Pakistan J. Sci. Ind. Res., Vol. 23, Nos. 1-2, February-April, 1979

THE FATE OF SOIL-APPLIED ZINC AND THE EFFECT OF SELECTED SOIL PROPERTIES ON ZINC AVAILABILITY IN ALKALINE CALCAREOUS SOILS

F. HUSSAIN and A. RASHID,

Soil Science Division, Nuclear Institute for Agriculture and Biology, Faisalabad

(Received April 4, 1978 ; revised August 21, 1978)

Abstract. In a soil incubation study on twenty-two alkaline calcareous soils, it was found that the fixation of Zn proceeded rapidly up to 3 days of contact but thereafter it increased gradually and reached a slow steady state after 7 days. Average recovery of added Zn with DTPA (diethylenetriaminepentaacetic acid) after 14 days was about 63%. This fraction presumably would be available for plant uptake.

DTPA-extractable native Zn showed a significant correlation with clay and organic matter content of the soils. Native soil Mn extracted with DTPA, and $NaHCO_3$-extractable P correlated negatively ($P < 0.05$ and $P < 0.01$ respectively) with Zn fixed after 14 days' incubation.

Introduction

Micronutrient deficiencies in Pakistan have been widely reported in various crops[1-6, 28]. Particularly Zn deficiency has been increasingly observed in rice and maize.[2,6-9, 28] Experimental methods to correct Zn deficiency included soil applications of Zn containing materials.[2] Soil applications had given good results in some instances and poor results in others.[10] Hence a better understanding of the behaviour and fate of soil-applied Zn and the soil factors affecting its availability is needed.

Detailed reviews of the subject have been given by a number of researchers.[11-13] Suffice to say that N[14], P[15], K[16], pH[17], organic matter[18], Ca $CaCO_3$[12, 14] and clay content[19] have all been attributed to affect Zn reactions and its availability in soils. Since little information is available about the fate of soil-applied Zn and the factors affecting its availability in Pakistan soils, studies on these lines were thought quite imperative. The present study was carried out to get information upon the fixation of added Zn as a function of contact time by 22 alkaline calcareous soils. An attampt was also made to correlate various soil properties with Zn availability in these soils.

Materials and Methods

Twenty two surface soils (0-15 cm) collected from wheat and maize growing tracts of the Punjab were utilized in the present study. The soils were air-dried, crushed in a wooden mortar and passed through a 2-mm plastic sieve. Some physico-chemical properties of the soils are given in Table 1. Soil texture was determined by the Bouyoucos hydrometer method classifying the soils according to the International Textural Triangle.[29] pH of the saturated soil paste was measured by using glass electrode, electrical conductivity by conductivity meter and $CaCO_3$ by neutrilization with HCl.[30] Organic matter was determined by dichromate oxidation and available P by Olsen's method[31] and DTPA-extractable Fe and Mn by the method developed by Lindsay and Norvell.[32] Incubation study was carried out by treating 25 g portions of the soils with two levels of Zn (0 and 10 ppm Zn as $ZnSO_4.7H_2O$) to standardize the time of contact that may be necessary for maximum fixation of Zn. The soils in plastic vessels treated with aqueous solution of $ZnSO_4.7H_2O$ were maintained at 75% of their respective field capacities throughout the course of the study. The soils were incubated at $30 \pm 1°$ for varying periods of time intervals, viz. 1, 2, 3, 7 and 14 days. The treatments were effected in triplicate. At the end of the fixed incubation period, Zn/Cu of each soil, extracted with 0.005 *M* DTPA (soil, extractant ratio; 1:2), was determined by atomic absorption spectrophotometery.[20] All the experimental apparatus were washed successively with 0.2 *M* EDTA (ethylenediaminetetraacetic acid), deionized water, 10% HNO_3 and again deionized water.[21]

In this paper the term *fixed Zn* denotes that amount of the adsorbed Zn which could not be released when extracted with 0.005 *M* DTPA.

