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Full Length Research Paper

Ammonia volatilization in corn crop as a result of the application of different nitrogenous fertilizers

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The experiment was carried out in a greenhouse with samples of Eutroferric Red Latosol. On each of these samples, an amount of 800 mg/kg of N was superficially added in the soil. The experiment consisted of five industrial sources of nitrogen, urea (45% of N), urea plus (45% of N), ammonium sulfate (20% of N and 24% of S), Yarabela® (27% of N) where we assessed the volatilization 1, 2, 5, 7, 10, 14, 18 days after the application of the doses. Two methodologies were tested, semi-open static system and the method developed by Miyazawa (2007). After the volatilization assessment of each source, we cultivated a corn plant on each vase for 30 days to evaluate the residual effect of the fertilizer in the crop development through the plant height, stem diameter, dry biomass production of the aerial part and content of N in the vegetal tissue of the aerial part. The urea and the urea plus showed higher volatilization in both ammonium collecting systems and the ammonium sulfate and Yarabela® had the lower volatilization rate. The spectrophotometer detected low levels of nitrogen in comparison to the distillation method.

Key words: Nitrogen, volatization, urea, residual effects.

INTRODUCTION

Maize (*Zea mays* L.) is one of the most economically important crops and one of the most studied due to the nutritional value of the grain, considering its importance in human and animal feed and its raw material for industry. Among the various factors which contribute to rhe low productivity, the incorrect management of mainly nitrogenous fertilizers has stood out (Portugal 2012).

According to Silva et al. (2005) nitrogen is the most required nutrient by corn crop, and the dose to be applied may vary depending on the preceding crop, the expected grain yield and the content of organic matter in the soil. The loss of nitrogen by volatilization of ammonia (NH_3) into the atmosphere is one of the most important factors responsible for the low efficiency of urea applied to the soil surface. In order to provide ammonia volatilization, the presence of ammonia and high pH simultaneously is necessary in the soil (Ernani et al., 2001). The nitrogen losses to the environment are associated with the concentration of soluble nitrogen forms or shapes which is more susceptible to losses. One way to increase the

Table 1. Chemical and physical analysis of the soil.

P	M O	pH CaCl$_2$	H+Al$_2$	Al^{3+}	K+	Ca	Mg^{2+}	SB	CTC	V
Mg dm^{-3}	g dm^{-3}	0.01 mol L^{-1}	------------------------------Cmol$_c$dm^{-3}------------------------------------							%
18.45	23.24	5.63	2.98	0.00	0.75	6.69	2.06	9.50	12.48	76.12

Particle size analysis		
Sand%	Silt%	Clay%
60	15	25

(1)pH in CaCl$_2$, the ratio 1:2.5, [(2)]Extractor kCl mol L^{-1}, [(3)]Extractor calcium acetate 0.5 mol L^{-1} pH 7.0, puller Mehlich^{-1}, the hydrometer method (EMBRAPA, 2009).

efficiency of nitrogen fertilizers is the use of slow or controlled release fertilizers. To minimize losses and increase productivity in a profitable and sustainable manner using nitrogen sources, formulas were developed with slow release of nutrients which reduce the losses that normally occur with the use of urea. This gradual release of nutrients is achieved by coating the nitrogen fertilizer with polymers, increasing crop yields and fertilizer efficiency (Cantarella, 2007).

Leon (2008) in ammonia volatilization resulted from the application of urea in corn, verified reduction of nitrogen volatilization and urease activity for the treatments in which was used urea coated with polymer when compared to the conventional urea in the fertilization in the corn crop. In this sense, Sousa and Loubato (2004) advocated that the quality of the fertilizer, the type of solute and the time of application of the fertilizer are factors associated with soil moisture, the cultivated plant species and crop management, which can interfere with fertilization efficiency and cause loss of nutrients and consequently waste of financial resources. However, according to Lara Cabezas and Trivelin (1990), it is possible to estimate the losses by soil ammonia volatilization from the application of nitrogen fertilizers through direct or indirect methods. One way to verify the dynamics of nitrogen, from the nitrogen sources in the soil, is made through the study of nitrogen transformations in soil with the use of stable isotopes. To determine the loss of NH$_3$ by volatilization coming from nitrogen fertilizer in Brazilian conditions, researchers have developed NH$_3$ collectors to volatilization measures. Indirect methods can be carried out through the use of isotopically labeled fertilizer (^{15}N), isotopic measurements show high cost, but they can be used in the calibration of direct methods using collecting chambers (Trivelin and Franco, 2011).

The closed-static systems, closed-dynamic and static semi-open are used in the determination by direct methods. Closed systems may make it impossible to obtain observations of volatilization under natural conditions, because they modify the environment at the soil surface (Lara Cabezas and Trivelin, 1990). The collectors described by Nönmik (1973), with static semi-

open system, are used in field studies. The semi-static open collector, however, also has limitations. These limitations were evaluated by Lara Cabezas and Trivelin (1990), who found that the presence of the semi-static open collector system influenced significantly, by reducing the percentage and amount of volatilized ammonia of the fertilizer. Thus, it can be verified, the importance of using correction factors to determine the static semi-open collector, the N-NH$_3$ volatilized (Mattos, 2011). Considering the importance of studying different methods to assess the quantity and ammonium speed volatilized by different nitrogen sources, this study aimed to evaluate the amount of ammonia volatilized from each source of N tested by two methods, the static semi-open system and the method developed by Miyazawa (2007).

MATERIALS AND METHODS

The experiment was conducted in the soil fertility laboratory and mineral nutrition of Plants at Universidade Estadual do Oeste do Paraná - UNIOESTE, Campus de Marechal Cândido Rondon / PR. For each vase, we used 6 kg of an Eutroferric Red Latosol (Table 1). On each of these vases, it was added 800 mg/kg of N in the soil surface, where the volatilization was evaluated within 18 days of five sources of N: Urea (45%), ammonium sulfate (20% N and 24% O) Yarabela® (27% N), urea plus (46% N) and super N (45% N).

Five industrial sources of nitrogen were tested by two methodologies applied in coverage and witness, each treatment was composed by four repetitions, totaling 40 vases. The capture of volatilized NH$_3$ was made by two methods; one of them was the method in closed chambers developed system. For this system, we used transparent plastic bottles of polyethylene terephthalate (PET) with capacity of 2 L and basal diameter of 10 cm. The bottles were sealed at the top, with their bases removed, so that the gases enter therein after their introduction to the soil. Inside the middle part of them, it was placed a plastic centrifuge tube of 50 ml, which is suspended by a wire bracket connected at its upper part, fixed by the lid. Inside this tube it was placed H$_2$SO$_4$ solution (0.05 mol L^{-1}), glycerin (2%, v/v) and a strip of filter paper (2 × 20 cm), in order to increase the contact surface of NH$_3$ with H$_2$SO$_4$, according to the method described by Miyazawa (2007). The ammonia retained on the paper was determined by salicylate blue spectrophotometry method (Miyazawa, 2007), salicylic acid 5% solution: 50 g of salicylic acid, 50 g of Na citrate and 21 g of NaOH in 100 ml flask and the remaining volume was completed with water, Na nitroprusside solution in 0.1%: 0.2 g of Na nitroprusside in 200 ml of H$_2$O and 0.15%: 6 ml of NaOCl 5% NaOCl in 200 ml of

H_2O. In a test tube we added 1 ml of the sample, 1 ml of the salicylic acid solution, 1 ml of Na nitroprusside solution in 0.1%, 1 ml of 0.15% NaOCl solution and 6 ml of water and then the test tubes were agitated and after 60 min the spectrophotometer reading at 697 nm was made. The NH_3 retained on the paper was also determined by vapor dragging, in semi-micro Kjeldahl apparatus (Tedesco et al., 1995).

The other form of assessment of the volatilization of N was by a semi open static system proposed by Nömmik (1973) with some modifications described by Marcondes (2007). Collectors were made with PVC pipes with a diameter of 15 cm, containing two polyurethane foam discs soaked in 50 ml of sulfuric acid 0.25 mol, more Glycerin 3% (v/v). The amount of volatilized $N-NH_3$ was determined by drag vapor in semi-micro Kjeldahl apparatus (Tedesco et al., 1995). The foams were exchanged in the same time interval when performed by Trivelin (2002), and the volatilization of NH3 was evaluated at 1, 2, 5, 7, 10, 14, and 18 days after application of treatments, in each of the experiments. During the collection period, the soil moisture was maintained between 70% of water retention in the soil. The collectors were taken to the soil fertility laboratory and mineral nutrition of plants for evaluations. The determination of ammonia retained in the absorber was performed by distillation and titration. The foam of each sample was cut in 2 pieces and placed in a distiller balloon with 1-liter capacity, where it was also added about 100 ml of distilled water and 20 ml of NaOH. We collected the distillate volume containing ammonia retained by the absorber, in a boric acid 2% solution titrated with standardized HCl solution.

After assessing the volatilization of each source, we cultivated a corn plant in each vase to evaluate the residual effect of the fertilizer. After 30 days of cultivation, we evaluated the growth of plants through the assessments of height, plants length, stem diameter and dry biomass production of the aerial part. We also evaluated the N content in the aerial part of the plant tissue according to Tedesco et al. (1995), which consists of the digestion with H_2O_2 and H_2SO_4 and distillation by vapor dragging into semi-micro Kjeldahl apparatus. We used simple linear correlation analysis (Pearson) to determine the relationship between the collecting systems and methods for the determination of $N-NH_3$. The collected data were submitted to analysis of variance and regression and the comparison between sources by 5% Tukey test, SAEG 8.0 (1999).

RESULTS

By the spectrometry method of determination of ammonia volatilization there was no significant difference between urea, urea plus, super N and Yarabela[®] in the first and fourth collection as shown in Table 2. The urea ammonium sulfate, urea plus, super N and Yarabela[®] presented an increase in the fourth collection and then dropped in the $N-NH_3$ content, this may be due to temperature oscillation during the collection period, because the temperature during the experiment oscillated with periods of cold days (16°C) and high temperatures (40°C). In the second and fifth day there was no significant difference between urea, urea plus, the same occurred between the ammonium sulfate and yarabela who had the lower volatilization. This result can be explained by the presence of S in the ammonium sulfate and in the Yarabela[®] source.

