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THE EFFECT OF DECOMPOSING ORGANIC MATTER ON

ZINC LEVEL IN SOIL AND PLANTS

by

Kamilia Shoukry Mohamed Shoukry

A dissertation submitted in partial fulfillment of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Soil Chemistry

UTAH STATE UNIVERSITY Logan, Utah

318,24A

ACKNOWLEDGMENTS

I express my deep appreciation and gratitude to Dr. R. L. Smith for his encouragement and helpful counsel throughout my study. I will always remember the encouragement and personal consideration he has given me during my stay at Utah State University. I sincerely appreciate my acquaintance with him and the chance of working under his excellent guidance.

My appreciation is also given to Dr. Harris O. Van Orden, Dr. Gene W. Miller, and Dr. Keith R. Allred for serving as committee members.

Most of all I am deeply grateful to my husband, Abdel Wahhab, for his great support and continual encouragement.

This dissertation is dedicated to my parents for their great sacrifices and help, especially to my father, the late Dr. M. Shoukry, for his incredible encouragement and inspiration to pursue my studies.

Kamilia S. M. Shoukry

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INTRODUCTION

That proportion of the total zinc (Zn) in the soil that is available to plants is variable, and little is known about the various forms of Zn or even the extent to which it occurs. Because of the complexity of the problem, most workers have approached the problem of availability of Zn to plants from the opposite point of view, that is, the forms in which the added or available Zn becomes unavailable.

The unavailable forms of Zn are believed to be:

1. Those that are bound tightly as an adsorbed ion on the mineral fractions of soil or actually enter the crystal lattice of these fractions.

2. Those that are precipitated as relatively insoluble compounds.

3. Those that are complexed by an organic component of the soil.

Many investigations in the laboratory and field were designed to study the postulation that a portion of the organic matter in the soil sometimes exists as a compound or compounds that are capable of forming insoluble complexes with polyvalent metals such as Zn. The results of these many studies have not entirely elucidated questions which have arisen concerning this postulate.

An unusual condition of Zn deficiency occurred in the Portneuf silt loam soil which comprises a large area of crop-land in the Snake River Valley of southern Idaho. It had been observed that a Zn deficiency was apparent in beans grown on land where the tops from a previous sugarbeet crop had been turned under. A foliar application of ZnSO₄ to the affected beans corrected the deficiency symptoms. In a laboratory study with this Portneuf soil, DeRemer and Smith (1964) substantiated these observations. They found that the addition of sugarbeet tops induced Zn deficiency symptoms in beans only if the organic material was allowed to incubate in the soil for at least 6 weeks before planting. Consequently, as a result of their preliminary studies, several questions have arisen, and some points were found to need more investigation.

This experiment was initiated to answer the following questions: 1. What is the effect of different sources of organic matter on the inactivation of Zn in soil?

2. Does the inactivation of Zn by sugarbeet tops occur in soil not known to have Zn deficiency problems, does it occur only in Zn deficient soils, or is there something specific about the Portneuf soil that the Zn deficiency occurs following sugarbeets?

3. What is the effect of time on the Zn that appears to be inactivated?

4. Where is the added Zn found in the different fractions of soil?

5. What is the relationship between the amount of Zn in soil and the amount taken up by plants?

REVIEW OF LITERATURE

As early as 1869, Raulin presented strong evidence that Zn was essential in the culture medium for at least some fungi. He thought it was not merely a stimulant but an essential element, and that growth when Zn was not added to the medium was due to the presence of Zn as an impurity. Javillier (1912) emphasized this point of view and showed that besides being an impurity in the purest chemicals, Zn was apt to be present in glassware.

In a series of nutrient culture experiments, Mazé (1914) furnished the first convincing evidence that Zn is essential for higher plants. The work of Sommer and Lipman (1926) and Sommer (1927, 1928), in which great care was used to prevent the plants from obtaining a Zn supply from the glassware, the water, the dust of the greenhouse, or the chemicals in the nutrient solution, seemed to establish beyond question the requirement of Zn as a nutrient for some, of not for all, plants.

During the period of 1931 to 1935, different groups of workers (Alben et al., 1932; Chandler et al., 1931, 1932; Finch and Kinnison, 1933; Barnette and Warner, 1935) discovered independently that treatment with Zn through the soil and in other ways will cure a serious disease in various fruit trees and many other crops. Since that time, intensive studies have been done to clarify the Zn problem.

It has been found that two factors govern the ability of a soil to provide enough Zn to a growing plant. These are the total supply of Zn in the soil and its availability to the plant. Most soils

usually have more than enough Zn to meet the requirements of normal plant growth, but crop plants may have Zn deficiency disease. Thus, the major problem appears to be one of availability. Because of this, most of the recent work in soil Zn has been devoted to the study of the factors affecting the Zn availability.

Many soil factors have been found associated with the deficiency of Zn in plants.

pH and Lime

There is enough evidence in the literature to establish conclusively that soil pH and lime content have a definite effect on the ability of plants to obtain adequate Zn from the soil. As early as 1939 Lott wrote that the more acid the soil, the greater was the concentration of Zn in the soil solution. Peech (1941) concluded from his experiment that as the pH of the soil was increased with CaCO₃, the amount of extractable Zn diminished and that virtually all the Zn was fixed at pH 9.0. Also Epstein and Stout (1951) showed that the uptake of Zn by plants increased with increasing proportions of complimentary H ions and decreasing Ca ions.

In 1955 Jurinak and Thorne reported titration curves with alkali hydroxides for dilute solutions of Zn in equilibrium with Utah bentonite. The reduced availability of Zn as the pH of the soil increased was generally thought to be a function of the formation of insoluble Zn hydroxide. The increased solubility of Zn with the NaOH and KOH as the pH exceeded 6.5 was taken as evidence of the formation of soluble zincate ions. The absence of increased solubility under calcium conditions was consistent with the low solubility of calcium zincate.

Wear (1956) found a highly significant relationship between pH value of the soil and the amount of Zn taken up by the plants; high pH caused less Zn uptake. He also indicated that a soluble form of Zn at a lower pH may be converted to a less soluble and less available form in the soil at higher pH values. Boawn et al. (1960) noted that Zn uptake by certain plants was influenced to a marked degree by changes in soil pH resulting from the various nitrogen carriers and nitrogen rates.

Leyden and Toth (1960) concluded that as the pH of the soil was increased, the Zn content of tomato tops decreased. They also showed that as the pH increased, less fertilizer Zn was absorbed and more came from the soil. More recently Brown and Tiffin (1962) emphasized that Zn deficiency in plants occurs on soils with a pH 6.0 or higher.

Lime minerals include primarily calcite $(CaCO_3)$, dolomite $[CaMg(CO_3)_2]$ and magnesite $(MgCO_3)$. Peech (1941) concluded that the indiscriminate use of lime to raise the pH value of the soil to the point favorable to fixation of ions into non-exchangeable and nonavailable forms may offset any benefits derived from liming. Among the elements that are rendered unavailable by overliming is Zn.

The possibility that lime minerals in the soil may constitute a potential adsorptive phase for certain cations was recognized by Leeper (1952), who postulated that in calcareous soils, calcium carbonate may be an important adsorbent of heavy metals. Another possibility for the effect of lime on Zn availability was proposed by Jurinak and Bauer (1956). They indicated that the similarity of the usually quoted ionic radii of the magnesium and Zn ions of 0.78% and 0.83%, respectively, suggests that Zn should fit well into the MgCO₃ lattice, whereas it is

too small to fit into holes of $CaCO_3$ -type lattice where 1.06 Å is the radius of Ca.

Walta (1953) found that increasing rates of application of limestone resulted in a progressive reduction of Zn^{65} uptake; for example, the activity per gram of plant tissue was 335 and 40 counts per minute as the limestone level was raised from 2,000 to 10,000 pounds an acre. Thus, if the available Zn present in the soil was near the critical level, the presence of appreciable amounts of lime minerals might present an additional hazard to proper Zn nutrition of plants.

Phosphate

Considerable work has been done to clarify the effect of phosphate fertilization on the availability of Zn to plants. However, disagreement still exists as to the relative importance of applied P in relation to Zn uptake by plants.

Chapman et al. (1940) emphasized that the high levels of phosphate in the soil will give Zn deficiency symptoms on citrus. Regers (1948) also found that the Zn content of the plants decreased to an almost constant value with increasing rates of application of phosphate while the P content increased regularly in a direct ratio to that applied. Bingham (1958) found noticeable reductions in Zn concentration of citrus plants with heavy applications of calcium phosphate. Langin et al. (1962) indicated that the more effectively the applied P was utilized by the crop, the more severe was the curtailment of Zn uptake. They added that low P rates rather than heavy infrequent application are likely to give less damaging effects.

The mechanism involved in the induction of Zn deficiency by P

fertilizations is not fully understood. There is little evidence to indicate how and under what conditions such a phenomenon occurs. Several mechanisms can and have been postulated. The immobilization of Zn by forming insoluble phosphate compounds is one. No evidence supports this view, and a consideration of the Zn requirements of plants and the solubility of even a compound such as $2n_3(PO_{l_4})_2$ makes such an explanation doubtful. Another explanation for the effect of phosphate on Zn uptake and the production of Zn deficiency symptoms appears plausible. It has been suggested that calcium from the super phosphate may have an inhibiting effect on Zn in the absorption process. Precipitation of zinc phosphate or other Zn complexes on root surfaces, in roots, and in conducting tissues may occur. Beawn et al. (1954) found that plant roots contain six times more Zn than do the aerial parts.

Langin et al. (1962) concluded that the damaging effect of P on Zn utilization was physiological or within the plant, perhaps in plant root cells, where increased levels of P blocked the absorption of Zn and vice versa. They also suggested that it is very possible that some Zn-activated enzyme involved in growth is associated; however, its effect would seem secondary to the absorption concept.

Meanwhile, there have been many results which contradict the theories on Zn-P interaction. Peech (1941) and Nikilin and Raimey (1952) claimed that P was neither detrimental nor beneficial to the absorption of Zn by plants. Boawn et al. (1954) indicated that their data did not support the idea that phosphate had an adverse effect on Zn adsorption or utilization; they also concluded that phosphate applications had no effect on the uptake of either applied Zn or native

soil Zn by plants. More than doubling the concentration of phosphate in the plant tissue failed to produce Zn deficiency symptoms or reduce the yield of dry matter of beans grown in greenhouse pots. They found that the amount of extractable phosphate in the soil was not related to the appearance of Zn deficiency symptoms.

Other groups of workers have tried to bring the two approaches together. Seatz (1960) suggested that the form in which phosphate is applied may have considerable effect. He showed that as the monocalcium phosphate content of the soil increased, the Zn content of plants increased; but when tricalcium phosphate was increased in the soil, the Zn content of plants decreased. Seatz explained the difference in degree of Zn uptake by the influence of the rate and source of phosphate on the soil pH. With monocalcium phosphate, the pH of the soil decreased from 7.2 to 6.1 as the P rate was increased from 1,000 to 20,000 pounds P_2O_5 per acre, while with tricalcium phosphate the soil pH changed from 7.0 to 7.3 for the same increase in phosphorus application.

