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Heavy metal accumulation in soils under long term fertilization

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Abstract
Investigations were made on the accumulation of DTPA extractable and total cadmium and lead in surface soils (0-15cm) from a 'Long Term Fertilizer Experiment' in progress since 1972 in a medium black soil at Coimbatore, India under irrigated condition. The experimental soil is a sandy clay loam with a pH of 8.2 and 2.0 percent calcium content. The organic carbon content is 0.3 percent. The treatments consist of NPK application at 50, 100 and 150 percent of optimal level, 100 percent optimal level of NPK without herbicidal addition through sulphur free sources, with zinc sulphate at 25 kg ha^{-1} and with cattle manure at 10 t ha^{-1}. There are two other treatments in addition to unfertilized control, *viz*., application of NP alone and N alone at 100 percent of optimal level. Each treatment is being replicated four times in a randomized block design and has a net plot size of 200 m^2. A fixed crop rotation of finger millet - maize –cowpea (since deleted from 2000) in a year is being followed. Soil samples are being collected after each crop, stored and evaluated for various parameters since 1992. The results of 1992, 2000 and 2008 revealed that the treatments effects on the concentration of DTPA extractable cadmium and lead were non-significant during 1992 but significant during 2000 and 2008. The results of 2000 and 2008 showed that the accumulation of DTPA and total Cd and Pb were the highest in the plots which received NPK at 150 percent. The least, in general, was in the control. Continuous fertilization for 36 years has not resulted in toxic concentrations of Pb and Cd.

Keywords: Long-term fertilization, heavy metal, accumulation

Introduction

Modern agriculture is highly productive, but highly dependent on nonrenewable resources, and is responsible for large-scale environmental contamination. Soil is the most basic of all natural resources, and its quality affects both agricultural productivity and environmental quality [2]. Increased environmental concern is expressed nowadays about the concentration of heavy metals, especially cadmium (Cd) and lead (Pb) in soils and their possible effect on human beings after entering into the food chain [13] through the food crops raised in such heavy metal contaminated soils [8]. Land disposal of solid wastes like sewages, land mining and deposition from the atmosphere are the major sources for heavy metal accumulation in the soil. Incorporation of fertilizers containing heavy metals is another source of contamination in cultivated soils. Phosphatic fertilizers like single superphosphate are the chief sources of heavy metals like Cd and Pb. Cadmium is a biologically non-essential element which is one of the most dangerous environmental contaminants because of its diverse toxic effects. Lead is another heavy metal which also finds its way to the soil through phosphatic and zinc fertilizers in addition to the major contamination sources like petroleum emission from motor vehicles. Countries like United Kingdom and Germany have suggested maximum permissible limits of Pb concentration in soil. In India the maximum permissible limit for Pb in fertilizers is 0.003 percent by weight as Pb [4]. Though their concentration in soils, as of now, may be negligible, in the long run, incorporation of fertilizers may pose serious problems. The best tool to monitor the heavy metal accumulation in agricultural soils is the permanent manurial / long term fertilizer experiments, wherein each treatment receives specified quantity of fertilizers every crop season. With a view to assess the effect of continuous fertilizer and manure application on the total and DTPA extractable Cd and Pb levels in the soil, surface soil samples (0-15 cm) from the 'Long Term Fertilizer Experiment' (LTFE) in progress since 1972 at Tamil Nadu Agricultural University Farm, Coimbatore, India were evaluated for Cd and Pb concentrations.

