THE ZINC FERTILITY
OF SASKATCHEWAN SOILS

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ABSTRACT

Field, growth chamber, and laboratory studies were conducted to investigate the zinc fertility of Saskatchewan soils. These studies included an examination of Zn spatial variability, a survey of DTPA-extractable Zn levels of soils from across the province, a variety of experiments on Zn fertilizers, and investigations on the mechanisms of P X Zn interaction in wheat (Triticum aestivum L.) and beans (Phaseolus vulgaris L.). In addition, the distribution and plant availability of native and applied Zn in various soil Zn fractions were investigated in three soils that varied widely in physical and chemical properties.

DTPA-extractable micronutrients (Zn, Cu, Mn and Fe) in fields of level topography showed a high degree of variability in samples taken along transects and geostatistical analyses (semivariograms) indicated that the extractable micronutrients were randomly distributed. In contrast, DTPA-extractable Zn and tissue Zn concentration in undulating topography showed spatial structure with a range of 25 m in all except one of the transects considered. DTPA-extractable Zn and organic C levels were highly correlated and had similar spatial structure.

Current criteria for predicting Zn deficiency in Saskatchewan soils are based on DTPA-extractable Zn values. DTPA-extractable Zn levels in 12% of 1200 samples taken across Saskatchewan contained $<0.5 \text{ mg Zn kg}^{-1}$ soil and would be classified as potentially Zn deficient. However, 23 field trials in 1982, 1983 and 1984 with spring wheat (Triticum aestivum L.), barley (Hordeum vulgare L.), lentils (Lens esculenta Moench.), peas (Pisum sativum L.), alfalfa (Medicago sativa L.), corn (Zea mays L.), and flax (Linum usitatissimum L.) produced only one significant response to Zn

fertilization.

The relative effectiveness of ZnSO_4 , ZnEDTA, low-yield ammonium-based lignosulphonate (ZnLY) and high-yield ammonium-based lignosulphonate (ZnHY) for bean production was tested in growth chamber and incubation experiments. ZnLY was more effective than ZnEDTA and ZnHY in correcting Zn deficiency of bean plants. While biomass production was best with ZnSO_4 , ZnLY was more effective in increasing Zn content of the foliage.

Field and growth chamber studies were carried out to elucidate the mechanisms of P X Zn interaction in the nutrition of wheat and beans, respectively. In the field, residual P levels from 80 or 160 kg P ha⁻¹ applied in 1979 to a Sutherland soil (Dark Brown Chernozemic) increased wheat yield significantly. In the presence of P, soil and foliage applied Zn in 1984 resulted in significant increase in grain yield and Zn uptake into grain. High levels of P in the soil increased tissue P concentration but Zn concentration was decreased significantly. DTPA-extractable soil Zn levels in the non-Zn amended treatment were independent of P application rate. A close relationship was obtained between Zn levels in the above ground plant parts and vesicular-arbuscular mycorrhizal (VAM) infection. VAM infection of wheat roots was significantly lower in high P treatments than in the control.

In the growth chamber, the P X Zn interaction in roots and above ground parts of bean was studied in the Sutherland (Dark Brown Chernozemic), Carrot River (Dark Gray Chernozemic) and Meota (Black Chernozemic) soils. The P X Zn interaction on dry matter yield of above ground parts was significant for the Sutherland and Carrot River soils only. Applied Zn increased yield only when P was applied. Application of P reduced Zn concentration in tops below the critical levels at 1/10 bloom

growth stage in the Sutherland and Carrot River soils. In the 0 applied Zn treatment, a response was obtained with P application but translocation of Zn from roots to tops was inhibited at both the 80 and 160 mg applied P kg^{-1} . Thus both Zn dilution in the plant and reduced translocation of Zn from roots to tops accounted for the P X Zn interaction observed. Phosphorus absorption by roots and accumulation of P in above ground plant parts was markedly reduced by Zn application. However, in the absence of applied Zn, P levels in bean tissue never reached toxic levels.

Native and applied Zn in three soils (used for P X Zn interaction experiment with beans) were separated into water soluble plus exchangeable (EX), specifically adsorbed (ExAD), organically bound (OM), Mn-oxide bound (MnOX), Fe-oxide bound (FeOX) and residual (RES) fractions. The major proportion of native Zn in all soils was recovered in the RES and FeOX fractions. The EX, ExAD, OM and MnOX fractions accounted for only a small portion of native Zn. In contrast, most of the applied Zn in the Meota and Carrot River soils was recovered in the ExAD fraction, whereas in the Sutherland soil in the OM and FeOX fractions. The amount and percent distribution of applied Zn in the OM, FeOX and MnOX fractions of all soils varied directly with the organic C and Fe- and Mn-oxide contents, respectively. The distribution of applied Zn in various fractions was independent of applied P. The distribution of applied Zn in various Zn fractions in combination with Zn plant uptake indicated that the EX and ExAD fractions were the most potentially plant available pools.

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Dedicated to my father

Late Sh. Hari Singh

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1. INTRODUCTION

Early assessment of the micronutrient fertility status of Saskatchewan soils showed that most of the province's soils were adequately supplied with micronutrients for cereal crops (Stewart 1969). However, recent analysis of soil and plant samples submitted to the Saskatchewan Soil Testing Laboratory (SSTL) suggested that micronutrients could be a yield limiting factor (Tomasiewicz and Stewart, 1982). Thus, research has accelerated in the last few years and an attempt has been made to either verify or reject the hypothesis that there is no need for micronutrient fertilization of Saskatchewan soils. As a result of this, Cu deficiencies in some mineral soils and Cu and Mn deficiencies in organic soils have already been uncovered (Karamanos et al., 1984a, 1985, 1986; Kruger et al., 1985).

Zinc deficiency is one of the most common micronutrient deficiencies in agricultural crops on a global basis. It is becoming increasingly significant affecting a wide variety of plants and soils. The susceptibility of plants to Zn deficiency varies greatly among plant species and even among cultivars (Viets et al., 1954a; Brown et al., 1972). Zinc deficiency has been observed extensively in the United States, Australia and many tropical countries (Thorne, 1957; Lindsay, 1972; Kanwar and Youngdahl, 1985). Low Zn levels have also been shown to occur in the soils of several European countries (Aubert and Pinta, 1977). The Zn nutritional problem for fruit trees in Canada has long been delineated in the provinces of Ontario and British Columbia (Woodbridge, 1954; Heeney et al., 1964) and has now been confirmed in isolated cases for agricultural crops in prairie

soils (Crepin, 1983; Loewen-Rudgers et al., 1983).

In Saskatchewan, Stewart and Tahir (1971) found that DTPA-extractable Zn levels in soil were highly correlated with plant Zn concentrations especially at the tillering stage. Multiple regression analysis relating available Zn to various soil chemical properties led to the conclusion that the Zn status of a soil could be predicted from the information that can be obtained from Saskatchewan soil survey reports. In preliminary soil test calibration work, Edlin et al. (1983) evaluated four Zn extraction methods (DTPA, EDTA, 1 M NH_4OAc and 0.1 M HCl) for their ability to separate responding from non-responding soils in a growth chamber experiment using alfalfa as a indicator plant. The DTPA test (Lindsay and Norvell, 1978) was found to be most suitable as an index of Zn deficient soils with a critical value of 0.55 mg kg^{-1} of soil. This was slightly higher than the critical value of $0.5 \text{ mg Zn kg}^{-1}$ of soil adopted by the Saskatchewan Soil Testing Laboratory (SSTL). The need of verification of these values as well as of Zn fertilization under field conditions is of primary agronomic and economic importance.

The plant availability of Zn is conditioned by a number of soil and environmental factors: pH, adsorption on surfaces of clay, organic matter, carbonate, and oxide minerals, complexation by organic matter, interaction with other nutrients, and climatic conditions (Lindsay, 1972; Olsen, 1972; Stevenson and Ardakani, 1972; Shuman, 1980). Factors such as high pH and high clay, organic matter, oxide and carbonate contents favour Zn fixation and also affect the distribution of Zn among different forms. Separation of various forms of Zn in soil has been useful in studying the retention and release of

Zn by the soil to the plant. Zinc associated with different soil fractions varies in plant availability. The zinc present in water-soluble, exchangeable, and adsorbed fractions is readily available, whereas Zn associated with primary and secondary minerals is relatively unavailable to plants (Viets, 1962). In determining the distribution of Zn, one can find better extractants that remove Zn in proportion to that removed by plant. The dynamics of Zn transformations from one chemical form to another, in response to changing soil conditions, can be answered by studying the distribution of Zn in various forms.

There are widespread reports that high phosphorus availability in soil induces Zn deficiency. This interaction occurs mainly when plants are grown in soil or culture media low in available Zn (Olsen, 1972). Many of the results have been confusing because the accentuated symptoms of Zn deficiency were not always accompanied by reduction in Zn concentration in plant tops (Olsen, 1972). In Saskatchewan, Wagar et al. (1986) studied the effect of single broadcast fertilizer P applications on wheat yield and nutrient uptake in a Sutherland soil (Dark Brown Chernozemic) over a period of six years. They observed that high P rates significantly reduced Zn levels in plant tissue and suspected that Zn disorder could be a yield limiting factor in their study.

In the past two years, a number of field experiments on micro-nutrient requirements of various crops have been conducted in different parts of Saskatchewan. In a number of cases, no yield response were obtained in spite of soil test values indicating deficient levels (Karamanos et al., 1984b). Although this behavior

may be attributed to several factors, spatial variation of micronutrients appeared to be the most likely one. The heterogeneity of soil fertility has been stressed by Peck and Melsted (1967), who have further suggested that sampling plans should be designed in such a manner as to reveal variation within each field. This is essential in the proper interpretation of a soil test, especially since recommendation of nutrient application relies on the nutrient value determined for a composite sample.

The general objectives of this research were, therefore:

(i) to study the spatial variability of Zn in Saskatchewan soils of both uniform and undulating topographies,

(ii) to examine the importance of Zn to crop nutrition and production of common crops in Saskatchewan, and

(iii) to understand the transformations of native and added Zn in soils and their distribution among different soil Zn fractions in relation to plant availability.

2. LITERATURE REVIEW

2.1 Zinc in Plant Physiology

Zinc is one of the more dissociated metal ions in xylem fluid but it can sometimes be bound to organic complexes (Tiffin, 1972). The form in which Zn is translocated from roots to the upper plant parts is not well understood. Electrophoretic evidence indicates that Zn in xylem fluid is not bound to stable ligands. Zinc is slightly cathodic and is not translocated as citrate since Zn citrate complexes are anodic (Tiffin, 1972).

The Zn requirement of plants is generally small but plant species differ in their Zn requirements (Lindsay, 1972) and in their sensitivity to Zn deficiency (Viets et al., 1954a). Carroll and Loneragan (1969) obtained maximum or near maximum yield of eight different plant species in flowing water culture experiments with Zn concentrations in the range of $0.01 \times 10^{-6}M$ to $2.5 \times 10^{-6}M$. Maximum yield of plants was obtained with an uptake of between 10-30 ng atom of Zn per gram of fresh root material per day.

It is now generally accepted that Zn uptake is metabolically controlled (Moore, 1972). Schmid et al. (1965) and Bowen (1969) using barley roots and sugarcane leaf tissue concluded that metabolic Zn uptake by plants was characterized by a steady state rate. Zinc uptake was considerably reduced by low temperature and by metabolic inhibitors.

Essential functions of Zn in plants have been identified and characterized. Zinc deficiency symptoms show wide variations in different plant species. The common symptom of Zn deficiency are

chlorosis in the interveinal area of the leaf. These are pale green, yellow or even white followed by the appearance of brown necrotic spots in young leaves by stunting and delayed vegetative and reproductive development (Mengel and Kirkby, 1982).

How Zn deficiency explicitly influences these symptoms is not well understood. Some Zn enzymes which perform essential functions in plants have been identified and characterized. Zinc is an essential component of cellular membranes and is also present in a number of metalloenzymes, particularly in carbonic anhydrase, various dehydrogenases, proteinases and and peptidases (Vallee and Wacker, 1970; Jacobson et al., 1975). One of the effects of Zn deficiency may well be related to the reduction of net photosynthesis. Ohki (1978) found reduced photosynthesis and carbonic anhydrase activity in Zn deficient soybean plants. Seethambaram and Das (1985) observed a decline in net photosynthetic rate and CO_2 fixation with Zn deficiency in Oryza sativa L. and Pennisetum american L. They attributed this to lowered levels of carbonic anhydrase, energy and reducing power in the former, but to lowered energy and reducing power alone in the latter. Clearly carbonic anhydrase, a chloroplast enzyme, catalyzes the reaction between CO_2 and H_2O to form $\text{H}^+ + \text{HCO}_3^-$ in photosynthesis (Jacobson et al., 1975).

The levels of carbohydrates in the plant are also affected. Seethambaram and Das (1985) reported lower levels of reducing sugar in leek (Pennisetum american L.) plants presumably due to the effect of Zn on photosynthesis.

Zinc is closely involved in the N metabolism of the plants. Price et al. (1972), in a review article, cited a number of references

indicating that the possible causal event in the case of Zn deficiency is a sharp decrease in the concentrations of RNA and ribosome in cells. This reduction in RNA synthesis leads to an inhibition of protein formation while glucose, non-protein N and DNA are relatively increased. Zinc is also required in the synthesis of tryptophan. Under Zn deficiency, concentration of indoleacetic acid is decreased possibly due to inhibited synthesis of tryptophan (Salami and Kenefick, 1970). In sharp contrast to these results, Takaki and Kushizaki (1970) found higher levels of tryptophan in Zn deficient maize plants and concluded that Zn is required in the synthesis of indoleacetic acid from tryptophan. However, a causal relationship between Zn, tryptophan and indoleacetic acid has yet to be established (Price, 1970).

According to Jyung et al. (1975) Zn has a possible role in plant metabolic processes associated with starch formation. These authors compared the behaviour of two cultivars of navy bean (Phaseolus vulgaris), one susceptible to Zn deficiency and the other not, grown under Zn deficiency conditions. The starch content, the activity of the starch synthetase enzyme, and the number of starch grains of the susceptible cultivar were all more depressed compared to the non-susceptible one. Further, a very close inverse relationship between the degree of Zn deficiency and starch formation was established. Whether this effect on starch formation is a primary result of Zn deficiency still remains an open question.

Zinc deficiency may influence N_2 fixation directly by affecting nodule nutrition and indirectly by affecting host nutrition (Demeterio et al., 1972). Rhoden and Allen (1982) found a significant increase

in N_2 fixation with application of Zn. Rate of N_2 fixation was highly correlated with nodule number. They argued that, since both nodulation and N_2 fixation peaked at the same rate of Zn, increased rate of N_2 fixation could have been directly associated with the increased nodulation.

2.2 Zinc Containing Minerals and Zn Content in Soils

The average Zn content of the lithosphere is 80 mg kg^{-1} , whereas the Zn content of normal soils ranges from 10-300 mg kg^{-1} (Hodgson, 1963). The Zn content of soils varies widely. Shuman (1980) cited a number of references reporting lower and also much higher values for total Zn content of soils, reflecting differences in parent materials, age and type of soil, and climatic, topographic and biological conditions.

The abundance of Zn in the parent material is one of the major factors determining Zn content in soils, particularly in younger soils. Zinc in igneous rocks tends to concentrate in mafic rather than in felsic rocks because it can substitute in silicates for Mg^{2+} and Fe^{2+} and occurs in the form of small grains of sphalerite in the mafic rocks. The largest Zn concentration in sedimentary rocks is found in shales where Zn is held in adsorbed form and in the lattice structure of clay minerals (Krauskopf, 1972). Igneous rocks such as basalt and granite contain on an average 100 mg kg^{-1} and 40 mg kg^{-1} of Zn, respectively. Among sedimentary rocks, shale contains more Zn (95 mg kg^{-1}) than either limestone (20 mg kg^{-1}) or sandstone (16 mg kg^{-1}) (Krauskopf, 1972).

Minerals of Zn include sphalerite (ZnS), smithsonite ($ZnCO_3$)

and hemimorphite ($\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$). Zinc occurs chiefly as the single sulfide mineral sphalerite which indicates the metal is largely chalcophile. The Zn ion, with an ionic radius of 0.83Å, does substitute to some extent for Mg (0.78Å) and Fe (0.83Å) in silicate minerals, so that it is partly lithophile as well. Zinc most commonly shows four-fold coordination in mineral structure but in some minerals it has 6-coordination with oxygen (Krauskopf, 1972).

Tiller and Pickering (1974) synthesized Zn silicates in weathering environments. They formed stevensite and concluded that neither willinite nor hemimorphite are important in controlling chemical reaction of Zn in soils. Both Krauskopf and Lindsay (1972) are of the opinion that sphalerite (ZnS) is unstable under normal oxidizing conditions. Kittrick (1976), however, suggested that Zn in soil solution could be controlled by ZnS if the soil was in equilibrium with atmospheric H_2S , since ZnS is the only Zn mineral insoluble enough to control Zn at ppb levels.

Weathering of Zn minerals releases Zn^{2+} into soil solution. The Zn ions released may combine with anions in the soil solution to form a new solid phase as Zn carbonate or Zn hydroxide. Alternatively, Zn ions may be adsorbed on different soil minerals and subsequently fixed irreversibly. All the above Zn compounds are too soluble to account for the small concentration of Zn found in most soil solutions (Lindsay, 1979). Adsorption and desorption by clay minerals, oxides, carbonates and organic matter are much more likely mechanisms controlling Zn concentration in soil solution (Brummer et al., 1983).

2.3 Zinc Species in Soil Solution

The levels of Zn in soil solution are very low. Hodgson et al. (1965, 1966) measured Zn levels in soil solution displaced from 20 Colorado and four New York soils. The total Zn concentration averaged <2 ppb and 74 ppb for the Colorado and the New York soils, respectively. They separated soil solution Zn into ionic and complexed form and reported that on an average 60% and 55% of the soluble Zn occurs presumably in soluble Zn organic complexes for the Colorado and the New York soils, respectively.

McBride and Blasiak (1979) observed that the proportion of Zn complexed in solution increased as soil pH increased. At soil pH values above 6.5, much of the Zn in solution was complexed with soluble organic material. This may explain the differences between the New York and the Colorado soils as reported by Hodgson et al. (1965, 1966) since the latter had much higher average pH values than the former. Stevenson and Ardakani (1972) reviewed the micronutrient organic matter reactions and concluded that soluble Zn organic complexes are mainly associated with amino, organic and fulvic acids, while insoluble organic complexes are derived from humic acid.

Numerous ionic and complexed ionic species including those of Zn^{2+} hydrolysis are found in soil solution (Lindsay, 1979). The Zn hydrolysis species in equilibrium with soil Zn are depicted in Figure 2.1. The predominant species below pH 7.7 is Zn^{2+} , whereas above this pH, ZnOH^+ is more prevalent. The neutral species Zn(OH)_2 is the major species at pH values above 9.1, whereas the species Zn(OH)_3^- and Zn(OH)_4^{2-} are never major solution species in the pH range of soils. Zinc also forms complexes with chloride, phosphate, nitrate, and

Figure 2.1 The hydrolysis species of Zn^{2+} in equilibrium with soil Zn (adapted from Lindsay, 1979).

sulfate. These complexes except ZnSO_4 do not contribute significantly to total zinc in solution. However, in neutral and calcareous soils the species ZnHPO_4 may be significant depending upon pH and the activity of phosphate.

The solubility of zinc is highly pH dependent and decreases 100-fold for each unit increase in pH (Lindsay and Norvell, 1969). This relationship is represented by the equation:

which gives $\log \text{Zn} = 6.0 - 2 \text{ pH}$.

Zinc moves to plant roots mainly by diffusion (Wilkinson et al., 1968; Elgawhary et al., 1970; Schwartz et al., 1985), where it is taken up principally in the divalent form (Zn^{2+}) although some monovalent forms (ZnOH^+) may also be taken up (Thorne, 1957). Halvorson and Lindsay (1977) confirmed the hypothesis that Zn is adsorbed by plant roots as Zn^{2+} , since chelated Zn is not readily absorbed. They further observed that chelation aids in the transport and movement of Zn ions to plant roots. Both natural and synthetic chelates aid in Zn transport from parent material and other relatively insoluble phases to plant roots (Zunino and Martin, 1977).

2.4 Forms and Distribution of Soil Zinc

Separation of various forms of Zn in soils has been a useful tool in studying the retention of Zn by the soil and its release to plant. Generally Zn in soils has been partitioned into forms (Hodgson, 1963) or pools (Viets, 1962), primarily on the basis of ways that Zn is bound in soil or held against extraction by various chemical agents. These forms may be (i) water soluble (both ionic and complexed species), (ii) on exchange sites of reactive soil components, (iii) complexed with organic matter (water insoluble), (iv) occluded by soil oxides and hydroxides, and (v) entrapped in primary and secondary minerals.

The distribution of Zn among different forms may vary significantly depending on the soil. Several attempts have been made to separate the various physical and chemical forms of Zn in soils. White (1957) carried out fractionation of Zn in 14 Tennessee soils and

reported that 1 to 7% of the Zn was in the exchangeable form, 30 to 60% in the Fe-oxide fraction, 20 to 45% in clay fraction, and 10 to 40% was associated with organic matter or resistant minerals. Shuman (1979) reported that 1 to 7% of the Zn in ten Georgia soils was in the exchangeable form and on an average 40% and 20% in the clay and Fe-oxide fractions, respectively. The percentage of Zn in the organic matter, sand, and silt fractions were almost similar (12%). However, fine textured soils contained higher amounts of Zn associated with the clay fraction compared to coarse textured soils, in which more Zn was proportionately associated with the organic fraction.

Iyengar et al. (1981) studied the distribution of Zn among different fractions for 19 soils, which varied widely in chemical and physical properties. There was wide variation in the magnitude of Zn fractions among these soils. On average most of the total Zn was present in the Fe-oxide (25%) and residual (70%) fractions. The exchangeable (non-specifically and specifically adsorbed), organically bound and Mn-oxide bound Zn fractions averaged 3.7 (0.4 and 3.3), 2.5 and 2.0% of total Zn, respectively.

Sedberry and Reddy (1976) found that an average of 1.7, 0.9, 2.6, 4.4 and 86.4% of the Zn in ten Louisiana soils was in the water soluble, exchangeable, chelated, organic and residual mineral fractions, respectively. The high values for residual mineral Zn fraction reported for these soils was probably associated with soil oxides and hydroxides as the fractionation technique followed by the authors did not account for Zn associated with these fractions.

Variation in soil environments causes a redistribution of Zn among different fractions. Sims and Patrick (1978) found that Zn was

higher in the exchangeable and organic fractions at low pH and Eh than at high pH and Eh, whereas the amounts of Zn in the water soluble and Mn- and Fe-oxide fractions were greater at high pH and Eh values. More recently, Shuman and Hargrove (1985) studied the effect of tillage on the distribution of Zn fractions. The exchangeable fraction was the only fraction in which Zn was significantly lower for conventional tillage compared to minimum tillage.

Zinc is especially sensitive to soil pH. The exchangeable fractions increases as soil pH decreases, but the specifically adsorbed and Mn-oxide Zn fraction increase with increases in soil pH (Iyengar et al., 1981). In a study with 19 soils (Iyengar et al., 1981), the organic Zn fraction was found to increase as the organic matter content increased and much of the residual Zn was present in clay-sized minerals. Similarly, Shuman (1979) reported that residual Zn was mostly associated with the clay fraction of fine textured soils. It seems likely that exchangeable Zn would decrease when the cation exchange capacity and clay content decrease because fewer exchange sites would be available for adsorption. However, Shuman (1985) reported an unusual increase in exchangeable Zn with a decrease in cation exchange capacity and silt and clay content.

Zinc in different soil fractions varies in plant availability (Viets, 1962). Iyengar et al. (1981) attempted to relate different fractions of Zn to plant availability. Zinc uptake varied directly with exchangeable Zn and organically-bound Zn and inversely with oxide-bound Zn. One interesting finding of their study was a highly significant positive correlation between the residual Zn form and Zn plant uptake. In contrast to this, Iyengar and Deb (1977) reported

that the residual mineral Zn fraction does not contribute significantly to plant uptake and that complexed, water soluble, exchangeable and organically bound Zn were the most important fractions contributing to plant uptake.

Stanton and Burger (1967) reported that hydrous Fe-oxides, in the presence of phosphate ions, fixed Zn in a plant unavailable form. In the absence of phosphate ions, however, the oxides had a strong affinity for Zn, but Zn fixation in unavailable forms did not occur. Goethite, on the other hand, fixed Zn against plant uptake irrespective of the absence or presence of phosphate ions. In sharp contrast to these results, Marinko and Igue (1972) found that treatment of volcanic ash soils and oxisols with large quantities of P fertilizer led to neither enhancement of Zn adsorption nor depression in Zn uptake by corn plants grown on these soils. Cavallaro (1982) observed lowered Zn adsorption by soil clays when clay surfaces were saturated with P.

In comparing these studies, it is important to consider the quantities of adsorbed Zn and phosphate relative to the surface capacity for adsorption, as well as the ionic medium, which the metal ions were adsorbed from. Phosphate adsorption increases the negative charges of soil clays containing oxides as demonstrated by electrophoretic mobility measurements (Cavallaro, 1982). Hence, enhanced metal ion adsorption by electrostatic attraction might be expected. However, specific adsorption of Zn could simultaneously be reduced because of the occupation of fixation sites by phosphate. The actual mechanism still remains unknown.

2.5 Zinc Adsorption by Soil and Inorganic Constituents

2.5.1 Whole soils

Adsorption of Zn by soils has been the subject of research by several investigators. In general, Zn adsorption is found to be pH-dependent and related to soil cation exchange capacity. Sharpless et al. (1969) found that 75% of the added Zn adsorbed at a one minute reaction period was accounted for by the cation exchange capacity. In some soils, however, 2/3 of the exchangeable Zn became fixed in non-exchangeable forms after a certain period. According to Kalyanasundaram and Mehta (1970), the availability of applied Zn varied inversely to the proportion of finer fractions of the soil. Fixation was high (57%) in a clayey soil, medium (44%) in a medium-textured soil, and low (35%) in a light-textured soil.

Adsorption isotherms have been used for many years to describe the nature of various types of adsorption phenomena. An adsorption isotherm describes the amount of solute adsorbed by an adsorbent as a function of the equilibrium concentration of the solute. The quantity of ion adsorbed has generally been found to be dependent, within limits, on the concentration of ion in solution. Despite some limitations, these adsorption isotherms can give good qualitative information upon which certain conclusions can be based (Shuman, 1975).

Zinc adsorption often follows the Langmuir model, which can be used to obtain estimates of sorption maxima (capacity) and bonding energy for different soils. Udo et al. (1970) found that Zn adsorption at low concentration in calcareous soils was described by the Langmuir adsorption equation (Fig. 2.2). The calculated Langmuir adsorption maxima were related to the carbonate and organic matter

Figure 2.2 Langmuirian adsorption of zinc by three calcareous Arizona soils (adapted from Udo et al., 1970).

contents of the soils. When the added Zn exceeded the adsorption maxima, the Zn concentration at soil pH above 7.5 appeared to be governed by the solubility of Zn hydroxides or carbonates. However, this was not a factor in most soils.

The objection to precipitation as a mechanism in controlling the concentration of Zn in soil has been based on the fact that most of the precipitates considered, except Zn sulfide (ZnS), are too soluble in the soil solution (Lindsay, 1979). Brummer et al. (1983) reported that concentration of Zn in soils at pH values below 7 are determined exclusively by adsorption-desorption reactions. Even at pH values above 7, the formation of other Zn compounds is unlikely in most soils because additions of large amounts of Zn are required to ensure saturation of the adsorption sites of different soil components before the Zn concentration in the soil solution can increase

sufficiently to bring about the precipitation of a definite compound.

Shuman (1975) studied the adsorption of Zn on four soils of varying texture. He found that Zn adsorption conformed to the Langmuir isotherm and that there were two linear portions on the curve (Fig. 2.3). The adsorption sites for the lower linear portion had very high bonding energy coefficients and low adsorptive capacities compared with the adsorption sites of the upper linear portion corresponding to higher Zn concentration. Soils high in clay or organic matter had higher adsorption capacities and higher bonding energy for Zn than sandy soils low in organic matter. Low pH reduced Zn adsorption more for sandy soils than for those high in colloidal material.

Figure 2.3 Langmuir isotherm for Zn adsorption by Decatur A horizon and Cecil A B_{2t} horizons (adapted from Shuman, 1975).

Kuo and Mikkelsen (1979) reported that at extremely low Zn concentration, Zn sorption by two alkaline soils could be described by

either Langmuir or Freundlich sorption isotherms. However, at higher Zn concentration only a Freundlich equation could describe the sorption. Zinc sorption by four different California soils conformed only to the Freundlich equation (Kurdi and Doner, 1983).

Harter (1983) reported that differences among soils in the amounts of Zn sorbed at any given Zn concentration did not directly correspond with soil cation exchange capacity. One would expect to obtain such results if the amounts of sorbed Zn were more affected by final pH than by soil cation exchange capacity. As noted by Kurdi and Doner (1983), Zn sorption differences among the soils were more related to equilibrium pH than to cation exchange capacity. Soil pH has a strong effect on Zn adsorption (McBride and Blasiak, 1979). The minimal Zn concentration in solution occurred between pH 7 and 8. Concentration of Zn in solution decreased 30-fold for every unit of pH increase in the pH range 5 to 7.

2.5.2 Layer silicates

Soil clays play an important role in the adsorption of Zn and this adsorption is controlled by cation exchange capacity and pH (Ellis and Knezek, 1972). Nelson and Melsted (1955) found that 50-70% of the adsorbed Zn is replaced by neutral salts and that an additional 15-20% can be extracted by acid. Some of the adsorbed Zn cannot be replaced by acid or salt solution. It is considered that this portion of Zn is incorporated into the lattice structure, since the ionic radius is similar to that of Mg in the octahedral lattice. Reddy and Perkins (1974) studied the fixation of Zn by bentonite, illite and kaolinite and found that kaolinite clay fixes less Zn than either

bentonite or illite and that fixed Zn was not substituted for lattice ions since X-ray and DTA (differential thermal analysis) did not reveal mineralogical changes. Although Zn fixation has been attributed to lattice substitution (Elgabaly, 1950), clay adsorption of Zn without fixation is most likely an exchange process.