Brown and Tiffin (1962) indicated that the P effect also depended on the type of the plants. The addition of P accentuated Zn deficiency symptoms in some plants like cotton, red kidney beans, tomatoes, and okra. Dill plants, in the same soil, developed severe Zn deficiency symptoms on all treatments even without adding any phosphate.

Burteson (1961) concluded that P fertilization may induce Zn deficiency in some crops under certain soil and climatic conditions. Phosphorus-induced Zn deficiencies are probably enhanced by cold, wet soils during the early part of the growing season. It is thought that there was a restriction of root development near to the zone of

fertilizer placement.

Ellis (1964) noted that a decrease in soil temperature decreased yield of corn plants and decreased the Zn concentration in the plants. The P concentration in the corn was not affected significantly by soil temperature.

Soil Minerals

The mineral fractions of soil play an important role in the availability of soil zinc. Jurinak and Bauer (1956) concluded that the similarity of the usually quoted ionic radii of the Mg and Zn ions suggests that Zn should fit well into the MgCO₃ lattice. Seatz and Jurinak (1957) indicated that Zn ions can be strongly adsorbed on commonly occurring lime minerals. They also added that the effect of liming with calcite and dolomite limestone on acid soils not only lowers Zn availability by increasing soil pH, it may also increase, temporarily, the adsorptive capacity of the soil for Zn. The ability of the lime minerals to increase the adsorptive capacity for any given soil, whether acid or alkaline, for Zn ions would probably be important only in soils of coarse texture where clay was not the dominating fraction of the soil.

Chandler (1935) found that trees growing on soils high in clay and with reactions as high as pH 8 to 9 rarely showed Zn deficiency, whereas trees on sandy, well-drained soils with reactions as low as pH 5.9 showed deficiency symptoms. Holmes (1943) reported that the Zn contents of the soil correlated quite closely with clay content.

Elgabaly and Jenny (1943), working with montmorillonite clays, found that Zn adsorption from Zn chloride solutions involves the ions Zn⁺⁺, ZnCl⁺, and ZnCH⁺, but the release of Zn from Zn clay is restricted mainly to Zn⁺⁺. Some of the Zn adsorbed could not be replaced with salt solution. Later Elgabaly (1950) explained that in minerals with Si-Al structural patterns, ions may enter the lattice through the holes produced by the distorted Al-octahedra on the a-b planes. In minerals with Si-Al-Si structures, entrance of the ion through Si-O planes seems improbable. In such cases the easiest way for an ion to be incorporated within the lattice is to pass through holes on the broken surfaces.

In their experiment, Nelson and Melsted (1955) added Zn^{65} to clays with different exchangeable ions and measured Zn adsorption. Their data supported Zn fixation in clay lattices. They showed that Zn was retained by soils in the following relation to other cations.

H > Zn > Ca > Mg > K

They concluded that a large part of the Zn added to soils and clay is converted to a form which is non-exchangeable, but which can be extracted with dilute acids. The proportion of Zn in this form increased with calcium saturation, time of reaction, and with decreasing quantities of Zn.

Organic Matter and Microorganisms

Many studies have been conducted in order to investigate the effect of organic matter on the availability of Zn. Jones, Call, and Barnette (1936) placed saw grass peat on the top of columns of soils and leached with a Zn solution. The peat was found to retain most of the Zn added.

Hibbard (1940a) showed that the surface 2 inches of the soil had a much higher Zn content than was found in lower layers. He found that

In was not readily leached from the soil and reasoned that accumulation resulted from the decomposition of organic matter. He also determined the Zn content of leaves of three woody species in various stages of decomposition. The Zn content of oak leaves was found to vary from 40 ppm in freshly fallen leaves to 98 ppm in leaves showing much decomposition. Pine varied from 34 ppm to 180 ppm and redwood from 39 to 97 ppm. This would show that Zn is retained by the organic matter and not leached as the organic matter decomposes.

Peech (1941) noted that the formation of humates of Cu and Zn in Florida soils was the major cause of reduced availability of these elements on the acid soils, particularly where the exchange capacity was seated primarily in the organic matter fraction.

Himes and Barker (1947) concluded that soil organic matter has a high affinity for Zn. They found that the removal of organic matter by oxidation destroyed the ability of the soil to chelate Zn. Miller and Ohlrogg (1958) indicated that Zn supplied as the organic complex is less available to plants than that supplied in the ionic form.

Recently DeRemer and Smith (1964) found that addition of organic matter in the form of sugarbeet tops to the soil tended to make the Zn present in the soil more difficult for the plant to obtain if the organic matter was allowed to partially decompose.

On the other hand, the effect of organic matter in increasing the availability of Zn has also been reported. Barnette et al. (1936) showed that the addition of organic manures to soils producing Zn deficient plants corrected the deficiency. Camp (1945) wrote that the increase in the number of Zn deficient soils in Florida may be due to the change from the use of organic manures to the use of mineral

fer ilizers.

It has been believed that microorganisms in a soil in which the Zn level is low absorb so much of what is available that higher plants suffer from the lack of Zn (Hibbard, 1940). The same idea was presented by Ark (1937). Ark found that the sterilization of a Zn deficient soil was effective in correcting the unfavorable Zn condition. Plants grown in the sterilized soil were healthy, while those grown in the untreated soil were severely deficient. This observation led him to the conclusion that there was a relationship between soil microflora and Zn availability in soil to plants.

Organo-Clay Complex

Attention has recently been given to the interaction between organic matter, which is believed to chelate or complex Zn, and the clay fraction in soil.

DeRemer and Smith (1964) found that the silt and sand size particles seemed to retain more Zn than the clay size particles. Also, Henry (1966) reported similar findings during his experiment. He concluded that organic matter seemed to bind clay size particles together and produce silt size particles. He added that if this were the case, the bonding of organic material to the mineral fraction was so firm that it resisted the extraction by hydrogen peroxides and other reagents.

There are many evidences in the literature to support the hypothesis that organic matter interacts with soil mineral fractions. It was indicated that a certain amount of organic substance is firmly bound with clay. A remarkable property acquired by clay under the influence

of humus is the decrease of solubility. Schloesing (1902), on the basis of his observations, thought that the colloids of humus take up clay and form some undefined compounds in a way that there was a decrease in the capability of clay to dissolve under the influence of water. Sidiri (1936) noted that humus was irreversibly adsorbed by clay. and thus raised the tenacity of the aggregates. This was not in the same degree for every clay. Meyers (1937) believed that the electronegative properties which are possed by soil colloids would serve as polarizing materials for the humic compounds which are polar and would attract the positive end of the polar compounds toward their surfaces. He also emphasized the effect of amphoteric compounds such as aluminum hydroxide on forming a chemical union between the positive valences of the compound and the negative valences of the colloidal organic acids. In addition, there would probably be oriented packing around the aluminum hydroxide particles since the organic colloidal particles, because of their relatively large size, would need to be packed very closely in order to satisfy the valence requirements of the positively charged particles.

Tyulin (1938) found that, besides the organic matter which was loosely attached to the organo-mineral gels in soils, there were considerable quantities of organic substances that were more firmly held. The N and the P of the strongly attached humus were only slightly unavailable to microorganisms.

Hendricks (1941) has presented evidences that the organic molecules may be held on clay surfaces by Van der Waals forces.

Bradley's (1945) opinion was that the organic molecules may be withdrawn by the clay from rather dilute solutions and, in becoming

adsorbed on the clay surfaces, may displace hydrogen-bonded water. He concluded that the interaction between hydrogen atoms of the organic matter with oxygen ions of the silicate surface involves energy comparable in magnitude with that of the O-H...O bonds of a natural water system.

EXPERIMENTAL METHODS

Description of the Soils

The three different soils used in this experiment (Table 1) were Portneuf silt loam soil in which Zn deficiency was found in field beans when the tops from a previous sugarbeet crop were turned under, Taumton sandy loam soil which is known to have a Zn deficiency on most sensitive crops, and Millville silt loam soil which has not shown any Zn deficiency problems.

	Soil							
Determination	Portneuf silt loam	Taunton sandy loam	Millville silt loam					
рН	7.8	8.2	7.9					
Organic matter (%)	1.8	0.5	2.2					
Cation exchange capacity (me/100 g)	23.3	13.8	13.6					
Available Zn Dithizone (ppm)	1.5	0.5	4.2					
EDTA (ppm)	1.3	0.5	4.3					
<pre>1/3 atmosphere moisture (%)</pre>	29.3	13.7	16.2					
Clay (<0.002) %	26.0	8.0	19.0					
Silt (%)	64.0	35.0	52.0					
Sand (%)	10.0	57.0	29.0					

Table 1. Physical and chemical characterization of the three soils used in these studies

Preliminary Study

This experiment was conducted in order to observe the visual deficiency symptoms on plants on Portneuf soil and compare them with Zn deficiency symptoms that appeared on plants growing on Taunton soil. Another purpose for the preliminary experiment was to develop an easy and efficient fractionation method for the soils.

Ground dried sugarbeet tops were added to the three soils (Portneuf, Taunton, and Millville) at two rates, zero and 30 ton/acre (2 x 10^6 lbs soil) on a green weight basis. The soils were allowed to incubate for 6 weeks by adding deionized water to bring the soil to field capacity and maintaining the temperature at 30 ± 1° C. Then beans were planted and allowed to grow for another 6 weeks.

The plants in Taunton soil showed chlorosis in the lower older leaves at 3 weeks, and the chlorosis was more severe in the older leaves than the young leaves. The deficiency symptoms started by the appearance of light green, yellow, or white areas between the veins of the leaves followed by browning of these areas and necrosis. The growth of the plants was not vigorous, and especially the new leaves were very small. These symptoms were observed in both the zero and 30 tons organic matter treatments. In the case of Portneuf soil, however, the plant growth was fairly good, although the same symptoms of Zn deficiency that were seen on the plants grown in Taunton soil appeared in plants grown on the Portneuf soil at the age of 4 weeks. This was only in the treatment where organic matter was added. Plants grown on Millville soil did not show any chlorosis and the growth was vigorous throughout the experimental period. Plants were harvested after 6 weeks of growth, and the soils were allowed to dry for a week. Different methods of extraction were tried and compared. The extraction of the available Zn by dithizone (Shaw and Dean, 1952) was compared with 1 percent aqueous solution of disodium ethylene diamine-tetra-acetate (EDTA) extraction (Allen, 1961). The Zn extracted by dithizone was compared with that extracted with EDTA for the three soils before applying any treatment. The values are shown in Table 1. Both methods gave almost the same values; therefore, in this study Zn extracted by 1 percent EDTA was used as the available fraction.

Five grams of soil were extracted successively with water to give the water soluble Zn fraction, then with neutral, normal ammonium acetate to give the exchangeable Zn (Baughman, 1956), then with copper acetate (0.05 N) for the complexed Zn (Baughman, 1956; Himes and Barker, 1957). The organic matter was then destroyed by treating with hydrogen peroxide and the soil extracted with water to give the Zn complexed by organic matter fraction. Finally the soil was treated with EDTA again to give the available Zn remaining in the soil.

