academic Journals

Vol. 7(8), pp. 115-122, August, 2016 DOI: 10.5897/JSSEM2016.0551 Articles Number: 2752EC959789 ISSN 2141-2391 Copyright ©2016 Author(s) retain the copyright of this article http://www.academicjournals.org/JSSEM

Journal of Soil Science and Environmental Management

Full Length Research Paper

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

B. Masanza¹, J. H. A. Maida^{2*}, A. D. C. Chilimba³, M. W. Lowole² and P. C. Nalivata²

¹National food Reserve Agency, Private Bag B450, Lilongwe, Malawi.

²Lilongwe University of Agriculture and Natural Resources, Bunda Campus, P. O. Box 219, Lilongwe, Malawi. ³Lunyangwa Agricultural Research Station, P. O. Box 59, Mzuzu, Malawi.

Received 19 January 2016, Accepted 22 February 2016

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 functions, other 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 μ g 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 μ g g⁻¹ bw day⁻¹. In Malawi, selenium intake is low (20 to 30 μ g Se per day), compared with 50 to 70 μ g 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-

*Corresponding author. E-mail: jhamaida@africa-online.net.

Author(s) agree that this article remain permanently open access under the terms of the <u>Creative Commons Attribution</u> License 4.0 International License 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 immunocompetence, 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[–], H₂Se_{aq}), elemental selenium-0 (S⁰), selenites-IV (SeO₃^{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 (HSe¹⁻) 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 innersphere metal-O-Se covalent bond is formed by replacement of hydroxyls on the edges of layer silicate clavs 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 μ g Se per day) in Malawi in Malawi is low when compared with 50 to 70 μ g 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 μ g g⁻¹ day⁻¹) and toxic levels (>900 μ g 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 P₂O₅ + 20 K₂O + (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 $(25 \pm 2^{\circ}C)$ 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_2SeO_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 (K₂Cr₂O₇) 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 CaCl₂.2H₂O and 14.2 g of

Lime rate	Organic matter	Ν			Р	Ca	Mg	κ
	g kg ⁻¹		- pH _{κci}	рН _{Н2О}	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

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

**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 nonexchangeable 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 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,

Lime rate (t/he)	Se	Maan			
Lime rate (t/ha) -	0.0 5.0		10.0	Mean	
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				

Table 2. Effect of liming and selenium application on exchangeable AI contents (mg kg⁻¹) of soil samples after maize harvest.

*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 NO₃⁻ 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 (AI) 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 AI contents of the soils. However, the liming effects as observed from the differences in exchangeable AI 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 ir ١V deprotor

 $>AI-OH_2]^{+\frac{1}{2}} + OH^- = >AI-OH_1^{-\frac{1}{2}},$

leaving negatively charged OH⁻ ions in place of the OH₂ 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 noncrystalline 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

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

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

Lime rete (t/he)		Mean		
Lime rate (t/ha) —	0.0	5.0	10.0	wean
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		
LimexSelenium	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 $pH_{\!_{H,O}}$ 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

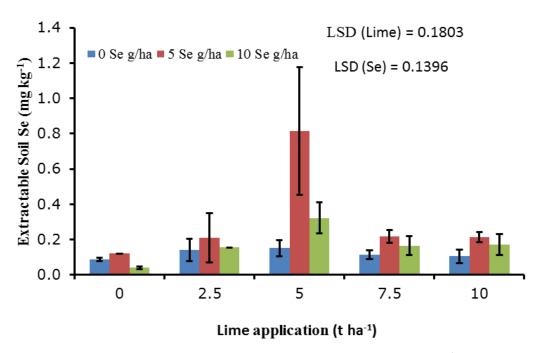


Figure 1. Effect of lime application and Se application on soil Se concentration (mg kg⁻¹).

than double of the world mean concentration of Se $(0.4 \text{mg Se kg}^{-1})$ 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.

ACKNOWLEDGEMENTS

The senior author gratefully acknowledges the financial support from the Alliance for Green Revolution in Africa (AGRA) which made it possible for her to undertake the postgraduate training programme that lead to an award of a Master of Science (MSc) degree in soil science. The authors are also grateful to Mr. Austin Ngwira, Director of the Clinton Development Initiative (CDI) Anchor Farm Business Development Project, for his permission to have soil samples for the present study collected from one of the CDI-funded farmers' farms in the Mchinji district of Malawi, to Messrs L. K. Chirwa, B. Msukwa and S. Khombe for their assistance during the execution of the laboratory investigations, and to the Head of Chitedze Agricultural Research Station for grating the senior author permission to use the station's facilities for incubation experiments.

