# Manganese solubility due to compaction in soils under corn and soybean

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# Abstract

Manganese has a complicated redox chemistry which plays an essential role in the uptake of soil manganese by the plants. Mn is the only element that can be both deficient and toxic in the same site during a growing season. Manganese is present in different redox forms in soils Mn(II) Mn(III) and Mn(IV), where Mn(II) (as $Mn^{2+}$) is the most available form for plants.

In this study Mn solubility in two different soils was investigated, one came from a field cultivated with corn and the other from a field cultivated with soybeans. The objectives of the study were to evaluate if extractable soil manganese was reliable on the bulk density in the soils and if there was any difference in extractable soil Mn concentrations between the two different species. It was also investigated whether the water content of the soil correlated with the plant available Mn. In a first experiment cylinder piles with soils from the two crops was set up with different bulk densities. In the cylinder piles a gradient in water content was supposed to be established. In a second experiment, the effect of bulk density was investigated with single cylinders. The manganese solubility was obtained from a sequential extraction procedure consisted of: (i) 1 M ammonium acetate (pH 7), (ii) 1 M ammonium acetate (pH 3) and (iii) 0.018 M Hydroquinol in 1 M pH 7 $NH_4OAc$.

The manganese solubility was higher in the samples with the highest bulk density. This was probably a result of a more rapid depletion of oxygen at the higher bulk densities. The Mn concentration was consistently higher in the corn than in the soybean soils. One possible explanation is that this is due to a special fungus that exists in the soil under soybean, which would be able to decrease the availability to plant hosts.

No relationship between the Mn solubility and water content was found at constant bulk density. This could be due to the fact that the water content only was measured at the end of the experiment. Practical problems in some cases when measuring the water content at high degree of saturation could have contributed to the lack of correlation.

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# 1. Introduction

Manganese is a micronutrient element that exists in the terrestrial environment and it is essential for plants and animals. It is the only element that in the same area during a growing season can be deficient for a plant or become toxic, depending on its concentration, various environmental factors, the plant specie and the type of soil (Marshner, 1995).

There has been a lot of work about Mn oxidation and reduction for a long time. Manganese has a very complex chemistry in soils and much is still to be learned about what controls Mn availability to plants. Mn is an element that is "collaborating" with the microorganisms in the oxidation of organic material (Barlett, 1988; McKenzie, 1989). Mn has three different oxidation states and both the reduction to $Mn^{2+}$ and the oxidation to $Mn^{3+}$ and $Mn^{4+}$ appear to be mediated of microorganisms. It has been found that soluble $Mn^{2+}$ added to a soil as $MnSO_4$ can become oxidized and made insoluble by microorganisms after only a few hours (Marshner, 1995).

Manganese is reduced and made very soluble when soils become saturated and reduced. In year 2003 a project was going on with soil samples from soybean and corn fields at Purdue University's Agronomy Center for Research and Education (ACRE), with the purpose to analyze plant available Mn (experiment made by Wm. C. Smith, 2003). The samples were taken during a very wet spring and some of the samples were even taken in the mud. Instead of getting high concentrations of extractable Mn that would have been suspected when a soil become saturated, the extractable Mn was lowest when the soil was wettest. To found out whether this phenomenon could be repeated an experiment was performed on new samples taken from a similar site. This was the background for my project.

The objectives of this thesis were to determine how extractable soil Manganese is related to bulk density and compaction grade of the soil and at the same time see if any difference in Mn concentrations between soils under soybean and corn existed. The aim was also to determine whether the extractable soil Mn responded to water content and the moisture in the soil.

# 2. Background

## 2.1. The chemistry of Manganese

Manganese is the eleventh most common element in the soil of the earth and it is essential for both plants and animals. Mn is a red to silver gray metal which is rather hard and that in many ways are similar to iron both in its looks and in its reactions (Lide, 2000).

The content in the lithosphere is approximately 900 mg/kg whereas the amount in the soil can vary from 20 to 3000 mg/kg with an average on 600 mg/kg. The way that it appears is in compounds of $Mn^{2+}$ and $Mn^{3+}$ (Lindsay, 1979). The factors that determine the amount and the distribution of the different compounds are parent materials, soil forming processes and the fluctuations in the water table during the year. Another factor is biocycling that makes the manganese to accumulate in the surface soils. In the sand and silt fractions biocycling and furthermore fertilization makes the Mn appears in nodules and surface coatings (Mc Kenzie, 1979).

The mineralogy of manganese is complicated because it appears in several different forms of oxides and hydroxides. Mn exists of three oxidation states in the aqueous environment of soils and plants. These states are $Mn^{2+}$, $Mn^{3+}$, and $Mn^{4+}$ (Figure 1). $Mn^{2+}$ is soluble and taken up by plants from the soil solution as the most dominant state of Mn in plants. $Mn^{3+}$ is insoluble and unstable in the soil solution and therefore not available to plants. It is instead often spontaneously transformed into $Mn^{2+}$ or $Mn^{4+}$, dependent on redox potential. $Mn^{4+}$ is also insoluble and precipitates into various Mn oxides and hydroxides, which means that it is physiologically unavailable to plants (Marshner, 1995).
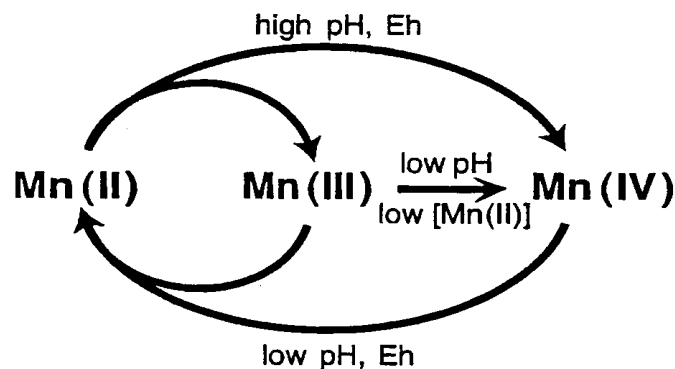


Figure 1. The cycle of the oxidation states of manganese found in nature (Tebo et al., 2004).

Thermodynamically the $Mn^{2+}$ is stable when $O_2$ is depleted and the pH is low. The opposite environment with presence of oxygen and higher pH favor $Mn^{3+}$ and $Mn^{4+}$. They occur as insoluble Mn oxyhydrooxides and oxides (Kleiwicki and Morgan, 1998, 1999).

There are a large number of oxides and hydroxides of manganese but the most common one of crystalline Mn-oxide in soils are Birnessite, Vernadite, Lithiophorite and Hollandite. The minerals appear as coatings on soil particles but even in cracks and veins of a different mineral. They are often mixed with Fe-oxides or other soil particles in nodules (Dixon and Weed, 1989).

## 2.2. Redox reactions and pE-pH diagrams

A chemical reaction in which electrons are transferred from one species to another species is called redox reaction. Redox is shortening for reactions that contain oxidation of one element and reduction of another element. One example is when $MnO_2$ in solid form are reduced to $Mn^{2+}$ in the reduction half reaction:

½ $MnO_2$ (s) + 2$H^+$ (aq) + $e^-$ → ½ $Mn^{2+}$ (aq) + $H_2O$ (l)          Eh° = 1.23 V (Reaction 1)
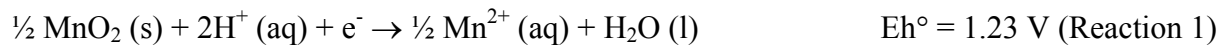
This reaction can then be combined with an oxidation half reaction and the new reaction is a redox reaction (Sposito, 1989). Each half-reaction has a pE that is the negative logarithm of the free electron activity, pE = -log ($e^-$). This is also called the redox intensity and it measures the relative tendency that solutions have to accept electrons. Solutions that tend to donate electrons to other species in the solution have a low pE (high electron activity) and are reducing. The opposite, that a solution has a tendency for accepting electrons happens in the oxidizing solutions (McBride, 1994). The relation between the Standard Electrode Potential, Eh°, and pE is:

$$pE = Eh \text{ (Volts)} / 0.059 \qquad \text{(Equation 1)}$$

The mineral that is most stable under well oxidized circumstances is Pyrolusite, β-$MnO_2$. There are also other minerals as Birnessite, Manganite and Hausmannite that can be found in the soil environment. One way to evaluate the stability of different Mn forms is by constructing a stability diagram or pE-pH diagram. As an example, the stability line for $MnO_2$ (s) can be obtained from reaction 1 above. The Nernst Equation (McBride, 1994) gives the electrode potential:

$$E_h = E_h° - \frac{0.059}{2} \log \frac{(Mn^{2+})}{(H^+)^4} \qquad \text{(Equation 2)}$$

In a logarithmised form it can be rewritten:

$$E_h = 1.23 – 0.0295 \log (Mn^{2+}) – 0.118 \text{ pH} \qquad \text{(Equation 3)}$$

If we write this in terms of pE according to Equation 1 the relationship with pH is:

$$pE = 20.8 – 0.5 \log (Mn^{2+}) – 2 \text{ pH} \qquad \text{(Equation 4)}$$

If then assuming that the $Mn^{2+}$ activity has a certain value the corresponding pE can be calculated and the relationship be drawn in a pE – pH axis system also called stability diagram. The most common and simple pE –pH diagram with manganese are the one showed in Figure 2. This shows at which pH and pE different forms are stable. Soluble $Mn^{2+}$ is stable when pH is <8. Above pH 8 $Mn^{2+}$ will precipitate as solid $MnCO_3$ if there are reducing conditions (McBride, 1994).

