Extractable Zinc in Particle Size Fractions of Soils from Western Australia and Queensland

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Abstract

The zinc (Zn) content of particle size fractions of 12 mainly Zn deficient soils was measured by extraction with three contrasting extractants. The soils, which ranged from sands to a black earth, were from Western Australia and Queensland and particle size fractions (clay, silt, fine sand, coarse sand) were obtained by sieving and sedimentation after ultrasonification of soil suspended in deionized water. The extractants were concentrated $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{HClO}_4$ (acid extractable or AE-Zn), DTPA and 0.002 M CaCl_2 . For each extractant, Zn contents of the fractions and whole soils were correlated with organic carbon and ammonium oxalate extractable Fe and Al.

The AE-Zn concentrations in whole soils were 0.6–132 mg kg⁻¹ and high clay soils had higher concentrations (mean 54 mg kg⁻¹) than low clay soils (mean 2 mg kg⁻¹). After fractionation, lowest AE- and DTPA-Zn were found in coarse sand fractions and concentrations increased with decreasing particle size. Clay plus silt fractions contained 60–99% of the whole soil AE-Zn and 76–93% of the whole soil DTPA-Zn. The CaCl_2 -Zn concentrations were very low (< 5.0 µg kg⁻¹) for all soils. In whole soils, DTPA-Zn was only a small proportion, 3.2% and 1.8%, of the AE-Zn in the low clay and high clay soils, respectively. The CaCl_2 -Zn was generally less than 2% of the DTPA-Zn in whole soils.

In whole soils, AE-Zn was correlated with oxalate extractable Fe and with oxalate Al ($r=0.72$ and 0.71 , respectively; $P<0.01$), whereas DTPA-Zn was correlated with oxalate extractable Fe ($r=0.82$; $P<0.01$). The AE- and DTPA-Zn were correlated with organic carbon only in some fractions. The DTPA- and CaCl_2 -Zn were not correlated with AE-Zn content, nor was DTPA-Zn correlated with CaCl_2 -Zn in whole soils or fractions ($P<0.05$).

Dispersion of the soils with ultrasonification in the absence of dispersing agents was not as effective as dispersion with conventional mechanical/chemical dispersion. The percentage of the soil recovered in the clay fraction after sonification was 23–78% of that recovered by the conventional method. Fine and coarse sand contents were similar for either method, indicating that incomplete dispersion of clay by ultrasonification resulted in higher silt contents.

Introduction

Most of the zinc (Zn) in soils is on surfaces of clays, hydrous oxides and organic matter, rather than in solution. Zn deficiency in plants is caused either by inherently low concentrations in the soil or because reactions with soil components make Zn unavailable to plants. Reactions of Zn with individual components of the soil are reasonably well documented (e.g. Ghanem and Mikkelsen 1988), but the relative importance of the components in controlling Zn availability is not clear. The soil components that react with Zn can be

present in different forms which may be distinguished according to their size. For example, iron oxides may occur as discrete particles in the clay size fraction or as coatings on larger grains. Organic matter may be present in the sand size fraction binding small particles together, or as discrete, finer particles. In both cases, it is not known if Zn reacts with each form of the soil constituent in a similar manner or to an equivalent extent. Both these considerations are important for assessing the availability of Zn to plants.

Zn in soils may be divided into unavailable (Zn released by soil surfaces too slowly to provide an adequate source for plants), potentially available (Zn released by soil surfaces) and readily available Zn (Zn in the soil solution). The total amount of Zn in a soil is measured by extraction with concentrated acids, while chelating agents such as DTPA are reported to measure potentially available Zn (Lindsay and Norvell 1978). Readily available Zn can be measured by extraction of the soil solution, but the use of dilute CaCl_2 has many analytical advantages. Across a range of soil types, it may be necessary to measure a combination of intensity and quantity to predict the response of plants to Zn fertilizer because of the failure of quantity tests alone (Tiller *et al.* 1972; McGrath *et al.* 1985).

We do not know if unavailable Zn tends to be associated with a certain size fraction and/or represents a higher proportion of total Zn than other forms. Similarly, we do not know if potentially available Zn comes mainly from one size fraction because it accumulates there, or because it accumulates to an equal extent in all size fractions but is not equally extractable from them. The source of available Zn may also be elucidated by knowing the size fraction from which readily available Zn is most easily replenished.