Lara Cabezas et al. (2005) and Lara Cabezas and Couto (2007) found that ammonium sulfate in relation to urea gave a higher yield of maize, the authors attributed to the cause of the observed response, S present in the ammonium. By ribbon distillation methodology, there was no significant difference in volatilization in the 1st, 2nd and 7th gathering; in the 3rd, 4th and 5th collects the ammonium sulfate and Yarabela[®] showed similar behavior to that presented in the distillation of foam and the spectrophotometer not differing statistically from each other with the least amount of evaporation.

Manzoni and Trivelin (2003) when comparing absorbed paper to the method of ^{15}N balance, observed that paper absorbs only estimated actual losses of NH_3 by volatilization in high volatilization conditions. On the fifth day, urea plus had the highest $N-NH_3$ volatilized content differing from the other treatments in the distillation method of tape and foam. In the distillation of the foam there was no significant difference between urea, urea plus and Yara bela® on the first day, result that was also observed by the spectrophotometry method. The results found in the second collection by spectrophotometry and distillation of the foam are similar, there was no significant difference between super N ammonium sulfate and Yarabela®. The volatilization of urea and urea plus did not differ statistically and the super N volatilization was similar to urea plus in the seventh day. In the tenth collection, super N volatilization showed a content of $N-NH_3$ higher than others. In the 14th gathering there was no significant difference between the $N-NH_3$ levels for urea, urea plus and super N when measured by the distillation of tape and foam.

By the foam distillation in the 18th collection, volatilization of Super N was similar to urea, a result also found by spectrophotometry among the ammonium sulfate and Yarabela® there was only significant difference in the spectrophotometry method, where the ammonium sulfate showed high $N-NH_3$ content in the first day, in the seventh day and in the 14th day, a result similar to that was found in foam distillation on the first day. The ammonium sulfate and Yarabela[®] in both methodologies had the lowest $N-NH_3$ volatilized values. The length showed a significant difference in the collector tape system and the treatment with super N was superior to the others (Table 3). The nitrogen content did not differ statistically in the collecting system of $N-NH_3$ by the foam distillation, but in the evaluation of the tape distillation system, the leaf nitrogen content in the treatment with Yarabela[®] was lower than the other treatments. There was a positive correlation between capture systems of volatilized ammonia as shown by correlation analysis presented in Table 4, however, in the methods of determining the volatilized nitrogen, the assessment made by the spectrophotometer detected low levels of nitrogen compared to the distillation method.

DISCUSSION

Tasca et al. (2011) says that the greatest NH_3 losses

Table 2. Ammonia volatilization in function of days after the application of fertilizers, assessed by different collectors and methods of N determination.

Fertilizers	Collection (days)						
	1	2	5	7	10	14	18
Collector Tape- Spectrophotometer (g kg^{-1})							
Urea	0.06^b	7.8^a	10.44^a	4.18^a	7.97^a	2.77^b	2.17^a
Urea plus	0.04^b	8.28^a	14.88^a	4.1^a	6.77^{ab}	2.35^b	1.94^{ab}
Super N	0.03^b	1.48^b	9.66^{ab}	4.1^a	3.75^{bc}	4,26^a	1.65^{ab}
Ammonium S.	0.65^a	0.09^b	0.19^b	0.23^b	0.07^c	0.07^c	0.09^b
Yarabela®	0.08^b	0.06^b	0.12^b	0.1^b	0.23^c	0,03^c	0.04^b
F Values	114.9**	10.38**	9.5**	16.78**	17.08**	37. 094**	5.17*
CV (%)	28.62	72.69	60.76	41.66	46.8	31.09	77.11
Collector tape-distillation (g kg^{-1})							
Urea	1.08	4.4	86.76^b	43.56^A	53.5^a	29.41^a	2.76
Urea plus	0.96	5.97	96.82^a	28.67^A	5.42^b	35.39^a	2.82
Super N	0.71	5.23	9.97^c	35.76^A	4.37^b	6.16^b	2.23
Ammonium S.	0.65	3.34	2.42^d	4.68^B	2.66^b	3.13^b	2.11
Yarabela®	0.93	2.54	1.66^d	3.59^B	1.92^b	2.89^b	1.98
F Values	0.3^{ns}	1.67^{ns}	11.14**	27.4	9.92**	40.83	0.18^{ns}
CV (%)	76.04	49.91	7.27	29.96	104.6	31.96	23.52
Collector foam-distillation (g kg^{-1})							
Urea	0.56^b	50.35^a	14.56^a	63.74^A	14.35^b	35.26^a	25.03^a
Urea plus	0.31^b	55.01^a	17.35^a	63.07^{Ab}	12.01^b	30.36^a	2.69^b
Super N	0.09^b	9.2^b	20.95^a	41.71^B	22.92^a	4.67^b	25.1^a
Ammonium S.	2.35^a	0.56^b	0.72^b	1.09^C	0.71^c	0.92^b	0.46^b
Yarabela®	0.55^b	0.64^b	0.83^b	0.29^C	0.53^c	0.28^b	0.47^b
F Values	26.55**	45.54**	32.09**	43.93**	52.37**	15.02**	13.41**
CV (%)	45.6	34.86	30.83	28.11	26.16	61.61	66.58

Means followed by the same letter in the column do not differ by Tukey test at 5%.

occurred proportionally with the increase in temperature. In an experiment conducted in the laboratory, it was observed that when urea was put in a surface at a temperature of 18°C there was a reduction of 4.6 times lower than when put at 35°C. In wet soils, near field capacity, the gaseous ammonia losses accompany the process of evaporation of water.

Silva and Vale (2000) in nitrate availability in Brazilian soils under the influence of liming and sources and doses of nitrogen explains that cause elevation of pH around the granule which slows volatilization of ammonia. The volatilization of urea, urea plus, super N did not differ statistically from each other on the second day. Trivelin (2001), the methods with chambers are relatively simple and suitable for an experiment with small amount and various treatments in the same area. One of the disadvantages of this system is the formation of microclimate with the modification of the environmental conditions inside as intensity, light wavelength, temperature, relative humidity, ventilation and the formation of dew, which certainly influence the volatilization of NH3 when compared to natural conditions (Table 2).

For the variables dry matter and plant height shown in Table 3, there was no significant difference for the different methods of determination of N-NH$_3$ volatilization. Regarding the diameter, the ammonium sulfate showed significant difference with larger diameter compared with other sources in determining the collector. This fact can be explained by Koprivova et al. (2000) who reported the importance of the N and S metabolism that are directly related. The assimilation of N and S are well coordinated and the deficiency of one of them can affect the assimilation of the other.

Conclusion

Urea showed the highest loss by volatilization by both evaluation methods: spectrophotometry and distillation

Table 3. Leaf dry matter production, diameter, height, length, leaf N of corn by collector system with the use of filter paper tape and polyurethane foam.

Fertilizer	Leaf dry matter (g/kg)		Diameter (mm)		Height (cm)		Length (cm)		N leaf (%)	
	Foam	Tape	Foam	Tape	Foam	Tape	Foam	Tape	Foam	Tape
Urea	0.21	0.21	8.2	8.1[ab]	39.63	38.4	65.08	66.63[b]	2.84	2.67[ab]
Urea plus	0.21	0,21	8.6	9.03[ab]	40.88	42.6	66.25	76.65[ab]	3.08	3.24[a]
Super N	0.21	0.21	7.4	9.55[a]	38.88	44.4	58.75	82.85[a]	3.19	2.89[a]
Ammonium S.	0.21	0.21	8.4	7.03[b]	41.83	39.3	71.13	64.35[b]	2.98	3.04[a]
Yarabela®	0.21	0.21	8.1	7.75[ab]	39	36.9	63.68	64.93[b]	2.84	1.48[b]
F Values	0.95[ns]	1.17[ns]	0.44[ns]	4.09[*]	0.19[ns]	1.8[ns]	0.76[ns]	7.45[**]	0.12[ns]	5.4[*]
CV (%)	2.9	2.26	15.89	12.01	14.77	11.6	15.83	8.51	29.36	22.42

Means followed by the same letter in the column do not differ by Tukey test at 5%

Table 4. Correlation array between systems of volatilized ammonia and N determination method.

Correlation	FIESP	FIDEST	ESPDEST
FIESP	-	-	-
FIDEST	0.90[**]	-	-
ESPDEST	0.94[**]	0.90[**]	-

[**] Correlation significant at a level of 1% probability by T test. FIESP: tape by spectrophotometry; FIDEST: tape by distillation ESPDEST: foam by distillation.

dragging vapors. The nitrogen content in the leaf tissue by the collector-tape determination in the treatment with Yarabela® was lower than the other treatments. The ammonium sulfate and Yarabela® in both methodologies had the lowest $N-NH_3$ volatilized values. The spectrophotometer detected low levels of nitrogen compared to the distillation method.

Conflict of interests

The authors have not declared any conflict of interests.

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Full Length Research Paper

Soil management effects on phosphorus sorption and external P requirement in oxisols of Malawi

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Oxisols are one of the major soils of Malawi and they are high in P sorption. Conservation agriculture has been practiced on this soil for some years now but soil management effects on P sorption and external P requirement (EPR) of Oxisols in Malawi have not, however, been determined. Soil management effects on P sorption and EPR of Oxisols in Malawi were therefore determined in the present study. The effects studied were conventional tillage (CT), no-tillage (NT) and crop rotation (CR). The soils differed considerably in their sorption characteristics, with the sorption maxima ranging from 413 to 345 mg P kg^{-1}. Differences in sorption maxima and affinity due to soil management effects were statistically significantly ($P \le 0.05$). The sorption affinity (b) values ranged from 0.48 to 0.72 dm^3 mg^{-1} and differences due to soil management effects were statistically significant ($P \le 0.05$) only between conventional tillage (CT) and no tillage (NT) or crop rotation (CR). The sorption affinity due to NT was not statistically significant from that of CR. The b values were the highest in soils that had been subjected to CT.

Key words: Oxisols, soil management effects, sorption affinity, sorption maxima, external P requirement.