Results and Discussion

Time of incubation versus DTPA-extractable Zn (native). The amount of DTPA-extractable Zn in most of the soils decreased ($P < 0.01$, Table 2) with an increase in the time of incubation. In a few soils, however, soil incubation either had no effect or tended to increase it. The average DTPA-extractable Zn decreased significantly after one-day incubation and no further change occurred up to 2 days. Extractable Zn again decreased signifi-

cantly after the 3rd day and then remained unchanged up to one week's period. The complexing of available soil Zn in an unavailable form by its biological fixation in the tissue of microorganisms probably accounts for the subsequent decreased extractability of Zn with an increase in the time of incubation.[14] At the end of 14 days' incubation, DTPA-extractable Zn increased significantly (Table 2) as compared with that of one-week incubation. The mineralization of organic materials present in the soils could be responsible for this increased availability of Zn. The results of Stanton[13] are parallel to these findings. He applied maize leaves to the soils, incubated the soils at 28°C for the required decomposition periods and then planted with Japanese millet. He noted an initial increase of available Zn resulting from organic matter application. The highest Zn levels in the plant material were attained for the two-week period on all soils.

Fixation of native plus added Zn as a function of time. Zinc fixation increased considerably with the passage of the time of incubation ($P<0.01$, Table 3). Fixation proceeded rapidly up to 3 days of contact but thereafter it was slow. Though maximum fixation took place within the first 3 days of contact, it increased gradually upto 7 days. There was a little further increase in fixation after 7 days. Fig. 1 plotted from the data of some random soils

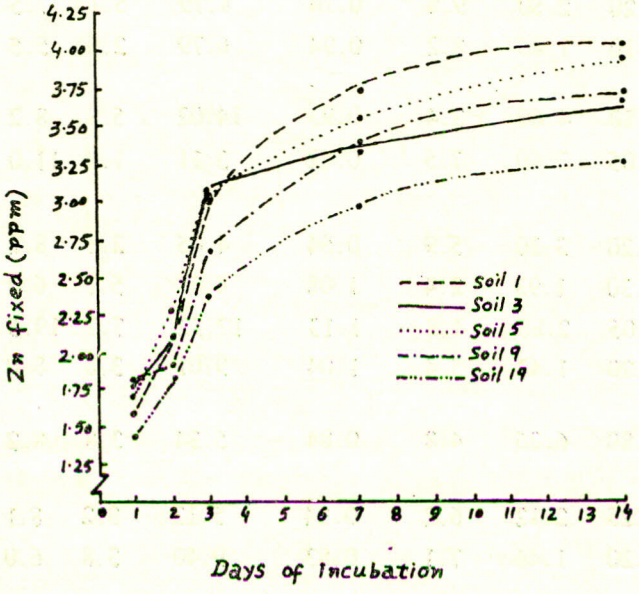

Fig. 1. Effect of time of contact on the fixation of Zn by some randon soils.

gives a general picture of Zn fixation as a function of time. Therefore, as a practical approach to the equilibrium, 13-days incubation period was taken as the optimum time of contact for maximum fixation. Tiller and Hodgson,[22] while studying the specific sorption of Zn by layer silicates, observed that equilibrium is not readily attained but tends to approach a slow steady state after several days.

Effect of selected soil properties on Zn availability in soils. DTPA-extractable native soil Zn varied considerably depending upon the properties of soils. It correlated significantly with clay and organic matter content of the soils ($r=0.514$ and 0.464 respectively). The correlation of the soil Zn content with clay and organic matter content indicated that these two soil components may contribute towards the retention of native Zn in these calcareous soils.[23] Higher Zn content have been found to be related to clay content and organic matter distribution in many soils.[17, 19, 23] A correlation coefficient of 0.81 has been reported between Zn content and organic matter distribution of different soils.[18] Other soils properties, like $CaCO_3$ content, electrical conductivity and $NaHCO_3$-extractable P did not reveal any significant correlation with DTPA-extractable native Zn of the soils.