After dispersal of 15 soils from the United States with an ultrasonic probe and separation of fractions, Khan (1979) found that concentrations of DTPA extractable Zn were generally highest in clay and lowest in sand fractions. Distribution of Zn among particle size fractions has not been reported for Australian soils. The objective of our research was to establish with which size fractions Zn was associated, the chemical extractability of the Zn in each fraction and whether Zn extracted by the same solution was equally extractable from different size fractions. We fractionated soils with a wide range of pH and clay contents into different size fractions by sonification and then extracted the fractions with concentrated acids, DTPA and CaCl_2 .

Materials and Methods

Twelve surface (0–10 cm) soils that were mainly Zn deficient (Armour *et al.*, in preparation) were collected from Western Australia and Queensland and separated into clay, silt, sand and coarse sand fractions. The soils were sieved to <2 mm and ranged from sand to sandy clay loam (W.A.) and clay loam to clay (Qld; Tables 1 and 2). Acid extractable Zn, DTPA-Zn and CaCl_2 -Zn were measured in the whole soil and fractions.

Particle Size Separation

Particle size separation was achieved by ultrasonification [essentially the procedure of Khan (1979), a modification of the method of Genrich and Bremner (1974)] and also by a conventional chemical/mechanical dispersion method for comparison.

Table 1. Some soil properties (0–10 cm, air-dry basis)

Soil	Location	Soil classification ^A	pH (1:5 H ₂ O)	OC ^B (%)	AE-Zn ^C (mg kg ⁻¹)	DTPA-Zn (mg kg ⁻¹)	CaCl ₂ -Zn (μg kg ⁻¹)	Fe ^D (%)	Al ^D (%)
<i>Western Australia</i>									
1	Swan Coastal Plain	Uc2·33	5·3	2·99	0·6	0·03	1·3	<0·01	<0·01
2	Wongan Hills	Uc5·22	6·2	0·50	1·9	0·05	5·0	0·02	0·02
3	Bramley	Dy3·61	7·4	0·92	1·4	0·06	1·3	0·01	0·12
4	Talbot	Dy3·81	6·5	3·04	7·1	0·04	<0·5	0·05	0·43
5	Dandaragan	Uc5·21	6·8	0·47	1·4	0·05	0·5	0·02	0·02
6	Merredin	Dr2·33	6·9	1·56	10·1	0·66	3·5	0·03	0·06
<i>Queensland</i>									
7	Murray Upper	Gn2·21	6·1	1·92	40·4	0·50	4·0	0·23	0·12
8	Walkamin	Gn3·11	6·3	2·84	73·7	1·56	4·5	0·68	0·20
9	Tolga	Gn3·14	5·6	1·72	132·0	0·18	4·0	0·31	0·62
10	Kingaroy	Gn3·74	5·7	2·11	18·2	0·16	1·3	0·18	0·21
11	Emerald	Uf6·33	7·4	0·57	58·3	0·68	<0·5	0·17	0·23
12	Miles	Ug5·24	8·0	1·01	48·0	0·26	3·0	0·13	0·11

^A Northcote (1971).

^B Organic carbon.

^C Acid extractable Zn.

^D Acid ammonium oxalate extraction.

Table 2. Particle size distribution for ultrasonic and conventional dispersion methods

Soil	Texture	Dispers. method ^A	Fractions (%)						
			< 2	2-20	20-45	2-63	45-212	63-212	> 212 μm
1	sand	C	6.5	2.1	0.9		7.1		83.4
		U	4.1			3.0		7.1	85.9
2	sand	C	7.7	0.8	0.5		25.0		76.1
		U	1.8			4.0		14.5	79.7
3	sand	C	8.3	2.9	1.5		16.7		70.6
		U	4.5			12.0		16.3	67.1
4	gravelly sandy loam	C	14.8	5.9	3.0		27.1		49.2
		U	6.1			16.0		25.4	52.5
5	sandy loam	C	9.4	1.1	0.7		11.3		77.6
		U	2.9			5.3		8.6	83.2
6	sandy clay loam	C	21.0	6.9	3.5		20.7		47.9
		U	10.8			19.7		19.7	49.8
7	clay loam	C	24.7	21.0	9.3		13.4		31.6
		U	14.3			43.4		11.7	30.6
8	clay	C	48.2	21.1	4.7		7.6		18.3
		U	22.7			42.4		9.4	25.3
9	clay	C	60.9	16.2	4.1		12.2		6.6
		U	37.2			42.4		13.2	7.2
10	clay	C	30.0	19.4	7.9		15.1		27.7
		U	16.9			38.1		14.3	30.1
11	clay	C	65.0	15.8	5.6		9.1		4.4
		U	50.9			23.0		16.0	10.0
12	clay	C	47.6	17.9	5.3		13.7		15.4
		U	36.4			34.1		13.3	16.2

^A C, chemical dispersion; U, ultrasonic dispersion.

