The Effect of Municipal Sewage Sludge and
Inorganic Cadmium on Cadmium
Bioavailability to Wheat and on the
Chemistry of Soil Cadmium.


by

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A thesis submitted to the University of Manitoba
in partial fulfllment of the requirements
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THE EFFECT OF MUNICIPAL SEWAGE SLUDGE AND INORGANIC
CADMIUM ON CADMIUM BIOAVAILABILITY TO WHEAT AND
ON THE CHEMISTRY OF SOIL CADMIUM


BY


ALAN BRUCE HASTIE


A Thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements for the degree of


MASTER OF SCIENCE


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ABSTRACT

Application of sewage sludge (SS) to agricultural land is a practical and economical approach for its disposal. As cadmium (Cd) is the heavy metal present in SS most insidious to human health, its addition to the soil must be studied in order to determine its effects on soil chemistry, crop growth and ultimately its bioavailability.

Studies were conducted using lysimeters in the field, and laboratory adsorption experiments on Red River clay and Lakeland clay loam soils. Both soil series are common to areas near the City of Winnipeg. The SS was a batch from the City of Winnipeg Water Pollution Control Plant.

The Lysimeter study involved amending the soils with four rates of SS, viz., 0, 50, 100 and 200 t ha$^{-1}$. A similar lysimeter study was conducted with five rates of CdCl$_2$, 0, 2, 4, 8 and 16 kg Cd ha$^{-1}$. Both studies were conducted over a three year period. Neither sewage sludge nor CdCl$_2$ affected the yield of wheat over the study period. The Cd concentration in the straw and grain did increase from the application of SS and CdCl$_2$ during the first year. The Cd concentration in the grain of the wheat grown on the Red River soil amended with SS increased from 0.027 ug g$^{-1}$ to 0.057 ug g$^{-1}$ and amended with CdCl$_2$ from 0.027 ug g$^{-1}$ to 1.869 ug g$^{-1}$. The Cd concentration in the grain of wheat grown on the Lakeland soil amended with

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SS increased from an undetectable level to 0.024 ug g$^{-1}$ and amended with CdCl$_2$ from an undetectable level to 0.667 ug g$^{-1}$. By the third year, the bioamplification of Cd in the grain had returned to background (control) levels.

The yield of wheat grown on SS-amended soil and the Cd concentration in the tissue were also studied under adverse environmental conditions, such as flooding and acidification. The yields and Cd concentrations were not significantly affected by either, flooding or acidification.

A sequential extraction procedure was used (H$_2$0, KNO$_3$, KF, NaP$_2$O$_7$, EDTA and HNO$_3$) to determine the distribution of Cd in the treated soil. Very small amounts of Cd were extracted using H$_2$O and < 5% of the Cd was extracted using KNO$_3$ in both soils. For the Red River soil approximately 11% of the Cd was extracted with KF, 79% with NaP$_2$O$_7$, 1% with EDTA and 7% with HNO$_3$. For the Lakeland soil about 4% of the Cd was extracted with KF, 80% with NaP$_2$O$_7$, 3% with EDTA and 5% with HNO$_3$. The percentage of total Cd applied to the soil that was extracted was, on average, 41% for both soils.

Analysis was conducted on the oxide-bound Cd in the CdCl$_2$ treated soils. Citrate-dithionate-bicarbonate (CDB) was used to determine the concentration of Cd associated with the oxide fraction. On the Red River soil 7 to 14% of the total Cd

applied to the soil was extracted using CDB. On the Lakeland soil 9 to 11% was extracted. There was a close relationship between oxide bound Cd and the amount of Cd added ($r^2 = 0.89$).

Further study revealed that the adsorption of Cd by goethite increased as the pH of the system increased. The ratio of the moles $H^+$ released/$Cd^{2+}$ adsorbed was $2.44 \pm 0.04$. Once adsorbed to the goethite, Cd was held relatively tightly and was not readily desorbed by a neutral salt ($CaCl_2$).

The adsorption of Cd by SS was a two step process. There was an initial rapid step within the first 30 min where approximately 95% of the Cd added was removed from solution. The second step followed first order reversible kinetics where Cd removal from solution proceeded at a slower rate. The equilibrium reactions depended on the initial Cd concentrations. Some of the adsorbed Cd was released back to solution after 48 hrs of equilibrium.

It was derived from this study that the application of SS to agricultural land for the purposes of grain production would not affect the yield or quality of the grain due to the high levels of Cd contained in the SS. The results suggest that the soil and the SS itself, tie up the Cd making it unavailable for plant uptake.

## ACKNOWLEDGEMENTS

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# I. INTRODUCTION

The issue of sewage sludge (SS) disposal is a fundamental problem for the swelling urban and industrial areas of the world. With both heightened interest in environmental awareness and stricter legislation imposed against pollution, more environmentally acceptable methods must be sought to dispose of SS sensibly and efficiently. Disposal methods such as incineration, landfill and ocean/river dumping are no longer acceptable as they do not utilize the beneficial aspects of SS and are also the source of much environmental pollution. However, the use of SS for agricultural purposes may prove to be a satisfactory alternative for dealing with its disposal in both environmental and economical terms.

Sewage sludge is the by-product of primary, secondary and even tertiary treatment of human waste. It contains a myriad of organic and inorganic constituents that can vary greatly in quantity from one SS to another depending on its source and the treatment process. In general, SS is composed of some decomposable organic materials, nutrients (nitrogen, phosphorous, sulphur), surfactants, microorganisms, synthetic organic compounds and heavy metals (Environment Canada, 1984). Typically it is a suspension in nature with a solid content of 2 to 9% (Webber, 1984). However the latest SS treatment processes have been found to increase the solid content to

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approximately 30%. On average, about 1% of the total flow
entering a sewage plant is ultimately produced as SS by the
end of the treatment processes (Lester et al., 1983).
According to Webber (1984), SS production in Canada in 1973
was approximately 100 000 dry tonnes $yr^{-1}$ with projected
production levels for the year 2000 estimated at 1 000 000 dry
tonnes $yr^{-1}$. An estimated 141 municipalities across Canada
applied SS to agricultural land in 1983 (Environment Canada,
1984).

There are certain environmental concerns associated with the
use of SS for agricultural purposes. It is a possible source
of several potentially toxic heavy metals such as Cd, Pb, Cu
and Zn (Berrow and Webber, 1972), toxic synthetic organics
such as pesticides and polychlorinated biphenyls (PCB's)
(Sommers and Barbarick, 1988), pathogenic micro-organisms such
as Salmonella (Burge and Marsh, 1978) and of high N levels
that may promote $NO_3$ leaching and consequently contaminate
underlying groundwater (Stewart et al., 1975). All these
factors present environmental health risks to humans and
animals.

As land application is a natural way to recycle waste products
back the environment, efforts should be made to efficiently
use SS so that there is as little adverse impact on the
environment as possible. Due to the aforementioned concerns

associated with SS, limits have been set in Canada for the amount of SS that can be applied to agricultural fields. For the City of Winnipeg this limit has been set at 56 t ha$^{-1}$ on an annual basis.

With respect to heavy metals, Cd is of the greatest concern. Cadmium has no physiological function in human, animals or plants. However Cd can be the cause of serious health problems to humans if present in the body at high concentrations. Food is the main source of Cd to humans (Schroeder and Balassa, 1961), therefore the concern lies in plant bioavailability of Cd in SS-amended soil.

There is a paucity of information on the bioavailability of Cd and its fate in the soil when SS is applied to fields in Manitoba. This study was undertaken, therefore, to examine the bioavailability of Cd in SS-amended soil to wheat and its effects on yield. Selected soil constituents were studied in an effort to determine what soil fraction the Cd was strongly associated with and to what extent this Cd would become occluded/bioavailable in future years.

# II. LITERATURE REVIEW

## 2.1 BENEFITS OF SEWAGE SLUDGE APPLICATION TO THE SOIL

The use of soil as a repository for SS disposal has received
much attention over the past few decades (Zwarich and Mills,
1979; Sommers and Barbarick, 1988; King, 1988; Sims and Kline,
1991). Consequently, research into the distribution and
speciation of nutrients and pollutants in SS and their
potential impact on the soil environment has escalated
accordingly. An extensive study conducted by Sommers (1977),
analyzing more than 250 SS samples from approximately 150
treatment plants, determined that the median composition for
certain constituents of both aerobically treated and
anaerobically digested SS were as follows. For the
aerobically treated SS the values were: Organic C, 29.5 %; N,
4.8 %; P, 2.7 %; K, 0.4%; Pb, 300 ug $g^{-1}$; Zn, 1800 ug $g^{-1}$; Cu,
970 ug $g^{-1}$; Ni, 31 ug $g^{-1}$; and Cd, 16 ug $g^{-1}$. For the
anaerobically digested SS the values were: Organic C, 26.8 %;
N, 4.2 %; P, 3.0 %; K, 0.3%; Pb, 540 ug $g^{-1}$; Zn, 1890 ug $g^{-1}$;
Cu, 1000 ug $g^{-1}$; Ni, 85 ug $g^{-1}$; and Cd, 16 ug $g^{-1}$. These data
show that SS contains significant quantities heavy metals.
Subsequently, the land application of such a metal-laden
matrix has created certain concerns with regards to
environmental contamination. Nevertheless, the high organic
C, N and P content, also characteristic of SS, is beneficial

for agricultural purposes.

Research has shown favourable yield responses from the application of SS to the soil due to its high N and P content. Increased yields have been obtained for many crops including barley (Milne and Graveland, 1972), wheat (Linmann et al., 1973; Chang et al., 1982), corn (Stewart et al., 1975; Magdoff and Amadon, 1980), rye (Kelling et al., 1977) and certain forages (Kelling et al., 1977; Stark and Clapp, 1980). In some cases yield increases from SS-amended soil were comparable to yields obtained from using chemical fertilizer (Webber and Bole, 1979; Goda et al., 1986). Further, short term residual effects over 2 or 3 growing seasons have also been measured (Kelling et al., 1977; Webber and Bole, 1979; Stark and Clapp, 1980).

Less work has been conducted on the effect SS has on the physical properties of the soil. However, SS has favourable effects on soil tilth and may prove to be a means of maintaining the organic C content in soils (Metzger and Yaron, 1987). In addition SS can enhance the water retention capacity, (Gupta et al., 1977; Khaleel et al., 1981), reduce the bulk density (Gupta et al., 1977; Kladivko and Nelson, 1979), increase the total porosity (Pagliai et al., 1981), promote aggregate stability (Epstein, 1975; Wei et al., 1985), increase the hydraulic conductivity (Epstein, 1975; Wei et

al., 1985) and may improve the infiltration rate (Kladivko and Nelson, 1979; Wei et al., 1985) of the soil. Therefore, SS application to fine textured soil may enhance seedbed preparation for seeding and seedling emergence and improve aeration. Also, SS can improve the soil's water holding capacity and reduce the potential erodibility of coarse textured soils.

In summary, the beneficial aspects of SS to agriculture lie in its ability to fertilize and condition the soil, as it contains considerable amounts of N, P, S, micronutrients and organic matter.

## 2.2 HEAVY METAL CONTENT OF SEWAGE SLUDGE

Much research has been conducted in an attempt to understand the extent to which SS-amended soils endanger animal and human health through the contamination of the soil with heavy metals (Zwarich and Mills, 1979, Wolnik et al., 1983; Goda et al., 1986). The problem lies in the fact that SS contains significantly higher amounts of heavy metals than is typically present in the soil. In particular, the concentration of Cd, Cu, Hg, Pb, Zn, Ag, Sn and Bi are far higher in SS than in most soils (Lake, 1987). One factor that affects the amount of metals found in SS is the treatment process used by the sewage plant. A process commonly used in SS treatment is

anaerobic digestion. This process stabilizes SS (Gibbs and Angelidis, 1988) and can reduce its organic content by 40 to 50% (Webber, 1984; Environment Canada, 1984). However, the metal content of SS is also increased considerably by this treatment process (Lester et al., 1983). Although the solid fraction of the SS decreases significantly, its total metal content does not change. Therefore the metals are concentrated into a smaller volume increasing the concentration. One of the main reasons, however, for the presence of significant amounts of heavy metals in SS is due to their formation with, or association with settleable solids during primary and secondary treatment processes (Sterritt and Lester, 1983). Again this process merely acts as another method by which metals accumulate in the organic matrix. Once amassed in the SS, the forms of metals present appear to consist partly of stable inorganic solids, precipitates of the more insoluble metals, adsorbed species in the form of moderately stable metal-polymer complexes and to a lesser extent soluble organic complexes with only a small fraction of the metal in free ionic forms (Sterritt and Lester, 1983). The most potentially hazardous metals to the food chain that are present in SS are Cd, Zn, Cu, Ni, Co, Mo and Se (Webber, 1984). The degree of toxicity that these metals present to the food chain ultimately depends upon their bioavailability. In most cases, the plant itself shows severe toxicity symptoms before the concentration of a given metal, such as Zn or Cu,

reaches levels high enough in the plant tissue to be detrimental to human health if consumed. This provides a good buffer from large concentrations of metals entering the food chain. However, Cd can be taken up by plants to concentrations that are far in excess of what is considered safe for human consumption but show no signs of toxicity. Consequently Cd poses a more serious and insidious problem to the food chain than other metals.

## 2.3 CADMIUM: HEALTH CONCERNS

Cadmium is a relatively rare heavy metal not found in a pure metallic state in nature (Page and Bingham, 1973). First discovered in 1817 (Tiller, 1989), Cd is found in electroplating of metal surfaces, pigments, stabilizers in plastics, alkaline batteries and alloys (Page and Bingham, 1973; WHO, 1977). The principal source of Cd to the human body is from food and tobacco. Cadmium has no known biological function. Its importance to the food chain lies in the fact that it can reach concentrations in the plant that are far in excess of that considered safe for human or animal consumption without showing any indication of toxicity to the plant itself (Webber, 1984; King, 1988). Further, depending on its speciation, Cd can be quite mobile in the soil and as such is readily taken up and translocated by plants (Alloway and Tills, 1983). It is evident, therefore, that an external

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source of Cd, such as that provided by SS application to soil, can potentially elevate concentrations of Cd in plants to hazardous levels.

Cadmium can cause serious health problems in animals and humans. It is virtually absent in newborns but accumulates with age in the liver and kidneys of adults (Schroeder and Balassa, 1961; WHO, 1977). It has been estimated (WHO, 1977) that the human daily intake of Cd in non-polluted areas is 10 to 80 ug $d^{-1}$ whereas for certain polluted areas it can be as high as 180 to 390 ug $d^{-1}$. The effects of Cd on human health has been studied and reviewed extensively (Schroeder and Balassa, 1961; Goyer and Cherian, 1979; Ryan et al., 1982). The degree of illness in humans caused by Cd depends on the extent and duration of exposure as summarized by Rudd (1987). Chronic exposure affects primarily the gastro-intestinal tract and to a lesser extent the kidney, bone, heart, pancreas, testes and haematopoietic system. Prolonged exposure primarily affects the kidney. Exposure at low concentrations can cause vomiting, diarrhoea and colitis. Prolonged exposure at low concentrations may result in hypertension, heart enlargement and death.

## 2.4 CADMIUM IN SOILS

Heavy metals occur naturally in the soil and are derived mainly from the underlying parent material. The parent material of the soil in turn reflects the properties imparted to it from the underlying rock. Page and Bingham (1973) determined that soils derived from igneous rocks contain 0.1 to 0.3 ug $g^{-1}$ Cd, soils derived from metamorphic rock 0.1 to 1.0 ug $g^{-1}$ Cd, and soils derived from sedimentary rock 0.3 to 11 ug $g^{-1}$ Cd.

Quantifying the background levels of metals in uncontaminated soil is the first step towards protecting the soil environment from excessive SS amendments. By monitoring the metal content of SS-amended soils, the concentration of metals added to the soil can be regulated, and consequently prevented from reaching toxic levels. Such preliminary work has already been conducted in many areas of the world including Canada. McKeague and Wolynetz (1980) conducted an extensive study of 53 soils across Canada from the Podzolic, Gleysolic and Luvisolic Orders. The average total concentration of various metals for the soils analyzed were: Zn 74, Cu 22, Ni 20 and Pb 20 ug $g^{-1}$. Cadmium was below the detection limits of 0.3 ug $g^{-1}$. A similar study was conducted by Zwarich and Mills (1979) for soils in Manitoba representative of the Chernozemic and Regosolic soil orders. The total concentrations of Zn, Ni and

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Cd were slightly higher than those found by McKeague and Wolynetz (1980) with values of 116, 42 and 0.9 ug g$^{-1}$, respectively. The total concentrations of Pb and Cu however, were very similar at 17 and 25 ug g$^{-1}$, respectively. Mills and Zwarich (1975) noted that the metal concentrations in the surface soil was closely related to concentrations in the soils parent material. For Ontario soils Frank et al. (1976) determined that the total concentrations of Zn, Cu, Ni, Pb and Cd were 53.5, 25.4, 15.9, 14.1 and 0.56 ug g$^{-1}$, respectively. Values of Zn, Cu, Ni, Pb and Cd for Alberta soils, from well to poorly drained soils representative of the Black, Brown and Gray soil zones, ranged from 5.7-26, 1.8-7.4, 1.2-8.1, 1.8-7.4 and 0.09-0.40 ug g$^{-1}$ respectively (Dudas and Pawluk, 1977). As compared to the findings of other researchers, metal concentrations reported by Dudas and Pawluk (1977) were considerably lower. However, some of the values obtained by the other authors were uncharacteristically high for expected natural background levels of metals in soil, for example 8.1 ug g$^{-1}$ Cd (Frank et al. 1976).