REFERENCES

- Anderson JM, Ingram JSI (1993). TSBF: A handbook of methods of analysis. CAB International. Wallingford, UK.
- Barrow NJ, Whelan BR (1989). Testing a mechanistic model VIII. The effects of time and temperature of incubation on the sorption and subsequent desorption of selenite and selenate by a soil. J. Soil Sci. 40:29-37.
- Blakemore LC, Searle PL, Daly BK (1987). Methods for Chemical Analysis of Soils. New Zealand Soil Bureau. Scientific Report 80. P 103.
- Bolan NS, Adriano DC, Curtin D (2003). Soil acidification and liming interactions with nutrient and heavy metal transformation and bioavalability. Adv. Agron. 78:215-272.
- Bolan NS, Syers JK, Tillman RW and Scotter DR (1988). Effect of liming

and phosphate additions on sulphate leaching in soils. J. Soil Sci. 39:493-504.

- Broadley MR, White PJ, Bryson RJ, Meacham MC, Bowen HC, Chilimba ADC (2011). Potential for safe and efficient biofortification of maize crops with selenium in Malawi. PhD Thesis. University of Nottingham, Uk.
- Das R, Saha D (2013). Changes in non-exchangeable K in an acid and corresponding limed soil as affected by addition of nitrogenous and potassic fertilizers. J. Crop Weed 9(1):99-102.
- Day PR (1965). Particle fractionation and particle-size analysis. Methods of Soil Analysis. Part 1. Physical and mineralogical properties, including statistics of measurement and sampling, (methodsofsoilana), pp. 545-567.
- Dhillon SK, Dhillon KS (2000). Selenium adsorption in soils as influenced by different anions. J. Plant Nutr. Soil Sci. 163:577-582.
- Doran JW (1982). Microorganisms and the biological cycling of selenium. In Adv. Microb. Ecol. Springer US. pp. 1-32.
- Eich-Greatorex S, Sogn TA, Øgaard AF, Aasen I (2007). Plant availability of inorganic and organic selenium fertiliser as influenced by soil organic matter content and pH. Nutrient Cycling in Agroecosystems 79(3):221-231.
- Elrashidi MA, Adriano DC, Workman SM, Lindsay WL (1987). Chemical equilibria of selenium in soils: A theoretical development. Soil Sci. 144:141-152.
- Environment Agency (2009c). Human health toxicological assessment of contaminants in soil. Science Report SC050021/SR2. Bristol: Environment Agency.
- Environment Agency (2009d). Contaminants in soil: updated collation of toxicological data and intake values for humans. Selenium. Science Report SC050021/SR TOX10. Bristol: Environment Agency.
- Fordyce F (2005). Selenium deficiency and toxicity in the environment. In: Selinus O, Alloway BJ (Eds.). Essentials of medical geology: Impacts of the natural environment on public health. Academic Press, London, UK pp. 373-415.
- Fordyce F (2007). Selenium geochemistry and health. AMBIO: J. Hum. Environ. 36(1):94-97.
- Fordyce FM, Zhang G, Green K, Liu X (1998). Soil, Grain and Water Chemistry and Human Selenium Imbalances in Enshi District, Hubei Province, China. British Geological Survey Overseas Geology Series Technical Report WC/96/54.
- Fordyce FM, Zhang G, Green K, Liu X (2000b). Soil, Grain and Water Chemistry and Human Selenium Imbalances in Enshi District, Hubei Province, China. Appl. Geochem. 15(I):117-132.
- Foster HD (2003). Why HIV-1 has diffused so much more rapidly in Sub-Saharan Africa than in North America. Med. Hypotheses 60(4):611-614.
- Ge K, Yang G (1993). The epidemiology of selenium deficiency in the etiological study of endemic diseases in China. Am. J. Clin. Nutr. 57:259S-263S.
- Goh K, Lim T (2004). Geochemistry of inorganic arsenic and selenium in a tropical soil: effects of reaction time, pH and competitive anions on arsenic and selenium adsorption. Chemosphere 55:849-859.
- Goldberg S (2014). Macroscopic experimental and modelling evaluation of selenite and selenate adsorption mechanisms on gibbsite. Soil Sci. Soc. Am. J. 78:473-479.
- Hoffman JE, King MG (1997). Selenium and selenium compounds. In: Kroschwitz JI, Howe-Grant MH, (Eds.). Encyclopedia of chemical technology. New York, NY: John Wiley & Sons, pp. 686-719.
- Johnson SE, Hawkesford MJ, McGrath SP, Zhao FJ, Breward N, Harriman M (2006). Biofortification of UK food crops with selenium. Proc. Nutr. Soc. 65(02):169-181.
- Jump RK, Sabey BR (1989). Soil test extractants for predicting selenium in plants. Selenium in Agriculture and the Environment, (seleniuminagric), pp. 95-105.
- Kupka R, Msamanga GI, Spiegelman D, Morris SW, Mugusi F, Hunter DJ, Fawzi WW (2004). Selenium status is associated with accelerated HIV disease progression among HIV-1-infected pregnant women in Tanzania. J. Nutr. 134:2556-2560.