It was found that Zn level in the hydrogen peroxide solution was very low, even in the organic matter treated pots. Also, it was observed that Zn in final EDTA extraction in some cases was more than that in the EDTA extraction at the beginning. These observations led to the conclusion that after the organic matter was destroyed with H_2O_2 , part of the released Zn reacted with the soil and not all the Zn complexed with the organic matter fraction came out in the hydrogen peroxide solution. So extractings with water, ammonium acetate, and copper acetate followed the destroying of the organic matter in order to obtain all the Zn released from the organic fraction even if it did react with certain soil fractions.

Also it has been found that 20 ml extractions for 2 hours was adequate to extract all the Zn in a certain fraction.

As a result of the preliminary experiment, the fractionation method given in Figure 1 was used.

Primary Experiment

An intensive long-term incubation research study using the three soils was set up in order to investigate the several objectives.

Three organic matter treatments were applied to the soils; no organic matter, or ground alfalfa, or sugarbeet tops at the rate of 30 tons per acre equivalent green weight. Zn was added to the soils at rates of 0 or 20 lbs Zn per 2 x 10^6 lbs soil as ZnSO_4 . At the same time, Zn^{65} was introduced to all the soils as a tracer at the rate of 79 µc per kg.

The soils were mixed thoroughly with the organic matter and Zn fertilizer and then were placed in quart plastic containers with 1 kilogram per pot.

This experiment was set up with four incubation periods (no incubation, 6 weeks, 6 months, and 1 year). Water was added to bring the soil to field capacity where it was maintained with deionized water and were stirred occasionally. The temperature was maintained at $30 \pm 1^{\circ}$ C.

After each incubation period, small white bean seeds were planted, six seeds per pot. A week after planting, the plants in each pot were thinned to three of the most uniform plants with regard to size, color, and shape. This experiment was carried on in the growth chamber



Figure 1. Flow sheet describing the extraction procedures for obtaining the different soil fractions

(DeRemer and Smith, 1964) at a photoperiod of 13 hours and a nyctoperiod of 11 hours. The phototemperature was 30° C and a nyctotemperature of 23° C. The equivalent of 100 pounds of N as $\mathrm{NH}_4\mathrm{NO}_3$ per acre furrow slice was added to the soil and mixed at the time the organic matter residues were applied. The experiment, therefore, consisted of 72 treatment combinations with two replicates, so the total number of pots was 144.

The plants were harvested after 6 weeks of growth.

Plants and soils analysis

<u>Plants</u>. The plants were harvested, dried at 60° C, weighed, then separated into aerial parts and roots. The tops were pelleted, weighed, and the Zn⁶⁵ content determined by counting. The pellets were then digested in a mixture of 17 ml of concentrated nitric acid and 3 ml of 72 percent perchloric acid. The volume was completed to 50 ml and total Zn was determined on a Perkin-Elmer 303 atomic absorption spectrophotometer.

<u>Soils</u>. After harvesting the plants, the pots were left in the growth chamber for a week to allow the soils to become air dry. Two 5-gram samples of soil from each pot were obtained and analyzed for Zn according to the diagram in Figure 1.

In each extraction Zn^{65} was counted with Baird atomic multiscaler model 132 attached to RIDAL model 33-1 and single channel spectrometer model 139-2, connected to sodium iodide well detector, and total Zn was determined as ppm by using the Perkin-Elmer model 303 atomic absorption spectrophotometer. In the case of the residue, just the Zn^{65} was determined.

The total Zn and Zn^{65} in the EDTA extraction of the soils before

planting were also determined in the last two incubation periods.

RESULTS AND DISCUSSION

Soil Analyses

EDTA extractable or available Zn

The level of the EDTA extractable form of Zn was affected by the three organic matter treatments and by the three different soils (Figures 2, 3, and 4). The soils where sugarbeet tops and alfalfa were incubated always had less Zn^{65} in the available form than the soils where no organic matter was added. The recovery of the Zn^{65} extracted by this EDTA was least for the Taunton soil (Figure 2); intermediate for the Portneuf soil (Figure 3), and greatest for the Millville soil (Figure 4). This may suggest that both the Taunton and Portneuf soils had the ability to inactivate a greater part of the "available" Zn than did the Millville soil.

It should be pointed out that after the 32 weeks' incubation period, the amount of Zn recovered as available in the Portneuf and Taunton soils increased in the case of both the sugarbeet and alfalfa treatments and that the level of Zn approached that of the no organic matter treatment at the 58-week period. The amount in the Millville soil did not change with time after the 32-week sampling. This also may support the suggestion that both the Taunton and Portneuf have the ability to inactivate the available Zn but with time this ability decreases.

Soil fractionations

The most important objective of this study was to determine the rate, mode, and magnitude of the inactivation of Zn in the soil brought



Figure 2. The effect of organic matter treatments on the amount of EDTA extractable (available) ${\rm Zn}^{65}$ in the Taunton sandy loam at the end of each of the four incubation periods



Figure 3. The effect of organic matter treatments on the amount of EDTA extractable (available) ${\rm Zn}^{05}$ in the Portneuf silt loam at the end of each of the four incubation periods


Figure 4. The effect of organic matter treatments on the amount of EDTA extractable (available) ${\rm Zn}^{95}$ in the Millville silt loam at the end of each of the four incubation periods

about by, or at least during, the decomposition of organic material. So the effect of each of the three organic treatments on the different fractions of each soil was plotted; also each fraction was plotted in detail in order to give a clear picture of the effect of organic matter on the behavior of the soils.

<u>Taunton soil</u>. The amount of Zn^{65} recovered in the different fractions of the Taunton soil (Figure 5) where no organic matter was added, was in the following order: residue > complexed > EDTA > organic > exchangeable > water soluble. The addition of organic matter only changed the relative position of two of the fractions, EDTA extractable and Zn in the organic fraction. When sugarbeet tops (Figure 6) or alfalfa (Figure 7) were added, the Zn^{65} recovered in the different fractions was: residue > complexed > organic > EDTA > exchangeable > water soluble. Where figures 6 and 7 are compared, it is clear that the addition of either sugarbeet tops or alfalfa affected the relative order of Zn^{65} recovered in the soil fractions in the same manner. The Zn^{65} level in the treatment with no organic matter was always higher than the treatments with sugarbeet tops or alfalfa in all fractions except that in the residue and organic fractions.

The percentage of the $2n^{65}$ in the water soluble (Figure 8) and exchangeable (Figure 9) fractions was small when compared to the other soil fractions. The amount in these two fractions increased gradually with increasing time of incubation irrespective of whether or not organic matter was added. Between the two incubation periods of 32 and 58 weeks, the $2n^{65}$ increased rapidly in the water soluble and exchangeable fractions. The presence of organic matter in the soil decreased the recovered $2n^{65}$ in both fractions.



Figure 5. The effect of zero organic matter additions on the distribution of $2n^{0.5}$ in various fractions of Taunton sandy loam at the end of each of the four incubation periods



Figure 6. The effect of added sugarbeet tops on the distribution of Zn^{65} in various fractions of Taunton sandy loam at the end of each of the four incubation periods



Figure 7. The effect of added alfalfa on the distribution of ${\rm Zn}^{65}$ in various fractions of Taunton sandy loam at the end of each of the four incubation periods



Figure 8. The effect of organic matter treatments on the percent of the total recovered Zn^{05} that was found in the water soluble fraction of the Taunton sandy loam at the end of each of the four incubation periods



Figure 9. The effect of organic matter treatments on the percent of the total recovered $2n^{05}$ that was found in the ammonium acetate extraction (exchangeable) of the Taunton sandy loam at the end of each of the four incubation periods

The addition of sugarbeet tops or alfalfa decreased the amount of Zn^{65} recovered in the copper acetate extraction (complexed Zn). In the earlier incubations the presence of sugarbeet tops decreased the Zn^{65} in this fraction more than did the addition of alfalfa (Figure 10).

The Zn^{65} recovered in the organic matter fraction was initially at a high level, but then decreased with time (Figure 11). When no organic matter was added, the percentage was 8.7 at 6 weeks and 5.0 at 58 weeks. With additions of sugarbeet tops and alfalfa, the percentage was 15.0 and 13.2 at the first incubation. The percentage decreased to 6.5 and 6.1, respectively, at the 58-week period.

The $2n^{65}$ recovered in the EDTA extraction (remaining available Zn) was also affected by the addition of organic matter and the length of incubation period (Figure 12). The percentage of $2n^{65}$ in this fraction was much higher without organic matter than when organic matter was added. The amount of $2n^{65}$ recovered in this fraction from the treatments involving the two organic matter additions, sugarbeet tops and alfalfa, continued to decrease till the 32-week incubation period, but then increased rapidly at the 58-week period.

Figure 13 shows the effect of organic matter treatments on the percent of the total recovered $2n^{65}$ that was found in the residue fraction of the Taunton sandy loam at the end of each of the four incubation periods. Like the organic fraction, the addition of organic matter always caused more $2n^{65}$ to show up in this fraction. The 32-week incubation period marked the end of the increasing amount of $2n^{65}$ recovered in the residue fraction. After this time the amount decreased so that at the end of the 58-week incubation period, the amount in this fraction was actually lower for both the no organic matter treatment



Figure 10. The effect of organic matter treatments on the percent of the total recovered ${\rm Zn}^{05}$ that was found in the copper acetate extraction (complexed) of the Taunton sandy loam at the end of each of the four incubation periods







Figure 12. The effect of organic matter treatments on the percent of the total recovered Zn^{65} that was found in the EDTA extraction (remaining available) of the Taunton sandy loam at the end of each of the fourincubation periods



Figure 13. The effect of organic matter treatments on the percent of the total recovered Zn^{05} that was found in the residue fraction of the Taunton sandy loam at the end of each of the four incubation periods

and the alfalfa treatment that had been found originally.

<u>Portneuf soil</u>. The effect of each organic matter treatment on the distribution of Zn^{65} in the various fractions of this soil at the end of the incubation periods is presented in Figure 14 for the zero organic matter, Figure 15 for the case where sugarbeet tops were added, and Figure 16 for the case where alfalfa was added.

The amount of Zn^{65} recovered in the different soil fractions where no organic matter (Figure 14) was added was in the following order; residue > EDTA > complexed > organic > exchangeable > water soluble. The relative position of the organic, complexed, and EDTA Zn^{65} fractions in the case of the sugarbeet tops and alfalfa treatments varied with the length of incubation period. In general, however, when organic matter was added, the following order persisted (Figures 15 and 16): residue > organic = complexed = EDTA > exchangeable > water soluble.

As in the treatments where Taunton sandy silt soil was used, the $2n^{65}$ level in the no organic matter treatment was always higher than where sugarbeet tops or alfalfa were added in all fractions except the organic and residue fractions.

The percentage of the Zn^{65} that was recovered in the water soluble (Figure 17) and exchangeable (Figure 18) fractions was very small compared to the other soil fractions; however, the amount increased gradually with time irrespective of whether or not organic matter was added. This was true except at the end of the 12-week incubation period where Zn^{65} in these fractions decreased in the treatments where organic matter was added.