It is evident that the Cd content of Canadian soils varies greatly from area to area. This spatial variability is not unexpected due to the capricious nature of soils. However the Cd concentration of uncontaminated soils in Canada generally falls within the range of 0.09 to 1.0 ug g$^{-1}$. This range is consistent with other estimated values for Cd concentrations

of < 1.0 ug g$^{-1}$ for uncontaminated soil (WHO, 1977).

## 2.5 FATE OF SOIL CADMIUM

The fate of Cd applied to the soil in SS is an important area
of research in soil science. Although the total concentration
of heavy metals in SS-amended soils may be relatively high,
this measure does not give any indication as to the fate,
distribution or speciation of Cd in the soil. It certainly is
not considered a reliable guide to the bioavailability of
soil-borne metals (Oake et al., 1984; Lake, 1987). Cadmium
can exist in the soil in many forms. These forms can be
summarized as follows: water soluble (both ionic and
complexed), exchangeable, extractable from organic and
inorganic sites not released to extractants of exchangeable
ions, precipitates, occluded by soil oxides and hydroxides,
held in biological residues and living organisms, components
of lattice structures of primary and secondary minerals
(Hodgson, 1963; McLaren and Crawford, 1973; Sims and Patrick,
1978). Soluble Cd exists in the soil solution as free ions or
as ions adsorbed on suspended colloids (Viets, 1962).
Exchangeable Cd is held predominantly by electrostatic forces
on negatively charged sites on clays, other minerals or
organic matter, or on amorphous materials with a low point of
zero charge (PZC) such as some oxides or solid organo-mineral
complexes (Beckett, 1989). Sorbed Cd is held relatively

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strongly on inorganic sites such as those on clay surfaces mainly by covalent or electrostatic attraction (Ellis and Knezek, 1972). Cd can also exist as precipitates of carbonates, sulfides, phosphates and hydroxides.

Organically held Cd involves Cd immobilized by organic material, such as plant residues or soil microflora, and consists mainly of Cd complexed or chelated by organic materials, either recently synthesized or the resistant residues from microbial metabolism (Beckett, 1989). The complexed Cd may vary in stability from immediately mobile, to easily decomposed, to moderately resistant or resistant to decomposition (Adriano, 1986). Thus the strength by which Cd is retained by organic substances varies greatly depending on the degree of organic matter decomposition and resynthesis in the soil ie. the degree of humification. The importance of organic matter in metal retention is based on the known chelating ability of soil organic constituents. Examples of this are humic and fulvic acid extract; high correlations between metal sorption or micronutrient deficiencies and organic matter content of soils; and reduction in sorption or increase in extractability of metals after treatment of soils with hydrogen peroxide to destroy the organic matter (Keeney and Wildung, 1977). The functional groups involved in retaining Cd are weak acids mainly carboxyls (-COOH), the phenolic and alcoholic hydroxyls (-OH), primary, secondary and

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tertiary amino groups (-N, -NH, -NH$_2$) and sulfhydryls (-SH) (Sposito and Page, 1984). The functional group configuration offers the opportunity for chelation as these groups bind metals very strongly (Hodgson, 1963).

## 2.6 SOIL OXIDES

One of the most important soil constituents for retaining metals are the oxides of iron, aluminium or manganese. Oxides play an important role in the adsorption or occlusion of metals. Adsorption equilibria governs the ionic concentrations of trace elements in the soil solution when the concentration of ions are not high enough to exceed the solubility limit (Quirk and Posner, 1975). At metal concentrations common to surface soils, precipitation phenomena does not control metal solubility (Cavallaro and McBride, 1978). Therefore, under conditions where precipitation does not occur, adsorption is a significant process and it consequently controls the availability of metals in the soil solution.

Oxides occur in the soil in various forms: as discrete particles, as cements which bond soil particles together into amorphous concretions or as coatings on clay minerals (Adriano, 1986; Russel, 1988). When the surface of the oxide comes in contact with an aqueous environment such as the soil

solution, it becomes hydroxylated and subsequently a charge evolves (Gast, 1979). Gast (1979) explained that these surface charges evolve as edge effects on the oxide surface just as on crystalline clay minerals or interlayers on crystalline clay minerals. Furthermore, the co-precipitation of Fe and Al, and the resulting perturbation of the crystal structure, can create site vacancies, increase the specific area and change the PZC of oxides making them more adsorptive (Goh et al., 1986). It is this surface charge coupled with the abundance of oxides in the soil that represents the significance of soil oxides in metal retention.

Iron oxides are the most widespread form of oxides in soil (Russel, 1988). Eight naturally occurring iron oxides or hydroxides predominate namely, magnetite, haematite, maghemite, akaganeite, limonite, ferrihydrite, geothite and lepidocrocite (Allen and Hajek, 1989).

Of these eight Fe oxides, goethite is the most thermodynamically stable and is therefore the final solid phase expected in soils (Sposito, 1989). Further, goethite occurs in almost every soil type and climatic region (Schwertzmann and Taylor, 1989). It is not unexpected therefore that geothite is one of the most commonly used oxides for research purposes (Forbes et al., 1976; Parfitt and Russel; 1977).

Cadmium therefore may exist in the soil in many forms; from ionic ($Cd^{2+}$) and labile, to strongly complexed and residual. The forms that are readily available for plant uptake exist in equilibrium between the exchangeable and water soluble fractions. However, the organic and oxide-bound fractions in the soil dictate the extent to which metals are present in these two forms. With time, metals associated with the oxide or organic fractions can become increasingly labile or, as is perhaps more common, occluded permanently.

It is apparent therefore, that the oxide and organic fractions play an integral role in metal retention and inevitably govern the fate of Cd applied to the soil. However, due to the intricate nature of the interactions that exist between oxides and organic matter (Goh, 1983; Goh et al., 1986), the fundamental factor governing the fate of Cd in the soil may be better described as the organo-mineral complex. However the organo-mineral complex may behave in a completely different manner in its ability or capacity to retain Cd as compared to the oxides or organics individually. If both oxides and organics are present in the soil in proximity, synergistic or even antagonistic effects can significantly influence the extent to which, or the mechanism by which, Cd is retained in the soil. However, the first step in forming any concepts for a problem of such complexity is to develop a fundamental understanding of the basic constituents involved.

## 2.7 IMPORTANCE OF SOIL OXIDES

The importance of oxides in governing the availability of metals was stressed by Jenne (1968). Although much research (Petruzzelli et al., 1978; Gerritse and Van Driel, 1984) has suggested that organic matter plays a more dominant role in governing metal availability, Jenne (1968) tends to dispute its significance in heavy metal retention. Jenne (1968) hypothesized that organic matter plays a more indirect role in controlling oxide-retained metals in the soil. That is, the organic matter creates a periodically reduced environment that maintains oxides in a hydrous microcrystalline condition. In fact the initial destruction of organic matter by peroxide may cause the release of oxide bound metals and be misconstrued as metals associated with organic matter. This hypothesis has since been supported by later research (Quirk and Posner, 1975; Kalbasi et al., 1978; Goh et al., 1986; King, 1988). Jenne's (1968) hypothesis is further borne out with respect to Cd, by the fact that Keefer et al. (1984) found no appreciable Cd associated with any organic fraction from a SS-amended soil analyzed for organically held Cd with N,N dimethylformahide and sodium pyrophosphate. Nevertheless, the importance of organic matter in retaining metals has been observed by many researchers (Haghiri, 1974; Levi-Minzi, 1976; Elliot et al., 1986). The work documented indicates a strong relationship between metal retention and O.M. but suggests that the

retaining power of the O.M. is predominantly through its CEC
property rather than its chelating ability.

It is apparent therefore that some controversy exists as to
the significance of O.M. in metal retention and permanent
fixation in the organic phase. As the organic content of a
SS-amended soil comprises a large percentage of the total
mass, its importance should not be underestimated. The
chemical properties of organic colloids predisposes the matrix
to retain metals but perhaps in a more exchangeable form.

Carbonates have also been studied in great depth as a direct
site for metal retention (Abboud, 1987) but again Jenne (1968)
suggested that carbonates are more important with regards to
their effect on soil pH. As the charge on oxides is pH
sensitive (Parks, 1965), so is their adsorptive capacity.
With increasing pH, Cd adsorption by oxides increases.
Carbonates may indirectly appear to be controlling the
adsorption or desorption of metals through their direct
influence on soil pH.

2.8 ADSORPTION OF CADMIUM TO SOIL OXIDES

Initially the Cd would be held in an exchangeable form, but
these may be held in more covalent (specific) forms with time
(Beckett, 1989). The adsorption mechanisms by which oxides

retain metals has been schematically represented using Zn and Fe oxides as follows (Quirk and Posner, 1975; Kalbasi et al., 1978).

1.

$$Fe\begin{array}{c} OH_2 \\ \\ OH_2 \end{array} \quad + \; ZnCl^+ \quad \longrightarrow \quad Fe\begin{array}{c} OH - ZnCl + H^+ \\ \\ OH_2 \end{array}$$

2.

$$O\begin{array}{c} Fe\begin{array}{c} OH \\ \\ OH \; H \end{array} \\ \\ Fe\begin{array}{c} OH \; H \\ \\ OH \end{array} \end{array} \quad + \; Zn^{2+} \quad \longrightarrow \quad O\begin{array}{c} Fe\!-\!O^H \\ \\ Fe\!-\!O \end{array}\begin{array}{c} OH \\ \\ Zn + 2H^+ \\ \\ OH \end{array}$$
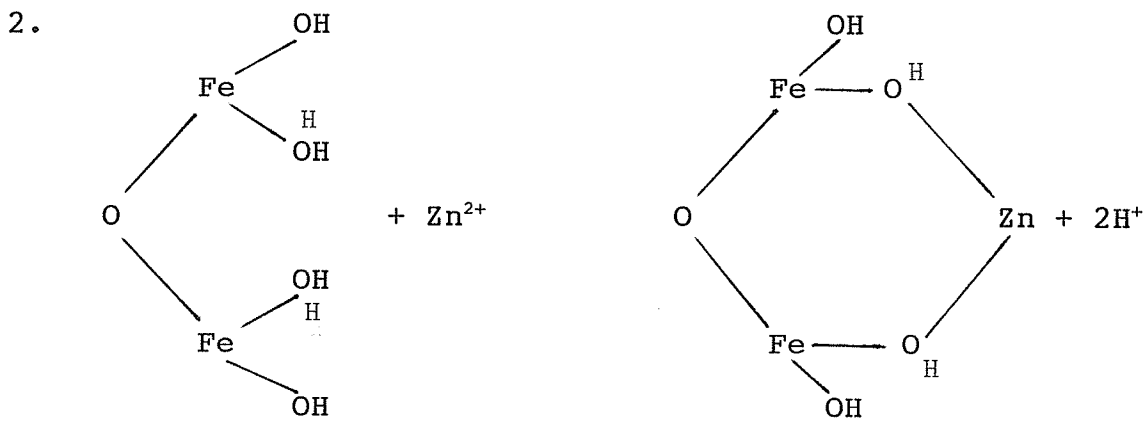
Kalbasi et al. (1978) explained that the first mechanism likely involved the adsorption of $Zn^{2+}$ and $Cl^-$ or $ZnCl^+$ along with the release of one $H^+$ for each adsorbed $ZnCl^+$. In this form, the Zn is not held relatively tightly and is readily replaced by a neutral salt. This form of adsorption is called non-specific.

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The second mechanism of metal adsorption (Quirk and Posner, 1975) likely involved adsorption of $Zn^{2+}$ and the release of two $H^+$ for each $Zn^{2+}$. Here an olation bridge and ring structure is postulated. This type of adsorption can be regarded as a growth or extension of the surface and its properties would accord with the lack of complete reversibility of such an adsorption. In this case it is assumed that the Zn is held by a strong chemical bond making it more resistant to desorption (Kalbasi et al. 1978) and is called specific adsorption. Research has indicated (Forbes et al., 1976) that the molar ratio for $H^+/Cd^{2+}$ is actually 2.0 suggesting that Cd is specifically adsorbed by geothite. Therefore the second mechanism of metal retention for oxides probably holds for Cd.

## 2.9 CHEMICAL EXTRACTION OF HEAVY METALS

As only the water soluble and exchangeable forms of metals are immediately available for plant uptake, some method of analysis should be used to evaluate the various forms in which metals exist in soil. This would provide a more valuable indicator of potential metal toxicity to plants. Analytical procedures are required for the precise separation of metals into their specific chemical forms but chemical reagents have been used in an attempt to partition solid phase metals into chemically similar forms (Emmerich et al., 1982).

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When a single chemical reagent is used for soil analysis, to determine metal concentration, its specificity is usually aimed at the extractable or available fraction of the metal. The reagents most commonly used for this determination are acetic acid, EDTA or DTPA (Beckett, 1989). The use of sequential extractions rather than single extractants may be of greater value in determining metal distribution in SS-amended soils whereby metals are separated into their various forms. Using a sequence of chemical extractants in order of increasing strength but with decreasing specificity to extract complete and discrete fractions is not, however, feasible. The chemical reagents are not selective nor specific enough to distinguish apart and consequently extract a given form of Cd in the soil without dissolving, to some extent, other forms of Cd. Overlap between fractions results but the technique still represents a potential tool for the examination of the interrelationship between metals in SS-amended soil (Oake et al., 1984).

Several sequential extraction procedures have been proposed (McLaren and Crawford, 1973; Silviera and Sommers, 1977; Garcia-Miragaya et al., 1981; Emmerich et al., 1982) most of which are a variation or adaptation of the other. A commonly used procedure (Sposito et al., 1982; Rudd et al., 1988; Oake et al., 1984) was devised by Stover et al. (1976). Extractants were used to estimate the exchangeable, sorbed,

organic, carbonate and sulfide forms of metals present. However the procedure was initially established to be used in the analysis of the metal fractions in SS. As a procedure to be used in soil analysis, it appears to neglect the most important constituent controlling metal availability in the soil, namely the oxide fraction. This procedure tends to place importance on the ability of carbonates to retain metals in SS-amended soils (Sposito et al., 1982; Oake et al., 1984). The analysis of SS itself again suggests that the carbonate fraction plays a predominant role in metal retention (Stover et al., 1976; Rudd et al., 1988).

If the concentration of Cd in the soil solution is less than its solubility product, precipitation of Cd-carbonates will not occur and adsorption is the predominant reaction. Consequently, as oxides play a predominant role in soil adsorption processes, their presence should be accounted for in any sequential extraction procedure. Studies that take the oxide fraction into consideration (McLaren and Crawford, 1973; Garcia-Miragaya, 1980; McLaren et al., 1986) tend to support the importance of the oxides in metal retention. Commonly used extractants for Cd removal from oxides in soils are acidified ammonium oxalate and citrate-dithionite-bicarbonate (McKeague and Day, 1966).

# 3. EXPERIMENTAL

## 3.1 THE EFFECT OF SEWAGE SLUDGE, CADMIUM AND SIMULATED ENVIRONMENTAL CONDITIONS ON THE CONTENT AND DISTRIBUTION OF CADMIUM IN THE SOIL AND ON CROP GROWTH

### 3.1.1 MATERIAL AND METHODS

Field trials were established, using open-ended lysimeters, for a three-year period starting in the spring of 1988. The experiments were conducted on two soils in a randomized complete block design with four replicates. The soils used were a Red River clay (Gleyed Rego Black) and a calcareous Lakeland clay loam (Gleyed Carbonated Rego Black). Selected properties of the soils are shown in Table 3.1.

The pH of the soil was measured electrometrically in suspensions of soil: 0.01M $CaCl_2$ in a 1:2 ratio. A suspension of 10 g of soil and 20 ml $CaCl_2$ were thoroughly mixed and the pH measured with an Accumet 950 pH/ion meter.

Organic C was determined using a procedure developed by Yeomans and Bremner, 1988. The procedure involved digestion of the soil sample with an acidified dichromate ($K_2Cr_2O_7$-$H_2SO_4$) solution for 30 min. Unreacted dichromate was estimated by titration of the cooled digest with an acidified solution of

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Table 3.1. Chemical characteristics of a Red River clay and a
Lakeland clay loam, 0 - 7.5 cm depth, and Municipal
Sewage Sludge from the City of Winnipeg.

| Chemical Property | | Red River | Lakeland | Sewage Sludge |
|---|---|---|---|---|
| pH | | 6.2 | 7.2 | 5.9 |
| Organic C | $(g kg^{-1})$ | 36.5 | 56.7 | 234.8 |
| CEC | $(meq 100g^{-1})$ | 33.8 | 28.7 | - |
| Carbonates | (CCE%)* | 0 | 18.1 | 15.7 |
| Total N | $(g kg^{-1})$ | 3.0 | 4.9 | 16.1 |
| Phosphates | $(\mu g g^{-1})$ | 25.2 | 23.8 | - |
| Total Cd | $(\mu g g^{-1})$ | 0.15 | 0.11 | 7.0 |

* CCE% = calcium carbonate equivalent percent

ferrous ammonium sulfate with use of N-phenylanthranilic acid as an indicator.