INTRODUCTION

It has been observed that due to an increasing demand of agricultural production for phosphorus (P) and the fact that the peak in global P production may soon occur, P is now receiving more attention than ever before as a non-renewable resource (Cordell et al., 2009; Gilbert, 2009). Soils serve as the principal reservoir of P in terrestrial systems. They contain P ranging from 35 to 5,300 mg kg^{-1}, with a median concentration of 800 mg kg^{-1} (Bowen, 1979; Sparks, 2003). In soils, P exists in various chemical forms including inorganic and organic P forms. These P forms differ in their behaviour and fate in soils (Hansen et al., 2004; Turner et al., 2007).

Inorganic P usually accounts for 35 to 70% of total P in soil. Primary P minerals including apatites, strengite, and variscite are very stable, and the release of available P from these minerals by weathering is generally too slow to meet the demand of annual crops through direct application of phosphate rocks. In contrast, secondary P minerals including calcium (Ca), iron (Fe), and aluminium (Al) phosphates vary in their dissolution rates, depending on size of mineral particles and soil pH (Pierzynski et al., 2005; Oelkers and Valsami-Jones, 2008). With decreasing soil pH, solubility of Fe and Al phosphates decreases while the solubility of Ca phosphate decreases with increasing soil pH except for pH values above 8 (Hinsinger, 2001).

The strong affinity of phosphate ions for the solid phase of soils causes P to be very low in its effective

concentration in soil solutions where it is in dynamic equilibrium with the solid phase. In highly weathered soils of the tropics and subtropics, limited availability of soil P is often the main constraint to plant growth. In Malawi, the fertilisers smallholder farmers add to their soils invariably carry, among other essential elements, nitrogen and phosphorus in order to optimise crop production. For maize (*Zea mays* L.) production, P fertilisation is usually aimed at maintaining an effective concentration of 0.02 mg P kg^{-1}. Phosphate ions introduced into soil solutions, which are not absorbed by the growing plant or immobilized by soil microbes, however, are subject to various chemical reactions. These include precipitation and dissolution (mineral equilibria or pseudo-equilibria) and sorption and desorption (interactions between P in solution and soil solid phases).

The kinetics of dissolution and precipitation of P minerals, such as variscite ($AlPO_4 \cdot 2H_2O$) and strengite ($FePO_4 \cdot 2H_2O$) that form and become stable in acid soils or octocalcium phosphate [$Ca_8H(PO_4)_{6.5}H_2O$] and hydroxyapatite [$Ca_5(PO_4)_3OH$] that form and become stable in alkaline soils govern the effective concentration of phosphate ions in soil solution. The solubilities of the aluminium-bound phosphate (Al-P) mineral and iron-bound phosphate (Fe-P) mineral decrease with increasing acidity whereas the calcium-bound phosphate (Ca-P) minerals decrease with decreasing hydrogen ion (H^+) concentration.

The P concentration in soil solution is also influenced by sorption and desorption. The combined processes of desorption and dissolution influence the bioavailability of phosphate ions in soil solutions. Both desorption and precipitation occur in response to disequilibria established in solution by removal of P from solution (disequilibria desorption); or in response to the action of ligands exchanging with phosphate or dissolving phosphate-bearing compounds (ligand desorption). Bioavailable desorbable P is commonly indexed by extracting a portion of the labile pool of P with chemical extractants, such as Bray 1, Mehlich 1 or 3, or Olsen's Solution (Ziadi et al., 2001). Soil P tests can, however, be used as indices of P availability, able to accurately predict the amount of P that is available for plant uptake, only after they have been subjected to, and selected from, correlation and calibration studies using laboratory, greenhouse and field experimental data. Because soil tests serve as an index to P bioavailability and do not define the pattern of P release, or the influence of P desorption on the soil solution concentration, they have limited utility in the mechanistic modelling of P bioavailability and uptake by plants.

Whereas the combined processes of desorption and dissolution do generally influence the bioavailability of phosphate ions in soil solutions, in highly weathered soils, such as those that occur in the tropics, it is the degree of phosphate sorption that largely controls the effective concentration and therefore P bioavailability of

phosphate ions in soil solutions. Phosphate (P) adsorption is the process in which the ions are held on the active sites of the soil particle surfaces. The amount of P adsorbed by soil increases as the effective concentration of phosphate ions in solution increases and vice versa. Adsorption affects the fate of P-source and the availability of phosphate to plants. Adsorbed or precipitated inorganic phosphate undergoes desorption or dissolution reactions when moving from the solid to the solution phase.

The relationship between P sorbed on the solid phase and P in the solution phase defines what is known as adsorption isotherm. Adsorption isotherm can be described as the equilibrium relationship between the amounts of adsorbed and dissolved species of phosphate at constant temperature in quantitative terms. The P adsorption isotherm is a useful, descriptive characteristic of soil that provides information on the ability of the soil to hold P in reserve and release it into solution as the phosphate ions are removed from the solution. Phosphorus sorption relationships are commonly used in the determination of external phosphorus requirement (EPR) of crops. The EPR of crops has been defined as the concentration of P in solution known to be non-limiting to plant growth (Henry and Smith, 2004). For most crops, the amount of P in equilibrium with 0.2 mg P dm^{-3} ($P_{0.2}$) has been shown to be the threshold over which no response to P is observed (Iyamuremye et al., 1996; Nziguheba et al., 1998). The P requirements, estimated in this manner, aim at building up the status of soil phosphorus by a single application to a level which, thereafter, only requires maintenance application to replenish losses due to plant uptake, removal by erosion or continuing slow reactions between phosphate and soil (Henry and Smith, 2003).

Most of the upland soils (Oxisols and Ultisols) in Malawi are dominated by the poorly buffered 1:1 kaolinite and halloysite and oxides of iron and aluminium, reflecting that the soils are highly weathered and leached (Maida, 1973; Mwandemere and Robertson, 1975; Ntokotha, 1974). The poorly buffered soils account for over 40% of soils in Malawi. Mughogho (1975) conducted P sorption studies on Oxisols and Ultisols collected from several sites in Malawi. The Oxisols have since then been subjected to conventional tillage (CT). The extent to which CR influences P sorption and EPR characteristics of the Oxisols has, however, not been determined in Malawi. The main objective of the present investigations therefore was to determine the capacity of the Oxisols to sorb P and the EPR of crops after they have been subjected to four years of crop rotation.

MATERIALS AND METHODS

Description of the experimental site and soil sampling

This study was carried out in Nkhotakota district which lies between

33°22' east and 34°10 east and between 13°20' south and 3°40' south in the central part of Malawi. It is located at just 82 km away from Lilongwe University of Agriculture and Natural Resources. Topographically, it is divided into two parts: the eastern part is predominantly hilly while the western part is low. The hilly eastern part is well drained by small streams which flow into Lake Malawi. The average annual rainfall ranges from 750 to 1,000 mm and the temperature is within the range of 15° to 35°. Soil samples used in the present study were collected from an experimental site where soils had been subjected to no-tillage (NT) and to crop rotation (CR) for three years. Twelve representative top soils (0 to 20 cm) were randomly collected in a zigzag manner from the site, air-dried, and ground to pass through a 2-mm sieve.

Soil characterization

The soils were analyzed for pH in a 1:2.5 soil to water slurry using a pH electrode as outlined by Blakemore et al. (1987), particle size distribution using the Bouyoucos hydrometer method (Day, 1965) as described by Anderson and Ingram (1993). The soil organic carbon contents were determined using the potassium dichromate ($K_2Cr_2O_7$) oxidation method of Walkley and Black (1934) as described by Anderson and Ingram (1993) by multiplying the total soil organic carbon with 1.724. Total nitrogen was determined using the Kjeldhal wet oxidation process as described by Anderson and Ingram (1993).

Total P was estimated following wet digestion with H_2O_2/H_2SO_4 (Okalebo et al., 2002), while P in the clear extracts was determined colorimetrically by the ascorbic acid method (Murphy and Riley, 1962) on a Perkin Elmer Lambda 25 UV/VIS spectrometer. Exchangeable Ca^{2+}, Mg^{2+}, and K^+ were extracted using Mehlich-3 method (Mehlich, 1984) and determined by atomic absorption spectrophotometer. Exchangeable acidity ($Al^{3+} + H^+$) was extracted with 1.0 M KCl and titrated with 0.05 M NaOH (Okalebo et al., 2002).

Phosphate sorption isotherms

Two grams of air-dried and ground (<2 mm) soil samples were weighed in triplicates into 50 ml centrifuge tubes and suspended in 30 ml of 0.01 M $CaCl_2$ of supporting electrolyte containing various concentration of P as KH_2PO_4 to give 0, 100, 200, 300, 400, and 500 P mg kg^{-1} of soil for six days at a room temperature. Three drops of toluene were added to minimize microbial activity. Suspensions were shaken twice daily for 30 min and at the end of the sixth day, they were centrifuged at 10,000 rev min^{-1} and filtered through Whatman No. 42 filter paper. Phosphorus content in the clear supernatant solution was determined colorimetrically by the ascorbic acid method (Murphy and Riley, 1962) on a Perkin Elmer Lambda 25 UV/VIS spectrometer.

The amount of P remaining in solution was taken to be the equilibrium concentration (C) and expressed as mg P dm^{-3}. The amount of P sorbed (mg P kg^{-1} soil) was estimated as the difference between equilibrium P concentration and initial P added. One of the models that quantitatively describe adsorption isotherm is that of Langmuir (Pant and Reddy, 2001; Essington, 2003; Dossa et al., 2008). The sorption data were fitted to the following linearized form of the Langmuir equation:

$$\frac{C}{S} = \frac{1}{S_{max} \times b} + \frac{C}{S_{max}}$$

Where C is the P equilibrium P concentration (mg dm^{-3}), S is the total amount of adsorbate (adsorbed P) taken up per unit mass of adsorbent (mg kg^{-1}) = adsorption maximum mg kg^{-1}. B is a constant

related to the bonding energy of the soil for P or affinity constant (Uzoho and Oti, 2005).