The data in Figure 19 indicate that the addition of organic matter decreased the Zn⁶⁵ that was complexed up to the end of the 32-week







Figure 15. The effect of added sugarbeet tops on the distribution of Zn^{65} in various fractions of Portneuf silt loam at the end of each of the four incubation periods



Figure 16. The effect of added alfalfa on the distribution of Zn^{65} in various fractions of Portneuf silt loam at the end of each of the four incubation periods



Figure 17. The effect of organic matter treatments on the percent of the total recovered Zn^{65} that was found in the water soluble fraction of the Portneuf silt loam at the end of each of the four incubation periods



Figure 18. The effect of organic matter treatments on the percent of the total recovered Zn^{05} that was found in the ammonium acetate extraction (exchangeable) of the Portneuf silt loam at the end of each of the four incubation periods



Figure 19. The effect of organic matter treatments on the percent of the total recovered Zn^{05} that was found in the copper acetate extraction (complexed) of the Portneuf silt loam at the end of each of the four incubation periods

period. The Zn^{65} in this fraction then increased at the end of the 58-week period. The decrease in Zn^{65} recovered in this fraction when alfalfa was added was less pronounced than when sugarbeet tops were used.

The incubation for 12 weeks increased the $2n^{65}$ obtained in the organic fractions of the Portneuf silt loam for the three organic matter treatments (Figure 20). After this, the amounts of $2n^{65}$ in this fraction declined rapidly. It is important to point out again that the level of $2n^{65}$ in the organic and residue fractions was higher in the organic matter treatments than when no organic matter was added.

The Zn^{65} recovered in EDTA extraction (remaining available Zn) was decreased by the addition of organic matter and by longer incubation periods (Figure 21). At the end of the 58-week period, the level of Zn^{65} in this fraction increased to a level approximately equal to that obtained at the end of the 6-week period.

The data in Figure 22 indicate that the addition of organic matter increased the amount of $2n^{65}$ recovered in the residue fraction. The length of incubation time also caused an increased percent of $2n^{65}$ in this fraction up to the 32-week incubation period, then there was a decrease noted at the end of the 58-week incubation.

<u>Millville soil</u>. The effect of organic matter treatments on the distribution of Zn^{65} in the various fractions of this soil at the end of each of the four incubation periods is shown in Figure 23 for the zero organic matter, Figure 24 for the case where the sugarbeet tops were added, and Figure 25 for the case where alfalfa was added. It is noticed that, in general, this amount of Zn^{65} recovered in the different soil fractions where no organic matter was added follow the following



Figure 20. The effect of organic matter treatments on the percent of the total recovered Zn^{05} that was found in the organic fraction of the Portneuf silt loam at the end of each of the four incubation periods



Figure 21. The effect of organic matter treatments on the percent of the total recovered $2n^{65}$ that was found in the EDTA extraction (remaining available) of the Portneuf silt loam at the end of each of the four incubation periods



Figure 22. The effect of organic matter treatments on the percent of the total recovered $2n^{05}$ that was found in the residue fraction of Portneuf silt loam at the end of each of the four incubation periods



Figure 23. The effect of zero organic matter additions on the distribution of Zn^{65} in various fractions of Millville silt loam at the end of each of the four incubation periods



Figure 24. The effect of added sugarbeet tops on the distribution of Zn^{65} in various fractions of Millville silt loam at the end of each of the four incubation periods



Figure 25. The effect of added alfalfa on the distribution of $2n^{65}$ in various fractions of Millville silt loam at the end of each of the four incubation periods

order: residue > EDTA > complexed > organic > exchangeable = water soluble. The addition of sugarbeet tops and alfalfa affected the amounts of Zn^{65} recovered in the organic, complexed, and EDTA (remaining available Zn) fractions. The organic matter additions produced the following order of Zn^{65} in the different fractions: residue > organic = complexed = EDTA > exchangeable = water soluble.

The data for the percent of the total $2n^{65}$ recovered in the individual soil fractions for the Millville soil following each of the four incubation periods are presented graphically in Figures 26 to 31. The data in Figure 26 show that the additions of organic matter to this soil brought about reductions in Zn in the water soluble fraction. The overall level of Zn in this particular fraction is higher than that found in the Taunton soil (Figure 8) or the Portneuf soil (Figure 18), but the reduction in Zn is still evident. There are similarities and differences in the three soils in the effects of organic matter additions on the distribution of Zn in the various soil fractions. These will be brought out in detail in the next section.

The difference between soils

Although these data have all been presented previously in graphical form under the sections for the various soils, it was felt that it would be profitable to compare directly the Zn status in the various fractions of each soil found at the end of the four incubation periods. There are striking similarities in the Zn status in these soils as influenced by organic matter additions. There are differences, too, and these similarities and differences take on patterns that might be related to specific properties of the soils. Since there was little



Figure 26. The effect of organic matter treatments on the percent of the total recovered Zn^{65} that was found in the water-soluble fraction of the Millville silt loam at the end of each of the incubation periods



Figure 27. The effect of organic matter treatments on the percent of the total recovered Zn^{05} that was found in the ammonium acetate extraction (exchangeable) of the Millville silt loam at the end of each of the four incubation periods



Figure 28. The effect of organic matter treatments on the percent of the total recovered Zn^{05} that was found in the copper acetate extraction (complexed) of the Millville silt loam at the end of each of the four incubation periods



Figure 29. The effect of organic matter treatments on the percent of the total recovered Zn^{65} that was found in the organic fraction of the Millville silt loam at the end of each of the four incubation periods



Figure 30. The effect of organic matter treatments on the percent of the total recovered $Zn^{0.5}$ that was found in the EDTA extraction (remaining available) of the Millville silt loam at the end of each of the four incubation periods



Figure 31. The effect of organic matter treatments on the percent of the total recovered Zn^{05} that was found in the residue fraction of Millville silt loam at the end of each of the four incubation periods

di ference noted between alfalfa or sugarbeet tops on their effect on the Zn distribution in these soils, for clarity the data for the alfalfa treated soils will be omitted.

The first EDTA extraction was to give an overall measure of the available Zn. It can be seen that the Millville soil was better supplied with available Zn at all times and under all treatments than was the Portneuf soil which in turn was better supplied than was the Taunton soil (Figure 32). There was, however, a reduction in the available Zn for all soils when organic matter was added. The amount of available Zn in the Millville soil to which the organic matter had been applied was still greater than in the unammended Portneuf soil. This pattern was also found between the Portneuf and the Taunton soils. The available Zn level in the Portneuf soil, even though it was reduced by the addition of sugarbeet tops, was still greater than the available Zn in the Taunton soil to which no organic matter was added. The greatest reduction of available Zn, brought about by the addition of sugarbeet tops was in the Portneuf soil. It is possible that the effect of added organic matter on the EDTA extractable Zn illustrates enough of the similarities and differences that exist between the three soils. However, the data obtained when the soils were fractions ted and the Zn determined the various areas might be useful in explaining the differences noted in both the available Zn level in the soils and the growth of plants on these soils. For that reason, the water-soluble Zn, the exchangeable Zn, the copper acetate extractable Zn, the second EDTA extractable Zn, the Zn released when the organic matter was destroyed, and the Zn remaining in the residue will be presented so the differences between the soils can be observed.



Figure 32. The effect of organic matter treatments on the Zn content (ppm) that was found in the EDTA extractable or available fraction of the three soils, Taunton sandy loam, Portneuf silt loam, and Millville silt loam, at the end of each of the four incubation periods

There was less Zn found in the water-soluble fraction than any other. As far as the three soils were concerned, it can be seen that the Zn recovered from the Millville soil was greater than that recovered from the Portneuf soil, and this, in turn, was greater than that recovered from the Taunton soil (Figure 33). In this respect, this fraction follows the pattern observed with the available Zn (Figure 32). In the case of the water-soluble Zn, however, there was a greater effect of added organic matter on reducing the Zn level in the Millville than had been observed with the EDTA-extractable Zn. The water soluble Zn in the unammended Millville soil remained quite constant with time while that in the ammended Millville soil and in both the treated and untreated Portneuf and Taunton soils increased with time. There was, therefore, a striking narrowing with time of the watersoluble Zn levels between the treated and non-treated Millville soil. This narrowing of the water-soluble Zn found in the soil where no organic matter was added and that found in the soil upon addition of organic matter was also noted with the other two soils. The other point that should be noted is that the water-soluble Zn in the treated Portneuf soil dropped materially between the first and second incubation periods.

The ranking of the soils as far as Zn recovered in the case of the water-soluble Zn was also observed with the exchangeable Zn (Figure 34). That is: Millvile > Portneuf > Tanton. It should be noted that in the unammended soils there was only slightly more exchangeable Zn than water-soluble Zn for the Millville soil, while for the Portneuf soil there was a difference of 1.5 times and for Taunton soil a difference of nearly two times. In all cases, both treated and


Figure 33. The effect of organic matter treatments on the percent of the total recovered Zn^{05} that was found in the water soluble fraction of the three soils, Taunton sandy loam, Portneuf silt loam, and Mill-ville silt loam at the end of each of the four incubation periods



Figure 34. The effect of organic matter treatments on the percent of the total recovered Zn^{65} that was found in the exchangeable fraction of the three soils, Taunton sandy loam, Portneuf silt loam, and Mill-ville silt loam, at the end of each of the four incubation periods

untreated, there were increases of exchangeable Zn with time except for the ammended Portneuf soil between the first and second incubation periods. There was also a reduction of exchangeable Zn with the addition of organic matter in all soils. There was a narrowing of the level of exchangeable Zn between treated and non-treated soils with time. Thus, because of the increase of exchangeable Zn in all cases with time and because there was a narrowing of this Zn level between the treated and untreated soils with time, the level of exchangeable Zn in the treated soils at the last incubation period was always higher than that found for the unammended soil at the first incubation.

The pattern of Zn removed from the three soils with copper acetate at the end of each of the four incubation periods is given in Figure 35. The ranking of the three soils for this particular Zn extraction is: Taunton > Millville > Portneuf. It is not known how available this Zn might be for plants, but it is suspected it is not readily available. There was also a reduction in the Zn level in this fraction by the addition of organic matter. Although the particular curves of Figure 35 might appear to be closer together than those noted with water... soluble Zn (Figure 33) and exchangeable Zn (Figure 34), they are actually much further apart. It is interesting to note that for the Zn deficient Taunton soil from 23 to 30 percent of the Zn recovered was in this fraction. For Millville soil the range was from 17 to 24 percent, and for Portneuf soil from 14 to 19 percent. The Portneuf soil was the only soil that showed a reduction of Zn in this fraction with time, and this was at the second and third incubation periods.

The addition of organic matter to the three soils caused Zn to be added to the organic fraction (Figure 36). The surprising observation



Figure 35. The effect of organic matter treatments on the percent of the total recovered Zn^{65} that was found in the complexed fraction of the three soils, Taunton sandy loam, Portneuf silt loam, and Millville silt loam, at the end of each of the four incubation periods



Figure 36. The effect of organic matter treatments on the percent of the total recovered Zn^{65} that was found in the organic fraction of the three soils, Taunton sandy loam, Portneuf silt loam, and Millville silt loam, at the end of each of the four incubation periods

is that there was so much Zn in the organic fraction of the treated Millville soil. In all cases, except for the Portneuf soil, there was a decrease of Zn in this fraction with time. With the Portneuf soil, especially the treated soil, the Zn in this fraction increased at the second incubation period.