The lower line in the Mn diagram is pH + pE = 0, which stands for the reduction limit of the protons. In turn the upper line is pH + pE = 20.78. This is the limit for the forming of oxygen from water at one atmospheric pressure (Marshner, 1995).

The chemistry of manganese has many similarities with iron. One of the most observable is the high solubility of the reduced species $Mn^{2+}$ and $Fe^{2+}$ in comparison to the oxidized species

$Mn^{3+}/Mn^{4+}$ and $Fe^{3+}$, which will precipitate as oxides, hydroxide and oxyhydrooxide minerals (Sposito, 1989).
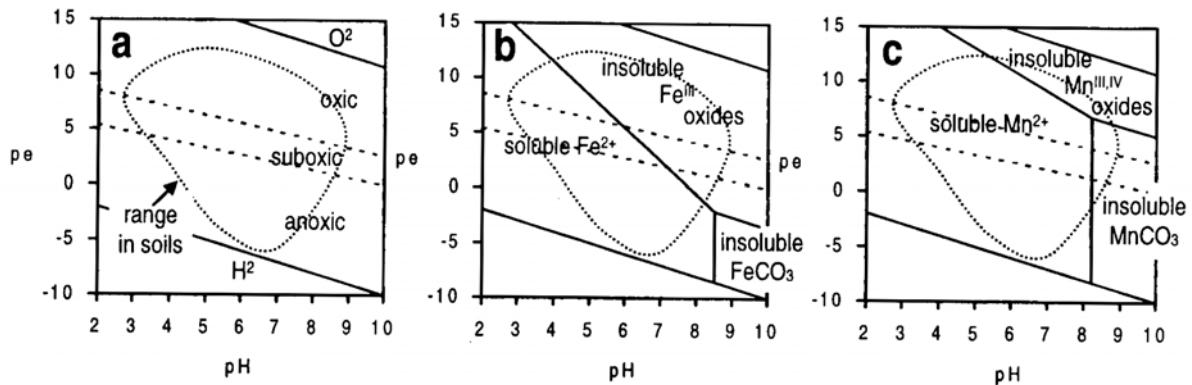


Figure 2a) Stability field diagram of the range in soils with oxic -anoxic systems. b) Stability field diagram or even called pE – pH diagram showing the soluble and insoluble Fe forms. c) pE – pH diagram with manganese (Sposito, 1989).

Even if there are similaries there are differences as well which can be showed in the simplified pE–pH diagrams of iron and manganese. If you compare Mn with Fe, the insoluble $Fe^{3+}$-oxide phases are thermodynamically favored over the pH-range in soils with a pH around 5-8 when there are oxic conditions, which means that oxygen is present. On the other hand the reduction of Fe to soluble $Fe^{2+}$ requires suboxic or anoxic conditions. In contrast insoluble Mn-oxide minerals are stable only at the highest pE's and pH's and soluble $Mn^{2+}$ is thermodynamically stable even under oxic conditions. In general, $Fe^{2+}$ spontaneous oxidizes to $Fe^{3+}$ in the presence of $O_2$ at pH values below 3 (Cornell and Schwertmann, 1996), while Mn in the same situation needs a pH around 8.5 - 9.0 to get a spontaneously oxidation. At pH values around neutral the kinetics of Mn redox reactions can be quite slow and $Mn^{2+}$ ions can persist in solution even though thermodynamically thoughts would suggest that Mn should oxidize (McBride, 1994).

Manganese is an element that oxidizes more easily in a strong alkaline environment if air is available. Mn that are oxidized in the biologically way takes part because of a various number of bacteria and fungi (McKenzie, 1979).
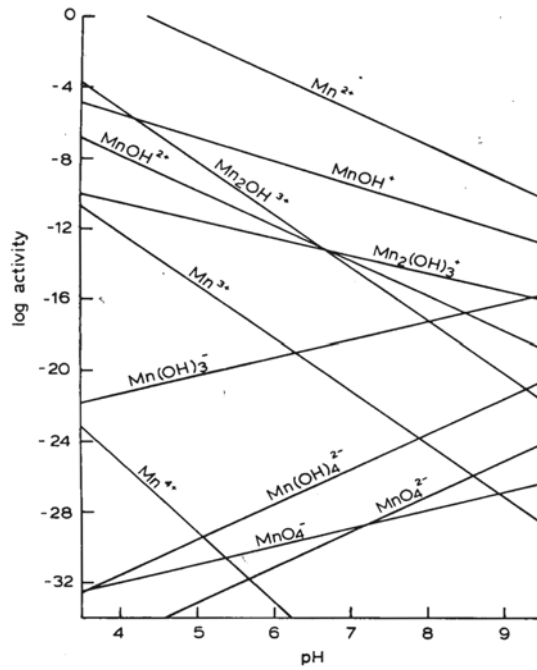
Figure 3. Manganese and its solution species in soils in equilibrium with Manganite and Pyrolusite at pE + pH of 16.62 (Lindsay, 1979).

In Figure 3, Manganese and the formation of many solution species is showed at pE + pH = 16.62 at equilibrium with Manganite and Pyrolusite. As illustrated, $Mn^{2+}$ is the predominant species in the solution. All the other hydrolysis species of Mn are of less importance. At this redox the moves to lower redox can be showed along the Manganite equilibrium lines and if moves to higher redox are made they can be showed along the Pyrolusite equilibrium line.
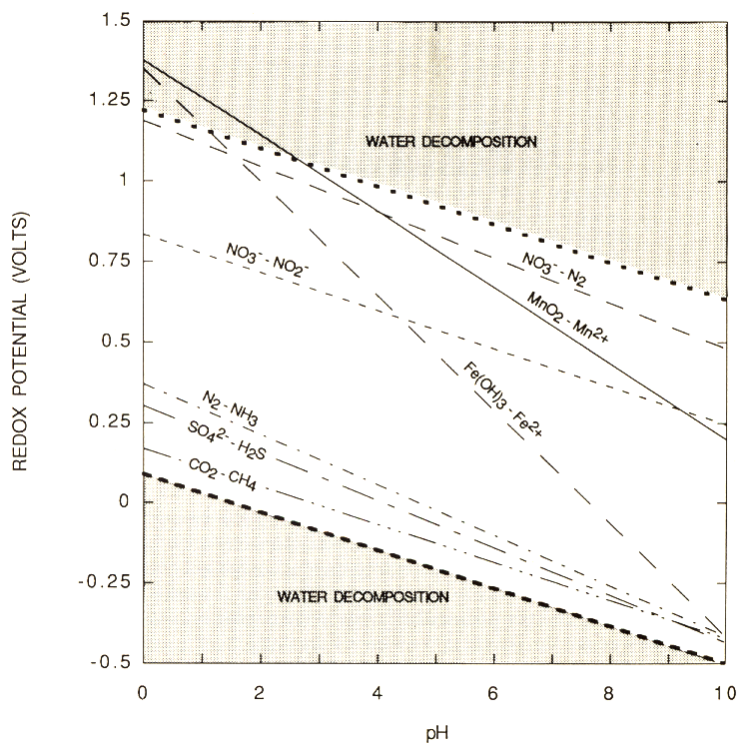


Figure 4. Half-cell reactions of important elements in water and the relationship between the redox potential, $E_h$, and pH. The bold dotted lines in the diagram refer to when water is oxidized to $O_2$ (above) and reduced to $H_2$ (under).

Figure 4. shows the stability of the reducing or the oxidizing species in a redox couple for not just manganese, but for nitrogen, iron, sulphur and carbon. The figure shows that the sequence for reduction at intermediate pH values (4-6) are: $NO_3^-$, $MnO_2$, $Fe(OH)_3$ and $SO_4^{2-}$. Thus, it is just $NO_3^-$ that is being reduced more easily than $MnO_2$.

