CHAPTER 6

Changes in Ammonium Nitrate (NH_4NO_3) and Ammonium EDTA (NH_4EDTA) Extractable Metals from Two Long-Term Biosolids Disposal Soils due to Intensive Liming and Incubation

6.1 Abstract

Sacrificial disposal of metal containing biosolids leads to a build-up of organic material, acidity and metals in soils. Preliminary investigations have indicated that intensive liming of these soils could lead to an increase in metal extractability. Two acid soils ($pH_{(water)}$ 4) were collected from different sacrificial sites and incubated in open containers with regular wetting and drying cycles over periods of 0, 1, 2, 4, 6, 8, 12, 16, and 20 weeks. One set of treatments for each soil received the equivalent of 27 tons ha^{-1} $CaCO_3$ (AR) while another was incubated without lime. On the samples a pH ($CaCl_2$) determination and NH_4NO_3 and NH_4EDTA extractions were performed and the metals Al, Fe, Mn, Cd, Cr, Cu, Ni, Pb, and Zn determined in the extracts. The lime reaction was complete within three days after application. Most of the metals indicated a slight increase in NH_4NO_3 extractability over the incubation period in the unlimed treatments and this was positively correlated with a decrease in pH. All the metals showed a significant decrease in NH_4NO_3 extractability after liming. The EDTA extractability of the metals did not correlate with the slight decrease in pH over the incubation period. The EDTA extractability of all the metals (except Ni), however, indicated varying degrees of increase after liming. Liming of sacrificial soils is considered a sound practice due to the significant decrease in extractability of the metals by NH_4NO_3, or exchangeable metal fraction, even though the EDTA extractability of the metals increased after liming. The correlation between the NH_4NO_3 and EDTA extractable metals and plant metal uptake is not known and should be investigated.

6.2 Introduction

Sacrificial biosolid soils are often polluted with high levels of metals that could pose a threat to the environment due to their low pH and high pH buffer capacity. One of the possible approaches to decrease the mobility of the heavy metals in these soils is liming, as it is often used as a rehabilitation strategy in metal polluted soils (Logan, 1992). The most important factor controlling the mobility of metals in soils is pH (Sauerbeck, 1991; Smith, 1994; Hooda et al., 1997) mainly due to its influence on the adsorption of metals on clay minerals (Jinadasa et al., 1995; Kaupenjohann and Wilcke, 1995; Straalen and Bergema, 1995; Schwarz et al., 1999, Yin et al., 2000) as well as the pH stability of organo-metalic complexes (Schnitzer, 1978; Stevenson, 1982; Clapp et al., 1993). Several workers (Hue, 1995; Moore, 1997), though, have cautioned against this strategy in soils that are polluted with metals and that also contain elevated levels of organic matter. The reason for the cautionary approach is the increase in solubility of organic matter (and therefore organo-metalic complexes) upon lime addition and the fear of the migration of these complexes into lower soil horizons or even groundwater.

In this context Van der Waals et al. (2005) have indicated in a previous study that the intense liming of two sacrificial biosolids disposal soils lead to a decrease in most of the $BaCl_2$ extractable metals. However, the EDTA extractability of several of the metals increased when compared to unlimed treatments. In a subsequent study (Chapter 5) it was found that the increased metal extractability in EDTA showed a good correlation with organic matter extracted from the soils. This was due to the characteristics of the EDTA (known as an organic matter extractant) as well as the influence of pH on the solubility of organic matter in soil.

The trials reported on by Van der Waals et al. (2005) and in Chapter 5 represent a once-off sampling of the soils with no further indication as to the influence of incubation time on extractability. Other studies have shown that metal mobility or extractability decreases with time after application due to the precipitation or adsorption of the metals on soil mineral surfaces in increasingly stable complexes or forms (Grove and Ellis, 1980; Bibak et al., 1995).

In order for longer-term data to be applicable to conditions experienced in the field, it is necessary that the effect of liming on the mobility of the metals be investigated under controlled conditions that closely resemble field conditions. The rainfall in the Gauteng province varies between 650 and 750 mm per year and is mainly in the form of thunderstorms that vary in intensity. Topsoil horizons often dry out completely before the follow-up rainfall events due to low relative humidity and high average maximum temperatures (ranging from 28 º – 34 ºC). The soils therefore experience numerous and intense wetting and drying cycles during a season that lead to a rapid mineralization of unstable organic matter. The aim of this study, therefore, was to determine the changes in extractability of metals in the two acid sacrificial soils reported on by Van der Waals et al. (2005) and in Chapter 5 as a function of lime addition and incubation time with repeated wetting and drying cycles.

Under wetting and drying cycle conditions with exposure of the soil and drying to the atmosphere it would not be possible to determine the products of organic matter mineralization, such as gaseous CO_2 emissions, and therefore also impossible to determine its influence on metal extractability. Terry et al. (1979) indicated that mineralization of the unstable organic matter fraction was mostly complete within 28 days after sludge application to soil and that a major component (55 to 80 %) was resistant to decomposition. Due to the "aged" nature of the biosolids in the experimental soils it was concluded that organic matter mineralization would not be significant in the soils and its omission from the study was therefore considered justified.

6.3 Materials and Methods

6.3.1 Incubation With and Without Lime

The soils that were used for the trials reported on in Chapters 4 and 5 were also used for this trial. The reaction of the two soils on incubation with and without lime was determined by incubating 150 g of each soil in plastic containers for a period of 20 weeks. For the lime treatment 1 g $CaCO_3$ (AR) was added to the 150 g soil (equivalent to 27 tons ha^{-1} if incorporation to a depth of 0.3 m is assumed in a soil with a bulk density of 1.5 g cm^{-3}). The samples were thoroughly mixed with a glass rod and four replicates were prepared for each soil (limed and not limed) for every sampling period of 0, 1, 2, 4, 6, 8, 12, 16 and 20 weeks. At the beginning of the trial all the samples received de-ionised water (100 ml – in excess of saturation) and were thoroughly mixed. The Week 0 samples were removed immediately after the addition of the water and dried at 65 ºC. The remaining samples were left to dry to the atmosphere in a constant temperature room at 27 ºC (approximately 5 – 6 days). These remaining samples received 50 ml de-ionised water (water to soil ratio of 1:3 – roughly equivalent to field capacity) every week, were stirred with a glass rod and left to dry. This was repeated weakly up to Week 20 to simulate repeated wetting and drying cycles in the field. At every interval the assigned samples were removed and dried at 65 ºC. After drying, the samples were stored in sealed polyethylene bags until analysis.