Following the destruction of the organic matter and recovery of the Zn released, the soils were extracted with EDTA. The addition of organic matter caused a reduction in the amount of the Zn that showed up in this fraction (Figure 37). Even after the exhaustive extractions that preceded this one, as much as 35 percent of the recovered Zn was in this fraction. There was a greater range of Zn recovered in this EDTA extraction between the soils than had been noted for any previous extraction. The taunton soil had very little Zn in this fraction and Millville and Portneuf soils showed almost the same amounts. The addition of organic matter to these soils caused a greater reduction of the EDTA extractable Zn for the Millville and Portneuf soils than was the case for the Taunton soil. For the treated soils there was a great increase in the Zn in this fraction between the third and fourth incubation periods while for the non-treated soils the Zn in this fraction remained fairly constant after the second incubation period.

There was a tremendous variation in the Zn found in the residue for the three soils (Figure 38). The ranking of the unammended soils for the Zn in the residue was Taunton > Portneuf > Millville for all incubation periods. For the ammended soils the amount of Zn in the residue of the Portneuf soil far exceeded that of the Taunton soil only at the third incubation. In general there was an increase in Zn in this fraction for all soils up to the third incubation. There followed,



Figure 37. The effect of organic matter treatments on the percent of the total recovered $Zn^{0.5}$ that was found in remaining available fraction (EDTA extraction) of the three soils, Taunton sandy loam, Portneuf silt loam, and Millville silt loam, at the end of each of the four incubation periods



Figure 38. The effect of organic matter treatments on the percent of the total recovered $2n^{65}$ that was found in the residue fraction of the three soils, Taunton sandy loam, Portneuf silt loam, and Millville silt loam, at the end of each of the four incubation periods

then, a decrease at the time of the last incubation. It is not evident why there was the increase of Zn in the residue of the non-treated soils.

ZnSOL treatment

As indicated before, the soils in one-half of the pots had received only $2n^{65}$ and those in the other half had received $2nSO_{l_1}$ labelled with $2n^{65}$. There was no significant difference between the percentage of $2n^{65}$ in soil fractions in the two Zn treatments. In general, similar fractions in both treatments gave the same trend and behavior. There was some indication that the water soluble, exchangeable, and complexed fractions showed a little increase in $2n^{65}$ percent when $2nSO_{l_1}$ was included. On the other hand, the organic fraction, the Zn remaining as available, and that in the residue fraction had less $2n^{65}$ when $2nSO_{l_1}$ was added.

The total Zn (ppm) in the soil fractions was always higher in the treatments where ZnSO₁, fertilizer was applied.

The plants reacted differently when $2nSO_{l_1}$ was added than when it was omitted. There were much higher counts in plants grown in the tracer alone (no added $2nSO_{l_1}$). This may be due to the dilution effect of the added $2nSO_{l_1}$ as another source of Zn besides the $2n^{65}$ and the indigenous Zn found in the soil. This observation was clearly noticed in the case of the two soils which did not have high Zn content originally, namely the Taunton and Portneuf soils. In the case of the Millville soil the difference between the two Zn treatments on $2n^{65}$ uptake was small and the uptake of $2n^{65}$ by the plants was much lower than in the case of the other two soils.

Plant Analysis

The complex relationship between the composition of the plant and that of the soil has never been fully understood, although investigations of those relationships have been conducted for many years. Doubtless the factors influencing the intake of any given nutrient by a plant are so numerous as to make it difficult enough to use plant composition of this mutrient as a guide to its level in soil, although Woodbridge (1961) noted that evidence indicates that each plant species has a limiting minimum concentration of each element. Little is known about the optimum levels or the values of Zn associated with deficiency symptoms in the tissues of different crops. Teakle and Turton (1943) reported that the Zn supply was inadequate when the leaves of subterranean clover at flowering contain as low as 10 to 15 ppm. For oats at 6 to 8 weeks of age, 20 ppm Zn in the whole top was said to be normal. Viets et al. (1954) found that Zn content in the total top of deficient bean plants varies from 10 to about 22 ppm. They also found that the In content for tops of symptomless plants and deficient plants overlap in the range of 15 to 22 ppm.

One of the purposes of this investigation was to study the relationship between the amount of Zn in soil and the amount taken up by plants and to observe the effect of this soil Zn on the growth and yield of plants. Viets et al. (1954), on the basis of their experiment, listed beans at the top of the most sensitive crops toward Zn. It has already been noted that this crop exhibited Zn deficiency symptoms in the field after turning under sugarbeet tops in Portneuf soil (DeRemer and Smith, 1964). Small white beans, Phaseolus vulgaris, were, therefore, chosen to be used in this experiment.

Visual observations

Plants grown in Taunton soil in all the treatments without the addition of ZnSO_L showed Zn deficiency symptoms. The Zn deficiency symptoms started on the lower older leaves early and were more severe than on the younger leaves. The deficiency symptoms were observed first as the appearances of light green, yellow, or white areas between the veins of the leaves. This was followed by browning of these areas and eventually necrosis. The new young leaves were smaller in size than those that first appeared. Even though all the symptoms appeared at the earlier incubation periods, no change of plant color appeared when the soils were incubated for 1 year.

Concerning the Portneuf soil, Zn deficiency symptoms appeared only in the soil treated with organic matter; when no organic matter was added, none of these symptoms showed up on the plants. This behavior occurred in the first three incubation periods (no incubation, 6 weeks, and 6 months), but at the end of the incubation period of 1 year, the growth of all plants was normal and no symptoms appeared.

Plants grown in Millville soil did not exhibit any Zn deficiency symptoms for any of the organic matter treatments or incubation periods and the growth was quite normal.

The yield

The dry matter yield for the beans grown on the three soils following the various incubation periods (no incubation, 6 weeks, 6 months, and one full year) are shown in Figures 39, 40, and 41. This experiment revealed that, in general, the persistent Zn deficiency symptoms of the



Figure 39. The effect of organic matter treatments on the dry matter weight (g) of small white beans grown for 6 weeks in Taunton sandy loam at the end of each of the four incubation periods



Figure 40. The effect of organic matter treatments on the dry matter weight (g) of small white beans grown for 6 weeks in Portneuf silt loam at the end of each of the four incubation periods



Figure 41. The effect of organic matter treatments on the dry matter weight (g) of small white beans grown for 6 weeks in Millville silt loam at the end of each of the four incubation periods

plants were correlated with lowered yield. This observation was also obtained by Judy et al. (1964).

The yield of bean plants grown on the Taunton soil (Figure 39) showed the effect of the added $2nSO_{l_1}$ in the four incubation periods. The yields were lowest on this soil when compared with that obtained with the two other soils. This may be a result of some other fertility factors besides the low level of indigenous Zn.

In Portneuf soil (Figure 40) the effect of $ZnSO_{\downarrow}$ on increasing plant growth was large. This was particularly so in the case of no incubation, 6 weeks, and 6 months incubation. At the end of 1 year of incubation, this effect of $ZnSO_{\downarrow}$ on plant growth was not evident, and the plants grown on soil without added $ZnSO_{\downarrow}$ gave a yield comparable to the soil $ZnSO_{\downarrow}$ applied. In Portneuf and Taunton soils, there appeared to be some depressing effect on plant growth due to the added organic material when $ZnSO_{\downarrow}$ was not supplied.

The growth of plants in the Millville soil showed the least variation in yield at all the incubation periods. It also did not show the effect of organic matter or added ZnSO₄ on plant growth (Figure 41).

Zinc content in plants

In the case where plants were grown in the Taunton soils without added ZnSO_{l_1} (Figure 42), the Zn content varies from 5.7 to 15.0 ppm. The organic matter treatments, in general, lowered the Zn level in the plants. The amount of Zn in the plants, however, increased with each succeeding incubation period. When ZnSO_{l_1} was added to this soil, the Zn content ranged from 19.2 to 23.2 ppm.



Figure 42. The effect of organic matter treatments on the Zn content ppm, in small white beans grown for 6 weeks in Taunton sandy loam at the end of each of the four incubation periods The striking effect of added organic material in the absence of additional Zn on the level of Zn in plants is shown with the Portneuf soil (Figure 43). The Zn content of the plants ranged from 15.6 to 20.9 ppm when no organic matter was added to the soil; in the case where sugarbeet tops were added, the range was 6.5 to 18.9 ppm, and when alfalfa was added, it was 8.1 to 19.2 ppm. It should be noticed that in the case of organic matter additions, when we compare the plants grown at the end of the one year's incubation with those grown earlier, the amount of Zn in the plants was doubled. This may be an indication of the releasing of more available Zn to plants by the decomposing organic matter as the incubation period increases.

The Zn content in the plants grown in the Millville soil was much higher, in general, than in the plants grown in the other two soils (Figure 44). In this soil the Zn in the plants continuously increased with time. Adding ZnSO₄ increased the Zn in plants. No effect of the organic matter was observed. The Zn in plants ranged from 26.4 to 31.9 ppm without added ZnSO₄; and when ZnSO₄ was added, it was 34.8 to 40.8 ppm.

If we were to set Zn levels to distinguish between deficient and normal bean tops, the result of this experiment would suggest the following:

For Taunton sandy loam

... less than 9.5 ppm total Zn would produce Zn deficiency symptoms.

...more than 9.5 ppm to less than 19 ppm total Zn, no change in color appeared on plants but growth was stunted (marginal).

...more than 19 ppm total Zn would produce no Zn deficiency



Figure 43. The effect of organic matter treatments in the Zn content (ppm) in small white beans grown in Portneuf silt loam at the end of each of the four incubation periods



Figure 44. The effect of organic matter treatments on the Zn content (ppm) in small white beans grown in Millville silt loam at the end of each of the four incubation periods

(normal).

For Portneuf silt loam

...less than 10 ppm total Zn would produce Zn deficiency symptoms. ...10 ppm to 14 ppm total Zn (marginal).

...more than 14 ppm total Zn would produce no Zn deficiency (normal).

The plants grown on the two soils, Portneuf silt loam and Taunton sandy loam, showed deficiency symptoms at different upper limits of Zn content. Plants grown on Portneuf soil containing less than 14 ppm of total Zn showed Zn deficiency symptoms; on the other hand, plants grown on Taunton soil showed deficiency when they contained less than 19 ppm of total Zn. Therefore, a common upper level of Zn deficiency in all soils may not be applicable.

The relation between Zn level in soils and plants

The data of this experiment suggested that the amount of Zn in the EDTA extraction (available) for the three soils was the most representative value of the Zn content in the plants (Figures 45, 46, 47 vs. 42, 43, 44).