Inorganic C content was determined using a procedure developed by Bundy and Bremner, 1972. The procedure involved treating the soil sample with 2M HCl at room temperature for 16-24h in a stoppered bottle containing 2M KOH in a small beaker. The $CO_2$ released by the carbonates is determined by titration of the KOH solution in standard HCl to the phenolphthalein endpoint (pH 8.3) to convert carbonates in this solution to bicarbonate. The $KHCO_3$ is then determined by a further titration to the bromocresol endpoint (pH 3.8) with standard HCl.

Cation exchange capacity (CEC) was determined using a procedure developed by Polemio and Rhoades, 1977. The procedure involved saturating the cation exchange sites with Na by four successive "equilibriations" of the soil with 33 ml increments of a pH 8.2, 60% ethanol solution of 0.4M NaOAc-0.1M NaCl (saturating solution). The saturated sample is then extracted with three 33 ml increments of 1.0M, pH 7.0 magnesium nitrate. Total Na and Cl is determined in the extracted solution. Chloride is determined so that the soluble Na, from the excess saturating solution carried over from the saturation step to the extraction step, may be deducted from the total Na to obtain exchangeable Na, which is

equivalent to the CEC.

Total N was determined using a procedure outlined by Keeney and Nelson, 1982. The procedure involved heating oven dried plant tissue in digestion tubes. The plant tissue was digested twice on the digestion rack: Initially for 45 min with potassium permangante, dilute sulfuric acid, octyl alcohol and reduced Fe, then again for 5 h with a catalyst ($K_2SO_4$) and concentrated sulfuric acid.

Total phosphates were determined using a procedure developed by Olsen and Sommers, 1982. Charcoal was added to the soil samples, which were then treated with 0.5M $NaHCO_3$. Mixtures were shaken, fitered and pH adjusted using 2,4-dinitrophenol and concentrated $H_2SO_4$. A reagent was added to promote colour development and samples read on a spectrometer.

Total Cd in the soil was determined in digests using a 2.5 ml concentrated $HNO_3$ and 5.0 ml concentrated $HClO_4$ acid mixture added to 2 g of soil. The digests were filtered using Whatman No. 42 filter paper and diluted. The digested soil then underwent a clean-up process using dithizone-$CH_2Cl_2$ (Iu et al. 1979, Kamata et al., 1982). The following modifications were made to the procedure: 2-hydroxyethylethylenediaminetriacetic acid (HEDTA) was used to suppress interferences from Zn. The clean-up process involved complexing the Cd with dithizone

followed by the seperation of the dithizone complexes into aqueous and organic phases.

However, the amount of Zn in solution did not effect Cd recovery and thus HEDTA was not necessary. Methylene chloride was substituted for $CCl_4$ in the dithiozone solutions. The Cd concentration of the samples was determined using a Perkin-Elmer HGA 400 graphite furnace along with a Perkin-Elmer 560 Atomic Absorption spectrometer.

At each site, lysimeters constructed from PVC with a cross-sectional surface area of 483 cm$^2$ and a depth of 24 cm were embedded to a depth of 16 cm in the soil using a tractor with a front-end loader. After the soils in the lysimeters were amended with their respective SS or $CdCl_2$ treatments (section 3.1.2 and section 3.1.3), urea and monoammonium phosphate were added at rates of 150 kg N ha$^{-1}$ and 40 kg $P_2O_5$ ha$^{-1}$, respectively. Theses rates were far in excess of that required by the crop to eliminate nutrient deficiency as a growth limiting factor. The fertilizer was incorporated into the top 7.5 cm of soil. An indicator crop of Katepwa wheat was then sown at a rate of 100 kg ha$^{-1}$ and maintained till maturity. Weeds were controlled both manually and chemically. Chemical control was in the form of diclofop methyl bromoxynil (ester) (Hoe-grass 2; active ingredient of 310 g l$^{-1}$) which was sprayed twice during the growing season using a backpack

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sprayer at a rate of 3.5 l product ha$^{-1}$.

At harvest the wheat was cut at ground level and stored in burlap bags in a drying room at 70 C. When dry, grain and straw yields were measured. The grain was winnowed, then both winnowed grain and straw were ground to pass a 53 um screen and then stored for chemical analysis. Samples of soil were also collected to a depth of 7.5 cm from each lysimeter at harvest using an Oakfield soil sampler with a 2.5 cm diameter. The samples were air dried, ground with a mortar and pestel to pass through a 2 mm sieve and stored for chemical analysis.

During the second growing season, the mill used to grind the grain samples was replaced with a more recent model. However the new mill contained Cd in the grinding blade which contaminated the plant samples. This rendered the data from the second growing season useless and was subsequently disregarded from the study. The study was then extended to a third year. Stastistical analysis performed on the data was the least-significant-difference at the 5% level of significance.

## 3.1.1.1 Sewage Sludge Treatments

Sewage sludge obtained from the City of Winnipeg's Pollution Control Plant was applied to the lysimeters. Selected properties of the SS are given in Table 3.1. The rates of SS applied (containing 7.0 ug g$^{-1}$ Cd) were 0, 50, 100 and 200 t ha$^{-1}$ (dry weight basis) and were applied only once at the start of the study. The top 15 cm of soil was removed from each lysimeter. Sewage sludge was then incorporated uniformly into this soil and this mix was returned to the lysimeter.

To simulate certain environmental conditions that may enhance the availability of Cd to the plant, sub-plots of SS treatments were set up, as outlined above, then flooded or acidified (Table 3.2). One sub-treatment involved the flooding of the SS treatments twice during the growing season. Deionized water was used and the soil was flooded for five consecutive days at the seedling stage and again at anthesis.

To determine the effects of acidification, the following sub-treatments were conducted (Table 3.2). Deionized water, acidified to a pH of 3.5 with sulphuric acid, was added to SS-amended soil twice a week for 11 weeks. The amount of acidified water added was equivalent to 2.5 cm of precipitation. Initial and final pH readings were taken to determine the decline in pH (Table 3.3). The pH was measured

Table 3.2. Outline of Lysimeter Field Study Treatments

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**Sewage Sludge Experiment**

| | |
|---|---|
| SS Treatments | 0, 50, 100, 200 t ha$^{-1}$ |
| SS Subtreatments | 0, 50, 100, 200 t ha$^{-1}$:flooded |
| | 0, 50, 100, 200 t ha$^{-1}$:acidified |

**CdCl$_2$ Experiment**

| | |
|---|---|
| CdCl$_2$ Treatments | 0, 2, 4, 8, 16 kg Cd ha$^{-1}$ |
| CdCl$_2$ Subtreatments | 50 t ha$^{-1}$ SS plus 0 kg ha$^{-1}$ CdCl$_2$ |
| | 50 t ha$^{-1}$ SS plus 2 kg ha$^{-1}$ CdCl$_2$ |
| | 50 t ha$^{-1}$ SS plus 8 kg ha$^{-1}$ CdCl$_2$ |

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electrometrically in suspensions of soil: 0.01M CaCl$_2$ in a 1:2 ratio. A suspension of 10 g of soil and 20 ml CaCl$_2$ were thoroughly stirred then the pH taken on an Accumet 950 pH/ion meter. No crop was seeded on the acidified sub-treatments during the first growing season.

Table 3.3. The effect of water acidified to a pH of 3.5 on the pH of a Red River clay and a Lakeland clay loam amended with sewage sludge.

| Sewage Sludge (t ha$^{-1}$) | Red River pH | Lakeland |
|---|---|---|
| 0 | 5.8 | 7.3 |
| 50 | 5.9 | 7.1 |
| 100 | 6.0 | 7.1 |
| 200 | 5.9 | 7.1 |

## 3.1.1.2 Inorganic Cadmium Treatments

A second study was conducted using an inorganic source of Cd namely, $CdCl_2$ solution. Cadmium chloride was applied to the soil at rates of 0, 2, 4, 8 and 16 kg Cd $ha^{-1}$. The top 15 cm of soil in each lysimeter was removed, treated with the respective $CdCl_2$ solution, mixed and then subsequently returned to the lysimeter.

Sub-plots were established to determine the effect of SS on the availability and distribution of inorganic Cd in the soil (Table 3.2). The soil was amended with SS at the rate of 50 t $ha^{-1}$ and $CdCl_2$ was applied at two rates: 2 and 8 kg Cd $ha^{-1}$.

## 3.1.1.3 Plant Analysis

The Cd concentration in the grain and straw was determined as follows: 2 g of winnowed grain or straw material was digested using a 2.5 ml concentrated $HNO_3$ and 5.0 ml concentrated $HClO_3$ acid mixture (Isaac and Kerber, 1971). The digests were filtered using Whatman No. 42 filter paper and diluted. The digested plant tissue then underwent a clean-up process using dithizone-$CH_2Cl_2$ (Iu et al. 1979, Kamata et al., 1982) as outlined in section 3.1.1. The Cd concentration in the samples was determined using a Perkin-Elmer HGA 400 graphite furnace along with a Perkin-Elmer 560 Atomic Absorption

spectrometer.

Due to the complexity of the analysis required to determine Cd
in plant tissue and the need at the time for a better
analytical technique, grain and straw samples from 1988 were
used to develop a method to accurately determine the
concentration of Cd in plant tissue. Therefore, it was
necessary to combine grain and straw samples from 1988 from
which statistical analysis could not be performed. The method
of detecting and analyzing low levels of Cd increased in
sensitivity over the three year period which included the use
of a graphite furnace and the development of a clean-up
process with dithizone-$CH_2Cl_2$ by Dr. Geza Racz, Dr. Tee Boon
Goh and Val Huzel. As it took over two years to develop this
process, error and variability in values were initially high
but improved with time.

3.1.1.4 Sewage Sludge and Soil Analysis

To examine the fate of Cd applied to the soil, 7 g of ground
soil was treated with six reagents in a pre-determined
sequence. Each reagent is designed to extract Cd from a
specific soil fraction. The method was adapted from Stover et
al. (1976) and is outlined as follows with corresponding
soil/solution ratios: deionized water, 7:1; 1M $KNO_3$, 10:1;
0.5M KF, 10:1, pH 6.5; 0.1M $Na_4P_2O_7$, 10:1; 0.1M NaEDTA, 6:1

twice, pH 4.8; 1M $HNO_3$ 10:1. The soil and extractant were shaken for 60 min and the suspensions centrifuged, then filtered through Whatman No. 42 filter paper. The filtrate was analysed for Cd concentration. Prior to analysis for Cd, all samples underwent the clean-up process outlined in section 3.1.1.

The sequence of extractants used by Stover et al. (1976) to fractionate Cd are: $H_2O$, $KNO_3$, KF, $Na_4P_2O_7$, NaEDTA and $HNO_3$. Deionized water and $KNO_3$ extract the soluble an exchangeble Cd from the soil. Potassium nitrate acts as a source of cations to displace trace metals held on inorganic or organic sites predominantly by electrovalent forces (Beckett, 1989). Due to the strong complexing power of the fluoride ion, KF theoretically has the ability to extract metals from amorphous (poorly formed) alumino-silicates, especially from the clay fraction (Bracewell et al., 1970; Loveland and Bullock, 1976). Stover et al. (1976) favoured the use of KF as it extracts the adsorbed fraction, dissolves negligible amounts of carbonates or sulfides and does not appear to mobilize metals from organic matter.

Pyrophosphate is used principally to extract organically bound metals especially from organic matter flocculated and complexed by Ca, or by Fe and Al, which it disperses by complexing the flocculating cations (Beckett, 1989).

Controversy exists in the literature as to whether pyrophosphate also dissolves significant amounts of oxides. Some researchers (Miller et al., 1986) suggest that pyrophosphate has little effect on extracting oxide metals. Other researchers differ in this view. McLaren and Crawford (1973) and Rappaport et al. (1986) indicated that pyrophosphate did extract appreciable amounts of metals associated with the amorphous oxide fractions. Further, Rendell et al. (1980) determined that pyrophosphate dissolves free oxides associated with organic colloids particularly Fe and Al but much less free Fe from inorganic materials.

Perhaps the most controversial reagent in the extracting sequence is NaEDTA. Metals extracted using EDTA have been associated with many fractions including carbonates and oxides. Stover et al. (1976) considered EDTA as a good extractant for carbonates. However, other researchers have used it as an extractant for amorphous oxides (Miller and McFee, 1983, McLaren et al., 1986). It is thus probable that NaEDTA extracts a significant amount of metals from both the oxide and carbonate fractions.

The final reagent used is $HNO_3$ which is a strong oxidizing agent. Although Stover et al. (1976) used it as an extractant specific for the sulfide fraction, it is more commonly referred to as the residual fraction.

The third year's soil samples were analysed for water soluble and exchangeable Cd using $H_2O$ and $KNO_3$ extractants sequentially. Soil samples from 1988 were analysed using citrate-dithionite-bicarbonate (CDB) to further study Cd associated with free oxides. CDB was added to 10 g of soil ground to pass a 100 mesh sieve following the procedure by Mehra and Jackson (1960). The suspension was then centrifuged, filtered using Whatman No. 42 filter paper and the filtrate analysed for Cd. Analysis was conducted using a Perkin-Elmer HGA 400 graphite furnace along with a Perkin-Elmer 560 Atomic Absorption spectrometer. The analysis underwent the clean-up process outlined in section 3.1.1.

3.1.2 RESULTS AND DISCUSSION OF PLANT ANALYSIS

3.1.2.1 Effect of Sewage Sludge on Crop Growth and

Accumulation of Cadmium in a Red River clay soil


Table 3.4 indicates that no statistical yield differences in grain or straw were obtained from growing wheat on a SS-amended Red River soil in either 1988 or 1990. In 1988 the average grain yield on the Red River soil was 20.8 g and the average straw yield was 19.2 g. In 1990 the average grain yield was 28.2 g and straw yield was 24.3 g. The yields were lower in 1988 due to the drought conditions and relatively high temperatures experienced during that growing season.

Wheat grown on the simulated flooded SS treatments on the Red River soil did not show any significant yield differences (Table 3.4) among flooded treatments nor among flooded and non-flooded SS treatments for grain or straw. This observation was consistent for years 1 and 3 (Table 3.4).

Wheat grown on the simulated acidified SS treatments on the Red River soil in 1990 did not show in any significant grain or straw yield differences (Table 3.4) among acidified treatments nor among acidified and non-acidified SS treatments.

Table 3.4. Yield of wheat grown on Red River clay treated with sewage sludge under normal and adverse environmental conditions.

| | Year 1 1988 | | Year 3 1990 | |
|---|---|---|---|---|
| SEWAGE SLUDGE RATE (t ha$^{-1}$) | Grain | Straw (g lysimeter$^{-1}$) | Grain | Straw |
| 0 | 21.4a* (2.8)** | 19.6a (3.0) | 27.0a (3.5) | 24.2a (2.6) |
| 50 | 19.6a (1.6) | 19.3a (3.4) | 32.4a (5.5) | 27.3a (3.1) |
| 100 | 19.4a (2.8) | 18.7a (5.0) | 21.1a (3.7) | 20.9a (4.3) |
| 200 | 22.7a (3.9) | 19.0a (3.1) | 32.5a (4.9) | 24.7a (3.7) |
| SEWAGE SLUDGE RATE + FLOODING | | | | |
| 0 | 18.5a (1.8) | 18.0a (1.5) | 37.8a (4.6) | 33.1a (2.9) |
| 50 | 20.8a (4.1) | 23.1a (2.6) | 39.9a (7.9) | 35.0a (6.3) |
| 100 | 17.7a (1.7) | 20.2a (1.9) | 31.2a (4.7) | 29.3a (3.9) |
| 200 | 16.5a (1.7) | 20.7a (4.0) | 21.0a (4.8) | 26.2a (3.6) |
| SEWAGE SLUDGE RATE + ACIDIFICATION | | | | |
| 0 | – | – | 18.5a (3.4) | 14.8a (5.4) |
| 50 | – | – | 26.3a (4.7) | 23.3a (3.7) |
| 100 | – | – | 25.3a (4.9) | 23.5a (4.8) |
| 200 | – | – | 25.5a (3.7) | 25.1a (5.1) |

* Means in each column followed by the same letter are not significantly different at the 0.05 level according to the LSD test.
** Standard deviation in brackets.

Table 3.5 shows the Cd concentration of grain and straw grown on Red River soil amended with SS. During the year of application (1988) the total Cd concentration in the grain more than doubled from 0.027 µg g$^{-1}$ for the control to 0.057 µg g$^{-1}$ for the 200 t ha$^{-1}$ rate of SS (Table 3.5). The concentration of Cd in the straw showed a similar increasing trend (Table 3.5). The Cd concentration in the check was 0.037 µg g$^{-1}$ and at the 200 t ha$^{-1}$ rate was over double at 0.081 µg g$^{-1}$. However even at the highest rate of SS applied, 200 t ha$^{-1}$, the concentration of Cd in the grain was still considerably lower than acceptable limits, 0.1 µg g$^{-1}$ (WHO, 1977).

The flooded treatments also showed an increasing trend in Cd concentration in grain and straw with the application of SS (Table 3.5). However the total concentration at each treatment was lower on average than for the SS treatments without flooding.