6.3.2 Soil Analysis

Each of the soil samples was analysed for pH ($CaCl_2$) according to the method described by the Non-Affiliated Soil Analysis Work Committee (1990) with a 0.01 M $CaCl_2$ solution. The metals Al, Fe, Mn, Cu, Zn, Cd, Cr, Ni, and Pb were determined through NH_4NO_3 and NH_4EDTA extractions. Ammonium nitrate and NH_4EDTA were chosen due to their frequency of use in studies on exchangeable and "potentially plant-available" metals in soils. The NH_4NO_3 extraction was as follows: 5 g of soil was shaken with 50 ml 0.2 M NH_4NO_3 in a stoppered glass bottle on a horizontal shaker for 1 hour and filtered afterwards. Aluminium, Fe, Mn, Cu, and Zn were determined through Atomic Absorption Spectrophotometry (AAS) and Cd, Cr, Ni, and Pb by ICP-AES due to levels being below the detection limits of AAS. For the EDTA extraction the volumes were adapted from the original 45 ml 0.02 M NH_4EDTA and 15 g soil stipulated by the Non-Affiliated Soil Analysis Work Committee (1990) to 50 ml 0.02 M NH_4EDTA and 5 g soil. This was done to ensure adequate EDTA in the presence of high metal levels. With this extraction all the metals were determined through AAS. In both cases an internal reference soil was included as every 9th determination. All the samples were analysed at the same time to reduce experimental error differences.

6.4 Results and Discussion

6.4.1 Change in pH Upon Incubation

Figure 6.1 presents the change in pH for the limed and unlimed soils upon incubation. In both the unlimed treatments there was a 0.3 to 0.4 pH unit decrease over the incubation period indicating that the processes driving the acidification of the soils (organic matter mineralization, nitrification) had not stabilised yet. In the limed treatments this trend was not as pronounced with an overall slight decrease over the incubation period.

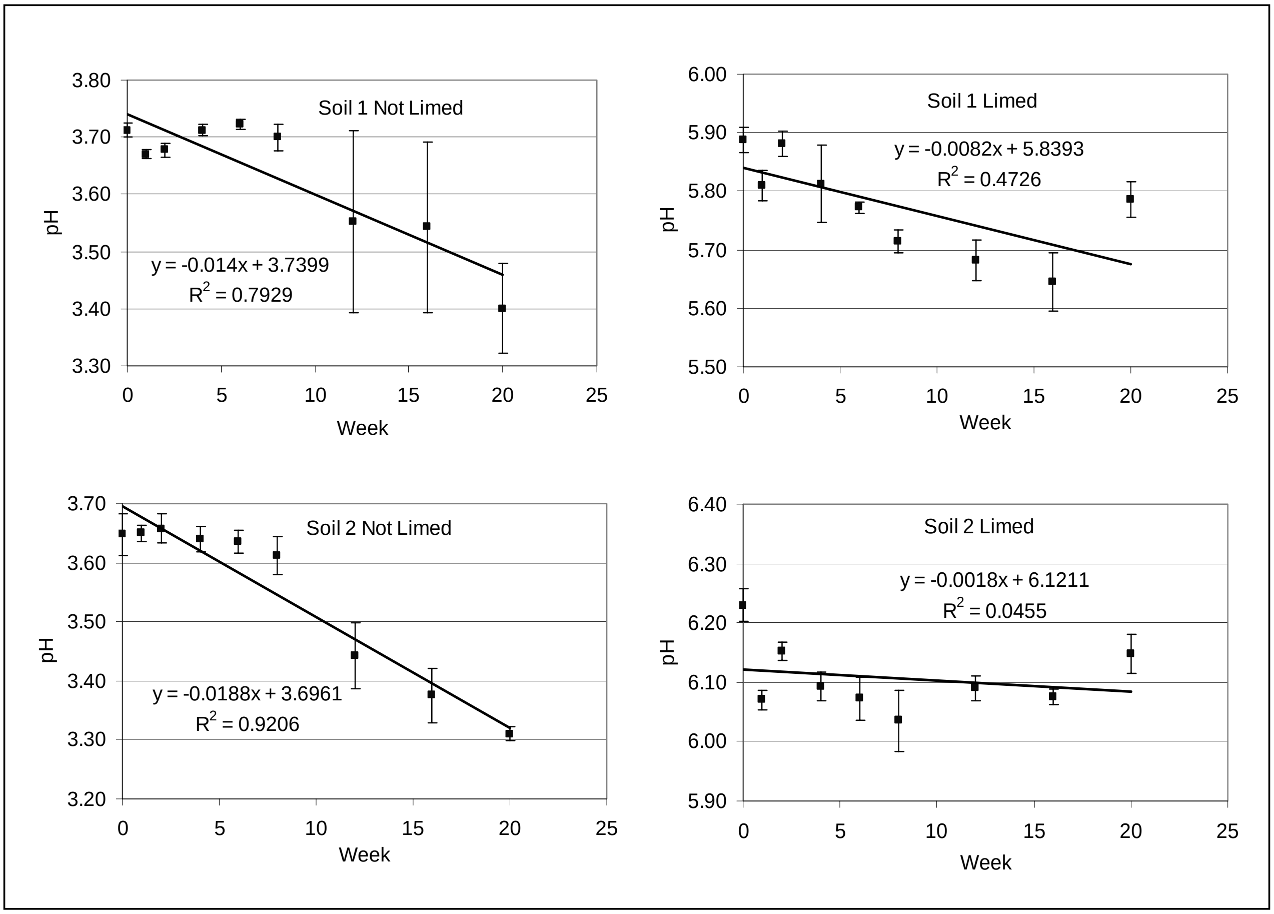

Figure 6.1. Change in pH ($CaCl_2$) over the 20 weeks incubation period for the limed and unlimed treatments. Vertical bars indicate + and – standard deviation.