In Taunton sandy loam when $ZnSO_{l_1}$ was added, the amount of Zn in EDTA extraction varied from 2.5 to 3.5 ppm; however, when $ZnSO_{l_1}$ was not added, the amount varied from 1.2 to 1.9 ppm (Figure 45). The same trend was obtained in the other two soils, Portneuf silt loam (Figure 46), and Millville silt loam (Figure 47), with some variation in the amount of Zn obtained. The amounts of Zn in EDTA extraction when $ZnSO_{l_1}$ was added to Portneuf and Millville soils, were 3.1 to 6.3 ppm and 5.0 to 7.0 ppm, respectively, and when no $ZnSO_{l_1}$ was applied,



Figure 45. The effect of organic matter treatments on the amount of EDTA extractable or available Zn in the Taunton sandy loam at the end of each of the four incubation periods when Zn was added to the soils at the rate of zero (-ZnSO_L) and 20 lb/acre (+ZnSO_L)



Figure 46. The effect of organic matter treatments on the amount of EDTA extractable or available Zn in the Portneuf silt loam at the end of each of the four incubation periods when Zn was added to the soils at the rate of zero (-ZnSO₄) and 20 lb/acre (+ZnSO₄)



Figure 47. The effect of organic matter treatments on the amount of EDTA extractable or available Zn on the Millville silt loam at the end of each of the four incubation periods when Zn was added to the soils at the rate of zero $(-ZnSO_{\rm h})$ and 20 lb/acre $(+ZnSO_{\rm h})$

the amounts were 1.5 to 3.2 ppm for the Portneuf and 4.1 to 5.3 ppm for Millville.

To reach a conclusion concerning the relationship between the plants content and soil supply with Zn is a hard task, but the available information obtained in this experiment may be helpful in setting this relation. It should be kept in mind, however, that these conclusions are valid only under the environment and conditions of this experiment. Flants vary greatly in their Zn requirements and their ability to obtain Zn from the different soils; therefore, what constitutes a normal Zn content of one plant may not be sufficient for some other plant. However, from the data presented in Tables 2 and 3 and from the observed deficiency symptoms, the following tentative list of Zn levels in soils and plants can be made:

Plant levels:

Total Zn ppm

10	or less	•	0	0	•		•	•	•	•	•	•	۰	deficient
10	to 19 .	0	•	o		•	٠	0	•	0	o	•	•	marginal
19	and more	o	0				0	0		0		0		normal

In the marginal range the deficiency symptoms may show dependency upon some other factors; for example, in the Taunton soil, when plants contained l4 ppm, the growth was not completely normal, but the plants grew normally in Portneuf soil when they had the same amount of Zn. Soil levels:

Zn EDTA-extractable (ppm)

1.9 or less deficient, soil not able to supply enough Zn for a normal plant growth

1.9 to 2.5 marginal, soil may or may not be able

		Taun	ton			Port	neuf		Millville			
Treatments	0 weeks	6 weeks	26 weeks	52 weeks	0 weeks	6 weeks	26 weeks	52 weeks	0 weeks	6 weeks	26 weeks	52 weeks
No organic + (Zn65)	8.1	8.4	9,5	14.2	15.6	14.2	16.1	20.9	27.2	29.2	29.5	31.6
No organic + (Zn ⁶⁵ + ZnSO ₄)	19.3	19.4	20.4	23.2	23.7	21.3	23.2	25.6	34,8	37.8	38.3	40.5
Sugarbeet + (Zn ⁶⁵)	5.9	5.7	8.1	13.1	7.9	6.5	9.0	19.0	27.6	28.8	29.2	31.9
Sugarbeet + $(Z_n^{65} + Z_nS0_4)$	19.2	19.7	19.9	22.7	22.9	20.2	22.3	24.8	36.9	37.7	38.4	40.8
Alfalfa + (Zn ⁶⁵)	6.6	6.0	8.4	15.0	9.2	8.1	10.1	19.2	26.4	28.8	28.5	31.4
Alfalfa + $(Zn^{65} + ZnS0_4)$	19.7	19.4	20.2	22.9	23.1	20.7	22.8	25.3	36.0	38.3	39.4	40.8

Table 2. Zn (ppm) content in small beans grown in Taunton, Portneuf, and Millville soils after the four incubation periods, 0, 6, 26, 52 weeks (average of two replications)

		Taunt	on			Port	neuf		Milíville			
Treatments	6 weeks	12 weeks	32 weeks	58 weeks	6 weeks	12 weeks	32 weeks	58 weeks	6 weeks	12 weeks	32 weeks	58 weeks
No organic + (Zn ⁶⁵)	1.4	1.5	1.8	1.9	2.8	2.5	2.9	3.2	4.9	4.9	4.9	5.3
No organic + $(Z_n^{65} + Z_n^{50}S_4)$	2.6	2.7	2.8	3.5	6.2	5.0	6.0	6.4	6.6	6.9	7.0	7.0
Sugarbeet + $(2n^{65})$	1.2	1.3	1.4	1.7	1.8	1.5	1.9	2.5	4.1	4.2	4.6	4.8
Sugarbeet + $(\mathbb{Z}n^{65} + \mathbb{Z}nSO_4)$	2.5	2.6	2.7	3.1	5.0	3.1	4.8	5.6	5.0	5.1	5.1	6.4
Alfalfa + (Zn ⁶⁵)	1.4	1.5	1.7	1.9	1.9	1.8	1.9	2.6	4.2	4.4	4.7	4.9
$\begin{array}{l} \text{Alfalfa +} \\ (\text{Zn}^{65} + \text{ZnSO}_4) \end{array}$	2.6	2.6	2.7	3.3	5.4	3.6	5.6	5.9	5.9	6.2	6.6	6.8

Table 3. Total Zn (ppm) in EDTA extraction (available) after the four incubation periods, 6, 12, 32, and 58 weeks (average of two replications)

to supply enough Zn for normal plant growth 2.5 or more normal, soil is able to supply enough Zn for normal plant growth.

As emphasized before, these levels were set for the conditions of this experiment. More work is required to arrive at a universal test of Z_n levels in different soils for different plants.

GENERAL DISCUSSION

Available Zn

The term available, as applied to nutrients, refers to their existence in the soil in a chemical condition in which they either may be absorbed directly by plants or may be readily converted into such a condition. Regardless of the many limitations that are obvious, testing for available mutrients in soil is a useful tool, especially when accompanied by plant tissue tests and observations of nutrient deficiency symptoms.

Many efforts have been made to determine the available supplies of nutrients in soils. For Zn several different methods have been used. Hibbard (1940b), working with California soils, used the equilibrium method with KCl solution acidified to pH 3.2. Lyman and Dean (1942) found a relationship between the amount of Zn extracted from acid soils with normal ammonium acetate acidified to pH 4.6. From acid soils of Alabama, Wear and Sommer (1947) found a correlation between the occurrence of Zn deficiency symptoms and the amount of Zn extracted with 0.04 N acetic acid and a 0.01 N HCl.

Shaw and Dean (1952) concluded that these methods were unsatisfactory for neutral or calcareous soils. Since none of these methods had been calibrated against a wide variety of soils, they performed an experiment with approximately 50 different soils which differed in pH, organic matter, clay, and total Zn content. Zn was extracted directly from these samples with a two-phase system of aqueous ammonium acetate and CCl_{\downarrow} containing dithizone. The amounts of Zn extracted were correlated with various crops grown on the soils. Their methods proved to be a useful procedure for predicting the capacity of many soils to supply plants adequately with Zn. Later, Allen (1961) defined the Zn in an EDTA extraction of the soil as the available Zn fraction. In the current experiment the dithizone- CCl_{\downarrow} extraction of Dean and Shaw (1952) was compared with the EDTA extraction of Allen (1961) for the three soils and both methods gave almost the same values. The EDTA extraction gave less variation in values. Therefore, in this study the EDTA method was used to characterize available Zn because it was much easier than the dithizone method.

The present study showed that the amount of Zn in this available fraction was related to plant yield, the content of Zn in the plant, and the visual appearance. As the Zn increased in the available fraction, more Zn was present in the tops of plants.

Water Soluble and Exchangeable Fractions

The percent of Zn extracted from the soils as water soluble or exchangeable was consistently low during the four incubation periods. It was clear that these two fractions were not able to supply the plants with Zn unless there was another Zn source that would supply Zn with time. This Zn might come from the readily and easily decomposable organic forms.

Copper Acetate Fraction (Complexed)

All ions adsorbed on the colloidal fraction of soils are not equally available to plants. Some are more easily replaced than the

others; also, all the ions of the same nature may not be equally accessible to plants. Some are held quite closely to the colloidal surface, while others move in the outer portions of the ionic swarm.

In order for Zn to be bound by the soil, it probably must enter into an exchange reaction with compounds or complexes present in the soil. The amount of exchange that occurs will depend on the relative concentrations of the exchangeable ion or ions, and the stability constants of the bond being broken and of the one being formed.

Baughman (1958) indicated that there are three levels or degrees of retention of Zn by the soil. These would be (1) simple exchange spots in which Zn replaces other easily exchangeable ions and is in turn replaced by the ammonium ion; (2) complexes in which Zn replaces other complexed ions and in turn can be replaced by copper; and (3) difficulty ionizable complexes in which Zn replaces other complexed ions and is not in turn replaced by copper.

The data of the present experiment indicate that a considerable percentage of Zn was found in the complexed fraction.

In addition to that of the Zn of the soil, the copper may react with part of the Zn in the easily ionizable organic complexes. Even if this is the case, that part of Zn which may come out of the organic matter would not be considered inactivated since it would probably be available for plant use.

Organic Fraction

The nature of the inactivation of heavy metals by organic matter is not understood. Soil organic matter may form complexes with metals by ion exchange, surface adsorption, chelation and complex coagulation and peptization reactions. Many studies have indicated that metal ions, like Zn, form chelating compounds with soil organic matter, and that this reaction may cause the inactivation of Zn.

Compounds responsible for Zn complexes

The major components of soil organic matter are mixtures of lignins polysaccharides, proteins, tannins, and other polyphenols. Most of the principal chelating donor groups, like amino, imino, keto, hydroxy, thioether, carboxylate, and phosphonate, are present in compounds which have been separated from soil organic matter.

A considerable number of investigators have tried to point out the most important compounds which are responsible for the chelation reactions. Himes and Barber (1957) concluded that the humic fraction of organic matter retained 59 percent and the fulvic fraction 12 percent of the total Zn applied to soils. Henry (1966) found that during the 30 weeks of a study on organic matter decomposition the concentration of Zn with the fulvic acid fraction was several times that in the humic acid fraction. The decline in Zn with time associated with the fulvic acid fraction showed a reciprocal increase in Zn associated with the mineral fraction.

Proteins are considered to be one of the groups responsible for chelation. Gurd and Wilcox (1956) concluded that in the proteins the side chains such as carboxyl, imidozole, and sulfhydryl are usually more important in binding metal ions than the terminal amino and carboxyl groups. Zinc has been found to form a complex with each of the 16 imidazole groups of the albumin molecule (Gurd, 1952).

Release of Zn from the organic fraction

It may be expected that certain amounts of organic compounds capable of forming chelates and complexes with Zn are constantly being released during the decomposition processes taking place in the soil. The rate of decomposition of the organic matter and the release of the different nutrients depends on the soil condition. This decomposition is largely affected by the temperature at which the decomposition takes place, and hence the composition and the activity of the soil microorganisms. Water supply and aeration also control the rate of decomposition.