Size limits for the fractions from sonification (chosen for convenience of separation) were clay (< 2 μm), silt (2-63 μm), fine sand (63-212 μm) and coarse sand (212-2000 μm). Soils were dispersed with a Braunsonic 1510 ultrasound at full power (300 W) for 15 min. A stirred suspension of 50 g soil 200 ml⁻¹ deionized water was cooled with a water jacket < 20°C during sonification. To minimize the potential for re-aggregation of dispersed material, the suspensions were washed through a 63 μm stainless steel sieve immediately after sonification until the filtrate was clear. The sieve contents (> 63 μm) were washed with a minimum of deionized water into containers and the excess water was removed after sedimentation. The washing of the size fractions with water would not have caused much disturbance of the equilibrium of Zn between the solution and surfaces because the majority of Zn in soils is strongly held at specific adsorption sites. After oven-drying at 40°C, the sand was sieved through a 212 μm stainless steel sieve. Material passing through the sieve was fine sand (63-212 μm), while coarse sand (> 212 μm) was retained on the sieve.

Clay and silt were separated by centrifugation (Khan 1979) within 24 h of dispersion. In our method, we concentrated the clay by centrifugation at a relative centrifugal force of 2600 (rather than by the use of filter candles) for 30 min and removed the supernatant by vacuum. This speed and time removed clay material of < 0.22 μm or with a specific gravity of < 2.61 g cm⁻³. The sand fractions were only kept under water for the 1-2 days required for the separation procedure. Silt and clay fractions were oven-dried at 40°C then gently crushed in an agate pestle and mortar.

Conventional particle size analysis was determined in duplicate by the pipette method after shaking the soil in a solution of 2.5% sodium hexametaphosphate in 0.1 M NaOH (Gee and Bauder 1986). The particle size limits for this method were < 2, 2-20, 20-45, 45-212 and 212-2000 μm for clay, silt, very fine sand, fine sand and coarse sand, respectively.

Soil Analyses

The whole soil and fractions were analysed in duplicate by the methods below. All equipment used for Zn analyses was soaked in 0.2 M Na₂EDTA, rinsed in deionized water, soaked in 2% HNO₃ and rinsed with deionized water.

Total Zn was estimated by digestion in concentrated HNO₃/H₂SO₄/HClO₄ and we have termed this fraction acid extractable (AE) Zn. This was the method of Baker and Amacher (1982), except that we omitted HF. The DTPA-Zn was determined by the method of Lindsay and Norvell (1978). The Zn extractable in 0.002 M CaCl₂ was measured on extracts obtained by shaking soil at a soil/solution ratio of 1:5 for 16 h. Supernatants from each extract were filtered (<0.45 µm) after centrifugation and read by flame (DTPA-, AE-Zn) or graphite furnace atomic absorption (CaCl₂-Zn, acidified to 0.01 M with 3 M HCl).

Organic carbon was determined by the method of Walkley and Black (1934) with the colorimetric finish of Sims and Haby (1971). Fe and Al were extracted with acid ammonium oxalate at a soil:solution ratio of 1:40 (McKeague and Day 1966) and analysed by atomic absorption (Searle and Daly 1977).

Results

Particle Size Separation

The particle size separation obtained by sonification differed from that obtained by conventional chemical/mechanical dispersion (Table 2). The percentage of the soil measured in the clay size fraction after sonification was 23–78% (mean 53%) of that measured by the conventional dispersion method. The proportion of the 2–63 µm fraction of sonified soils was generally larger than that of the 2–45 µm fraction in conventionally dispersed soils, while the content of the 63–212 µm fraction of sonified soils was similar to the content of the 45–212 µm fraction of conventionally dispersed soils. These comparisons, and the similarity in coarse sand contents for both dispersion methods, suggest that incomplete dispersion of the clay after sonification (shown by lower clay % in all soils) produced an increase in the 2–63 µm fraction rather than in the larger size fractions.

Extractable Zn Concentrations in Whole Soils and Fractions

The AE-Zn concentrations in whole soils were 0.6–132 mg kg⁻¹ (Table 1). The high clay soils (sandy clay loam–clay soils, soils 6–12) had much higher concentrations (mean 54 mg kg⁻¹) than the low clay soils (sandy–sandy loam soils, soils 1–5, mean 2 mg kg⁻¹).