A plot of C/(x/m) versus C gave a straight line equation with slope as 1/b and an intercept as 1/kb

Soil external P requirements

Soil external P requirements of crops were determined by substituting the desired P concentration (0.2 mg P dm^{-3}) into the following Langmuir equation (Dodor and Oya, 2000):

$$S = \frac{S_{max} \times bC}{1 + bC}$$

Where S, S_{max}, b and C are as defined as stated earlier.

Statistical analysis

The relationship between P sorption parameters and P sorbed at equilibrium with 0.2 mg P dm^{-3} with selected soil chemical properties was determined using simple regressions and correlations, and tested for significance at 0.01 and 0.05 probability levels using the 16th edition of GenStat statistical software. The contribution of soil properties to sorption parameters was examined using the stepwise model-building procedure. The differences in P sorption among the treatments within site and across sites was analysed using ANOVA and tested at significant level 0.05.

RESULTS AND DISCUSSION

Soil organic matter

Table 1 shows the selected properties of the Oxisols. The properties of the soils varied with soil management effects. The increase in soil organic matter (OM) contents observed in soils subjected to CR and NT was consistent with conclusions of Rasmussen (1999) and During et al. (2002) which attributed an increase in organic matter contents of the topsoil subjected to annual no-tillage to plant residues left on the soil surface. Lal (1997b) also observed soil organic carbon (SOC) to be significantly higher in the soil subjected to NT than the one that was under conventional tillage (CT) treatment.

Ali et al. (2006), however, observed OM and other soil variables such as N, P, K, Ca and Mg to have the lowest values recorded in CT plots. This finding was attributed to the inversion of topsoil during ploughing, which was postulated to have shifted less fertile subsoil to the surface, and to possible leaching. Busari and Salako (2013) observed in South Western Nigeria that soil, the soil organic C (SOC) and the effective cation exchange capacity (ECEC) were significantly higher at the end of a two-year study under NT than under CT. The present study also showed organic matter contents to be the lowest in the soil that had been subjected to CT (Table 1). In addition to the factors that have been cited by earlier workers referred to earlier as possible causes for the low organic matter contents in the soil that was under CT, the loosening of the soil caused by CT and the

Table 1. Selected soil characteristics.

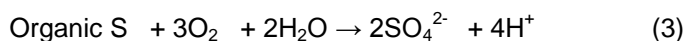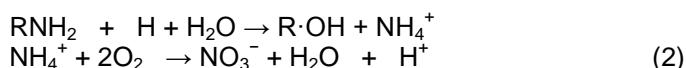| Soil properties	Treatment			Grand mean
	CR	NT	CT	
OM (g kg^{-1})	17.0	11.2	3.4	10.6
pH (water)	5.1	4.9	4.7	4.9
Al$_{(ex)}$ (cmol$_c$ kg^{-1})	3.3	2.6	7.9	4.6
N (%)	1.4	1.6	1.5	1.5
K (cmol$_c$ kg^{-1})	0.13	0.10	0.17	0.13
Mg (cmol$_c$ kg^{-1})	0.31	0.36	0.42	0.36
Ca (cmol$_c$ kg^{-1})	4.97	6.84	10.56	7.50
Total P (mg kg^{-1})	126.9	123.0	23.8	91.2

CR: Crop rotation; NT: no tillage; CT: conventional tillage.

resultant improvement in soil aeration may have also created a soil ambient which, under high soil temperatures, might have been favourable for increased microbial activities and OM biodegradation leading to the observed low OM values.

Soil pH

The soil that was under CT treatment had the lowest pH value (Table 1). Some of the earlier workers, for example Rasmussen (1999) observed no effects that could be attributed to tillage systems while other findings showed soil pH values to be lower in no-till (NT) systems than in soils that were under CT (Rahman et al., 2008). The lower pH in NT was attributed to accumulation of organic matter in the upper few centimetres under NT soil (Rhoton, 2000) causing increases in the concentration of electrolytes and reduction in pH (Rahman et al., 2008). Busari and Salako (2013) observed in South Western Nigeria that NT soil had a significantly higher pH at the end of the first year after tillage, but that the pH became significantly lower compared with the CT soil at the end of the second year after tillage. The latter appears to be in accord with the findings of the present work (Table 1), which are consistent with the findings of Cookson et al. (2008) that showed a decrease in surface soil pH with increasing tillage disturbance.

Earlier work of Lal (1997b) also showed a significantly higher soil pH in NT plots as compared to those in tilled plots. As indicated earlier, under high temperatures and heavy rainfall, CT results in the loosening of the soil, improved soil aeration and increased soil OM biodegradation. During the OM biodegeneration, the synthesis of organic acid (Equation 1) and the mineralisation of organically bound essential elements such as N (Equation 2) and S (Equation 3) lead to proton generations:

$$Organic\ C \rightarrow RCOOH \rightarrow \ RCOO^- + \ H^+ \tag{1}$$

$$RNH_2 \ + \ H + H_2O \rightarrow R\cdot OH + NH_4^+$$
$$NH_4^+ + 2O_2 \ \rightarrow NO_3^- + H_2O \ + \ H^+ \tag{2}$$

$$Organic\ S \ + 3O_2 \ + 2H_2O \rightarrow 2SO_4^{2-} \ + 4H^+ \tag{3}$$

The protons generated as shown in Equations 1 to 3 replace basic cations on the soil exchange complex, thus bringing the cations into soil solution from where they are susceptible to loss through crop uptake and leaching, leaving H^+ and Al^{3+} on the soil exchange complex, thus rendering the soil to be acidic in its reaction.

Phosphate sorption and external phosphate requirement

The linearized Langmuir equation gave a good fit for all the soils when C/(x/m) was plotted against equilibrium P concentration C, with coefficients of determination (R^2) values > 0.95 (Figures 1 to 3). Using the equations shown in Figures 1 to 3, the sorption maxima (S_{max}) and sorption affinity (b) were calculated. The soils differed considerably in their sorption characteristics, with the S_{max} ranging from 413 to 345 mg P kg^{-1} (Table 2). Differences in the observed sorption maxima and affinity (b) due to treatment effects were statistically significant ($P \leq 0.05$). The sorption affinity (b) values ranged from 0.48 to 0.72 dm^3 mg^{-1} and the b values of the soil under NT treatment were not significantly different from those of the soil under CR (Table 2).

Soil pH

The b values were the highest in soils that had been subjected to CT treatment and the trend was similar to that of the sorption maxima (S_{max}), the external phosphate requirement (EPR), and soil pH values (Table 2). The results suggest that the highest amounts of any soluble fertiliser P added to the soils would be sorbed by reactive surfaces of soils that have been subjected to CT.
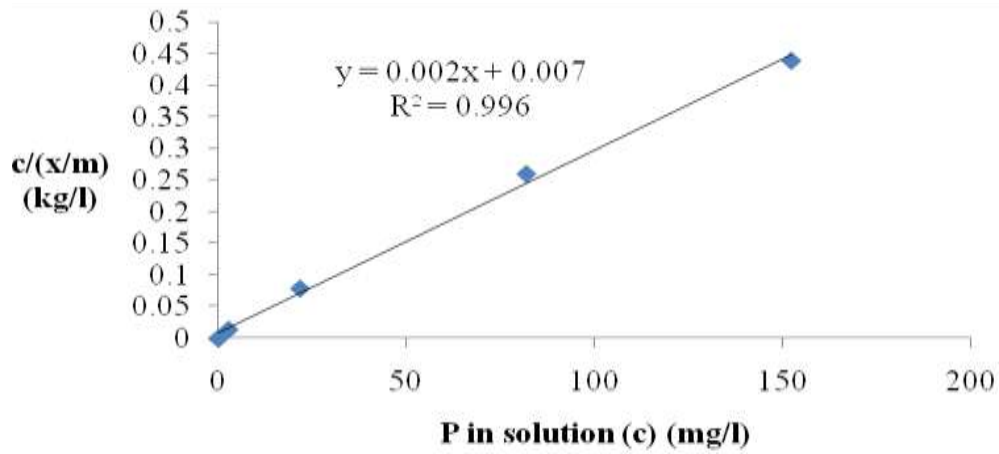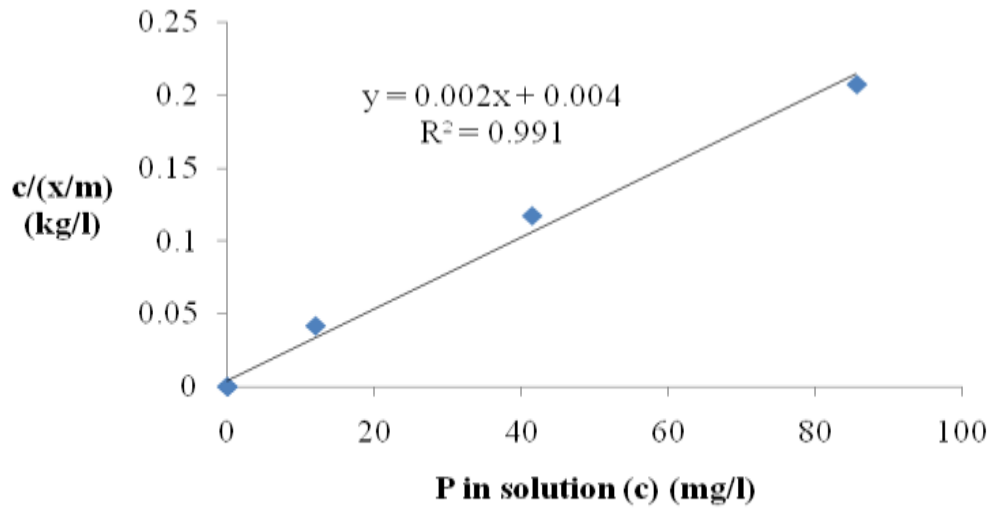
Figure 1. Crop rotation.
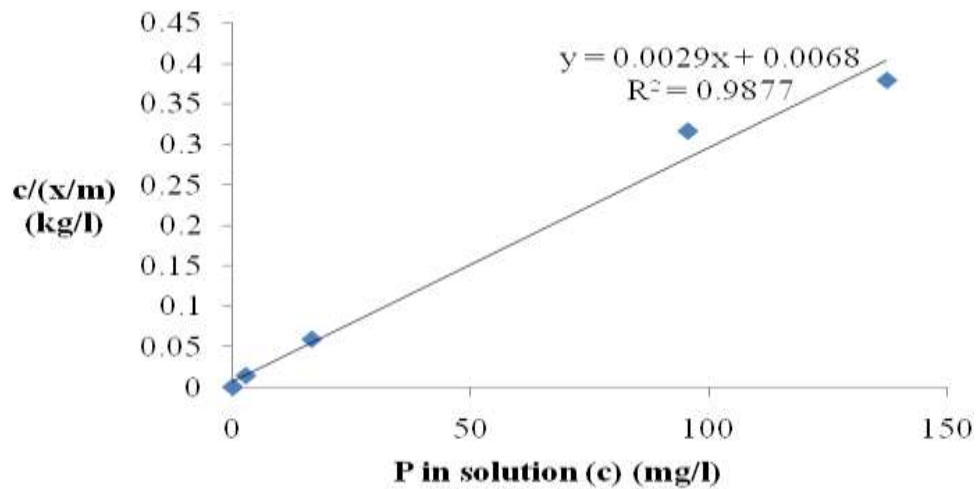

Figure 2. Conventional tillage.