6.4.2 NH_4NO_3 Extractable Metals

The NH_4NO_3 extractability of Al and Mn (Figure 6.2a), Cd and Zn (Figure 6.3a), and Cu and Ni (Figure 6.4a) increased slightly over the twenty weeks of incubation in the unlimed treatments – mainly due to a slight decrease in pH. Aluminium exhibited a significant increase in Soil 2 to the end of the incubation period. Aluminium and Mn (Figure 6.2b), Cd and Zn (Figure 6.3b), and Cu and Ni (Figure 6.4b) also exhibited a very good correlation with pH, with the trend line in Soil 2 having a steeper slope than the trend line in Soil 1 for most of these metals. The pH trend was very pronounced in Soil 2 (higher clay content than Soil 1) for Cd, Cu, and Zn where the R^2 values exceeded 0.8. The R^2 value that approaches 0 for Mn in Soil 1 is considered an artefact due to the near horizontal trend of the values while the data points had a very good linear fit.

The variability in the Cr and Pb values for both the limed and unlimed treatments in Soil 1 was very high (Figure 6.5a). This trend is not repeated in Soil 2 however. It is postulated that the higher clay content of Soil 2 influenced the extractability of the metals and led to a more clearly defined difference between the limed and unlimed treatments. The presence of more clay in Soil 2 than Soil 1 led to a larger stable surface area for adsorption during the increase in pH after liming, whereas the liming had little influence on the stability of Cr and Pb organic complexes in both soils. Both metals exhibited a clear higher extractability with decreasing pH in the unlimed Soil 2 treatments (Figure 6.5b) whereas the Soil 1 values had the opposite trend.

The extractability of Fe in the unlimed treatments (Figure 6.6a) was variable with a peak at 16 weeks of incubation and a poor correlation with pH in both soils (Figure 6.6b). If the Week 16 values were to be removed the data would indicate a slight decrease over the incubation period. The anomalous Week 16 values are ascribed to a humid climatic spell that could have influenced the water's rate of evaporation during the drying cycle. The Fe extractability probably influenced that of Cr and Pb in that the same trend is evident in the Cr and Pb values.

In most of the lime treated samples there was a very significant decrease in extractability compared to the unlimed treatments. It is also clear that the lime had an immediate effect on the pH of the soils in that the metal extractability decreased already from Week 0. The variability in the limed treatments was significantly lower than the unlimed treatments, except for Cr and Pb in Soil 1. This could be ascribed to the coarser nature of Soil 1 and the difficulty in obtaining a homogenous sample. There wasn't a significant correlation between the metal extractability and pH in the limed samples, with all R^2 values approaching 0 (a function of the slope approaching 0). The limed and unlimed values for Cr and Pb were very variable though for Soil 1 and are, as discussed earlier, attributed to the low clay content of the soil and the low extractability of the metals. All the other metals (except Ni) exhibited a larger decrease in Soil 2 than Soil 1 and this is also attributed to the higher clay content of Soil 2.

6.4.3 NH_4EDTA Extractable Metals

The EDTA extractability of Al and Fe (Fig. 6.7), Cd, Cr and Cu (Fig. 6.8), and Pb (Fig. 6.9) increased with liming and is consistent with the data reported by Van der Waals et al. (2005). Again the Cr values were very variable in Soil 1. The extractability of Mn increased in Soil 2 (Fig. 6.7) and that of Ni and Zn in Soil 1 (Fig. 6.9). Although the increases appear relatively small, they are significant in most cases. There wasn't a correlation between the pH of the soil samples and the EDTA extractability of the metals and the data will therefore not be presented here. The increased extraction of metals after liming in this trial is due to the increased extractability of organic matter as reported in Chapter 5.

6.5 Conclusions and Recommendations

The pH dependence of metal extraction is a well-known phenomenon – especially for neutral salt extractants. From the NH_4NO_3 data it is clear that liming had a significant influence on the extractability of most of the tested metals. Whereas the unlimed soils exhibited a systematic increase in extractability over the incubation period (in most cases linked to a decrease in pH), the limed soils exhibited no clear increases. This indicates that the liming of these soils would decrease the extractability of most metals and that this extractability will remain low after repeated wetting and drying cycles – such as field conditions.