DeMumbrum and Jackson (1956a) and Bingham et al. (1964) observed that montmorillonite, especially at neutral or alkaline pH, adsorbed Zn in excess of the cation exchange capacity. This phenomenon may be explained by two mechanisms, namely, adsorption of Zn in hydrolyzed forms or precipitation of $\text{Zn}(\text{OH})_2$. Brummer et al. (1983) reported that the adsorption capacity for specifically adsorbed Zn by the following components increased in the order of $\text{CaCO}_3 < \text{bentonite} < \text{humic acid} < \text{amorphous Fe and Al-oxide}$, thus limiting the possibility of reactions.

DeMumbrum and Jackson (1956b), using infrared techniques to study the reaction mechanism of Zn with layer silicates and peat, found that Zn saturation decreased the intensity of the 2.8μ infrared absorption band of the hydroxyl ions in montmorillonite, vermiculite, and kaolinite, indicating a reaction or bonding with the octahedral OH in layer silicates. This bond could be visualized as a Zn-O-Al or

$$\begin{array}{c} \text{OH} \\ | \\ \text{Zn-O-Al} \end{array}$$

in position, where access by the Zn ions is possible because of silica net openings, crystal defects or position at edges. These data, together with the observation by Hodgson (1963) that a large part of Zn adsorbed could be replaced by non-destructive dilute acid extraction, suggests that most of the specific adsorption occurs on exposed-OH groups and not by substitution into octahedral layer.

The dependence of Zn adsorption on pH is thought to be due to the competition effect of the H^+ ion and to the change of cation exchange capacity with pH. Abd-Elfattah and Wada (1981) determined the selective adsorption of Zn by different cation exchange material to be: Fe oxide, halloysite > kaolinite > humus > montmorillonite. Exchange between Ca^{2+} and Zn^{2+} and solubility product $[Zn^{2+}][OH^-]^2$ indicates that Zn is not precipitated as hydroxide but is adsorbed on cation exchange sites. Differences in specific Zn adsorption on different cation exchange materials is related to the cation exchange sites developed at pH values higher than 6.0 due to ionization of surface OH and COOH groups.

Farrah and Pickering (1977) found that Zn adsorption on kaolinite, illite, and montmorillonite varied with clay, pH, concentration of competing ions and nature of ligands present. Some ligands that form complexes with metal ions decrease adsorption by decreasing the concentration of adsorbing species—while other increase adsorption. Removal of iron oxides increased the capacity of clays to adsorb Zn in more instances than it decreased it and the adsorptive capacity was directly related to the cation exchange capacity values for clays (Shuman, 1976).

2.5.3 Oxides and hydroxides

Hydrous oxides of Fe and Al can be just as important as clay minerals in Zn adsorption in soils. The oxides are found either free in the soil or as coating on clay minerals (Thomas and Swoboda, 1963). The ubiquitous nature of the oxides in soil makes them more important to the retention and release of Zn in relation to plant availability.

Jenne (1968) has suggested that in very many situations, the levels of Zn in natural waters, including the soil solution, is controlled by adsorption on the surfaces of oxides.

Shuman (1977) equilibrated Zn solution with both fresh and aged Fe and Al oxides to measure Zn adsorption. Fresh Fe and Al oxide gels adsorbed ten times as much Zn as aged gels, corresponding to a tenfold difference in both cation exchange capacity and surface areas.

One of the most important properties of simple oxides is that they show a particularly strong tendency to adsorb Zn, even when the oxide surface has a net positive charge. Zinc adsorption was found to occur at pH values well below the isoelectric point of the oxides when the surfaces were positive and the Zn in a cationic form (Kinniburgh et al., 1976; Bolland et al., 1977).

Zinc can be adsorbed specifically and non-specifically on the crystalline oxide surface. Specific and non-specific adsorption on oxide surfaces accounted for 60 to 90% and 40 to 10% of the total Zn adsorption, respectively (Kalbasi et al., 1978). Adsorption of Zn by oxides occurs, although the exact mechanisms of adsorption on oxide surface are not clear. Quirk and Posner (1975) have suggested that the specific adsorption of Zn^{2+} involves the formation of a chelation bridge and ring structure which can be viewed as an extension of the oxide surface:

A second mechanism of non-specific adsorption of Zn at low pH values was postulated by Kalbasi et al. (1978) involve adsorption of ZnCl or Zn^{2+} plus Cl^- and the release of one H ion for each mole of Zn^{2+} adsorbed. They proposed the following adsorption reaction:

The adsorption of Zn by the hydrolytic product of Al is a process involving the formation of specific bonds (Goh et al., 1983). Well-crystallized Al hydroxides formed in the absence of tannic acid are least important in the adsorption of Zn (Goh et al., 1983). The presence of tannic acid contributes to the adsorption of Zn by perturbing the crystallization of hydrolytic products of Al and the subsequent increase in the specific surface and exposure of Al-OH, carboxylate and phenolic groups of the hydrolytic products.

In addition to Fe and Al hydrous oxides, Mn oxide can also adsorb Zn. Loganathan et al. (1977) found specific adsorption of Zn

by δMnO_2 at low and higher pH values. Zinc was exchanged with bound H^+ at pH values below 5. At higher pH values Zn adsorption increased abruptly and was related to hydroxylation. These workers proposed that $\text{Zn}(\text{OH})_2$ was nucleated at the surface.

A characteristic feature of the specific adsorption of Zn is that it is highly pH dependent. At trace concentration ($<10^{-7}$ M), Zn adsorption by ferrihydrite increased by about 45 times for each unit increase in pH (Kinniburgh and Jackson, 1982). This strong pH-dependence has been interpreted in terms of several mechanisms, namely, the preferential adsorption of ZnOH^+ , the formation of surface- $\text{Zn}(\text{OH})_2$ species or the exchange of Zn^{2+} for surface-bound protons. Whatever the particular mechanism, the net effect is that for adsorption of each Zn^{2+} there is a release of protons (Quirk and Posner, 1975; Forbes et al., 1976; Kalbasi et al., 1978; Goh et al., 1983; Kinniburgh, 1983). These studies show that approximately 2 moles of H^+ are released from the surfaces of well-crystallized gibbsite or goethite for every mole of Zn adsorbed. However, this stoichiometry was not observed for hydrolytic products of Al containing substantial amounts of poorly crystalline materials (Goh et al., 1983). If the adsorbed ions in the stern plane are close to the surface, the proton release is almost equivalent to the charge on the metal ions; as the distance increases, proton release decreases (Barrow et al., 1981).

2.6 Reaction with Organic Matter

The formation of complexes between organic matter and Zn is of fundamental importance in determining Zn mobility and plant availability. Soluble organic compounds such as simple aliphatic acids,

amino acids, phenolic acids, peptides and proteins, simple sugars and polysaccharides, and humic and fulvic acids complex the majority of Zn in soil solution. Although many of the complexing agents are short-lived in soils, biological processes are constantly replenishing them (Stevenson and Ardakani, 1972).

The role of organic matter on Zn availability may vary depending on the characteristics and amount of organic material involved. In many ways organic matter keeps Zn available to the plants. However, organic soils are often deficient in Zn. Matsuda and Ito (1970) found that the adsorption strength of Zn for humus increases as humification progresses. Insoluble Zn complexes are most likely bound to the humic acid fraction, while soluble Zn complexes are mainly associated with individual biochemical molecules (Stevenson and Ardakani, 1972).

Randhawa and Broadbent (1965) explained the strong pH dependence of complexed Zn as follows: Complexing agents, which may be considered as Lewis bases (electron donors), have considerable affinity for hydrogen ions as well as metal ions (electron acceptors). Hydrogen ions compete with the metal ion for the ligand. Thus a decrease in pH results in a reduction of the free ligand concentration and a decrease in the amount of metal complexed. The result is that, at higher pH values, more complexing sites are available on humic acid molecules for combination with Zn. Schnitzer and Skinner (1966) reported Zn-fulvic acid stability constants of 1.73 at pH 3.5 and 2.34 at pH 5.0. Since bonding of metals to fulvic acid involves carboxyl groups, the pH dependence of the stability constant reflects the competition with hydrogen ions. Whenever possible, it

would be preferable to eliminate the pH dependence of the metal-fulvic complexes in determining stability constants.

Binding of Zn^{2+} and Mg^{2+} on several humic and fulvic acid-like model polymers was studied by Zunino et al. (1979). Polymers containing carboxylic and phenolic OH groups show higher coordination power for Zn^{2+} than those containing only OH groups.

Complex reactions of Zn with organic matter extracted from sewage sludge were studied by Tan et al. (1971). They reported that both the complexing power and the stability constant of fulvic compounds increased with increasing pH. A shift in infrared characteristics of OH band from 3500 cm^{-1} to 3200 cm^{-1} and sharp increase in carboxyl stretching at 1650 cm^{-1} and 1400 cm^{-1} , indicated the formation of coordinate covalent bonds between OH groups and Zn and linkage between COO^- and Zn, respectively. The role of phenolic OH as Zn binding ligands has also been documented by Abd-Elfattah and Wada (1981) and Goh et al. (1983).

2.7 Phosphorus X Zinc Interaction

High levels of available P or the heavy application of P to the soil induce Zn deficiency in plants grown in soil or culture media low in available Zn (Olsen, 1972). This P X Zn interaction, generally known as "P induced Zn deficiency", has been recognized for many crops such as corn (Langin et al., 1962), potatoes (Boawn and Leggett, 1964); tomatoes (Martin et al., 1965); soybean (Paulsen and Rotimi, 1968); flax (Moraghan, 1980); and blackbeans (McKenzie and Soper, 1983).

Despite so many studies, elucidation of the mechanism of the P

X Zn interaction has been controversial. The effects of P treatment on plant response to Zn are numerous and complex involving a number of factors. In general, efforts have been concentrated on four possible causes: (i) a P X Zn interaction in the soil, (ii) a simple dilution effect on concentration in plant tops due to growth response to P; (iii) a slower rate of translocation of Zn from the roots to tops; and (iv) a metabolic disorder within the plant cells related to an imbalance between P and Zn (Olsen, 1972).

In earlier studies, the cause of P-induced Zn deficiency was suspected to be the formation of an insoluble $\text{Zn}_3(\text{PO}_4)_2$ in the soil, which reduced the concentration of Zn in the soil solution to deficiency levels. However, this was not observed in experiments testing the solubility of this compound (Jurinak and Inouye, 1962). Even when the solubility was at minimum, it was over 100 times greater than the Zn concentration required for maximum plant growth as determined by Carroll and Loneragan (1969). Moreover, $\text{Zn}_3(\text{PO}_4)_2$ is an effective Zn fertilizer (Boawn et al., 1957) and higher P rates either increased or did not affect extractable soil Zn levels (Pauli et al., 1968; Brown et al., 1970; Racz and Haluschak, 1974; Safaya, 1976). This evidence clearly indicated that precipitation in the soil is not likely to be the cause of a P-induced Zn deficiency in plants.

When the rate of plant growth exceeds the rate of uptake of a particular nutrient, the concentration of that nutrient in the tissue decreases or in other words dilution occurs. Several studies (Boawn et al., 1954; Loneragan et al., 1979; Moraghan, 1980) observed that a reduction in Zn content of crops as a result of applied P produced Zn deficiency symptoms. Applied Zn increased yield only when P was

applied. A response in yield was found for applied P. Hence, a dilution effect upon Zn largely accounted for this interaction. This explanation fits many cases of interaction, but not all. In general, this interaction occurs when the soil is deficient in P and marginal in Zn (Olsen, 1972). It is therefore likely to be a very important component of P X Zn interactions observed in the field.

Another mechanism related to P X Zn interaction was reported by Stukenholtz et al. (1966). They observed that although the concentration and uptake of Zn by corn roots increased with applied P, concentration and uptake in the leaves, nodes, and internodes declined. From an analogous experiment, Sharma et al. (1968) observed the distribution of Zn in corn and tomato roots and tops. Concentration and uptake of Zn in roots, in comparison to the tops, was higher in P treated plants. The findings of these studies suggested that applied P had little or no effect on Zn absorption by roots. The main effect was a physiological inhibition in the translocation of Zn from roots to tops.

Andriano et al. (1971) have shown that the root cell wall can bind Zn in sufficient amounts to prevent cytoplasmic toxicity due to Zn. Further, the binding capacity of root cell wall increases in the presence of high P levels (Youngdahl et al., 1977) resulting in less Zn available for transportation to the upper portion. The observation that soils high in Zn or soils that have been fertilized with Zn do not show the P-induced Zn deficiency can be explained since the binding sites in the cell wall are saturated, and any additional Zn would be available for metabolism.

A number of authors have also observed that P treatments

sometimes enhanced symptoms of Zn deficiency without reducing concentration in tops. The symptoms correlated with the ratio of concentration of P/Zn but not with Zn concentration (Boawn and Leggett, 1964; Watanabe et al., 1965; Boawn and Brown, 1968; Millikan et al., 1968). These observations suggest that increasing P concentration in plant tissue induces a higher physiological requirement for Zn. However, this phenomenon has been the most confusing one, since several other studies have tended to discount the concept of a critical P/Zn ratio (Stukenholtz et al., 1966; Sharma et al., 1968; Warnock, 1970; Loneragan et al., 1979; Moraghan, 1980).

More recently Loneragan et al. (1982) studying the P X Zn interaction in a solution culture experiment with okra clarified the above mentioned puzzling phenomenon responsible for P X Zn interaction. They showed that P-induced Zn deficiency lies not on Zn metabolism in the leaves but rather on P absorption and transport from roots. Under conditions of low Zn and high P supply, P accumulates to toxic levels in leaves inducing or accentuating symptoms resembling Zn deficiency. However, the relevance of P toxicity resembling Zn deficiency from solution culture experiments has yet to be established under field conditions.

Another factor which may be involved in the P X Zn interaction is mycorrhizal infection of plant roots. Tinker and Gildon (1983) cited a number of references reporting increased Zn uptake by crops due to mycorrhizal inoculation. High levels of P can inhibit infection of plant roots with vesicular-arbuscular mycorrhizae (VAM) (Hayman, 1978; Tinker, 1980). Therefore, it seems likely that one of the mechanisms operating to produce this antagonism is that P tends to

reduce VAM infection. Lambert et al. (1979) tested this idea with soybeans and corn and showed that adding P fertilizer significantly reduced Zn uptake in mycorrhizal plants.

2.8 Factors Affecting Zn Availability

The types of soils inherently low in available Zn include acid sandy soils, some organic soils, particularly peats and humic gley soils, calcareous soils, and subsoils exposed by land levelling operations or by wind or water erosion (Lucas and Knezek, 1972). Factors which limit the rate of diffusion of Zn to plant roots also reduce Zn availability. This perhaps is the most probable reason why Zn deficiency often occurs on compacted soils. As discussed earlier (Section 2.7), Zn deficiencies are also associated with soils with low Zn content and high available soil P levels.

Deficiencies are correlated not with total Zn in the soil but with a complex soil-plant system. A low total Zn level may be an important contributory factor but availability is the important limiting factor. Factors which favour Zn fixation, such as high pH, clay, organic matter, oxides, and carbonate content limit Zn availability. These factors are discussed in detail in Section 2.5 and 2.6.

Zinc deficiencies found during the early growing season often disappear by midseason. According to Lindsay (1972), Zn deficiencies in Colorado are most pronounced during cool, wet spring and disappear in July. He suggests that either the cool soil results in poorly established rooting system, thus restricting the feeding zone, or reduced microbial activity causes insufficient available Zn to be released from the organic matter.

Edwards and Kamprath (1974) considered that the detrimental effect of low soil temperature in suppressing Zn accumulation in corn was mainly due to lowered translocation from roots to tops. Decreased metabolic activity of plant roots at low soil temperatures was also advanced as a cause of early season Zn deficiency in corn (Giordano and Mortvedt, 1978).

Plants differ widely in their ability to obtain Zn from soil. Differences occur among both varieties and species. From a study of 25 annual crops and pasture plant varieties representing 21 species, Gladstones and Loneragan (1967) found that species differ characteristically in their feeding power for Zn. They suggested that relative differences among species are maintained over a wide range of soils. Differential susceptibility has been shown to occur in navy beans. Ambler and Brown (1969) found that the variety Sanilac was more susceptible to Zn deficiency than Saginaw. Massey and Loeffel (1967) found wide variations in the Zn levels of 31 inbred lines of corn. The nature of resistance to Zn deficiency for several inbreds and single corn crosses is believed to be under genetic control (Halim et al., 1968). Sensitivity of various crops to low levels of soil Zn is shown in Table 2.1.

2.9 Diagnosis of Zn Deficiency

2.9.1 Soil testing

Analysis of soil is one means of assessing the available supply of Zn. A wide variety of techniques and extractants have been tested for determining the available Zn levels of soils.

Accuracy in designating deficient areas is better achieved with

Table 2.1 Sensitivity of crops to low levels of available zinc in soil
(adapted from Tisdale et al., 1982).

Very sensitive	Mildly sensitive	Insensitive
Beans, lima and pea	Alfalfa	Asparagus
Castor beans	Barley	Carrots
Citrus	Clovers	Forage grasses
Corn	Cotton	Mustard and other crucifers
Flax	Potatoes	Oats
Fruit trees (deciduous)	Sorghum	Peas
Grapes	Sugar beets	Peppermint
Hops	Tomatoes	Rye
Onions	Wheat	Safflower
Pecans		
Pine		
Rice		
Soybeans		
Sundangrass		

extractions that estimate the available Zn in the soil. Soil Zn, which is extracted by neutral salt solutions such as $\text{Ca}(\text{NO}_3)_2$ or KCl is considered readily available to plant. This portion of Zn, however, is very small, especially in alkaline soils (Tiller et al., 1972). Extractable Zn extracted with Ca or K salts, is not considered useful in interpreting the Zn labile pool. Extraction with 2 N MgCl_2 was shown to be a very good estimate of the Zn supplying power of 20 soils that varied considerably in pH (5 to 7.6), organic matter content and soil texture (Stewart and Berger, 1965). Optimum growth of millet was obtained when the 2 N MgCl_2 extractable Zn was greater than 0.4 mg kg^{-1} . Martens (1968) extracted 16 soils with 2 N MgCl_2 and 0.1 and 1.0 N HCl to predict Zn uptake by greenhouse corn. He found that 2 N MgCl_2 extractable Zn was closely related to Zn uptake.

Weak acids such as 0.1 N HCl have also been evaluated as an

index of Zn availability. Wear and Evans (1968) compared the effectiveness of 0.1 N HCl, dilute acid mixture of 0.05 N HCl + 0.025 N H₂SO₄ and 0.05 M EDTA at pH 7 as a means of predicting Zn uptake by corn plants. The correlation coefficients were 0.89 for dilute acid mixture, 0.82 for 0.1 N HCl and 0.62 for EDTA. Although the dilute acid, 0.1 N HCl, was found equally effective as Aspergillus niger (Tucker and Kurtz, 1955) and was highly correlated with chelating agents (Tiller et al., 1972), this test extracts an excess of Zn from calcareous soils, which is doubtful that it is available to plants. The use of the acid extraction may not be applicable in calcareous soils (Trierweiler and Lindsay, 1969).

Chelating reagents as Zn extractants are most frequently used to estimate labile Zn pool. Dithizone-ammonium acetate (Shaw and Dean, 1952), EDTA-ammonium acetate (Viro, 1955; Tucker and Kurtz, 1955), EDTA-ammonium carbonate (pH 8.6) (Trierweiler and Lindsay, 1969), and DTPA (Lindsay and Norvell, 1978) have been used. The dithizone method shows a high degree of correlation with extractable Zn and uptake of Zn by plants (Marten et al., 1966) and is capable of separating Zn deficient from non-deficient soils (Trierweiler and Lindsay, 1969). The EDTA-ammonium carbonate (pH 8.6) method was also found to be effective in predicting soil available Zn (Trierweiler and Lindsay, 1969; Brown et al., 1971; Haq and Miller, 1972).

The DTPA method (Lindsay and Norvell, 1978) seems promising because it simultaneously extracts Zn, Fe, Mn and Cu. This test was able to successfully separate 42 Colorado soils into Zn deficient and non-deficient categories for corn. The critical level for this crop was established at 0.8 mg kg⁻¹. Halvin and Soltanpour (1981)

evaluated the NH_4HCO_3 -DTPA soil test developed by Soltanpour and Schwab (1977). Their results indicate that the NH_4HCO_3 -DTPA soil test is as good as the DTPA soil test of Lindsay and Norvell (1978) for predicting plant available Zn in Colorado soils. However, the NH_4HCO_3 -DTPA soil test is more economical because it simultaneously extracts both macro- and micronutrients.

Lindsay and Norvell (1978) cited a number of references reporting on the success of the DTPA method. However, they have clearly suggested that critical levels must be determined separately for each crop using standardized procedures for soil preparation, grinding and extraction. The importance of sample handling, soil drying, soil grinding, suspension shaking and filtering, soil to solution ratio and reaction time in developing a soil test method has been well documented (Soltanpour et al., 1976; Khan and Soltanpour, 1978; Leggett and Argyle, 1983). The use of composite samples, which is the normally recommended procedure, can provide mean DTPA-extractable micronutrient levels, but offers no indication of spatial variation within a field. The latter is of great importance in the case of micronutrients as sufficiency and deficiency criteria often lie within narrow limits.

2.9.2 Plant tissue analysis

Plant tissue analysis reflects the nutrient uptake conditions of the soil. As such, it represents another approach in determining the soil nutrient availability. The diagnosis of nutrient deficiencies, and the prediction of fertilizer requirements from plant analysis, are based on the critical concentration (Farhoomand and

Peterson, 1968) of a nutrient within plant or some plant part, below which growth or crop yield is restricted. Critical nutrient concentrations have been defined as the nutrient concentration of tissue associated with 10% reduction from maximum growth due to deficiency (Ulrich and Hills, 1973).

Zinc deficiency occurs in many plants when the leaf concentration in mature plants is less than 20 mg kg^{-1} in the dry matter (Jones, 1972). Different plants and plant parts vary considerably in the levels of Zn that accompany Zn deficiencies. For making diagnosis a part of the plant, usually recently matured leaves is preferred for determining Zn (Viets et al., 1954b; Ohki, 1977, 1984). However, Melsted et al. (1969) favoured the analysis of the whole plant at boot stage for wheat.

The concentration of Zn in a plant is dependent on the physiological stage of the plant. Thus, sampling time is important in the interpretation of plant tissue analysis. Bates (1971) suggested that most C-shaped growth curves could be avoided if the tissue of the same physiological age and the same plant parts are analyzed. Sillanpaa (1982) studied the effect of sampling time on the Zn content of wheat. Plants were sampled twice a week throughout the growing season. Zinc content of wheat remained relatively constant during the growing season. Thus sampling time may not be as critical for wheat as for other crops (Jones, 1972; Jacques et al., 1975).

The time of sampling is particularly important when plants are under stress, and especially when they are initially affected. When deficiency problems are suspected, comparative analysis of normal plant can aid the interpreter (Jones, 1972). However, caution should

be exercised to select similar plant tissue at the same stage of development (Bates, 1971). Suggested sampling procedures listing growth stage, plant part to be sampled and number of plants to be sampled for field and vegetable crops are summarized by Jones (1972).

Often Zn deficiencies are associated with cool or excessively wet conditions early in the season, but the plants grow out of the deficiency later on (Lindsay, 1972). Calibration studies using plant analysis from experiments in such cases are difficult and the likelihood of a response to a Zn fertilizer is probably dependent on the yield potential and the length of the deficiency period (Moraghan, 1985). Nutrient interaction and environmental variables such as moisture supply can markedly alter the nutrient content of the plants (Bates, 1971). Therefore, the blind acceptance of individual critical values or ranges must be viewed with caution.

2.10 Zinc Fertilizers and Correction of Zn Deficiency

Zinc deficiencies are relatively easy to correct using foliar or soil applied Zn or trunk injection to trees. Recommended rates of Zn vary considerably depending upon the crop, the source, the soil, the severity of deficiency, and the methods of application (Murphy and Walsh, 1972). Typical application rates for foliar Zn sprays are 0.9-4.5 kg of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ per 378 liters of water applied at early stages and repeated as required (Lindsay, 1972). Soil Zn application rates vary from 2 to 22 kg Zn ha^{-1} and 0.3 to 6 kg Zn ha^{-1} for inorganic and organic sources, respectively.

Both band and broadcast and incorporated applications of Zn are effective in correcting Zn deficiency. Boawn (1973) reported that

banded chelates are 2.5 times more effective than Zn sulfate. On the other hand, banded Zn sulfate has lower availability coefficient than Zn sulfate broadcast and plowed down. Zinc applied as inorganic salts is relatively immobile in soils (Brown et al., 1962). Surface application of Zn has been proven in several cases to be relatively ineffective for upland crops as compared to applications that involve mixing into the soil (Barrow et al., 1960; Brown et al., 1962; Boawn, 1973).

Foliar applied Zn is usually considered as a temporary, annual corrective measure taken after deficiency symptoms occur (Murphy and Walsh, 1972). According to Chapman (1966), foliar applications have been most successful for correcting Zn deficiency in trees. Boawn and Leggett (1963) could not correct Zn deficiency in Russet Burbank potatoes by Zn sprays after deficiency symptoms had developed. In contrast, Murphy and Walsh (1972) reported success by other workers. For example, Zn deficiency in corn in Australia could be controlled if the crop was sprayed one or two times with a solution of 0.5, 1.0 or 1.5% ZnSO_4 beginning 5 weeks after emergence.

Among inorganic sources, Zn sulfate is one of the most commonly used Zn fertilizers. Other inorganic compounds such as ZnO , ZnCO_3 and $\text{Zn}_3(\text{PO}_4)_2$ are sufficiently soluble to supply available Zn to plants (Lindsay, 1972). Attempts have been made to compare the relative efficiency of organic and inorganic Zn fertilizers. Boawn et al. (1957) reported that when 2 mg Zn kg^{-1} was applied to an alkaline silt loam in pots, bean plants took up 3.5 times more Zn from ZnEDTA than from Zn sulfate. Brown and Krantz (1966) and Shukla and Morris (1967) using pot cultures, reported that Zn uptake by corn from ZnSO_4 and

ZnEDTA was comparable when the sources were mixed into the soils. However, when Zn sources were banded under the seed, ZnEDTA was more effective than Zn sulfate (Brown and Krantz, 1966; Boawn, 1973).

Gallagher (1978) reported that organic Zn sources supply more Zn to the plants grown on acid soil at low temperature but high temperature reversed this trend. The organic Zn sources were slightly more effective than inorganic sources on calcareous soils at both temperatures.

3. MATERIALS AND METHODS

To meet the objectives of this thesis a number of field, growth chamber and laboratory experiments and exploratory surveys were carried out. Analytical procedures adopted for soil and tissue analysis common in all these studies are described in a separate section (3.4) under "Analytical Procedures".

3.1 Spatial Variability of Zn

3.1.1 Spatial variability of Zn in relation to other micronutrients in uniform topography

To study the spatial variability of DTPA-extractable Zn, Cu, Fe, and Mn, two transects were sampled, one in a cultivated field and the other 8 m away in an adjacent native prairie field. Each transect was 46 m long located in a flat well-drained area. The fields were chosen for their apparent uniformity and the overall slope of each transect was less than 0.4%. The soils of both the transects were Brookings clay loam (Dark Brown Chernozemic) developed on a glacial parent material. Soil cores (76 mm diameter) were taken from the A and B horizon of both transects at 1 m intervals.

3.1.2 Spatial variability of Zn in undulating topography

This study was conducted to evaluate the influence of slope position on the spatial variability of DTPA-extractable Zn and wheat tissue Zn concentration at FEEKES-10 growth stage. Four transects were sampled from Weyburn loam soil (Dark Brown Chernozemic) with undulating topography as shown in Figure 3.1. Three transects A, B

Figure 3.1 Relative locations and elevations of the four transects sampled.

and C, each 50 m long were sampled at 1 m intervals across the slope on the upper, middle and lower slope positions, respectively. The fourth transect, D, 100 m long was sampled every 2 m along the slope. Three samples were collected from each site representing the 0 to 15 cm depth using a 25 mm diameter probe and composited for analysis. A flag was placed at each point of soil sampling. A composite sample of two plants was obtained adjacent to the point of soil sampling when the wheat was at FEEKES-10 growth stage.

3.1.3 Soil and plant tissue analyses

Soil samples from both studies were processed as described in Section 3.4.1 and were assayed for available Zn using the DTPA method (Section 3.4.1.7). In addition to Zn, soil samples from the uniform field were analyzed for DTPA extractable Cu, Fe and Mn and those from the undulating field for pH, texture, and inorganic and organic C (Sections 3.4.1.1, 3.4.1.2 and 3.4.1.6, respectively). Wheat tissue samples were analyzed according to the procedure outlined in Section 3.4.2.

3.1.4 Statistical Approach

3.1.4.1 Classical statistics

The classical statistical technique was used to describe the variability of the data by calculating mean, standard deviation, and coefficient of variation. The sample mean (U_E), standard deviation (S_E) and coefficient of variation (CV) were calculated from:

$$U_E = \sum X_i / n \quad [3.1]$$

$$S_E = [\sum (X_i - U_E)^2 / (n-1)]^{1/2} \quad [3.2]$$

$$CV = (S/U) \times 100 \quad [3.3]$$

Before calculation of sample numbers, the amount of skewness and kurtosis was examined in the data. Normal distribution was found for all the data except Mn in the A horizon of native prairie soil, which was log-normally distributed. An estimate of the number of samples necessary to estimate the mean within a given precision with a specific probability was obtained from the equation:

$$N = t_{\alpha}^2 s^2 / D^2 \quad [3.4]$$

where N = number of cores required, t_{α} = student t with $(n-1)$ degrees of freedom at the α probability level, s = standard deviation, and D is the specified limit of precision (Peterson and Calvin, 1965). This equation was used to calculate the number of samples required to estimate the mean within 5%, 10% and 20% at the 5% probability level.

3.1.4.2 Geostatistics

The classical approach to describe variability of soil parameters considers them as a simple random variable and includes only two characteristics, the mean and the variance. However, this approach neglects the spatial correlation structure inherent in soils. In these circumstances, the alternative is to use geostatistical methods which take into account the spatial structure of the data. The geostatistical approach applied in this study is described by Journel and Huijbregts (1978). Geostatistics is based on the theory of regionalized variables. A variable distributed in space and/or time is said to be regionalized. Corresponding to random function $Z(X)$, a random variable $Z(x_1)$ can be compared to another random variable $Z(x_1 + h)$ which is distance or time h away from $Z(x_1)$. The variable $Z(x)$ is a regionalized variable.