Figure 3. No-tillage.

Table 2. Means of P sorption parameters, organic matter, exchangeable aluminium and EPR ($P_{0.2}$) for crops
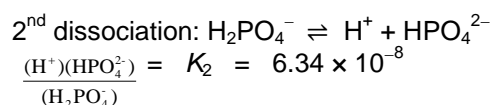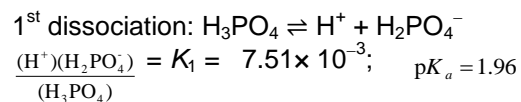
Treatment	Variables				
	OM (g kg^{-1})	Al$_{exc}$ (cmol kg^{-1})	S$_{max}$ (mg kg^{-1})	B (dm^3 mg^{-1})	EPR ($P_{0.2}$)
CR	17.0^a	3.33^a	342.1^a	0.48^a	30.2^a
NT	11.2^a	2.55^a	345.4^a	0.48^a	30.0^a
CT	3.4^b	7.90^b	413.0^b	0.72^b	52.2^b
Grand mean	10.57	4.59	366.8	0.56	37.5
LSD (0.05)	4.887	1.802	22.86	0.12	8.18
CV%	28.9	24.5	3.9	11.5	13.6

Means having different letters in the same column are statistically different at 0.05 probability level. CR: Crop rotation; NT: no tillage; CT: conventional tillage.
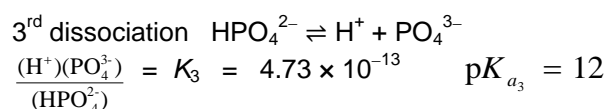
The relatively higher b, S_{max} and EPR values of the soils under CT may be attributed to the lower pH values, which is according to previous observations (Udo, 1981; Uzoho and Oti, 2005).

Plants take up P from the soil as $H_2PO_4^-$ and HPO_4^{2-} ions and the effective concentration of these ions in solution is a function of the pH of the ambient solution.

These phosphate ions are dissociation products of the orthophosphoric acid (H_3PO_4), which is a polyprotic, weak acid. The extent to which the relative concentrations of the phosphate ions in solutions is influenced by the pH of the ambient solution is self-evident from the following sequence for the dissociation of H_3PO_4:

1st dissociation: $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$

$$\frac{(H^+)(H_2PO_4^-)}{(H_3PO_4)} = K_1 = 7.51 \times 10^{-3}; \quad pK_a = 1.96$$

2nd dissociation: $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$

$$\frac{(H^+)(HPO_4^{2-})}{(H_2PO_4^-)} = K_2 = 6.34 \times 10^{-8}$$

$$pK_{a_2} = 6.80$$

3rd dissociation $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$

$$\frac{(H^+)(PO_4^{3-})}{(HPO_4^{2-})} = K_3 = 4.73 \times 10^{-13} \quad pK_{a_3} = 12$$

This shows that the sequence for the dissociation of H_3PO_4 yields products of diminishing acid strength and that the monovalent dihydrogen phosphate ($H_2PO_4^-$) species is dominant in solutions having pH 4.0 to 5.5, which suggests that this is the phosphate species that was dominant in the soils used in the present study (Table 1) and that the thermodynamic concentration of the phosphate ions in such an acid Oxisol would be governed by cations such as Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^+$, Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ that co-precipitate with phosphate ions. Besides precipitation and dissolution of P minerals and by the sorption and desorption of inorganic P. The data given in Table 1 show that the soil under CT whose pH was the lowest had the highest P sorption maxima and P sorption affinity values, which is consistent with earlier findings which show that in highly weathered soils like the Oxisols used in the present study, P sorption increased with decreasing pH (Udo, 1981; Uzoho and Oti, 2005) and decreases with increasing soil pH (Naidu et al., 1990).

The increase in P sorption and EPR with decreasing soil pH and the decrease in P sorption and EPR with increasing soil pH may be attributed to the amphoteric behaviour of soil colloids in such soils. The Oxisols usually contain hydrous metal oxides which like organic materials, have ionisable functional groups at their surfaces. Surface charge can develop as a result of the dissociation of these functional groups. Proton exchange reactions for surface functional groups of metal oxide minerals may be illustrated as follows:

$$\equiv]OH_2^+ \rightleftharpoons \equiv]OH^O + H^+$$
$$\equiv]OH^O \rightleftharpoons \equiv]O^- + H^+$$
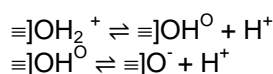
where $\equiv]OH^O$ is a surface-binding site and $\equiv]OH_2^+$ and $\equiv]O$ are proton-exchange surface complexes. The charge at the surface is a unction of the pH of the surrounding water. Neutral or alkaline pH conditions generally will result in a net negatively charged surface while under acidic conditions, excess protons generally are retained at the surface yielding a net positively charged surface as follows:

$$\equiv]OH_2^+ \quad \rightleftharpoons \quad \equiv]OHO \quad \rightleftharpoons \quad \equiv]O^-$$
(low pH) (high pH)

It is the net increase in positive charge on the surfaces with decreasing soil pH that results in the increase in P sorption, while the decrease in P sorption with increasing soil pH may be attributed to the colloidal surfaces becoming increasingly negative charge with increasing soil pH, resulting in greater coulombic (electrostatic) repulsion and decreased P sorption (Bowden et al., 1980; Haynes, 1982). The increase in the reactive colloidal surfaces with decreasing soil pH will require more P to

Table 3. Regression of sorption maxima with exchangeable aluminium, OM and soil pH.

Variable (x)	Functions best fitting data	R^2
Exchangeable aluminium	$Y = 307.66 + 12.88\ Al_{ex}$	87.6
Organic matter	$Y = 417.9 - 46.15\ OM$	68.8
pH (water)	$Y = 914 - 112.3\ pH$	50.8

satisfy the colloidal surface and this may explain the observed EPR values observed in soils that had been subjected to CT.

Soil organic matter

Besides electrostatic repulsion between the increasingly negative surface charge with increasing soil pH as a factor contributing to the observed decrease in P affinity, P sorption and external P requirement, the implication of soil organic matter contents in P sorption and external P requirement cannot be ruled out. As a consequence of the non-export of crop residues from the land under CR and NT, the soils under these treatments had high organic matter contents (Table 1). The P sorption affinity, P adsorption maxima and EPR values were much lower in these soils than in the soils under CT. The low biodegradation of these high contents of organic matter may have, as some of its products, humic substances such as organic acid anions such as citrate and tartarate whose concentrations in the rhizosphere may reach a level high enough to enable them compete strongly with phosphate anions for adsorption sites on reactive surfaces of solid constituents such as oxides of Fe and Al (Holford and Mattingly, 1975). Polyanionic organic complexants can also complex reactive surfaces of solid constituents such as oxides of Fe and Al.

The concentrations of organic acids in the soil solution are usually low (10^{-3} to 4×10^{-4} mol dm^{-3}), but greater amounts are found in the rhizosphere of crop plants (Vance et al., 1996). It has been observed that the organic acids (the tri-carboxylic and di-carboxylic acids) that most commonly occur in soils are effective in reducing phosphate sorption, whereas monocarboxylic acids have little effect on phosphate sorption (Hingston et al., 1971; Earl et al., 1979; Yuan, 1980; Sibanda and Young, 1986; Violante et al., 1991, 1996). These properties of organic acids that occur in soils may explain the observed lower S_{max} values.

Exchangeable aluminium

The data given in Table 1 show that exchangeable aluminium (Al_{ex}) contents in the soil subjected to CR and NT were less than half of the Al_{ex} contents of the soil that was under CT. The sorption maxima increased linearly with increasing exchangeable Al contents which accounted for about 88% of the total variations in sorption maxima (Table 3). These findings are consistent with previous observations (Udo, 1981; Bubba et al., 2003).

The significance of the inclusion of the soil variables organic matter (OM) and pH in equation after sorption maxima was regressed on exchangeable Al (Al_{ex}):

$$Y = 307.66 + 12.88\ Al_{ex}\quad (R^2 = 876) \tag{4}$$

was tested and the following linear regression equation was obtained:

$$S_{max} = 609.0 + 5.76\ Al_{ex} - 18.45 OM - 50.6 pH\ (R^2 = 970) \tag{5}$$

The increase in the coefficient of determination ($\Delta R^2 = 106$) brought about by the inclusion of OM and pH in Equation 1 was statistically significant ($P \leq 0.05$), and the combined effects of Al_{ex}, OM and pH accounted for 97% of the total variation in sorption maxima. These findings are consistent with previous observations (Gichangi et al., 2008; Agbenin, 2003; Henry and Smith, 2002; Duffera and Robarge, 1999).

