CHAPTER 7

Heavy Metal Uptake by Wheat from Two Sacrificial Biosolids Disposal Soils at Differential Liming Rates

7.1 Abstract

In previous studies it has been shown that intensive liming of sacrificial biosolids disposal soils leads to an increase in many EDTA extractable metals. This aspect is a cause for concern in that many studies have indicated that plant metal levels could be correlated with EDTA extractable metal levels in soil. To determine the influence of intensive liming of sacrificial soils on plant metal content a dedicated trial was conducted. A new bulk sample of the two soils used in the previous studies was collected and incubated with $CaCO_3$ (AR) in pots at lime application rates equivalent to 0, 12, 24, and 36 tons ha^{-1}. Spinach and wheat were planted and harvested before flowering. The spinach plants did not grow in the 0 lime application treatment and grew poorly in the lime treatments and the wheat plants were therefore the only ones analysed for their metal content. The soils from the pots were sampled and analysed for NH_4NO_3 and NH_4EDTA extractable metals. The NH_4NO_3 extractable metals decreased with increasing lime rate whereas the NH_4EDTA extractable metals generally increased, especially in the one soil. Plant metal levels were better correlated with NH_4NO_3 than with NH_4EDTA metal levels. This indicates that liming leads to a decreased risk of plant metal uptake from sacrificial soils and that it should be introduced into the management of these soils. The use of EDTA in guideline metal levels as well as to determine "potentially plant available" metals is discouraged.

7.2 Introduction

In previous chapters it has been shown that intensive liming influenced the extractability of metals in two sacrificial biosolids disposal soils. The NH_4NO_3 extractable fraction decreased after liming during incubation as expected. However, the EDTA extractable metal fraction increased after intensive liming as well as with increasing lime rates of two sacrificial biosolids disposal soils during incubation. The increased extractability was correlated with an increase in extractability of organic matter at increasing lime rates.

This increase leads to concern regarding the desirability of liming of acid sacrificial soils, especially in the light of a number of studies that have reported a correlation between EDTA extractable metals in soils and plant metal content. In this regard Hooda et al. (1997) and Cajuste and Laird (2000) have indicated that EDTA is a reliable test for predicting plant-available metals. Earlier Bruemmer and Van der Merwe (1989) stated that the NH_4-EDTA-extractable heavy metal concentration gives a good estimate of those potentially plant-available, and even suggested it to be used in the establishment of preliminary threshold values for heavy metals in South African soils. Weaker extractants such as neutral salts extract exchangeable metals (Beckett, 1989; McLaughlin et al., 2000) and is considered to give a good indication of the immediately bioavailable fraction (LeClaire et al., 1984; Mullins et al., 1986).

In light of the above the question arose regarding the plant availability of the metals in the soils after intensive liming. It was therefore decided to conduct a dedicated trial to determine the extent of plant metal uptake from the two sacrificial soils at four increasing lime application rates.

7.3 Materials and Methods

For this trial a new bulk sample of 300 kg per soil was collected. The sample of Soil 1 was collected in the same area as the bulk sample for the previous trials. The Soil 2 sample had to be collected from within the vicinity due to a fresh application of biosolids on the original site. The alternative site was the driest that could be found but still had visible undecomposed or decomposing biosolids mixed into it. The bulk samples were dried, sieved and weighed off into 4 kg nursery pots. For each pot the specified amount of AR $CaCO_3$ for an equivalent lime application rate of 0, 12, 24, and 36 ton ha^{-1} was weighed and thoroughly mixed with the soil. Each treatment was replicated four times. Deionised water was added to the pots and the soils were left to dry to the atmosphere. After drying, the soil of each pot was mixed again to ensure an even distribution of limed soil and it was watered again afterwards. This was deemed necessary due to previous incomplete mixing as well as possible precipitation of Ca-salts at the surface of the soil upon drying.

Four wheat and four spinach seeds were planted per pot and the soils kept moist during the growing season to ensure adequate growth. Spinach was chosen as test crop due to its known ability to accumulate metals to higher levels than many other crops (also reported by Hooda et al., 1997). The wheat cultivar (Tugela DN) is known for its Al and acid tolerance and was included to be certain of harvestable plant material at the zero lime application rate. The plants were harvested before the flowering stage (approximately 2 months of growth) and dried at 65 ºC for 48 hours. The dry matter was milled and analysed for heavy metals through the dry ashing procedure described by Soon (1998). Copper, Fe, Mn and Zn were determined in the digest solutions through AAS and Cd, Cr, Ni, and Pb determined by ICP-MS.