### 2.3. Plant physiological aspects on Manganese

Manganese is an essential element for the plants since it is a cofactor for some enzymes. The $Mn^{2+}$ activates the enzymes in the cells of the plants. For example it is a cofactor that is very important as a Mn-prot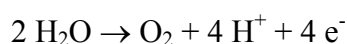ein in the photo system II governing the oxidation of water to oxygen (Marshner, 1995). The water is oxidized to oxygen according to the following reaction (Yachandra et al, 1996):

$$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$$

In the reaction four electrons are removed from two molecules of water to one oxygen molecule. This is an energy consuming reaction because water is a very stable molecule. This is the only biochemical system that carries out this reaction (Taiz and Zeiger, 1998). The oxygen evolution starts with a flashing light and something that is called the S state mechanism. It is five increasingly oxidized states in the water oxidizing system, $S_0 - S_4$ and they appear when a sample of dark-adapted chloroplasts is exposed to a serie of flashes (Kok et al., 1970). Here, Mn is involved in a protein called D1 that stores positive charges. The structure is a cluster of four Mn atoms that are linked together with amino acids, oxygen, chloride and calcium (Taiz and Zeiger, 1998).

Manganese is the only essential micronutrient that can be deficient and toxic to plants in the same soil at different times during the growing season. The major symptom of Mn-deficiency is chlorosis that is intervenous together with some small necrotic spots (Taiz and Zeiger, 1998). It is no special time during the plant growth period when the chlorosis appears; it can appear in both young and old leaves. It mostly depends on the plant species and the rate of growth. A high pH, above 6.5, leads in most cases to Mn deficiency, especially on sandy soils. The Mn toxicity has its most diagnostic feature in darkening of leave veins that mostly appears in older foliage. The darkening is due to an accumulation of dark crystals of insoluble Mn in tissues or in veins. The toxicity mostly occurs at low pH (Schubert, 1992).

### 2.4. Analytical methods

The method used in this thesis was a sequential extraction procedure outlined by Guest et al. (2002). The sequence is designed to extract increasingly less soluble fraction of manganese from the samples. There were three different steps containing 1 M $NH_4OAc$ at pH 7 that mainly extracts water soluble and exchangeable $Mn^{2+}$. The soluble Mn contains both free cations and cations complexed with organic and inorganic ligands. The exchangeable Mn is the cations that are electrostatically bound mostly to clay minerals and organic matter (Stevenson, 1986). $Mn^{2+}$ is the form of Mn that is available for plants. The second step is an extraction with 1 M $NH_4OAc$ at pH 3 which extracts an acid soluble $Mn^{2+}$ fraction. The third step is an extraction with 0.018 M hydroquinol in 1 M $NH_4OAc$ at pH 7 that extracts easily reducible $Mn^{3+}$ and $Mn^{4+}$ oxides. To determine the Mn concentration in the extract Atomic Absorption Spectroscopy (AAS) can be one alternative.

There are two methods that are used with the Atomic Absorption Spectrophotometer, flame or electrothermal, for example graphite furnace. When analyzing Manganese in soil and plants the flame method is the most common method. The AA Spectrophotometer uses the absorption of

light to measure the concentration in the sample. It contains a hallow cathode, which is a type of discharge lamp that produce narrow emission from atomic species. In this case there is a lamp which emits light with wavelength that is typical for Mn.

While the samples are liquid the ions or the molecules must be dissolved and vaporized in a gas flame to be determined. The extract is sucked into the gas flame and in the heat the sample is decomposed. When the atoms absorbs light the incoming energy excites electrons to a higher energy level, this depends of the wavelength. The amount of light that the sample absorbs is proportional to the concentration of the element in the sample. This means that the more light a sample absorbs the more Mn the sample contains.
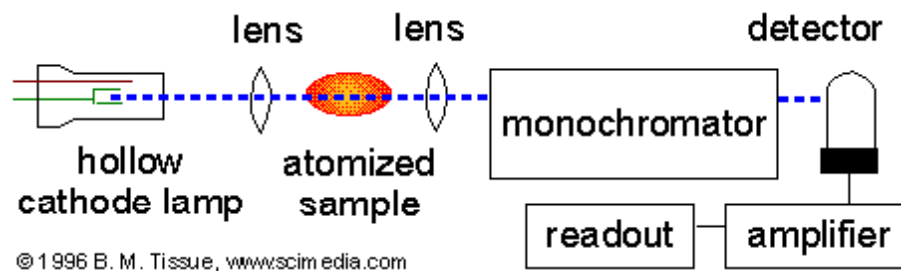


Figure 5. A schematic picture over an Atomic Adsorption Spectroscopy machine.

To identify manganese minerals in soils one of the primary techniques used by mineralogists is Powder X-ray diffraction. The data is represented in a collection of single-phase X-ray powder diffraction patterns for the three most intense D values. In form of interplanar spacings (D) for the most common Mn oxides and hydroxides and relative intensities (I/Io) the mineral and its name can be determined (McKenzie, 1979).

Another method with X-ray is X-ray Absorption Near Edge structure Spectroscopy, XANES. This method can be used also for the oxides that have lower concentrations or lower crystallinity that cannot be analyzed with powder X-ray diffraction (Schulze, 1995). This is an element specified method that makes it capable of probing the local environment of manganese and it does not require any special sample preparation. Theoretical multiple scattering calculations are compared with experimental XANES spectra in order to determine the geometrical arrangement of the atoms surrounding the absorbing atom (Koningsberger and Prins, 1998). Interpretation of XANES spectra is complicated but it is in wide use for many studies of complex, disordered and heterogeneous systems (Schulze et al., 1995).

One study made by Guest et al (2002) showed that XANES spectroscopy can recognize changes in Mn oxidation state that not shows up in wet-chemical extractions.

In some cases Infrared Spectroscopy (IR), a more simple method, can be used to determine a mineral in soils. This sort of spectroscopy is sensitive to amorphous components and also to more crystalline materials with short range order. Because of this data about minerals can be detected with IR that is not possible to detect with X-ray methods (McKenzie, 1979).

## *2.5. Metal and radionuclide sorption by Mn Oxides*

Manganese oxides are an important component in soils and sediments. Metals like copper, cadmium, zinc, nickel, uranium, mercury and lead can be strongly adsorbed by Mn oxides or be incorporated in the soil (Tebo et al., 2004).

With a model for cation binding called SCAMP, Surface Chemistry Assemblage Model for particles, the capacity in metal-binding in manganese oxides, iron oxides and aluminum oxides were compared. The strength of the different phases increased in the following order: aluminum oxide < ferric oxide < manganese oxide. The Mn oxides are the oxides with the strongest metal binding ability, due to its reactive hydroxyl group. One factor that plays an important role in the metal binding is the presence of organic matter, also called humic substances, which largely determines the surface charge on the oxides (Lofts and Tipping, 1998).

# 3. Materials and Method

### 3.1 Soil Samples

Soil samples were collected from two different fields 4 kilometers northwest of Purdue University, West Lafayette, Indiana. The fields were approximately 300 × 600 m each. One of the fields had been cultivated with corn (*Zea mays* L.) and the other one had been cultivated with soybean (*Glycine Max* (L.) Merr.). The fields were chosen because they had different crops which might have affected the soil properties differently.

The soil is mapped as a Starks - Fincastle complex, two soils that are essentially the same, but the Starks series has some water-worked material at the base of the pedon, while there is glacial till at the base of the Fincastle series. The soil is a brown silt loam which is somewhat poorly drained with a high available water capacity. The topsoil has a base saturation of 52 %, a pH at 6.2 and the amount of organic carbon is 0.87 % (Ziegler and Wolf, 2004).

In each field, samples were collected from six locations, chosen randomly. Each sample consisted of the topsoil, approximately down to 20 cm under the surface. The soil from the fields was dug up with a spade and put in two buckets covered with tight lids. The soil was stored field moist, in order to minimize changes in redox conditions.

### 3.2. Experiment 1: Mn Solubility in a water potential gradient

To see the different behavior of the manganese due to bulk density and at the same time due to the water content a cylinder pile experiment was set up. Before using the soil samples in the lab the soil was sieved through a 2-mm sieve, to get a homogenized sample. Additional water was added to the soils to get a little bit more sticky soil, so it could easily be packed in cylinders of rigid plastic.

The soil was then put into the small plastic cylinders 1 cm in height, 4 cm in diameter and with a volume of approximately 13 cm$^3$. The rings were made by cutting a plastic pipe in one cm pieces and then polished with very fine sandpaper to get a smooth surface for fitting on top of each other. The size of the cylinders was chosen to make the soil stuck well in the cylinders even if they were moved. The plastic cylinders were packed with soil with a special bulk density determined for each cylinder pile. The weight of soil in each cylinder was calculated from the moisture content together with the bulk density.

The soil was compacted using a piece of rigid plastic having exactly the diameter of the cylinders. Cylinder piles were made in duplicates of each bulk density in both soil under corn and soil under soybean. (See Table 1 for the different bulk densities obtained).

The cylinder pile was made of 15 rings stacked on each other into a pile and patched together with tape. The number of rings was decided with help from the soil physic professor, Eileen Kladivko, Purdue University. The height of 15 rings, approximately 15 cm, should be enough to get a gradient in the cylinder pile from the bottom to the top. To improve the connection between the soils in the different rings the soil was scratched so it got a rough surface. The cylinder pile of the rings was put into a small bucket and water was added slowly from underneath until the three lowest rings were covered with water.