- Lyons G, Stangoulis J, Graham R (2003). Nutriprevention of disease with high selenium wheat. J. Australas. College Nutr. Environ. Med. 22(3):3.
- Maclean AJ, Halstead RL, Finn BJ (1972). Effects of Lime on extractable Aluminium and other soil properties and on Barley and Alfalfa grown in pot tests. Can. J. Soil Sci. 52:427-438.
- Mandala ŴL, Ngwata CE, Chilalire LJ, Lakudzala DD (2004). Effects of fractional liming on soil properties and on yield of Tobacco. Agricultural Research and Extension Trust, Lilongwe, Malawi.
- Mayland HF (1994). Selenium in Plant and Animal Nutrition. In Selenium in the Environment (Frankenberger WT, Benson S Eds.). Marcel-Dekker, New York, pp. 29-47.
- Mayland HF, Gough LP, Stewart KC (1991). Chapter E: Selenium mobility in soils and its absorption, translocation, and metabolism in plants.
- Mchinji District Assembly (2008). Mchinji District socioeconomic profile. Malawi Government Printer, Zomba.
- Meda AR, Pavan MA,Cassiolato ME, Miyazawa M (2002). Dolomite lime's reaction applied on the surface of a sandy soil of the Northwest Parana, Brazil. Braz. Arch. Biol. Technol. 45(2):219-222.
- Mehlich A (1984). Mehlich 3 soil test extractant: a modification of Mehlich 2 extract. Commun. Soil Sci. Plant Anal. 15(12):1409-1416
- Murphy J, Riley JP (1962). A modified single solution method for the determination of phosphate in natural water. Anal. Chem. Acta 27:31-36.
- Neal RH (1995). Selenium. In Heavy Metals in Soils (2nd edn.) (ed. B.J. Halloway). London: Blackie Academic & Professional.
- Ngwira A (2011). An Update on the Clinton Development Initiative (CDI) Anchor Farm Business Development Project, CDI/AGRA/07/2011.
- Rayman MP (2000). Review: The importance of selenium to human health. The Lancet 356:233-241.
- Rayman MP (2002). The argument for increasing selenium intake. Proc. Nutr. Soc. 61:203-215.
- Rechcigl JE (Ed.). (1995). Soil amendments and environmental quality, 2. CRC Press.
- Sime D (2001). Lime: The essential element in New Zealand agriculture . The Northland lime Millers Associaion. New Zealand.
- Spallholz JE (2001). Selenium and the prevention of cancer, Part II: Mechanisms for carcinostatic activity of Se compounds. The bulletin of Selenium and Tellurium, pp. 1-12.
- Tardos THF, Lyhlema J (1969). The Electrical Double Layer on silica in the Presence of Bivalent Counter-Ions. J. Electroanal. Chem. Interfacial Electrochem. 22:1-7.
- Uexkull HRV (1986). Efficient fertilizer use in acid upland soils of the humid tropics. Food and Agriculture Organization of the United Nations, Rome.
- Walkley A, Black CA (1934). An examination of the digestion method for determining soil organic matter and proposed acid titration method. Soil Sci. 37:29-38.
- Yang G, Wang S, Zhou R and Sun S (1983). Endemic selenium intoxication of humans in China. Am. J. Clin. Nutr. 37:872-881.
- Yang G, Xia M (1995). Studies on human dietary requirements and safe range of dietary intakes of selenium in China and their application to the prevention of related endemic diseases. Biomed. Environ. Sci. 8:187-201.