After harvesting the pots were left to dry to the atmosphere and afterwards a representative soil sample was collected from each pot. The pH ($CaCl_2$) and NH_4NO_3 and NH_4EDTA extractable metals were determined according to the same methods as described in Chapter 6. Due to the set-up of the trial the calculation of standard deviation and regression analysis of the data was considered to be adequate statistical analysis.

7.4 Results and Discussion

7.4.1 Soil pH and Dry Matter Yield

The pH results of the four liming rates in the two soils are presented in Table 7.1. The results for Soil 1 compare favourably with those reported in Chapter 5 but those for Soil 2 do not. It is postulated that the reason for the difference is the decomposing organic matter in the bulk sample from Soil 2 and that this could indicate more recent biosolids additions than for the sample used previously. The higher pH value for the zero lime rate confirms this postulation as it is expected that fresh anaerobically digested material will have a pH in excess of 7 and that the pH will decline after prolonged exposure to the atmosphere due to mineralization, nitrification and leaching of N.

Table 7.1. The pH ($CaCl_2$) of the two soils at four liming rates (n = 4; values in brackets denote the standard deviation)

Soil	Lime application rate (ton ha^{-1})			
	0	12	24	36
1	4.06 (0.02)	4.40 (0.02)	5.42 (0.04)	5.91 (0.01)
2	4.73 (0.04)	5.24 (0.03)	5.71 (0.03)	5.90 (0.03)

The dry matter yield per plant of the spinach and wheat is presented in Figures 7.1 and 7.2 respectively. The yield of the spinach was erratic with no yields at the zero lime application rate due to the low pH in the soils. For this reason the spinach dry matter was not analysed further due to the lack of a zero lime rate “control”. The wheat yield was also erratic but the general trend indicated an increase in yield with pH. Growth at the zero lime rate was significantly inhibited compared to the lime treatments.

7.4.2 Wheat Metal Content

The metal content of the wheat plants (Table 7.2) shows a decrease with increasing lime rate. The values for the zero lime rate are often significantly higher than those of the different lime rates and could be due to a concentration effect related to the low yield at the low pH treatments. This effect is often more pronounced in Soil 2 and lead to R^2 values that are generally lower than those of Soil 1. In Soil 1 the increasing lime rates lead to a consistent decrease in plant metal content. In Soil 2, though, the 36 ton ha^{-1} lime rate exhibited an increase in plant metal content compared to the 24 ton ha^{-1} rate for Cd, Cr, Fe, Ni, and Pb, albeit not significantly in most cases.

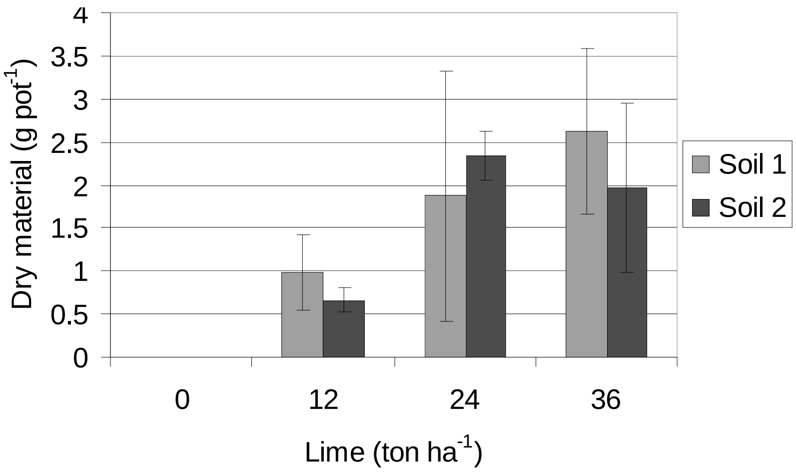

Figure 7.1. Spinach dry matter yield per pot (vertical bars indicate the standard deviation).