Unlike most classical statistics, the assumption of independence is

not made, thus the random variables $Z(x)$ and $Z(x + h)$ may or may not be dependent. According to the regionalized variable theory, a variogram function (which is basic to geostatistics) is defined as:

$$\gamma(h) = \text{var} [Z(x) - Z(x + h)] \quad [3.5]$$

Taking a simplistic one-dimensional case, e.g. along a transect, and assuming stationarity (i.e. $E[Z(x)]$ equals a constant) we define the semivariogram by

$$\gamma(h) = 1/2 E [Z(x) - Z(x + h)]^2 \quad [3.6]$$

and the sample semivariogram by

$$\gamma(h) = \frac{1}{2n} \sum_{i=1}^n [Z(x_i) - Z(x_i + h)]^2 \quad [3.7]$$

where γ is a function of h , the distance between samples. The semivariogram is developed by plotting semivariance with respect to h .

The resulting semivariograms can be fitted to mathematical models which are necessary for subsequent applications, e.g. kriging. Valid possibilities include linear, spherical, exponential, Gaussian and power models. To date there is not a foolproof, purely objective method for fitting models to sample semivariograms. As a result, models are fitted subjectively by weighting more heavily where large numbers of sample pairs are available and pairs relatively close together. Journel and Huijbregts (1978) suggested that distance intervals (h) should be selected to provide at least 25 to 30 pairs of points in each interval to arrive at stable estimates of the semivariogram. The sample semivariograms for this study are modelled using a linear equation ($y = a + bx$) weighted for the number of pairs in each distance interval (h).

The shape of semivariogram gives an indication of the spatial dependence of the soil property. If for all values of lag greater than zero, $\gamma(h)$ is approximately constant, the semivariogram indicates that the observations are spatially independent. If, on the other hand, values of $\gamma(h)$ approach the variance gradually or in some consistent manner as the value of lag increases, the observations are spatially dependent.

The linear semivariogram model is given as Figure 3.2. The semivariance starts at C_0 for $h = 0$, where C_0 is called the "nugget" value and is due to inherent variability of the characteristic, type of sampling and or laboratory analysis error. From C_0 the value increases linearly with distance between samples, h , to maximum "sill" value, $C_0 + \Delta C$, where ΔC is the h dependent change in semivariance.

Figure 3.2 A linear semivariogram model.

The sill value remains constant with intersample distances greater than or equal to the "range", a . Thus, samples are dependent for distances up to range " a " where semivariance then remains constant with increasing distances between samples and samples achieve independence.

3.2 Importance of Zn to Crop Nutrition and Production of Common Crops

3.2.1 Zinc status of Saskatchewan soils

3.2.1.1 Exploratory surveys

DTPA-extractable Zn levels (Section 3.4.1.7) from approximately 1200 fields from the province of Saskatchewan were compiled using soil samples submitted by individual farmers to the Saskatchewan Soil Testing Laboratory (SSTL) and others collected by our research team from field research sites. The proportion of samples with low levels of extractable Zn is probably greater than the proportion of farmland with low levels of extractable Zn. This would be since the survey was primarily based on submissions to SSTL by farmers, who are more likely to test their fields if they suspect Zn is limiting yields or if reports of Zn deficiency occur in their area. Nonetheless, representation from a wide range of soil types covering many areas of the province was achieved (Fig. 3.3).

Soils in the population studied were arbitrarily classified into three groups on the basis of DTPA-extractable Zn. Class 1 (<0.5 mg Zn kg⁻¹) included soil samples with extracted Zn levels below the critical level adopted by the SSTL. Class 2 included extracted Zn levels in the marginal range ($0.5 - 1.0$ mg Zn kg⁻¹) and Class 3 adequate levels (>1.0 mg Zn kg⁻¹) of DTPA-extractable Zn.

Figure 3.3 Distribution of micronutrient sampling sites in Saskatchewan (1982-83).

Following classification of the soils in the three classes above, the population of the samples was superimposed on soil maps to establish Zn levels trend in various soil associations.

3.2.1.2 Field experiments with Zn fertilizers

3.2.1.2.1 Experimental design

Twenty-three field trials that were established in 1982 and 1983 on a number of Saskatchewan soils of diverse soil characteristics (Table 3.1) were considered in order to assess crop responses to applied Zn.

Basal applications of N, P and K were applied to each field trial according to soil testing recommendations to ensure that available macronutrients did not limit yield. Sulfur was applied in two different ways. In 1982, a treatment of Na_2SO_4 containing amounts equivalent to those added by ZnSO_4 was included in all experiments where this fertilizer form was used. In 1983, basal applications of 30 kg S ha^{-1} as ammonium sulfate were applied over the whole experimental site. The experiments were designed as completely randomized demonstration strips ($3.05 \text{ m} \times 30.5 \text{ m}$ plot size) in 1982 and randomized complete block design ($3.05 \text{ m} \times 6.10 \text{ m}$ plot size) in 1983. With the exception of S application, the basic design included a control and one or more Zn treatments. Zinc was broadcast either as Zn oxide or Zn sulfate shelf chemical or as Zn sulfate fertilizer at a rate of 10 kg Zn ha^{-1} or sprayed as Zn-chelate (polylignosulphonic acid) on the soil or foliage at a rate of 1 or $0.35 \text{ kg Zn ha}^{-1}$, respectively. Soil application of fertilizers or shelf chemicals was always followed by incorporation. Foliar applications for all cereals

Table 3.1 Soil characteristics of experimental sites for 0-15 cm depth.

Site No.	Soil Association	Texture	pH	EC m^{-1}	Organic C g kg^{-1}	Inorganic C g kg^{-1}	DTPA-Zn mg kg^{-1}
1	Asquith	s	8.5	0.1	1.7	0.6	0.42
2	Asquith	fsl	8.0	0.1	9.1	1.5	0.35
3	Canora	sil	7.5	0.1	42.3	0.6	6.80
4	Carrot River	vfs	7.7	0.3	11.6	0.8	1.60
5	Carrot River	lvfs	7.5	0.3	15.7	0.6	3.00
6	Carrot River	vfs	7.6	1.1	23.8	5.8	0.70
7	Carrot River	fsl	7.9	0.2	11.9	1.2	0.40
8	Carrot River	fsl	7.7	0.2	19.1	0.4	0.60
9	Carrot River	fsl	7.6	0.3	24.1	0.4	0.40
10	Elstow	l	7.2	0.3	11.0	0.0	0.70
11	Elstow	l	7.0	0.4	18.0	0.0	2.60
12	Elstow	l	7.2	0.3	15.2	0.0	0.60
13	Hatton	fsl	7.8	0.2	10.0	0.0	0.55
14	Meota	fsl	7.3	0.2	29.0	0.0	4.00
15	Regina	hvc	7.4	0.7	20.3	0.0	0.90
16	Sceptre	hvc	7.6	0.2	5.4	2.0	0.54
17	Sceptre	hvc	7.3	0.6	18.0	1.1	0.50
18	Sceptre	c	7.4	0.3	25.5	0.2	0.78
19	Sceptre	c	7.5	0.2	18.7	1.8	0.75
20	Sylvannia	fsl	7.0	0.2	12.4	0.0	0.30
21	Weirdale	cl	7.6	0.6	42.3	1.8	1.70
22	Weirdale	l	7.7	0.3	30.7	4.2	0.92
23	Yorkton	l	7.3	0.2	26.7	0.8	1.10

were applied at the FEEKES-6 (first node of stem visible at the basis of shoot) and/or FEEKES-10 (sheath of the last leaf extended with the ear swollen but not yet visible) growth stages and for corn at the mid whirl stage. All treatments were replicated four times. In 1984, crops were grown in four of the experiments initiated in 1983 to assess residual effects of Zn fertilizers. Basal applications of macronutrient fertilizers were made according to corresponding 1983 schedule.

3.2.1.2.2 Soil and plant tissue sampling and analyses

Composite soil samples (0-15 cm) were taken from the whole experimental site in 1982 and from each block in 1983 prior to fertilizer applications. In 1984, four 20-mm in diameter by 150-mm deep cores were obtained from each plot in all 1983 experiments in which residual fertilizer was assessed. Composite samples were then made on a per treatment basis (4 plots) in all experiments.

Plant tissue samples were collected once during the growing season in 1982 and twice in 1983 at the growth stage at which foliar Zn applications were made (Section 3.2.1.2.1) and prior to the foliar application. In certain cases, separate whole plant and flagleaf samples were obtained at FEEKES-10 growth stage. One-half of each plot was utilized for the tissue sampling program. Tissue samples at each of the two growth stages sampled in 1983 were obtained from a separate one-quarter of each plot. At maturity, above ground plant materials from a 1.6 m² area in the remaining half of each plot were harvested, dried and grain or seed separated. The DTPA extraction (Section 3.4.1.7) was used to assess available Zn levels in all

experiments. Zinc in extracts was determined by atomic absorption spectrophotometry. Harvested plant materials were processed according to the procedure outlined in Section 3.4.2.

3.2.1.2.3 Statistical analysis

All yield and tissue content data were subjected to analysis of variance for a completely randomized design in 1982 and a randomized complete block design in 1983 and 1984. Duncan's multiple range test was used to separate significantly different means.

3.2.2 P X Zn interaction in wheat

3.2.2.1 Experimental design

This study was conducted on an ongoing field experiment, which was established in 1979 to assess the residual effect of a single broadcast application of a large amount of P fertilizer for crop growth. The site had been established on a Sutherland soil (Dark Brown Chernozemic) with clay texture, pH 7.3, organic C of 34.3 g kg⁻¹, CEC of 46 cmoles kg⁻¹ and <3 mg P kg⁻¹ soil of NaHCO₃-extractable P (Olsen et al., 1954) in the 0-15 cm depth. A single application of 0, 20, 40, 80 or 160 kg P ha⁻¹ from triple superphosphate (0-45-0) was broadcast on the main plots (13.7 m x 30.5 m) arranged in a 5 x 5 latin square design and incorporated in the spring of 1979 prior to first seeding of a continuous hard red spring wheat (Triticum aestivum L. cv. Neepawa) system.

In 1984, three factorial experiments were created by maintaining the 0, 80 and 160 kg P ha⁻¹ treatments as main plots and superimposing various rates of soil applied Zn-sulfate or Zn-chelate

(polylignosulfonic acid), or foliar application of Zn-chelate as 2.74 m x 2.74 m subplots within the main plots. Soil applied treatments of Zn-sulfate (0, 5, 10 and 20 kg Zn ha⁻¹) and Zn-chelate (0, 0.5, 1.0 and 2.0 kg Zn ha⁻¹) were broadcast or sprayed, respectively, on the soil surface and incorporated with a small cultivator. Two rates of Zn-chelate (0 and 0.35 kg Zn ha⁻¹) were applied on foliage either at FEEKES-6 or at FEEKES-10 growth stage. All plots received basal application of N prior to seeding in accordance with the Saskatchewan Soil Testing Laboratory recommendations.

3.2.2.2 Soil and plant tissue sampling and analyses

Prior to Zn application, composite soil samples (0-15 cm) from each main plot were collected and analyzed for DTPA-extractable Zn (Section 3.4.1.7) and resin extractable P (Section 3.4.1.5). One-half of each subplot (1.37 m x 2.74 m) was used for tissue sampling and the remaining half for harvest at maturity. Composite plant tissue samples were obtained from the S.W. quarter (1.37 m x 1.37 m) of each subplot at FEEKES-6 and from the S.E. quarter at FEEKES-10 growth stages, respectively.

At maturity, above ground plant material and roots were harvested from the north half of each subplot. The above ground plant material was oven-dried at 60°C for 72 h, the grain was separated and grain and straw weight determined. Grain, straw and tissue samples were assayed for Zn and P according to the procedure outlined in Section 3.4.2.

3.2.2.3 Mycorrhizal infection

To assess vesicular-arbuscular mycorrhizal (VAM) infection, root samples were rinsed in water, cleaned in hot 10% KOH and dipped into 0.01 N HCl to neutralize KOH. Twenty 1-cm root sections were selected at random from roots collected at each subplot and stained in 0.05% trypan blue in lactophenol (Phillips and Hayman, 1970) and VAM infection was assessed microscopically. The number of infected microscopic fields was expressed as a percentage of the total number of microscopic fields observed.

3.2.2.4 Statistical analyses

Analyses of variance were performed for a randomized complete block split-plot design. Orthogonal contrasts were used to partition the sum of squares for P and Zn effects and interaction into single degrees of freedom. Orthogonal polynomials were used for the rates of each soil applied Zn source only, since the control and the high rates of initially applied P selected for this study as well as the foliar Zn treatments were considered discrete.

3.2.3 P X Zn interaction in beans

3.2.3.1 Experimental design

A factorially arranged completely randomized design was used in this experiment. Samples from the surface layer (0-15 cm) of three soils from different areas in Saskatchewan (Table 3.2) were used as growth media. The treatments for Meota (Black Chernozemic) and Carrot River (Dark Gray Chernozemic) soil associations consisted of four levels of P (0, 40, 80 and 160 mg P kg⁻¹) and two levels of Zn (0 and

Table 3.2 Physical and chemical characteristics of the soil used.

Characteristics	Soils		
	Sutherland	Meota	Carrot River
pH	7.5	7.6	6.4
Inorganic carbon (g kg^{-1})	1.0	0.9	0.1
Organic carbon (g kg^{-1})	17.8	19.1	7.7
CEC (cmoles kg^{-1})	41.6	12.2	5.7
Available P (mg kg^{-1})	11.0	19.0	16.0
DTPA-Zn (mg kg^{-1})	0.96	1.69	0.45
Sand (g kg^{-1})	86	844	890
Silt (g kg^{-1})	336	88	65
Clay (g kg^{-1})	579	68	45
Free Fe (g kg^{-1})	8.7	4.8	4.5
Free Mn (g kg^{-1})	0.5	0.2	0.2

5 mg Zn kg^{-1}) in all possible combinations. For the Sutherland soil (Dark Brown Chernozemic) association, the treatments consisted of all possible combinations of four levels of P (0, 40, 80 and 160 mg P kg^{-1}) and three levels of Zn (0, 5 and 10 mg Zn kg^{-1}).

3.2.3.2 Treatment application

The soil samples used were air-dried at room temperature, ground with a wooden rolling pin and passed through a 2 mm polyethylene sieve. The treatments were applied to 4.5 kg (oven-dry basis) portions. Each kilogram of soil received a blanket application of other nutrients: 100 mg N, 200 mg K, 86 mg Ca, 5 mg Mg, 5 mg S, 5

mg Fe, 1 mg Cu, 4 mg Mn, 0.5 mg B, and 0.6 mg Mo according to TVA recommendations (Allen et al., 1976).

All Zn and P treatments were duplicated as either radioisotope labelled (^{65}Zn and ^{32}P) or non-labelled and replicated four times. The Zn-labelled treatments corresponded with the P non-labelled ones and vice versa.

Zinc as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was applied at specific activities of 12 and 6 $\mu\text{Ci } ^{65}\text{Zn mg}^{-1}$ of ^{64}Zn for the 5 and 10 mg Zn kg^{-1} soil treatments, respectively. Phosphorus was applied in KH_2PO_4 form at specific activities of 1.88, 0.94 and 0.47 $\mu\text{Ci } ^{32}\text{P mg}^{-1}$ of ^{31}P for the 40, 80 and 160 mg P kg^{-1} soil treatments, respectively. All nutrients were applied in solution form to dry soil, the soil was allowed to air-dry and was subsequently mixed in a rotary tumbler for 2 h. The treated soils were transferred to polyethylene pots in 1-kg (oven-dry basis) portions.

3.2.3.3 Establishment of the experiment

The potted soils were wetted to field capacity with deionized water and incubated for 7 days prior to seeding. Four seeds of beans (Phaseolus vulgaris cv. Pinto) were sown in each pot.

3.2.3.4 Maintenance of the experiment

Sixteen h light and 8 h dark periods were used for the duration of the experiment at a constant temperature of $22 \pm 2^\circ\text{C}$. The pots were watered daily to near field capacity. Evaporation from the surface of the pots was reduced by placing a layer of "perlite" beads on the soil surface. After establishment the seedlings were thinned to two plants per pot.

3.2.3.5 Plant tissue sampling and analyses

Plant tissue was sampled at two stages during the course of the experiment. Two of the four replications selected at random from each treatment but including two Zn-labelled and two P-labelled ones were harvested at 1/10 bloom stage. The remaining two replicates were sampled at maturity. Roots, tops, grain and straw were separated and washed with deionized water. Plant samples were dried at 60°C and weighed. For mature samples, the total dry matter and grain yields were determined and straw yields were calculated by difference. Each replicate from each harvest was analyzed separately for total P and Zn and where applicable for ^{32}P and ^{65}Zn activity (Section 3.4.2).

3.2.3.6 Statistical analysis

All data were subjected to a two-way analysis of variance. Orthogonal polynomial and/or contrasts were used to partition the sum of squares for P and Zn effects and interaction into single degree of freedom.

3.2.4 Effectiveness of zinc fertilizers

Several Zn sources have been tested to correct Zn deficiency in crops (Anderson, 1964; Boawn, 1973; Gallagher et al., 1978). Zinc chelate, particularly ZnEDTA, has been the most frequently used to correct Zn deficiencies in field experiments. However, the relatively high cost of ZnEDTA has precluded its widespread use. Consequently, forms such as Zn lignosulphonates have also been considered. Since the relative effectiveness of various types of Zn fertilizers has not been determined, two Zn lignosulphonates were compared directly with

Zn sulfate (ZnSO_4) and Zn EDTA (ZnEDTA). This was done by comparing dry matter yield and Zn uptake of a selected plant species in a growth chamber experiment.

Lignosulphonates are acid sulfite pulping by-products removed during the isolation of cellulose from wood. In Canada alone, some 2×10^6 tonnes of these by-products are produced annually, most of which are returned untreated to the environment. Currently, sulfite wood-pulping operations are classified as either low-yield (LY, $0.4\text{--}0.5 \text{ kg kg}^{-1}$), medium yield (MY, $0.5\text{--}0.6 \text{ kg kg}^{-1}$), high yield (HY, $0.65\text{--}0.75 \text{ kg kg}^{-1}$), or ultra-high (UHY, 0.76 kg kg^{-1}) processes; the term "yield" refers to the quantity of cellulosic fibers obtained from the wood source. A further subdivision can also be made depending upon the cationic species used (e.g. ammonium, sodium, magnesium or calcium) in conjunction with sulfurous acid.

In this investigation the lignosulphonates used were from low-yield (0.44 kg kg^{-1}) ammonium-based and high-yield (0.75 kg kg^{-1}) sodium-based processes. The wood used in both cases was obtained from softwoods (conifers). The corresponding Zn-modified forms were then prepared, i.e. ZnLY and ZnHY, respectively. The chemical composition of these technical lignosulphonates is shown in Table 3.3.

3.2.4.1 Experimental design

Beans (Phaseolus vulgaris cv. Pinto) were used as a test crop and the surface soil sample (0-15 cm) obtained from a Regosolic very fine sandy loam was used as a growth medium (Table 3.4). In addition to the Regosolic very fine sandy loam, three other surface (0-15 cm) soil, namely a Chernozemic loamy very fine sand, a Chernozemic loam

Table 3.3 Chemical composition of zinc-lignosulphonates prepared from low-yield ammonium based (ZnLY), and high-yield sodium based (ZnHY) lignosulphonates[†].

	ZnLY g kg ⁻¹	ZnHY g kg ⁻¹
Lignosulphonate	653.0	336.0
Total carbohydrate	197.0	192.0
Nitrogen	31.0	0.3
Phosphorus	0.4	0.07
Ash	1.0	23.8
Sulfate	40.7	11.1
Thiosulfate	1.6	5.4
Sulfite	68.3	169.0
Zinc ^ε	50.0	50.0

[†]Analyses provided by Dr. N.G. Lewis, Pulp and Paper Institute of Canada, Point Claire, Quebec

^εZinc sulfate was added to the above samples to give a zinc concentration of 5%

and a Chernozemic silt loam were used in an incubation experiment (Table 3.4). All soils used were air-dried at room temperature, ground and sieved (2 mm).

Two experiments were conducted to assess various Zn sources, namely ZnSO₄, ZnEDTA, low yield ammonium based Zn-lignosulphonate (ZnLY), and high yield sodium based Zn-lignosulphoante (ZnHY). In the first experiment, the treatments were established in 1.5 L polyethylene pots containing 1.0 kg of Regosolic very fine sandy loam. Zinc in organic forms was applied at a rate of 2.5 mg kg⁻¹ of soil and

Table 3.4 Physical and chemical characteristics of the soils used.

Great Group	Texture	pH	Clay ₁ g kg ⁻¹	Organic matter ₁ g kg ⁻¹	CEC cmol kg ⁻¹	Exchangeable Ca ²⁺ (1/2 Ca ²⁺) kg ⁻¹	DTPA-extractable Zn mg kg ⁻¹
Regosolic ¹	vfs1	8.5	33	6.9	3.8	3.2	0.25
Chernozemic	lfs	7.9	74	50.0	21.6	18.7	0.65
Chernozemic	l	7.4	124	39.7	19.8	16.7	1.01
Chernozemic	sil	6.0	322	44.8	25.3	17.4	4.71

¹ Soil used in growth chamber experiments

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ form at a rate of 5 mg kg^{-1} of soil. Controls (no zinc added) were also established for each source as a matter of routine.

Blanket application of other nutrients included 117 mg N, 40 mg P, 133 mg K, 167 mg Ca, 5 mg Mg, 33 mg S, 5 mg Fe, 5 mg Mg, 0.5 mg B, and 0.8 mg Mo per kg of soil according to TVA recommendations (Allen et al., 1976). The nutrients were applied to the surface of the potted soils in solution form and the soil was allowed to equilibrate for one week. All treatments were arranged in a completely randomized design with four replicates. Four seeds of bean were sown in each pot. The surface of the soils was kept damp by repeated application of water to the surface. After establishment, the seedlings were thinned to two plants per pot. The pots were watered daily to field capacity with deionized water. During the growth period, the chamber was maintained at $20 \pm 2^\circ\text{C}$ with a 16 h photoperiod.

In the second experiment, only ZnSO_4 and ZnLY treatments were established in 2 L polyethylene pots containing 1.5 kg of the same Regosolic very fine sandy loam soil. Zinc in both forms was applied at four rates (0, 0.5, 2.5 and 5.0 mg kg^{-1} soil). Other nutrients were applied at the same rates used in the first experiment. This experiment was established in the same manner as the first experiment.

In a separate incubation experiment, 100 g samples of each of the four soils (Table 3.4) were treated with 10 mg Zn kg^{-1} of soil in the form of ZnSO_4 , ZnEDTA, ZnLY or ZnHY. Four replicates of each treatment were incubated at field capacity for 5 wk at a constant temperature of $25 \pm 1^\circ\text{C}$.

3.2.4.2 Soil and plant tissue sampling and analyses

Plants in both experiments were harvested at 1/10 bloom stage. In the first experiment, the top three leaves were collected separately from the remaining shoot material. In addition, root material was removed manually from all pots of the first experiment and washed free of soil. Harvested plant material was processed and digested for total Zn using the method outlined in Section 3.4.2. Soil samples obtained at the completion of the experiments were analyzed for DTPA-extractable Zn (Section 3.4.1.7).

3.2.4.3 Statistical analysis

Analysis of variance were performed for a randomized complete design. Duncan's multiple range test was used to compare treatment mean effects.

3.3 Distribution of Native and Applied Zinc

The distribution of native Zn among different Zn forms was examined in the three soils used for P X Zn experiment with beans (Section 3.2.3). To study the distribution of added Zn, 5 mg ^{65}Zn kg^{-1} with 0 mg ^{31}P kg^{-1} and 5 mg ^{65}Zn kg^{-1} with 160 mg ^{31}P kg^{-1} treatments were selected from the same experiment. Soil samples were collected before seeding, after 1/10 bloom stage harvest, and after harvesting the beans at maturity. The fractionation scheme is given in Figure 3.4 and the analytical methods involved are described in Sections 3.4.1.9 through 3.4.1.9.7.

Figure 3.4 Fractionation procedure for native and applied Zn.

3.4 Analytical Procedures

3.4.1 Soil sample collection and preparation

Composite soil samples collected for soil analysis were air-dried at room temperature, ground with a wooden rolling pin and passed through a 2 mm polyethylene sieve before analysis.

3.4.1.1 pH and electrical conductivity

Soil suspensions (1:1 soil:water ratio) were shaken for 30 min on a reciprocating shaker. The pH and electrical conductivity of the suspension were determined using standard pH and conductivity meters, respectively.

3.4.1.2 Soil texture

Particle size distribution was determined by the hydrometer method as outlined by McKeague (1978). Samples were pretreated with sodium hexaphosphate and dispersed for 5 min in a Hamilton Beach blender. Corrections were made for organic matter content.

3.4.1.3 Cation exchange capacity

Soil cation exchange capacity was determined by leaching a Ba saturated soil sample with 1 M ammonium acetate (McKeague, 1978) and determining Ba by atomic absorption spectrophotometry.

3.4.1.4 0.5 M NaHCO_3 -extractable P

0.5 M NaHCO_3 extractable-P was determined in a 1:20 soil to 0.5 M NaHCO_3 (pH 8.5) suspension by the method of Olsen et al. (1954).

3.4.1.5 Resin extractable P

Resin P was extracted by the method as outlined by Hedley et al. (1982). 0.4 g resin (Dowex 1 x 8-50, >319 μm , in bicarbonate form) in nylon bag and 30 ml of deionized water were added to 0.5 g of soil in a 50 ml centrifuge tube. After shaking the mixture for 16 h, the resin bag was removed and then shaken overnight with 20 ml of 0.5 M HCl. Phosphorus was determined on 10 ml of extract using the reagents of Murphy and Ripley (1962).

3.4.1.6 Inorganic and organic carbon

Inorganic C was determined by placing finely ground soil samples into a flask and adding 10 ml of approximately 6 M HCl (Tiessen et al., 1983). After the initial reaction subsided, the flask was heated to bring the reaction mixture to a gentle boil for about 7 min and the evolved CO_2 was collected in 0.15 M NaOH in an absorption tower and titrated between pH 8.3 and 3.7. Organic C was determined using the dry combustion method after carbonate removal (Tiessen et al., 1983).

3.4.1.7 Available zinc

Available Zn was extracted according to the method described by Lindsay and Norvell (1978). The DTPA extracting solution was prepared to contain 0.005 M diethylenetriaminepentaacetic acid (DTPA), 0.01 M calcium chloride (CaCl_2), and 0.1 M triethanolamine (TEA). The final solution was adjusted to $\text{pH } 7.30 \pm 0.05$ with dilute HCl. Ten g of air-dry soil were placed into acid washed 125 ml conical flask. Twenty ml of the DTPA extracting solution was added to the flask. The flasks

were covered with parafilm and secured upright in a horizontal shaker with a stroke of 6 cm oscillating at 120 cycles min^{-1} . The samples were shaken for 2 h and filtered by gravity through Whatman #42 filter paper into vials. Zinc in the filtrates was determined by atomic absorption spectrophotometry.

3.4.1.8 Free Fe and Mn

Free Fe and Mn were determined by the method developed by De Endredy (1963) as modified by McLaren and Crawford (1973). One hundred ml of Tamm's solution (0.1 M oxalic acid and 0.175 M ammonium oxalate, pH 3.25) were added to 2 g of soil in a 250 ml beaker. The mixture was placed in a hot water bath (100°C) for 2.5 h. During extraction, the suspension was stirred intermittently with a glass rod, and the liquid level in the beaker was maintained near 100 ml with deionized water. After extraction, the suspension was transferred into a 250-ml centrifuge bottle with another 50 ml of Tamm's solution reagent and centrifuged. After centrifugation, the Fe and Mn in the supernatant were determined by atomic absorption spectrophotometry.

3.4.1.9 Zinc fractionation technique

Zinc in different soil fractions was extracted using a modified version of the sequential fractionation scheme proposed for Cu by McLaren and Crawford (1973). The methods followed for the fractionation procedure were as follows:

3.4.1.9.1 Exchangeable (non-specifically adsorbed) (EX)

Twenty grams of soil and 200 ml 0.05 M CaCl_2 were shaken in a 250-ml polycarbonate centrifuge bottle for 24 h and centrifuged.

3.4.1.9.2 Exchangeable (specifically adsorbed) (ExAD)

The soil residue from the EX extraction (Section 3.4.1.9.1) was washed twice with 100 ml of deionized water and shaken with 200 ml of 2.5% acetic acid for 24 h and centrifuged.

3.4.1.9.3 Organically bound Zn (OM)

This Zn fraction was determined on a second subsample of soil using the procedure described by Bascomb (1968). Two grams of soil were shaken with 200 ml of 0.1 M $\text{K}_4\text{P}_2\text{O}_7$ for 16 h in a 250-ml polycarbonate centrifuge bottle. Organically bound Zn was calculated as Zn in the supernatant minus the Zn present in the previous two fractions (Section 3.4.1.9.1 and 3.4.1.9.2).

3.4.1.9.4 Mn-oxide bound Zn (MnOX)

The soil residue from OM extraction (Section 3.4.1.9.3) was washed twice with 100 ml of deionized water. Zinc occluded by oxides and hydroxides was determined following the methods of Chao (1972). A 100 ml extracting solution (0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 0.01 M HNO_3 , pH 2) was added to the centrifuge bottle containing the soil residue after washing and the content shaken for 30 min and centrifuged.

3.4.1.9.5 Fe-oxide bound Zn (FeOX)

Residue from the MnOX extraction (Section 3.4.1.9.4) was washed

twice with 100 ml of deionized water and transferred into a 250-ml beaker with 100 ml of Tamm's solution (0.1 M oxalic acid and 0.175 M ammonium oxalate at pH 3.25). The mixture was placed in a hot water bath (100°C) for 2.5 h. The liquid level was maintained during digestion with deionized water. After extraction, the suspension was transferred to a centrifuge bottle with another 50 ml of Tamm's solution and centrifuged.