Fixation of Zn after 14 days incubation varied considerably from soil to soil. It correlated negatively with $NaHCO_3$- extractable P ($r=-0.599$, $P<0.01$) and with DTPA-extractable native soil Mn only with a small correlation coefficient ($r=<0.399$, $P-0.05$). Brown *et al.*[15] measured the effect of fertilizer P on ammonium acetate dithizone-extractable Zn in two alkaline soils. They observed that rate of P did not greatly affect extractable Zn but tended to increase the Zn rather than decrease it. Shukla[24] has also reported an increase in Zn availability of many soils with KH_2PO_4 application. The sorption of heavy metals by the oxides of Mn may probably hinder Zn fixation by soils.[25] Other soil properties like clay, organic matter and $CaCO_3$ contents did not have any correlation with Zn fixed after 14 days incubation. Fixation of heavy metals at pH above 7 seems to be a serious problem which induces their deficiency under these conditions. In this study correlation between pH and extractable Zn was not calculated since the soils had very narrow pH range i.e., 7.7 to 8.5.[26]

Effect of time and Zn application on the availability of native Cu in soils. Like Zn, the availability of DTPA-extractable native Cu in most of the soils decreased ($P<0.01$, Table 4) after 14 days' incubation. This decreased Cu availability with the passage of time could be attributed to its biological fixation in the tissue of microorganisms. Zinc addition tended to increase the DTPA-extractable Cu in most of the soils ($P<0.01$) which might be due to the replacement of adsorbed Cu by added Zn. In black, red and alluvial soils treated with Zn, Misra *et al.*[27] noted a rise in HCl-extractable Cu as the amount of Zn increased.

Conclusions

The present study was primarily of a preliminary nature to establish which factor could affect Zn availability in these soils. With the passage of time, the availability of native Zn/Cu decreased showing that the fixation of available Zn and Cu is increased

TABLE 1. SOILS USED AND SOME OF THEIR PHYSICO-CHEMICAL PROPERTIES

Soil No.	Location	Clay	Texture	pH_s	$EC_e \times 10^3$	$CaCO_3$ equiv.	Organic matter	$NaHCO_3$ extractable P	0·005 *M* DTPA-extractable Fe	0·005 *M* DTPA-extractable Mn
		—%—				—%—		ppm		
1.	Govern. Agr. Farm, Jhang	14.8	Loam	8.15	2.22	7.1	0.62	5.06	2.6	7.5
2.	Chimranwali, Jhang	9.6	Sandy loam	8.25	1.55	6.3	0.52	5.20	1.9	5.5
3.	Thikriwala, Faisalabad	13.8	Sandy loam	8.20	2.20	4.1	0.67	6.51	3.2	9.5
4.	Gojra Seed Farm, Gojra	17.6	Sandy clay loam	8.25	3.60	6.1	0.66	9.22	3.8	10.0
5.	Alhar Pind, T. T. Singh	17.8	Sandy clay loam	8.05	1.67	5.7	0.84	4.17	3.8	7.5
6.	Saraba, T. T. Singh	15.6	Sandy clay loam	8.02	5.00	6.5	1.09	8.85	3.8	16.7
7.	Chak 285/JB, Rejana	8.8	Sandy loam	8.70	1.55	6.5	0.46	6.34	1.9	7.1
8.	Mauza Chaddar, Kamalia	26.6	Loamy clay	8.15	2.62	4.6	1.31	6.56	9.0	7.5
9.	Chak 17/11-L, Chichawatni	8.8	Sandy loam	8.40	1.75	6.5	0.47	8.23	2.6	11.2
11.	Chab Chauki, Kacha Khuh	9.6	Loamy sand	8.00	3.35	4.6	0.24	4.84	3.2	6.0
12.	Burewala Textile Mills	18.8	Clay loam	8.20	2.50	9.8	0.76	8.79	5.1	7.5
13.	Mohammad Nagar Farm, Arifwala	10.6	Sandy loam	8.10	1.85	8.2	0.94	6.79	2.6	5.5
15.	Qadirpur Rawan, Multan	15.6	Clay loam	7.80	4.60	3.4	0.93	14.02	5.8	8.2
16.	Chak 133/16-L, Mian Channu	9.6	Sandy loam	8.05	3.40	7.5	0.62	3.11	1.9	11.0
17.	Chak 187/9-L, Harrapa	10.8	Sandy loam	8.20	3.20	5.9	0.54	4.45	2.6	8.2
18.	Chak 118/9-L, Arifwala	14.8	Loam	8.30	1.93	2.4	1.08	4.78	5.1	6.0
19.	Maize Farm, Yousafwala	20.8	Clay loam	8.05	2.85	4.8	1.13	12.52	7.7	19.5
20.	Iqbal Nagar, Mian Channu	16.8	Sandy clay loam	8.20	1.42	5.4	1.04	9.01	3.8	8.0
21.	Chah Din Mohd Wala, Kabirwala	22.8	Clay loam	7.80	6.25	4.8	0.84	5.34	3.8	8.2
22.	Chak 84/10-R, Khanewal	12.3	Sandy loam	8.25	2.12	6.2	0.94	5.12	3.2	8.1
23.	Nawab Iftikhar Farm, Jhang City	9.6	Sandy loam	8.20	1.46	7.1	0.83	9.40	3.8	6.0
24.	NIBA, Faisalabad	5.6	Loamy Sand	7.70	1.34	—	0.31	10.70	5.5	7.3