Conclusion

The results confirm that soil disturbance by conventional tillage (CT) leads to a decrease in soil organic matter contents, and to an increase in soil exchangeable aluminium (Al_{ex}), P sorption affinity (b), soil P adsorption maxima (S_{max}) and soil external P requirements (EPR). The decrease in soil organic matter contents on soils subjected to CT suggests that continued conventional tillage can impact adversely on soil quality. The increased contents of organic matter in soils under no-tillage confirm that not only maintenance of an improved soil health, but also reduction in emissions of CO_2 into the atmosphere can be achieved if the soil is not disturbed. The decrease in EPR of the soils under crop rotation (CR) and no-tillage (NT) treatments suggests that, of the three treatments used in the present study, P will be bioavailable more in soils that have been subjected to either CR or NT than in soils under CT. These results show that, because of their higher sorption capacity, soils under conventional tillage require more external P compared to the other two. This further suggests the need for the promotion of soil cropping under CR or NT

rather than CT for use by resource-poor smallholder farmers in order for them to get good value from their investment in the purchase of the small quantities of phosphatic fertilisers they apply for crop production.

Conflict of Interests

The authors have not declared any conflict of interests.

ACKNOWLEDGEMENTS

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Full Length Research Paper

Liming and selenium application impact on plant available selenium in selected soils of Malawi

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Selenium (Se) is an essential micronutrient for humans and other animals. Its deficiency in food can cause cancer, cardiovascular and other diseases in humans. In high concentrations, Se is toxic for humans, animals and plants. The bioavailability of Se in soils largely determines the Se level in food, feed and therefore throughout the nutrition chain. Selenium content in soils is highly variable. The objective of this study was to quantify effects of applying Se to limed and unlimed soils using soils that were inherently deficient in Se. Application rates ranging from 0 to 10 g ha^{-1} did not increase available soil Se beyond the level of 0.121 mg Se kg^{-1} obtained after lime had been added at the rate of 5 t ha^{-1}. The differences in extractable Se due to combined Se and lime applications were statistically significant (P <0.05). This study has reinforced the need to avoid soil management practices that increase available soil Se to levels that are potentially toxic to humans, animals and plants.

Key words: Soil acidity, liming effects, extractable selenium, adsorption, toxicity.

INTRODUCTION

Selenium is an essential trace element to humans and other animals. In animals, selenium is a component of glutathione peroxidase, which detoxifies peroxides as well as superoxide and hydroxide free-radicals, preventing damage to tissues, especially cell membranes (Spallholz, 2001; Rayman, 2000). This trace element therefore complements the function of vitamin E and has other functions, including participation in the mitochondrial electron transport system in muscles. The adult oral mean daily intake (MDI) for Se from food and water combined is 35 µg day^{-1} (Environment Agency, 2009d), which is equivalent to 0.5 µg g^{-1} body weight (bw) day^{-1} for a 70 kg adult. For 20 kg child (aged six) who ingests 74% of the adult dietary intake (Environment Agency, 2009c), the estimated daily oral intake would be 1.3 µg g^{-1} bw day^{-1}. In Malawi, selenium intake is low (20 to 30 µg Se per day), compared with 50 to 70 µg Se per person recommended in most countries as dietary reference intake (DRI) (Chilimba et al., 2011).

Selenium deficiency has been linked to cancer and cardiovascular diseases in humans (Spallholz, 2001; Rayman, 2000) and to Keshan disease and Kaschin-

Beck disease (Fordyce et al., 2000b; Lyons et al., 2003). Keshan disease is named after the Chinese province where it was first described. It occurs mainly in children and women of child-bearing age, and impairs cardiac functioning (Ge and Yang, 1993). Kaschin-Beck disease is an osteoarthropathy that causes deformity of affected joints (Fordyce et al., 2000b; Lyons et al., 2003). Selenium toxicity (selenosis), which results in hair and nail loss and nervous system disorders in the human population, has also been recorded (Yang et al., 1983). An increased interest in Se contents of human diets stems from observations that marginal intakes of Se can have adverse health effects, that low dietary intakes of Se have been associated with the HIV/AIDS epidemic (Rayman, 2000, 2002; Kupka et al., 2004), that suboptimal intakes of Se have been associated with, *inter alia*, increased cancer mortality and reduced immuno-competence, and that the low HIV/AIDS incidence in Senegal is associated with the relatively high Se contents of soils of that country (Foster, 2003).

Selenium contents in soils are highly variable, but they most frequently range from 0.05 to 0.5 mg kg^{-1} (Kabata-Pendias and Mukherjee, 2007) with 0.4 mg kg^{-1} as a world mean concentration (Fordyce, 2005). The six naturally occurring stable isotopes of Se are 74Se, 76Se, 77Se, 78Se, 80Se and 82Se with approximate abundances of 0.87, 9.02, 7.58, 23.52, 49.82, and 9.19% respectively (Hoffman and King, 1997). Depending upon the physical and chemical properties of the soils, Se can exist in four oxidation states as selenide–II (Se^{2-}, HSe^-, H_2Se_{aq}), elemental selenium-0 (S^0), selenites-IV (SeO_3^{2-}, $HSeO^{3-}$, H_2SeO_3aq) and selenates-VI (SeO_4^{2-}, $HSeO_4^-$, H_2SeO_4aq) in inorganic compounds and organic Se (Selenomethionine, Selenocysteine) in organic compounds. In wet, acidic, or humus-rich soils, elemental Se and the insoluble reduced forms of Se (H_2Se and HSe^-) predominate, thus restricting the mobility and bioavailability of Se.

On the basis of equilibrium reactions and constants they have developed for 83 Se minerals and solution species, Elrashidi et al. (1987) have defined Se solubility in soils. They have observed that the redox potential of soils, as defined by pe + pH (that is, the sum of the negative logarithm to base 10 of electron (pe) and the negative logarithm to base 10 of hydrogen ion in soil solution (pH)) generally controls selenium speciation in solution. On the basis of their observations, these workers have suggested that soils may be classified into three categories: (1) arid regions with high redox (pe + pH >15.0) where selenate is most common; (2) humid regions with medium redox range (pe + pH =7.5 to 15.0) where depending on pH, either selenite or biselenite ($HSeO_3^{1-}$) predominate; and (3) gley soils or wetlands with a low redox (pe + pH <7.5), where monohydrogen selenide (HSe^{1-}) is the major solution species (Elrashidi et al., 1987, 1989). It has further been noted that only in

acid soils do H_2Se species contribute significantly to selenium in solution.

Between pH 4 and 8, selenium solubility is governed by adsorption (Mayland et al., 1991). Selanates bond only weakly to oxides and other minerals, and the bonding strength increases with increasing acidity (Goldberg, 2014). Selanates are the dominant form of Se occurring in alkaline, oxidized soils while the selenite species (HSeO3- and SeO_3^{2-}) are dominant in suboxic or mildly oxidizing soils, and in oxygenated, acidic (pH < 6) soils with low redox potential (Eich-Greatorex et al., 2007). Selenite species are less mobile than selanates in such acidic soils. In acid soils, the negatively charged selenite (SeO_3^{2-}) ions, with two nucleophilic centres and the potential to act as a bidentate ligand, may have a great affinity for the positively charged soil surfaces that develop at low soil pH in the highly weathered soils that display variable-charge characteristics.

Selenium is adsorbed on the soil colloids by ligand exchange. Such an exchange results when an inner-sphere metal–O–Se covalent bond is formed by replacement of hydroxyls on the edges of layer silicate clays and the surfaces of insoluble oxides of Al, Fe, and/or Mn, such chemisorption induces the Se to be nonlabile. Increasing soil pH through liming therefore causes a gradual decrease in Se adsorption, hence making Se readily available for plant uptake. Large application of selenium in form of sodium selenate which is less adsorbed to soil minerals may be lost from the soil through direct leaching, biological and non-biological reduction to selenite and subsequent sorption (Mayland et al., 1991); hence, inefficient utilization of applied selenium by plants. Bioavailability of Se in soils is a function of sorption and desorption of Se. Both sorption and desorption of Se are, in turn, determined mainly by the soil pH, redox potential, microbial activity, mineralogy, soil organic matter, and other anions such as phosphate, sulphate, oxalate, and molybdate for adsorption sites (Dhillon and Dhillon, 2000; Goh and Lim, 2004). Selenite is sorbed more strongly than selenate onto clays, but not as strongly as phosphate or fluoride (Barrow and Whelan, 1989). Sorption of both selenite and selenate decreases with increasing pH.

As indicated earlier in this introduction, the daily Se intake (20 to 30 µg Se per day) in Malawi in Malawi is low when compared with 50 to 70 µg Se per person recommended in most countries as dietary reference intake (DRI) (Chilimba *op. cit.*). This suggests that Malawians are exposed to potential risks of cancer and cardiovascular diseases among others due to their daily low Se intake. Since it is from the soils that most of the Se is transferred to humans by plants, interest in establishing the bioavailability of soil Se has increased since the essentiality of Se to humans had been established during the 1950s. This interest has been underpinned by the knowledge that Se is toxic to humans

at high doses and that the range between deficiency levels (<11 μg g^{-1} day^{-1}) and toxic levels (>900 μg g^{-1} day^{-1}) in susceptible people is very narrow (Yang and Xia, 1995). Soils in Malawi are generally acidic in their reaction and need for liming the soils has increased with time. There is, however, sparse knowledge about the Se status of the Malawi soils and the extent to which liming effects affect the mobility and therefore bioavailability of Se in the soils. The present investigations were conducted to enhance this knowledge.

MATERIALS AND METHODS

Description of the study site

The study was carried out on Mpherero Estate, one of the sites where the Clinton Development Initiative (CDI) was multiplying seed for Malawian farmers under the Alliance for Green Revolution in Africa (AGRA) project. Mpherero Estate is in Mchinji district (Latitude: 13° 46' 19" S Longitude: 33° 00' 03" E), about 150 km from Lilongwe University of Agriculture and Natural Resources, to the west of Malawi's Capital city, Lilongwe. The site topographically lies between 1200 and 1829 m above sea level and has two distinct terrains: the hilly western part, comprising the Mchinji Mountain ranges with gentle slopes where almost all rivers found in the district originate from and the rest of the district lying within a plain of mostly arable land that is generally drained by water ways and there are some *dambos* which are permanently or seasonally inundated wetlands characterized by grasses, rushes and sedges, contrasting with surrounding woodland such as Miombo *(Brachystegia)* woodland.