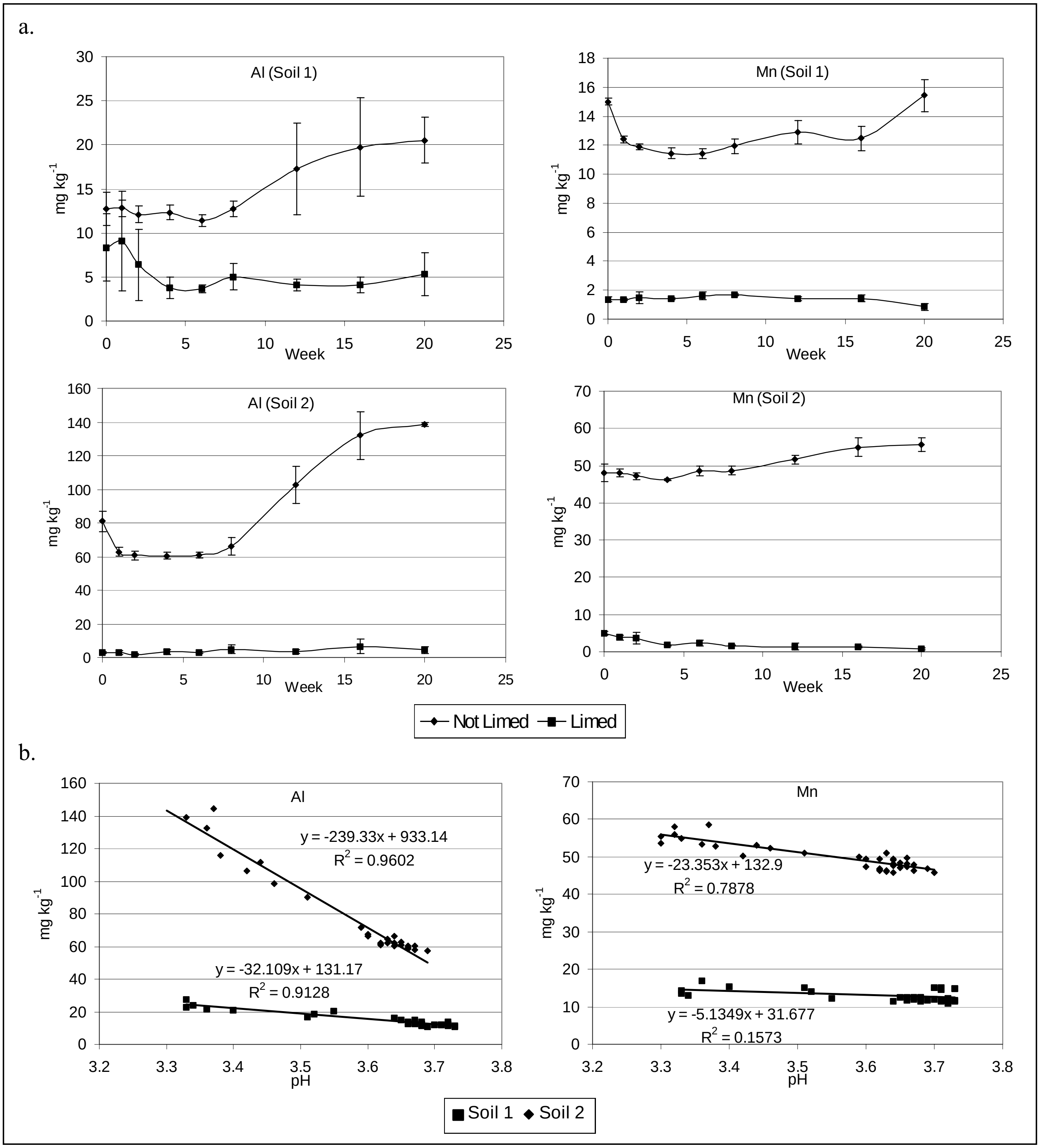

Figure 6.2. Aluminium and manganese levels (NH_4NO_3) for Soils 1 and 2 extracted at intervals over 20 weeks with and without liming (a) and correlation between extractability and pH ($CaCl_2$) for the unlimed treatments (b). Vertical bars indicate + and – standard deviation.

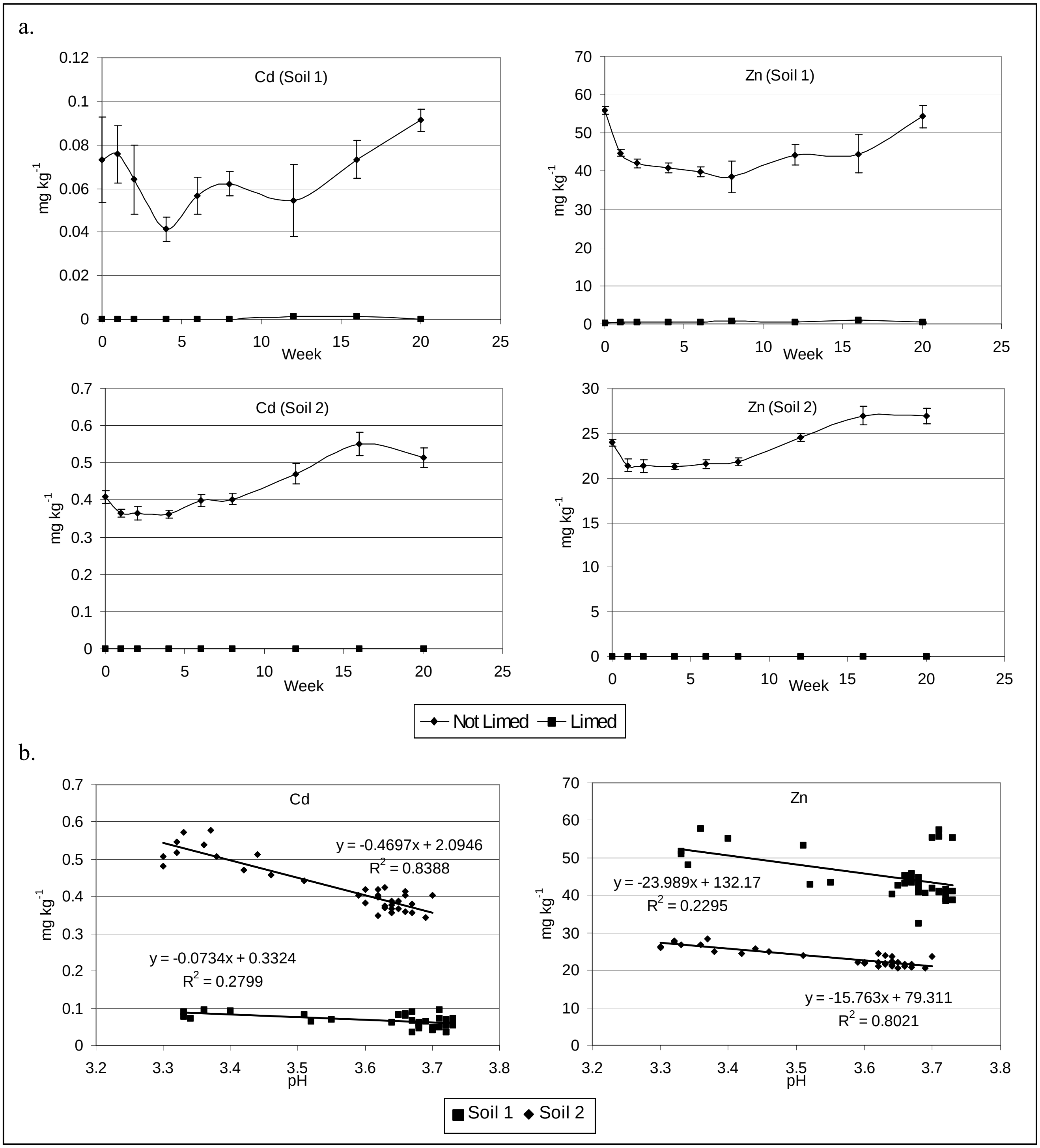

Figure 6.3. Cadmium and zinc levels (NH_4NO_3) for Soils 1 and 2 extracted at intervals over 20 weeks with and without liming (a) and correlation between extractability and pH ($CaCl_2$) for the unlimed treatments (b). Vertical bars indicate + and – standard deviation.