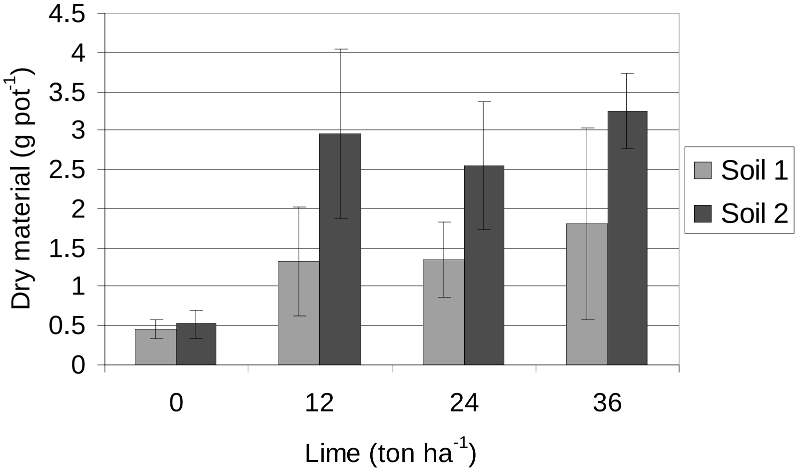

Figure 7.2. Wheat dry matter yield per pot (vertical bars indicate the standard deviation).

Table 7.2. Plant metal content (mg kg^{-1} wheat dry matter) and regression equations for the lime treatments and soils

Metal	Soil	Lime rate (ton ha^{-1})				Regression Equation (plant metal content vs. lime rate	R^2 Value
		0	12	24	36		
Cd	1	1.31 (0.14)	1.07 (0.32)	0.49 (0.12)	0.46 (0.21)	$y = -0.3132x + 1.6172$	0.91
	2	3.19 (0.90)	0.94 (0.43)	0.91 (0.11)	0.92 (0.10)	$y = -0.6844x + 3.2017$	0.61
Cr	1	23.1 (2.3)	5.45 (0.59)	5.37 (1.47)	3.22 (0.96)	$y = -5.972x + 24.216$	0.69
	2	6.65 (0.97)	1.76 (1.20)	0.86 (0.36)	1.01 (0.31)	$y = -1.7847x + 7.032$	0.70
Cu	1	71.2 (20.6)	49.6 (23.7)	34.6 (7.2)	28.4 (7.1)	$y = -14.326x + 81.756$	0.94
	2	72.9 (55.9)	49.8 (14.0)	47.7 (13.1)	46.2 (7.7)	$y = -8.2197x + 74.696$	0.71
Fe	1	218 (61)	200 (82)	148 (78)	138 (69)	$y = -29.449x + 249.55$	0.93
	2	293 (52)	162 (24)	125 (28)	149 (23)	$y = -47.017x + 299.76$	0.65
Mn	1	65.5 (12.4)	51.0 (3.6)	39.7 (8.7)	30.6 (6.9)	$y = -11.611x + 75.717$	0.99
	2	243 (27)	37.9 (10.0)	24.8 (18.6)	17.7 (2.7)	$y = -68.971x + 253.31$	0.67
Ni	1	7.54 (1.49)	5.91 (1.37)	6.03 (0.65)	3.40 (0.91)	$y = -1.2298x + 8.7956$	0.86
	2	67.7 (20.0)	13.4 (6.0)	7.55 (4.17)	12.2 (3.7)	$y = -17.245x + 68.346$	0.61
Pb	1	3.35 (0.99)	2.47 (0.60)	2.86 (0.55)	0.99 (0.30)	$y = -0.6699x + 4.0907$	0.72
	2	6.75 (2.26)	3.12 (1.70)	1.29 (0.86)	2.64 (0.63)	$y = -1.4148x + 6.9893$	0.61
Zn	1	171 (27)	103 (13)	55.6 (12.1)	45.0 (9.8)	$y = -42.368x + 199.39$	0.92
	2	400 (19)	170 (11)	112 (14)	99.0 (11.7)	$y = -96.272x + 436.12$	0.79

7.4.3 Soil Metal Levels

The NH_4NO_3 and NH_4EDTA extractable metal levels for the two soils are presented in Tables 7.3 and 7.4 respectively. Included in the tables are the regression equations and R^2 values obtained from graphs of the metal extraction values versus soil pH. With the NH_4NO_3 extraction most of the metals decreased significantly in extractability (except Cr and Pb in both soils, Cu in Soil 1, and Fe in Soil 2) with increasing lime rate. The non-significant decrease in Cr and Pb extractability is due to a high variability in the data as was the case in Chapters 5 and 6. In most cases the decrease in extractability was more pronounced in Soil 2 than Soil 1 with steeper slopes of the regression equations and could be the result of Soil 2 originally containing more undecomposed material than Soil 1. Upon liming the material would have undergone accelerated decomposition with a consequent large influence of the lime on metal extractability.