When the soils were separated into fractions, lowest concentrations of AE-Zn were found in coarse sand fractions and the concentration increased with decreasing particle size of the fraction (Fig. 1a). The AE-Zn concentrations in the clay and silt fractions of the high clay soils were generally much higher than in the fractions of the low clay soils. The mean percentage of whole soil AE-Zn in the clay and silt fractions was 44% (range 20–83%) and 36% (range 16–53%) respectively (Fig. 1b). Clay plus silt fractions contained between 60 and 99% of whole soil AE-Zn. The mean value of the sum of AE-Zn in each fraction multiplied by the proportion of each fraction in soil was 96% of the AE-Zn of the whole soil (range 64–168%).

The DTPA extractable Zn concentrations were very low in the low clay soils (<0.1 mg kg⁻¹) and variable in the high clay soils (0.2–1.6 mg kg⁻¹; Table 1).

Fig. 1. Plots of (a) acid extractable Zn concentration in clay, silt, fine sand and coarse sand fractions (standard error of the mean is 1.1), and (b) proportion of acid extractable Zn in whole soils in clay, silt, fine sand and coarse sand fractions.

After fractionation, the concentration of DTPA-Zn increased with decreasing particle size of the fraction of all soils except in the north Queensland euchrozem (soil 8; Fig. 2a). In this soil, the highest Zn concentration was found in the fine sand. Even though there was far less DTPA-Zn in the whole low clay soils, the concentration in each size fraction was similar for the two groups of soils. Only in the coarse sand fractions were the DTPA-Zn concentrations of low clay soils consistently lower than in the high clay soils.

The percentage of whole soil DTPA-Zn found in each fraction generally increased with decreasing particle size of each fraction (Fig. 2b). An average of 49% (range 20–70%) of the whole soil DTPA-Zn was found in the clay fraction and

Fig. 2. Plots of (a) DTPA extractable Zn concentration in clay, silt, fine sand and coarse sand fractions (standard error of the mean is 0.05), and (b) proportion of DTPA extractable Zn in whole soils in clay, silt, fine sand and coarse sand fractions. (Legend as for Fig. 1.)

38% (range 19–56%) was in the silt fraction. Clay plus silt fractions accounted for 76–93% of the whole soil DTPA-Zn. The mean value of the sum of DTPA-Zn in each fraction multiplied by the percentage of each fraction in the soil was 246% (range 88–1030%) of whole soil DTPA-Zn.

The proportion of AE-Zn extracted by DTPA was higher in the low clay soils and fractions than in the high clay soils and fractions. In whole soils, DTPA-Zn was only a small proportion, 3.2% and 1.8%, of the AE-Zn in the low clay and high clay soils, respectively. In silt and in clay fractions, DTPA-Zn was approximately 20% of the AE-Zn for the low clay soils and 3% for the high clay soils, respectively.

Fig. 3. The CaCl_2 extractable Zn concentrations in clay, silt, fine sand and coarse sand fractions (standard error of the mean is 0.4; legend as for Fig. 1).

Zn extractable in 0.002 M CaCl_2 was very low for all soils (from <0.5 to $4.5 \mu\text{g kg}^{-1}$) and there were no consistent trends in the distribution of CaCl_2 -Zn with particle size (Fig. 3). Data for the proportion of whole soil CaCl_2 -Zn found in each fraction was not presented because the concentration of Zn in some fractions and whole soils was less than $0.5 \mu\text{g kg}^{-1}$ soil.

The DTPA- and CaCl_2 -Zn were not correlated with AE-Zn content, nor was DTPA-Zn correlated with CaCl_2 -Zn in the fractions or the whole soil ($P > 0.05$).

Correlation of Extractable Zn in Whole Soils and Size Fractions with Soil Properties

In whole soils, AE-Zn was correlated with oxalate extractable Fe and with oxalate extractable Al ($r = 0.72$ and 0.71 , respectively; $P < 0.01$). In fractions, AE-Zn was correlated with oxalate extractable Fe in coarse sand fractions ($r = 0.94$; $P < 0.01$) and with oxalate extractable Al in fine sand fractions ($r = 0.92$; $P < 0.01$). The AE-Zn was correlated with organic carbon in coarse sand fractions ($r = 0.95$; $P < 0.01$). The DTPA-Zn was correlated with oxalate extractable Fe ($r = 0.82$; $P < 0.01$) in whole soils and after fractionation with Fe in fine sand ($r = 0.85$; $P < 0.01$) and with Al in coarse sand fractions ($r = 0.68$; $P < 0.01$). Data for ammonium oxalate extractable Fe and Al and organic carbon contents are not presented.

The AE-Zn and CaCl_2 -Zn concentrations were not related to organic carbon in soils or fractions. The DTPA-Zn was correlated with organic carbon contents in silt and coarse sand fractions ($r = 0.64$ and 0.70 , respectively; $P < 0.05$).