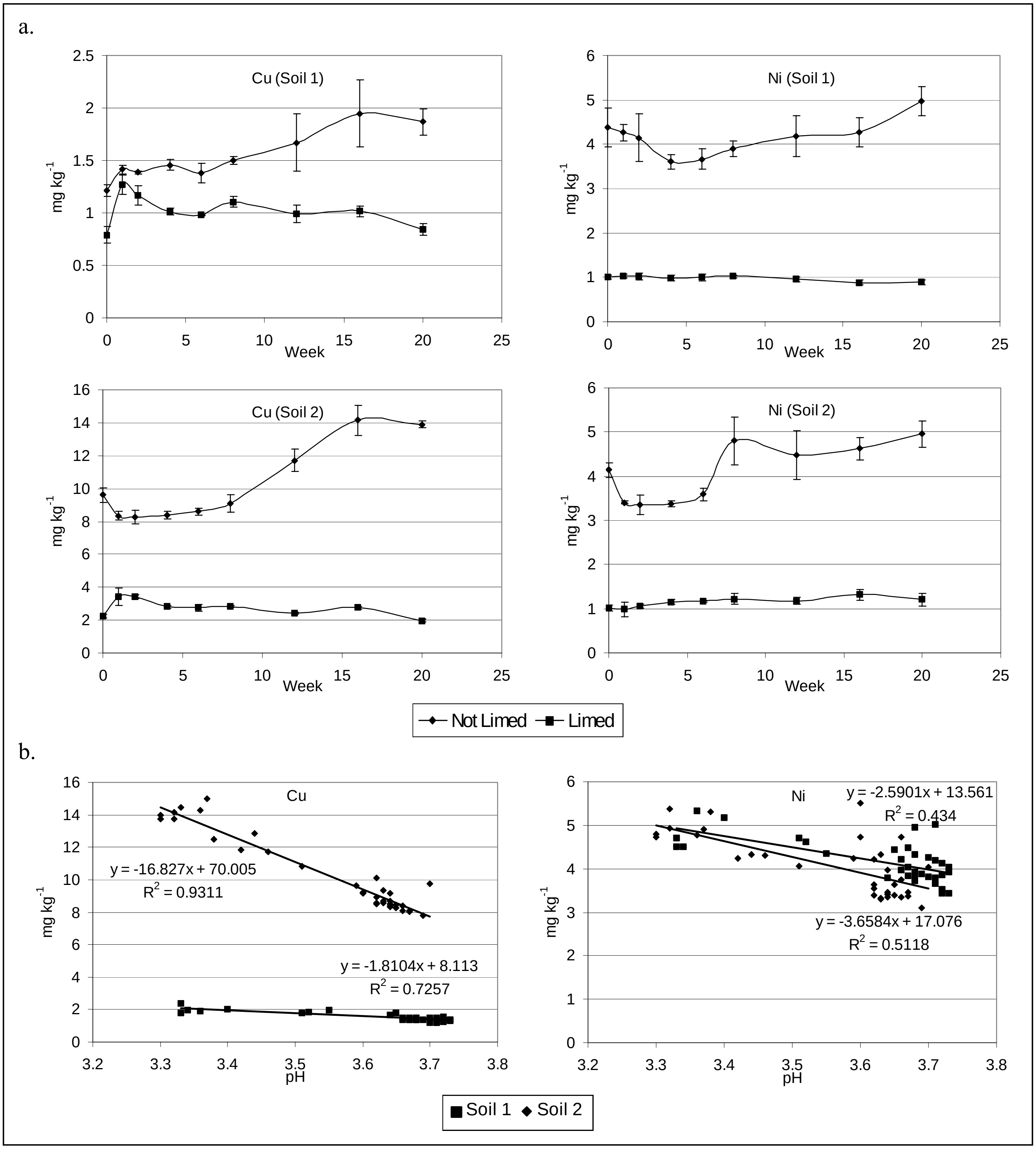

Figure 6.4. Copper and nickel levels (NH_4NO_3) for Soils 1 and 2 extracted at intervals over 20 weeks with and without liming (a) and correlation between extractability and pH ($CaCl_2$) for the unlimed treatments (b). Vertical bars indicate + and – standard deviation.