Table 7.3. NH_4NO_3 extractable metal levels and regression equations for the two soils (mg kg^{-1}, n = 4, the values in brackets denote the standard deviation)

Metal	Soil	Lime rate (ton ha^{-1})				Regression Equation ([Metal] vs. pH)	R^2 Value
		0	12	24	36		
Cd	1	0.87 (0.05)	0.53 (0.06)	0.22 (0.04)	0.16 (0.07)	y = -0.3584x + 2.2179	0.88
	2	1.91 (0.23)	0.93 (0.10)	0.42 (0.10)	0.37 (0.04)	y = -1.3249x + 8.0573	0.92
Cr	1	0.15 (0.02)	0.13 (0.08)	0.10 (0.05)	0.14 (0.08)	y = -0.011x + 0.1841	0.02
	2	0.30 (0.08)	0.20 (0.06)	0.18 (0.03)	0.20 (0.08)	y = -0.0815x + 0.6583	0.25
Cu	1	0.81 (0.16)	0.62 (0.06)	0.71 (0.04)	0.74 (0.10)	y = -0.0046x + 0.7396	0.001
	2	2.93 (0.09)	2.57 (0.14)	2.48 (0.06)	2.46 (0.11)	y = -0.3921x + 4.7268	0.72
Fe	1	4.53 (0.48)	3.08 (0.41)	2.65 (0.79)	2.08 (0.41)	y = -1.0995x + 8.5234	0.65
	2	0.77 (0.47)	0.85 (0.12)	1.09 (0.50)	1.17 (0.24)	y = 0.3573x - 0.9573	0.21
Mn	1	2.81 (0.09)	2.11 (0.06)	0.73 (0.05)	0.17 (0.07)	y = -1.4027x + 8.3925	0.99
	2	32.3 (5.4)	10.4 (0.6)	3.56 (0.36)	2.80 (0.64)	y = -25.002x + 147.16	0.87
Ni	1	1.17 (0.08)	0.68 (0.05)	0.51 (0.09)	0.32 (0.04)	y = -0.3854x + 2.5759	0.81
	2	18.8 (2.2)	9.6 (0.4)	4.6 (0.4)	4.0 (0.3)	y = -12.763x + 78.114	0.93
Pb	1	0.23 (0.17)	0.15 (0.12)	0.08 (0.03)	0.09 (0.06)	y = -0.0736x + 0.4999	0.24
	2	0.09 (0.08)	0	0	0	y = -0.07x + 0.3988	0.38
Zn	1	13.7 (0.3)	6.86 (0.22)	1.12 (0.31)	0.13 (0.05)	y = -6.8326x + 39.261	0.89
	2	15.8 (2.58)	8.67 (0.42)	1.21 (0.35)	0.82 (0.21)	y = -13.362x + 78.704	0.95

The EDTA extractable Cd, Cu, Fe, Mn, Pb, and Zn in Soil 1 increased significantly in most cases whereas Cu, Fe, and Pb increased non-significantly in Soil 2 after liming. The extractability of Ni was opposite between the soils but the trends were non-significant for both as was the case for the previous trials reported in Chapters 5 and 6. As reported in these chapters the variability in Cr levels was too large to determine any significant trends. The overall trend was reversed in Soil 2 with a limited decrease in extractability of Cd and Mn and a non-significant decrease in Zn. The reversed trend in the Soil 2 EDTA extractable metal levels could possibly be ascribed to the same factors that lead to the somewhat unexpected pH results. It would appear that the undecomposed biosolids acted differently to material that had undergone changes in the soils after prolonged exposure to the climatic and atmospheric factors.

Table 7.4. NH_4EDTA extractable metal levels and regression equations for the two soils (mg kg^{-1}, n = 4, the values in brackets denote the standard deviation)