TABLE 2. AVAILABILY OF NATIVE SOIL Zn AS INFLUENCED BY TIME OF INCUBATION

Period of incubation	0.005 *M* DTPA-extractable Zn in soils**										
	1	2	3	4	5	6	7	8	9	11	12
days	ppm										
0	0.70	0.28	0.46	0.46	0.42	0.50	0.32	0.62	0.42	0.36	0.38
1	0.57	0.35	0.29	0.37	0.38	0.43	0.24	0.36	0.39	0.31	0.45
2	0.56	0.37	0.32	0.36	0.39	0.43	0.27	0.34	0.42	0.30	0.48
3	0.59	0.28	0.25	0.28	0.35	0.34	0.17	0.30	0.35	0.22	0.38
7	0.53	0.35	0.23	0.24	0.29	0.33	0.20	0.34	0.32	0.22	0.34
14	0.56	0.30	0.29	0.33	0.34	0.41	0.19	0.36	0.34	0.24	0.40

Period of incubation	0.005 *M* DTPA-extractable Zn in soils**											
	13	15	16	17	18	19	20	21	22	23	24	Means*
days	ppm											
0	0.38	0.56	0.36	0.42	0.46	0.46	0.52	0.50	0.62	1.66	0.46	0.5182a
1	0.37	0.43	0.43	0.69	0.39	0.52	0.43	0.39	0.39	1.23	0.39	0.4455b
2	0.42	0.45	0.42	0.55	0.37	0.49	0.42	0.38	0.40	1.30	0.39	0.4468b
3	0.27	0.43	0.38	0.54	0.35	0.49	0.42	0.30	0.32	1.18	0.34	0.3877d
7	0.31	0.39	0.37	0.47	0.32	0.47	0.38	0.33	0.34	1.17	0.33	0.3759d
14	0.34	0.39	0.39	0.45	0.40	0.52	0.40	0.35	0.38	1.50	0.34	0.4191c

*Means followed by the same letter do not differ significantly at the 5% level of probability.
**The values are the average of three replicates.