Mchinji experiences annually mean temperatures ranging from 17 to 20°C. Lowest temperatures are experienced in June while high temperatures are experienced during the months of October and November. The district receives average rainfall of between 800 and 1230 mm per annum with the wet rainy season running from November to April (Mchinji District Assembly, 2008).

Cropping history

The site topographically lies between 1200 and 1829 m above sea level and has two distinct terrains: the hilly western part, comprising the Mchinji Mountain ranges with gentle slopes where almost all rivers found in the district originate from, and the rest of the district lying within a plain of mostly arable land that is generally drained by water ways and there are some *dambos* which are permanently or seasonally inundated wetlands characterized by grasses, rushes and sedges, contrasting with surrounding woodland such as Miombo *(Brachystegia)* woodland. The experimental site is an area where the Anchor Farm Project, which is a Clinton Development Initiative (CDI)-operated commercial farm, was conducted. The CDI-sponsored project partners with thousands of neighbouring smallholder farmers and provides them with access to quality inputs for maize and soy production, as well as training and market access.

Farmers in the project have access to improved soy seed and to training in advanced agronomic techniques. The farm manager of the commercial farm observed that crop yields were far below 2 t ha^{-1} and that a plant locally known as "Nzobwe" (*Terminalia superb*), which is an indicator of acid soils (Bolan et al., 1988), was thriving well on this site. After incorporating dolomitic limestone into the soil at a rate of 2 t ha^{-1} and Super D (10.5 N + 24 P$_2$O$_5$ + 20 K$_2$O + (6 S and 0.15 B) at the rate of 300 kg ha^{-1}), the farm manager observed that the crop yield increased significantly to an average of 2.9 t ha^{-1} of soybean seed from an average of 1.5 t ha^{-1}

that was obtained from the plots that had not been limed (Ngwira, 2011). It was, however, impossible to conclude on whether the 2 t ha^{-1} of lime that was applied represented the maximum rate of dolomitic lime required to improve indices of chemical soil fertility to optimum yield of the soybean seed at the site.

Soil sampling and incubation

Top (0 to 0.15 m) soil samples were randomly collected from 20 spots and mixed together to form a composite sample weighing 1,000 kg. The composite soil samples were air dried at room temperature (25 ± 2°C) and sieved to pass through a 2 mm sieve mesh. The sieved samples were used for the incubation experiment that was conducted at Chitedze Agricultural Research Station. The incubation experiment entailed mixing thoroughly 24 kg of the sieved soils with three levels (0, 5, and 10 g Se ha^{-1}) of sodium selenate and five levels (0, 2.5, 5.0, 7.5, and 10 t ha^{-1}) of dolomitic limestone and placing the mixture in 25-L plastic pots. The experiment was replicated three times and the treatments were arranged in a randomized complete block design and conducted in a micro-environment climate in a glasshouse at Chitedze Agricultural Research Station.

The soils were then incubated at 30°C for 30 days. Before incubation started, water was added to the pots to reach field capacity and throughout the incubation process the pots were kept at field capacity. After 30 days of incubation, soil samples were taken and analysed. Sodium selenate (Na$_2$SeO$_4$) was then applied to the incubated soils at top dressing as per treatments and the soils were crop to maize (*Zea mays*). After maize harvest, aliquots of the soils were taken after maize harvest, and were analysed for selenium.

Characterisation of physical and chemical properties of the soils

After the sieved soil samples were incubated for 30 days, aliquots of the soils were taken and analysed to assess liming effects on soil chemical properties after the incubation period. The soils were analysed for pH in a 1:2.5 soil to water slurry using a pH electrode as outlined by described by Blakemore et al. (1987), particle size distribution using the Bouyoucos hydrometer method (Day, 1965) as described by Anderson and Ingram (1993). The organic carbon contents of the soils were determined by the potassium dichromate (K$_2$Cr$_2$O$_7$) oxidation method of Walkley and Black (1934) as described by Anderson and Ingram (1993). Organic matter was estimated by multiplying the total soil organic carbon with 1.724.

Total nitrogen was determined using the Kjeldhal wet oxidation process as described by Anderson and Ingram (1993), while available phosphorus was extracted by the Mehlich 3 method (Mehlich, 1984) and P in the clear extracts was determined colorimetrically by the ascorbic acid method (Murphy and Riley, 1962) on a Perkin Elmer Lambda 25 UV/VIS spectrometer. The extract obtained by the Mehlich 3 method (Mehlich, 1984) was used for the determination of K by flame emission photometry at a wavelength of 766.5 nm, and of both Ca and Mg using Atomic Absorbance Spectrophotometer model 6200 at a wave length of 422.7 and 285.2 nm, respectively (Anderson and Ingram, 1993).

Determination of extractable soil selenium

Aliquots of the soils, 30 days after they had been incubated and then after the soils were cropped to maize, were taken for extractable Se determinations. The extracting solution used in this study was prepared by mixing 1.97 g of diethylene triamine pentaacetic acid (DTPA), 1.47 g of CaCl$_2$.2H$_2$O and 14.2 g of

Table 1. Effects of liming on some soil chemical properties after 30-day incubation period.

Lime rate	Organic matter	N	pH$_{KCl}$	pH$_{H2O}$	P	Ca	Mg	K
	g kg^{-1}				mg kg^{-1}	cmol$_c$ kg^{-1}		
0.0	1.92	0.10	4.84[d]	5.26[d]	52.5[b]	1.7[c]	0.4[c]	0.25
2.5	1.88	0.09	5.87[c]	6.13[c]	52.5[b]	2.3[cb]	0.6[bc]	0.21
5.0	1.86	0.09	5.98[c]	6.23[c]	57.4b[a]	2.6[b]	0.7[b]	0.22
7.5	1.93	0.10	6.18[b]	6.61[b]	58.1[a]	2.8[ab]	0.8[b]	0.20
10	1.73	0.09	6.37[a]	6.78[a]	57.5b[a]	3.4[a]	1.1[a]	0.19
F pr.	0.36[ns]	0.41[ns]	<0.001**	<0.001**	0.007*	<0.001**	<0.001**	0.083[ns]
LSD	0.21	0.01	0.16	0.12	4.0	0.6	0.2	0.04
CV (%)	1.2	1.2	2.9	2.0	7.5	2.4	3.3	2.18

**Highly significant, *Significant, ns: not significant, means with different subscripts along a column are significantly different.

triethylamine (TEA) as described by Jump and Sabey (1989). An aliquot of 40 ml of extracting solution was added to 5 g of air dried, 2-mm sieved soil in a plastic shaking bottle and covered tightly to avoid leakages. The bottles were then shaken for 2 h on a reciprocal shaker. After shaking, the suspension was filtered into clean plastic bottles. The filtrates were then packed for selenium concentration determination using Atomic Absorption Spectrometer.

Statistical analysis

Data collected from the experiment were subjected to statistical analysis using Genstat statistical software 14th edition. The differences between and within treatments were analysed using analysis of variance (ANOVA) at 0.05 probability level and Fisher's least significant difference (LSD) was used to separate means.

RESULTS AND DISCUSSION

Liming effects on soil properties after 30 days of incubation

The data summarized in Table 1 show that the incubation of the limed soils for 30 days had significant effects on soil reaction and the levels of exchangeable Mg, Ca and Al. Soil acidity decreased significantly with increasing rates of lime application while exchangeable Mg and Ca increased, as expected, with increasing rate of dolomitic lime application. It has been observed that selenium (Se) deficiency occurs when this element is not readily available for plant uptake (Fordyce et al., 1998, 2007). The bioavailability of Se is a function of the effective concentration of Se in the soil solution. The effective concentration of Se in soil solution is determined by soil properties including soil pH, organic matter, soil texture, redox potential, the speciation of the element, and the presence of other ions in soil solution.

The addition of dolomitic limestone to the soils resulted in exchangeable Ca to be higher than exchangeable Mg, and this may be ascribed to the fact that selectivity of the colloidal negative sites is higher for Ca than for Mg (Meda et al., 2002). The differences in exchangeable K due to liming effects were not statistically significant (Table 1).

This is consistent with results of Mandala et al. (2004). Research has shown that liming increases non-exchangeable K contents due to precipitation of hydroxyl aluminium and hydroxyl iron polymers by blockage that could cause difficulties in the release of K from initially non exchangeable position (Das and Saha, 2013).

Liming also decreases soil exchangeable K, which has been attributed to the conversion of exchangeable K into non-exchangeable form or to enhanced power of the soil colloids to adsorb K from the soil solution (Uexkull, 1986). The effect of cations such as Mg^{2+}, Ca^{2+} and K$^+$ on the effective concentration of any of the Se species in soil solution is not yet well known but anions such as phosphate and sulphate affect the bioavailability of Se through their competition with Se for adsorption on the surface of soil colloids.

In the present investigations, extractable (available) P increased with increasing rate of lime application and the difference between the P value extracted from the unlimed soil and the P extracted after 7.5 t ha^{-1} dolomitic limestone was incorporated into the soil was statistically significant at the 5% probability level. Phosphate ions in the soil solution readily adsorb on the sorptive surface of soil colloidal particles thus decreasing the sorption of Se on the soil surface and increasing the bioavailability of Se. It has also been observed that increased phosphate concentration dilutes the Se content of plants by inducing increased plant growth (Jacobs, 1989; Mayland, 1994; Neal, 1995). The increase in P bioavailability due to liming effects is in accord with past findings (Rechcigl, 1995; Sime, 2001).

This study showed that the Malawi soils were low in extractable Se, suggesting that the utilisation of Se by microorganisms degrading the soil organic matter would have decreased the extractable Se status of the soils. The differences in organic matter contents due to liming effects observed in the present study were not, however, statistically significant (Table 1). The bioavailability of Se in soils is influenced by soil organic matter contents through the biodegradation of organically bound Se, which results in the release of inorganic Se. It has,

Table 2. Effect of liming and selenium application on exchangeable Al contents (mg kg $^{-1}$) of soil samples after maize harvest.

