend to accumulate in the surface soil if materials applied to the soil contain significant quantities of these elements.

The Cd concentrations for romaine lettuce and sweet corn, in relation to the rates of Cd applied to the soil in LC#1 and P.D., are shown in fig. 3. Note the difference in Cd concentration of the corn leaves and the romaine lettuce, and the rather steep curve for Cd in romaine lettuce.

Assuming an application rate of 10 lb Zn per acre is adequate, then 33 lb of LC#1 would provide this amount of Zn. At the same time, 0.046 lb Cd would be applied to an acre of soil. An annual rate of this magnitude would contribute 0.46 lb Cd per acre in 10 years; or if applied only once every 5 years, it would require 50 years to reach 0.46 lb Cd per acre. By this time, corn leaves or romaine lettuce would have concentrations of Cd of approximately 1 ppm.

In the case of P.D., however, the situation is more hazardous. The 10 lb per acre Zn rate would require 150 lb of material, which would add 0.82 lb of Cd per acre. An annual application for 10 years would contribute 8.2 lb of Cd per acre, or if applied once every 5 years, would reach 8.2 lb Cd per acre in 50 years. At this level of soil Cd, sweet corn leaves would contain 2 to 4 ppm Cd, while romaine lettuce would contain 5 to 6 ppm Cd.

Analysis of soil samples taken from each pot after three crops were grown showed that Cd concentration, as determined by DTPA extraction, was increased in relation to the amount applied to the soil. Thus, Cd accumulations in the soil can readily be detected by appropriate chemical analysis.

Pb and Mn concentrations of sweet corn, where LC#1 and P.D. were com-

pared to  $ZnSO_4$ , indicated that neither of these elements poses a hazard. Pb concentrations were all below 5 ppm and Mn concentrations were all below 100 ppm, and neither was affected by the application of LC#1 or P.D., even at the highest rate of 64 ppm Zn. It would appear, on the basis of the Cu content, that Cu would not be a hazard at normal rates of application.

## Conclusions

Many of these miscellaneous Zn sources could be used in agriculture if they do not contain significant quantities of heavy metals, which are likely to accumulate in soils to the point of being hazardous to human health. The availability of the Zn, unless present as ZnS, appears to be comparable to ZnSO<sub>4</sub> when applied in powder form.

Before such materials are used for soil applications, they should be analyzed rather completely so that the hazardous elements or hazardous quantities of elements may be identified. It would seem prudent, in light of present knowledge, to apply reasonably pure compounds for correcting micronutrient deficiencies. In this manner, the accumulation of harmful elements or harmful quantities of elements would be kept to a minimum. One can be guided by the complete analysis of the material before application.

LC#1 does not appear to pose a hazard for Cd, if normal recommended rates for Zn are followed. However, if by chance, an application rate were increased 10-fold, there may be a health hazard, depending upon the crop being grown. For the P.D., a hazard would exist even with a single normal Zn application rate for many crops. The problem would be even greater if these materials were applied to soils that already had marginally high Cd levels. The levels of Pb, Mn, and Cu (copper) in the materials studied do not appear to constitute any hazard.

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