Metal	Soil	Lime rate (ton ha^{-1})				Regression Equation	R^2 Value
		0	12	24	36	([Metal] vs. pH)	
Cd	1	0.46 (0.03)	0.61 (0.06)	0.72 (0.04)	0.72 (0.04)	y = 0.1329x - 0.031	0.73
	2	5.23 (0.23)	5.00 (0.14)	4.84 (0.14)	4.63 (0.17)	y = -0.4669x + 7.445	0.65
Cr	1	0.21 (0.19)	0.19 (0.09)	0.20 (0.15)	0.22 (0.13)	y = 0.0086x + 0.1641	0.003
	2	1.04 (0.25)	0.76 (0.07)	0.80 (0.09)	0.64 (0.14)	y = -0.2866x + 2.3553	0.43
Cu	1	23.4 (1.0)	27.3 (2.9)	31.7 (2.0)	32.7 (1.7)	y = 4.742x + 5.3206	0.76
	2	306 (11)	317 (9)	325 (7)	318 (14)	y = 11.721x + 253.29	0.23
Fe	1	147 (25)	208 (32)	304 (15)	359 (33)	y = 109.31x - 286.3	0.91
	2	592 (35)	635 (18)	668 (68)	606 (48)	y = 29.493x + 466.1	0.07
Mn	1	3.79 (0.17)	3.72 (0.35)	4.27 (0.23)	4.32 (0.21)	y = 0.3448x + 2.3197	0.55
	2	316 (12)	313 (13)	297 (5)	282 (12)	y = -28.07x + 453.47	0.59
Ni	1	2.97 (0.71)	4.24 (0.36)	4.52 (0.50)	3.95 (0.65)	y = 0.4479x + 1.7055	0.19
	2	57.1 (3.2)	57.5 (9.0)	47.1 (1.7)	53.2 (4.5)	y = -6.0736x + 86.468	0.20
Pb	1	4.92 (0.69)	7.06 (0.84)	11.6 (0.8)	12.8 (0.3)	y = 4.267x - 12.006	0.95
	2	107 (11)	115 (14)	113 (9)	123 (8)	y = 10.241x + 59.316	0.18
Zn	1	32.4 (1.2)	34.8 (3.5)	42.2 (3.0)	46.9 (3.0)	y = 7.6558x + 1.2286	0.84
	2	380 (13)	371 (7)	373 (7)	368 (19)	y = -8.3823x + 418.18	0.11

7.4.4 Correlation Between Plant and Soil Metal Levels

The plant-uptake metal levels correlated with the NH_4NO_3 and NH_4EDTA extraction values are presented in Table 7.5. From the R^2 values it is clear that the NH_4NO_3 extraction data correlated better with the plant metal levels than the NH_4EDTA data for all the metals except Cu, Fe, and Pb where both extractants performed equally poor. For all the metals except Fe in Soil 2 there was a direct relationship between the amounts taken up by the plants and the amounts extracted from the soil with NH_4NO_3. This was not the case for NH_4EDTA where there was an inverse relationship (indicating a very poor correlation) between the plant content and that extracted from the soil. This inverse relationship diminishes the fear concerning the increased extractability of metals with EDTA at increasing lime rates.

Table 7.5. Regression equations of plant metal content (mg kg^{-1} dry matter) versus NH_4NO_3 and NH_4EDTA extractable metal levels (mg kg^{-1} soil) respectively

Metal	Soil	NH_4NO_3 extractable metals		NH_4EDTA extractable metals	
		Regression Equation (plant vs. soil metal content)	R^2 Value	Regression Equation (plant vs. soil metal content)	R^2 Value
Cd	1	y = 1.2645x + 0.2715	0.77	y = -2.705x + 2.5285	0.58
	2	y = 1.3642x + 0.2443	0.68	y = 1.9215x - 7.9807	0.24
Cr	1	y = 28.769x + 5.5477	0.04	y = 3.6672x + 8.5275	0.003
	2	y = 20.638x - 1.9775	0.41	y = 7.2404x - 3.3301	0.35
Cu	1	y = 72.572x - 6.0811	0.14	y = -3.4446x + 145.07	0.42
	2	y = 24.618x - 10.944	0.05	y = -1.2063x + 435.18	0.32
Fe	1	y = 27.418x + 91.356	0.15	y = -0.2683x + 244.19	0.10
	2	y = -52.509x + 231.74	0.07	y = -0.5173x + 504.21	0.14
Mn	1	y = 12.291x + 28.827	0.75	y = -20.255x + 128.22	0.22
	2	y = 7.2817x - 8.7041	0.88	y = 3.0583x – 843	0.29
Ni	1	y = 3.67x + 3.2637	0.43	y = -0.9261x + 9.3525	0.16
	2	y = 3.6695x - 8.9181	0.74	y = 1.3697x - 48.49	0.11
Pb	1	y = 4.6099x + 1.789	0.25	y = -0.1902x + 4.147	0.35
	2	y = 29.584x + 2.8702	0.40	y = -0.1195x + 17.188	0.29
Zn	1	y = 9.0652x + 43.964	0.91	y = -6.6132x + 352.05	0.64
	2	y = 18.045x + 76.062	0.85	y = 3.4358x – 1086	0.11

7.5 Conclusions and Recommendations

From the data it is clear that liming at increasing rates decreased the NH_4NO_3 extractable metals but lead to an increase in many of the NH_4EDTA extractable metals, especially in Soil 1. The data confirms the data generated through separate studies that have been reported in Chapters 5 and 6.