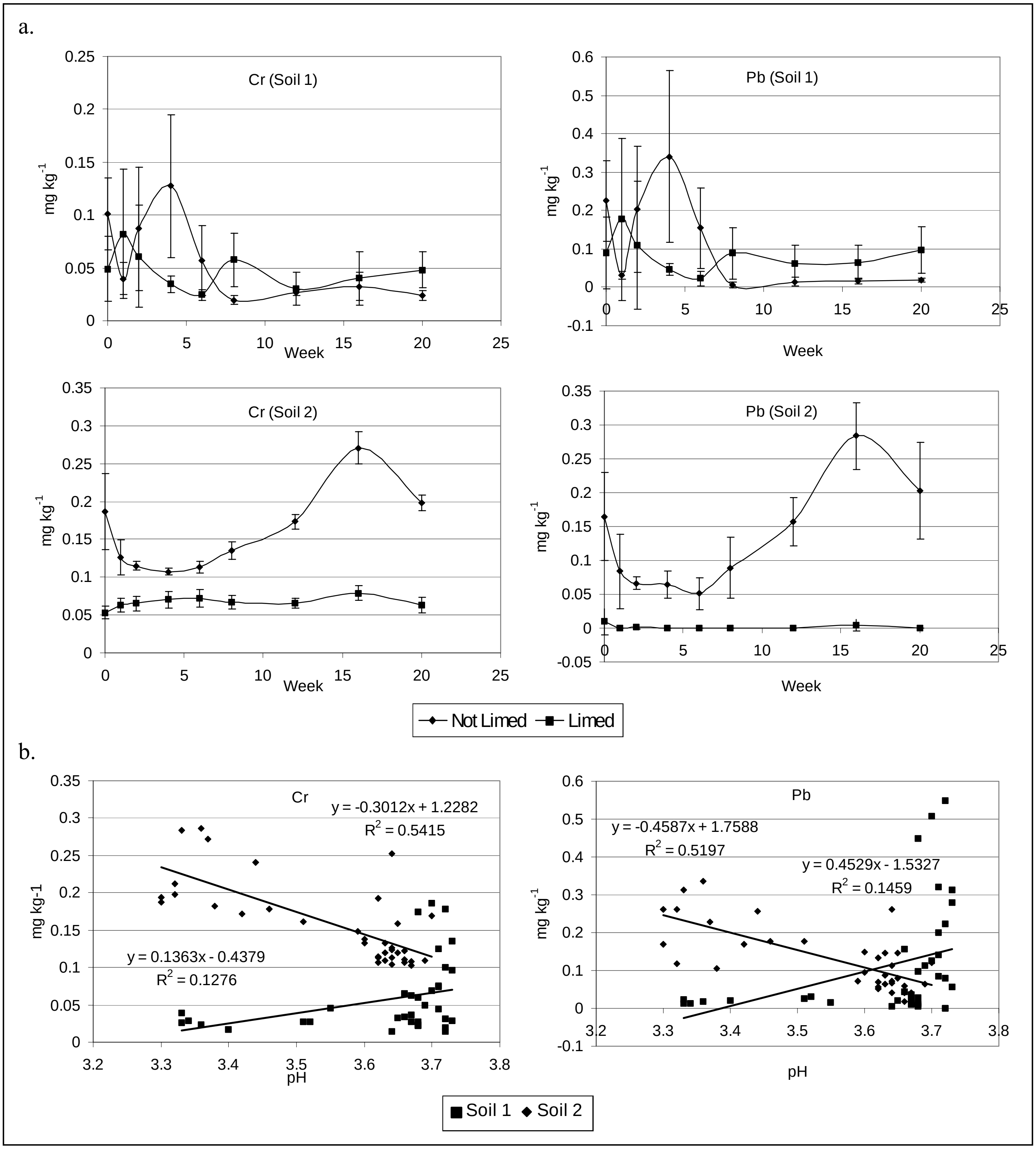

Figure 6.5. Chromium and lead (NH_4NO_3) levels for Soils 1 and 2 extracted at intervals over 20 weeks with and without liming (a) and correlation between extractability and pH ($CaCl_2$) for the unlimed treatments (b). Vertical bars indicate + and – standard deviation.

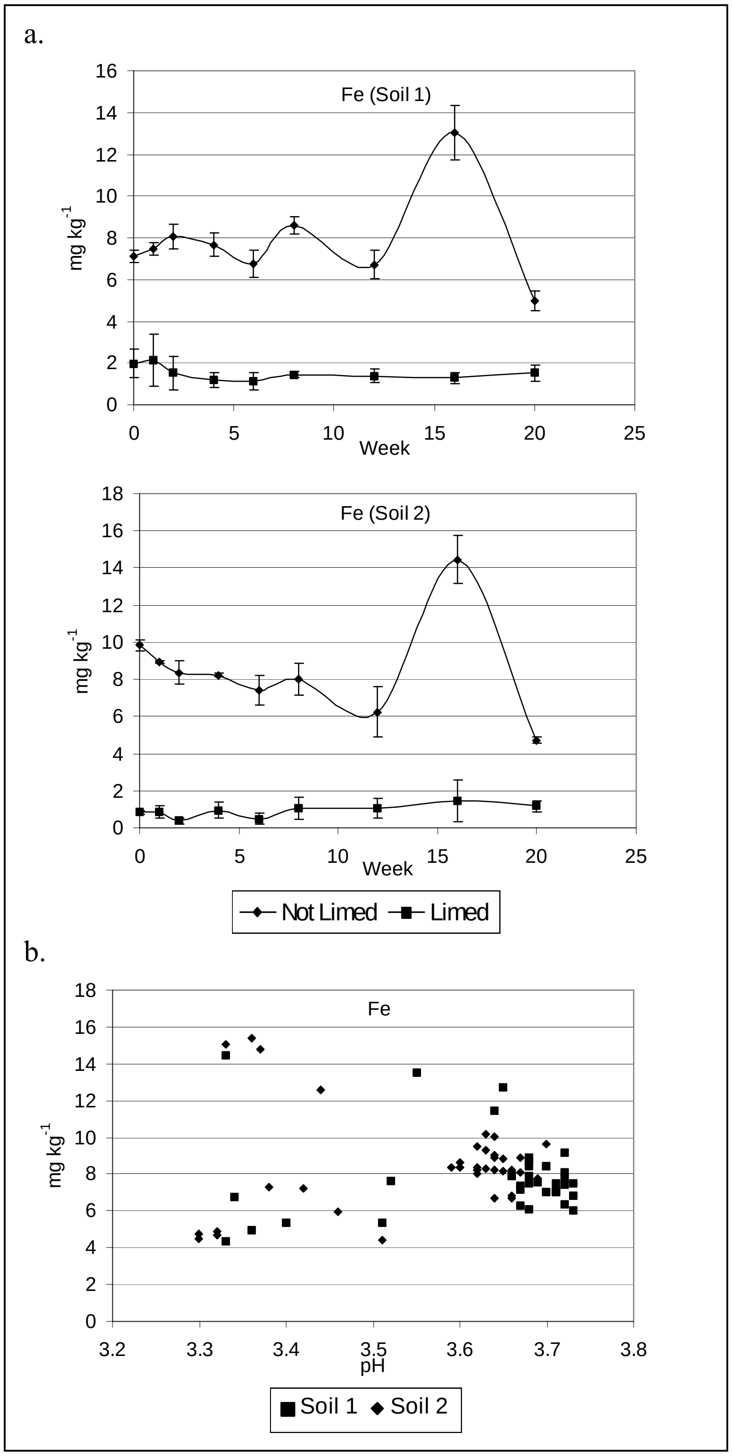

Figure 6.6. Iron levels (NH_4NO_3) for Soils 1 and 2 extracted at intervals over 20 weeks with and without liming (a) and correlation between extractability and pH ($CaCl_2$) for the unlimed treatments (b). Vertical bars indicate + and – standard deviation.