Materials and Methods

This LTFE soil is medium black (Vertic Ustropept), sandy clay loam with a pH of 8.2 and cation exchange capacity of 26.0 cmol (p+) kg^{-1}. The organic carbon content is around 0.3 per cent and total calcium content of 2.0 per cent. Its ten treatments each in a net plot size of 200 m^2 and replicated four times in a randomized block design are unfertilized control, addition of NPK at 50, 100 and 150 percent optimal level, 100 percent optimum NPK without any herbicidal application, 100 percent optimum NPK + $ZnSO_4$ @ 25 kg ha^{-1}, 100 percent optimum NP, 100 percent optimum N alone, 100 percent optimum NPK + cattle manure at 10 t ha^{-1} and 100 percent NPK through sulphur free sources. A fixed crop sequence of Finger millet (*Elusine coracana*)- Maize (*Zea mays*) -Cow pea (*Vigna unguiculata*) (Since deleted from 2000 onwards) in a year is being followed. Maize alone receives $ZnSO_4$ while cattle manure is applied only to finger millet. The optimum doses of N, $P_2O_5$and K_2O applied, based on soil test are, 90: 45: 17.5, 135: 67.5: 35 kg ha^{-1} in the form of urea, single superphosphate and muriate of potash for finger millet and maize respectively. For the sulphur free sources of NPK, phosphorus is applied in the form of diammonium phosphate. The herbicides being applied are Atrazine (50 %) at 0.5 kg ha^{-1} and Butachlor (50 %) at 2.0 L ha^{-1} for maize and finger millet, respectively. The mean Cd and Pb contents of single superphosphate, the P source, are 70 and 106 mg kg^{-1} respectively. The irrigation water had <1.0 mg L^{-1} of Cd. Commencing from the year 1992 after harvest, surface soil samples after each crop are collected and preserved for future evaluation. Soil samples from 1992 and 2000 crop seasons were evaluated for DTPA extractable and total cadmium and lead contents following the methods suggested by [9] and [18] respectively and published earlier [14]. The results obtained during 2008 are presented and discussed in this paper.

Results and Discussion

The DTPA extractable cadmium concentration of soil did not statistically differ among the treatments during the year 1992 (Table 1). Statistically non-significant differences in the concentration of Pb and Cd were also observed by [3] who could not detect toxic level even after 28 years of continuous fertilization. In contrast, significant differences in the DTPA extractable cadmium concentration could be observed during 2000. The highest concentration was in those plots which received NPK at 150 percent of optimum level while the least was in the control. During 2008 also a similar trend was observed. The experimental field was under dry land agriculture prior to the initiation of this experiment. Twenty-eight years of cultivation and fertilization could result in significant changes in the concentration of DTPA extractable Cd. The concentrations of Cd in the present experiment are in close agreement with those reported for European [7] and United States [6] soils.

Addition of Cd through Cd containing fertilizers and animal manure apart from crop residue incorporation in the last thirty six years, however has resulted in considerable buildup of total Cd. The highest total Cd concentration was under NPK at150 percent optimal level, while the least was in control. The increase in the total as well as DTPA extractable Cd in this treatment was due to the addition of Cd through single super phosphate which contained on an average about 70 mg kg^{-1} of Cd. The total quantum of single superphosphate applied to 150 percent optimal NPK level in a year accounts for about 1500 kg and in terms of Cd it is 105 g ha^{-1} yr^{-1}. From the analysis of 77 samples of commercial fertilizers marketed in the Kingdom of Saudi Arabia for their heavy metal concentrations, [11] reported Cd content upto 36.8 mg kg^{-1} of fertilizer. [15] analyzing soils from the Rothamsted Permanent Manurial Experiment in England and one in New Zealand reported annual additions of 5 g Cd ha^{-1} for P addition at the rate of 33 kg ha^{-1} for England and 20 g Cd ha^{-1} for 35 kg P addition in New Zealand. However, [12] is of the opinion that it is very difficult to estimate the accumulation of Cd and other heavy metals applied to agricultural soils with P fertilizers because the mechanism of addition and removal cannot be assessed easily. The quantum of Cd added in the present study is considerable and naturally, there is an increase in the Cd content of soil. Cadmium accumulation due to phosphatic fertilizer addition to soil has been very well documented. [10] while studying the effect of continuous addition for 10 years of four phosphatic fertilizers of differing cadmium content and solubility on New Zealand pasture soils reported that single super phosphate addition resulted in higher plant available and total Cd than other phosphatic fertilizers tried. Since the control plot does not receive fertilizer, addition there was the least concentration of Cd.

Some countries have set tolerance limits on heavy metal additions to soil in the absence of information on the long term effects of these on soils. These limits usually are set for plough layer of soil where most root activity occurs. The limit values for potentially toxic elements (PTE proposed by The Council of European Economic Committee [16] for cadmium concentration in soils is 1-3.0 mg kg^{-1} of dry soil and the maximum annual addition of total cadmium to the soils is 150 g ha^{-1}. The determined values in this investigation are within the limits. However, under supra optimal doses of NPK, the total Cd is nearing the limit values. This implies that in the long run balanced fertilization at optimum levels, with a close monitoring is essential to prevent Cd concentration in the soil to toxic levels.