3.4.1.9.6 Residual Zn (RES)

Residue from the FeOX extraction (Section 3.4.1.9.5) was washed twice with deionized water and three times with 0.5 M $(\text{NH}_4)_2\text{CO}_3$ to remove the oxalate. It was subsequently dried in a forced air oven at 110°C for 24 h, and ground to pass a 150 μm stainless steel sieve. A 0.5 g subsample was placed in a teflon beaker containing enough deionized water to cover the bottom. After adding 15 ml concentrated HF and 10 ml concentrated HNO_3 , the beaker was covered and allowed to stand for 2 h. Two ml of concentrated HClO_4 were added and the mixture heated on a hot plate at low temperature until the dense fumes of HClO_4 subsided (to dryness). After cooling, the sides of the beaker were washed with a small quantity of deionized H_2O . The mixture was evaporated to dryness, the residue dissolved in 4 ml 1:1 HCl, and then diluted to 10 ml volume with 1:1 HCl.

3.4.1.9.7 Total Zinc

A sample of soil was ground to pass through a 150 μm stainless steel sieve. A 0.5 g subsample was then added to a teflon beaker and treated as outlined in the residual Zn extraction (Section 3.4.1.9.6).

3.4.1.9.8 Zinc determination in soil fractions

Total Zn in each fraction was determined by atomic absorption spectrophotometry. To determine the activity of ^{65}Zn , one-ml of supernatant was counted with 10 ml of scintillation cocktail (ready solv. TM) in scintillation vials using a Beckman LS9000 liquid scintillation counter. The amounts of added Zn associated with each fraction were calculated as follows:

$$\frac{\text{mg Zn kg}^{-1} \text{ (standard)}}{\text{CPM (standard)}} = \frac{\text{mg Zn kg}^{-1} \text{ (sample)}}{\text{CPM (sample)}} \quad [3.8]$$

where CPM = counts min^{-1} .

3.4.2 Plant tissue analysis

Harvested plant material was dried in a forced air oven at 60°C and ground to $<425 \mu\text{m}$ in a Wiley mill prior to chemical analysis. Ground plant material was digested using a wet-ashing technique involving an acid mixture of H_2O_2 and H_2SO_4 described by Thomas et al. (1967). Zinc and P concentration of plant material was determined using a Beckman spectrospan plasma arc emission spectrometer. To determine the activity of ^{65}Zn and ^{32}P , one ml of tissue digest was counted with 10 ml of scintillation cocktail (ready solv. TM) in scintillation vials using a Beckman LS9000 liquid scintillation counter. The amounts of P and Zn in plants derived from fertilizer sources were calculated from:

$$\frac{\text{mg P or Zn kg}^{-1} \text{ (standard)}}{\text{CPM (standard)}} = \frac{\text{mg P or Zn kg}^{-1} \text{ (sample)}}{\text{CPM (sample)}} \quad [3.9]$$

Percentage of plant P or Zn derived from fertilizer (% Pdf or % Zndff) was calculated using the relationship:

$$\% \text{ P or Zndff} = \frac{{}^{32}\text{P or } {}^{65}\text{Zn in plant}}{\text{P or Zn total in plant}} \times 100 \quad [3.10]$$

4. RESULTS AND DISCUSSION

4.1 Spatial Variability of Zn

4.1.1 Spatial variability of Zn in relation to other micronutrients in uniform topography

The large spatial variation of DTPA-extractable micronutrients along the sampled transects is readily shown from the plots of extracted values versus distance on the transects (Figures 4.1 to 4.4).

A statistical summary of the micronutrient data (mg kg^{-1}) obtained for the A and B horizons and total solum (calculated from A and B horizons) of both transects is given in Table 4.1.1. Coefficients of variation (CV) for all micronutrients (mg kg^{-1}) in the cultivated soil were larger in the B than the A horizon. The largest CV in the cultivated A horizon was obtained for extractable Cu (32%) and the lowest was obtained for Fe (22%). However, in the A horizon of the native prairie soil, the largest CV was obtained for extractable Fe (43%). The CV's for the rest of the micronutrients in the A horizon of the native prairie soil were similar (36%). A similar trend for iron was observed in the B horizon as well. However, the patterns of the other three micronutrients in the B horizons differed considerably from those in the A horizon.

Calculated mean micronutrient concentration values (mg kg^{-1}) in the solum of the cultivated soil exhibited similar CV's to those of the A horizon but significantly lower than those of the B horizon. In the native soil, the CV's for the Cu, Mn and Fe in the solum were lower than those in either the A or B horizons, but for Zn the CV was

Figure 4.1 Distribution of DTPA-extractable zinc in the A and B horizons of a 46 m transect of soils sampled every meter; (a) native prairie, (b) cultivated field.

Figure 4.2 Distribution of DTPA-extractable manganese in the A and B horizons of a 46 m transect of soils sampled every meter; (a) native prairie, (b) cultivated field.

Figure 4.3 Distribution of DTPA-extractable iron in the A and B horizons of a 46 m transect of soils sampled every meter; (a) native prairie, (b) cultivated field.

Figure 4.4 Distribution of DTPA-extractable copper in the A and B horizons of a 46 m transect of soils sampled every meter; (a) native prairie, (b) cultivated field.

Table 4.1.1 Statistical summary for DTPA-extractable micronutrients in soils.

Micronutrient	Sample No.	Cultivated field			Native prairie		
		Mean mg kg ⁻¹	SD ±	CV %	Mean mg kg ⁻¹	SD ±	CV %
<u>A horizon</u>							
Copper	46	1.94	0.63	32	1.91	0.70	37
Zinc	46	4.34	1.10	25	5.09	1.88	37
Manganese	46	49.51	13.10	27	40.19	14.73	37
Iron	46	134.51	29.23	22	96.47	41.84	43
<u>B horizon</u>							
Copper	43	1.92	0.88	46	1.87	0.67	36
Zinc	43	0.47	0.23	49	0.39	0.10	26
Manganese	43	20.87	8.73	42	25.55	7.85	31
Iron	43	35.81	13.55	38	33.36	15.16	45
<u>Solum</u>							
Copper	43	1.84	0.48	26	1.83	0.46	25
Zinc	43	2.04	0.63	31	2.14	0.72	34
Manganese	43	32.81	7.98	24	31.27	8.53	27
Iron	43	77.39	17.53	23	58.35	21.91	38

lower only in the B horizon.

The CV values were used to compare variability of micronutrients between cultivated and native prairie transects. The comparison was done with a t-test. The variance associated with each CV was calculated from the formula:

$$s_{CV}^2 = [(CV^2)/2 N][1 + 2 (CV/100)^2] \quad [4.1]$$

where N is sample size (Sokal and Rohlf, 1969).

A direct comparison of the two adjacent transects reveals that spatial variation of DTPA-extractable micronutrients (mg kg^{-1}) was greater in the A horizon of the native prairie soil than in the cultivated one. In contrast, the spatial variation of Cu, Zn and Mn in the B horizon was larger under cultivated conditions. The change of variability patterns under cultivation may in part be attributed to the redistribution of soil organic matter and clay within the soil profile. A significant ($P < 0.01$) positive relationship was found between soil organic matter and both Zn and Mn under both systems examined (Table 4.1.2). However, significant spatial redistribution of surface soil due to tillage translocation has occurred during the initial years of cultivation (Kachanoski, 1984), which would also tend to reduce local differences in concentration values at the surface. A significant positive correlation between Cu and organic carbon was obtained only for the A horizon of the native prairie soil whereas no correlation existed between Fe and organic carbon (Table 4.1.2). However, there was a significant negative correlation between Fe and the bulk density of the cultivated soil B horizon (Table 4.1.2).

There was no relationship between horizon thickness in the cultivated field and the concentration of Cu, Zn and Mn (Table 4.1.2), which implies that these nutrients were homogeneously distributed in each of the two horizons sampled. However, approximately 15% of the variation in Fe concentration in the A horizon could be attributed to variation in the thickness of this horizon. The organic carbon content in the A horizon of both cultivated and native prairie soils was significantly but inversely correlated with the thickness of the horizon sampled (Kachanoski, 1984). Thus, higher concentrations of

Table 4.1.2 Correlation coefficients among micronutrients (mg kg^{-1}) and organic carbon (g kg^{-1}), bulk density (kg m^{-3}) and depth (cm) of soil horizon sampled.

Micronutrient	Organic Carbon		Bulk density		Thickness	
Horizon	A	B	A	B	A	B
<u>Native prairie</u>						
Cu	0.38**	0.11	-0.24	0.09	-0.35*	-0.25
Zn	0.66**	0.12	-0.35*	-0.31*	-0.47**	-0.28
Mn	0.31*	0.37*	-0.30*	-0.25	-0.31*	-0.03
Fe	0.26	0.27	-0.04	0.11	0.38**	0.33**
<u>Cultivated</u>						
Cu	-0.22	-0.17	-0.29	-0.05	-0.11	-0.04
Zn	0.45**	0.41**	-0.20	-0.32*	-0.04	0.27
Mn	0.29	0.62**	-0.09	-0.34*	0.02	-0.12
Fe	-0.05	0.19	-0.10	-0.35*	0.38*	0.04

*, ** Significant at the 0.05 and 0.01 probability levels, respectively

organic carbon were associated with less soil mass in the A horizon. This is probably associated with the mode of deposition of organic litter in the upper few centimeters of the soil. The micronutrients that exhibited significant positive correlation with organic C content in the A horizon of the native prairie soil also exhibited significant but inverse correlation with A horizon thickness (Table 4.1.2). This would also imply association of those micronutrients with organic matter and, thereby, partial dependence of their variation on the variation of organic carbon in the A horizon. However, this dependence as far as distribution is concerned, appears to have been disturbed under cultivation. No significant correlation was found

between B horizon thickness and organic carbon concentration (Kachanoski, 1984) or Cu, Mn and Zn concentrations.

The mean content (mg kg^{-1}) of Zn, Mn and Fe was higher in the A than in the B horizon, under both native prairie and cultivated conditions (Table 4.1.1). This trend has also been reported for Zn in various soils of the province of Saskatchewan by Stewart and Tahir (1971). The mean concentration of Cu in both horizons under both conditions was similar.

Another feature in Table 4.1.1 is the association of larger CV's with lower mean values of DTPA-extractable micronutrients. This is of extreme importance as an increased number of sampling cores would be required to obtain an estimated mean value as deficiency limits are approached.

The number of samples required to achieve 95% confidence limits for a range about the mean value of ± 5 , ± 10 and $\pm 20\%$ for Cu, Zn, Mn and Fe are given in Table 4.1.3. As standard procedures for soil testing involve taking samples at constant depth (usually 0-15 cm) and since there was no correlation between Cu, Zn and Mn concentration and depth in the cultivated soil (Table 4.1.2), the concentration of these micronutrients was calculated for the 0-15 cm depth, assuming that they are homogeneously distributed in each horizon. The number of samples required for constant depth sampling are given in Table 4.1.4. The results in Tables 4.1.3 and 4.1.4 reveal large differences among the number of samples required for each micronutrient in order to obtain estimates with the same degree of precision. Thus, the number of samples must vary depending on the micronutrient to be evaluated. Conversely, if the same number of samples is used for determination of

Table 4.1.3 Number of soil samples to give mean DTPA-extractable micronutrient values with specified confidence limits.

Specified confidence limits (95%) as percentage variation from mean	Cultivated field				Native prairie			
	Copper	Zinc	Manganese	Iron	Copper	Zinc	Manganese	Iron
	<u>A horizon</u>							
+ 5%	159	99	111	72	206	207	206	289
+ 10%	40	25	28	18	52	52	52	72
+ 20%	10	6	7	5	13	13	13	18
	<u>B horizon</u>							
+ 5%	322	368	269	220	197	101	145	317
+ 10%	81	92	68	55	49	25	36	79
+ 20%	20	23	17	14	12	6	9	20
	<u>Solum</u>							
+ 5%	105	149	91	79	97	174	114	217
+ 10%	26	37	23	20	24	43	29	54
+ 20%	7	9	6	5	6	11	7	14

Table 4.1.4 Number of constant depth (0-15 cm) soil samples from the cultivated field to give mean values of DTPA-extractable micronutrients with specified confidence limits.

Specified confidence limits (95%) as percentage variation from mean	Copper	Zinc	Manganese
$\pm 5\%$	134	115	111
$\pm 10\%$	34	29	28
$\pm 20\%$	9	7	7

all DTPA-extractable micronutrients the results for each micronutrient will be at different level of precision. The need for varying sample size according to the micronutrient under investigation has also been documented by Khan and Nortcliff (1982). Hence, it is important the the desired level of precision be determined prior to field sampling. For example, five samples are required to obtain a DTPA-extractable Fe value with no more than 20% variation from the true mean (Table 4.1.3). However, if no more than 5% variation is desirable, the sample size must be increased to 72 (Table 4.1.3). Calculation of Cu, Zn and Mn concentrations on a constant depth basis had virtually no effect on the number of samples required to obtain a true mean value for these micronutrients.

A statistical summary of the "total" DTPA-extractable micronutrients for the A and B horizons and total solum are given in Table 4.1.5. "Total" here refers to the content of extractable micronutrients in the total mass of each horizon or the solum. If

Table 4.1.5 Statistical summary for the "total" DTPA-extractable micronutrients in soils.

Micronutrient	Sample size No.	Cultivated field			Native prairie		
		Mean _{g m⁻²}	SD ±	CV %	Mean _{g m⁻²}	SD ±	CV %
<u>A horizon</u>							
Copper	46	0.49	0.26	53	0.36	0.16	43
Zinc	46	1.17	0.67	58	0.94	0.30	32
Manganese	46	13.10	6.81	52	7.72	2.90	38
Iron	46	37.24	20.15	54	18.69	8.23	44
<u>B horizon</u>							
Copper	43	0.61	0.28	46	0.57	0.23	41
Zinc	43	0.16	0.10	61	0.12	0.05	37
Manganese	43	7.18	3.34	47	8.05	3.84	48
Iron	43	11.91	5.40	45	11.16	7.72	69
<u>Solum</u>							
Copper	43	1.11	0.38	34	0.93	0.28	30
Zinc	43	1.33	0.71	53	1.06	0.32	30
Manganese	43	20.28	7.34	36	15.77	4.36	28
Iron	43	49.14	20.30	41	29.85	12.97	43

assessment of the micronutrient status of a field were to be based on the "total" amounts of micronutrients in the soil, a considerably larger number of samples would be required under cultivated conditions. However, under native conditions, the variability in the "total" amounts was of the same magnitude as for micronutrient concentration.

An important application of the variability information is in

the design of an efficient sampling plan. Peck and Melstead (1967) discussed the desirability of an accurate knowledge of soil variability in determining fertilizer requirement. If the variation is very large, a considerable portion of a field may remain deficient in a nutrient even though the extracted mean nutrient value may appear above critical levels of deficiency. Conversely, considerable portions of a field may contain adequate levels of a nutrient, in spite of a mean value indicating deficiency, thus resulting in waste of fertilizer. An illustration of the above can be offered by assuming that the B horizon of the cultivated soil is the medium for growth of a field crop. The mean Zn content in this horizon is 0.47 mg kg^{-1} , which is just below the critical level of 0.5 mg kg^{-1} used by the Saskatchewan Soil Testing Laboratory for a variety of crops. If a 5% precision with 95% confidence limit is required (i.e. $\pm 0.01 \text{ mg kg}^{-1}$ of DTPA-extractable Zn), 368 samples will be required. However, if the common practice of obtaining 12 samples is followed, the mean will have only a $\pm 28\%$ level of precision, i.e. $0.47 \pm 0.13 \text{ mg kg}^{-1}$ and could represent either deficient or sufficient levels of Zn in soil.

The large sample number suggested in this study to obtain estimates of micronutrient spatial variation may never be practical. However, knowledge of this variation is essential to properly interpret soil tests as well as results of field experimentation. The use of composite samples, which is the normally recommended procedure, can provide mean DTPA-extractable micronutrient levels, but offers no indication of spatial variation within the field. The latter is of great importance in the case of micronutrients as sufficiency and deficiency criteria often lie within narrow limits.

Statistical methods applied in this study to evaluate the spatial distribution of DTPA-extractable micronutrients are based on the assumption that the observations of a given variate are statistically independent regardless of their spatial position. However, this approach neglects the spatial correlation structure inherent in natural soils. Therefore, semivariograms were computed (Eq. 3.7, Section 3.1.4.2) to analyze structure of all the micronutrients in the A and B horizon of native and prairie soils. All the micronutrients were found to be randomly distributed, with the semivariograms showing no spatial dependence.

4.1.2 Spatial variability of Zn in undulating topography

The means, standard deviations, and coefficients of variation of DTPA-extractable soil Zn levels as well as Zn tissue concentration at FEEKES 10 growth stage for all the four transects are summarized in Table 4.1.6. Analysis for skewness and kurtosis was performed on all data to test the hypothesis that a given set of observations has been drawn from a population with normal distribution. The results of the

Table 4.1.6 Statistical summary for DTPA-extractable soil Zn levels and tissue Zn concentration at FEEKES 10 growth stage.

Transect	Sample No.	DTPA-extractable Zn			Tissue Zn conc.		
		Mean mg kg ⁻¹	SD ±	CV %	Mean mg kg ⁻¹	SD ±	CV %
A	50	0.56	0.33	59	12.3	4.2	35
B	50	0.65	0.22	34	16.6	3.6	22
C	50	3.51	0.62	18	37.9	5.2	14
D	50	1.01	0.77	76	19.3	8.1	42

analysis indicated insignificant amount of skewness and kurtosis, therefore, normal distribution was assumed. The importance of number of samples required to obtain a given precision with specific probability in level area has been discussed in detail (Section 4.1.1.). The number of samples required to estimate the mean of DTPA-extractable soil Zn levels and Zn tissue concentration with a specific probability at a given level of precision is given in Table 4.1.7. Similarly to the uniform topography field, a large number of samples were required to estimate DTPA-extractable soil Zn levels within 5, 10 and 20% of mean at the 95% confidence level.

As mentioned in Section 4.1.1, CV values with the help of the t-test can be used to compare the variability of the same parameter

Table 4.1.7 Number of samples to give mean DTPA-extractable soil Zn levels and tissue Zn concentration at FEEKES 10 growth stage with specified confidence limits.

Specified confidence limits (95%) as percentage variation from mean	Transects			
	A	B	C	D
<u>DTPA-extractable Zn</u>				
+ 5%	560	185	50	913
+ 10%	140	46	13	228
+ 20%	35	12	3	57
<u>Tissue Zn concentration</u>				
+ 5%	192	77	31	277
+ 10%	48	19	8	69
+ 20%	12	5	2	16

between either fields or mapping units. The same test can be used to compare two properties within a field. Equation 4.1 (Section 4.1.1) was used to compare the variability of DTPA-extractable soil Zn with that of tissue Zn concentration of a particular transect. Results of the t-test analysis for each transect indicated that DTPA-extractable soil Zn exhibited greater variability compared to tissue Zn concentration. This conclusion is supported by the smaller number of samples required to estimate the mean of tissue Zn concentration compared to that of soil Zn levels (Table 4.1.7). One would have expected that the variability of tissue Zn concentration is equal to or greater than that of DTPA-extractable soil Zn levels, since plant Zn uptake depends on other factors in addition to available soil Zn. However, since a great deal of variation can be avoided if specific plant parts or the whole plant is sampled at the same physiological stage (Bates, 1971), the smaller variability of tissue Zn concentration may be the result of the sampling procedure.

To examine whether there was a spatial dependence of DTPA-extractable soil Zn levels and tissue Zn concentration semivariograms were drawn (Eq. 3.7, Section 3.1.4.2) for transects A, B and C (Section 3.1.2). Since a semivariogram is only valid from about a half to about a third of the total sampling length (Journel and Huijbregts, 1978) semivariograms were computed only up to a lag of 25 m. Computation of semivariograms requires that the data should be stationary (Journel and Huijbregts, 1978), i.e. the expected value $E[Z(x)]$ of a random variable $Z(x)$ is constant and the covariance for each pair of random variable $[Z(x), Z(x+h)]$ is the same all over the field of interest and depends on distance (h). DTPA-extractable Zn in

transect D increased from 0.2 in the knoll position to 3.04 mg kg^{-1} at the depression and did not fulfill the requirement of data stationarity. Similarly the tissue Zn concentration ranged from 8.4 in the knoll to 47.5 mg kg^{-1} in the depression and did not meet the stationarity requirement. Hence, no semivariograms for transect D were computed.

Several theoretical models of conditionally positive definite type could be fitted to the experimental semivariogram. The experimental and theoretical (fitted) semivariograms of DTPA-extractable soil Zn levels and tissue Zn concentration are given in Figures 4.5, 4.6, 4.7 and 4.8. Using the minimum mean square deviation criterion, a linear model ($\gamma(h) = C_0 + b|h|$) with discontinuity at the origin (nugget effect) best fits the experimental semivariograms of DTPA-extractable soil Zn levels for all the transects. The semivariograms of tissue Zn concentration fits the linear model for transects A and C only. The fitted models (solid lines) show linear increase up to a lag of 25 m for transects A, B and C, respectively (Figures 4.5, 4.6, 4.7a and 4.8), except for tissue Zn concentration of transect B (Fig. 4.7b) indicating that they were spatially dependent up to 25 m. Therefore, samples separated by 25 m or more are generally not correlated to each other.

Although by definition $\gamma(h) = 0$ when $h = 0$, the lines in Figure 4.5 through 4.10 do not pass through the origin. Instead, there appears to be finite value, the nugget variance (C_0) to which $\gamma(h)$ approaches as h approaches zero. The nugget effect indicates micro-regionalization which may be due to both measurement error and to microvariabilities at scale which is less than the smallest distance

(a)

(b)

Figure 4.5 Experimental (black dots) and fitted models (solid lines) semivariograms for soil Zn; (a) transect A, (b) transect B.

Figure 4.6 Experimental (black dots) and fitted model (solid line) semivariogram for soil Zn of transect C.

(black dots) and fitted model (solid line)
 as for plant Zn; (a) transect A, (b) transect B.

Figure 4.8 Experimental (black dots) and fitted model (solid line) semivariogram for plant Zn of transect C.

between the sample points.

Statistical correlations between DTPA-extractable Zn levels and selected soil and plant parameters were quantitatively estimated by means of linear correlation. Linear correlation coefficients are given in Table 4.1.8. The amount of Zn extracted by DTPA was positively correlated with organic C and silt and negatively correlated with sand in all the transects. There was a significant negative correlation between DTPA-extractable Zn and soil pH or lime content in two of the four transects studied.

Table 4.1.8 Correlation coefficients between DTPA-extractable Zn and selected soil and plant parameters.

Transects	Plant-Zn mg kg ⁻¹	pH	Org. C	Inorg. C	Sand g kg ⁻¹	Silt	Clay
A	0.77**	-0.35*	0.69**	-0.20	-0.33*	0.31*	0.12
B	0.37**	-0.24	0.57**	-0.52**	-0.38**	0.39**	0.08
C	0.58**	-0.26	0.87**	-0.20	-0.58**	0.38**	0.10
D	0.73**	-0.52**	0.84**	-0.07	-0.34*	0.48**	0.04

*, ** Significant at the 0.05 and 0.01 probability levels, respectively.

Since a consistent and highly significant correlation between soil Zn and organic C (Table 4.1.8) was obtained in all the transects, an attempt was made to find out the spatial correlation between these two variables. This was done by making use of a cross-semivariogram (Eq. 4.2). An unbiased estimate for the cross-semivariogram between two soil properties u and v , $\gamma(uv)$, is obtained by assuming constant expectation for both u and v (Journel and Huijbregts, 1978).

$$\gamma_{uv}(h) = \frac{1}{2nh} \sum_{i=1}^{n(h)} ([u(x_{i+h}) - u(x_i)][v(x_{i+h}) - v(x_i)]) \quad [4.2]$$

The experimental cross-semivariograms between soil Zn and organic C for transects A, B and C are given in Figures 4.9 and 4.10. Linear models with discontinuity at the origin best fit the experimental cross-semivariograms. Organic matter supplies complexing agents which promote the availability of certain elements (Hodgson, 1963). The fact that extractable Zn was correlated with organic C indicates that organic C has a major effect on DTPA-extractable Zn. The cross-semivariograms presented in Figures 4.9 and 4.10 demonstrate that the two parameters have the same spatial structure. This also suggests that the spatial structure of soil Zn can be inferred from the spatial structure of organic C for a particular soil mapping unit or soil site. This conclusion agrees with the earlier findings of Stewart and Tahir (1971), who found a highly significant positive correlation between DTPA-extractable soil Zn levels and organic C contents in 24 soils of Saskatchewan.

A significant correlation was obtained between DTPA-extractable soil Zn and plant Zn (Table 4.1.8). This indicates that soil variability was reflected in plant Zn content.

Figure 4.9 Experimental (black dots) and fitted models (solid lines) cross-semivariograms between soil Zn and organic carbon; (a) transect A, (b) transect B.

Figure 4.10 Experimental (black dots) and fitted model (solid line) cross-semivariogram between soil Zn and organic carbon for transect C.

4.2 Importance of Zn to Crop Nutrition and Production of Common Crops

4.2.1 Zinc status of Saskatchewan soils

4.2.1.1 Exploratory surveys

Approximately 12% of the soil samples in the population examined had Zn levels below the critical value of 0.5 mg kg^{-1} soil (Class 1) adopted by the SSTL, while approximately 37% belonged to Class 2 (Table 4.2.1). DTPA-extractable Zn levels ranged between 0.2 and 10.0 mg kg^{-1} with an average value of 1.7 mg kg^{-1} ($\text{SD} \pm 1.6$). In contrast to Cu, where most soil samples containing marginal levels belonged to identifiable soil associations (Kruger et al., 1985), soils in Zn Class 1 represented localized conditions rather than generalized areas and had the following characteristics: They were either (i) loams with lime present and/or pH between 7.9 and 8.2, or (ii) clay loams, clays and heavy clays (within the Fox Valley, Sceptre, Echo, Ardill, Amulet, Trossachs and Regina soil associations (Mitchell et al., 1944; Ellis et al., 1965b)) with lime present (>70% of the cases) and/or with pH in the range of 7.8 to 8.3 (>85% of the cases), or (iii) sands with pH 7.0 to 8.0.

Table 4.2.1 Distribution of DTPA-extractable Zn levels.

Class	DTPA-extractable Zn levels (mg kg^{-1})	Distribution (%)
1	<0.50	12
2	0.50-1.0	37
3	>1.0	51

There are a number of reports that suggest that Zn availability is highly related to pH and calcium carbonate content of soils. Both Zn solubility (Lindsay and Norvell, 1969) and Zn adsorption by soil colloids (Shuman, 1980) are strongly pH dependent. Further, since Zn is strongly adsorbed on calcium carbonate (Udo et al., 1970), this may explain why low DTPA-extractable soil Zn levels were associated with high lime content soils. Furthermore, it has been shown that liming of acid soils decreased the concentration of soluble Zn (MacLean et al., 1972) and that DTPA-extractable Zn levels were inversely related to calcium carbonate content of soils (Mashhady, 1983).

4.2.1.2 Field experiments with Zn fertilizers

A number of field trials were conducted during 1982, 1983 and 1984 on several soils belonging to the three classes in Table 4.2.1. Detailed results of all 1982 and 1983 experiments grouped on the basis of soil Zn levels are presented in Tables 4.2.2, 4.2.3 and 4.2.4 and are summarized on a per crop and Soil Zone basis in Table 4.2.5. The results indicate that crops grown on mineral soils in Saskatchewan are not likely to respond to Zn fertilization. Eleven experiments (27 treatments) with spring wheat (hard red or soft red or white), six experiments (12 treatments) with barley and six experiments (15 treatments) with lentils, peas, alfalfa, corn and flax produced only one significant yield increase (Table 4.2.5), i.e. <2% of the treatments applied. Similar results have been found in the neighboring province of Manitoba, where seven experiments with black beans and 16 with corn have only produced one significant yield response to Zn for each crop, while yields of cereals, flax and alfalfa in a number of

Table 4.2.2 Crop yield responses to Zn fertilization on soils in Class 1 of soil Zn levels

Site [†] no.	Crop	Part	Control	Mg ha ⁻¹			CV %	SE
				Zn sulfate (shelf-chemical) 10 kg Zn ha ⁻¹	Zn sulfate (fertilizer) 10 kg Zn ha ⁻¹	Zn chelate (fertilizer) 1 kg Zn ha ⁻¹		
1	Spring wheat	Grain	1.92a ^ε	1.92a	-	2.36a	38.4	0.18
		Straw	2.72b	2.82a	-	3.52b	37.0	0.24
2	Spring wheat	Grain	2.29a	2.08a	-	2.36a	13.2	0.07
		Straw	2.84a	2.70a	-	2.89a	18.0	0.13
7	Barley	Grain	3.04a	3.18a	3.53a	-	15.2	0.12
		Straw	4.19b	6.96a	6.29a	-	23.1	0.34
9	Barley	Grain	3.46a	3.31a	-	3.26a	10.8	0.09
		Straw	2.92a	2.85a	-	2.79a	14.0	0.10
20	Spring wheat ^ψ	-	-	-	-	-	-	-

[†]See Table 3.1 for soil characteristics.^εMean followed horizontally by the same letter are not statistically different at P < 0.05 (Duncan's Multiple Range Test).^ψSite lost in 1983 due to midge infection.

Table 4.2.3 Crop yield responses to Zn fertilization obtained on soils in Class 2 of soil Zn levels.