The increasing lime rates generally lead to a decrease in the metal content of wheat plants grown in the soils. The plant metal data was better correlated with the NH_4NO_3 extractable metal levels than those of NH_4EDTA as is reflected in the slopes and R^2 values of the regression equations.

The fact that the plant metal content was better correlated with the NH_4NO_3 extractable metals and that both of these sets of data indicated a decrease with increasing lime rate indicates a decreased risk of metal mobilisation through liming. The first implication of the data is that sacrificial soils can be limed to increase pH levels and thereby decrease threats posed by the metals to the environment.

The second implication of the data is that the widely held notion that EDTA is a good predictor of plant metal availability is not valid for sacrificial soils. The setting of guideline EDTA extractable metal levels is therefore discouraged unless it involves extensive testing in different soils under a wide range of conditions and the linking of these conditions to the guideline levels. EDTA extract values are imperical and are restricted in the sense that it is influenced by factors other than those determining metal plant availability. The use of NH_4NO_3, on the other hand, is encouraged due its better correlation with plant metal content.

CHAPTER 8

Concluding Remarks and Recommendations

The lack of management of sacrificial soils (especially pH management) is a source of grave concern. The potential risk include metal leaching into groundwater, removal of metals by plants that are in turn consumed by animals or humans, distribution of metals through wind blown particles to neighbouring fields and human settlements, as well as leaching of acid water percolating through the soils into groundwater. The last aspect mentioned here could cause the accelerated formation of sinkholes in underlying dolomite and is a very real threat in the case of Soil 2.

The most obvious pH management approach is the addition of lime to the acidified soils. The increased NH_4EDTA extractability of metals from sacrificial soils due to intensive liming as reported by Van der Waals et al. (2005) lead to concerns regarding the rehabilitation and management of these soils. The results also lead to a number of questions regarding the cause of the increased extractability and the implications thereof on the proposed management of sacrificial soils.

Several trials were conducted to quantify the increased extractability as well as to determine the influence of liming application rate and incubation of the soil with lime on metal extractability and plant metal availability. The following conclusions were reached from the different trials:

1. The addition of lime at increasing rates to sacrificial soils to increase the pH to acceptable levels leads to increased NH_4EDTA extractable metals but decreased NH_4NO_3 metal levels.
2. The increased extractability of metals with NH_4EDTA is ascribed to the ability of EDTA to extract organic matter from the soil. This ability seems to be correlated also with increasing soil pH.
3. Incubation of soils with and without lime over a 20-week period with regular wet and dry cycles lead only to a small influence on metal extractability. This was mainly due to a small change in pH over the incubation period. Liming had the same effect on NH_4EDTA extractable metal levels as in two previous trials.

4. Plant metal levels after a pot trial were better correlated with NH_4NO_3 extractable metal levels that with NH_4EDTA metal levels. This indicates that the NH_4NO_3 extractable metal level is a more realistic indication of plant metal availability than NH_4EDTA metal levels.

From the data it can safely be advised that sacrificial soils should be limed to decrease the risk of metal leaching and uptake by plants. The management of future sacrificial (or rehabilitated) sites should as a matter of principle include the regular addition of lime to prevent excessive build-up of acidity.

The use of EDTA as extracting agent in guidelines should be discouraged unless extensive investigations under different conditions have been conducted. These conditions should include a wide range of polluted soils that are enriched with organic matter. The fact that EDTA also extracts organic matter from soils means that factors influencing organic matter extractability will determine metal extraction levels instead on factors controlling the mobility of the metals. Furthermore, EDTA extract values are imperical and are restricted in the sense that it is influenced by factors other than those determining metal plant availability. This is especially so in the case of high organic matter soils where and increase in pH has opposite effects on plant metal uptake and EDTA metal extractability.

It is suggested that NH_4NO_3 be used as extracting agent to determine the risk of plant metal uptake in polluted soils. The fact that it is a neutral salt implies that it also gives an indication of the metal fraction that poses a risk of leaching in soils.