The soil samples were left for six days at room temperature, 22 C°, in the bucket covered with Parafilm. Small holes were made in the film to let in some air. After the incubation the cylinders were taken apart and analyzed separately. From each cylinder a 10-gram aliquot was

Table 1. Cylinder piles made from soil under corn under soybean with each bulk density.

| Cylinder pile | Species | Bulk density (g/cm$^3$) |
|---|---|---|
| 1 | Corn | 1.5 |
| 2 | Corn | 1.5 |
| 3 | Corn | 1.3 |
| 4 | Corn | 1.3 |
| 5 | Soybean | 1.4 |
| 6 | Soybean | 1.4 |
| 7 | Soybean | 1.3 |
| 8 | soybean | 1.3 |

weighed, dried at 105º C for 24 hours and weighed again to determine water content. Five grams of soil from each segment was used for an immediate analysis of Mn (see above).

The water contents of the soils were obtained by drying at 105º C for 24 hours and calculated as:

$$\text{Gravimetric moisture content (\%)} = \frac{((\text{can} + \text{soil})-(\text{can} + \text{oven dry soil}))\ (\text{g})}{((\text{can} + \text{oven dry soil}) - \text{can})(\text{g})}$$

The pH of the soils was measured by adding water to obtain a 1:2 soil to solution ratio. The soil suspensions were shaken for five minutes before pH was measured with a pH-meter.

### 3.3. Experiment 2: Mn solubility as a function of bulk density
An investigation was also made to see if there was any correlation between the extractible Mn concentration in the soil and the degree of compaction, measured as bulk density. Instead of using the cylinder piles duplicates were made of one cylinder with soil sample that were put into the bottom of a box with a covering lid. Between the box and the lid a small plastic tube was set to let in some air. Both soils from under corn and soils from under soybean were used. The bulk densities obtained were:

0.6; 0,8; 1,0; 1,2; 1,3; 1,4; 1,6; 1,7; 1,8; 1,9 g /cm$^3$

All soil samples of soybean had the same water content at 26 volume-percent when they were put in the box. The corn samples had a water content of 27 volume-percent. It was rather hard to fit the soil samples with high bulk density in the cylinders. Because the soil was as moist as it was from the beginning it became very elastic, especially the soybean soil and it almost had to be forced out of the cylinders. The rings were incubated for six days in the box before 5 grams of every sample was extracted with the sequential extraction procedure outlined by Guest et al. (2002). The water content was measured again after the incubation time, but unfortunately it had decreased in all the cylinders. The new calculation of the water content ranged between 10-15 %.

### 3.4. Sequential extraction procedure
Manganese was analyzed using the sequential extraction procedure outlined by Guest et al. (2002), to represent the range of plant available Mn.

- 1 M NH$_4$OAc at pH 7 that mainly extracts water soluble and exchangeable Mn$^{2+}$. Mn$^{2+}$ is the form of manganese that is available for plants.

- 1 M NH$_4$OAc at pH 3 which extracts an acid soluble Mn$^{2+}$ fraction.
- 0.018 M hydroquinol in 1 M NH$_4$OAc at pH 7 that extracts easily reducible Mn$^{3+}$ and Mn$^{4+}$ oxides.

When Mn is present at toxic levels an increase in the first fraction can be anticipated. This occurs particularly in acid soils, lacking oxygen due to e.g. flooding. The exchangeable Mn in almost all soils can be seen as the readily available (plant available) Mn. In the third step the easily reducible Mn can be seen as the total Mn of the soil. A large part of the Mn present as oxides and hydroxides are included in this group (Adams, 1965).

The procedure for preparing solutions for the sequential extraction procedure was as follows: 1 M $NH_4OAc$ solution at pH 7 was prepared by stirring 77.08 g of $NH_4OAc$ in 1 L of deionized water. A pH-meter was used to register the pH; to increase the pH $NH_4OH$ was used and to decrease the pH acetic acid was used. To prepare the solution with 1 M $NH_4OAc$ at pH 3 57.5 mL glacial acetic acid was mixed with deionized water to get a total volume of 1 L. Initially the pH was around 2.4 and was then adjusted to 3 by the addition of $NH_4OH$. To prepare the third solution 1.98 g of 0.2 % hydroquinol was mixed with 1 L deionized water. This solution is light sensitive so a bottle of dark glass with aluminum foil was used during the preparation, which should be fresh for the day. The solution had to be stirred for half an hour to be completely dissolved.

In the sequential extraction procedure, a moist aliquot of 5-gram was taken from each plastic cylinder after the incubation time of six days. It was weighed into a 50-mL centrifuge tube and shaken 30 minutes in a reciprocating shaker, together with 40 mL of the first extractant at pH 7. The soil sample was then centrifuged for 5 minutes at 1000 rpm. The solution was filtered through a Whatmann filter paper and after removing the solution from the supernatant, another 20 mL of the extractant was added and ones more the sample was centrifuged for 5 minutes.
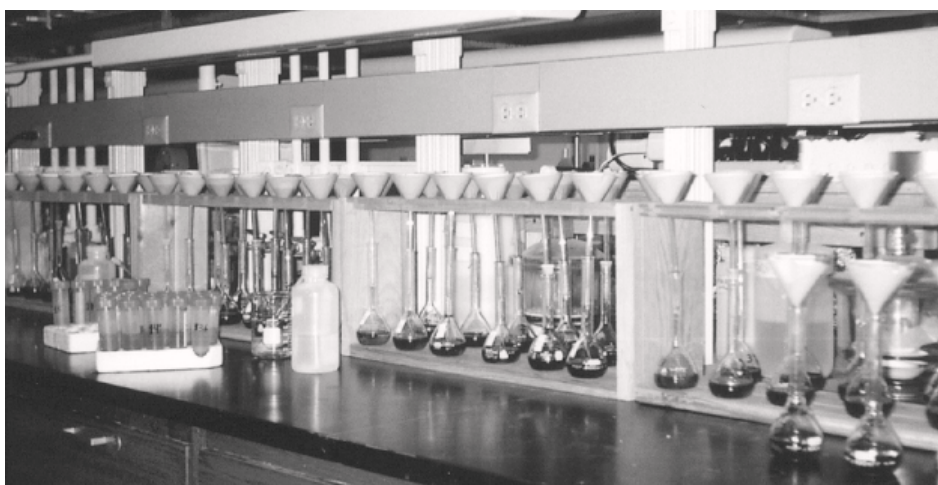


Figure 6. From every soil sample and extraction the solution was filtered into volumetric flasks a 100 mL.

The solution was filtered into a volumetric flask at 100 mL. The filter paper and the funnels were washed with 20 mL deionized water and the flasks were finally filled up with more deionized water to make up total volume. The residual soil was further used in the next two steps with 1 M $NH_4OAc$ at pH 3 and 0.018 M hydroquinol in 1 M $NH_4OAc$ at pH 7 of the sequential extraction procedure. For each tube a vortex mixer was used between the steps to loosen the cake of soil. The extracts were stored in plastic bottles, not longer than 24 hours before analysis using Atomic Absorption Spectroscopy. If left longer the extract could change in manganese concentrations.

### 3.5. Analysis of Mn in extracts

The manganese concentrations in the extracts were determined using Atomic Absorption Spectroscopy. Before the extracts were analyzed the bottles were shaken to get a homogeneous solution.

Standard solutions were used to calibrate the machine at each time a cylinder pile was analyzed. The six standards were made from a 100 mg/L Mn standard solution diluted with a solution of 60 % 1 M NH$_4$OAc solution at pH 7 and 40 % deionized water to match the ionic composition of the samples. Then the standards were made from 1 to 6 mg/l in volumetric flasks of 100 mL. For every turn of analyzing 15 samples, one cylinder pile, a check sample was analyzed at the same time to check for instrumental drift.