The AE-Zn in whole soil was related to % clay plus silt by the equation

$$y = 0.8810 \times 1.0635^x, \quad r^2 = 0.92,$$

where y = AE-Zn and x = % clay plus silt. Conversely, AE-Zn decreased as the proportion of coarse and fine sand increased.

Zn extracted by any methods was not correlated with pH in whole soils.

Discussion

The highest concentrations and proportions of whole soil AE- and DTPA-Zn were found in the clay and silt fractions. These results are consistent with the higher reactivity of small particles, but the Zn concentrations in the fractions could not be consistently related to any of the measured properties of the fractions.

As concentrations of DTPA-Zn in the soil have been related to plant growth (e.g. Lindsay and Norvell 1978), it can be considered to be an estimate of plant available Zn, although consideration of the soil pH is required for acid soils (Haq and Miller 1972; Haynes and Swift 1983). These results have shown that DTPA-Zn is only a small proportion of the whole AE-Zn and they confirm that plant availability is related not only to the quantity in the soil but to adsorption reactions. Although there was less total Zn in the low clay soils than in the high clay soils, a greater proportion of the total Zn was extracted by DTPA. The lack of correlation of DTPA- or CaCl_2 -Zn with AE-Zn suggests that unavailable Zn may be in a different form from available Zn, rather than the latter being just a proportion of all forms of Zn which are present. Further evidence for this hypothesis may be seen in the correlation of DTPA-Zn with oxalate extractable Fe in contrast to the correlation of AE-Zn with oxalate extractable Fe and Al in whole soils.

The very low concentrations of CaCl_2 -Zn in the whole soil are consistent with its low ionic strength, and the lack of relationship with particle size suggests that it is a true intensity measure. The low concentrations in the fractions were expected because the fractionation procedure involved suspending the fractions in large quantities of water.

After the particle size separation of the soils, the mean value of whole soil AE-Zn calculated from the fractions was less than that measured in whole soils, while the mean of DTPA-Zn was higher. The general decrease in AE-Zn was expected because of the unavoidable loss of some fine clay and organic matter during the final centrifugation of the clay suspension and discarding of the supernatant. Soil 3 had an unusually high calculated AE-Zn of 168% (for AE-Zn from fractions as a percentage of whole soil AE-Zn) which cannot be explained. The increase in availability of DTPA-Zn may be due to the exposure of fresh surfaces during sonification, either due to disintegration of organic matter or of clay particles. Soil 1, a peaty sand, had a whole soil DTPA-Zn of 0.03 mg kg^{-1} compared with a calculated value of 0.26 mg kg^{-1} for the sum of the fractions and this produced a very high 'recovery' of 1030%. The sum of AE-Zn for the fractions of this soil was 69% of the whole soil AE-Zn and shows that contamination was not the reason for the high DTPA concentrations in the fractions. Khan (1979) suggested that the reported higher concentrations of DTPA-Zn after intense sample grinding and higher shaking speeds (Soltanpour *et al.* 1976) may have been due to disintegration of microaggregates.

In these soils, 49% of the whole soil DTPA-Zn was in the clay fraction and 38% was in the silt fraction. Khan (1979) also found that the highest DTPA-Zn concentrations were found in clay and silt fractions of 15 United States soils.

However, the proportion of DTPA-Zn in these fractions was higher in the U.S. soils, as 68% of the whole soil DTPA-Zn was in the clay fraction and 22% was in the silt fraction. The DTPA-Zn concentrations were between 4 and 7 times higher than in the fractions of these soils. The differences in distribution may be due to differences in the efficiency of ultrasonic particle dispersion, although comparisons between ultrasonic and conventional dispersion were not given by Khan (1979).

Considering AE-Zn as an estimate of total Zn in the soil, our results are in the ranges reported in an extensive review of Zn concentrations on Australian soils (Tiller 1983), except for the peaty sand (soil 1) which had a lower AE-Zn than the range reported for deep sands. The DTPA-Zn concentrations were within the ranges reported for Australian soils (Radjagukguk *et al.* 1980; Standley *et al.* 1981; Haddad and Weir 1985).

The low clay contents obtained with ultrasonic dispersion compared with conventional mechanical/chemical dispersion differ from other published data (Genrich and Bremner 1972, 1974; Curtin *et al.* 1987). No other work on Australian soils has published comparisons between ultrasonic and conventional dispersion techniques in the absence of dispersion agents. Despite the differences that we have found between the two techniques, sonification is currently the best method available to disperse soils without the addition of dispersing agents.

Acknowledgments

The senior author completed this research while on Study Leave from the Queensland Department of Primary Industries. We thank Mr W. J. Simmons for technical advice.

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