In 1990, the Cd concentration in the grain and straw of wheat grown on the Red River soil treated with SS did not differ significantly among treatments (Table 3.5). The average concentration of Cd in the grain for the four treatments was 0.054 µg g$^{-1}$ and in the straw for the four treatments was 0.10 µg g$^{-1}$.

Table 3.5. Cd content of wheat grown on Red River clay treated with sewage sludge under normal and adverse environmental conditions.

| SEWAGE SLUDGE RATE (t ha$^{-1}$) | Year 1 1988 | | Year 3 1990 | |
|---|---|---|---|---|
| | Grain | Straw (ug Cd g$^{-1}$) | Grain | Straw |
| 0 | 0.027 | 0.037 | 0.077a* (.016)** | 0.176a (.146) |
| 50 | 0.031 | 0.055 | 0.045a (.009) | 0.049a (.017) |
| 100 | 0.044 | 0.049 | 0.051a (.010) | 0.056a (.029) |
| 200 | 0.057 | 0.081 | 0.045a (.026) | 0.110a (.051) |
| **SEWAGE SLUDGE RATE + FLOODING** | | | | |
| 0 | 0.011 | 0.049 | 0.144a* (.075) | 0.455b (.023) |
| 50 | 0.014 | 0.037 | 0.080a (.050) | 0.263ab (.149) |
| 100 | 0.017 | 0.057 | 0.174a (.096) | 0.426b (.199) |
| 200 | 0.025 | 0.049 | 0.054a (.091) | 0.154a (.105) |
| **SEWAGE SLUDGE RATE + ACIDIFICATION** | | | | |
| 0 | – | – | 0.055a (.014) | 0.170a (.178) |
| 50 | – | – | 0.047a (.018) | 0.151a (.146) |
| 100 | – | – | 0.045a (.036) | 0.187a (.181) |
| 200 | – | – | 0.038a (.024) | 0.108a (.052) |

* Means in each column followed by the same letter are not significantly different at the 0.05 level according to the LSD test.
** Standard deviation in brackets.

The Cd concentration in the grain in the flooded and the acidified treatments on the Red River soil (Table 3.5) were also not significantly different. The Cd concentration in the straw however did show statistical differences in the flooded treatments. The control had the highest concentration of Cd at 0.455 $\mu g\ g^{-1}$. This tends to suggest that this sample was contaminated from an external source prior to analysis.

3.1.2.2 Effect of Sewage Sludge on Crop Growth and

Accumulation of Cadmium in a Lakeland clay loam soil

Significant grain and straw yield differences were obtained in 1988 from SS applications to the Lakeland soil (Table 3.6). The application of 50 tonnes of SS outyielded the check by 6.7 g of grain and by 6.0 g of straw. No significant yield differences were observed between the 50, 100 and 200 t $ha^{-1}$ SS treatments for the grain or straw (Table 3.6).

The flooded treatments in 1988 showed a similar trend for grain yields. The straw yield however was significantly higher at the 200 t $ha^{-1}$ SS rate than all the other treatments weighing 42.7 g compared to the flooded check at 23.4 g (Table 3.6).

By 1990 there were no significant grain or straw yield differences from the SS-amended soil (Table 3.6). The average

Table 3.6. Yield of wheat grown on Lakeland clay loam treated with sewage sludge under normal and adverse environmental conditions.

| SEWAGE SLUDGE RATE (t ha$^{-1}$) | Year 1 1988 | | Year 3 1990 | |
|---|---|---|---|---|
| | Grain | Straw | Grain | Straw |
| | (g lysimeter$^{-1}$) | | | |
| 0 | 22.4a (2.9) | 24.1a (4.0) | 31.9a (1.8) | 24.3a (3.9) |
| 50 | 29.1b (3.7) | 30.1b (0.8) | 44.2a (6.8) | 35.0a (4.8) |
| 100 | 28.7b (5.8) | 32.1b (2.4) | 33.5a (2.6) | 26.2a (2.1) |
| 200 | 34.5b (8.8) | 34.7b (3.6) | 33.4a (3.5) | 28.5a (1.9) |
| **SEWAGE SLUDGE RATE + FLOODING** | | | | |
| 0 | 21.3a (1.8) | 23.4a (3.6) | 24.5a (7.2) | 21.8a (4.6) |
| 50 | 33.0b (3.8) | 34.8b (4.2) | 33.6a (1.2) | 32.1a (5.6) |
| 100 | 32.7b (1.0) | 36.2b (2.6) | 32.2a (1.8) | 26.1a (2.4) |
| 200 | 39.2b (1.0) | 42.7c (4.6) | 30.4a (4.7) | 25.9a (1.2) |
| **SEWAGE SLUDGE RATE + ACIDIFICATION** | | | | |
| 0 | - | - | 32.6a (1.8) | 24.3a (2.7) |
| 50 | - | - | 35.5a (2.9) | 33.5a (5.9) |
| 100 | - | - | 37.1a (4.6) | 26.5a (1.2) |
| 200 | - | - | 30.6a (1.8) | 25.4a (2.2) |

\* Means in each column followed by the same letter are not significantly different at the 0.05 level according to the LSD test.
\*\* Standard deviation in brackets.

grain yield in 1990 was 35.7 g and average straw yield was 28.5 g.

The flooded treatments and the acidified treatments did not result in significant grain and straw yield differences in 1990 either (Table 3.6) when comparing among SS rates within each sub-treatment.

Table 3.7 shows the Cd concentration of grain and straw grown on SS-amended Lakeland soil. During the year of application (1988) the Cd concentration in the grain was negligible for all the SS applications including the flooded treatments. The Cd concentration in the straw however increased slightly at the 0 and 50 t ha$^{-1}$ application rates to 0.006 µg g$^{-1}$ at the 100 t ha$^{-1}$ rate to 0.024 µg g$^{-1}$ at the 200 t ha$^{-1}$ rate. Cadmium concentration in the straw grown on the flooded treatments were all negligible in 1988 (Table 3.7).

In 1990 (Table 3.7), the concentration of Cd in the grain and straw for wheat grown on the SS-amended Lakeland soil had increased from 1988 but no significant differences were found among rates of SS applied. The average Cd concentration in the grain was 0.024 µg g$^{-1}$ and in the straw was 0.044 µg g$^{-1}$.

In the flooded treatments, the Cd concentration in the straw differed significantly but reasoning points again to

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Table 3.7. Cd content of wheat grown on Lakeland clay loam treated with sewage sludge under normal and adverse environmental conditions.

| SEWAGE SLUDGE RATE (t ha$^{-1}$) | Year 1 1988 Grain | Straw (ug Cd g$^{-1}$) | Year 3 1990 Grain | Straw |
|---|---|---|---|---|
| 0 | nd* | nd | 0.011a** (.006)*** | 0.026a (.009) |
| 50 | nd | nd | 0.020a (.006) | 0.040a (.009) |
| 100 | nd | 0.006 | 0.017a (.003) | 0.038a (.013) |
| 200 | nd | 0.024 | 0.050a (.040) | 0.072a (.053) |
| **SEWAGE SLUDGE RATE + FLOODING** | | | | |
| 0 | nd | nd | 0.211b (.150) | 0.367bc (.270) |
| 50 | nd | nd | 0.043a (.033) | 0.079a (.044) |
| 100 | nd | nd | 0.259b (.058) | 0.428c (.146) |
| 200 | 0.003 | 0.009 | 0.081a (.070) | 0.142ab (.123) |
| **SEWAGE SLUDGE RATE + ACIDIFICATION** | | | | |
| 0 | – | – | 0.032a (.032) | 0.026a (.006) |
| 50 | – | – | 0.075a (.069) | 0.205bc (.246) |
| 100 | – | – | 0.075a (.065) | 0.186ab (.159) |
| 200 | – | – | 0.043a (.033) | 0.069a (.055) |

*nd = non-detectable
** Means in each column followed by the same letter are not significantly different at the 0.05 level according to the LSD test.
*** Standard deviation in brackets.

contamination of samples rather than differences in Cd availability to the plant as the values vary randomly and are high at low SS application rates. The Cd concentrations of the grain and straw were not significantly affected by the acid treatments.

### 3.1.2.3 Effect of Inorganic Cadmium on Crop Growth and accumulation of Cadmium in a Red River clay soil

Wheat grown on the Red River soil treated with $CdCl_2$ (Table 3.8) showed no grain or straw yield response to inorganic Cd in 1988 or 1990 even at rates as high as 16 kg $ha^{-1}$. The addition of 50 t $ha^{-1}$ of SS to the $CdCl_2$ treatments also had no effect on the grain or straw yields (Table 3.8).

However, there is a distinct increasing trend in the Cd concentration in the grain and straw of wheat grown on the Red River soil with increasing rates of $CdCl_2$ applied, (Table 3.9). The Cd concentration of the grain at the check was 0.027 $\mu g$ $g^{-1}$ and increased to 1.869 $\mu g$ $g^{-1}$ at the 16 kg $ha^{-1}$ treatment. The grain at the 2 kg $ha^{-1}$ treatment contained 0.513 $\mu g$ $g^{-1}$ of Cd and with the addition of 50 t $ha^{-1}$ SS the grain contained 0.234 $\mu g$ $g^{-1}$ (Table 3.9). At the 8 kg $ha^{-1}$ treatment, the Cd concentrations were 1.386 and 0.895 $\mu g$ $g^{-1}$ for the $CdCl_2$ treatment and the $CdCl_2$ plus SS treatment respectively. This suggests that the addition of an organic

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Table 3.8. Yield of wheat grown on Red River clay treated with $CdCl_2$ and $CdCl_2$ plus 50 t ha$^{-1}$ sewage sludge.

| $CdCl_2$ RATE (kg Cd ha$^{-1}$) | Year 1 1988 | | Year 3 1990 | |
|---|---|---|---|---|
| | Grain | Straw | Grain | Straw |
| | | (g lysimeter$^{-1}$) | | |
| 0 | 21.4a* (2.8)** | 19.6a (2.9) | 27.0a (3.5) | 24.3a (2.6) |
| 2 | 21.5a (5.2) | 22.8a (2.9) | 26.9a (2.3) | 23.0a (1.8) |
| 4 | 22.8a (5.3) | 23.9a (5.9) | 23.1a (1.8) | 13.8a (6.3) |
| 8 | 22.8a (4.6) | 20.0a (0.9) | 33.6a (5.7) | 28.3a (4.7) |
| 16 | 19.4a (3.2) | 15.3a (6.5) | 29.6a (4.8) | 25.8a (3.6) |
| $CdCl_2$ RATE + SEWAGE SLUDGE | | | | |
| 2 | 20.9a (1.9) | 20.2a (7.3) | 21.8a (2.1) | 21.8a (2.4) |
| 8 | 22.7a (4.1) | 18.4a (2.5) | 33.5a (6.2) | 33.5a (6.1) |

* Means in each column followed by the same letter are not significantly different at the 0.05 level according to the LSD test.
** Standard deviation in brackets.

Table 3.9. Cd content of wheat grown on a Red River clay
treated with $CdCl_2$ and $CdCl_2$ plus 50 t $ha^{-1}$
sewage sludge.

| CdCl₂ RATE (kg Cd ha⁻¹) | Year 1 1988 | | Year 3 1990 | |
|---|---|---|---|---|
| | Grain | Straw | Grain | Straw |
| | | | (ug Cd g⁻¹) | |
| 0 | 0.027 | 0.037 | 0.077a* (.016)** | 0.176a (0.146) |
| 2 | 0.513 | 0.984 | 0.041a (.003) | 0.033a (.017) |
| 4 | 0.837 | 1.822 | 0.049a (.016) | 0.045a (.003) |
| 8 | 1.386 | 1.408 | 0.038a (.007) | 0.044a (.030) |
| 16 | 1.869 | 3.067 | 0.050a (.027) | 0.075a (.047) |
| **CdCl₂ RATE + SEWAGE SLUDGE** | | | | |
| 2 | 0.234 | 0.398 | 0.047a (.024) | 0.066a (.004) |
| 8 | 0.895 | 1.767 | 0.043a (.013) | 0.042a (.011) |

\* Means in each column followed by the same letter are not significantly
   different at the 0.05 level according to the LSD test.
\*\* Standard deviation in brackets.

matrix such as SS reduces the availability of Cd to the plant. However this is not strictly the case with Cd concentration in the straw. Comparing the 2 kg ha$^{-1}$ treatment of $CdCl_2$ with and without SS, indicates that the SS treatment is again lower at 0.398 $\mu$g g$^{-1}$ compared to 0.984 $\mu$g g$^{-1}$ (Table 3.9). At the 8 kg ha$^{-1}$ treatment, the $CdCl_2$ plus SS is higher at 1.767 $\mu$g g$^{-1}$ compared to 1.408 $\mu$g g$^{-1}$ without the SS. In the absence of a statistical analysis, it is difficult to draw definite conclusions but the Cd data for 1988 suggests that the level of Cd in grain or straw tissue is not affected by the presence of SS. This is definitely the case for Cd in both the grain and straw in 1990. There are no statistical differences among any of the Cd treatments for grain or straw including the $CdCl_2$ rates that were applied with and without SS (Table 3.9). The average Cd concentration in the grain in 1990 was 0.051 $\mu$g g$^{-1}$ and in the straw, 0.075 $\mu$g g$^{-1}$.

3.1.2.4 Effect of Inorganic Cadmium on Crop Growth and accumulation of Cadmium in a Lakeland clay loam soil

The application of $CdCl_2$ up to 16 kg ha$^{-1}$ did not significantly effect the yield of wheat grown on Lakeland soil in 1988 or 1990 (Table 3.10). The data also show that the application of 50 t ha$^{-1}$ of SS along with the $CdCl_2$ had little effect on straw or grain yield (Table 3.10).

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Table 3.10. Yield of wheat grown on a Lakeland clay loam treated with $CdCl_2$ and $CdCl_2$ plus sewage sludge.

| CdCl₂ RATE (kg Cd ha⁻¹) | Year 1 1988 | | Year 3 1990 | |
| --- | --- | --- | --- | --- |
| | Grain | Straw | Grain | Straw |
| | | (g lysimeter⁻¹) | | |
| 0 | 21.4a* (2.8)** | 19.6a (3.0) | 31.9a (2.5) | 24.3a (6.1) |
| 2 | 22.8a (5.2) | 21.5a (2.9) | 37.7a (5.7) | 28.2a (3.4) |
| 4 | 23.9a (5.3) | 22.8a (5.9) | 34.3a (3.8) | 33.3a (2.4) |
| 8 | 20.0a (4.6) | 22.8a (0.9) | 33.0a (2.1) | 33.1a (2.6) |
| 16 | 15.3a (3.2) | 19.4a (6.5) | 36.6a (4.2) | 37.9a (6.5) |
| CdCl₂ RATE + SEWAGE SLUDGE | | | | |
| 2 | 20.2a (1.9) | 20.9a (7.3) | 30.2a (2.6) | 28.4a (4.9) |
| 8 | 18.4a (4.1) | 22.7a (2.5) | 36.9a (4.6) | 31.3a (2.8) |

\* Means in each column followed by the same letter are not significantly different at the 0.05 level according to the LSD test.
\*\* Standard deviation in brackets.

The amount of Cd in the grain grown on the Lakeland soil (Table 3.11) increased with increasing levels of $CdCl_2$ from non-detectable in the control to 0.667 $\mu$g g$^{-1}$ in the 16 kg ha$^{-1}$ treatment. The Cd concentration in the straw also increased with amount of Cd applied. The addition of 50 t ha$^{-1}$ of SS to the 2 and 8 kg ha$^{-1}$ treatments did not have any effect on the Cd concentration in the grain or straw (Table 3.11). This supports the conclusion derived from the data on the Red River soil (Table 3.9). At the 2 kg ha$^{-1}$ treatment, the Cd concentration in the grain was 0.152 $\mu$g g$^{-1}$ and 0.127 $\mu$g g$^{-1}$ without and with SS, respectively for the grain. At the 8 kg ha$^{-1}$ treatment the Cd concentration for the grain was 0.537 $\mu$g g$^{-1}$ and 0.545 $\mu$g g$^{-1}$ without and with SS, respectively. For the straw, the Cd concentrations without and with SS were 0.256 $\mu$g g$^{-1}$ and 0.477 $\mu$g g$^{-1}$, respectively, at the 2 kg ha$^{-1}$ treatment and 1.199 $\mu$g g$^{-1}$ and 1.469 $\mu$g g$^{-1}$, respectively, at the 8 kg ha$^{-1}$.

The differences in the Cd concentration in the grain and straw in 1990 were not statistically significant among $CdCl_2$ treatments (Table 3.11). The Cd concentration in the grain averaged 0.022 $\mu$g g$^{-1}$ and the straw, 0.034 $\mu$g g$^{-1}$ over all treatments. Again the addition of 50 t ha$^{-1}$ of SS did not have a significant effect on the Cd concentration in the tissue.