## 4. Results & Discussion

### 4.1. Mn concentration due to compaction in Experiment 1

The result shows that in both the cylinder piles with soil under corn and the cylinder piles with soil under soybean could be seen an effect of bulk density on the extractable manganese concentrations. A higher bulk density gave higher concentrations of extractable Mn in the soil samples (Figure 7). Cylinder piles number 1 and 2, with a bulk density of 1.5 g/cm$^3$, reached twice the concentration of that obtained in cylinder piles 3 and 4 with a bulk density of 1.3 g/cm$^3$. In the cylinder piles with soybean the effect of bulk density had the same effect. This suggests that the compaction grade strongly affects the amount of plant available Mn. The graphs in Figure 7 show the first extractant (pH 7) that is the most sensitive, and are believed to be best related to the plant available fraction (Guest et al., 2002).
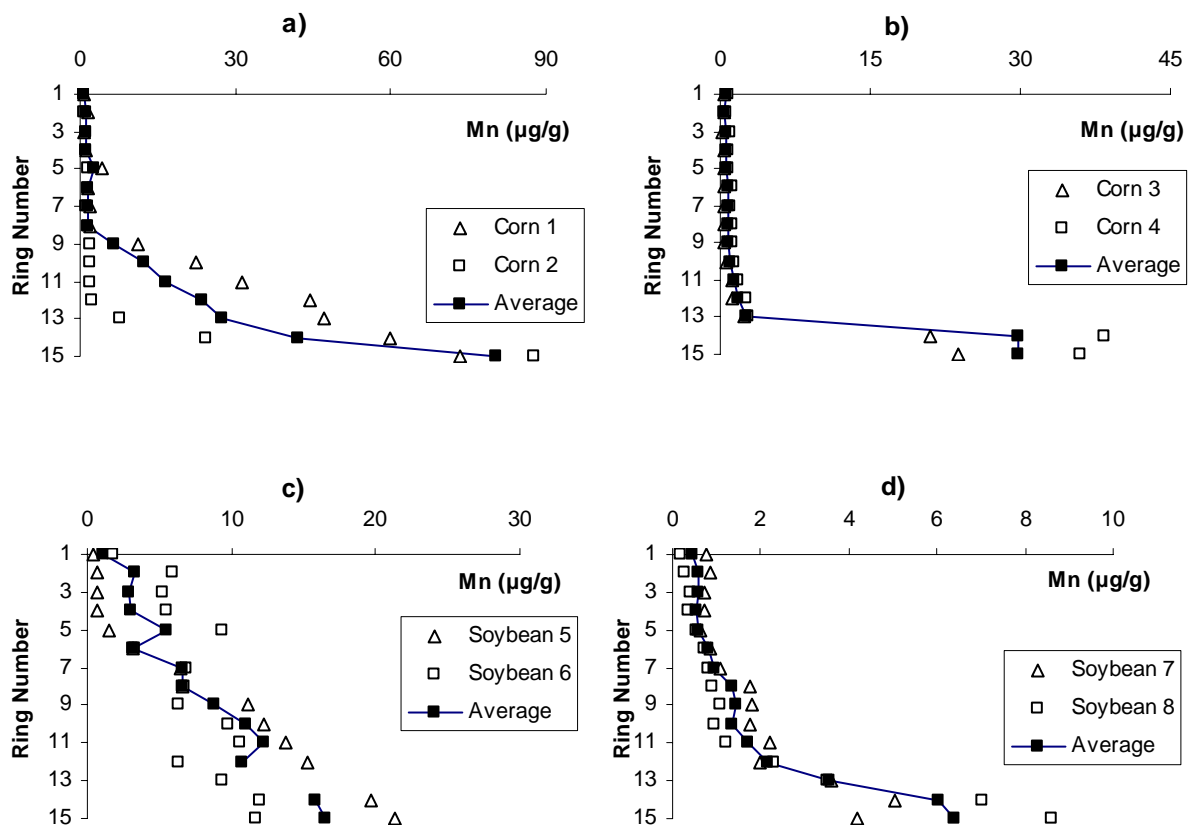


Figure 7. Both cylinder piles under corn and cylinder piles under soybean show that there is an increase of manganese with increasing bulk density in extraction with NH$_4$OAc at pH 7.The Mn concentration also increases in the cylinders that have been saturated with water in the bottom of the piles.  a) Cylinder piles 1 and 2 of corn with the bulk density 1.5 g/cm$^3$. b) Cylinder piles 3 and 4 under corn, bulk density 1.3 g/cm$^3$. c) Cylinder piles 5 and 6 under soybean, bulk density 1.4 g/cm$^3$. d) Cylinder piles 7 and 8 under soybean, bulk density 1.3 g/cm$^3$.
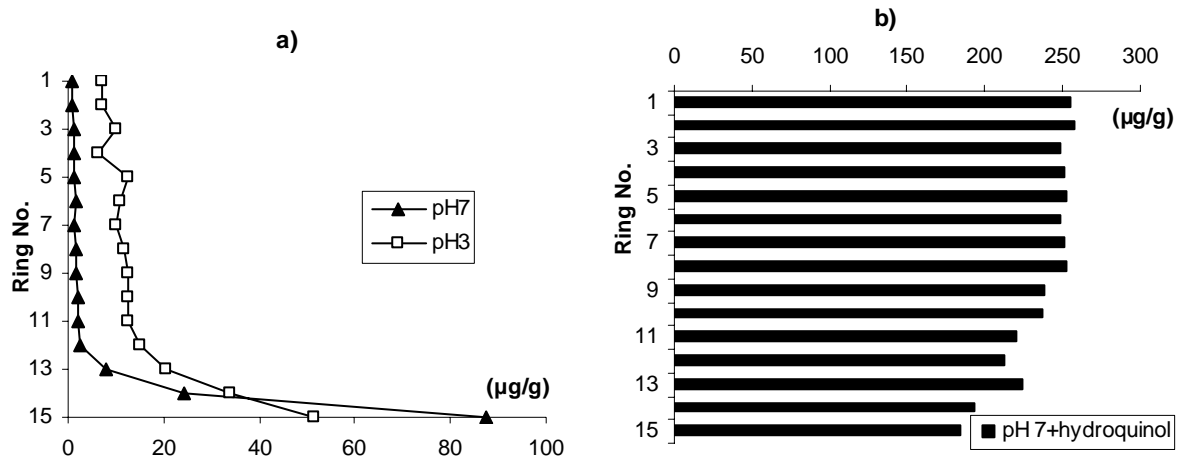
Figure 8a). Extractible Mn in cylinder pile 2 with soil under corn and bulk density 1.5 g/cm$^3$. pH 7 and pH 3 are shown in the diagram with their different concentrations (µg/g), b). The third extraction with pH 7 plus hydroquinol in cylinder pile 3 under corn. The graph is reversed with comparison to the graphs in figure 7, with pH 7 and pH 3.

The manganese concentrations were lower in the first extraction at pH 7 than at pH 3 (Figure 8a). When the pH was lowered from 7 to 3 it probably resulted in a partial reduction of $Mn^{4+}$ to $Mn^{3+}$ (Guest et al., 2002) which explained the lower concentrations at pH 3 extraction, but the two graphs still followed each other. In the third extraction with the hydroquinol at pH 7 (Figure 8b), the graphs were always the opposite; it decreased, instead of increased with depth. This is due to the fact that a larger part of the Mn already had been extracted with the weaker extractants at the lower depths. The hydroquinol extracts the easily reducible $Mn^{3+}$ and $Mn^{4+}$ oxides and can be seen as the total amount of all Mn (Adams, 1965). Thus, only a small fraction of Mn is soluble in these soils at normal conditions. All data from Experiment 1 are presented in Appendices 1-4.

### 4.2. Mn concentration due to compaction in Experiment 2

Also in the second experiment, performed with only one cylinder, one could see a tendency of increasing concentration with increasing bulk density. The effect is clearer in the NH$_4$OAc extractable fraction at pH 7 (Figure 9a) than at pH 3 (Figure 9b). The soil with higher bulk density (1.6 g/cm$^3$-1.9 g/cm$^3$) was really hard to fit in the cylinders because the soil got very elastic with the added water.
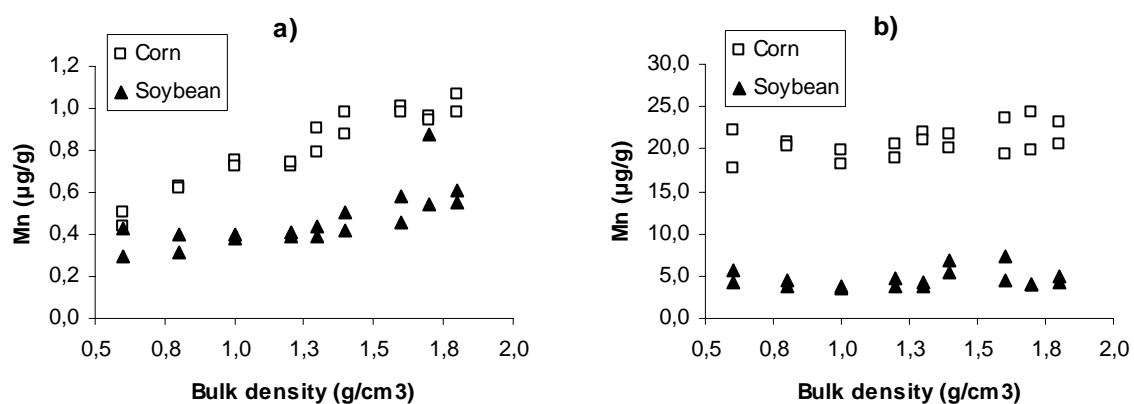


Figure 9a). The increase of the extractible Mn concentration in pH 7 due to the increased bulk density g/cm$^3$ and b) the increase of the extractible Mn concentration in pH 3 due to the increased bulk density g/cm$^3$.

A classic effect that shows how compaction influence on the manganese availability for the plant is in a field there the tire tracks from a sprayer or a fertilizer spreader showing up as green strips in the faded green-yellow crop. The compaction from the vehicle has created conditions there just enough Mn is released to keep the crop from showing deficiency (Taiz and Zaiger, 1998).