The three soils of the present study were kept under the same conditions during the incubation periods. The temperature was about 30° C, and the soils were kept moist with deionized water to about the one-third bar moisture suction for each soil.

The Zn in the organic fraction in the two soils, Millville silt loam and Taunton sandy loam, was at its highest level after 6 weeks incubation. The organic fraction in Portneuf soil, however, retained more Zn at 12 weeks than at 6 weeks. After reaching the maximum level, the Zn in all soils was continuously released from the organic fraction. At the end of 58 weeks, the level of Zn in the organic fraction was quite low. This may indicate that the compounds which are capable of forming complexes with Zn in the organic fraction are subjected to decomposition or change in such a way that the Zn is gradually released.

EDTA Fraction or Remaining Available Zn

The nature of Zn in this fraction is not quite known. Zn in this

extraction is assumed to be representative of the Zn chelated or complexed by soil in a way that the EDTA solution forms a more stable compound with it than had been the case where it was in the soil.

The Zn in this fraction was always less than that found in the original available fraction. This led to the conclusion that part of the so-called available Zn had been removed when the soil was extracted for the Zn in the water soluble, exchangeable, complex, and organic fractions.

The percentage of Zn in this final EDTA extraction was affected by the different treatments of the soils. In general, there was a reciprocal relation with the Zn in this fraction and that in both the organic and residue fractions.

Zinc in the Residue

Zinc in this fraction was not replaced by the various extractions applied to the soil previously. The amount of Zn in the residue presumably forms extremely stable and unavailable forms of Zn as far as plant growth is concerned.

The residue in the three soils retained a high percentage of the added Zn under all treatments. The observation that the organic matter interacts with soil residue and forms an organo-clay complex may be demonstrated here to a certain degree. When sugarbeet tops and alfalfa were added to the soils, there was an increase of Zn over the zero organic additions, in the residue fraction. This increase was greater in the two soils, Millville and Portneuf, which have higher clay content.

Henry (1966) found that during a 19 weeks' incubation period, the

silt and sand size particles retained more Zn than the clay size particles. He concluded that these results were due to the presence of organic matter binding clay particles together, thus producing silt size particles with more Zn attached to them.

The present study showed that time affected the amount of Zn found in the residue. The percent of Zn in this fraction continued to increase during the 32 weeks' period, and then it gradually decreased. This latter decrease was not greatly significant, but may be due to the breaking down of some of the organo-clay particles with time.

SUMMARY AND CONCLUSIONS

The effect of different organic matter treatments on the inactivation of zinc in three different soils was studied. The three soils were Portneuf silt loam, in which zinc deficiency was found in field beans following sugar beets, Taunton sandy loam, known to show Zn deficiency on most sensitive crops, and Millville silt loam, no known Zn deficiency problem. Organic matter was added as alfalfa and sugarbeet tops at the rate of zero or 30 tons equivalent green weight per acre (2 x 10^6 lbs.). Zinc treatments were zero or 20 lbs. per acre as $ZnSO_{4^{\circ}}$ Zinc⁶⁵ was added to all soils as a tracer. There were four incubation periods, zero time, 6 weeks, 6 months, and 1 year. After each incubation period beans were grown for 6 weeks. The plants were harvested, dried, weighed, separated into aerial parts and roots, digested in acid, and the total Zn determined on an atomic absorption spectrophotometer.

Two 5-gram samples of dry soil from each pot were obtained and analyzed for Zn according to a fractionation procedure that would give the Zn found in each fraction. These fractions were the available or EDTA extractable Zn, the water soluble Zn, the exchangeable Zn, the complexed or copper acetate extractable Zn, the Zn in the organic fraction (organic matter destroyed by H_2O_2), the Zn that came out with a second EDTA extraction, and the Zn remaining in the residue or mineral fraction.

The decomposing organic matter increased Zn inactivation in all soils. This effect was not specific for sugarbeet tops, but was also noted with alfalfa. The degree of inactivation brought on by the

decomposing organic matter was not always the same for the two organic sources. This may be due to the difficulty in establishing exactly the same amount of organic matter when additions are made on a green wieght basis.

The amount of Zn inactivated in the three soils by organic matter was different, but in general the Zn inactivation increased when organic matter was added.

A large part of the zinc in the organic fraction and soil residue was released by time, particularly at the end of a 1-year incubation period. The growth of bean plants was not depressed by the added organic matter following the last incubation period, and a relatively high level of Zn was found in the tops of the plants.

There was a considerable amount of Zn found in the organic fraction of the soils in the 6- and 12-week incubation periods. The amount of Zn in this fraction then gradually decreased with time. A high percentage of the added Zn was found in the soil residue, and the Zn in this fraction varied greatly with time and type of soil. Zinc in the water-soluble and exchangeable fractions was very low in comparison to that found in other fractions. The amount in both fractions increased with time.

Zinc deficiency symptoms of the plants were always accompanied by low yield, low Zn in the plant tops, and low Zn in the available or EDTA fraction of the soil.

The information obtained from this experiment led to the conclusion that the particular Zn deficiency observed in the Portneuf soil was a result of more than one factor. It is suggested that although the level of available Zn in the Portneuf soil was not as low as that found
in the Taunton soil, it was at or approached the critical values for growth of a zinc-sensitive plant. The addition of sugarbeet tops, or any large amount of organic matter, caused a decrease in the available Zn. It was shown that at least part of this Zn that was removed from the available pool by the decomposing organic matter would be released for plant uptake in time.

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APPENDIX

I. EDTA Extraction Before Planting

During the course of the experiment, and after completing the analysis of soils at 6 and 12 weeks, the idea of determining Zn in soil before planting was introduced. The purpose was to evaluate how much Zn was actually found in the soil before any uptake by the plants, and what was the difference between the level of Zn before and after planting. The results are listed in Table 4.

It has been noticed that in all treatments EDTA extraction before planting had more Zn than after planting; however, the same trend was found in both extractions toward adding organic matter, ZnSO_{4} , and also the period of incubation.

It is expected that during the growth period plants utilize part of the Zn in EDTA extraction and as a result, the level of Zn after harvesting the plants is always less than before planting.

II.

The percentage of Zn^{65} of total recovered in various fractions of the three soils, Taunton sandy loam, Portneuf silt loam, and Millville silt loam, at the four incubation periods (6, 12, 32, and 58 weeks) of the two Zn treatments (Zn^{65} and $Zn^{65} + 20$ lb Zn as $ZnSO_{l_4}$ per acre) are presented in Tables 5 through 16.

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	Portn	euf	Taun	ton	Millville			
Treatments	6 months	l year	6 months	l year	6 months	l year		
the a contract the function of the second	parts per million							
No organic + Zn ⁰⁵	3.6	4.1	1.9	2.0	6.1	6.3		
No organic + (Zn ⁰⁵ + ZnSO ₄)	7.2	7.7	3.1	4.1	8.3	9.0		
Sugar beet + Zn ⁶⁵	2.1	2.8	1.8	1.9	5.6	6.2		
Sugar beet + (Zn ⁶⁵ + ZnSO ₄)	5.8	6.5	2.9	3.9	7.0	8.3		
Alfalfa + Zn ⁶⁵	2.2	3.6	1.8	1.9	5.8	6.2		
Alfalfa + (Zn ⁶⁵ + ZnSO ₄)	6.7	7.1	3.0	4.0	8.6	8.8		

Table 4. Total Zn in the EDTA extractions (available) after the two incubation periods, 6 months and 1 year, before planting (average of two replications)

Treatments	Water soluble	Exchange- able	Com- plexed	Organic	Remaining available	Residue
No organic + Zn ⁶⁵	2.0	2.6	25.0	8.5	19.3	42.6
	1.9	2.6	25.7	8.8	18.5	42.7
No organic +	2.0	2.7	27.0	8.7	18.3	41.3
(Zn ⁰⁵ + ZnSO ₄)	2.1	2.8	27.0	9.0	18.7	40.4
Sugar beet +	1.3	1.9	23.3	14.6	14.8	44.1
Znoy	1.4	1.8	23.2	15.4	14.6	43.5
Sugar beet +	1.4	2.0	25.4	14.7	13.4	43.1
$(2n^{\circ}) + 2nSO_{4})$	1.5	1.9	24.6	14.1	14.3	43.6
Alfalfa +	1.6	2.1	24.4	13.2	15.7	43.0
Znoy	1.7	2.2	24.7	13.3	14.5	43.6
Alfalfa +	1.7	2.3	26.6	12.5	15.7	41.2
$(Zn^{05} + ZnSO_{\downarrow})$	1.8	2.4	25.8	11.9	15.2	42.9

Table 5. Zn⁶⁵ percent of total recovered in various fractions of Taunton soil at 6 weeks incubation period^a

aValues are given for two replications.

Treatments	Water soluble	Exchange- able	Com- plexed	Organic	Remaining available	Residue
No organic +	2.0	2.6	27.0	8.4	17.2	42.8
Znog	2.0	2.4	28.2	8.6	16.2	42.6
No organic +	2.1	2.8	28.8	8.7	16.8	40.8
$(Zn^{0} + ZnSO_{4})$	2.1	2.8	28.3	8.6	17.3	40.9
Sugar beet +	1.5	2.0	25.6	14.1	11.5	45.3
Znog	1.6	2.1	25.3	14.0	11.4	45.6
Sugar beet +	1.6	2.2	26.5	13.3	11.5	44.9
$(2n^{\circ} + 2nSO_{4})$	1.7	2.4	26.5	13.7	11.4	44.3
Alfalfa +	1.9	2.2	26.4	12.2	13.4	43.9
Zn ^{OD}	1.8	2.3	27.8	12.2	12.1	43.8
Alfalfa + (Zn ⁶⁵ + ZnSO ₄)	1.9	2.6	28.8	10.9	12.4	43.4
	1.9	2.7	28.4	11.1	12.0	43.9

Table 6. Zn⁶⁵ percent of total recovered in various fractions of Taunton soil at 12 weeks incubation period^a

Treatments	Water soluble	Exchange- able	Com- plexed	Organic	Remaining available	Residue
			20.1		- / -	
No organic + Zn ⁶⁵	2.0	2.8	28.4	7.1	16.5	43.2
	2.2	2.7	28.2	7.0	16.3	43.6
No organic +	2.4	2.9	29.9	7.0	16.2	42.6
(2n ⁰) + 2n 30 ₄)	2.4	3.0	30.2	7.0	16.0	41.4
Sugar beet +	1.7	2.1	27.7	12.1	9.0	47.4
21-2	1.8	2.2	27.7	12.6	9.1	46.6
Sugar beet +	2.0	2.3	28.7	11.4	9.9	45.7
$(2n^{0}) + 2nSO_{4}$	1.9	2.5	28.5	12.0	9.2	45.9
Alfalfa +	1.9	2.6	27.8	11.4	10.6	45.7
211->	2.0	2.5	28.5	11.6	10.6	44.8
Alfalfa +	2.2	2.8	29.4	10.9	10.8	43.9
$(2n^{\circ}) + 2n^{\circ}(1)$	2.2	2.7	28.4	11.1	10.8	44.8

Table 7. \mathbf{Zn}^{65} percent of total recovered in various fractions of Taunton soil at 32 weeks incubation period^a

Treatments	Water soluble	Exchange- able	Com- plexed	Organic	Remaining available	Residue
No organic +	3.0	3.7	29.3	5.3	17.0	坦。7
	2.9	3.6	29.6	4.6	18.6	40.7
No organic +	3.4	3.5	30.6	4.9	17.5	40.1
(2n ⁰) + 2n ⁵ 0 ₄)	3.2	3.7	29.2	4.9	18.7	40.3
Sugar beet +	2.9	3.1	27.3	6.4	15.3	45.0
Znoy	2.8	3.3	27.8	6.7	14.8	44.6
Sugar beet +	3.1	3.6	28.9	6.6	14.3	43.5
$(2n^{\circ}) + 2nSO_{4}$	3.1	3.5	29.2	6.7	14.8	42.7
Alfalfa +	2.9	3.3	27.2	6.1	18.2	42.3
Znoo	2.8	3.3	28.1	6.1	18.3	41.4
Alfalfa +	3.1	3.7	28.4	6.4	15.7	42.7
$(2n^{\circ}) + 2nSO_{4}$	3.3	3.8	29.2	6.7	15.7	41.3

Table 8. $2n^{65}$ percent of total recovered in various fractions of Taunton soil at 58 weeks incubation period^a

aValues are given for two replications.