Table 3.11. Cd content of wheat grown on a Lakeland clay loam
treated with $CdCl_2$ and $CdCl_2$ plus 50 t $ha^{-1}$ sewage
sludge.

| CdCl₂ RATE (kg Cd ha⁻¹) | Year 1 1988 | | Year 3 1990 | |
|---|---|---|---|---|
| | Grain | Straw (ug Cd g⁻¹) | Grain | Straw |
| 0 | nd | nd | 0.011a (.006) | 0.026a (.009) |
| 2 | 0.152 | 0.256 | 0.017a (.006) | 0.032a (.006) |
| 4 | 0.224 | 0.753 | 0.023a (.009) | 0.053a (.013) |
| 8 | 0.537 | 1.199 | 0.021a (.009) | 0.025a (.005) |
| 16 | 0.667 | 1.468 | 0.037a (.035) | 0.032a (.010) |
| CdCl₂ RATE + SEWAGE SLUDGE | | | | |
| 2 | 0.127 | 0.477 | 0.014a (.010) | 0.046a (.004) |
| 8 | 0.545 | 1.469 | 0.014a (.007) | 0.025a (.011) |

\* Means in each column followed by the same letter are not significantly
   different at the 0.05 level according to the LSD test.
\*\* Standard deviation in brackets.

3.1.2.5 Discussion of the Effects of Cadmium from Sewage
         Sludge and from Inorganic Cadmium on Crop Growth
         and Plant Tissue Levels of Cadmium


Favourable yield responses by crops to soil amended with SS
are well documented (Milne and Graveland, 1972; Chang et al.,
1982).    However  no  significant  yield  differences  were
established from the application of SS to either the Red River
soil or the Lakeland soil.   This lack of yield response was
expected due to the high rates of nitrogen and phosphorus
fertilizers applied to the lysimeters. This in effect negated
the   beneficial   nutrient   response   associated   with   the
application of SS to crops.


An exception to the lack of yield response was the increase in
grain  and  straw  yields  on  the  Lakeland  soil  with  the
application of SS during the year of application. This can be
explained as follows.  The Lakeland soil due to its clay loam
texture had a low moisture holding capacity and a relatively
fast  infiltration  rate.    With  the  application  of  SS,  the
soil's infiltration rate slowed considerably.  Therefore more
water was available to the crop in the lysimeters amended with
SS and a response in grain and straw yield resulted.  This did
not occur in the lysimeters from the Red River soil due to the
inherently  high  moisture  holding  capacity  and  slow
infiltration rate of that soil.   The growing season of 1990

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was not as dry as 1988. Therefore, the moisture holding capacity and the infitration rate of the Lakeland soil did not play as important a part in affecting yields in 1990.

Cadmium is not a plant nutrient and its presence in plant tissue has not been shown to be of beneficial physiological importance. The application of $CdCl_2$ to the soil therefore was not expected to increase wheat yields. This was the case as the results from the $CdCl_2$ study indicate. However relatively high amounts of Cd (eg. 1.869 $\mu g$ $g^{-1}$) were found in the wheat tissue at the higher rates of $CdCl_2$. The Cd concentration of the grain grown on the Red River and Lakeland soil with no applications of SS or $CdCl_2$ ranged from 0.027 to 0.077 $\mu g$ $g^{-1}$ and from non-detectable to 0.011 $\mu g$ $g^{-1}$, respectively. These values agree with findings by other researchers (Bingham et al., 1975; Chang et al., 1982) and the WHO (1977) value of < 0.1 $\mu g$ $g^{-1}$ for Cd concentrations typical for wheat. However the presence of high levels of Cd did not lower wheat yields on either soil. This is an indication of the insidious nature of Cd in the food chain. High levels of Cd in plant tissue is not evident unless analysis for Cd is conducted. The absence of visual symptoms in wheat to high levels of Cd has been found by others (Haghiri, 1973).

Cunningham et al. (1975) advised caution when attempting to use results derived from inorganic salt treatments to evaluate

metal uptake from SS-amended soils. Metals in an inorganic form are more bioavailable and phytotoxic. However, the data from the inorganic Cd study does indicate that by the third year after application, the Cd was no longer readily available to the crop, even at the higher rates applied. This suggests that when the SS decomposes in the soil and the Cd is released, it is tied up by the soil and is not readily bioavailable.

The application of SS to a Lakeland soil had a negligible effect on the Cd concentration in the grain and straw tissue in 1988 or 1990. The Cd concentration of the grain and straw grown on the SS-amended Lakeland soil was lower than the grain or straw grown on the Red River soil. This was expected due to the difference in pH of the two soils. Cadmium bioavailability depends on pH (Linnman et al., 1973). The lower the pH, the more bioavailable the Cd. Studies have shown that Cd is more available on acid soils than calcareous ones (Mahler et al., 1980). As the pH of the Red River soil is 6.2 compared to 7.3 for the Lakeland soil, it follows that the Cd concentration of wheat grown on SS-amended Red river soil would be higher. The flooded treatments did not significantly affect the yield of grain or straw on either the Red River or Lakeland soils. Cadmium availability to plants can be enhanced by reducing conditions due to flooding (Sims and Patrick, 1978). However, the Cd concentration in the

grain or straw tissue on the Red River or Lakeland soil did not differ significantly. These findings suggest, therefore, that during an unusually wet growing season the application of SS to these soils will not effect the growth of wheat nor increase the bioavailability of Cd.

Contrary to what was expected, the acidified treatments did not significantly effect the yield of grain or straw grown on SS-amended Red River or Lakeland soil. Studies have shown a strong relationship between pH and Cd bioavailability. Linnman et al. (1973) illustrated that as the pH of the soil was raised by applying CaO, the Cd concentration in plants declined. However the Cd concentration in the grain or straw tissue on either the Red River or Lakeland soil was not elevated significantly from the acidified treatments. The acidifying treatments did not lower the pH of the Lakeland soil substantially (Table 3.3) and therefore Cd availability to the plants remained the same. The pH of the Red River soil, however, decreased slightly from 6.2 to 5.9 (Table 3.3). However, the pH decline did not effect Cd bioavailability. This suggests, therefore, that both the Red River soil and the Lakeland soil, treated with SS, can withstand considerable acidifying conditions before the pH of either soil will drop low enough to increase the concentration of Cd in the tissue of wheat.

3.1.3 RESULTS AND DISCUSSION OF SOIL ANALYSIS

3.1.3.1 Effect of Sewage Sludge on the Content and
        Distribution of Cadmium in a Red River Clay Soil

Table 3.12 shows the total extractable Cd from a Red River soil amended with SS for 1988 after the crop was harvested. The total Cd extracted increased from 0.095 $\mu g\ g^{-1}$ in the check to 0.340 $\mu g\ g^{-1}$ at the 200 t $ha^{-1}$ SS rate. For the flooded SS treatments, the total Cd extracted increased from 0.126 $\mu g\ g^{-1}$ to 0.457 $\mu g\ g^{-1}$ for the same rates of SS. Further, the amount of Cd extracted by the various extractants from the flooded SS treatments were similar to the SS treatments without flooding.

Table 3.12 also gives some indication as to the distribution of the extractable Cd in the soil. Very little Cd was extracted with water. Generally less than 3% of the Cd was extracted using $KNO_3$ and less than 2% using EDTA. Most of the Cd was extracted using $Na_4P_2O_7$, 76% on average. The amount of Cd removed by the various extractants from the flooded SS treatments was similar to the SS treatments without flooding.

At harvest in 1990, the $H_2O$- and $KNO_3$-extractable Cd in the SS-amended Red River soil (Table 3.13) were still very low and concentrations were not statistically different among treatments. The average amount of Cd extracted over all SS

Table 3.12. Total Cd extracted and the distribution of Cd in a Red River clay treated with sewage sludge under flooded and non-flooded conditions during the initial year of application using a sequential extraction procedure.

| SEWAGE SLUDGE RATE (t ha$^{-1}$) | $H_2O$ | $KNO_3$ | KF | $NaP_2O_7$ | EDTA | $HNO_3$ | TOTAL (ug g$^{-1}$) |
|---|---|---|---|---|---|---|---|
| | | | (% of total extracted) | | | | |
| 0 | nd* | 4.3 (0.0) | 9.7 (0.5) | 80.6 (25.7) | 1.1 (1.0) | 4.3 (1.6) | 0.095 (.021) |
| 50 | nd | 2.8 (0.0) | 8.3 (4.7) | 76.1 (29.2) | 1.7 (0.0) | 11.6 (10.5) | 0.170 (.074) |
| 100 | nd | 2.4 (0.8) | 9.1 (3.5) | 66.3 (20.5) | 1.0 (0.0) | 20.9 (14.5) | 0.308 (.107) |
| 200 | nd | 2.3 (0.0) | 8.8 (4.5) | 78.3 (16.5) | 0.8 (0.0) | 9.7 (7.1) | 0.340 (.084) |
| **SEWAGE SLUDGE RATE + FLOODING** | | | | | | | |
| 0 | nd | nd | 5.6 (0.0) | 87.3 (34.1) | 1.2 (1.0) | 6.3 (4.4 | 0.126 (.050) |
| 50 | nd | nd | 7.7 (0.3) | 86.7 (9.6) | 1.6 (0.0) | 4.0 (1.3) | 0.188 (.049) |
| 100 | nd | 2.0 (0.0) | 7.8 (0.6) | 78.7 (8.2) | 1.2 (0.0) | 10.2 (8.8) | 0.244 (.002) |
| 200 | nd | 1.7 (0.8) | 10.5 (0.5) | 54.7 (44.1) | 7.6 (7.1) | 25.3 (8.4) | 0.457 (.061) |

* nd = non-detectable
** Standard deviation in brackets.

Table 3.13. $H_2O$ and $KNO_3$ extractable Cd of a Red River clay and a Lakeland clay loam treated with sewage sludge under normal and adverse conditions.

| | Red River | | Lakeland | |
|---|---|---|---|---|
| SEWAGE SLUDGE RATE (t ha$^{-1}$) | $H_2O$ | $KNO_3$ | $H_2O$ | $KNO_3$ |
| | | (ug Cd g$^{-1}$) | | |
| 0 | 0.002a* | 0.005a | 0.004a | nd |
| 50 | 0.005a | 0.005a | 0.003a | nd |
| 100 | 0.003a | 0.005a | nd | 0.002a |
| 200 | 0.008a | 0.006a | 0.005a | 0.002a |
| SEWAGE SLUDGE RATE + FLOODING | | | | |
| 0 | 0.002a | 0.005a | 0.006a | nd |
| 50 | 0.002a | 0.003a | nd | 0.004a |
| 100 | nd | 0.006a | nd | 0.003a |
| 200 | 0.002a | 0.005a | nd | 0.002a |
| SEWAGE SLUDGE RATE + ACIDIFICATION | | | | |
| 0 | nd | 0.005a | 0.002a | 0.002a |
| 50 | 0.006a | 0.003a | 0.002a | 0.002a |
| 100 | 0.005a | 0.005a | 0.002a | 0.002a |
| 200 | nd | 0.006a | 0.002a | nd |

* Means in each column followed by the same letter are not significantly different at the 0.05 level according to the LSD test.

treatments, with no flooding or acidification, using $KNO_3$ was 0.005 $\mu g$ $g^{-1}$. Under flooded and acidified conditions the concentration of Cd extracted was not statistically different among treatments nor from the SS-amended soil.

3.1.3.2 Effect of Sewage Sludge on the Content and
       Distribution of Cadmium in a Lakeland clay loam soil

The total Cd extracted after harvest from the SS-amended Lakeland soil is given in Table 3.14. The total Cd extracted increased from 0.039 $\mu g$ $g^{-1}$ for the check to 0.347 $\mu g$ $g^{-1}$ for the 200 t $ha^{-1}$ SS treatment. In the flooded treatments, the Cd extracted also increased with increasing SS rates (Table 3.14) similar to the non-flooded treatments.

The distribution of Cd extracted from the Lakeland soil under flooded and non-flooded conditions was similar to the trends observed for the Red River soil. Again most of the Cd was extracted using $Na_4P_2O_7$, 82% on average. Water extractable Cd was very low, and generally < 2% of the Cd was extracted using $KNO_3$ and generally < 5% with EDTA.

At harvest in 1990 (Table 3.13), $H_2O$- and $KNO_3$-extractable Cd from the Lakeland soil amended with SS did not differ significantly with increasing rates of SS. The $H_2O$-extractable Cd ranged from negligible to 0.005 $\mu g$ $g^{-1}$ and the

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Table 3.14.  Total Cd extracted and the distribution of Cd in a Lakeland clay loam treated with sewage sludge under flooded and non-flooded conditions during the initial year of application using a sequential extraction procedure.

| SEWAGE SLUDGE RATE (t ha⁻¹) | H$_2$O | KNO$_3$ | KF | Na$_4$P$_2$O$_7$ | EDTA | HNO$_3$ | TOTAL |
|---|---|---|---|---|---|---|---|
| (t ha⁻¹) | | | (% of total Cd extracted) | | | | (µg g⁻¹) |
| 0 | nd* | 17.9 (16.0)** | nd | 64.1 (0.0) | 9.0 (0.0) | 9.0 (3.8) | 0.039 (.015) |
| 50 | nd | 2.0 (2.0) | nd | 96.0 (12.2) | 1.5 (0.0) | nd | 0.197 (.023) |
| 100 | nd | 2.0 (0.0) | 2.4 (0.0) | 76.0 (8.6) | 2.4 (0.0) | 3.4 (3.3) | 0.296 (.065) |
| 200 | nd | 0.9 (0.9) | 2.4 (0.0) | 92.2 (6.6) | 2.0 (0.0) | 2.3 (2.3) | 0.347 (.039) |
| **SEWAGE SLUDGE RATE + FLOODING** | | | | | | | |
| 0 | nd | nd | 12.1 (10.3) | 48.3 (18.3) | 24.1 (0.0) | 15.5 (15.0) | 0.029 (.013) |
| 50 | nd | 13.1 (1.9) | 4.4 (1.9) | 72.5 (69.1) | 4.4 (0.0) | 5.0 (1.9) | 0.160 (.108) |
| 100 | nd | 2.3 (2.5) | 3.2 (0.0) | 87.3 (9.5) | 1.4 (0.0) | 5.4 (1.8) | 0.221 (.020) |
| 200 | nd | nd | 7.7 (1.4) | 76.1 (37.8) | 3.2 (0.0) | 13.1 (1.0) | 0.222 (.036) |

* nd = non-detectable
** standard deviation in brackets

KNO$_3$-extractable Cd ranged from negligible to 0.002 μg g$^{-1}$.
The effect of flooding or acidifying on extractable Cd was not
significant (Table 3.13).


3.1.3.3 Effect of Inorganic Cadmium on the Content and
          Distribution of Cadmium in a Red River clay soil


Total Cd extracted after harvest from the Red River soil
treated with CdCl$_2$ increased from 0.095 μg g$^{-1}$ for the check to
3.896 μg g$^{-1}$ for the 16 kg ha$^{-1}$ treatment.  The application of
SS to the CdCl$_2$ treatments nearly doubled the total amount of
Cd extracted (Table 3.15).


As Table 3.15 indicates, the distribution of Cd extracted was
very similar to that of the SS-amended Red River soil (Table
3.12).  Most of the extractable Cd was removed with Na$_4$P$_2$O$_7$,
82% on average.  Negligible amounts were extracted with water,
KNO$_3$ extracted generally < 3% and KF < 13%.  The trends did
not vary greatly among treatments.  The addition of SS to the
CdCl$_2$ treatment increased the total Cd extracted but did not
significantly effect the distribution of Cd in the soil.


At harvest in 1990 (Table 3.16), there was a slight increase
in total extractable Cd by H$_2$O from 0.002 μg g$^{-1}$ to 0.009 μg g$^{-1}$
but is not staistically significant.  The KNO$_3$-extractable Cd
also increased by 1990 with CdCl$_2$ rate from 0.005 μg g$^{-1}$ to

**Table 3.15.** Total Cd extracted and the distribution of Cd in in a Red River clay treated with $CdCl_2$ and $CdCl_2$ plus 50 t $ha^{-1}$ sewage sludge using a sequential extraction procedure.

| $CdCl_2$ RATE (kg Cd $ha^{-1}$) | $H_2O$ | $KNO_3$ | KF | $Na_4P_2O_7$ | EDTA | $HNO_3$ | TOTAL (ug $g^{-1}$) |
|---|---|---|---|---|---|---|---|
| | | (% of total Cd extracted) | | | | | |
| 0 | nd* | 4.3 (0.0)** | 9.7 (0.5) | 80.6 (25.7) | 1.1 (1.0) | 4.3 (1.6) | 0.095 (.021) |
| 2 | nd | 1.4 (0.3) | 12.8 (1.5) | 82.8 (19.5) | 0.7 (0.0) | 2.0 (1.5) | 0.525 (.021) |
| 4 | nd | 1.7 (0.5) | 13.9 (2.6) | 82.5 (14.9) | 0.3 (0.0) | 1.5 (1.5) | 1.517 (.105) |
| 8 | nd | 1.4 (1.3) | 13.9 (2.2) | 81.1 (23.3) | 0.4 (0.0) | 2.0 (0.7) | 1.521 (.250) |
| 16 | 0.1 (0.0) | 2.3 (0.2) | 12.2 (1.3) | 82.8 (0.2) | 0.2 (0.0) | 2.4 (0.1) | 3.896 (.037) |
| **$CdCl_2$ RATE + SEWAGE SLUDGE** | | | | | | | |
| 2 | nd | 0.6 (0.1) | 7.0 (1.2) | 91.8 (50.8) | 0.3 (0.0) | nd | 1.036 (.513) |
| 8 | nd | 1.3 (0.2) | 12.3 (1.3) | 86.1 (19.3) | 0.2 (0.0) | nd | 2.039 (.426) |

* nd = non-detectable
** standard deviation in brackets

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Table 3.16. $H_2O$ and $KNO_3$ extractable Cd of a Red River clay and a Lakeland clay loam treated with $CdCl_2$ and $CdCl_2$ plus 50 t $ha^{-1}$ sewage sludge.

| CdCl$_2$ RATE (kg Cd ha$^{-1}$) | Red River | | Lakeland | |
| --- | --- | --- | --- | --- |
| | $H_2O$ | $KNO_3$ | $H_2O$ | $KNO_3$ |
| | | (ug Cd g$^{-1}$) | | |
| 0 | 0.002a* | 0.005a | 0.004a | nd |
| 2 | 0.005a | 0.009a | nd** | 0.005a |
| 4 | 0.005a | 0.016a | 0.005a | 0.002a |
| 8 | 0.006a | 0.032a | 0.005a | 0.006a |
| 16 | 0.009a | 0.080a | 0.007a | 0.006a |
| CdCl$_2$ RATE + SEWAGE SLUDGE | | | | |
| 2 | 0.005a | 0.056a | 0.003a | 0.004a |
| 8 | 0.006a | 0.024a | 0.006a | 0.007a |

* Means in each column followed by the same letter are not significantly different at the 0.05 level according to the LSD test.
** nd = non-detectable

0.080 µg g$^{-1}$ but again these differences were not statistically significant.