### 4.3. Mn concentration due to kind of corn

Both experiments clearly showed that the amount of extractable manganese was higher under corn than under soybean (Figures 7, 9 and 10; Table 2). This shows the impact of the current crop or the impact of the crop which has been cultivated on the soil. In table 2 below there is a comparison between the cylinder piles and the range of Mn concentration in soil samples under corn and soil samples under soybean in the extraction with $NH_4OAc$ at pH 7, which shows the differences in amount.

That manganese is more plant available under corn than under soybean has also been shown in the work from William C. Smith, 2003 (personal communication). A three months study was made to evaluate the effects of crop rotation and soil on available soil Mn. The results showed that samples analyzed from soil under corn were found to have a higher Mn concentration than in the samples with soil under soybean and that the current crop had a clear impact on the Mn availability. There are experiments that have showed that this is depending on a special fungus that exists in the soil under soybean. There is also evidence that Mn deficiency is more common in soybean than in corn. The availability of soil Mn correlates with the severity of some important fungal diseases.

The same result with less plant available manganese under soybean than under corn can be seen in analyzes done by William Smith, in year 2003 (personal communication). An investigation about an accumulation and oxidation of Mn by fungi at the resolution of individual hyphae has been made by Thompson et al. (2004). Mn is the only element that shows close cooperation with the fungal hyphae. All other elements (Fe, Zn, Cu, Cr and As) were randomly distributed in the investigation, which shows the possibility of a network between Mn and fungal hyphae (Thompson et al., 2002).

Further evidence for a biological explanation for the difference between the crops is that the corn soil had a higher extractable concentration of Mn despite higher pH and a lower "total" concentration of Mn (see Appendices 1-5)

Table: 2 Concentrations in Mn µ/g in soil under corn and in soil under soybean in $NH_4OAc$ at pH 7. All data are presented in Appendices 1-5.

|  | Bulk density g/cm³ | Range [Mn] µg/g |
|---|---|---|
| **Corn** | 1.5 | 73 - 87 |
|  | 1.3 | 24 - 38 |
| **Soybean** | 1.4 | 12 - 21 |
|  | 1.3 | 5 - 9 |
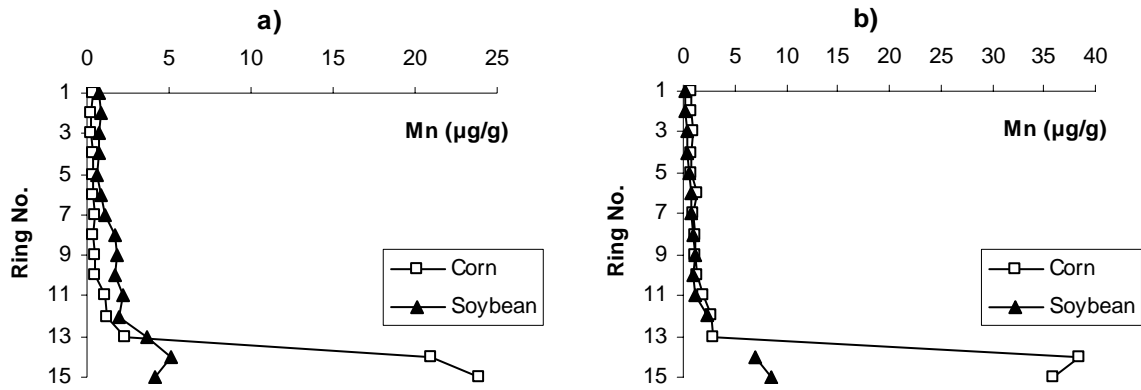
Figure 10. An example that shows how the concentration amount of manganese differ under dissimilar crops. Here in a) cylinder pile 3 under corn and cylinder pile 7 under soybean and in b) cylinder pile 5 under corn and cylinder pile 8 under soybean both with 1.3 g/cm³.

### *4.4. Mn concentration due to water content (Experiment 1 & 2)*

The idea behind the experimental set-up in Experiment 1 was to establish a water potential gradient in the cylinder pile, with the highest water content in the bottom of the cylinder pile. Unfortunately it was very hard to obtain such a gradient (Appendices 1-4). Probably some air got stacked in between the soil particles and therefore affected the water content in the cylinders.

Another reason could be that the soil was unevenly packed in the rings despite the great effort to get it evenly. The lack of distinct gradients in water content is in contrast to the distinct gradient in Mn solubility obtained (Figure 7). Thus, no correlation between the water content and the available plant Mn could be seen (Figure 11). This is surprising since water content is believed to be the key variable that limits diffusion of $O_2$, thus controlling the redox potential (Turner and Patrick, 1968). One contributing factor could be that there were practical problems in some cases when measuring the water content at high degree of saturation.

Another possible explanation could be that the water content measured just reflected to situation at the end of the experiment (after 6 days), i.e. no information on the dynamics is available. Since $O_2$ depletion takes some time (it has to be consumed by the micro organisms) the duration of a certain state ought to be an important factor (Turner and Patrick, 1968). With the information available, Mn solubility itself is probably the indicator of the redox status in the experiment. Judging from that indicator, a clear gradient in redox was obtained in the cylinder piles.
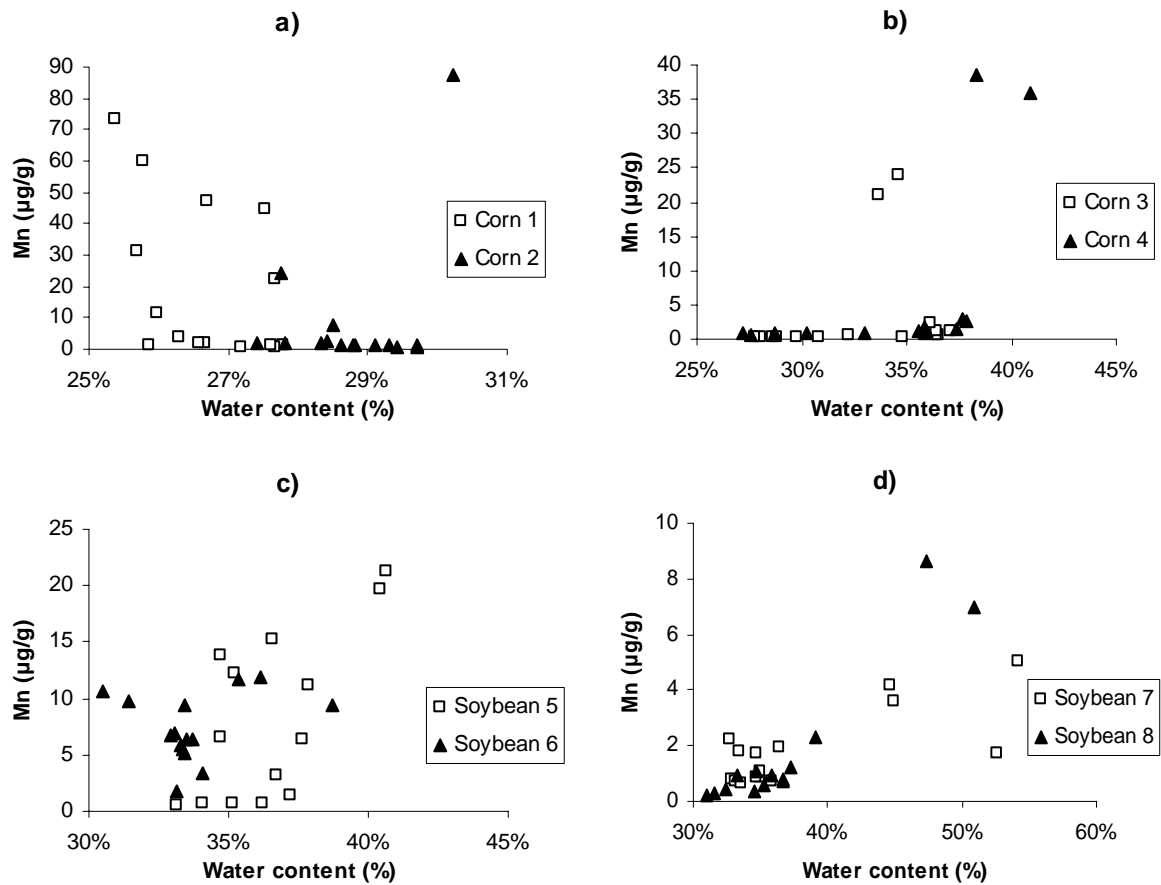
Figure 11. The data from the water content is plotted against the manganese concentration. All together the figures show that there is no true correlation between these two factors. a) Cylinder piles 1 and 2 under corn, 1.5 g/cm$^3$, b) Cylinder piles 3 and 4 under corn, 1.3 g/cm$^3$, c) Cylinder piles 5 and 6 under soybean, 1.4 g/cm$^3$, d) Cylinder piles 7 and 8 under soybean, 1.3 g/cm$^3$.