As in the case of Cd, the DTPA extractable Pb concentration did not statistically differ among the treatments during the year 1992, while marked differences were observed during the years 2000 and 2008, wherein the addition of supra optimal dose of NPK resulted in higher DTPA Pb content. The total Pb concentration on the other hand differed significantly among the treatments from 1992l. Tiller (1991) reported a range of 8-160 mg kg^{-1} in the pasture and virgin surface soils (0.5 cm) of the Mt. Lofty ranges in Australia while concentration upto 10 and 20 mg kg^{-1} have been reported in other soils of the world. Since the single superphosphate, contributes on an average about 106 mg of Pb kg^{-1} of the fertilizer there is build up in the total lead content of soil.

The content of Pb in the single super phosphate which is higher than that (2-71 mg kg^{-1} as reported by [19]. There is an increase in the Pb content of soil over a period of sixteen years (1992-2008) in all the treatments including control. The increase in the control as well as N alone plots could be due to the input from other sources like irrigation water and atmospheric deposits. The experimental field is adjacent to an industrial area and hence considerable contribution would be expected. Emission from combustion of petrol in motor vehicles is the main global source of Pb [5]. [1] reported sizeable concentration of lead in the surface layer of road side soils (45-455 mg kg^{-1} as against the 0-25 mg kg^{-1} of normal soils). Of course, the rate of input from this source depends upon the intensity of traffic, wind direction and distance from the road. Since the experimental field is within the city limits and has two roads one on the southern and the other on the eastern sides with heavy traffic there would be natural increase in the Pb content of soil. Lead concentrations in the soils of present investigation in those treatments which received optimal level of NPK are within the limits proposed by the Council of European Economic Committee (5- 300 mg $kg^{-1}$of dry soil). At the current rate of increase, however, in treatments, which involve supra optimal dose toxic concentrations are likely to occur which needs close monitoring.

Table1: Effect of long term fertilization on DTPA and Total Cadmium content (mg kg^{-1}) of soil.

Treatments	DTPA Cadmium			TOTAL Cadmium		
	1992	2000	2008	1992	2000	2008
T1-50%NPK	0.020	0.025	0.029	0.83	1.13	1.67
T2-100%NPK	0.021	0.029	0.030	1.30	1.56	1.71
T3-150%NPK	0.018	0.031	0.068	2.43	3.06	2.52
T4-100%NPK+HW	0.021	0.028	0.028	1.43	1.60	1.96
T5-100%NPK+Zn	0.022	0.029	0.018	2.36	2.60	1.96
T6-100%NP	0.017	0.023	0.020	1.63	1.86	1.98
T7-100%N	0.019	0.022	0.030	0.73	0.76	1.98
T8-100%NPK+FYM	0.020	0.027	0.020	1.73	2.16	2.01
T9-100%NPK-S	0.019	0.027	0.023	1.93	2.30	1.69
T10-Control	0.023	0.020	0.020	0.16	0.26	0.43
CD (0.05)	NS	0.005	0.008	0.29	0.37	0.89

Table 2: Effect of long term fertilization on DTPA and Total Lead content (mg kg^{-1}) of soil.

Treatments	DTPA Lead			TOTAL Lead		
	1992	2000	2008	1992	2000	2008
T1-50%NPK	0.11	0.12	0.21	24.0	32.4	44.6
T2-100%NPK	0.12	0.13	0.23	34.2	37.0	70.5
T3-150%NPK	0.12	0.14	0.23	47.2	63.2	74.2
T4-100%NPK+HW	0.12	0.12	0.26	46.3	55.7	67.9
T5-100%NPK+Zn	0.11	0.13	0.25	42.7	61.4	70.1
T6-100%NP	0.11	0.11	0.24	36.8	49.0	73.4
T7-100%N	0.10	0.11	0.19	36.0	40.7	70.3
T8-100%NPK+FYM	0.11	0.12	0.14	36.2	45.4	59.8
T9-100%NPK-S	0.12	0.13	0.25	39.0	52.8	64.3
T10-Control	0.11	0.10	0.12	19.8	21.7	50.9
CD (0.05)	NS	0.02	0.06	5.03	1.83	2.37

HW-Hand weeding only. Zn-Zinc sulphate. FYM-Cattle Manure S-Sulphure free source

Conclusion

Continuous incorporation of phosphatic fertilizers resulted in the gradual buildup of Cd and Pb concentration in surface soils. Accumulations in higher concentrations of these heavy metals are associated with higher level of single superphosphate addition. Though the concentration of these two heavy metals in soil has not reached toxic levels even after 36 years, the rate of increase necessitates close monitoring the production systems involving single superphosphate and zinc application in order to sustain them.

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