The Na$_4$P$_2$O$_7$ clearly extracted the most Cd from the SS- or CdCl$_2$ amended-soil. This suggests that the Cd was predominantly bound by the organo-mineral fraction (Stover et al., 1976). Consequently, citrate-bicarbonate-dithionite, an extractant specific for oxides (Mehra and Jackson, 1960) was used to further analyze the oxide fraction in the CdCl$_2$ treated soil. Table 3.17 indicates that as the concentration of Cd applied to the soil increased, so did the amount of oxide-bound Cd. For the Red River soil, the concentration of Cd associated with the oxide fraction increased from 0.01 µg g$^{-1}$ to 1.09 µg g$^{-1}$. However, although there is a close relationship between the concentration of Cd in the soil and the amount of Cd extractable using CDB (r$^2$=0.89) (Fig. 3.1), the fraction of Cd extracted represented only 7-14% of the total Cd applied to the soil. The proportion of Cd associated with the oxide fraction increased from 7% at the check to 14% at the 2 kg ha$^{-1}$ treatment. However, there was no significant difference among the CdCl$_2$ treatments. Furthermore the application of SS to the CdCl$_2$ treatment did not differ significantly from the aforementioned trend.

Table 3.17. Cd concentration and proportion of total Cd applied as determined using citrate-dithionate-bicarbonate on a Red River clay and a Lakeland clay loam treated with $CdCl_2$ and $CdCl_2$ plus 50 t ha$^{-1}$ sewage sludge during the initial year of application.

| $CdCl_2$ RATE (kg Cd ha$^{-1}$) | Red River | | Lakeland | |
|---|---|---|---|---|
| | µg Cd g$^{-1}$ | % | µg Cd g$^{-1}$ | % |
| 0 | 0.01a | 7 | 0.01a | 9 |
| 2 | 0.16b | 14 | 0.09ab | 8 |
| 4 | 0.30c | 14 | 0.18b | 9 |
| 8 | 0.52d | 13 | 0.47d | 11 |
| 16 | 1.09f | 13 | 0.97e | 12 |
| $CdCl_2$ RATE + SEWAGE SLUDGE | | | | |
| 2 | 0.13ab | 9 | 0.13ab | 9 |
| 8 | 0.72e | 16 | 0.44d | 10 |

* Means in each column followed by the same letter are not significantly different at the 0.05 level according to the LSD test.
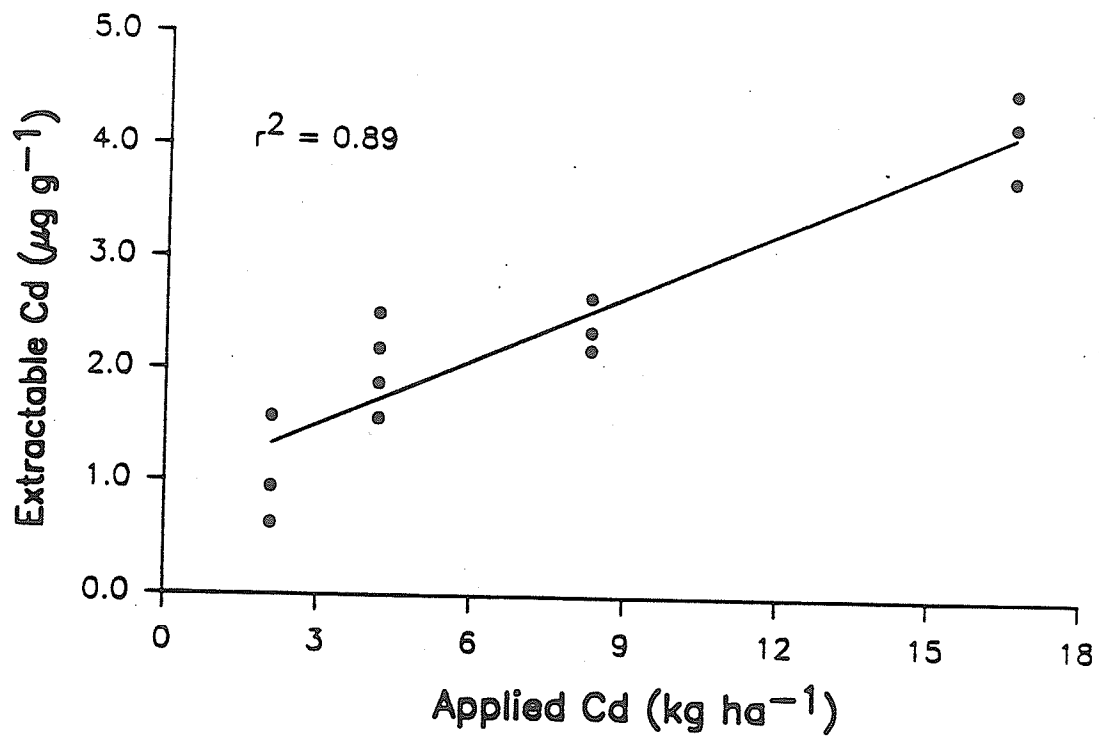
Figure 3.1. CDB-extractable Cd from a Red River clay
amended with inorganic Cd.

3.1.3.4 Effect of Inorganic Cadmium on the Content and

   Distribution of Cadmium in a Lakeland clay loam soil


Total extractable Cd from the Lakeland soil treated with $CdCl_2$ increased from 0.039 $\mu$g g$^{-1}$ on the check to 2.413 $\mu$g g$^{-1}$ at the 16 kg ha$^{-1}$ treatment (Table 3.18). The distribution of extractable Cd was similar to that observed for the Red River clay (Tables 3.12 and 3.13). Again most of the Cd, 77% on average, was extracted using $Na_4P_2O_7$. Negligible amounts of Cd were extracted with water and < 2% was extracted using $KNO_3$ (with the exception of 18% at the control). Less than 4% of the Cd was extracted using EDTA. The application of SS to the $CdCl_2$ treatments did not affect the distribution of extracted Cd from the soil although the total Cd extracted did increase.

At the harvest in 1990 (Table 3.16), there was a slight increase in total extractable Cd by water from 0.004 $\mu$g g$^{-1}$ to 0.007 $\mu$g g$^{-1}$ but the differences were not significant. The $KNO_3$-extractable Cd ranged from negligible to 0.006 $\mu$g g$^{-1}$ by 1990 (Table 3.16) but again there were no statistical differences among $CdCl_2$ treatments.

Table 3.17 shows the amount of Cd extracted using CDB from a Lakeland soil treated with $CdCl_2$. The concentration of Cd increased from 0.01 $\mu$g g$^{-1}$ for the check to 0.97 $\mu$g g$^{-1}$ at the 16 kg ha$^{-1}$ treatment. The relationship between Cd applied and

Table 3.18. Total Cd extracted and the distribution of Cd in a Lakeland clay loam treated with $CdCl_2$ and $CdCl_2$ plus 50 t $ha^{-1}$ sewage sludge using a sequential extraction procedure.

| $CdCl_2$ RATE (kg Cd $ha^{-1}$) | $H_2O$ | $KNO_3$ | KF | $Na_4P_2O_7$ | EDTA | $HNO_3$ | TOTAL |
|---|---|---|---|---|---|---|---|
| | | | (% of total Cd extracted) | | | | ($\mu g\ g^{-1}$) |
| 0 | nd | 17.9 (16.0) | nd | 64.1 (0.0) | 9.0 (0.0) | 9.0 (3.8) | 0.039 (.015) |
| 2 | nd | 0.5 (0.0) | 1.5 (0.2) | 94.8 (31.9) | 1.2 (0.0) | 2.5 (1.0) | 0.604 (.169) |
| 4 | nd | 1.8 (1.8) | 43.0 (4.2) | 2.0 (0.8) | 4.0 (0.0) | 48.5 (16.5) | 0.165 (.070) |
| 8 | nd | 2.3 (0.0) | 26.1 (17.7) | 60.7 (12.6) | 2.3 (0.0) | 8.3 (0.6) | 0.298 (.134) |
| 16 | nd | 0.2 (0.1) | 6.0 (5.6) | 89.9 (52.3) | 0.4 (0.0) | 3.7 (0.7) | 2.413 (.089) |
| $CdCl_2$ RATE + SEWAGE SLUDGE | | | | | | | |
| 2 | nd | nd | 3.0 (0.2) | 94.6 (5.6) | 0.8 (0.0) | 1.6 (1.6) | 0.897 (.043) |
| 8 | nd | nd | 3.7 (0.2) | 94.1 (1.3) | 0.2 (0.0) | 0.2 (0.5) | 3.270 (.051) |

\* nd = non-detectable
\*\* standard deviation in brackets

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oxide-bound is strong ($r^2$=0.88) (Fig. 3.2). Nevertheless, the oxide fraction of Cd represents only 9 to 11% of the total Cd applied to the soil. The application of SS to the $CdCl_2$ treatment was not statistically different from the $CdCl_2$ treatment without SS.

3.1.3.5 Discussion of the Effect of Cadmium from Sewage Sludge
         and from Inorganic Cadmium on the Content and
         Distribution of Cadmium in the Soil

There is no doubt that much ambiguity and controversy exists in the validity and specificity of the chemical reagents used in sequential extractions. It is apparent that although the procedure of Stover et al. (1976) neglects the oxide fraction, review of the literature does tend to suggest oxide-associated metals are extracted by three of the extractants used, namely KF, $Na_4P_2O_7$ and NaEDTA. This has perhaps led to the underestimation of oxides as a sink for metals in much of the research conducted using the procedure of Stover et al. (1976) and the overestimated importance of carbonates.

The SS and $CdCl_2$-amended Red River and Lakeland soils were low in water soluble and exchangeable Cd. This strongly suggests that Cd is not readily available to the plant during the year of application nor in the immediate years following. However, there was a slight increase in $H_2O$ soluble Cd by 1990 compared
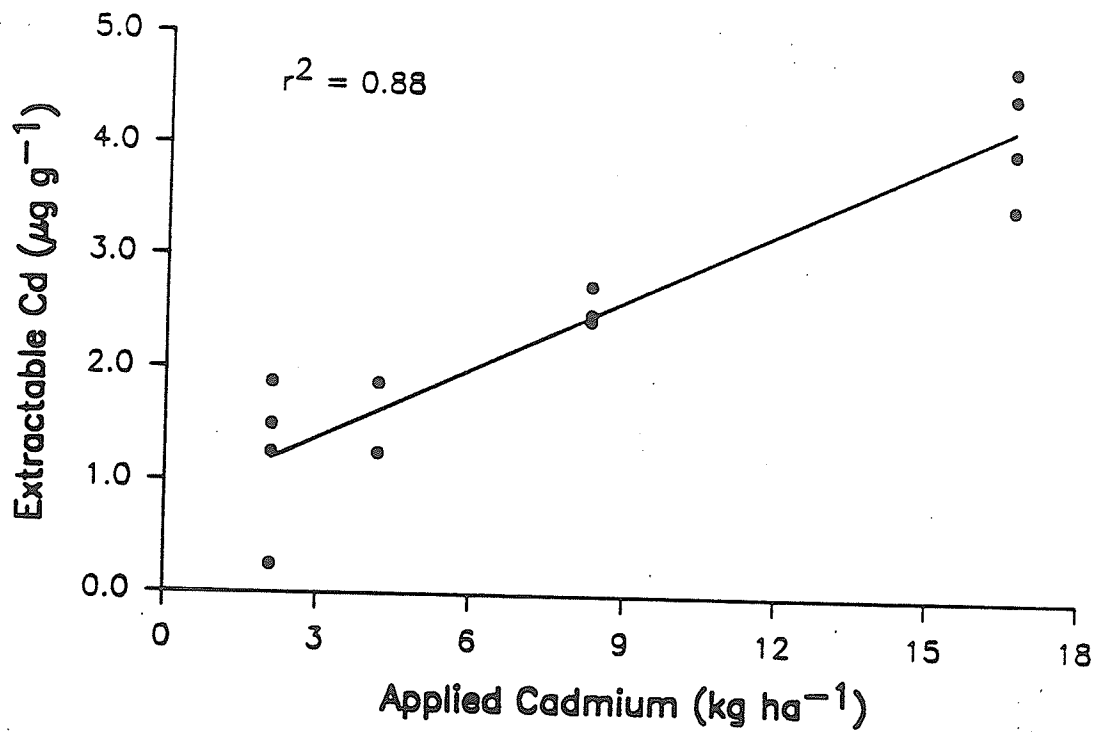
69

Figure 3.2. CDB-extractable Cd from a Lakeland clay
loam amended with inorganic Cd.

to 1988. Furthermore for the CdCl$_2$ treatments, H$_2$O soluble Cd increased with increasing Cd applied. However, as observed in section 3.1.2, the increase in H$_2$O soluble Cd did not translate into an increase in Cd concentration in the wheat crop grown. The KNO$_3$, on the other hand, extracted less or equal concentrations of Cd in 1990 compared to 1988.

The fact that Cd is not readily available for crop uptake has been shown by other research (Emmerich et al., 1982; Sposito et al., 1982; Sims and Kline, 1991). Studies have shown that, especially in calcareous soils, free Cd is rapidly adsorbed or precipitated in the solid phase and the solution concentration remains low (Hirsch and Banin, 1990). However Silviera and Sommers (1977) concluded that low levels of H$_2$O- or KNO$_3$-extractable Cd was more an indicator of metal mobility in the soil than of bioavailability. This may explain why the H$_2$O soluble Cd increased over time but did not become more bioavailable.

The Cd distribution for both soils across the four experiments showed very similar trends with approximately 80% of the Cd extracted with Na$_4$P$_2$O$_7$. This suggests most of the Cd applied to the soil is associated with the organo-mineral fraction. Very little Cd was extracted using EDTA from the Red River soil. This may have been expected as the Red River soil contains no carbonates. However, the SS has a CCE of 15.7%

(Table 3.1) and this should have increased the amount of Cd adsorbed by the carbonate fraction in the soil. The Lakeland soil is calcareous with a CCE of 18.1%, yet < 4% of the Cd was extracted using EDTA.

Using this sequential extraction on SS, Stover et al.(1976) recovered approximately 81% of the total Cd present. Other recoveries associated with the use of sequential extractions are 64% (Sims and Kline, 1991), 79% (Rudd et al., 1988), 100% (Sposito et al., 1982) and 110% (Emmerich et al., 1982). Therefore the sequential extraction procedure is successful to varying degrees. However, the amount of Cd extracted using the sequential extraction in this study ranged from 26 to 84% of the Cd applied both as $CdCl_2$ and SS (the average for all the SS and $CdCl_2$ treatments was 41%). Numerous studies (Williams et al., 1980; Emmerich et al., 1982) have indicated that Cd does not move out of the zone of incorporation therefore leaching is not a problem.

The findings of this sequential extraction did not compare favourably with other research. Rudd et al. (1988) established the following ranking of Cd extractability: EDTA > $HNO_3$ > $Na_4P_2O_7$ > KF > $KNO_3$. Stover et al. (1976) found a similar order of extractability but the findings of my experiments showed that $Na_4P_2O_7$ extracted the most Cd with EDTA extracting very little.

A similar study using a sequential extraction consisting of $KNO_3$, $H_2O$ (the exchangeable fractions), NaOH (organically-bound fraction, EDTA (carbonate fraction) and $HNO_3$ (residual fraction) was conducted on SS-amended soils (three Atlantic coastal plain soils amended with four rates of SS ranging from 0 to 44 Mg $ha^{-1}$) by Sims and Kline (1991). They determined that most of the Cd was extracted with EDTA and $HNO_3$. The distribution was as follows [$KNO_3$ + $H_2O$] (20-27%), NaOH (1-5%), EDTA (23-28%) and $HNO_3$ (40-56%). The distribution of Cd was more uniform between the extractants and one extractant was not as dominant as was $Na_4P_2O_7$ in this study. Sposito et al. (1982) amended two arid zone soils for four years with 45 t $ha^{-1}$ SS and found that the Cd was primarily distributed among the NaOH (25-26%), EDTA (39-46%) and $HNO_3$ (24-32%). Less than 1% of the Cd applied was extracted by [$KNO_3$ + $H_2O$].