## 5. Conclusions

The objectives of the study were to evaluate if extractable soil manganese was reliable on the bulk density in the soil and if there was any difference in extractable soil Mn concentrations between the two different species soybean and corn. It was also a question if the water content of the soil correlated with the plant available Mn. The conclusions are:

(i) In both the first and the second experiment the results showed that the compaction played an important role in controlling the Mn solubility. The cylinders packed with the highest bulk density showed the highest concentrations of extractable Mn ($NH_4OAc$, pH 7).

(ii) The Mn concentration was consistently higher in the corn than in the soybean soils. One possible explanation is that this is due to a special fungus that exists in the soil under soybean, which would be able to decrease the availability to plant hosts.

(iii) No relationship between the Mn solubility and water content was found at constant bulk density. This could be due to the fact that the water content only was measured at the end of the experiment. Practical problems in some cases when measuring the water content at high degree of saturation could have contributed to the lack of correlation. To make a better investigation about the influence of the water content on the Mn solubility, the aspect of time should have been included and followed during the six days that the soil samples were incubated. In such a case the dissolved oxygen concentration in the poor water would have been an important additional measurement in order to understand the mechanisms controlling the Mn solubility.

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Appendix 1. Data from cylinder piles 1 and 2 under corn in Experiment 1, bulk density 1.5 g/cm$^3$.

| Ring No. | Moisture content | pH | Mn concentration |
| --- | --- | --- | --- |

|  | (%) |  | NH4Ac pH 7 | NH4Ac pH 3 | hydroquinol |
|---|---|---|---|---|---|
|  |  |  |  | µg/g |  |
|  |  | Cylinder pile 1 |  |  |  |
| 1 | 27,2 % | 6,68 | 0,73 | 10,0 | 255 |
| 2 | 27,8 % | 6,54 | 1,41 | 12,9 | 258 |
| 3 | 27 7 % | 6,65 | 0,83 | 11,8 | 248 |
| 4 | 27,6 % | 6,74 | 1,33 | 12,6 | 251 |
| 5 | 26,3 % | 6,78 | 4,06 | 20,3 | 253 |
| 6 | 25,9 % | 6,82 | 1,42 | 12,8 | 248 |
| 7 | 26,7 % | 6,75 | 1,86 | 12,5 | 252 |
| 8 | 26,6 % | 6,59 | 1,75 | 14,8 | 253 |
| 9 | 26,0 % | 6,78 | 11,4 | 24,4 | 238 |
| 10 | 27,7 % | 6,72 | 22,5 | 28,6 | 237 |
| 11 | 25,7 % | 6,59 | 31,2 | 33,4 | 221 |
| 12 | 27,5 % | 6,49 | 44,4 | 38,2 | 212 |
| 13 | 26,7 % | 6,60 | 47,2 | 38,8 | 224 |
| 14 | 25,8 % | 6,69 | 60,0 | 42,5 | 194 |
| 15 | 25,4 % | 6,65 | 73,5 | 51,5 | 184 |
|  |  | Cylinder pile 2 |  |  |  |
| 1 | 29,4 % | 6,68 | 0,94 | 7,2 | 259 |
| 2 | 29,7 % | 6,77 | 0,85 | 7,1 | 289 |
| 3 | 29,1 % | 6,60 | 1,20 | 9,8 | 272 |
| 4 | 28,8 % | 6,69 | 1,27 | 6,5 | 262 |
| 5 | 29,3 % | 6,59 | 1,42 | 12,5 | 307 |
| 6 | 28,8 % | 6,49 | 1,56 | 10,7 | 271 |
| 7 | 29,7 % | 6,58 | 1,22 | 10,2 | 264 |
| 8 | 28,6 % | 6,59 | 1,53 | 11,9 | 275 |
| 9 | 28,3 % | 6,78 | 1,84 | 12,5 | 287 |
| 10 | 27,8 % | 6,59 | 1,89 | 12,4 | 262 |
| 11 | 27,4 % | 6,55 | 2,08 | 12,7 | 289 |
| 12 | 28,4 % | 6,62 | 2,45 | 14,9 | 296 |
| 13 | 28,5 % | 6,64 | 7,81 | 20,6 | 289 |
| 14 | 27,8 % | 6,63 | 24,4 | 33,8 | 237 |
| 15 | 30,2 % | 6,65 | 87,5 | 51,6 | 170 |

Appendix 2. Data from cylinder piles 3 and 4 under corn in Experiment 1, 1.3 g/cm$^3$.

| Ring No. | Moisture content | pH | Mn concentration | | |
|---|---|---|---|---|---|
|  | (%) |  | NH4Ac pH 7 | NH4Ac pH 3 | hydroquinol |

| | (%) | | NH4Ac pH 7 | NH4Ac pH 3 | hydroquinol |
|---|---|---|---|---|---|
| | | | | µg/g | |
| | | Cylinder pile 3 | | | |
| 1 | 28,0 % | 6,68 | 0,32 | 4,02 | 275 |
| 2 | 28,7 % | 6,59 | 0,30 | 4,33 | 267 |
| 3 | 27,8 % | 6,78 | 0,30 | 3,84 | 268 |
| 4 | 28,8 % | 6,72 | 0,39 | 3,78 | 264 |
| 5 | 29,7 % | 6,59 | 0,40 | 3,88 | 270 |
| 6 | 30,8 % | 6,49 | 0,38 | 4,39 | 266 |
| 7 | 32,3 % | 6,58 | 0,45 | 4,14 | 266 |
| 8 | 34,8 % | 6,75 | 0,31 | 4,39 | 269 |
| 9 | 36,5 % | 6,81 | 0,46 | 4,81 | 253 |
| 10 | 36,4 % | 6,59 | 0,50 | 4,31 | 269 |
| 11 | 36,4 % | 6,55 | 1,12 | 10,0 | 287 |
| 12 | 37,1 % | 6,77 | 1,17 | 11,4 | 258 |
| 13 | 36,1 % | 6,60 | 2,34 | 15,4 | 255 |
| 14 | 33,7 % | 6,69 | 21,0 | 33,2 | 227 |
| 15 | 34,6 % | 6,65 | 23,9 | 39,5 | 222 |
| | | Cylinder pile 4 | | | |
| 1 | 27,2 % | 6,75 | 0,76 | 4,03 | 262 |
| 2 | 27,6 % | 6,81 | 0,70 | 3,69 | 263 |
| 3 | 28,7 % | 6,59 | 0,94 | 4,12 | 259 |
| 4 | 30,2 % | 6,55 | 0,86 | 4,19 | 260 |
| 5 | 33,0 % | 6,77 | 0,77 | 4,17 | 275 |
| 6 | 35,6 % | 6,59 | 1,28 | 5,23 | 255 |
| 7 | 35,9 % | 6,49 | 1,02 | 4,42 | 264 |
| 8 | 35,8 % | 6,58 | 1,11 | 4,19 | 258 |
| 9 | 36,0 % | 6,60 | 1,16 | 4,59 | 260 |
| 10 | 37,3 % | 6,69 | 1,37 | 7,17 | 255 |
| 11 | 35,8 % | 6,64 | 1,85 | 13,0 | 251 |
| 12 | 37,8 % | 6,49 | 2,62 | 10,9 | 252 |
| 13 | 37,7 % | 6,58 | 2,90 | 13,0 | 239 |
| 14 | 38,3 % | 6,75 | 38,4 | 43,6 | 194 |
| 15 | 40,9 % | 6,81 | 35,9 | 42,3 | 202 |

Appendix 3. Data from cylinder piles 5 and 6 under soybean in Experiment 1, 1.4 g/cm$^3$.

| Ring No. | Moisture content | pH | | Mn concentration | |
|---|---|---|---|---|---|
| | (%) | | NH4Ac pH 7 | NH4Ac pH 3 | hydroquinol |
| | | | | µg/g | |

### Cylinder pile 5

| | | | | | |
|---|---|---|---|---|---|
| 1 | 33,2 % | 6,32 | 0,46 | 12,2 | 325 |
| 2 | 34,1 % | 6,35 | 0,63 | 17,1 | 310 |
| 3 | 35,2 % | 6,45 | 0,64 | 22,0 | 359 |
| 4 | 36,2 % | 6,36 | 0,64 | 16,7 | 327 |
| 5 | 37,2 % | 6,38 | 1,49 | 24,4 | 316 |
| 6 | 36,7 % | 6,38 | 3,15 | 27,3 | 314 |
| 7 | 37,6 % | 6,51 | 6,40 | 34,7 | 292 |
| 8 | 34,7 % | 6,32 | 6,64 | 35,6 | 280 |
| 9 | 37,9 % | 6,36 | 11,2 | 0,00 | 306 |
| 10 | 35,2 % | 6,45 | 12,3 | 43,8 | 291 |
| 11 | 34,7 % | 6,46 | 13,8 | 45,8 | 279 |
| 12 | 36,6 % | 6,39 | 15,2 | 45,2 | 304 |
| 13 | 51,0 % | 6,37 | 18,0 | 48,5 | 310 |
| 14 | 40,4 % | 6,43 | 19,6 | 50,2 | 293 |
| 15 | 40,6 % | 6,46 | 21,3 | 50,7 | 282 |