Treatments	Water soluble	Exchange- able	Com- plexed	Organic	Remaining available	Residue
No organic +	2.3	3.4	17.2	10.9	31.0	35.2
2	2.4	3.6	17.7	11.4	30.1	34.8
No organic +	2.6	3.9	20.4	10.2	28.4	34.5
(2n°) + 2nSO(4)	2.6	3.7	20.0	10.4	30.0	33.3
Sugar beet +	2.0	3.2	16.9	17.5	22.2	38.2
2n°2	1.9	3.3	17.2	17.9	22.2	37.5
Sugar beet +	2.0	3.5	20.0	17.1	21.1	36.3
$(2n^{05} + 2n^{0})$	2.0	3.6	20.0	17.2	19.8	37.4
Alfalfa +	2.1	3.4	17.4	15.5	24.9	36.7
Znos	2.0	3.4	17.3	15.9	24.2	37.2
Alfalfa +	2.1	3.7	20.1	15.1	22.9	36.1
$(2n^{0} + 2n^{0})$	2.2	3.8	20.1	13.9	24.3	35.7

Table 9. $2n^{65}$ percent of total recovered in various fractions of Portneuf soil at 6 weeks incubation period^a

Treatments	Water soluble	Exchange- able	Com- plexed	Organic	Remaining available	Residue
No organic +	2.4	3.4	16.8	11.2	28.0	38.2
011	2.7	3.7	17.1	12.0	26.7	37.8
No organic +	2.9	3.8	20.1	10.7	27.6	34.9
(2110) + 21130(4)	2.9	3.9	19.4	10.9	27.4	35.5
Sugar beet +	0.9	1.9	15.0	24.0	14.6	43.6
Znoy	0.9	2.2	16.1	24.6	14.8	41.4
Sugar beet +	1.4	2.6	18.9	23.5	15.3	38.3
$(2n^{\circ}) + 2n^{\circ})_{1}$	1.5	2.3	17.9	24.6	14.3	39.4
Alfalfa +	1.8	2.9	16.7	21.3	17.7	39.6
ZnOS	1.8	2.6	16.4	22.0	17.0	40.2
Alfalfa •	1.9	3.0	18.9	19.8	17.7	38.7
$(2n^{\circ}) + 2nSO_{4})$	1.9	3.1	19.8	21.3	17.5	36.4

Table 10. ${\rm Zn}^{65}$ percent of total recovered in various fractions of Portneuf soil at 12 weeks incubation period^a

Treatments	Water soluble	Exchange- able	Com- plexed	Organic	Remaining available	Residue
No organic +	2.5	3.6	16.4	10.6	26.6	40.3
	2.7	3.8	17.6	10.6	25.2	40.1
No organic +	3.2	4.0	21.6	9.5	23.4	38.3
(2110) + 21130(4)	3.2	4.1	20.4	9.5	23.2	39.6
Sugar beet +	1.8	3.1	13.6	18.4	9.3	53.8
21105	1.9	3.2	14.2	17.4	10.7	52.6
Sugar beet +	2.1	3.0	15.6	16.8	11.5	51.0
$(2n^{\circ}) + 2nSO_{4}$	1.9	3.2	16.4	17.3	10.3	50.9
Alfalfa +	2.0	3.2	15.3	17.0	15.9	46.6
Znoo	2.1	3.2	14.6	15.8	15.5	48.8
Alfalfa +	2.0	3.9	18.6	15.2	14.9	45.4
$(Zn^{05} + ZnSO_{1})$	2.1	3.8	17.6	16.0	14.0	46.5

Table 11. Zn⁶⁵ percent of total recovered in various fractions of Portneuf soil at 32 weeks incubation period^a

Treatments	Water soluble	Exchange- able	Com- plexed	Organic	Remaining available	Residue
No organic +	3.7	4.3	19.0	8.2	25.6	39.2
211-2	3.5	4.8	19.5	8.0	26.3	37.9
Nor organic +	4.0	4.7	21.9	7.2	23.9	38.3
$(Zn^{65} + ZnS0_{4})$	4.2	4.8	20.7	6.9	24.8	38.6
Sugar beet +	3.2	4.1	17.8	11.3	19.7	43.9
Znog	3.0	4.1	17.4	11.7	19.5	44.3
Sugar beet +	3.7	4.4	18.8	10.9	18.5	43.7
$(2n^{05} + 2nSO_{4})$	3.8	4.2	19.7	11.4	19.6	41.3
Alfalfa +	3.4	4.1	18.6	10.8	22.7	40.4
Znob	3.5	4.4	17.7	10.9	22.4	41.1
Alfalfa +	3.8	4.4	18.5	10.8	22.7	39.8
$(2n^{\circ} + 2nSO_{4})$	3.9	4.6	18.9	11.0	22.4	39.2

Table 12. \mathbf{Zn}^{65} percent of total recovered in various fractions of Portneuf soil at 58 weeks incubation period^a

aValues are given for two replications.

Treatments	Water soluble	Exchange- able	Com- plexed	Organic	Remaining available	Residue
No organic +	3.9	3.9	17.7	12.3	35.0	27.2
	3.9	4.0	17.9	12.4	34.5	27.3
No organic +	4.1	4.6	22.7	11.6	30.2	26.8
$(2n^{\circ} + 2nSO_{4})$	4.0	4.6	22.0	11.6	30.4	27.4
Sugar beet +	1.8	2.6	17.0	29.0	20.1	29.5
Znoy	2.0	2.4	17.2	27.8	20.9	29.7
Sugar beet +	2.4	2.9	20.7	26.3	19.1	28.6
$(2n^{\circ}) + 2nSO_{1}$	2.5	2.9	21.1	26.3	18.7	28.5
Alfalfa +	2.9	3.4	17.0	22.8	24.7	29.2
Znog	2.7	3.7	17.5	24.2	23.9	28.0
Alfalfa +	3.0	3.9	21.4	21.3	22.2	28.2
$(2n^{0} + 2n^{0})$	3.2	4.2	21.8	22.9	21.1	26.8

Table 13. Zn^{65} percent of total recovered in various fractions of Millville soil at 6 weeks incubation period^a

Treatments	Water soluble	Exchange- able	Com- plexed	Organic	Remaining available	Residue
No organic + Zn65	4.1	4.0	20.9	12.0	29.0	30.1
	3.9	4.0	19.7	12,0	28.8	31.6
No organic +	4.2	4.8	23.4	11.6	22.1	33.9
(2110) + 21130(1)	4.1	4.9	24.2	11.1	21.5	34.2
Sugar beet +	2.2	2.9	18.8	25.4	11.7	39.0
21105	2.1	3.0	19.1	26.0	11.2	38.6
Sugar beet +	3.6	3.0	22.8	23.1	11.1	36.4
$(2n^{\circ}) + 2nSO_{1}$	3.8	3.1	23.4	22.6	10.8	36.3
Alfalfa +	3.0	3.9	19.1	21.4	16.2	36.4
ZnOS	3.2	3.7	19.8	20.3	16.7	36.3
Alfalfa +	3.9	4.0	23.5	19.8	13.3	35.5
$(2n^{\circ} + 2nSO_{4})$	3.8	4.3	23.5	19.5	14.1	34.8

Table 14. Zn⁶⁵ percent of total recovered in various fractions of Millville soil at 12 weeks incubation period^a

Treatments	Water soluble	Exchange- able	Com- plexed	Organic	Remaining available	Residue
New WHERE CAR AND AN AND A CONTRACT OF A CONTRACT OF						
No organic +	4.0	4.2	21.0	10.9	23.8	36.1
	3.9	4.3	21.1	11.1	24.2	35.4
No organic +	4.2	5.0	26.1	10.1	20.3	34.3
$(2n^{O_2} + 2nSO_4)$	4.3	5.0	26.3	10.0	18.8	35.6
Sugar beet +	3.2	3.8	19.4	18.2	10.6	44.8
Zn	3.4	4.0	19.2	17.8	11.4	44.2
Sugar beet +	3.9	4.1	24.2	16.7	11.5	39.6
$(2n^{05} + 2nS0_{4})$	3. 8	4.2	25.6	17.0	10.2	39.2
Alfalfa +	3.8	3.8	20.9	16.9	12.3	42.3
Znog	3.7	4.2	20.5	16.1	13.6	41.9
Alfalfa +	4.1	4.3	24.8	15.4	13.6	37.8
$(2n^{\circ} + 2nSO_{\downarrow})$	4.1	4.4	26.6	14.9	13.2	36.8

Table 15. Zn⁶⁵ percent of total recovered in various fractions of Millville soil at 32 weeks incubation period^a

Treatments	Water soluble	Exchange- able	Com- plexed	Organic	Remaining available	Residue
No organic + Zn ⁶⁵	4.2	4.8	23.7	8.0	27.3	32.0
	4.3	4.7	23.8	8.7	26.1	32.4
No organic + (Zn ⁶⁵ + ZnSO ₄)	4.4	5.1	25.1	8.5	25.4	31.5
	4.4	5.1	26.7	7.7	25.9	30.2
Sugar beet + Zn ⁶⁵	3.8	4.5	19.9	10.6	21.5	39.7
	3.8	4.7	20.1	11.3	20.7	39.4
Sugar beet + (Zn ⁶⁵ + ZnSO ₄)	4.1	4.7	22.4	10.0	20.3	38.5
	4.3	4.7	23.8	9.8	20.1	37.3
Alfalfa + Zn ⁶⁵	4.1	4.5	20.0	10.2	25.9	35.3
	4.1	4.7	21.6	10.0	23.0	36.6
Alfalfa → (Zn ⁶⁵ → ZnSO ₄)	4.3	4.8	23.9	9.7	22.5	34.8
	4.3	4.9	24.6	9.5	22.3	34.4

Table 16. Zn⁶⁵ percent of total recovered in various fractions of Millville soil at 58 weeks incubation period^a