Silviera and Sommers (1977) incubated two Indiana soils with SS for 28 days. The water soluble and $KNO_3$ extractable Cd was below detection limits, whereas 58% and 42% of the soil Cd was extracted using DPTA or $HNO_3$.

Research tends to indicate therefore that EDTA will extract the largest proportion of Cd from SS-amended soils. This was not observed in this study, however, here < 4% of the Cd extracted was with EDTA. The findings of this study indicate that $Na_4P_2O_7$, referred to as the organo-mineral fraction, is

the reagent that extracted the most Cd in a Red River or Lakeland soil amended with SS or $CdCl_2$. As the CDB analysis showed, there was a strong relationship between free oxides in the soil and Cd applied, although < 15% of the Cd applied to either soil as $CdCl_2$ was extracted.

It is apparent from the data that the $H_2O$ and $KNO_3$ extractants extracted very little Cd as expected. Cadmium extracted by KF was very similar to values in the literature. The EDTA did not appear to be effective in extracting Cd. Consequently the extraction of total Cd was low. One reason for this could be that some of the Cd could have precipitated prior to analysis therefore giving low readings.

In conclusion, the oxides in the soils play an important part in retention of free Cd. However, free Cd in the soil constitutes a small proportion of the total Cd present. This is due to the propensity of SS to tightly bind Cd and thus not release it into the soil. Studies using sequential extraction procedures on SS-amended soil tend to suggest that the Cd applied to the soil is strongly associated with the carbonate fraction. However the Red River soil is void of carbonates thus little Cd would be expected to be extracted by EDTA. Cd contained in SS is strongly held by the carbonate fraction (Stover et al., 1976; Oake et al., 1984). Therefore, a large proportion of the Cd in the SS is probably still associated

with the carbonate fraction after incorporation into the soil, but once released is held by the soil oxides. This suggests, therefore, that the EDTA was not effective in extracting Cd. This is supported by the fact that very little Cd was extracted from the carbonate fraction of the calcareous Lakeland soil. This could explain why < 50% of the Cd applied, on average, was extracted.

3.2 THE BONDING MECHANISM BETWEEN CADMIUM AND SOIL OXIDES

3.2.1 MATERIAL AND METHODS

3.2.1.1 Adsorption of Cadmium by Goethite

The pH dependence of cadmium adsorption by goethite ($\alpha$-FeOOH) was studied. The goethite was a sample purchased from Ward's Scientific and was ground to pass a 400 mesh sieve. Suspensions of 200 mg of goethite in a background electrolyte made up of 20 ml of 0.1 mol l$^{-1}$ KNO$_3$ were contained in 100 ml polypropylene centrifuge tubes. The initial pH of the suspensions as adjusted by addition of 5 ml of KOH at varying concentrations. Thus the initial pH of the adsorption experiment ranged from 5.5 to 9.0. To each of these suspensions, 1 ml of CdCl$_2$ was added so that the Cd concentration at the start of the adsorption study was 40 ug ml$^{-1}$ after the adjustment for pH with KOH. The samples were run in duplicate. Preliminary studies indicated that the adsorption maxima of Cd on goethite occurred within 30 h. Therefore, the suspensions were gently shaken for 8 h and then left to equilibrate for a further 25 h. The pH of the suspensions were measured at the end of the equilibration period with an Accumet 950 pH/ion meter. The suspensions were then centrifuged at 30,000 g for 30 min, the supernatant collected and analysed for Cd by atomic absorption spectroscopy. The amount of Cd adsorbed by goethite was assumed to be equal to the difference between the initial and

final Cd concentrations in the supernatant. The residue was then washed three times with 2 ml of acetone/water (80/20 vol %). The supernatant was discarded after each wash. The final residue, containing goethite and adsorbed Cd only, was air-dried in the centrifuge tube and kept for further studies.

## 3.2.1.2 Release of Cadmium Adsorbed by Goethite

To each of the centrifuge tubes containing the residue of goethite with adsorbed Cd, was added 26 ml of 0.01 mol. $l^{-1}$ $CaCl_2$. The suspensions were then shaken and left to equilibrate as for the adsorption study, centrifuged and the supernatant analysed for Cd released.

## 3.2.1.3 $H^+/Cd^{2+}$ Stoichiometry during Adsorption of Cadmium by Goethite and the Bonding Mechanism

Specific adsorption of trace elements is accompanied by a reduction in pH of the system (Qirk and Posner, 1975; Goh et al., 1986). Consequently, the mechanism of bonding can often be inferred from the mole ratio of protons released to metal adsorbed (Quirk and Posner, 1975; Cavallaro and McBride, 1978, Kalbasi et al., 1978; Goh et al., 1986). The amount of protons released upon adsorption can be determined from pH data and calculation of the ionic activities (e.g. Quirk and Posner, 1975; Goh et al., 1986) or from titration curves,

(e.g. Kalbasi et al., 1978).

To 200 mg of goethite in a beaker were added 20 ml of the background electrolyte 0.01 M $KNO_3$, 5 ml of KOH of varying concentrations and 1 ml of deionized water. The suspensions were shaken for 30 min and then left to stand for 33 h prior to the measurement of pH electrometrically. From these data, the pH versus base-added-curve (absence of specific adsorption) was constructed. Another duplicate set was run but this time, 1 ml of 0.012 M $CdCl_2$ was added in place of the deionized water. The pH was measured as above and a pH versus base-consumption-curve constructed (presence of specific adsorption). The difference in base consumption at the same pH for the two curves is due to the proton released during the adsorption of Cd. The amount of Cd adsorbed at a particular pH was determined from the adsorption curves obtained in the adsorption study. The mole ratio of $H^+$ released to $Cd^{2+}$ adsorbed was calculated.

3.2.2. RESULTS AND DISCUSSION OF CADMIUM BONDING MECHANISM TO
     SOIL OXIDES

3.2.2.1 Adsorption and Bonding Mechanism between Cadmium and
     Goethite

The results of the Cd adsorption study are shown in Table 3.19. The values for pH ranged from 5.50 to 10.30. Adsorption of Cd by goethite increased linearly with pH ($r^2$ = 0.97) as illustrated in Figure 3.3. At pH 5.50 no Cd was adsorbed by the goethite.

As the pH increased beyond 5.50 Cd was adsorbed by the oxide and $H^+$ ions were desorbed. The molar ratio of $H^+$ released to $Cd^{2+}$ adsorbed was 1.43 when the pH of adsorption was 6.5. As the pH increased, the adsorption of $Cd^{2+}$ and desorption of $H^+$ ions increased accordingly. From pH 6.75 to 9.00, the adsorption of $Cd^{2+}$ increased from 1.71 to 4.30 mmoles 100 $g^{-1}$ and the desorption of $H^+$ ions from 4.17 to 10.18 mmoles 100 $g^{-1}$. From the pH of 6.75 to 9.00 the molar ratio of $H^+$ released to $Cd^{2+}$ adsorbed ranged from 2.37 to 2.55 with an average value of 2.44 with a standard deviation of 0.04. At pH 10.0 the molar ratio dropped to 1.68.

The desorption of $Cd^{2+}$ by $Ca^{2+}$ is shown in Figure 3.3. The amount of $Cd^{2+}$ desorbed at given pH was relatively small. As Figure 3.3 illustrates, the amount of $Cd^{2+}$ desorbed as a

Table 3.19. Adsorption of Cd by geothite suspended in aqueous solutions of varying pH.

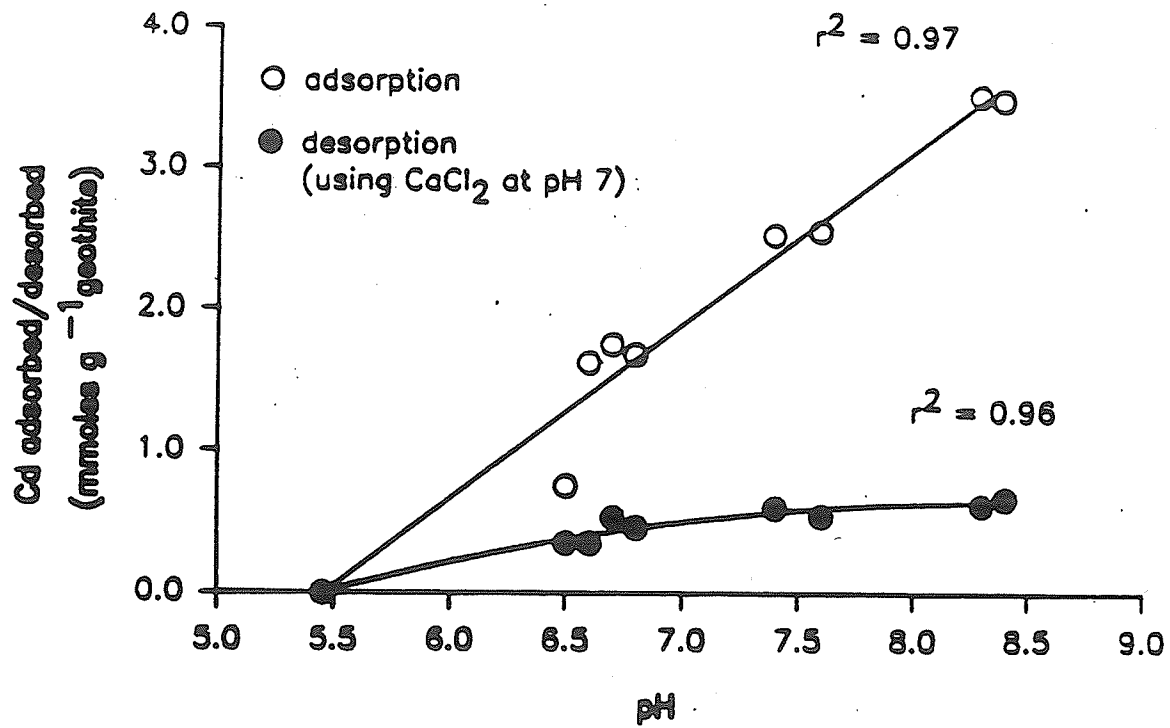| Final Suspension pH | H$^+$ released (A) | Cd$^{2+}$ adsorbed (B) | A/B |
|---|---|---|---|
| ..... mmoles 100 g$^{-1}$ ..... | | | |
| 5.50 | 0 | 0 | 0 |
| 6.50 | 1.70 | 1.19 | 1.43 |
| 6.75 | 4.17 | 1.71 | 2.44 |
| 7.00 | 4.90 | 1.92 | 2.55 |
| 7.25 | 5.53 | 2.24 | 2.47 |
| 7.50 | 6.21 | 2.50 | 2.48 |
| 7.75 | 6.85 | 2.84 | 2.41 |
| 8.00 | 7.55 | 3.16 | 2.39 |
| 8.35 | 8.55 | 3.52 | 2.43 |
| 9.00 | 10.18 | 4.30 | 2.37 |
| 10.30 | 7.74 | 4.60 | 1.68 |

Figure 3.3. The effect of pH on the adsorption/desorption
of Cd by goethite.

function of pH increases at a decreasing rate ($r^2 = 0.96$).
Further, at low levels of adsorbed $Cd^{2+}$, 35% of the Cd was
desorbed by Ca (Fig. 3.3). As the amount of $Cd^{2+}$ adsorbed
increased with pH, the proportion of Cd desorbed decreased to
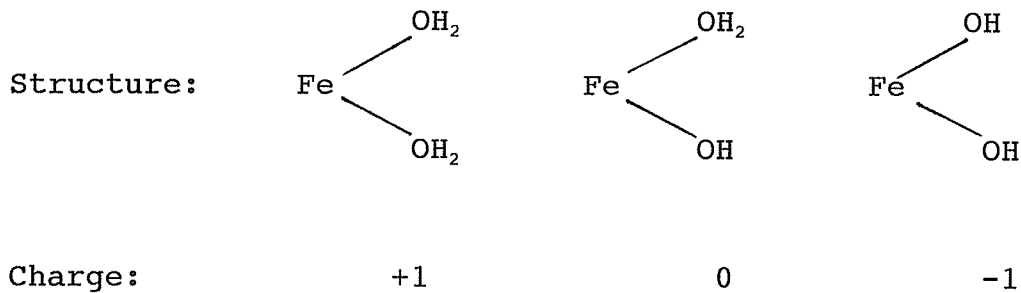15%.

## 3.2.2.2 Discussion

The importance of oxides in metal retention lies in their
surface charge. Schwertzmann and Taylor (1989) explained
these properties as follows. In the presence of water, Fe
atoms located on the surface of an oxide complete their ligand
shell with hydroxyl ions so that the surface becomes
hydroxylated or hydrated:
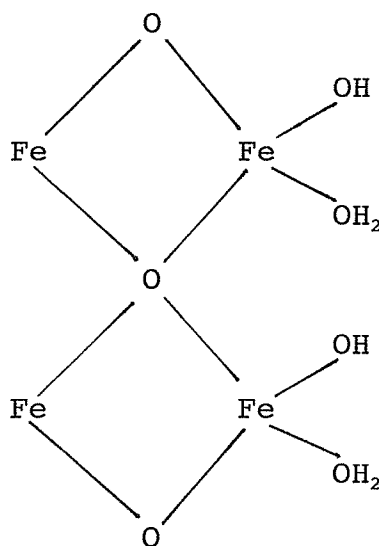
At the hydroxylated or hydrated surface, the adsorption or desorption of $H^+$ or $OH^-$ gives the surface a positive or negative charge; this results in a surface potential.

The pH at which the surface charge is zero is called the zero point of charge (ZPC) (Parks, 1965). At this pH the number of OH and $OH_2$ groups present on the oxide surface are equal and therefore the surface charge is zero.

The process by which a surface charge is established may be schematically represented as follows (Parks and Bruyn, 1962):

Structure:

$$Fe \Big\langle {}^{OH_2}_{OH_2} \qquad Fe \Big\langle {}^{OH_2}_{OH} \qquad Fe \Big\langle {}^{OH}_{OH}$$

Charge:          +1         0         -1

It is obvious from the above diagram that the pH of the solution surrounding the oxide is of utmost importance with regards to the charge on the oxide. As a soil becomes more acidic, surface charge density becomes more positive. Consequently the ability of the oxide to retain metals declines. The pH above which metals start to become strongly

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retained by oxides is about 6.5. Schwertzmann and Taylor (1989) also noted that the surface charge depends on the concentration of the electrolyte and the ionic strength, but the most important factor determining the extent of adsorption is pH.

The results of the Cd adsorption study are in accordance with the literature. At a pH less than 6.5, no Cd was adsorbed by the goethite. The charge of the oxide is positive and therefore repels the $Cd^{2+}$. The ZPC of the goethite is around pH 7.0 as suggested by Parks and Bruyn (1962) and Schwertzmann and Taylor (1989).

At pH 6.75 and greater the adsorption of Cd increased linearly with pH. This is expected as $H^+$ ions are released from the oxide to neutralize the OH- groups in solution. Now the negative charge density on the surface of the oxide increases and $Cd^{2+}$ is able to bond to the oxide. The molar ratio of $H^+$ to $Cd^{2+}$ provides valuable information regarding the bonding mechanism.

The average molar ratio of $H^+$ ions released to $Cd^{2+}$ adsorbed for the pH range 6.75 to 9.0 was 2.4. This agreed with the findings of Forbes et al. (1976) and Kalbasi et al. (1978). Forbes et al. (1976) determined that the ratio of $H^+$ released to $Cd^{2+}$ adsorbed was 2.2 ± 0.6. The corresponding values

reported for Cu, Zn and Pb were $1.8 \pm 0.5$, $2.2 \pm 0.3$ and $2.4 \pm 0.5$, respectively. Kalbasi et al. (1978) determined that the mole ratio of $H^+/Zn^{2+}$ was 1.97.