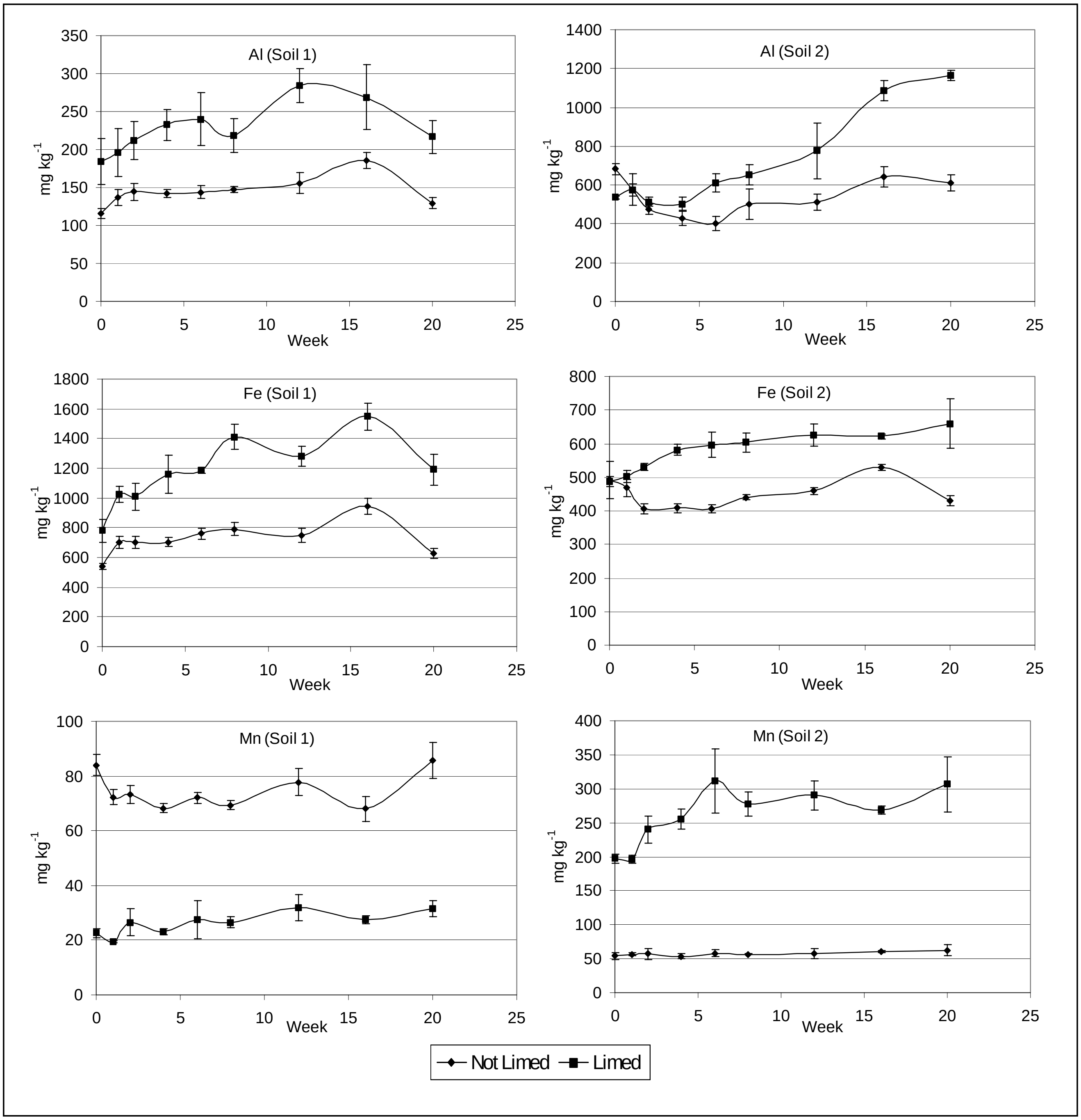

Figure 6.7. The EDTA extractability of Al, Fe, and Mn from two soils with and without liming over a 20-week incubation period. Vertical bars indicate + and – standard deviation.

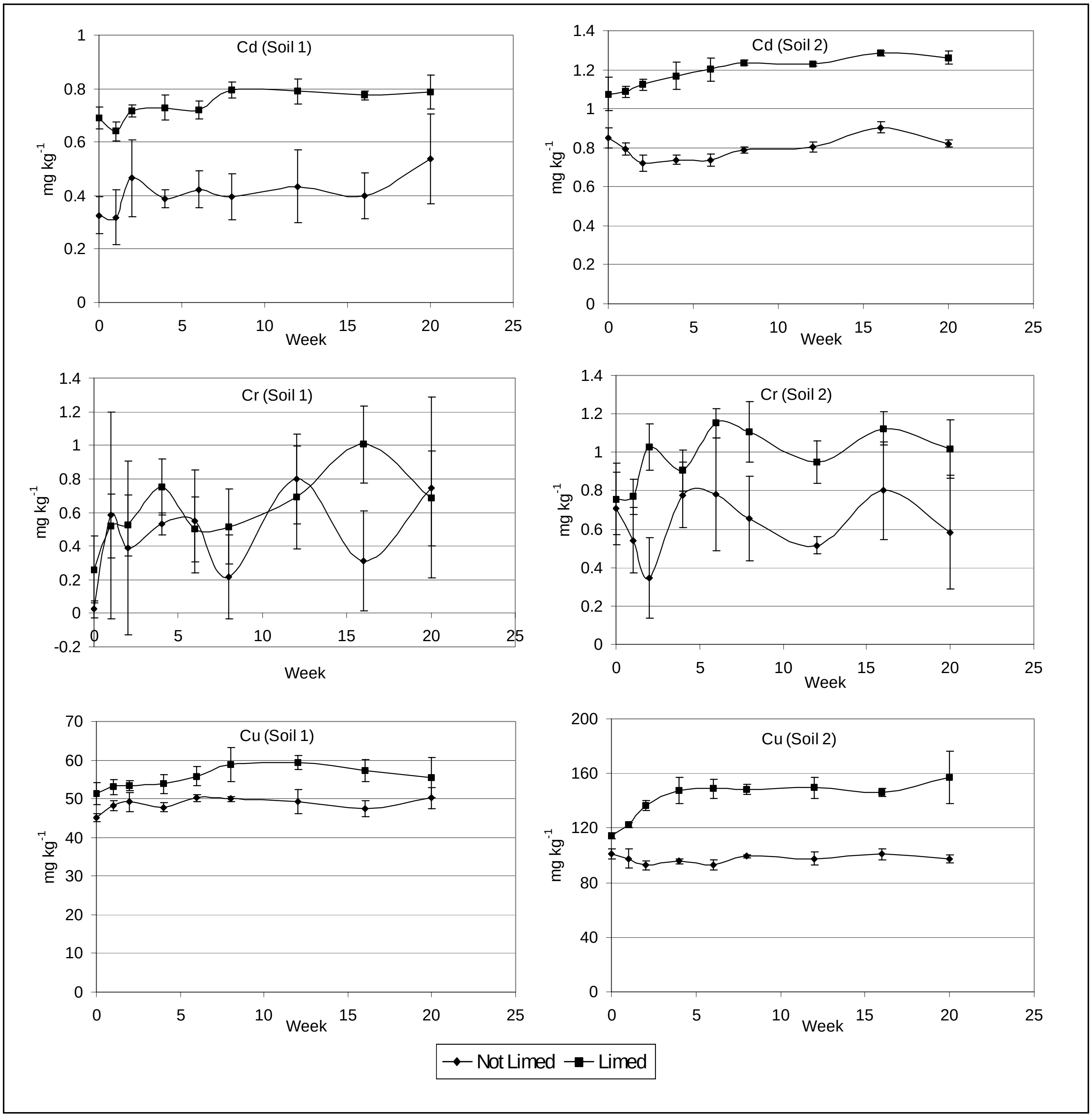

Figure 6.8. The EDTA extractability of Cd, Cr, and Cu from two soils with and without liming over a 20-week incubation period. Vertical bars indicate + and – standard deviation.