Site [†] no.	Crop	Part	Control	Na ₂ SO ₄	Zn oxide (shelf- chemical)	Zn sulfate (shelf- chemical)	Zn sulfate (fertilizer)	Zn chelate		CV %	SE
								Foliar 0.35 kg Zn ha ⁻¹	Soil applied 1 kg Zn ha ⁻¹		
Mg ha ⁻¹											
6	Spring wheat	Grain	3.30ab [†]	2.92bc	3.60a	3.13ab	2.75ab	2.54c	-	13.1	0.10
		Straw	6.01a	5.15a	5.17a	5.30a	4.78a	5.55a	-	11.9	0.16
8	Spring wheat [£]	-	-	-	-	-	-	-	-	-	-
10	Corn	Grain	1.26b	1.23b	1.04b	1.32b	1.04b	1.69a	-	20.7	0.65
		Stoves	5.96a	5.88a	6.91a	6.14a	5.81a	7.06a	-	10.4	0.16
12	Barley	Grain	5.17a	-	-	-	(2) [¶] 5.66a (4) [¶] 4.98a	-	-	11.4	0.15
		Straw	6.02a	-	-	-	(2) [¶] 6.08a (4) [¶] 5.72a	-	-	9.5	0.14
13	Spring wheat [£]	-	-	-	-	-	-	-	-	-	-
15	Lentils	Seed	1.37a	1.20a	1.41a	1.38a	1.31a	1.39a	-	7.6	0.05
		Vegetative	2.38a	2.69a	2.30a	2.43a	2.44a	2.52a	-	7.3	0.09
16	Spring wheat	Grain	2.08a	1.73a	2.18a	2.15a	2.38a	2.57a	-	18.1	0.10
		Straw	4.90a	3.53a	4.55a	4.87a	4.23a	5.42a	-	17.2	0.20
17	Spring wheat	Grain	3.25a	3.32a	3.31a	3.30a	3.31a	2.80b	-	7.0	0.06
		Straw	6.42a	5.76a	6.52ab	5.81bc	5.32bc	4.85c	-	12.8	0.19
18	Spring wheat	Grain	3.96a	-	-	-	4.23a	-	-	13.1	0.13
		Straw	6.40a	-	-	-	7.41a	-	-	15.0	0.26

Table 4.2.3 Continued.

Site no.	Crop	Part	Control	Na ₂ SO ₄	Zn oxide (shelf-chemical)	Zn sulfate (shelf-chemical)	Zn sulfate (fertilizer)	Zn chelate		CV %
								Foliar 0.35 kg Zn ha ⁻¹	Soil applied 1 kg Zn ha ⁻¹	
						10 kg Zn ha ⁻¹				
								Mg ha ⁻¹		
19	Spring wheat	Grain	2.42a	-	-	-	2.14a	(6) 2.04a (10) 2.14a (6+10) 2.19a	2.41a	13.6 0.08
		Straw	3.36a	-	-	-	2.75a	(6) 2.70a (10) 3.02a (6+10) 2.92a	3.23a	14.4 0.11
22	Peas	Seed	2.28a	-	-	-	2.55a	-	-	7.7 0.05
		Vegetative	3.82b	-	-	-	5.81a	-	-	24.0 0.29

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† See Table 3.1 for soil characteristics

‡ Mean followed horizontally by the same letter are not statistically different at P < 0.05 (Duncan's Multiple Range Test)

§ Seed placed at 2 or 4 kg Zn ha⁻¹

ε Site lost in 1983 due to midge infection

Table 4.2.4 Crop yield responses to Zn fertilization obtained on soils in Class 3 of soil Zn levels.

Site [†] no.	Crop	Part	Control	Na ₂ SO ₄	Zn oxide (shelf- chemical)	Zn sulfate		Zn chelate (foliar) 0.35 kg Zn ha ⁻¹	CV %	SE
						(shelf- chemical)	(fertilizer)			
						10 kg Zn ha ⁻¹				
						Mg ha ⁻¹				
3	Barley	Grain	1.61a ^ε	-	-	-	1.52a	-	12.6	0.05
		Straw	3.44a	-	-	-	3.76a	-	9.0	0.08
4	Barley	Grain	1.74a	1.88a	1.66a	1.95a	1.97a	1.99a	16.2	0.08
		Straw	5.89a	6.33a	7.05	6.39a	6.50a	6.23a	7.9	0.13
5	Barley	Grain	2.19a	-	-	-	1.80a	-	21.7	0.11
		Straw	6.19a	-	-	-	5.57a	-	15.6	0.23
11	Spring wheat	Grain	2.50a	-	-	-	2.46a	-	5.8	0.04
		Straw	3.69a	-	-	-	3.42a	-	9.0	0.08
14	Alfalfa	Whole	5.15bc	8.49a	4.82c	6.17ab	7.98a	-	26.2	0.43
21	Peas	Seed	1.89a	-	-	-	1.87a	-	6.1	0.03
		Vegetative	4.85a	-	-	-	4.37a	-	15.4	0.18
23	Spring wheat	Grain	2.21a	-	-	-	2.04a	-	15.7	0.08
		Straw	5.02a	-	-	-	4.48a	-	20.2	0.24

[†]See Table 3.1 for soil characteristics

^εMean followed horizontally by the same letter are not statistically different at P < 0.05 (Duncan's Multiple Range Test)

Table 4.2.5 Summary of Zn field experiments in Saskatchewan during 1982-84.

Crop	Soil zone	Total no. of experiments	No. of treatments			No. of treatments which responded		
			Soil	Foliar	Total	Soil	Foliar	Total
Spring wheat	Brown	6†	13	5	18	0	0	0
	D. Brown	4†	7	0	7	0	0	0
	Black	1	1	0	4	0	0	0
	Grey	1	3	1	4	0	0 ^E	0
	Sub total	12	24	6	30	0	0	0
Barley	D. Brown	1	2	0	2	0	0	0
	Black	1	1	0	1	0	0	0
	Grey	4	8	1	9	0	0	0
	Sub total	6	11	1	12	0	0	0
Lentil	D. Brown	1	3	1	4	0	0	0
Peas	Grey	2	2	0	2	0	0	0
Alfalfa	Black	1	3	0	3	0 ^ψ	0	0
Corn	D. Brown	1	3	1	4	0	1	1
Flax	Grey	1†	2	0	2	0	0	0
	Total	23	48	9	57	0	1	1

[†]Numbers include experiments carried out in 1984^εReduction in yield probably due to spray damage of the crop^ψBenefit from the sulfate component of Zn sulfate fertilizer observed

experiments were not increased as a result of micronutrient fertilizer application (Loewen-Rudgers et al., 1983). No responses to Zn fertilization have also been obtained in field studies with corn and sunflower in northern West Virginia and North Dakota soils in spite of soil test levels of Zn below the critical limit (Stout and Bennett, 1983; Hilton and Zubriski, 1985).

Zinc fertilization of field crops did not always increase the Zn concentrations in plant tissue during the growing season or those of grain and straw (Tables 4.2.6, 4.1.7 and 4.2.8). Only in 25% of the cases did Zn fertilization cause a significant increase in Zn levels in plant tissue of various crops (Table 4.2.9). These results would indicate that Zn from soil sources was sufficient to meet the Zn uptake requirements by various crops.

Soil applied Zn-sulfate had a residual effect as far as DTPA-extractable Zn soil levels are concerned (Table 4.2.11). Soil application of Zn-chelate resulted in increased DTPA-extractable Zn levels in two of the four experiments in spite of the low application rates (Table 4.2.11). No yield benefits were obtained, however, from residual Zn levels in either case (Table 4.2.10). This would indicate that Zn was not limiting grain yield. Relatively large soil applications of Zn have been found to exert an appreciable influence for a relatively long period of time. Boawn et al. (1960) reported that high proportion of Zn from 9 and 18 kg Zn ha⁻¹ application rates were still present in the acid extract of a Ritzville fine sand loam after 5 years. Application of 11 and 22 kg Zn ha⁻¹ as Zn sulfate reflected residual Zn availability by soil and plant analysis after 2 years (Ellis et al., 1965a). Ohki et al. (1976) observed increased corn

Table 4.2.6 Concentration of Zn in plant tissue of crops grown on soils in Class 1 of soil Zn levels.

Site no. †	Crop	Growth stage or plant part	Control	mg kg ⁻¹		CV %	SE
				Zn sulfate (shelf-chemical) 10 kg Zn ha ⁻¹	Zn chelate (fertilizer) 1 kg Zn ha ⁻¹		
1	Spring wheat	FECKES 6	24.9b ^ε	33.3a	34.4a	38.0	4.2
		Grain	27.0b	49.0a	37.0a	34.8	3.5
		Straw	13.6b	14.7b	12.2a	42.1	1.1
2	Spring wheat	FECKES 10 (whole)	22.6b	24.0a	25.80a	20.0	0.7
		FECKES 10 (flag leaf)	20.3a	26.4a	22.9a	21.2	1.2
		Grain	20.5a	28.8a	30.5a	28.3	1.9
7	Barley	FECKES 6	25.0a	33.0a	-	14.8	1.8
9	Barley	FECKES 6	26.5b	32.9a	34.1a	18.8	1.4
		Grain	29.8b	33.3ab	36.3a	12.6	1.1
20	Spring wheat	FECKES 6	25.3	30.9ab	34.8a	62.4	3.8

† See Table 3.1 for soil characteristics

ε Mean followed horizontally by the same letter are not statistically different at P < 0.05 (Duncan's Multiple Range Test)

Table 4.2.7 Concentration of Zn in plant tissue of crops grown on soils in Class 2 of soil Zn levels

Site no.	Crop	Growth stage or plant part	Control	Na ₂ SO ₄	Zn oxide (shelf- chemical)	Zn sulfate (shelf- chemical)	Zn sulfate (fertilizer)	Zn chelate		CV %	SE
								Foliar 0.35 kg Zn ha ⁻¹	Soil applied 1 kg Zn ha ⁻¹		

[†]See Table 3.1 for soil characteristics

[‡]Mean followed horizontally by the same letter are not statistically different at P < 0.05 (Duncan's Multiple Range Test)

[§]Seed placed at 2 or 4 kg Zn ha⁻¹

[‡]Foliar application made at FEKES 6 (6), FEKES 10 (10) or FEKES 6+10 (6+10) growth stages

Table 4.2.8 Concentration of Zn in plant tissue of crops grown on soils in Class 3 of soil Zn levels.

Site no.	Crop	Growth stage or plant part	Control	Na ₂ SO ₄	Zn oxide (shelf-chemical)	Zn sulfate (shelf-chemical)	Zn sulfate (fertilizer)	CV %	SE
						10 kg Zn ha ⁻¹			
4	Barley	FEEKES 6	31.0a ^ε	32.0a	34.0a	36.0a	34.0a	11.7	1.0
5	Barley	FEEKES 6	38.0a	-	-	-	43.0a	11.7	1.2
14	Alfalfa	Whole	28.0a	29.0a	35.0a	24.0a	32.0a	24.1	1.8
21	Peas	Flowering	20.0b	-	-	-	29.0a	26.3	1.6

[†] See Table 3.1 for soil characteristics

^ε Mean followed horizontally by the same letter are not statistically different at P < 0.05 (Duncan's Multiple Range Test)

Table 4.2.9 Summary of responses in plant tissue Zn concentrations in various crops.

	Growth state or plant part	Total no. of experiments	Total no. of treatments	No. of treatments with Zn levels higher than control
Cereals	FEKES 6	14	29	6
	FEKES 10 (whole)	1	2	2
	FEKES 10 (flag leaf)	1	2	0
	Grain	4	11	4
	Straw	4	11	7
Lentil, alfalfa, corn		3	9	0
Peas	Flowering	2	2	2
	Diagnostic stage			
	Total Class 1	5	11	7
	Total Class 2	11	25	2
	Total Class 3	4	5	1
	Total	20	41	10

Table 4.2.10 Crop yield responses to residual Zn in 1984 following 1983 application.

Site no. [†]	Crop	Part	Control	Mg ha ⁻¹			CV (%)	SE
				Zn sulfate ^ε	Zn chelate ^ψ	Zn chelate ^ψ		
2	Spring wheat	Grain	1.53a	1.94a	1.83a	1.83a	19.5	0.09
		Straw	3.19a	3.35a	3.33a	3.33a	12.1	0.10
8	Flax	Grain	1.24a	1.43a	1.31a	1.31a	23.5	0.08
		Straw	1.91a	2.16a	1.82a	1.82a	22.2	0.11
13	Spring wheat	Grain	1.37a	1.65a	1.93a	1.93a	24.0	0.10
		Straw	3.34a	2.60a	2.84a	2.84a	18.7	0.14
19	Spring wheat	Grain	1.75a	1.77a	1.84a	1.84a	26.7	0.10
		Straw	1.34a	1.34a	1.27a	1.27a	15.6	0.07

[†]See Table 3.1 for soil characteristics^εApplied at 10 kg Zn ha⁻¹^ψApplied at 1 kg Zn ha⁻¹

Table 4.2.11 DTPA-extractable Zn levels in soil samples (0-15 cm).

Site no.	Control (whole site)	Control	Zn sulfate†	Zn chelate‡
	-----1983-----	-----1984-----		
		mg kg ⁻¹		
2	0.35	0.40	1.54	0.77
8	0.60	1.10	1.60	1.68
13	0.55	0.55	2.28	0.64
19	0.75	0.60	1.50	0.65

† Applied at 10 kg Zn ha⁻¹‡ Applied at 1 kg Zn ha⁻¹

tissue Zn concentration and soil Zn levels at higher Zn rates indicating that residual effects were evident through the fourth growing year after Zn application. However, plant dry weight and grain yield were not affected significantly by residual Zn levels.

4.2.2 P X Zn interaction in wheat

4.2.2.1 Yields

Phosphate applied in 1979 resulted in increased resin extractable P levels six years after application (18.6, 28.2 and 58 kg ha⁻¹ for the check and applied P rates of 80 and 160 kg P ha⁻¹, respectively). Grain and straw yield of wheat grown on P treatments only was significantly higher than the control (Tables 4.2.12 and 4.2.13). However, there was no significant difference in grain yield between 80 and 160 kg P ha⁻¹ treatments (Tables 4.2.12 and 4.2.13). Similar long-term responses to residual phosphate levels have been observed in northern Great Plains soils and crops (Read et al., 1973; 1977; Halvorson and Black, 1985a,b).

Mean grain yield responses to soil applied Zn were significant with both types of Zn fertilizers (Tables 4.2.12 and 4.2.13). Foliar application of Zn-chelate at either FEEKES 6 or FEEKES 10 growth stage was equally effective in increasing grain yield (Table 4.2.13). The P X Zn interaction was significant for each source of applied Zn as demonstrated in grain yield. In all three experiments, yield responses to P were significantly larger when Zn was applied. At 80 kg P ha⁻¹, addition of Zn-sulfate increased grain yield from 1.72 to 2.42 Mg ha⁻¹ (Tables 4.2.12 and 4.2.13). Addition of Zn-chelate at the same P treatment resulted in significant response from 1.72 to 2.12 Mg ha⁻¹ (Tables 4.2.12 and 4.2.13). On the check P plots however, there was no response to any source of applied Zn (Tables 4.2.12 and 4.2.13). A 42% increase in yield above the residual effect of 80 kg P ha⁻¹, or 0.72 Mg of grain ha⁻¹ could be attributed to foliar applied Zn in this treatment. The corresponding additional

Table 4.2.12 Effect of P applied in 1979 and Zn applied in 1984 on the grain and straw yield of wheat.

Sources of applied Zn											
Zn-sulfate				Zn-chelate				Zn-chelate foliar			
Treatment		Yield		Treatment		Yield		Treatment		Yield	
P	Zn	Grain	Straw	P	Zn	Grain	Straw	P	Zn	Grain	Straw
-kg ha ⁻¹ -		-----Mg ha ⁻¹ -----		-kg ha ⁻¹ -		-----Mg ha ⁻¹ -----		-----kg ha ⁻¹ -----		-----Mg ha ⁻¹ -----	
0	0	1.44	2.34	0	0	1.44	2.34	0	0	1.44	2.30
	5	1.47	2.19		0.5	1.34	2.15		0.35T [†]	1.43	2.27
	10	1.43	2.19		1.0	1.45	2.15		0.35F [‡]	1.48	2.39
	20	1.49	2.20		2.0	1.37	2.28				
80	0	1.72	2.44	80	0	1.72	2.44	80	0	1.72	2.44
	5	2.06	2.57		0.5	2.23	2.39		0.35T	2.32	2.89
	10	2.24	2.96		1.0	2.22	3.01		0.35F	2.44	2.90
	20	2.42	2.91		2.0	2.30	2.85				
160	0	1.89	3.09	160	0	1.89	3.09	160	0	1.89	3.09
	5	2.03	2.97		0.5	2.07	3.17		0.35T	2.25	3.28
	10	2.40	3.24		1.0	2.05	3.07		0.35F	2.53	2.95
	20	2.31	2.91		2.0	2.16	3.02				

^{†,‡} Zn applied at FEEKES-6 and FEEKES-10 growth stage, respectively.

Table 4.2.13 Mean squares from the analysis of variance for grain and straw yield of wheat.

Source	df	Sources of applied Zn						df	Source	Zn-chelate foliar		Yield	Straw
		Zn-sulfate			Zn-chelate								
		Grain	Yield	Straw	Grain	Yield	Straw						
<u>P effects</u>													
0 vs 80+160(P1)	1	6.09**	5.81**		6.15**	5.73**		0 vs 80+160(P1)	1	5.42**		3.57*	
80 vs 160(P2)	1	0.02	1.08*		0.06	1.69*		80 vs 160(P2)	1	0.03		1.00	
Error 1	8	0.06	0.19		0.02	0.33		Error 1	8	0.04		0.40	
<u>Zn effects</u>													
Zn linear	1	1.20**	0.06		0.41*	0.14		0 vs 0.35T+0.35F(Zn1)	1	1.53**		0.25	
Zn quadratic	1	0.20*	0.09		0.16*	0.01		0.35T vs 0.35F(Zn2)	1	0.17		0.03	
Zn cubic	1	0.01	0.25		0.03	0.15							
<u>Interaction effects</u>													
P1 x Zn linear	1	0.48**	0.16		0.29**	0.08		P1 x Zn1	1	0.70**		0.14	
P1 x Zn quadratic	1	0.14	0.20		0.08	0.02		P2 x Zn1	1	0.04		0.31	
P1 x Zn cubic	1	0.03	0.06		0.14*	0.02		P1 x Zn2	1	0.04		0.14	
P2 x Zn linear	1	0.07	0.55		0.08	0.51*		P2 x Zn2	1	0.03		0.14	
P2 x Zn quadratic	1	0.01	0.01		0.10	0.05		Error 2	24	0.07		0.15	
P2 x Zn cubic	1	0.07	0.00		0.02	0.38							
Error 2	36	0.04	0.16		0.03	0.11							

*,** Indicates 0.05 and 0.01 significance level, respectively

benefits with the application of Zn-sulfate and Zn-chelate were 30 and 31% yield increases or 0.52 and 0.53 Mg of grain ha⁻¹, respectively (Table 4.2.12).

4.2.2.2 Nutrient distribution in the foliage

The concentrations of P in wheat plant tissue at FEEKES 6 and FEEKES 10 growth stages was not affected by either Zn-source or Zn application rate (Tables 4.2.14 and 4.2.15). However, the P concentration was significantly higher in the treatments that received 80 and 160 kg P ha⁻¹ 6 years before than in the control.

The Zn concentration in wheat plant tissue responded to Zn rate for both soil applied sources at FEEKES 6 and at FEEKES 10 (Table 4.2.15). Foliar application of Zn-chelate at FEEKES 6 stage caused a significant increase in the Zn concentration at FEEKES 10 (Table 4.2.16). The residual amounts of P six years after application resulted in significant decrease in the Zn concentration of plant tissue at both growth stages. In addition, the Zn concentration at FEEKES 10 of plants grown on treatments where large amounts of P had been applied six years before (Tables 4.2.14 and 4.2.16), approached that considered critical (20 mg Zn kg⁻¹) for normal plant growth (Melsted et al., 1969; Radjagukguk et al., 1980).

4.2.2.3 Nutrient uptake and distribution at maturity

The residual soil P levels in the 80 or 160 kg P ha⁻¹ treatments resulted in a significant decrease in the Zn concentration and uptake in straw, but in grain, only the Zn concentration was decreased significantly (Tables 4.2.17 to 4.2.22). However, there

Table 4.2.14 Effect of P applied in 1979 and soil applied Zn in 1984 on tissue Zn and P concentration of wheat at FEEKES-6 and FEEKES-10 growth stages.

Treatment		Sources of applied Zn									
		Zn-sulfate					Zn-chelate				
		FEEKES-6		FEEKES-10		Zn conc.	FEEKES-6		FEEKES-10		Zn conc.
P	Zn	Zn conc.	P conc.	Zn conc.	P conc.		P conc.	P conc.	Zn conc.	P conc.	P conc.
--kg ha ⁻¹ --		mg kg ⁻¹	g kg ⁻¹	mg kg ⁻¹	g kg ⁻¹	mg kg ⁻¹	g kg ⁻¹	g kg ⁻¹	mg kg ⁻¹	g kg ⁻¹	g kg ⁻¹
0	0(0) [†]	29.7	3.11	34.3	1.82	29.7	3.11		34.3		1.82
	5(0.5)	48.1	3.04	31.9	1.69	52.6	3.05		36.8		1.88
	10(1.0)	53.4	3.09	35.1	1.75	44.5	3.05		38.6		1.80
	20(2.0)	48.1	3.20	35.8	1.84	44.6	3.01		34.3		1.97
80	0(0)	26.7	3.62	18.4	2.18	26.7	3.62		18.4		2.18
	5(0.5)	46.3	3.77	25.6	2.12	40.7	3.69		23.6		2.07
	10(1.0)	47.6	3.77	24.5	2.11	41.1	3.70		23.7		2.09
	20(2.0)	38.1	3.71	26.4	2.22	46.7	3.72		24.7		2.05
160	0(0)	23.0	3.82	16.2	2.69	23.0	3.82		16.2		2.69
	5(0.5)	37.0	4.11	21.5	2.49	44.1	3.96		17.3		2.61
	10(1.0)	33.3	3.96	19.5	2.68	38.3	3.98		20.8		2.61
	20(2.0)	44.8	3.97	20.6	2.60	38.1	4.19		21.1		2.60

[†] Rate of Zn-chelate applied

Table 4.2.15 Mean squares from the analysis of variance for tissue Zn and P concentration of wheat.

Source	df	Sources of applied Zn							
		Zn-sulfate				Zn-chelate			
		FEEKES-6		FEEKES-10		FEEKES-6		FEEKES-10	
		Zn conc.	P conc.	Zn conc.	P conc.	Zn conc.	P conc.	Zn conc.	P conc.
<u>P effects</u>									
0 vs 80+160(P1)	1	604.54**	7.10**	2144.61**	4.93**	405.17*	8.00**	2322.70**	3.29**
80 vs 160(P2)	1	0.00	0.60**	1778.16**	2.12**	658.82**	1.40**	0.00	2.37**
Error 1	8	55.09	0.03	44.64	0.10	50.47	0.12	17.39	0.10
<u>Zn effects</u>									
Zn linear	1	1571.27**	0.05	131.35*	0.01	1222.86**	0.09	120.48*	0.00
Zn quadratic	1	1639.36**	0.04	30.19	0.08	1236.40**	0.00	56.99	0.03
Zn cubic	1	145.75	0.04	204.09*	0.07	1048.75**	0.03	0.00	0.00
<u>Interaction effects</u>									
P1 x Zn linear	1	9.05	0.00	9.78	0.01	38.00	0.15	72.29	0.09
P1 x Zn quadratic	1	83.74	0.11	39.02	0.00	25.39	0.01	17.21	0.00
P1 x Zn cubic	1	35.03	0.06	76.91	0.00	49.58	0.01	2.51	0.04
P2 x Zn linear	1	177.86	0.00	15.58	0.01	74.29	0.12	2.16	0.00
P2 x Zn quadratic	1	411.44*	0.00	2.46	0.00	58.64	0.01	15.60	0.00
P2 x Zn cubic	1	687.06**	0.03	317.23**	0.07	486.91**	0.07	32.34	0.09
Error 2	36	65.98	0.08	29.20	0.03	44.59	0.03	23.33	0.03

*, ** Indicate 0.05 and 0.01 significance levels, respectively

Table 4.2.16 Effect of P applied in 1979 and foliarly applied Zn-chelate in 1984 on tissue Zn concentration at FEEKES 10 growth stage.

Treatment		FEEKES 10
P	Zn	Zn conc.
— kg ha ⁻¹ —		mg kg ⁻¹
0	0	34.3
	0.35T [†]	44.9
80	0	18.4
	0.35T	32.1
100	0	16.2
	0.35T	28.4

Statistical significance

Source	df	Mean square
<u>P effects</u>		
0 vs 80 + 160(P1)	1	1669.53 ^{**}
80 vs 160(P2)	1	43.51
Error 1	8	26.84
<u>Zn effects</u>		
0 vs 0.35T [†] (Zn)	1	1110.20 ^{**}
<u>Interaction effects</u>		
P1 X Zn	1	9.20
P2 X Zn	1	2.80
Error 2	12	39.59

[†] Zn-chelate applied at FEEKES 6 stage

^{**} Indicate 0.01 significance level

were no differences in the Zn concentration of grain or straw between the 80 and 160 kg P ha⁻¹ treatments. Application of Zn to the soil either as Zn-sulfate or Zn-chelate increased Zn concentration in the grain but generally had no effect on the Zn levels in the straw (Tables 4.2.17, 4.2.18, 4.2.20 and 4.2.21). In contrast, foliarly applied Zn increased Zn concentrations in both grain and straw at maturity (Tables 4.2.19 and 4.2.22). This increase was independent of the growth stage at which foliar Zn was applied (Table 4.2.22). In the 0 kg Zn ha⁻¹ treatment total uptake of Zn into the above ground plant parts (grain + straw) decreased from 107.2 g Zn ha⁻¹ in 0 kg P ha⁻¹ to 87.2 and 88.1 g Zn ha⁻¹ in the 80 and 160 kg P ha⁻¹ treatments, respectively. These decreases in the Zn concentration of total above ground dry matter amounted to 27 and 35% for the corresponding P treatments and can only be partly explained by the corresponding increase in total above ground dry matter yield of 10 and 32%. Hence, a P induced Zn deficiency in this experiment can only be partly explained by a dilution effect.

The significant P X Zn interaction on the grain yield was also accompanied by a significant interaction on Zn uptake for the Zn-sulfate and foliar Zn-chelate treatments (Tables 4.2.20 and 4.2.22). Zn uptake into the grain was increased only when Zn was applied in the presence of P (Tables 4.2.18 and 4.2.19).

The concentration and uptake of P into grain in all cases were affected significantly by both P and Zn rates (Tables 4.2.17 to 4.2.22). A significant P X Zn interaction on P uptake into grain was evident both with soil and foliarly applied Zn.

Table 4.2.17 Effect of P applied in 1979 and Zn-sulfate applied in 1984 on Zn and P concentration and uptake of wheat grain and straw.

Treatment		Grain				Straw			
P	Zn	Zn conc.	Zn uptake	P conc.	P uptake	Zn conc.	Zn uptake	P conc.	P uptake
-kg ha^{-1}		mg kg^{-1}	g ha^{-1}	g kg^{-1}	kg ha^{-1}	mg kg^{-1}	g ha^{-1}	mg kg^{-1}	kg ha^{-1}
0	0	49.8	72.1	2.8	4.00	15.0	35.1	90	0.20
	5	55.4	81.6	2.9	4.23	22.0	46.8	100	0.22
	10	55.4	79.2	2.8	3.97	21.2	49.0	90	0.20
	20	57.8	86.3	2.9	4.04	24.0	48.4	100	0.23
80	0	38.0	64.5	3.4	5.72	9.6	22.7	180	0.43
	5	40.6	83.3	3.7	7.55	7.0	17.8	200	0.56
	10	45.0	99.9	3.8	8.44	9.6	28.8	190	0.55
	20	45.4	109.7	3.7	8.98	10.2	28.6	240	0.66
160	0	34.6	65.1	4.0	7.48	8.0	23.0	350	1.00
	5	36.4	74.3	4.0	8.09	7.2	21.4	310	0.91
	10	37.6	90.0	3.9	10.29	7.8	25.5	320	1.02
	20	41.6	97.6	4.4	10.15	8.8	24.6	420	1.12

Table 4.2.18 Effect of P applied in 1979 and Zn-chelate applied in 1984 on Zn and P concentration and uptake of wheat grain and straw.

Treatment		Grain				Straw			
		Zn conc.	Zn uptake	P conc.	P uptake	Zn conc.	Zn uptake	P conc.	P uptake
P	Zn	mg kg ⁻¹	g ha ⁻¹	g kg ⁻¹	kg ha ⁻¹	mg kg ⁻¹	g ha ⁻¹	mg kg ⁻¹	kg ha ⁻¹
-kg ha ⁻¹									
0	0	49.8	72.1	2.8	4.00	15.0	35.1	90	0.20
	0.5	51.6	68.3	2.8	3.76	22.2	49.7	120	0.25
	1.0	55.0	79.7	2.7	3.88	15.0	32.5	90	0.18
	2.0	56.4	77.0	2.9	3.91	20.8	45.8	90	0.20
80	0	38.0	64.5	3.4	5.72	9.6	22.7	180	0.43
	0.5	45.4	101.5	3.7	8.25	10.0	23.2	260	0.59
	1.0	41.4	92.0	3.3	7.38	6.6	19.9	210	0.50
	2.0	42.8	99.1	3.3	7.55	7.8	20.9	160	0.47
160	0	34.6	65.1	4.0	7.48	8.0	23.0	350	1.00
	0.5	36.0	74.1	4.2	8.59	9.4	28.0	350	0.99
	1.0	39.0	83.6	4.0	8.09	8.2	23.1	320	0.91
	2.0	41.4	90.5	4.1	8.84	8.4	24.7	270	0.80

Table 4.2.19 Effect of P applied in 1979 and Zn-chelate applied on foliage in 1984 on Zn and P concentration and uptake of wheat grain and straw.

Treatment		Grain				Straw			
P	Zn	Zn conc.	Zn uptake	P conc.	P uptake	Zn conc.	Zn uptake	P conc.	P uptake
		mg kg ⁻¹	g ha ⁻¹	g kg ⁻¹	kg ha ⁻¹	mg kg ⁻¹	g ha ⁻¹	mg kg ⁻¹	kg ha ⁻¹
0	0	49.8	72.1	2.8	4.00	15.0	35.1	90	0.20
	0.35T [†]	55.8	78.8	2.7	3.79	23.4	52.6	100	0.22
	0.35F ^ψ	60.4	89.8	2.7	4.03	22.0	50.0	100	0.24
80	0	38.0	64.5	3.4	5.72	9.6	22.7	180	0.43
	0.35T	45.8	106.3	3.5	8.15	11.4	32.8	180	0.52
	0.35F	44.2	108.0	3.6	8.68	10.8	31.2	220	0.62
160	0	34.6	65.1	4.0	7.48	8.0	23.0	350	1.00
	0.35T	41.2	91.0	4.1	9.14	10.4	33.7	300	0.96
	0.35F	39.4	99.8	3.9	9.64	9.8	29.9	340	0.96

^{†, ψ} Foliar Zn applied at FEEKES-6 and FEEKES-10 growth stage, respectively.