Lime rate (t/ha)	Selenium (g ha^{-1})			Mean
	0.0	5.0	10.0	
0.0	1.03	0.70	0.90	0.88[b]
2.5	0.93	0.40	0.63	0.66[ab]
5.0	0.60	0.60	0.60	0.60[ab]
7.5	0.70	0.53	0.50	0.58[ab]
10.0	0.47	0.37	0.50	0.44[a]
Mean	0.75	0.52	0.63	0.63
F-Prob				
Lime	0.05*			
Selenium	0.11[ns]			
Lime*Selenium	0.86[ns]			
s.e.d (Lime)	0.1342			
CV(%)	45.1			

*Significant, ns: not significant, means with different subscripts along a column are significantly different.

however, been observed that microorganisms are capable of transforming the absorbed selenite into organic compounds (Doran, 1982), thus rendering the immobilised Se to be unavailable.

The differences in total N contents due to liming effects were not statistically significant. Liming soils with variable charge decreases the positive surface charges of these soils, causing electrostatic repulsion between the negatively charged soil surfaces and NO_3^- ions and resulting in an increase in the leaching of the nitrate (Bolan et al., 2003).

Effect of liming on exchangeable aluminium

Effects of liming materials on exchangeable aluminium (Al) after 30-days of incubation are presented in Table 4. After the 30-day incubation period, the differences in exchangeable Al contents of the soils were not significantly different. This suggests that the 30-day period of soil incubation was not long enough for the liming materials to effectively affect exchangeable Al contents of the soils. However, the liming effects as observed from the differences in exchangeable Al contents of soils that had been cropped to maize after they had been subjected to the 30-day period of incubation were statistically significant (Table 2).

Mean concentrations of exchangeable aluminium were reduced from 0.88 mg kg^{-1} in unlimed soil to 0.44 mg kg^{-1} in the soil to which lime added at the rate of 10 t ha^{-1}. As soil pH increases due to liming, the aluminol groups may deprotonate, thus:

$$>Al—OH_2]^{+\frac{1}{2}} + OH^- = >Al—OH]^{-\frac{1}{2}},$$
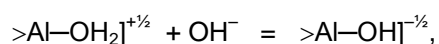
leaving negatively charged OH$^-$ ions in place of the OH$_2$ groups. The hydroxyl ions then react with Al in the solution to precipitate as aluminium hydroxide which over time may crystallize into gibbsite. The formation of insoluble aluminium hydroxide is favoured by pH between 5.0 and 7.5 (MacLean et al., 1972).

As noted earlier in this paper, Oxisols and Ultisols, such as those used in this study, contain minerals that include the crystalline and non-crystalline oxides and hydrous oxides of iron, aluminium, titanium and manganese, and kaolinite whose amphoteric surfaces have the charge density and sign of the surface charge that are pH-dependent. The crystalline and non-crystalline oxides and hydrous oxides of silicon, iron and aluminium have been observed to develop very high surface charge densities (Tardos and Lyhlema, 1969) that can sorb anions such as SeO_3^{2-}, $HSeO^{3-}$, SeO_4^{2-}, $HSeO_4^-$, SO_4^{2-}, $H_2PO_4^-$ and HPO_4^{2-} available in soil solutions.

Effect of liming on selenium availability after 30 days of incubation

The results obtained from the present study show that the differences in Se concentration due to liming effects after the soils had been subjected to a 30-day incubation period were not statistically significant (Tables 3). This observation may be attributed not only to the level of liming materials used in this investigation but also to the type of minerals contained in, and therefore the physical and chemical properties of, the soils used in this study.

As noted earlier in this paper, Oxisols and Ultisols such

Table 3. Effect of liming on Se availability in soils after 30 days of incubation.

Lime level (t ha^{-1})	Se Mean values ±SE (mg kg^{-1})
0	0.047±0.02
2.5	0.070±0.03
5.0	0.029±0.01
7.5	0.031±0.01
10.0	0.042±0.01
LSD$_{(0.05)}$	0.052
CV(%)	26.4

Table 4. Effect of liming and Se application on soil extractable Se (mg kg^{-1}) after the soils had been cropped.

Lime rate (t/ha)	Selenium (g ha^{-1})			Mean
	0.0	5.0	10.0	
0.0	0.09	0.12	0.04	0.08^b
2.5	0.14	0.21	0.16	0.17^b
5.0	0.15	0.82	0.32	0.43^a
7.5	0.11	0.22	0.17	0.17^b
10.0	0.11	0.21	0.17	0.16^b
Mean	0.12^b	0.32^a	0.17^b	0.20
	F pr.	**L.S.D.**		
Lime	0.01*	0.18		
Selenium	0.04*	0.14		
Lime×Selenium	0.16^{ns}	0.32		
CV (%)	21.7	-		

*Significant at 5% probability level, ns: not significant, means with different subscripts along a column are significantly different.

as those used in the present investigations contain minerals that include the crystalline and non-crystalline oxides and hydrous oxides of iron, aluminium, titanium and manganese, and kaolinite whose amphoteric surfaces have the charge density and sign of the surface charge that are pH-dependent. In such soils, applied liming materials are consumed to develop surface charge, requiring an inordinate quantity of lime to raise soil pH from an initial value near 5 to a final value of 7. This may explain why the pH_{H_2O} of the soils used in the present investigations increased from 5.1 for the unlimed soil to only 6.8 for the soil to which the liming material was applied at the rate of 10 t ha^{-1} and incubated for 30 days. These soil pH values indicate that the soils were still acidic in their reaction, and suggest that their surfaces were able to sorb the Se ions. After the incubated soils had been cropped, however, the extractable inherent Se contents of the soils (that is, the soils to which no Se was added) increased with increasing lime application from 0.09 mg kg^{-1} of the soil to which both Se and liming materials were not added to

0.15 mg kg^{-1} of the soil to which no Se was added but to which 5 t ha^{-1} of lime was added (Table 4 and Figure 1).

The extractable inherent Se contents of the soils, however, decreased with increasing lime application beyond the amount of 5 t of lime ha^{-1} which was applied (Table 4 and Figure 1). The extractable Se from the unlimed soils increased from 0.087 mg Se kg^{-1} of the soil to which no Se was added to 0.121 mg Se kg^{-1} of the soil to which 5 g ha^{-1} was added and then decreased after 10 g ha^{-1} was added. These results appear to be consistent with the findings of Chilimba (2011), which showed an increase in Se availability after an amount of 5 g Se ha^{-1} was applied.

It was, however, observed that extractable Se contents were highest (0.815 mg Se kg^{-1}) in soils to which both Se and liming materials were added at g ha^{-1} and 5 t ha^{-1}, respectively. The differences in extractable Se due to Se additions and liming effects were statistically significant ($P<0.05$) but the interaction between Se application and liming was not significant (Table 4).

The extractable Se value of 0.815 mg Se kg^{-1} is more
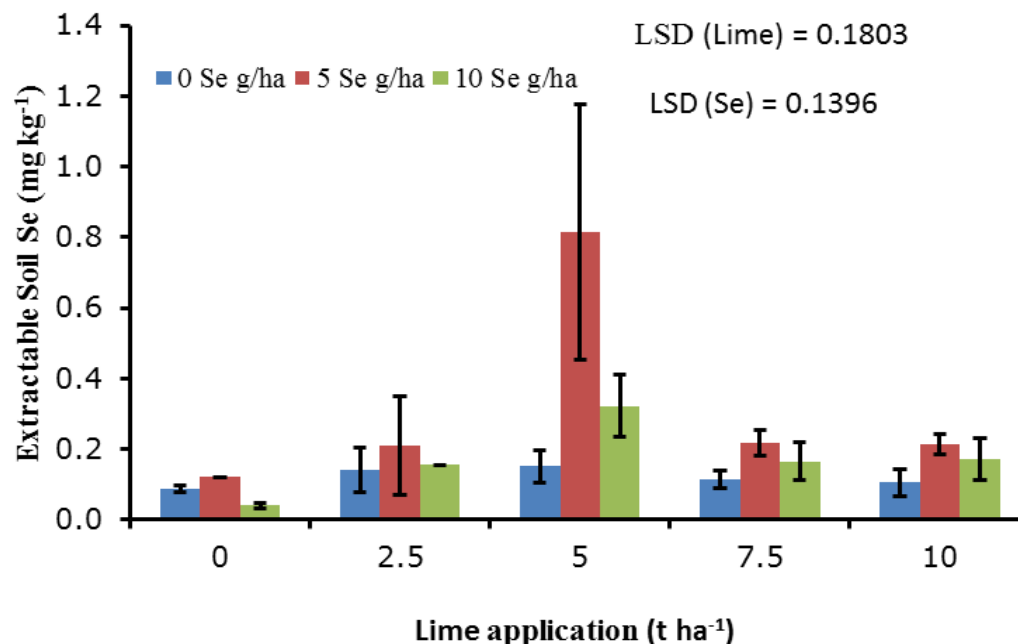
Figure 1. Effect of lime application and Se application on soil Se concentration (mg kg^{-1}).

than double of the world mean concentration of Se (0.4mg Se kg^{-1}) in soils is (Fordyce, 2005). Since the extractable Se vale of 0.087 g ha^{-1}) obtained from the soil to which both no Se and no liming materials were less than 0.127 mg kg^{-1}, the soils used in the present study can be said to be low in extractable Se (Broadley et al., 2006), while any of the soils that had extractable Se greater than 3 mg kg^{-1} can be said to have excess Se concentrations (Broadley et al., 2006)

Conclusion

Increasing additions of Se in the form of sodium selenate to the unlimed soils at rates ranging from 0 to 10 g ha^{-1} did not result in increasing extractable Se level beyond the 0.121 mg Se kg^{-1} obtained after adding the recommended 5 g ha^{-1}, thus suggesting that the increase in soil pH resulted in more of the Se added to these acid soils to be chemisorbed and therefore to become nonlabile. Addition of Se fertiliser to highly weathered, acid soils may not lead to an increase in Se bioavailability if the soils are overlimed. Comparative investigations are needed to establish the soil pH level at which Se a specific crop such as maize obtains optimal benefits from Se fertilisers. There is also need to establish the benefits that may accrue from adding Se fertiliser to soil relative to applying Se direct to crops.

Conflict of Interests

The authors have not declared any conflict of interests.

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