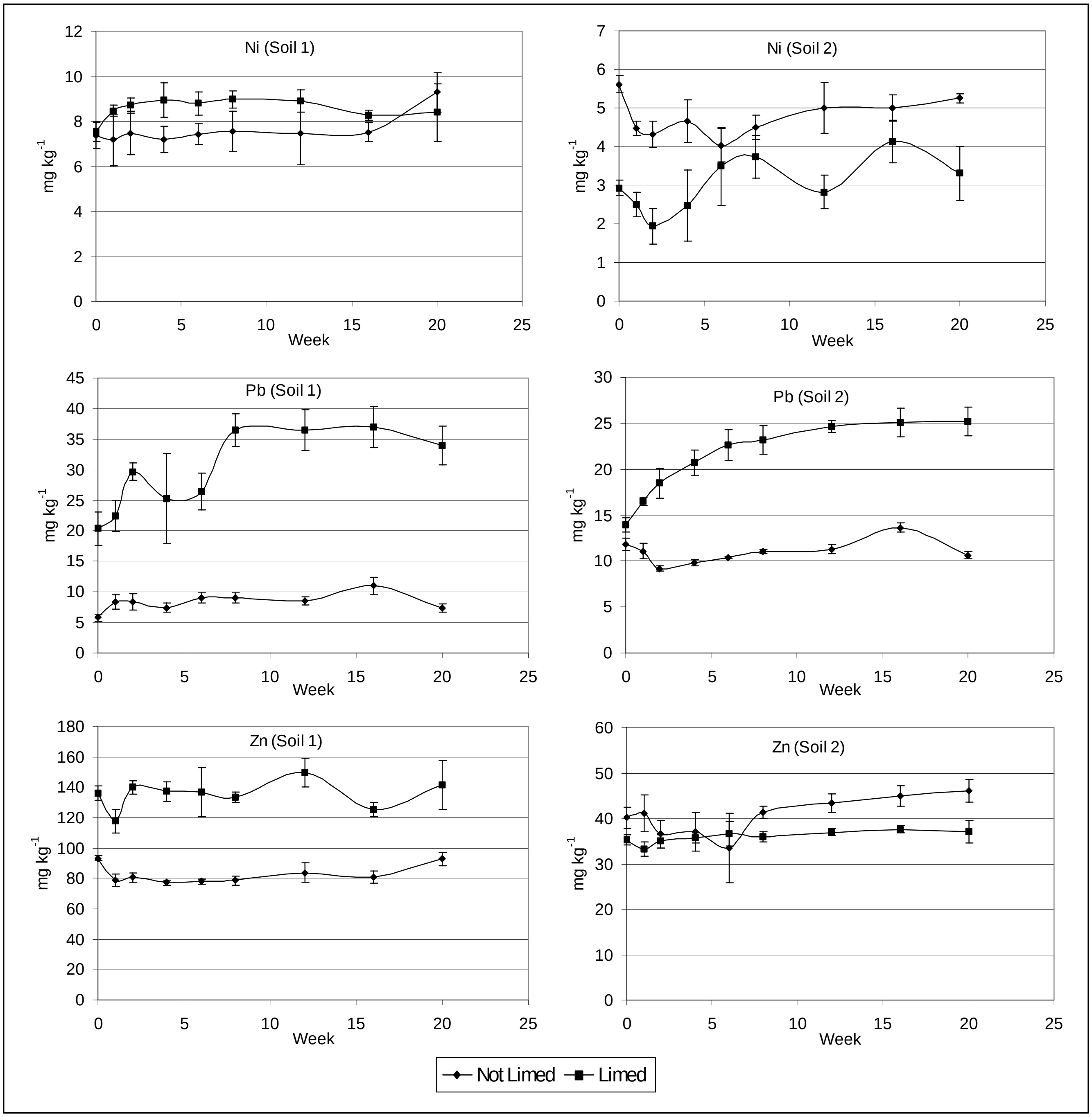

Figure 6.9. The EDTA extractability of Ni, Pb, and Zn from two soils with and without liming over a 20-week incubation period. Vertical bars indicate + and – standard deviation.

The lime reacted immediately after application and the increased EDTA extractability was observed just as rapidly. If decomposition of organic material had played a role in metal release, a slower increase in metal extractability would have been expected. As discussed earlier, significant organic material degradation was not expected due to the "age" and stability of the biosolids derived organic material.

The extracting agent EDTA is often used in heavy metal studies to determine the "potential plant-available" metal levels in soils. The motivation for its use is the correlation that is sometimes found between plant metal levels and extractable soil metal levels (Hooda et al., 1997). In the light of the increased EDTA extractability of certain metals from the two sacrificial soils after liming in this trial it might sound wise to discourage liming as a rehabilitation strategy for such soils. The NH_4NO_3 data, though, point to a very significant decrease in metal extractability after liming. The fraction extracted by the NH_4NO_3 is the immediately exchangeable fraction and therefore also the immediately plant-available fraction. In the light of these results liming can be strongly recommended as a rehabilitation strategy to decrease the immediate plant-availability as well as leachability of metals in these soils. The number of studies that have found a correlation between EDTA extractable metals and plant-uptake prompt the need for further trials to determine plant-uptake from the sacrificial soils after liming.

The incubation of the soil over 20 weeks indicates that unlimed soils have the potential to further acidify and that the metals could become more exchangeable. After liming the metals did not show an increase in NH_4NO_3 extractability over the incubation period indicating that this fraction is not likely to increase in the short-term. This aspect serves as a further motivation for the liming of sacrificial soils.