Table 4.2.20 Mean squares from the analysis of variance for Zn and P concentration and uptake of wheat grain and straw.

Source	df	Source of applied Zn: Zn-sulfate							
		Grain			Straw				
		Zn conc.	Zn uptake	P conc.	P uptake	Zn conc.	Zn uptake	P conc.	P uptake
<u>P effects</u>									
0 vs 80+160(P1)	1	2881.20**	440.83	13.67**	243.96**	1928.00**	5752.17**	438020.80*	4.28**
80 vs 160(P2)	1	0.02	579.91	3.79*	17.77	13.22	0.00	205699.16*	2.14
Error 1	8	107.51	596.69	0.76	5.14	21.93	129.19	43514.17	0.21
<u>Zn effects</u>									
Zn linear	1	417.19**	7280.05**	0.47*	31.23**	93.87	448.51	19201.19	0.13
Zn quadratic	1	30.17	567.70	0.00	6.67*	1.17	101.41	8766.23	0.01
Zn cubic	1	1.17	0.00	0.53*	0.51	0.16	82.31	1250.90	0.00
<u>Interaction effects</u>									
P1 x Zn linear	1	0.14	1274.90*	0.12	16.28**	71.76	61.20	7072.02	0.04
P1 x Zn quadratic	1	0.14	135.60	0.00	2.96	41.34	170.87	4095.77	0.00
P1 x Zn cubic	1	18.04	182.71	0.00	1.06	48.73	155.13	61.36	0.00
P2 x Zn linear	1	0.48	164.57	0.03	0.04	0.26	48.66	944.64	0.00
P2 x Zn quadratic	1	0.01	56.32	0.32	0.02	0.34	0.57	6040.58	0.02
P2 x Zn cubic	1	6.73	14.49	0.00	2.84	5.67	41.67	4892.27	0.04
Error 2	36	26.33	174.92	0.11	1.12	32.84	121.61	7651.39	0.05

*,** Indicate 0.05 and 0.01 significance levels, respectively

Table 4.2.21 Mean squares from the analysis of variance for Zn and P concentration and uptake of wheat grain and straw.

Source	df	Source of applied Zn: Zn-Chelate							
		Grain				Straw			
		Zn conc.	Zn uptake	P conc.	P uptake	Zn conc.	Zn uptake	P conc.	P uptake
<u>P effects</u>									
0 vs 80+160(P1)	1	2385.21**	1210.31	12.03**	197.63**	1267.50**	4124.27**	363000.00**	3.39**
80 vs 160(P2)	1	44.89	1197.83	4.35*	10.48*	0.00	92.98	165263.33*	1.85**
Error 1	.8	82.34	406.61	0.46	1.92	33.44	341.83	17131.67	0.09
<u>Zn effects</u>									
Zn linear	1	250.30*	3107.12**	0.01	4.69**	1.14	10.57	18010.71	0.05
Zn quadratic	1	33.22	809.19	0.00	2.53*	0.76	2.43	9562.77	0.02
Zn cubic	1	31.47	96.12	0.57	4.60*	131.61**	624.15*	12713.18	0.04
<u>Interaction effects</u>									
P1 x Zn linear	1	6.32	615.56	0.06	2.49*	40.02	85.57	5485.71	0.02
P1 x Zn quadratic	1	0.35	238.95	0.08	2.10	0.32	5.79	1820.35	0.01
P1 x Zn cubic	1	23.42	655.80	0.08	3.42*	71.28*	387.28*	27.27	0.00
P2 x Zn linear	1	24.55	1.15	0.03	0.02	7.14	7.80	2314.29	0.06
P2 x Zn quadratic	1	10.97	307.63	0.01	2.23	5.62	9.12	4058.44	0.01
P2 x Zn cubic	1	79.46	723.27	0.01	0.78	1.83	8.02	6097.27	0.01
Error 2	36	34.48	204.09	0.14	0.56	17.08	92.41	8083.61	0.04

*, ** Indicate 0.05 and 0.01 significance levels, respectively

Table 4.2.22 Mean squares from the analysis of variance for Zn and P concentration and uptake of wheat grain and straw

Source	df	Source of applied Zn: Zn-chelate foliar							
		Grain				Straw			
		Zn conc.	Zn uptake	P conc.	P uptake	Zn conc.	Zn uptake	P conc.	F
<u>P effects</u>									
0 vs 80+160(P1)	1	2190.40**	789.73	10.33**	175.98**	1026.84**	2895.67**	272250.00**	
80 vs 160(P2)	1	136.53	434.55	3.25*	11.45*	10.80	10.22	144501.11*	1.52**
Error 1	8	82.91	278.05	0.36	1.45	27.74	206.72	17122.78	0.08
<u>Zn effects</u>									
0 vs .35T+.35F(Zn1)	1	490.00**	8052.35**	0.01	22.65**	141.88**	1307.21**	0.00	0.02
0.35T vs .35F(Zn2)	1	1.19	386.39	0.16	1.30	5.63	56.96	481.78	0.01
<u>Interaction effects</u>									
P1 x Zn1	1	8.45	1308.42*	0.07	12.72**	77.36*	113.61	500.00	0.01
P2 x Zn1	1	2.82	253.38	0.04	1.03	0.60	0.42	4166.67	0.06
P1 x Zn2	1	66.15	55.10	0.00	0.13	1.06	0.02	2666.67	0.00
P2 x Zn2	1	0.05	56.63	0.06	0.07	0.00	5.61	1048.89	0.01
Error 2	24	23.50	210.53	0.16	1.06	17.76	149.44	7841.67	0.06

*,** Indicate 0.05 and 0.01 significance levels, respectively

4.2.2.4 Nature of P X Zn interaction

A number of possible explanations have been given for P X Zn interaction. Bingham (1963) suggested that the interaction was a result of chemical reactions that occur in the soil. This theory was deemed unsatisfactory by Olsen (1972), since the increase of added P to the soil did not cause a decrease in either water soluble or extractable soil Zn. This possibility was also discounted in our experiment for the same reasons. DTPA-extractable Zn in the non-Zn amended treatments varied between 0.96 and 1.02 mg kg⁻¹ and was independent of the P application rate.

Loneragan et al. (1982) observed that under conditions of high P and low Zn supply, P is absorbed by roots and transported in such excess that it becomes toxic and produces symptoms resembling Zn deficiency, while not changing Zn concentration in plant tops. The levels of P in the tissue, grain and straw of wheat in this experiment were well below the toxic level (Ozanne, 1980). Therefore, P toxicity was not a factor in this study. Moreover, high levels of P in this experiment decreased the concentration of Zn in plant tissue to near critical levels (Table 4.2.14).

Other explanations are based on the translocation of Zn from roots to shoots (Stukenholtz et al., 1966; Sharma et al., 1968; Safaya, 1976) or metabolic anomalies which are caused from a lack of equilibrium between two elements in the plants (Boawn and Leggett, 1964; Boawn and Brown, 1968; Millikan et al., 1968). The latter has been clarified through the work of Loneragan et al. (1982) who have shown that P-induced Zn deficiency is not due to Zn metabolism in the leaves, but rather to P absorption and transport from roots. Infec-

tion of roots with mycorrhizae has been reported to increase Zn uptake by the host plant (Benson and Covey, 1976). Cooper and Tinker (1978) using ^{65}Zn associated this with direct uptake of Zn by vesicular-arbuscular mycorrhizal (VAM) hyphae and subsequent translocation into the host. Further, it has been shown (Hayman, 1978; Tinker, 1980) that high levels of P can inhibit infection of roots with VAM. Hence, it is possible that increased P levels in the soil may lead to reduced Zn uptake via a reduction of VAM infection. More recently, Lambert et al. (1979), showed that P fertilization suppressed mycorrhizal uptake of Zn in corn and soybeans. Although translocation effects cannot be discounted in this experiment as a possible cause of reduced Zn uptake with addition of large P amounts, an attempt was made to identify the possible role of mycorrhizae in this interaction.

The effect of high P application rates on the mycorrhizal infection of wheat roots at the completion of the experiment is shown in Figure 4.11. Low mycorrhizal infection was associated with large P application rates.

The most significant finding in this study that could lead to a possible involvement of mycorrhizae in the P X Zn interaction observed was the close relationship between Zn levels in the above ground plant parts and mycorrhizal infection (Figure 4.12). Hence, high Zn levels in the foliage, grain and straw were associated with higher % mycorrhizal infection of wheat roots.

It would be difficult to single out any of the mechanisms described above as responsible for the P X Zn interaction observed. However, a portion of the decrease in Zn levels is indeed due to dilution. The remaining portion could be of a physiological nature

Figure 4.11 Relationship between mycorrhizal infection of wheat roots and rate of applied P.

Figure 4.12 Relationship between Zn levels in wheat plant tissue at FEEKES 10 and grain and straw and mycorrhizal infection of corresponding roots (open symbols indicate Zn-sulfate and darkened Zn-chelate treatments).

enhanced by reduced mycorrhizal infection in the roots of plants grown in treatments of high P application rates.

4.2.3 P X Zn interaction in beans

4.2.3.1 Yields

Dry matter yields (DMY) of all plant parts at both growth stages except the tops of beans grown on the Meota soil responded curvilinearly to P additions in all three soils (Tables 4.2.23 to 4.2.25). Maximum mean DMY in all cases was obtained with the addition of 40 mg P kg⁻¹. Response of DMY to Zn applications was not the same in all cases but was a function of both the soil and plant part. Hence, significant DMY increases due to Zn were obtained in the Sutherland (Table 4.2.23) and Carrot River (Table 4.2.24) soils for the above ground plant parts only.

Application of Zn alone without P application had no effect on DMY of beans. In contrast, significant DMY increases due to P application in the absence of Zn were observed in all three soils. The P X Zn interaction on DMY of above ground plant parts was significant for the Sutherland and Carrot River soils only (Tables 4.2.23 and 4.2.24). This interaction was expressed by larger yield responses to P when Zn was applied and larger responses to Zn when P was applied.

4.2.3.2 Zinc concentration and uptake in bean plants

The Zn concentration in the bean roots and tops at 1/10 bloom stage and in the roots, straw and seeds at maturity are presented in Tables 4.2.26, 4.2.27 and 4.2.28 for the Sutherland, Carrot River and

Table 4.2.23 Effect of P and Zn application on the yield of beans grown on Sutherland soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				g pot ⁻¹		
0	0	0.30	1.30	0.53	1.55	2.05
	5	0.33	1.20	0.53	1.40	2.00
	10	0.30	1.10	0.48	1.35	2.00
40	0	0.60	2.15	0.98	4.15	3.98
	5	0.63	2.78	1.05	5.48	4.98
	10	0.60	2.75	0.95	5.45	5.23
80	0	0.58	1.85	1.10	4.25	4.05
	5	0.65	2.93	0.95	5.35	5.33
	10	0.65	3.05	0.95	5.55	5.30
160	0	0.55	1.93	1.03	4.00	3.98
	5	0.55	3.15	1.08	5.70	5.65
	10	0.63	3.15	1.05	5.30	4.90

Statistical significance[†]

P rate	L,Q	L,Q,C	L,Q,C	L,Q,C	L,Q,C
Zn rate	NS	L,Q	NS	L,Q	L,Q
P X Zn	NS	*	NS	*	*

[†]Orthogonal contrast which are significant (P = 0.05) for P and Zn effects (L = linear; Q = quadratic; C = cubic)

NS - Not significant

* Indicate significant interaction at 0.05 level

Table 4.2.24 Effect of P and Zn application on the yield of beans grown on Carrot River soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				g pot ⁻¹		
0	0	0.30	1.63	0.85	1.75	2.93
	5	0.55	1.95	0.88	1.83	3.20
40	0	0.75	2.50	1.20	4.45	4.40
	5	0.68	3.08	1.15	5.63	5.25
80	0	0.70	2.35	1.25	4.08	4.45
	5	0.68	3.20	1.20	6.28	5.40
160	0	0.68	2.30	1.18	4.00	4.38
	5	0.75	3.33	1.26	6.03	5.63

Statistical significance[†]

P rate	L,Q	L,Q,C	L,Q	L,Q,C	L,Q
Zn rate	NS	*	NS	*	*
P X Zn	NS	*	NS	*	NS

[†] Orthogonal contrast which are significant (P = 0.05) for P effects (L = linear; Q = quadratic; C = cubic)

NS - Not significant

* Indicate 0.05 significance level for Zn and interaction effects

Table 4.2.25 Effect of P and Zn application on the yield of beans grown on Meota soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				g pot ⁻¹		
0	0	0.50	2.40	1.58	5.85	5.53
	5	0.43	2.20	1.58	6.00	5.73
40	0	0.70	2.93	1.98	8.20	6.90
	5	0.70	3.13	2.00	8.00	7.15
80	0	0.70	2.88	1.95	8.23	7.28
	5	0.73	3.10	2.03	8.48	7.78
160	0	0.68	3.28	1.90	7.98	7.33
	5	0.83	3.40	1.98	8.00	7.43

Statistical significance[†]

P rate	L,Q	L	L,Q	L,Q	L,Q
Zn rate	NS	NS	NS	NS	NS
P X Zn	NS	NS	NS	NS	NS

[†]Orthogonal contrast which are significant (P = 0.05) for P effects (L = linear; Q = quadratic)

NS - Not significant

Table 4.2.26 Effect of P and Zn application on the Zn concentration of beans grown on Sutherland soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				mg kg ⁻¹		
0	0	26.0	19.4	24.6	29.9	18.5
	5	44.5	37.8	39.6	37.9	27.3
	10	63.8	41.4	49.4	48.7	30.4
40	0	32.5	13.8	28.9	22.9	12.8
	5	34.0	21.9	30.1	22.9	13.9
	10	41.0	26.9	37.9	26.1	16.5
80	0	38.2	13.2	27.5	19.8	10.0
	5	34.6	21.9	34.3	22.8	16.2
	10	37.9	24.7	38.7	26.5	18.7
160	0	39.3	10.5	29.1	20.5	7.8
	5	39.1	21.6	31.5	24.8	16.2
	10	37.2	26.3	38.6	28.2	20.0
<u>Statistical significance</u> [†]						
P rate		L,Q,C	L,Q,C	L,Q	L,Q,C	L,Q,C
Zn rate		L	L,Q	L	L	L
P X Zn		*	*	*	*	*

[†] Orthogonal contrast which are significant (P = 0.05) for P and Zn effects (L = linear; Q = quadratic; C = cubic)

* Indicate significant interaction at 0.05 level

Table 4.2.27 Effect of P and Zn application on the Zn concentration of beans grown on Carrot River soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				mg kg ⁻¹		
0	0	33.7	20.3	27.2	31.3	18.7
	5	78.9	40.5	51.5	47.1	32.8
40	0	30.0	14.7	29.1	25.8	13.7
	5	67.8	30.1	50.6	31.2	26.6
80	0	35.8	13.7	33.5	25.9	11.7
	5	77.9	29.7	53.5	30.5	25.9
160	0	44.8	11.2	36.4	26.3	11.0
	5	67.4	29.8	53.6	33.1	26.0

Statistical significance[†]

P rate	C	L,Q,C	Q,C	L,Q	L,Q
Zn rate	*	*	*	*	*
P X Zn	*	*	*	NS	NS

[†] Orthogonal contrast which are significant (P = 0.05) for P effects (L = linear; Q = quadratic; C = cubic)

NS - Not significant

* Indicate 0.05 significance level for Zn and interaction effects

Table 4.2.28 Effect of P and Zn application on the Zn concentration of beans grown on Meota soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				mg kg ⁻¹		
0	0	35.2	20.9	35.9	22.4	14.3
	5	60.5	30.5	43.6	28.1	14.0
40	0	30.9	20.8	34.0	19.5	7.8
	5	61.6	27.1	45.1	22.3	11.8
80	0	31.7	20.7	33.1	18.9	7.3
	5	59.3	27.3	45.3	21.1	11.6
160	0	31.5	21.4	34.0	22.1	8.4
	5	62.3	30.4	49.0	23.3	11.9

Statistical significance[†]

P rate	NS	Q	Q	Q	L,Q
Zn rate	*	*	*	*	*
P X Zn	NS	NS	NS	NS	NS

[†] Orthogonal contrast which are significant (P = 0.05) for P effects (L = linear; Q = quadratic; C = cubic)

NS - Not significant

* Indicate 0.05 significance level for Zn

Meota soils, respectively.

The mean effect of either P or Zn application on the Zn concentration in all plant parts was significant at $P < 0.05$ (Tables 4.2.26 to 4.2.28) in all soils except for the roots of beans grown on the Meota soil at 1/10 bloom stage (Table 4.2.28). The expression of the mean effect, however, varied among soils and plant parts. In the Sutherland and Carrot River soils, the Zn concentration in the bean tops at 1/10 bloom stage was sharply reduced with the addition of 40 mg P kg⁻¹ of soil and remained more or less constant at higher P application rates (Tables 4.2.26 and 4.2.27). A similar trend was obtained for the roots of the beans at 1/10 bloom stage on the Sutherland soil only.

The mean effect of P on Zn concentration in the tops of beans at 1/10 bloom stage on the Meota soil (Table 4.2.28) and the roots on the Carrot River soil (Table 4.2.27) was less pronounced.

At maturity, Zn levels in the straw of plants grown in all soils were decreased sharply with 40 mg applied P kg⁻¹ of soil and remained more or less unaffected thereafter. A similar trend was also obtained for the seeds of plants grown on the Sutherland and Carrot River soils (Table 4.2.26 and 4.2.27) and the roots on the Sutherland soil (Table 4.2.26). In the remaining cases the effect of P on Zn concentration was very small.

A significant P X Zn interaction was obtained in the Sutherland and Carrot River soils only (Tables 4.2.26 and 4.2.27). A consideration of the Zn concentration in the tops of beans grown on these soils provides an insight into the P X Zn interaction observed for DMY. Responses of DMY to Zn in the presence of added P were a

consequence of the low Zn concentration in the tops of bean plants (Tables 4.2.26 and 4.2.27). For example, addition of 40 mg P kg^{-1} of soil caused a drop of Zn concentration of tops at 1/10 bloom stage from 19.4 and 20.3 to 13.8 and $14.7 \text{ mg Zn kg}^{-1}$ in the Sutherland and Carrot River soils, respectively (Tables 4.2.26 and 4.2.27). In contrast, P application on the Meota soil had no pronounced effect on Zn concentration in tops (Table 4.2.28). The non-occurrence of P X Zn interaction in the Meota soil can be explained since this soil apparently had enough "available" Zn to meet the requirement of growing plants.

The hypotheses that the decrease in the concentration of Zn in different plant parts of beans grown on the Sutherland and Carrot River soils was due to a dilution effect was tested by calculating total uptake of Zn by beans (Tables 4.2.29 to 4.2.31). Although application of P increased the yield of beans at all levels of applied Zn in the Sutherland and Carrot River soils (Tables 4.2.23 and 4.2.24), the uptake of Zn into different plant parts increased with increasing rates of applied P at 5 or 10 mg Zn kg^{-1} of applied Zn only. A critical examination of the Zn uptake into the above ground plant parts of non-Zn treatment reveals that 40 mg P kg^{-1} causes an increase in Zn uptake, whereas there was sharp reduction in Zn uptake at 80 and 160 mg P kg^{-1} of applied P (Tables 4.2.29 and 4.2.30). However, there was an increase in Zn uptake by roots with increasing P applications, indicating a reduced translocation to the above ground plant parts. Hence, both plant dilution effects and restricted translocation of Zn from roots to above ground plant parts seem to be the factor responsible for P-induced Zn deficiency in the Sutherland

Table 4.2.29 Effect of P and Zn application on the Zn uptake of beans grown on Sutherland soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				μg pot ⁻¹		
0	0	7.78	25.22	12.93	46.05	37.87
	5	14.43	45.78	20.74	53.35	54.16
	10	19.02	42.94	23.42	65.76	61.31
40	0	19.24	29.46	28.21	94.89	50.87
	5	21.35	60.43	31.55	124.63	68.64
	10	24.41	73.69	35.94	140.84	86.67
80	0	22.01	24.62	30.25	84.18	40.59
	5	22.44	63.81	32.69	121.99	85.61
	10	24.94	75.12	36.58	146.13	98.79
160	0	21.53	20.16	29.48	82.04	31.19
	5	23.94	68.45	33.57	140.67	90.90
	10	26.29	82.88	40.32	150.02	97.57

Statistical significance[†]

P rate	L,Q	L,Q	L,Q,C	L,Q,C	L,Q
Zn rate	L	L,Q	L	L	L
P X Zn	NS	*	NS	*	*

[†] Orthogonal contrast which are significant (P = 0.05) for P and Zn effects (L = linear; Q = quadratic; C = cubic)

NS - Not significant

* Indicate significant interaction at 0.05 level

Table 4.2.30 Effect of P and Zn application on the Zn uptake of beans grown on Carrot River soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				µg pot ⁻¹		
0	0	10.10	32.91	23.12	54.38	54.72
	5	43.37	78.66	45.45	86.56	103.18
40	0	22.50	36.38	34.92	114.70	60.67
	5	45.31	92.48	58.50	175.51	137.89
80	0	25.02	32.18	41.42	106.96	52.26
	5	52.28	94.79	66.88	192.05	138.72
160	0	30.18	25.49	43.05	105.19	48.54
	5	50.64	98.81	66.94	199.05	143.30

Statistical significance[†]

P rate	L,Q	NS	L	L,Q,C	Q
Zn rate	*	*	*	*	*
P X Zn	NS	*	NS	*	*

[†] Orthogonal contrast which are significant (P = 0.05) for P effects (L = linear; Q = quadratic; C = cubic)

NS - Not significant

* Indicate 0.05 significance level for Zn and interaction effects

Table 4.2.31 Effect of P and Zn application on the Zn uptake of beans grown on Meota soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				µg pot ⁻¹		
0	0	17.62	50.19	56.59	131.28	78.42
	5	25.51	67.09	68.81	167.87	80.19
40	0	21.67	60.69	67.11	160.67	53.86
	5	43.21	83.79	89.92	178.21	85.35
80	0	22.16	59.58	64.70	152.64	53.39
	5	43.59	84.64	91.62	179.16	86.45
160	0	22.10	70.10	64.32	176.40	60.94
	5	52.20	99.33	96.62	182.15	86.62

Statistical significance[†]

P rate	L	L	L	L	NS
Zn rate	*	*	*	*	*
P X Zn	NS	NS	NS	NS	*

[†] Orthogonal contrast which are significant (P = 0.05) for P effects (L = linear)

NS - Not significant

* Indicates 0.05 significance level for Zn and interaction effects

and Carrot River soils. Restricted translocation of Zn from roots to tops responsible for P-induced Zn deficiency has also been reported by Stukenholtz et al. (1966) and Sharma et al. (1968).

At high levels of P, the retention of more Zn in roots was probably due to the increased binding of Zn in root cell walls, resulting in less Zn available for transportation to the upper portion, as reported by Youngdahl et al. (1977). The observation that soils high in Zn or soils that have been fertilized with Zn do not show the P-induced Zn deficiency can be explained, since once the binding sites in the cell walls are saturated, any additional Zn would be available for metabolism.

4.2.3.3 Phosphorus concentration and uptake in bean plants

Application of P in all soils resulted in significant increase of the mean P concentration (Tables 4.2.32 to 4.2.34) and uptake (Tables 4.2.35 to 4.2.37) in all plant parts of beans at both sampling times. The expression of this increase varied among soils and plant parts. Linear increases in P concentration with P application rates were obtained at maturity only in the roots of beans grown on the Sutherland and Meota soils and in the seed on the Carrot River and Sutherland soils (Tables 4.2.32 to 4.2.34). P uptake was increased linearly with P application rate in the roots of mature beans grown on the Sutherland and Meota soils and the straw on the Meota soil.

Application of Zn had a variable effect on P concentration and uptake of beans. Thus, P concentration and uptake in above ground plant parts grown on the Sutherland and Carrot River soils decreased significantly with application of Zn (Tables 4.2.32, 4.2.33, 4.2.35

Table 4.2.32 Effect of P and Zn application on the P concentration of beans grown on Sutherland soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				g kg ⁻¹		
0	0	1.09	1.68	1.37	4.21	0.96
	5	1.11	1.75	1.40	4.17	0.98
	10	1.30	1.80	1.41	4.13	0.95
40	0	1.78	3.29	1.63	5.54	2.28
	5	1.83	2.11	1.83	3.70	1.50
	10	2.01	2.40	1.84	3.49	1.56
80	0	1.89	6.20	2.14	5.76	3.19
	5	2.06	3.41	2.49	3.78	2.16
	10	2.05	3.04	2.48	3.90	2.20
160	0	2.03	8.07	2.97	6.05	3.82
	5	2.33	4.60	3.56	4.07	2.27
	10	2.67	4.16	3.44	4.06	2.34

Statistical significance[†]

P rate	L,Q,C	L,Q,C	L	L	L,Q
Zn rate	L	L,Q	L,Q	L,Q	L,Q
P X Zn	*	*	NS	*	*

[†]Orthogonal contrast which are significant (P = 0.05) for P and Zn effects (L = linear; Q = quadratic; C = cubic)

NS - Not significant

* Indicate significant interaction at 0.05 level

Table 4.2.33 Effect of P and Zn application on the P concentration of beans grown on Carrot River soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				g kg ⁻¹		
0	0	1.84	2.34	1.94	4.05	2.10
	5	2.02	1.93	2.12	3.71	2.02
40	0	2.31	4.50	3.27	5.11	3.34
	5	2.63	3.30	3.67	3.42	1.98
80	0	2.72	6.23	4.82	6.26	3.88
	5	3.01	4.02	5.54	3.56	2.57
160	0	4.68	8.27	5.75	6.90	4.32
	5	5.58	5.15	6.05	3.78	3.06

Statistical significance[†]

P rate	L,Q,C	L,Q	L,Q,C	L	L,Q
Zn rate	*	*	*	*	*
P X Zn	*	*	NS	*	*

[†] Orthogonal contrast which are significant (P = 0.05) for P effects (L = linear; Q = quadratic; C = cubic)

NS - Not significant

* Indicate 0.05 significance level for Zn and interaction effects

Table 4.2.34 Effect of P and Zn application on the P concentration of beans grown on Meota soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				g kg ⁻¹		
0	0	1.40	1.97	1.86	2.85	1.47
	5	1.64	1.86	1.95	2.73	1.23
40	0	2.83	3.96	2.34	4.19	1.39
	5	3.51	3.71	2.42	3.91	1.24
80	0	3.95	4.93	3.16	5.03	2.04
	5	4.01	4.31	3.28	4.76	1.86
160	0	4.88	5.35	4.69	5.47	3.15
	5	4.41	4.88	4.83	5.38	3.10

Statistical significance[†]

P rate	L,Q	L,Q	L	L,Q	L,Q,C
Zn rate	NS	*	NS	*	*
P X Zn	NS	NS	NS	NS	NS

[†] Orthogonal contrast which are significant (P = 0.05) for P effects (L = linear; Q = quadratic; C = cubic)

NS - Not significant

* Indicate 0.05 significance level for Zn effects

Table 4.2.35 Effect of P and Zn application on the P uptake of beans grown on Sutherland soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				mg pot ⁻¹		
0	0	0.33	2.20	0.72	6.56	1.96
	5	0.35	2.11	0.73	5.90	2.02
	10	0.39	1.87	0.66	5.62	1.92
40	0	1.07	7.14	1.59	22.98	9.05
	5	1.15	6.16	1.92	20.08	7.51
	10	1.24	6.59	1.74	18.95	8.07
80	0	1.09	11.52	2.35	24.40	12.95
	5	1.33	10.88	2.36	20.19	11.45
	10	1.33	10.28	2.36	21.56	11.63
160	0	1.11	15.53	3.06	24.06	15.20
	5	1.27	14.33	3.82	23.20	12.63
	10	1.67	13.15	3.65	21.54	11.52

Statistical significance[†]

P rate	L,Q	L,Q	L	L,Q,C	L,Q
Zn rate	L	L	NS	L	L
P X Zn	NS	NS	NS	NS	*

[†]Orthogonal contrast which are significant (P = 0.05) for P and Zn effects (L = linear; Q = quadratic; C = cubic)

NS - Not significant

* Indicate significant interaction at 0.05 level

Table 4.2.36 Effect of P and Zn application on the P uptake of beans grown on Carrot River soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				mg pot ⁻¹		
0	0	0.55	3.82	1.65	7.21	6.20
	5	1.11	3.75	1.89	6.74	6.38
40	0	1.73	11.20	3.92	22.64	14.71
	5	1.76	10.20	4.22	19.34	10.41
80	0	1.91	14.58	6.05	25.48	15.96
	5	2.03	12.80	6.94	22.38	13.98
160	0	3.16	19.04	6.76	27.28	18.97
	5	4.17	18.08	7.57	22.90	17.49

Statistical significance[†]

P rate	L,Q	L,Q	L,Q	L,Q,C	L,Q
Zn rate	*	*	NS	*	*
P X Zn	*	NS	NS	NS	NS

[†] Orthogonal contrast which are significant (P = 0.05) for P effects (L = linear; Q = quadratic; C = cubic)

NS - Not significant

* Indicate 0.05 significance level for Zn and interaction effects

Table 4.2.37 Effect of P and Zn application on the P uptake of beans grown on Meeta soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				mg pot ⁻¹		
0	0	0.70	4.75	2.93	16.72	8.14
	5	0.70	4.09	3.06	16.21	7.05
40	0	1.98	11.58	4.62	34.24	9.53
	5	2.45	11.39	4.85	31.26	8.71
80	0	2.76	14.11	6.20	41.20	14.89
	5	2.91	13.38	6.65	40.27	14.42
160	0	3.28	17.49	8.95	43.78	22.97
	5	3.68	15.64	9.51	42.89	22.88

Statistical significance[†]

P rate	L,Q	L,Q,C	L	L,Q	L
Zn rate	NS	NS	NS	NS	NS
P X Zn	NS	NS	NS	NS	NS

[†]Orthogonal contrast which are significant (P = 0.05) for P effects (L = linear; Q = quadratic; C = cubic)

NS - Not significant

and 4.2.36). In the Meota soil, only the concentration of P in above ground parts was significantly decreased by Zn application (Table 4.2.34), whereas P uptake remained unaffected (Table 4.2.37). Application of Zn to the Sutherland and Carrot River soils caused an increase in root P at both growth stages but P uptake was increased only at 1/10 bloom stage (Tables 4.2.32, 4.2.33, 4.2.35 and 4.2.36). A significant P X Zn interaction on P concentration in root at 1/10 bloom stage and P concentration in above ground plant parts at both stages was obtained both in Sutherland and Carrot River soils (Tables 4.2.32 and 4.2.33). When no Zn was applied, P concentration in the tops of bean at 1/10 bloom stage increased from 3.29 at 40 mg P kg⁻¹ to 8.07 g kg⁻¹ at 160 mg P kg⁻¹ in the Sutherland soil (Table 4.2.32) and from 4.5 to 8.27 g kg⁻¹ in the corresponding treatment in the Carrot River soil (Table 4.2.33). In contrast, relatively small increases in P concentration (3.96 to 5.35 g kg⁻¹) were observed in the Meota soil as a result of raising P levels from 40 mg P kg⁻¹ to 160 mg P kg⁻¹ (Table 4.2.34). Application of Zn caused a significant decrease in P concentration in the above ground plant parts. This decrease was greater at 80 or 160 mg applied P kg⁻¹ of soil than at 40 mg applied P kg⁻¹ of soil. In contrast to the P concentration in above ground plant parts, root P concentration increased significantly with the application of Zn in the presence of P than in its absence. Thus applied Zn reduced concentration of P in the above ground parts at high rates of applied P but increased it in the roots. This decrease in concentration of P in the above ground plant parts can be attributed to a positive P X Zn interaction on the yield of beans as no significant P X Zn interaction was observed on the P uptake of the

above ground plant parts. Although statistical analysis indicated no significant effect of Zn on P uptake, there was a declining trend in P uptake with the application of Zn at all levels of applied P.