### Cylinder pile 6

| | | | | | |
|---|---|---|---|---|---|
| 1 | 33,2 % | 6,45 | 1,77 | 27,6 | 369 |
| 2 | 33,3 % | 6,51 | 5,92 | 26,3 | 370 |
| 3 | 33,4 % | 6,39 | 5,20 | 27,3 | 388 |
| 4 | 33,4 % | 6,40 | 5,53 | 29,4 | 360 |
| 5 | 33,4 % | 6,35 | 9,38 | 31,6 | 377 |
| 6 | 34,1 % | 6,36 | 3,31 | 29,4 | 376 |
| 7 | 33,1 % | 6,43 | 6,88 | 37,8 | 366 |
| 8 | 33,0 % | 6,38 | 6,69 | 37,8 | 367 |
| 9 | 33,5 % | 6,37 | 6,33 | 44,3 | 369 |
| 10 | 31,4 % | 6,39 | 9,83 | 41,0 | 364 |
| 11 | 30,5 % | 6,26 | 10,7 | 43,1 | 348 |
| 12 | 33,7 % | 6,46 | 6,33 | 46,6 | 336 |
| 13 | 38,7 % | 6,48 | 9,34 | 48,5 | 321 |
| 14 | 36,1 % | 6,38 | 11,9 | 49,1 | 249 |
| 15 | 35,3 % | 6,32 | 11,7 | 50,1 | 282 |

Appendix 4. Data from cylinder piles 7 and 8 under soybean in Experiment 1, 1.3 g/cm$^3$.

| Ring No. | Moisture content | pH | Mn concentration | | |
|---|---|---|---|---|---|
| | (%) | | NH4Ac pH 7 | NH4Ac pH 3 | hydroquinol |
| | | | | µg/g | |

|  | Cylinder pile 7 |  |  |  |  |
|---|---|---|---|---|---|
| 1 | 32,8 % | 6,46 | 0,76 | 22,1 | 332 |
| 2 | 34,9 % | 6,48 | 0,85 | 27,6 | 318 |
| 3 | 33,1 % | 6,39 | 0,71 | 26,1 | 295 |
| 4 | 35,8 % | 6,39 | 0,74 | 24,2 | 302 |
| 5 | 33,6 % | 6,39 | 0,65 | 23,4 | 308 |
| 6 | 34,7 % | 6,21 | 0,88 | 27,3 | 300 |
| 7 | 35,0 % | 6,45 | 1,10 | 30,9 | 303 |
| 8 | 34,7 % | 6,51 | 1,76 | 32,7 | 304 |
| 9 | 33,4 % | 6,37 | 1,80 | 35,7 | 291 |
| 10 | 52,5 % | 6,39 | 1,74 | 38,2 | 382 |
| 11 | 32,7 % | 6,26 | 2,20 | 35,1 | 289 |
| 12 | 36,3 % | 6,39 | 1,98 | 38,2 | 303 |
| 13 | 45,0 % | 6,28 | 3,62 | 37,8 | 289 |
| 14 | 54,2 % | 6,38 | 5,06 | 39,0 | 293 |
| 15 | 44,7 % | 6,32 | 4,19 | 39,9 | 342 |

|  | Cylinder pile 8 |  |  |  |  |
|---|---|---|---|---|---|
| 1 | 31,0 % | 6,45 | 0,19 | 14,9 | 360 |
| 2 | 31,6 % | 6,48 | 0,28 | 13,7 | 382 |
| 3 | 32,5 % | 6,38 | 0,42 | 13,3 | 396 |
| 4 | 34,6 % | 6,32 | 0,34 | 14,2 | 362 |
| 5 | 35,2 % | 6,35 | 0,55 | 15,1 | 380 |
| 6 | 36,7 % | 6,36 | 0,74 | 17,0 | 378 |
| 7 | 36,6 % | 6,43 | 0,79 | 14,2 | 373 |
| 8 | 35,8 % | 6,51 | 0,91 | 19,3 | 358 |
| 9 | 34,7 % | 6,39 | 1,08 | 19,5 | 371 |
| 10 | 33,2 % | 6,40 | 0,95 | 22,6 | 375 |
| 11 | 37,3 % | 6,35 | 1,22 | 26,4 | 366 |
| 12 | 39,2 % | 6,46 | 2,32 | 41,3 | 351 |
| 13 | 118 % | 6,48 | 7,69 | 70,3 | 505 |
| 14 | 50,9 % | 6,49 | 7,01 | 48,3 | 276 |
| 15 | 47,3 % | 6,32 | 8,62 | 51,4 | 311 |

Appendix 5. Data from Experiment 2 with rings under soybean and corn.

| Ring No. | Bulk density | Moisture content | pH |  | Mn concentration |  |
|---|---|---|---|---|---|---|
|  | (g/cm3) | (%) |  | NH4Ac pH 7 | NH4Ac pH 3 | hydroquinol |

| | | | | | μg/g |
|---|---|---|---|---|---|---|
| | | | Soybean | | | |
| 1a | 0,6 | 13,3% | 6,39 | 0,43 | 17,6 | 306 |
| 1b | 0,6 | 14,1% | 6,53 | 0,29 | 22,3 | 321 |
| 2a | 0,8 | 14,1% | 6,47 | 0,40 | 20,7 | 326 |
| 2b | 0,8 | 14,6% | 6,51 | 0,31 | 20,3 | 341 |
| 3a | 1,2 | 12,0% | 6,49 | 0,38 | 18,1 | 322 |
| 3b | 1,2 | 11,6% | 6,53 | 0,40 | 19,9 | 306 |
| 4a | 1,3 | 11,0% | 6,52 | 0,39 | 18,8 | 315 |
| 4b | 1,3 | 13,1% | 6,59 | 0,41 | 20,5 | 324 |
| 5a | 1,4 | 13,1% | 6,40 | 0,44 | 22,0 | 324 |
| 5b | 1,4 | 14,3% | 6,33 | 0,39 | 20,9 | 338 |
| 6a | 1,6 | 13,8% | 6,43 | 0,51 | 21,7 | 326 |
| 6b | 1,6 | 13,5% | 6,41 | 0,42 | 20,1 | 278 |
| 7a | 1,7 | 14,6% | 6,38 | 0,46 | 19,3 | 313 |
| 7b | 1,7 | 13,2% | 6,45 | 0,58 | 23,6 | 300 |
| 8a | 1,8 | 19,5% | 6,39 | 0,54 | 19,9 | 306 |
| 8b | 1,8 | 11,1% | 6,40 | 0,88 | 24,3 | 352 |
| 9a | 1,9 | 13,4% | 6,36 | 0,55 | 20,6 | 346 |
| 9b | 1,9 | 13,2% | 6,45 | 0,61 | 23,1 | 330 |
| | | | Corn | | | |
| 1a | 0,6 | 11,9% | 6,78 | 0,50 | 5,66 | 231 |
| 1b | 0,6 | 13,3% | 6,79 | 0,44 | 4,24 | 202 |
| 2a | 0,8 | 13,9% | 6,79 | 0,63 | 4,42 | 225 |
| 2b | 0,8 | 15,5% | 6,81 | 0,62 | 3,89 | 232 |
| 3a | 1,2 | 12,2% | 6,75 | 0,76 | 3,62 | 235 |
| 3b | 1,2 | 13,2% | 6,66 | 0,72 | 3,68 | 231 |
| 4a | 1,3 | 13,7% | 6,72 | 0,72 | 4,81 | 204 |
| 4b | 1,3 | 10,7% | 6,65 | 0,74 | 3,83 | 231 |
| 5a | 1,4 | 11,4% | 6,50 | 0,91 | 4,22 | 233 |
| 5b | 1,4 | 11,7% | 6,61 | 0,79 | 3,69 | 228 |
| 6a | 1,6 | 12,9% | 6,54 | 0,98 | 5,33 | 206 |
| 6b | 1,6 | 12,1% | 6,63 | 0,88 | 6,90 | 230 |
| 7a | 1,7 | 11,3% | 6,62 | 1,01 | 7,33 | 229 |
| 7b | 1,7 | 11,6% | 6,63 | 0,98 | 4,47 | 238 |
| 8a | 1,8 | 14,0% | 6,55 | 0,96 | 4,05 | 235 |
| 8b | 1,8 | 13,1% | 6,58 | 0,94 | 4,12 | 226 |
| 9a | 1,9 | 12,7% | 6,49 | 1,07 | 4,88 | 232 |
| 9b | 1,9 | 14,3% | 6,67 | 0,98 | 4,29 | 237 |