TABLE 3. EFFECT OF TIME OF CONTACT ON THE FIXATION OF Zn (NATIVE PLUS ADDED) BY SOILS TREATED WITH 10 PPM Zn AS $ZnSO_4.7H_2O$

Period of incubation	Zn fixed in the soils*										
	1	2	3	4	5	6	7	8	9	11	12
days	ppm										
1	1.58	1.25	1.77	1.77	1.69	1.38	1.54	1.99	1.81	1.79	1.62
2	2.10	1.46	2.10	2.02	2.28	2.15	2.13	2.33	1.90	2.05	2.03
3	3.00	2.61	3.07	3.04	3.01	2.67	2.66	2.98	2.66	3.02	2.71
7	3.74	3.28	3.32	3.51	3.52	3.38	3.52	3.55	3.38	3.40	3.27
14	4.03	3.50	3.66	3.85	3.94	3.82	4.02	4.15	3.72	4.03	3.78

Period of incubation	Zn fixed in the soils*										
	13	15	16	17	18	19	20	21	22	23	24
days	ppm										
1	1.65	1.40	1.33	1.52	1.39	1.43	1.49	1.82	1.63	—	1.64
2	1.99	1.66	1.46	1.90	1.78	1.82	1.75	1.82	1.76	—	1.64
3	2.84	2.17	2.43	2.66	2.90	2.37	2.59	2.85	2.64	—	2.86
7	3.35	2.82	3.28	3.42	3.33	2.97	3.06	3.33	3.28	—	3.28
14	3.82	3.21	4.00	3.94	3.85	3.27	3.65	4.15	3.91	—	4.16

*The values are the average of three replicates.

TABLE 4. AVAILABILITY OF NATIVE Cu AS INFLUENCED BY 10 PPM Zn APPLICATION AS $ZnSO_4.7H_2O$

Incubation time	Treatment	0.005 *M* DTPA-extractable Cu in soils**									
		1	2	3	4	5	6	7	8	9	11
days		ppm									
0	Control	1.74	0.68	1.08	1.70	1.40	1.84	0.64	2.86	0.74	0.54
14	Control	1.32	0.49	0.67	0.99	0.89	1.02	0.42	1.96	0.41	0.38
14	10 ppm Zn as $ZnSO_4.7H_2O$	1.31	0.49	0.68	1.09	0.98	1.11	0.48	1.80	0.45	0.43

Incubation time	Treatment	0.005 *M* DTPA-extractable Cu in soils**												
		12	13	15	16	17	18	19	20	21	22	23	24	Means
days		ppm												
0	Control	1.36	1.12	1.94	0.68	1.08	2.08	2.18	1.36	1.84	0.92	—	0.54	1.35a
14	Control	0.91	0.68	1.23	0.45	0.85	1.50	1.34	0.81	1.05	0.55	—	0.33	0.87c
14	10 ppm Zn as $ZnSO_4.7H_2O$	1.01	0.78	1.29	0.49	0.86	1.58	1.40	0.87	1.11	0.59	—	0.33	0.91b

*Means followed by the same letter do not differ significantly at the 5% level of probability.

**The values are the average of three replicates.

when proper soil moisture and temperature conditions prevail. Applied Zn also suffered in a similar way by the fixation processes. These studies revealed that 63% of the added Zn remained extractable with 0.005 *M* DTPA after 14 days' incubation. This fraction of the added Zn appears quite sufficient and presumably would be available for plant uptake.

In the present study, Zn content were found to have a positive correlation with clay and the organic matter content of the soils. Zinc fixed after 14 days had a negative correlation with $NaHCO_3$-extractable P and DTPA-extractable Mn determined in the original soil samples. Correlative studies of this kind while indicative of the contribution of some soil properties and not the others, may not necessarily give an accurate picture of the part they play in controlling Zn availability in soils. However, such positions must await further comprehensive experimentation. Certainly such a programme would aid in recommending the judicious Zn fertilization of these soils.

Acknowledgments. The authors are indebted to S. H. Mujtaba Naqvi, Director of the Institute for providing necessary facilities during the course of the study. Sincere thanks are due to Dr. M. Sharif and Mr. M. A. Kausar, Principal Scientific Officer and Scientific officer of this Division respectively, for critically reviewing the manuscript. Valuable suggestions by Dr. Shah Mohammad and Dr. R. H. Qureshi, Associate Professors of Soil Science Department, University of Agriculture, Faisalabad, are also gratefully acknowledged.