These results support the recent findings of Loneragan et al. (1982) that Zn deficiency may enhance P absorption and transport to such an extent that it may accumulate to higher levels in tops. However, these results do not agree with the hypothesis of Loneragan et al. (1982) that P toxicity may be a problem under conditions of low Zn and high P supply, for two reasons. First, the concentration of P in the tops of bean in this experiment were below the toxic level (Ozanne, 1980). Secondly, the P X Zn interaction was observed at all rates of P application. Moreover, high levels of P in this experiment decreased the concentration of Zn in the tops of bean to near critical levels (Tables 4.2.26 and 4.2.27) and the magnitude of reduction in Zn concentration was greatest at the 40 mg P kg⁻¹ rate. Only a small additional drop due to 80 or 160 mg P kg⁻¹ rate was observed.

4.2.3.4 Zinc and P derived from applied source

Doubling the amount of Zn fertilizer resulted in a significant increase in Zn derived from fertilizer (% Zndff) by roots and above ground parts of beans in the Sutherland soil at both growth stages (Table 4.2.38). The increase in % Zndff from the 5 mg Zn kg⁻¹ to the 10 mg Zn kg⁻¹ treatment, indicates a preferential uptake of the more readily available form of Zn fertilizer. The % Zndff by bean roots decreased significantly with P application in all soils but the effect was more pronounced in the Meota soil (Tables 4.2.38 to 4.2.40). In contrast to % Zndff in roots, the % Zndff in tops, seeds and straw in

Table 4.2.38 Zinc derived from fertilizer (% Zndff) by beans grown on Sutherland soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				% Zndff		
0	5	27.0	42.0	37.7	41.0	40.7
40	5	28.8	45.3	33.6	46.4	43.0
80	5	24.5	51.2	32.2	52.9	53.3
160	5	22.7	52.2	34.4	55.4	54.7
0	10	49.2	54.3	41.6	42.0	43.4
40	10	38.5	58.4	39.9	57.9	59.2
80	10	38.4	60.9	37.3	62.3	64.4
160	10	37.8	60.3	35.8	63.4	62.9

Statistical significance[†]

P rate	L	L	NS	L,Q	L,Q
Zn rate	*	*	*	*	*
P X Zn	NS	NS	NS	NS	NS

[†] Orthogonal contrast which are significant (P = 0.05) for P effects (L = linear; Q = quadratic)

NS - Not significant

* Indicate significant effect of Zn at 0.05 level

Table 4.2.39 Zinc derived from fertilizer (% Zndff) by beans grown on Carrot River soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				% Zndff		
0	5	51.7	41.9	51.7	49.1	52.8
40	5	53.6	46.5	51.5	52.5	54.0
80	5	49.6	48.1	48.1	58.7	54.5
160	5	47.8	49.0	47.7	59.6	55.2

Statistical significance[†]

P rate	L	L	NS	L	NS

[†] Orthogonal contrast which are significant (P = 0.05) for P effects (L = linear)

NS - Not significant

Table 4.2.40 Zinc derived from fertilizer (% Zndff) by beans grown on Meota soil.

Treatment		1/10 bloom stage		Maturity		
P	Zn	Roots	Tops	Roots	Seeds	Straw
mg kg ⁻¹				% Zndff		
0	5	44.6	29.4	17.0	24.1	26.9
40	5	23.5	24.1	8.9	24.7	24.0
80	5	21.8	24.0	7.9	24.9	22.0
160	5	18.4	21.4	8.4	24.4	23.9

Statistical significance[†]

P rate	L,Q,C	L	L,Q	NS	NS

[†] Orthogonal contrast which are significant (P = 0.05) for P effects (L = linear; Q = quadratic)

NS - Not significant

the Sutherland soil and tops and seeds in the Carrot River soil increased significantly with P application (Tables 4.2.38 and 4.2.39). In the Meota soil, however, it decreased significantly with P application at 1/10 bloom stage and remained unaffected at maturity (Table 4.2.40).

The % Zndff was affected by soil properties and native labile pool of Zn. Depending on P level, plant part, and growth stage, 22.7% to 55.4%, 41.9% to 59.6% and 7.9 to 44.6% of Zn was derived from applied sources (5 mg Zn kg^{-1}) by beans grown on Sutherland, Carrot River, and Meota soils, respectively (Tables 4.2.38 and 4.2.40). The higher values obtained in Carrot River and Sutherland soils compared to the Meota soil may well be related to their DTPA-extractable soil Zn levels. The DTPA-extractable Zn levels in three soils followed the sequence: Meota > Sutherland > Carrot River (Table 3.2, Section 3.2.3).

The P derived from fertilizer (% Pdf) in roots at 1/10 bloom stage increased significantly with Zn application in all three soils (Table 4.2.41). However, it was decreased with Zn application only in tops of beans grown on the Carrot River soil (Table 4.2.41). Yadav and Shukla (1982) have published autoradiographs that show more P retention in the roots when P and Zn were applied together compared to P application alone.

Phosphorus application increased % Pdf in both roots and tops of beans in all soils (Table 4.2.41). Similar increase in % Pdf with increasing amounts of P fertilizer has been reported by Nychas and Skarlou (1983). The % Pdf was also a function of soil properties. In the Sutherland soil, 56% to 90.6% and 59.6% to 80% of the P was

Table 4.2.41 Phosphorus derived from fertilizer (% Pdf) of beans at 1/10 bloom stage in three soils.

Treatment		Sutherland		Carrot River		Meota	
P	Zn	Root	Top	Root	Top	Root	Top
mg kg ⁻¹				% Pdf			
40	0	56.0	59.6	41.6	46.8	38.4	47.6
	5	58.2	59.2	43.0	44.9	40.0	44.7
	10	58.9	57.6	--	--	--	--
80	0	69.7	69.3	63.8	53.8	56.5	56.1
	5	72.2	67.0	65.0	50.5	57.4	54.4
	10	75.9	67.8	--	--	--	--
160	0	88.2	82.0	77.2	72.0	71.0	76.3
	5	90.6	80.0	82.0	70.4	76.3	74.5
	10	92.8	80.9	--	--	--	--

Statistical significance[†]

P rate	L,Q	L	L,Q	L	L,Q	L
Zn rate	L	NS	*	*	*	NS
P X Zn	NS	NS	NS	NS	NS	NS

[†] Orthogonal contrast which are significant (P = 0.05) for P and Zn effects (L = linear; Q = quadratic)

NS - Not significant

* Indicate significant effect of Zn at 0.05 level in Carrot River or Meota soil

derived from applied P in roots and tops, respectively. On the other hand, the % Pdf in roots and tops of the corresponding treatments in the Carrot River or the Meota soil was relatively less (Table 4.2.41). This may be attributed to lower levels of bicarbonate-extractable soil P in the Sutherland soil.

4.2.4 Effectiveness of Zn fertilizers

The data for dry matter yield (DMY), Zn concentration and uptake from Experiment 1 are provided in Table 4.2.42. There was a significant effect of Zn application on the production of above ground plant material (DMY) for all sources used but there was no effect on roots (Table 4.2.42). The Zn levels in the bean tissue of the control treatments (Table 4.2.42) were below the "desirable minimum Zn concentration", which is required to achieve good yields and rapid maturation of beans (Boawn, 1973).

Zinc concentration and uptake in tops and roots increased significantly over the control treatments with applied Zn (Table 4.2.42). It was interesting to note that the highest Zn concentration and uptake in roots and tops was achieved with low-yield ammonium based lignosulphonate (ZnLY) and zinc sulphate (ZnSO_4). The higher values obtained for ZnLY, when compared to those with high-yield sodium based lignosulphonate (ZnHY), are presumably a consequence of the lower lignin content (and, therefore, chelating ability) of this substrate (see Table 3.3, Section 3.2.4). This view is also supported by the relatively low DTPA-extractable Zn levels recovered in the ZnHY treatment in Experiment 1 (Table 4.2.42) and incubation experiment (Table 4.2.44). Of particular significance, however, is the

Table 4.2.42 Effect of Zn sources[†] on dry matter yield (DMY), Zn concentration and uptake by beans and DTPA-extractable soil Zn.

Variable	Fertilizer Source							
	ZnSO ₄		ZnLY		ZnHY		ZnEDTA	
	-Zn	+Zn	-Zn	+Zn	-Zn	+Zn	-Zn	+Zn
DMY shoots, g pot ⁻¹	2.23b	2.61a	2.07b	2.86a	2.19b	2.58a	1.68c	2.52a [‡]
DMY roots, g pot ⁻¹	0.88a	0.76a	0.81a	0.81a	0.83a	0.81a	0.67a	0.77a
Zn concentration, shoots mg kg ⁻¹	19.6d	85.4a	20.8d	74.8a	20.4d	52.2b	28.8c	65.1b
Zn concentration, roots mg kg ⁻¹	32.6d	132.0b	31.0d	153.4a	28.9d	71.5c	34.1d	87.6c
Zn uptake, shoots, µg pot ⁻¹	42.9d	215.1a	43.6d	217.9a	42.7d	130.1c	45.7d	155.4b
Zn uptake, roots, µg pot ⁻¹	28.3d	110.8b	25.2d	128.6a	24.8d	57.5c	22.6d	66.9c
Zn concentration, top leaves mg kg ⁻¹	18.9	68.7	22.0	82.20	15.0	42.0	21.9	46.8
Zn extracted by DTPA, mg kg ⁻¹	0.08	0.80	0.11	1.68	0.15	0.69	0.14	1.60
% recovery of applied Zn as DTPA-extractable Zn	--	28.8	--	62.8	--	21.6	--	30.8

[†] ZnSO₄ = zinc sulfate; ZnLY = low yield ammonium[†] based zinc lignosulfonate; ZnHY = high yield sodium based zinc lignosulfonate; ZnEDTA = zinc EDTA

[‡] Means followed horizontally by the same letter are not statistically different at P < 0.05 (Duncan's multiple range test)

recognition that zinc EDTA (ZnEDTA), the most commonly used Zn chelating agent in field studies, was less effective than ZnLY in this experiment.

The second experiment was conducted to investigate the relative efficiencies of ZnSO_4 and ZnLY at four Zn rates (0, 0.5, 2.5 and 5.0 mg kg^{-1} soil, respectively). Maximum yields were statistically obtained at different rates of applied Zn for the two sources (Table 4.2.43). Maximum yield with ZnLY was obtained with application of 2.5 mg Zn kg^{-1} of soil compared to 0.5 mg Zn kg^{-1} applied as ZnSO_4 . Dry matter yield obtained with Zn rates above these two levels with the corresponding sources was not significantly different. In contrast to yields, Zn concentration was significantly higher with ZnLY at 2.5 and 5 mg Zn kg^{-1} treatments compared to the same treatments of ZnSO_4 . Chelating agents are known to enhance the uptake of Zn by increasing the rate of diffusion in the immediate vicinity of plant roots (Elgawhary et al., 1970; Halvorson and Lindsay, 1977).

The amount of Zn extracted by DTPA after incubation varied with each Zn-source and soil (Table 4.2.44). At the end of the incubation period (5 weeks at $25 \pm 1^\circ\text{C}$), DTPA-extractable Zn ranged from 34.6 to 63.5% for the ZnSO_4 treatment, 49.5 to 70.3% for the ZnEDTA treatment, 90.1 to 94.4% for the ZnLY treatment, and 28.9 to 49.2% for the ZnHY treatment.

One significant feature of these results is that when Zn was applied as ZnEDTA, lower recoveries (49.5 to 57.5%) were obtained from soils with high organic matter and clay content and high calcium concentration (Table 3.4, Section 3.2.4). The mobility and fixation of Zn applied as ZnEDTA has been shown to be related to the Ca

Table 4.2.43 Effect of Zn rate of Zn-sulfate (ZnSO_4) and low yield ammonium based Zn-lignosulfonate (ZnLY) on dry matter yield (DMY), Zn concentration and uptake by beans and DTPA-extractable soil Zn.

Variable	Zn Rate (mg kg^{-1})							
	0		0.5		2.5		5.0	
	ZnSO_4	ZnLY	ZnSO_4	ZnLY	ZnSO_4	ZnLY	ZnSO_4	ZnLY
DMY shoots, g pot^{-1}	1.85b	1.99b	3.35a	2.67b	3.54a	3.32a	3.65a	3.52a [†]
Zn concentration, mg kg^{-1}	17.1e	14.7e	34.3d	35.2d	57.8c	82.4b	75.9b	107.0a
Zn uptake, $\mu\text{g pot}^{-1}$	31.5e	30.3e	115.8c	93.9c	236.4b	270.2a	274.5b	375.1a
Zn extracted by DTPA, mg kg	0.07	0.07	0.50	0.57	1.87	1.93	2.83	4.22
% recovery of applied Zn as DTPA-extractable Zn	--	--	86.00	100.0	72.0	74.40	55.2	83.0

[†] Means followed horizontally by the same letter are not statistically different at $P < 0.05$ (Duncan's multiple range test).

Table 4.2.44 Recovery of applied Zn by DTPA in the incubation experiment.

Soil	% recovery of applied Zn by DTPA			
	ZnSO ₄	ZnLY	ZnHY	ZnEDTA
Regosolic very fine sandy loam	34.6	90.1	28.9	70.3
Chernozemic loamy very fine sand	39.1	90.2	34.9	57.7
Chernozemic loam	50.5	93.0	42.7	55.9
Chernozemic silty loam	63.5	94.1	42.2	49.5

concentration, carbonate content and soil type (Hochberg and Lahav, 1978).

4.3 Distribution of Native and Applied Zinc

4.3.1 Distribution of native Zn

Amounts and percent distribution of native Zn among the water soluble plus exchangeable (nonspecifically adsorbed (EX)), exchangeable (specifically adsorbed (ExAD)), organic (OM), manganese oxide (MnOX), Fe oxide (FeOX) and residual (RES) fractions of the soils studied is summarized in Table 4.3.1. The sum of all Zn fractions rarely differed by more than 5% of the total Zn analysis.

The amounts and the percent distribution of total Zn in different fractions varied widely in three soils. The percentage of Zn in EX, ExAD, OM and MnOX fractions averaged 0.2, 0.7, 7 and 1.4%, respectively (Table 4.3.1). All three soils contained very low amounts of exchangeable (nonspecifically or specifically adsorbed) and

Table 4.3.1 Distribution of native Zn in different fractions.

Soils	Different fractions						Sum of fractions	Total analysis
	EX	ExAD	OM	MnOX	FeOX	RES		
	mg kg ⁻¹							
Carrot River	0.20+0.03 [†] (0.3) _ψ	0.55+0.04 (0.9)	3.25+0.11 (5.1)	1.10+0.14 (1.7)	14.30+1.13 (22.6)	43.82+1.25 (69.3)	63.22	65.56+2.12
Meota	0.20+0.00 (0.3)	0.90+0.14 (1.2)	4.90+0.14 (7.0)	1.15+0.07 (1.6)	14.85+1.02 (21.1)	48.40+0.35 (68.7)	70.40	67.98+2.26
Sutherland	0.13+0.02 (0.1)	0.13+0.05 (0.1)	9.24+0.35 (8.9)	1.10+0.06 (1.0)	28.97+1.48 (27.9)	64.10+1.15 (61.8)	103.67	107.50+1.98

[†]Averages of two replications with standard errors^ψFigures in parentheses indicate percent of the total Zn (sum of fractions)

MnOX native Zn. Relatively low amounts of exchangeable Zn have also been reported by other workers (Sedberry and Reddy, 1976; Shuman, 1979; Iyengar et al., 1981). Most of the Zn was associated with organic matter, Fe oxides and the residual mineral fractions. The OM fraction was significantly lower in the Carrot River soil compared to the Meota soil, which in turn was less than that of the Sutherland soil. This is in agreement with studies relating Zn in this fraction to soil organic matter levels (Iyengar et al., 1981).

The RES and FeOX fractions in the three soils averaged 66.6% and 23.9%, respectively, and constituted the major proportion of the native soil Zn. Fractionation of Zn in several Georgia (Shuman, 1979) and Virginia (Iyengar et al., 1981) soils has shown that up to 70% and 25% of the total Zn was associated with residual and Fe oxide fractions, respectively. Among the three soils in this study, the Sutherland soil had greater amounts of Zn in RES fraction compared to the Carrot River and Meota soils. Shuman (1979) has reported that a large portion of the total Zn is associated with clay-size fractions and considerably less with sand or silt fractions. However, the relatively high amounts of RES Zn present in the sandy soils (Carrot River and Meota soils) of this study indicate that a significant portion of the RES Zn could be associated with sand-size particles. The Sutherland soil was high in free iron content, therefore Zn associated with FeOX fraction was clearly high in this soil compared with the Carrot River and Meota soils.

4.3.2 Distribution of applied Zn

The distribution of applied Zn in various fractions of the

three soils after seven days incubation is shown in Table 4.3.2. The amount and percent distribution of applied Zn in OM, FeOX and MnOX fractions in all soils varied directly with organic carbon, Fe- and Mn-oxide contents. The greater proportion of Zn applied to the Carrot River soil was found to accumulate in ExAD (34.3%) and FeOX (26.2%) fractions (Table 4.3.2). In addition to ExAD (30.8%) and FeOX (26.1%) fractions, significant amounts of applied Zn to the Meota soil were recovered in the OM fraction (26.9%) (Table 4.3.2). In the Sutherland soil, however, most of the applied Zn was recovered in the OM (41.2%) and FeOX (35%) fractions (Table 4.3.2). In contrast to the Carrot River and Meota soils, the Sutherland soil had very low percentage of Zn in EX or ExAD fractions (Table 4.3.2). The percent recovery of Zn in MnOX fraction was 13.1, 11.8 and 16% in the Carrot River, Meota and Sutherland soils, respectively (Table 4.3.2).

Little Zn was found to be associated with the EX fraction in the Sutherland and Meota soils compared to the Carrot River soil (Table 4.3.2). This may be due to the much lower pH of the latter soil. Shuman (1975) reported increases in Zn sorption with increasing soil pH, particularly on coarser textured soils. Similar decreases in exchangeable Zn with an increase in pH were observed to be associated with shifts of Zn into organically complexed or oxides-bound fractions (Sims and Patrick, 1978; Iyengar et al., 1981; Sims, 1986). There was no consistent effect of pH on the ExAD fraction in this study.

Shuman (1979) has reported that high amounts of exchangeable Zn in soils are associated with high cation exchange capacity. This conclusion was not verified by the results of this study, since the soil with the highest cation exchange capacity (Sutherland) contained

Table 4.3.2 Distribution of added Zn in different fractions after 7 days incubation period.

Soils	Different fractions						Sum of fractions	Total analysis
	EX	ExAD	OM	MnOX	FeOX	RES		
	mg kg ⁻¹							
Carrot River	0.46+0.01 [†] (9.3) ^ψ	1.70+0.02 (34.3)	0.67+0.05 (13.5)	0.65+0.07 (13.1)	1.30+0.03 (26.2)	0.18+0.04 (3.6)	4.96	5.10+0.11
Meota	0.06+0.02 (1.2)	1.56+0.07 (30.8)	1.36+0.04 (26.9)	0.60+0.09 (11.8)	1.32+0.11 (26.1)	0.16+0.02 (3.2)	5.06	4.90+0.14
Sutherland	0.03+0.01 (0.6)	0.20+0.02 (4.0)	2.06+0.14 (41.2)	0.80+0.03 (16.0)	1.75+0.10 (35.0)	0.16+0.02 (3.2)	5.00	5.15+0.12

[†]Averages of two replications with standard errors^ψFigures in parentheses indicate percent of the total Zn (sum of fractions)

the least amount of exchangeable Zn (Table 4.3.2).

In spite of the low contents of free iron and manganese in the soils of this study (Table 3.2), oxides themselves appeared to have a marked effect on the distribution of applied Zn, since a major portion of the added Zn was found in FeOX fraction. It has been shown that Al-, Fe- and Mn-oxides adsorb considerable quantities of Zn (Kinniburgh et al., 1976; Loganathan et al., 1977; Shuman, 1977) and that the adsorbed Zn is largely non-exchangeable (Kalbasi et al., 1978). Cavallaro and McBride (1984) found that destruction of organic matter increased Zn sorption and concluded that the oxide component of the soil was more significant than the organic component in Zn sorption and fixation. Therefore, it seems likely that Zn is preferentially bonded to oxide fractions (Cavallaro and McBride, 1984).

One salient feature of the results of this study is that, in contrast to the distribution of native Zn (Table 4.3.1), only very small amounts of applied Zn (3.2 to 3.6%) were recovered with RES fraction (Table 4.3.2). Keefer and Estep (1971) found much higher amounts (30.7 to 58.2%) of applied Zn in the residual mineral fraction (clay-fixed nonexchangeable) of West Virginia soils compared with soils of this study. A portion of the clay-fixed Zn in their study probably was associated with Al-, Fe- and Mn-oxides and hydroxides, since the fractionation technique used by the authors did not account for these fractions. Although Zn fixation has been attributed to lattice substitution (Elgabaly, 1950), clay adsorption of Zn without fixation is most likely an exchange process (Reddy and Perkins, 1974).

Phosphorus application did not affect the distribution of Zn in various Zn fractions in any of the soils studied (Tables 4.3.3, 4.3.4 and

4.3.5). Stanton and Burger (1970) and Bolland et al. (1977) have shown that P addition enhances Zn adsorption on iron and aluminum oxides. In contrast to these studies, Zn in the FeOX fraction was not affected by P fertilization in the present study. Cavallaro (1982) found lower Zn adsorption following phosphate saturation of the soil clay surfaces.

The distribution of Zn in EX, MnOX and RES fractions remained almost unaffected with time (Tables 4.3.3, 4.3.4 and 4.3.5). The ExAD and OM Zn fractions tended to decrease with time with concomitant increases in Zn associated with FeOX fractions, particularly in the Sutherland soil (Table 4.3.5). Though values decreased with time, the reduction was great only at the maturity stage. These results indicate that part of Zn released from ExAD and OM fractions was taken up by plants and a part went to the FeOX fraction.

The limited number of soils did not permit a statistical assessment of relationships between Zn uptake and the various Zn fractions. The relative increases in total Zn uptake due to application of 5 mg Zn kg^{-1} of the Carrot River and Sutherland soils were 134 and 75% and 67.9 and 29.0% at 1/10 bloom stage and maturity, respectively. These results seem to indicate that EX and ExAD Zn fractions were the most available forms of Zn since the Carrot River soils had higher Zn contents in these fractions compared to the Sutherland soil. Plant uptake of Zn was primarily related to the exchangeable fraction (Sims, 1986). Iyengar et al. (1981) found that the adsorbed and organically bound Zn were more available than that occluded in Fe or Mn oxides. However, in the present study OM Zn fraction does not seem to contribute significantly to plant uptake as the Zn uptake in Sutherland soil was less in spite of high values for the OM fraction.

Table 4.3.3 The effect of time and P on the distribution of added Zn in Carrot River soil.

Treatment		Different fractions							Plant	Sum of fractions	Total analysis
P	Zn	EX	EXAD	OM	MnOX	FeOX	RES				
mg kg ⁻¹											
<u>Before seeding</u>											
0	5	0.46+0.01 [†] (9.3) _ψ	1.70+0.02 (34.3) _ψ	0.67+0.05 (13.5) _ψ	0.65+0.07 (13.1) _ψ	1.30+0.03 (26.2) _ψ	0.18+0.04 (3.6) _ψ	--	4.96	5.10+0.11 _ψ	
160	5	0.48+0.04 (9.7) _ψ	1.68+0.09 (33.9) _ψ	0.64+0.07 (12.9) _ψ	0.66+0.03 (13.3) _ψ	1.32+0.12 (26.7) _ψ	0.17+0.03 (3.4) _ψ	--	4.95	4.85+0.13 _ψ	
<u>At 1/10 bloom stage</u>											
0	5	0.49+0.02 (9.7) _ψ	1.66+0.05 (32.9) _ψ	0.70+0.07 (13.9) _ψ	0.62+0.06 (12.3) _ψ	1.33+0.06 (26.3) _ψ	0.19+0.05 (3.8) _ψ	0.06+0.02 (1.2) _ψ	5.05	5.16+0.15 _ψ	
160	5	0.50+0.06 (10.0) _ψ	1.65+0.10 (32.9) _ψ	0.68+0.04 (13.5) _ψ	0.61+0.04 (12.2) _ψ	1.34+0.09 (26.7) _ψ	0.17+0.10 (3.4) _ψ	0.07+0.02 (1.4) _ψ	5.02	4.90+0.09 _ψ	
<u>At maturity</u>											
0	5	0.50+0.04 (10.0) _ψ	1.58+0.08 (31.8) _ψ	0.58+0.12 (11.7) _ψ	0.64+0.02 (12.9) _ψ	1.36+0.02 (27.4) _ψ	0.19+0.03 (3.8) _ψ	0.12+0.00 (2.4) _ψ	4.97	5.08+0.08 _ψ	
160	5	0.52+0.08 (10.3) _ψ	1.56+0.04 (30.8) _ψ	0.57+0.07 (11.3) _ψ	0.64+0.05 (12.6) _ψ	1.35+0.08 (26.7) _ψ	0.19+0.09 (3.8) _ψ	0.23+0.04 (4.5) _ψ	5.06	5.10+0.10 _ψ	

[†] Average of two replications with standard errors

^ψ Figures in parentheses indicate percent of the total Zn (sum of fractions)

Table 4.3.4 The effect of time and P on the distribution of added Zn in Meeta soil.

Treatment		Different fractions						Plant	Sum of fractions	Total analysis
P	Zn	EX	ExAD	OM	MnOX	FeOX	RES			
mg kg ⁻¹										
<u>Before seeding</u>										
0	5	0.06+0.02 [†] (1.2) [‡]	1.56+0.07 (30.8) [‡]	1.36+0.04 (26.9) [‡]	0.60+0.09 (11.8) [‡]	1.32+0.11 (26.1) [‡]	0.16+0.02 (3.2) [‡]	--	5.06	4.90+0.14
160	5	0.06+0.03 (1.2) [‡]	1.56+0.07 (30.9) [‡]	1.35+0.12 (26.7) [‡]	0.59+0.08 (11.7) [‡]	1.34+0.02 (26.5) [‡]	0.15+0.03 (3.0) [‡]	--	5.05	5.20+0.17
<u>At 1/10 bloom stage</u>										
0	5	0.05+0.02 (1.0) [‡]	1.53+0.04 (30.3) [‡]	1.33+0.07 (26.3) [‡]	0.61+0.02 (12.1) [‡]	1.35+0.08 (26.7) [‡]	0.15+0.00 (3.0) [‡]	0.03+0.01 (0.6) [‡]	5.05	4.90+0.12
160	5	0.06+0.00 (1.2) [‡]	1.54+0.02 (30.2) [‡]	1.35+0.05 (26.5) [‡]	0.60+0.07 (11.8) [‡]	1.36+0.09 (26.7) [‡]	0.15+0.03 (2.9) [‡]	0.03+0.01 (0.6) [‡]	5.09	5.06+0.08
<u>At maturity</u>										
0	5	0.05+0.04 (1.0) [‡]	1.42+0.09 (29.0) [‡]	1.26+0.04 (25.7) [‡]	0.59+0.01 (12.0) [‡]	1.42+0.11 (29.0) [‡]	0.16+0.05 (3.3) [‡]	0.07+0.03 (1.4) [‡]	4.90	5.10+0.12
160	5	0.06+0.01 (1.2) [‡]	1.42+0.02 (28.3) [‡]	1.28+0.07 (25.5) [‡]	0.62+0.05 (12.4) [‡]	1.40+0.06 (27.9) [‡]	0.16+0.01 (3.2) [‡]	0.07+0.04 (1.4) [‡]	5.01	5.02+0.04

[†] Average of two replications with standard errors

[‡] Figures in parentheses indicate percent of the total Zn (sum of fractions)

Table 4.3.5 The effect of time and P on the distribution of added Zn in Sutherland soil.