References

1. F. M. Chaudhry, M. Sharif, A. Latif and R. H. Qureshi, Plant Soil, **38,** 573 (1973).
2. M. A. Kausar, F. M. Chaudhry, A. Rashid, A. Latif and S. M. Alam, Plant Soil, **45,** 397 (1976).
3. T. M. Chaudhry and G. R. Hisiani, Pakistan Cotton 15, 13 (1970).
4. H. M. Bhatti, Punjab Agr. Res. Inst., Lyallpur, Ann. Rep. (1969-70).
5. Agr. Chem. (Soil Fertility), Soil Fertility Surv. Soil Test. Inst., Lyallpur, Ann. Rep. (1971).
6. A. Tanaka and S. Yoshida, Intern. Rice Res. Inst., Techn. Bull. 10 (1970).
7. M. Shafi and A. Majid, Abstr., 23rd All Pakistan Sci. Conf., p. A (1971).
8. M. E. Raja and G. A. Shah, Abstr., 24th All Pakistan Sci. Conf., p. A (1972).
9. Project Director, Maize and Millets Res. Inst., Yousafwala, Sahiwal, personal communic. (1976).
10. A. L. Brown, B. A. Krantz and P. E. Martin, Soil Sci. Soc. Amer. Proc., **26,** 167 (1962).
11. A. F. Camp, Soil Sci., **60,** 157 (1945).
12. D. W. Thorne, Adv. Agron., **9,** 31 (1957).
13. D. A. Stanton, D. Sc. Thesis, Univ. Orange Free State, Bloemfontein.
14. D. A. Stanton and R. Du T. Burger, Agrochemophysica, 2, 33 (1970).
15. A. L. Brown, B. A. Krantz and J. L. Eddings, Soil Sci., **110,** 415 (1970).
16. K. N. Sharma and O. P. Meelu, J. Indian Soc. Soil Sci., **23,** 76 (1975).
17. J. F. Hodgson, Adv. Agron., **15,** 119 (1963).
18. H. L. Jensen and C. G. Lamm, Acta Agr. Scand., 11, 63 (1961).

19. M. Kurki, J. Sci. Agr. Soc., Finland, 46, 208 (1974).

20. W. L. Lindsay and W. A. Norvell, Agron. Abstr., p. 84 (1969).

21. F. M. Chaudhry and J. F. Loneragan, Exp. Bot., 23, 552 (1972).

22. K. G. Tiller and J. F. Hodgson, *Clays and Clay Minerals*, **9,** 393 (1962).

23. E. J. Udo., H. L. Bohn and T. C. Tucker, Soil Sci. Soc. Amer. Proc., **34,** 305 (1970).

24. U. C. Shukla, Agrochimica, **16,** 435 (1972).

25. R. R. McKenzie, Geoderma, **8,** 29 (1972).

26. A. L. Brown, J. Quick and J. L. Eddings, Soil Sci. Soc. Amer. Proc., **35,** 105 (1971).

27. S. G. Misra, P. C. Mishra and R. S. Pandey, Bhartiya Krishi Anusandham Patrica, 1, 1 (1973).

28. F. M. Chaudhry and M. Sharif, in *Isotope-aided Micronutrient Studies in Rice Production with Special Reference to Zinc Deficiency*, Proc. Combined Panel Res. Coord. Meeting, Vienna, Sept. 23-27, 1974, IAEA-172, p. 1 (1975).

29. G. J. Bouyoucos, Agron. J., **54,** 464 (1962).

30. U. S. Salinity Laboratory Staff, in *Diagnosis and Improvement of Saline and Alkali Soils*, Agriculture Handbook No. 60, U.S.D.A. (1954).

31. M. L. Jackson, in *Soil Chemical Analysis*, Prentice Hall, Inc. Englewood Cliffs, N. J. (1964).