Treatment		Different fractions						Plant	Sum of fractions	Total analysis
P	Zn	EX	EXAD	OM	MnOX	FeOX	RES			
mg kg ⁻¹										
<u>Before seeding</u>										
0	5	0.03+0.01 [†] (0.6) [‡]	0.20+0.02 (4.0) [—]	2.06+0.14 (41.2) [—]	0.80+0.03 (16.0) [—]	1.75+0.10 (35.0) [—]	0.16+0.02 (3.2) [—]	---	5.00	5.15+0.07
160	5	0.03+0.02 (0.6) [—]	0.19+0.03 (3.8) [—]	2.07+0.02 (41.6) [—]	0.79+0.05 (15.9) [—]	1.74+0.07 (35.0) [—]	0.15+0.04 (3.0) [—]	--	4.97	5.20+0.19
<u>At 1/10 bloom stage</u>										
0	5	0.02+0.01 (0.4) [—]	0.18+0.00 (3.6) [—]	2.01+0.09 (40.4) [—]	0.81+0.04 (16.3) [—]	1.80+0.03 (36.1) [—]	0.14+0.02 (2.8) [—]	0.02+0.01 (0.4) [—]	4.98	5.00+0.05
160	5	0.02+0.01 (0.4) [—]	0.18+0.02 (3.6) [—]	2.00+0.10 (39.7) [—]	0.82+0.04 (16.3) [—]	1.82+0.04 (36.1) [—]	1.82+0.04 (3.2) [—]	0.16+0.03 (0.8) [—]	5.04	4.92+0.08
<u>At maturity</u>										
0	5	0.02+0.00 (0.4) [—]	0.16+0.04 (3.2) [—]	1.80+0.05 (36.4) [—]	0.79+0.05 (16.0) [—]	1.98+0.12 (40.0) [—]	0.15+0.04 (3.0) [—]	0.05+0.01 (1.0) [—]	4.95	5.20+0.18
160	5	0.02+0.01 (0.4) [—]	0.16+0.04 (3.2) [—]	1.79+0.08 (35.7) [—]	0.78+0.05 (15.6) [—]	1.97+0.10 (39.3) [—]	0.15+0.04 (3.0) [—]	0.14+0.02 (2.8) [—]	5.01	5.15+0.02

[†] Average of two replications with standard errors

[‡] Figures in parentheses indicate percent of the total Zn (sum of fractions)

5. SUMMARY AND CONCLUSIONS

The objectives of this thesis were: (i) to study the spatial variability of Zn in Saskatchewan soils of both uniform and undulating topographies; (ii) to examine the importance of Zn in crop nutrition and production of common crops in Saskatchewan, and (iii) to understand the transformations of native and added Zn in soils and their distribution among different soil Zn fractions in relation to plant availability. To meet these objectives several field, growth chamber and laboratory studies were conducted.

DTPA-extractable micronutrients (Zn, Cu, Mn and Fe) in fields of level topography showed a high degree of variability in samples taken along transects and geostatistical analyses (semivariograms) indicated that the extractable micronutrients were randomly distributed. In contrast, DTPA-extractable Zn and tissue Zn concentration in undulating topography showed spatial structure with a range of 25 m in all except one of the transects considered. DTPA-extractable Zn and organic C levels were highly correlated and had similar spatial structure.

DTPA-extractable Zn levels from approximately 1200 fields from various parts of Saskatchewan were compiled using soil samples submitted by individual farmers to the Saskatchewan Soil Testing Laboratory (SSTL) and others collected by our research team from the field research site. Soils in the populations studied were classified into three groups arbitrarily on the basis of DTPA-extractable Zn. Class 1 ($<0.5 \text{ mg Zn kg}^{-1}$ soil) included soil samples with Zn levels below the critical level adopted by the SSTL. Class 2 included Zn

levels in the marginal range ($0.5 - 1.0 \text{ mg Zn kg}^{-1} \text{ soil}$) and Class 3 adequate levels ($>1.0 \text{ mg Zn kg}^{-1} \text{ soil}$) of DTPA-extractable Zn. DTPA-extractable Zn levels in 12% of the population examined had Zn levels below the critical level of 0.5 mg kg^{-1} (Class 1), while approximately 37% belonged to Class 2.

The validity of the DTPA-extractable Zn test was evaluated in field experiments. Zinc fertilizers in various forms were applied to soils belonging to the three DTPA-extractable Zn classes prior to seeding or to the foliage of growing crops. In none of the 23 field trials conducted with various crops was there a response to Zn fertilization except in one with corn. Soil applied Zn-sulfate had residual effects as demonstrated by DTPA-extractable soil Zn levels. However, there was no yield response to residual soil Zn levels.

The relative effectiveness of ZnSO_4 , ZnEDTA, low-yield ammonium-based lignosulphonate (ZnLY) and high-yield sodium-based lignosulphonate (ZnHY) for beans production was tested in two growth chamber experiments. In the first experiment, Zn in organic forms was applied at a rate of $2.5 \text{ mg kg}^{-1} \text{ soil}$ and ZnSO_4 form at $5 \text{ mg kg}^{-1} \text{ soil}$. A check treatment without Zn was included for each source. In the second experiment, ZnSO_4 and ZnLY were applied at four rates (0, 0.5, 2.5 and $5.0 \text{ mg Zn kg}^{-1} \text{ soil}$). In the incubation experiment, four soils were treated with $10 \text{ mg Zn kg}^{-1} \text{ soil}$ in the form of ZnSO_4 , ZnEDTA, ZnLY or ZnHY. Results of the growth chamber and incubation experiments indicated that ZnLY was more effective than ZnEDTA and ZnHY in correcting Zn deficiency of bean plants. Further while biomass production was best with ZnSO_4 , ZnLY was more effective in increasing Zn content in the foliage.

Clear evidence of Zn deficiency in wheat was recorded in previous work at one field site due to large applications of P and their residual effect. One-time heavy applications of P on Chernozemic soils can provide sufficient available P to sustain crop production over a period of several years, but may cause Zn nutritional problem for crops. Therefore, studies were conducted to determine the effect of Zn applied to wheat grown on residual P plots in the field and both P and Zn applied to beans, in a growth chamber study.

The field study was conducted in 1984, in a continuous wheat system, on a Sutherland soil (Dark Brown Chernozemic) that had received 0, 80 and 160 kg P ha⁻¹ in 1979. Three experiments were carried out using a split plot randomized complete block design with three levels of P as main plots and rates of soil applied Zn-sulfate (0, 5, 10 and 20 kg Zn ha⁻¹) or Zn-chelate (0, 0.5, 1.0, and 2.0 kg Zn ha⁻¹) or foliar applied Zn-chelate (0 and 0.35 kg Zn ha⁻¹) as subplots.

A one-time application of 80 or 160 kg P ha⁻¹ increased wheat yield significantly. In the presence of P, application of Zn resulted in a significant increase in grain yield and in Zn uptake into grain. Applied P increased soil P and tissue P concentration, but resulted in a significant decrease of tissue Zn concentration. DTPA-extractable soil Zn levels in the non-Zn amended treatment were independent of P application rate. Plant roots in high P treatments contained significantly lower levels of vesicular-arbuscular mycorrhizal (VAM) infection than the control. Further, a close relationship was observed between Zn levels in the above ground plant parts and VAM infection.

Interactions of soil applied P (0, 40, 80 and 160 mg ^{32}P kg $^{-1}$) and Zn (0, 5 or 10 mg ^{65}Zn kg $^{-1}$) in roots and above ground portions of bean at two growth stages were studied in the Sutherland (Dark Brown Chernozemic), Carrot River (Dark Gray Chernozemic) and Meota (Black Chernozemic) soils in the growth chamber. The P X Zn interaction on dry matter yield of above ground parts was significant for the Sutherland and Carrot River soils only. This interaction was expressed by larger yield responses to P when Zn was applied. The Zn concentration in tops was significantly reduced due to P application and the magnitude of reduction was greatest for the first increment of added P (40 mg P kg $^{-1}$). Translocation of Zn from roots to tops was inhibited in the 80 and 160 mg P kg $^{-1}$ treatments, as evidenced by reduction of Zn uptake into tops of non-Zn treatments. Plant dilution effects and reduced translocation of Zn from roots to tops were the two mechanisms responsible for the observed P-induced Zn deficiency in this study.

Added P increased the concentration and uptake of P in all plant parts at both growth stages in all soils. Increasing levels of Zn generally decreased the P concentration and uptake in the above ground plant parts. Root P concentration and uptake, however, increased with Zn application in the Sutherland and Carrot River soils only at 1/10 bloom stage. The increase in P concentration in the above ground plant parts was of greater magnitude with 80 or 160 mg P kg $^{-1}$ treatments in the absence than in the presence of applied Zn in the Sutherland and Carrot River soils. Thus Zn deficiency markedly enhanced P absorption by roots, transport and accumulation of P in above ground plant parts. However, P levels in bean tissue did not

reach reported toxicity levels.

The Zn derived from applied source (% Zndff) was affected by soil properties and the native labile pool of Zn. Depending on the P level, plant part and growth stage, 22.7 to 55.4%, 41.9 to 59.6% and 7.9 to 44.6% of Zn was derived from the applied source by beans in the Sutherland, Carrot River and Meota soils, respectively. The % Zndff was generally decreased in roots with P application whereas it was increased in the above ground portions of beans grown on the Sutherland and Carrot River soils only. Phosphorus application increased % Pdf in roots and tops in all soils. Application of Zn generally decreased the % Pdf in plant tops but increased it in the roots.

The distribution of native and applied Zn was studied in the Sutherland, Carrot River and Meota soils used for P X Zn experiment with beans. The distribution of added Zn ($5 \text{ mg } ^{65}\text{Zn kg}^{-1}$) was studied under two P treatments (0 and 160 mg P kg^{-1}) and soil samples were analyzed before seeding, after 1/10 bloom stage, and after harvesting the beans at maturity.

Total Zn was fractionated sequentially into water soluble plus exchangeable (EX), specifically adsorbed (ExAD), organically bound (OM), Mn-oxide bound (MnOX), Fe-oxide bound (FeOX) and residual (RES) forms. Most of the native Zn was present in RES (66.6%) and FeOX (23.9%) fractions. Among the three soils studied, the Sutherland soil had greater amounts of Zn in RES fraction compared to the Carrot River and Meota soils. The percentage of Zn in EX, ExAD, OM and MnOX fractions averaged 0.2, 0.7, 7.0 and 1.4%, respectively.

Added Zn was relatively higher in EX or ExAD fractions in the

Carrot River (9.3% or 34.3%) and Meota (1.2% or 30.8%) soils compared with the Sutherland soil (0.6% or 4.0%). In the Sutherland soil, most of the applied Zn was recovered in the OM (41.2%) and FeOX (35%) fractions. Very small amounts (3.2 to 3.6%) of applied Zn were associated with the RES fraction in all soils.

Addition of P did not affect the distribution of Zn in different forms in any of the soils studied. The OM, MnOX and FeOX fractions of the applied Zn in all soils varied directly with organic carbon, Mn- and Fe-oxide contents of the soils. Distribution of Zn in different fractions in three soils and Zn plant uptake data tended to indicate that plant uptake was primarily related to water soluble plus exchangeable and specifically adsorbed fractions.

The major conclusions of this thesis are as follows:

1. Under current cropping systems Zn deficiency in crops is not likely to occur in Saskatchewan, with the possible exception of special crops in localized areas or in soils with low levels of Zn where heavy applications of P are made.

2. Although a one-time application of large amounts of P on certain soils can provide sufficient available P to sustain crop production over a period of several years, it can also lead to Zn disorders in crops. In Saskatchewan, soil application of 10 kg Zn as $\text{ZnSO}_4 \text{ ha}^{-1}$ or foliar application of 0.35 kg Zn as Zn-chelate ha^{-1} are suggested as effective means of alleviating the adverse effect of high residual P in soil.

3. P-induced Zn deficiency observed in wheat and beans was found to be the result of plant dilution effects and physiological effects enhanced by reduced mycorrhizal infection. Neither P X Zn

interaction in the soil nor P toxicity in plant tops have been observed.

4. Examination of the forms and distribution of Zn in three representative Saskatchewan soils indicated that the water soluble plus exchangeable and the specifically adsorbed fractions are of importance in assessing plant Zn availability. Therefore, selection of extractants to identify Zn deficient soils should be based on the extractant's effectiveness in identifying these fractions. The DTPA soil test can be used successfully to determine the available Zn in sandy soils. However this test may not be successful in clayey soil. Hence, current soil testing criteria for the assessment of available Zn in Saskatchewan soils must be revised. The revision must proceed in two major directions, namely, (i) prediction of the Zn fertility of soils in which heavy rates of P have been or are being applied, and (ii) prediction of the Zn fertility of various types of Saskatchewan soils or crops other than small grain cereals.

5. Proper interpretation of soil Zn tests as well as of Zn field experimentation requires knowledge of the spatial variability of this nutrient in the field. Knowledge of the spatial variability of Zn in fields containing levels of Zn well above the critical level bears no significance to assessing the Zn fertility. However, at soil Zn levels near the critical level, knowledge of the spatial variability can prove an asset in determining fertilizer requirements in field research experiments. It is highly unlikely that in a routine soil testing program it will be possible to take sufficient samples to achieve high level of precision for Zn. However, current soil sampling practices recommended by the Saskatchewan Soil Testing

Laboratory appear to be adequate.

6. A great portion of the variation as well as spatial distribution of Zn can be inferred from that of organic C levels. This could be of major significance in assessing the Zn status of soils on a per map unit or soil site basis.

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A P P É N D I X

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Table A.1 Mean squares from the analysis of variance for the yield of beans grown on Sutherland soil.

Source	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>						
P linear (P-L)	1	0.28**	10.77**	1.31**	53.32**	34.89**
P quadratic (P-Q)	1	0.45**	6.30**	0.78**	50.54**	30.27**
P cubic (P-C)	1	0.06	1.71*	0.23*	12.26**	5.72**
<u>Zn effects</u>						
Zn linear (Zn-L)	1	0.01	3.99**	0.02	6.85**	5.70**
Zn quadratic (Zn-Q)	1	0.00	1.33**	0.00	3.01**	3.26**
<u>Interaction effects</u>						
P-L X Zn-L	1	0.01	1.99**	0.00	1.58*	0.54
P-L X Zn-Q	1	0.01	0.48	0.00	1.29	2.15*
P-Q X Zn-L	1	0.00	0.69*	0.00	1.44*	1.49
P-Q X Zn-Q	1	0.00	0.07	0.01	0.03	0.01
P-C X Zn-L	1	0.00	0.01	0.01	0.37	0.23
P-C X Zn-Q	1	0.00	0.00	0.03	0.37	0.00
Error	36	0.02	0.15	0.04	0.35	0.40

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table A.2 Mean squares from the analysis of variance for the yield of beans grown on Carrot River soil.

Source	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>						
P linear (P-L)	1	0.23**	2.97**	0.38*	29.35**	11.22**
P quadratic (P-Q)	1	0.17**	2.38**	0.30*	29.86**	7.81**
P cubic (P-C)	1	0.05	0.47*	0.03	5.76**	1.72
<u>Zn effects</u>						
0 vs. 5 (Zn)	1	0.03	3.85**	0.00	14.99**	5.53**
<u>Interaction effects</u>						
P-L X Zn	1	0.03	0.53*	0.01	3.83**	0.85
P-Q X Zn	1	0.07	0.04	0.02	1.76	0.10
P-C X Zn	1	0.02	0.00	0.00	0.07	0.04
Error	24	0.02	0.09	0.05	0.48	0.61

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table A.3 Mean squares from the analysis of variance for the yield of beans grown on Meota soil.

Source	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>						
P linear (P-L)	1	0.26**	3.94**	0.34**	11.95**	10.34**
P quadratic (P-Q)	1	0.12*	0.46	0.51**	16.44**	7.54**
P cubic (P-C)	1	0.02	0.55	0.10	1.75	0.17
<u>Zn effects</u>						
0 vs. 5 (Zn)	1	0.01	0.10	0.02	0.03	0.55
<u>Interaction effects</u>						
P-L X Zn	1	0.05	0.13	0.01	0.00	0.01
P-Q X Zn	1	0.01	0.11	0.00	0.00	0.12
P-C X Zn	1	0.00	0.02	0.00	0.23	0.04
Error	24	0.02	0.13	0.04	1.05	0.78

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table A.4 Mean squares from the analysis of variance for the Zn concentration of beans grown on Sutherland soil.

Source	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>						
P linear (P-L)	1	80.23**	816.63**	44.25**	369.75**	469.69**
P quadratic (P-Q)	1	160.33**	555.39**	66.24**	1021.58**	423.63**
P cubic (P-C)	1	53.49**	110.37**	16.14	161.84**	142.83**
<u>Zn effects</u>						
Zn linear (Zn-L)	1	485.10**	1954.69**	741.20**	660.66*	667.95**
Zn quadratic (Zn-Q)	1	20.41	150.25**	8.25	5.51	25.01
<u>Interaction effects</u>						
P-L X Zn-L	1	683.55**	22.60	75.99**	60.82*	7.86
P-L X Zn-Q	1	0.09	10.55	9.38	6.26	0.45
P-Q X Zn-L	1	322.63**	101.95**	60.03**	139.32**	47.07*
P-Q X Zn-Q	1	8.11	25.43	10.32	0.03	6.55
P-C X Zn-L	1	18.74	3.49	33.66**	74.18*	39.65*
P-C X Zn-Q	1	0.02	14.43	8.12	0.85	13.39
Error	36	6.89	11.15	4.38	12.22	17.48

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table A.5 Mean squares from the analysis of variance for the Zn concentration of beans grown on Carrot River soil.

Source	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>						
P linear (P-L)	1	12.15	311.65**	5.15	53.73*	174.35**
P quadratic (P-Q)	1	16.76	141.75**	37.56*	118.76**	88.71**
P cubic (P-C)	1	90.95**	23.12*	55.09**	14.43	7.75
<u>Zn effects</u>						
0 vs. 5 (Zn)	1	5428.01**	2467.53**	2187.90**	260.49**	1575.01**
<u>Interaction effects</u>						
P-L X Zn	1	243.54**	0.32	139.70**	1.67	1.90
P-Q X Zn	1	20.22	26.09*	63.96**	4.15	1.04
P-C X Zn	1	33.93	4.16	24.25	0.40	1.69
Error	24	12.45	5.30	6.93	8.28	7.09

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table A.6 Mean squares from the analysis of variance for the Zn concentration beans grown on Meota soil.

Source	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>						
P linear (P-L)	1	1.06	1.98	1.24	13.51	44.28**
P quadratic (P-Q)	1	10.68	22.85*	33.94	135.05**	62.10**
P cubic (P-C)	1	0.02	0.74	1.44	0.48	8.56
<u>Zn effects</u>						
0 vs. 5 (Zn)	1	3271.84**	501.65**	685.13**	60.50*	65.84**
<u>Interaction effects</u>						
P-L X Zn	1	9.36	0.02	1.59	19.03	9.79
P-Q X Zn	1	0.94	16.05	6.20	8.43	15.37
P-C X Zn	1	10.85	1.38	1.14	7.10	1.80
Error	24	50.48	5.22	6.57	8.99	4.77

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table 4.7 Mean squares from the analysis of variance for the Zn uptake beans grown on Sutherland soil.

Source	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>						
P linear (P-L)	1	139.25**	1669.20**	551.40**	20571.46**	2478.09**
P quadratic (P-Q)	1	177.16**	819.72**	246.02**	13311.21**	1776.94*
P cubic (P-C)	1	11.94	298.98	85.28*	5064.13**	42.36
<u>Zn effects</u>						
Zn linear (Zn-L)	1	104.19*	15344.02**	313.02**	19130.17**	16894.44**
Zn quadratic (Zn-Q)	1	2.53	1763.71**	3.05	848.65	1464.45*
<u>Interaction effects</u>						
P-L X Zn-L	1	41.39	1832.65**	0.36	2261.69*	2107.91**
P-L X Zn-Q	1	6.85	63.77	9.87	974.72	946.91
P-Q X Zn-L	1	15.59	266.90	13.79	527.43	165.42
P-Q X Zn-Q	1	0.39	6.70	16.14	9.62	24.64
P-C X Zn-L	1	0.14	66.37	0.10	0.42	80.92
P-C X Zn-Q	1	0.08	23.34	1.01	49.95	170.17
Error	36	14.84	98.66	19.71	423.49	250.61

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

4.8 Mean squares from the analysis of variance for the Zn uptake beans grown on Carrot River soil.

Source	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>						
P linear (P-L)	1	367.97**	87.64	536.19**	24368.37**	670.61
P quadratic (P-Q)	1	80.53*	213.97	113.25	17812.89**	861.17*
P cubic (P-C)	1	0.00	40.97	17.77	3897.70*	470.05
<u>Zn effects</u>						
0 vs. 5 (Zn)	1	2693.61**	28285.12**	2665.40**	32242.13**	47097.64**
<u>Interaction effects</u>						
P-L X Zn	1	57.73	780.26**	18.25	6001.54*	1939.60**
P-Q X Zn	1	4.37	19.42	20.19	1640.70	457.02
P-C X Zn	1	33.08	1.70	25.86	13.58	42.60
Error	24	17.85	99.37	64.11	787.15	178.56

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table 4.9 Mean squares from the analysis of variance for the Zn uptake beans grown on Meota soil.

Source	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>						
P linear (P-L)	1	404.41*	2455.59**	246.98**	2742.22*	30.38
P quadratic (P-Q)	1	81.58	52.33	103.37	24.12	387.06
P cubic (P-C)	1	43.60	141.68	48.64	1059.61	173.33
<u>Zn effects</u>						
0 vs. 5 (Zn)	1	1639.24**	4445.54**	2717.54**	2917.91*	4049.32**
<u>Interaction effects</u>						
P-L X Zn	1	212.38	144.35	62.66	825.99	419.26
P-Q X Zn	1	17.49	10.56	0.69	88.51	810.05*
P-C X Zn	1	22.88	3.06	1.65	71.60	16.35
Error	24	84.68	144.08	34.81	611.66	121.76

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table A.10 Mean squares from the analysis of variance for the P concentration of beans grown on Sutherland soil.

Source	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>						
P linear (P-L)	1	3.65**	103.21**	12.74**	2.23**	21.08**
P quadratic (P-Q)	1	0.53**	1.19**	0.01	0.00	3.25**
P cubic (P-C)	1	0.21**	1.85**	0.05	0.06	0.10
<u>Zn effects</u>						
Zn linear (Zn-L)	1	0.42**	30.77**	0.28**	17.89**	5.13**
Zn quadratic (Zn-Q)	1	0.00	7.89**	0.14*	5.37**	2.00**
<u>Interaction effects</u>						
P-L X Zn-L	1	0.09**	19.03**	0.10	2.46**	2.08**
P-L X Zn-Q	1	0.01	3.06**	0.09	1.07*	0.88**
P-Q X Zn-L	1	0.03	1.31**	0.01	2.06**	0.14
P-Q X Zn-Q	1	0.01	0.47	0.00	0.78*	0.08
P-C X Zn-L	1	0.02	1.05**	0.00	0.88*	0.03
P-C X Zn-Q	1	0.01	0.00	0.00	0.04	0.02
Error	36	0.01	0.12	0.03	0.17	0.06

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table A.11 Mean squares from the analysis of variance for P concentration of beans grown on Carrot River soil.

	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>						
P linear (P-L)	1	22.68**	85.01**	32.36**	9.71**	11.23**
P quadratic (P-Q)	1	1.04**	3.67**	3.52**	0.32	0.67*
P cubic (P-C)	1	0.09**	0.11	0.45**	0.20	0.02
<u>Zn effects</u>						
0 vs. 5 (Zn)	1	0.72**	22.92*	0.65**	31.01**	8.02**
<u>Interaction effects</u>						
P-L X Zn	1	0.28**	8.50**	0.01	7.80**	0.91*
P-Q X Zn	1	0.03	0.14	0.14	1.39*	1.08*
P-C X Zn	1	0.01	0.19	0.02	0.01	0.29
Error	24	0.02	0.19	0.04	0.25	0.15

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table A.12 Mean squares from the analysis of variance for the P concentration of beans grown on Meota soil.

	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>						
P linear (P-L)	1	18.78**	37.80**	18.64**	27.79**	15.79**
P quadratic (P-Q)	1	2.93**	9.22**	0.09	3.94**	0.90**
P cubic (P-C)	1	0.06	0.26	0.06	0.00	0.34**
<u>Zn effects</u>						
0 vs. 5 (Zn)	1	0.06	1.07*	0.05	0.30*	0.19*
<u>Interaction effects</u>						
P-L X Zn	1	0.43	0.16	0.00	0.01	0.03
P-Q X Zn	1	0.10	0.10	0.00	0.05	0.00
P-C X Zn	1	0.13	0.05	0.00	0.00	0.01
Error	24	0.15	0.14	0.10	0.05	0.04

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table A.13 Mean squares from the analysis of variance for the P uptake of beans grown on Sutherland soil.

Source	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>						
P linear (P-L)	1	2.38**	951.63**	24.38**	1323.30**	720.62**
P quadratic (P-Q)	1	1.11**	36.67**	0.43	814.00**	191.28**
P cubic (P-C)	1	0.22*	0.16	0.09	156.72**	0.07
<u>Zn effects</u>						
Zn linear (Zn-L)	1	0.27*	14.59*	0.12	53.23*	18.05*
Zn quadratic (Zn-Q)	1	0.00	1.30	0.21	8.01	4.26
<u>Interaction effects</u>						
P-L X Zn-L	1	0.13	5.73	0.20	0.67	13.88*
P-L X Zn-Q	1	0.01	0.06	0.11	0.44	0.42
P-Q X Zn-L	1	0.00	0.40	0.02	4.96	0.23
P-Q X Zn-Q	1	0.02	1.24	0.02	12.18	1.06
P-C X Zn-L	1	0.00	1.31	0.03	4.02	0.22
P-C X Zn-Q	1	0.01	0.56	0.07	2.73	0.45
Error	36	0.05	2.02	0.31	9.82	3.03

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table A.14 Mean squares from the analysis of variance for the P uptake of beans grown on Carrot River soil.

Source	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>						
P linear (P-L)	1	16.27	790.47**	61.38**	1087.97**	547.07**
P quadratic (P-Q)	1	0.05	65.71**	10.44**	531.27**	78.28**
P cubic (P-C)	1	0.27**	5.02	0.75	59.30*	3.61
<u>Zn effects</u>						
0 vs. 5 (Zn)	1	0.75**	11.59*	1.24	63.25*	39.81*
<u>Interaction effects</u>						
P-L X Zn	1	0.19**	3.58	0.23	12.30	0.31
P-Q X Zn	1	0.40	0.82	0.04	2.14	15.81
P-C X Zn	1	0.01	0.02	0.07	2.11	6.28
Error	24	0.02	2.22	0.43	13.87	9.26

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table A.15 Mean squares from the analysis of variance for the P uptake of beans grown on Meeta soil.

Source	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>						
P linear (P-L)	1	14.66**	542.34**	84.25**	2696.66**	1127.73**
P quadratic (P-Q)	1	2.22**	92.24**	0.27	811.04**	10.29
P cubic (P-C)	1	0.11	11.77*	0.01	9.71	16.04
<u>Zn effects</u>						
0 vs. 5 (Zn)	1	0.26	5.89	0.47	14.11	3.04
<u>Interaction effects</u>						
P-L X Zn	1	0.04	2.15	0.11	0.18	1.10
P-Q X Zn	1	0.01	0.70	0.00	1.66	0.01
P-C X Zn	1	0.10	0.17	0.00	5.63	0.01
Error	24	0.25	1.84	0.96	18.73	4.11

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table A.16 Mean squares from the analysis of variance for the Zn derived from fertilizer (% Zndff) by beans grown on the Sutherland soil.

Source	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>						
P linear (P-L)	1	116.85*	137.56*	39.96	605.07**	575.71**
P quadratic (P-Q)	1	26.18	36.60	23.45	172.42*	201.37*
P cubic (P-C)	1	0.46	0.37	0.36	1.52	4.77
<u>Zn effects</u>						
5 vs. 10 (Zn)	1	927.20**	467.10**	73.96*	224.25**	370.56**
<u>Interaction effects</u>						
P-L X Zn	1	8.60	12.70	5.60	11.06	1.58
P-Q X Zn	1	42.50	0.07	8.27	36.57	53.18
P-C X Zn	1	29.85	2.92	0.38	15.02	33.93
Error	8	11.68	14.67	12.43	19.24	18.96

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table 17 Mean squares from the analysis of variance for the Zn derived from fertilizer (% Zn_{dff}) by beans grown on the Carrot River and Meota soils.

Source	df	1/10 bloom stage		Maturity		
		Roots	Tops	Roots	Seeds	Straw
<u>P effects</u>		<u>Carrot River</u>				
P linear (P-L)	1	26.29*	45.86*	21.73	125.96*	5.44
P quadratic (P-Q)	1	1.38	14.01	1.19	18.65	0.53
P cubic (P-C)	1	10.38	0.85	4.65	7.20	0.06
Error	4	2.32	3.20	4.23	2.70	3.29
<u>P effects</u>		<u>Meota</u>				
P linear (P-L)	1	544.89**	54.03*	55.27**	0.04	7.69
P quadratic (P-Q)	1	239.50**	7.73	50.24**	0.69	16.64
P cubic (P-C)	1	61.59**	5.89	6.43	0.00	0.19
Error	4	2.03	3.61	2.27	4.40	4.19

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table 1.18 Mean squares from the analysis of variance for the P derived from fertilizer (% Pdf) by beans at 1/10 bloom stage grown on the Sutherland soil.

Source	df	Roots	Tops
<u>P effects</u>			
P linear (P-L)	1	3282.93**	1474.65**
P quadratic (P-Q)	1	60.35**	13.12
<u>Zn effects</u>			
Zn linear (Zn-L)	1	62.56**	7.05
Zn quadratic (Zn-Q)	1	0.03	2.56
<u>Interaction effects</u>			
P-L X Zn-L	1	0.64	0.38
P-L X Zn-Q	1	0.12	2.09
P-Q X Zn-L	1	4.80	0.03
P-Q X Zn-Q	1	1.10	1.84
Error	8	3.50	3.67

*, ** Indicate 0.05 and 0.01 significance levels, respectively.

Table A.19 Mean squares from the analysis of variance for the P derived from fertilizer (% Pdf) by beans at 1/10 bloom stage in Carrot River and Meota soils.

Source	df	Carrot River		Meota	
		Roots	Tops	Roots	Tops
<u>P effects</u>					
P linear (P-L)	1	2574.03**	1409.40**	2273.35**	1791.44**
P quadratic (P-Q)	1	240.29**	9.78	100.98**	1.09
<u>Zn effects</u>					
0 vs. 5 (Zn)	1	18.25*	12.81*	20.28*	13.65
<u>Interaction effects</u>					
P-L X Zn	1	7.04	0.01	8.78	0.44
P-Q X Zn	1	1.14	2.32	2.40	0.45
Error	6	2.69	2.09	1.70	2.75

*, ** Indicate 0.05 and 0.01 significance levels, respectively.