As the molar ratio of $H^+$ released to $Cd^{2+}$ adsorbed is approximately 2.0, this suggests $Cd^{2+}$ is adsorbed to the oxide by bidentate bonding. The mechanism of this adsorption can be represented as follows:
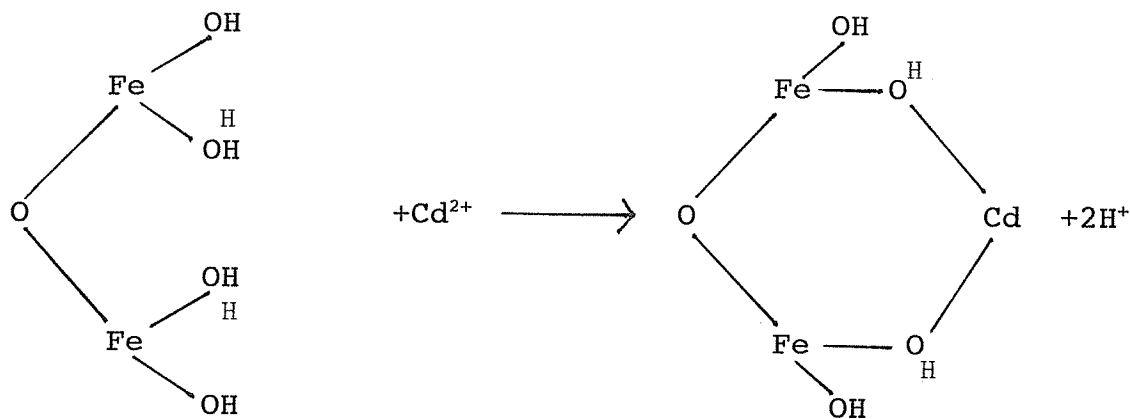


This is in accordance with the structure outlined by Quirk and Posner (1975) for Zn adsorption to oxides. Bidentate bonding is relatively stable and the sorbate is not readily released to solution. Therefore it is in a non-bioavailable state. The desorption study supports this finding as $Cd^{2+}$ was not readily desorbed $Ca^{2+}$. $Ca^{2+}$ at a relatively high concentration could displace only a small portion of the $Cd^{2+}$ adsorbed, and this portion decreased with increasing pH. This supports the findings of Kalbasi et al. (1978) with Zn.

At a pH of 10.3, the molar ratio of $H^+$ to $Cd^{2+}$ declined (Table 3.19) suggesting significant hydrolysis of $Cd^{2+}$. Adsorption of the hydrolysed species will result in a lower $H^+/Cd^{2+}$ stoichiometry (Cavallaro and McBride, 1978).

At pH 6.50 the molar ratio of $H^+$ to $Cd^{2+}$ was 1.43. The system was saturated with Cd, but at this pH the charge density on the oxide surface was not negative enough to facilitate the complete release of two $H^+$ in order to obtain bidentate bonding.

3.3. ADSORPTION OF CADMIUM BY SEWAGE SLUDGE

3.3.1 MATERIAL AND METHODS

3.3.1.1 Adsorption of Cadmium by Freeze-Dried Sewage Sludge

Sewage sludge was obtained from the Winnipeg North End Water Pollution Control Plant. Approximately one kilogram was placed in a freezer set at -50 C for one day. The frozen SS was then freeze dried for four days. The moisture content of the freeze dried SS was determined to be 8 wt.%. The pH of the freeze dried SS was determined on suspensions of 10 g SS and 30 ml $H_2O$ and 10 g SS and 30 ml 0.01 M $CaCl_2$.

The adsorption of Cd by SS was measured in duplicate: To 50 ml centrifuge tubes, 0.54g freeze dried SS and 35 ml of 0.01 M $KNO_3$, containing various concentrations of Cd, were added. The concentrations of Cd, as $Cd(NO_3)_2$, ranged from 0 to 50 ug $g^{-1}$. The suspensions were shaken for 30 minutes and after several different reaction periods were centrifuged at 16 000 g for 25 min. The reaction periods were 0, 0.5, 1, 2, 4, 6, 8, 12, 24 and 48 h.

The pH of the supernatants were recorded. The pH of the supernatant solution was measured using a combination glass electrode. The Cd content in solution was determined by atomic absorption spectrometry using a hollow Cd lamp. The amount of Cd adsorbed (or removed from solution) was

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calculated by subtracting the amount of Cd remaining in solution from the initial amount of Cd added.

## 3.3.2 RESULTS AND DISCUSSION OF CADMIUM ADSORPTION BY SEWAGE SLUDGE

The pH of the freeze-dried SS was 7.8. Table 3.20 gives the concentration of Cd adsorbed by the SS and the concentration of Cd remaining in solution for the various suspensions and equilibration periods. These data indicate that within the first 30 min. there was a large decline in the Cd concentration in solution. The rapid decrease was followed by a further slight decline in the Cd concentration which lasted for only 6 h for the Cd treatments of lower concentration (5 and 10 ug ml$^{-1}$) and for 24 h for the higher Cd treatments (25 and 50 ug ml$^{-1}$), before the Cd concentration in solution increased.

### 3.3.2.1 Theory of the Reaction Kinetics of Reversible Reactions at Equilibrium (Fitzgerald et al., 1992).

The rate at which Cd was removed from solution can be determined from the reaction times. The rate of a reaction determines the decrease in the amount of one of the reactants over a certain time interval, or conversely the increase in the amount of a product. A first order reaction is when the

Table 3.20. Effect of time on the concentration of Cd
remaining in solution (Cl) and the concentration
of Cd adsorbed (Cs) by the sewage sludge.

| Time of Adsorption (h) | Cadmium Treatment ($\mu g\ mL^{-1}$) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | | 5 | | 10 | | 15 | | 20 | | 25 | | 50 | |
| | Cl[*] | Cs[**] | Cl | Cs | Cl | Cs | Cl | Cs | Cl | Cs | Cl | Cs | Cl | Cs |
| 0.0 | 0 | 0 | 4000 | 0 | 8451 | 0 | 12200 | 0 | 16425 | 0 | 19002 | 0 | 39251 | 0 |
| 0.5 | 0 | 1 | 85 | 274 | 140 | 582 | 220 | 839 | 315 | 1128 | 365 | 1305 | 886 | 2686 |
| 1.0 | 5 | 1 | 80 | 274 | 130 | 583 | 225 | 838 | 260 | 1132 | 345 | 1306 | 775 | 2693 |
| 1.5 | 0 | 1 | 65 | 275 | 115 | 584 | 210 | 839 | 250 | 1132 | 340 | 1306 | 645 | 2702 |
| 2.5 | 0 | 1 | 60 | 276 | 135 | 582 | 190 | 841 | 205 | 1135 | 275 | 1311 | 590 | 2706 |
| 4.5 | 0 | 1 | 75 | 276 | 120 | 583 | 195 | 840 | 250 | 1132 | 315 | 1308 | 575 | 2707 |
| 6.5 | 0 | 1 | 60 | 276 | 115 | 584 | 235 | 838 | 245 | 1133 | 260 | 1312 | 525 | 2711 |
| 8.5 | 0 | 1 | 80 | 274 | 120 | 583 | 180 | 841 | 235 | 1133 | 255 | 1312 | 515 | 2712 |
| 12.5 | 5 | 0 | 100 | 273 | 155 | 581 | 215 | 839 | 260 | 1132 | 270 | 1311 | 560 | 2708 |
| 24.5 | 0 | 1 | 135 | 271 | 215 | 577 | 210 | 839 | 205 | 1135 | 230 | 1314 | 400 | 2720 |
| 48.5 | 5 | 0 | 130 | 271 | 285 | 572 | 445 | 823 | 435 | 1119 | 460 | 1298 | 510 | 2712 |

* Concentration of Cd in solution ($\mu g\ Cd\ L^{-1}$)
** Concentration of Cd adsorbed ($\mu g\ Cd\ g^{-1}$ sewage sludge)

rate of the reaction depends only on the first power of the concentration of a single reaction species. Therefore a first order rate equation for the decrease of Cd with time in solution (at a given temperature) can be written:

$$-\frac{d[Cd]}{dt} = k[Cd] \qquad (1)$$

This reaction, however, assumes the concentration of Cd will go to zero after a certain period of time. Since the Cd concentration in this experiment did not go to zero, it is possible that the reaction followed first-order reversible kinetics, in which an equilibrium was established between Cd in solution and that adsorbed by the SS. An equation for a first order reversible reaction between free Cd in solution (C) and adsorbed Cd (B) is:

$$-\frac{d[C]}{dt} = k_1[C] - k_2[B] \qquad (2)$$

The rate constants for the forward and reversible reactions are $k_1$ and $k_2$ respectively. For a reversible adsorption reaction to occur, the adsorbed Cd is released either by desorption (perhaps by ion exchange) or dissolution of surfaces by weathering or mineralization. It was assumed that the reaction will be reversible because there is a relatively

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large amount of solid (B), and thus the solid to liquid ratio is large. It was further assumed that the value of B was fixed because it is a solid and that there was no adsorbed Cd initially. The value for B can be represented by :

$$B = (Co - C)V/m$$

where Co is the initial amount of Cd added, C is the concentration of Cd in solution at time t, V is the total volume in which the reaction is taking place and m is the amount of adsorbent (ie. SS). Therefore equation 2 upon substitution becomes

$$-\frac{d[C]}{dt} = k_1C - \frac{k_2(Co-C)V}{m} \qquad (3)$$

This equation upon rearrangement and substitution becomes:

$$-\frac{dC}{dt} = k*C - \frac{k_2CoV}{m} \qquad (4)$$

where,      $$k* = k_1 + \frac{k_2V}{m}$$

When equilibrium occurs, $-\frac{dC}{dt} = 0,$

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therefore $C\alpha = \dfrac{k_2 CoV}{k*m}$

is the equilibrium concentration of Cd. Therefore, the equation for a first order reversible reaction can be written:

$$\dfrac{-dC}{dt} = k*(C-C\alpha) \qquad\qquad (5)$$

Integrating equation 5 yields:

$$-\ln(C-C\alpha) = k*t+K \qquad\qquad (6)$$

where K is a constant of integration.

The reaction is first order reversible if a plot of ln (C-Cα) versus time gives a straight line. For such a plot the slope of the line gives the specific rate constant for the first order reversible reaction.

## 3.3.2.2 Discussion

Figures 3.4, 3.5 and 3.6 show the kinetic plots obtained for the various initial concentrations of Cd. The equilibrium concentrations of Cd, Cα, were determined by graphical approximation to obtain the best fit line for the first order
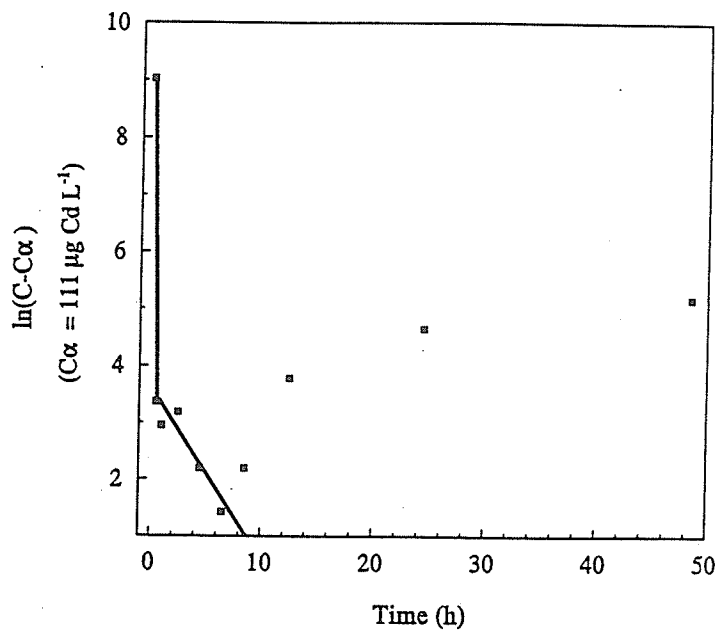
reversible plots.

It is evident from Figures 3.4, 3.5 and 3.6 that the decline of Cd from solution involves at least two rates:

    i. one rate within the first 30 minutes (dashed line) for the irreversible

   ii. one rate after 30 minutes which follows reversible reaction kinetics, albeit not necessarily at equilibrium

It is probable that most of the Cd removed from solution within the first 30 min was adsorbed and little desorption (or release) of Cd occurred. There were no rate constants determined for the initial 30 min as only two data points were obtained due to this being the timee alloted for shaking. After the first 30 min, the loss of Cd followed first- order reversible kinetics (Figs. 3.4, 3.5 and 3.6). There was some release of adsorbed Cd during this time period. However, the amount of Cd adsorbed was greater than the amount released, which resulted in a net decrease in the Cd concentration in solution. It is apparent from the graphs in Figs. 3.4, 3.5 and 3.6 that the length of time in which the loss of Cd from solution followed first order reversible kinetics depended on the initial amount of Cd added. Thus, for the lower concentrations of Cd studied (5 and 10 ug Cd ml$^{-1}$ treatment),
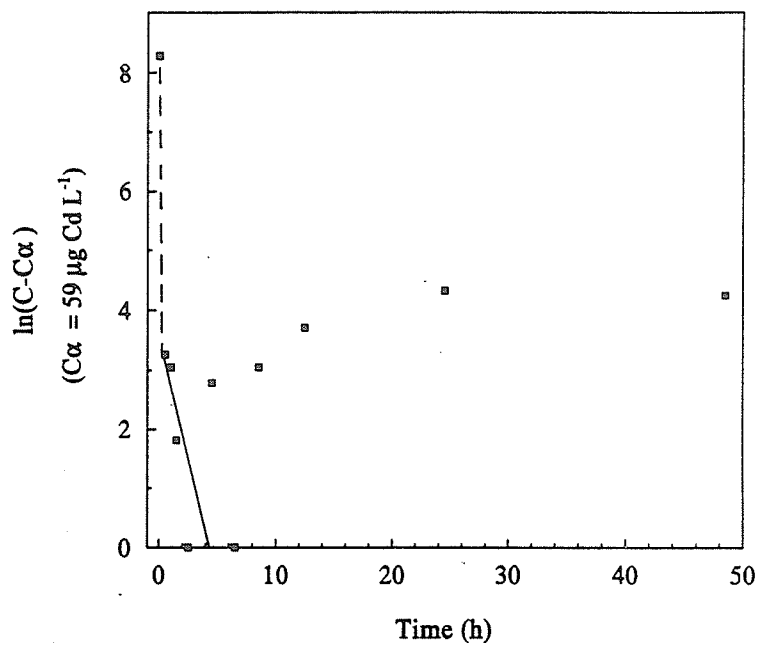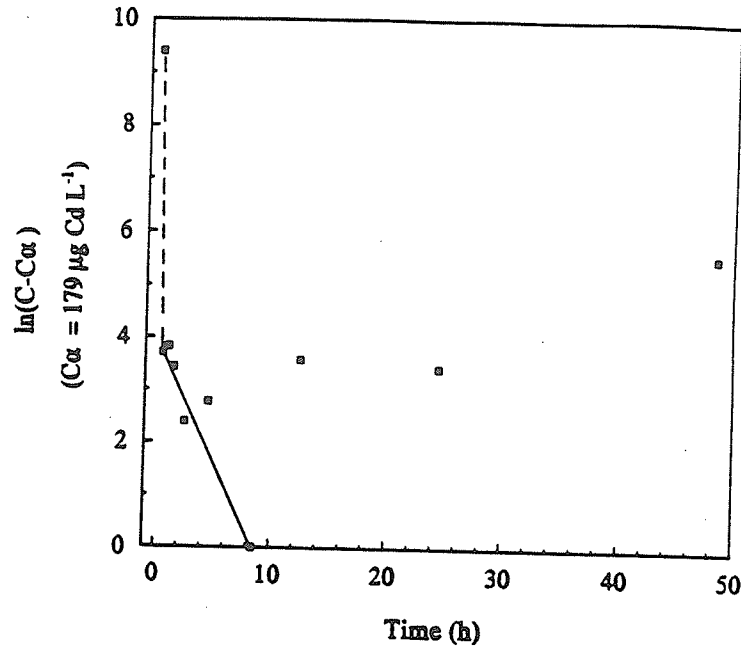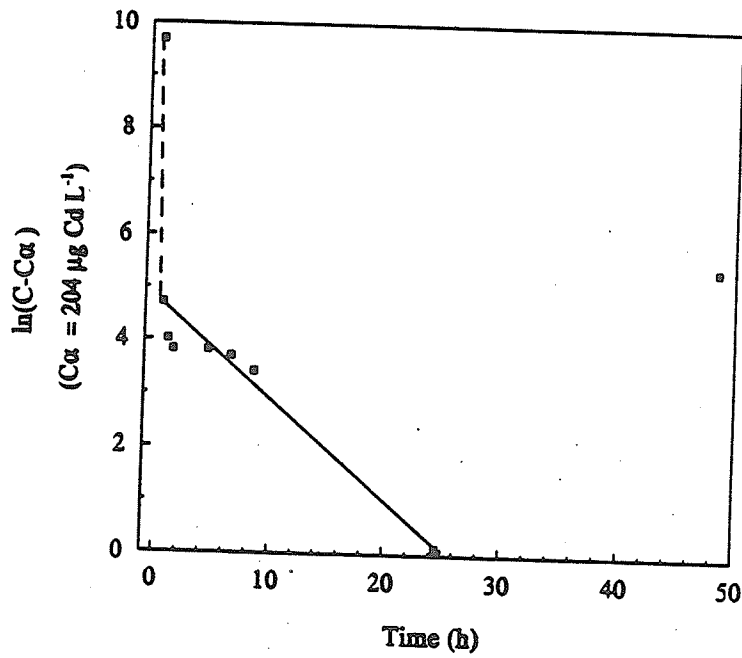
Figure 3.4. First order reversible plots for the decrease in the concentration of Cd in solution by Cd treatment. A. 5 ug Cd ml$^{-1}$   B. 10 ug Cd ml$^{-1}$.

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Figure 3.5. First order reversible plots for the decrease in the concentration of Cd in solution by Cd treatment. A. 15 ug Cd ml$^{-1}$   B. 20 ug Cd ml$^{-1}$.

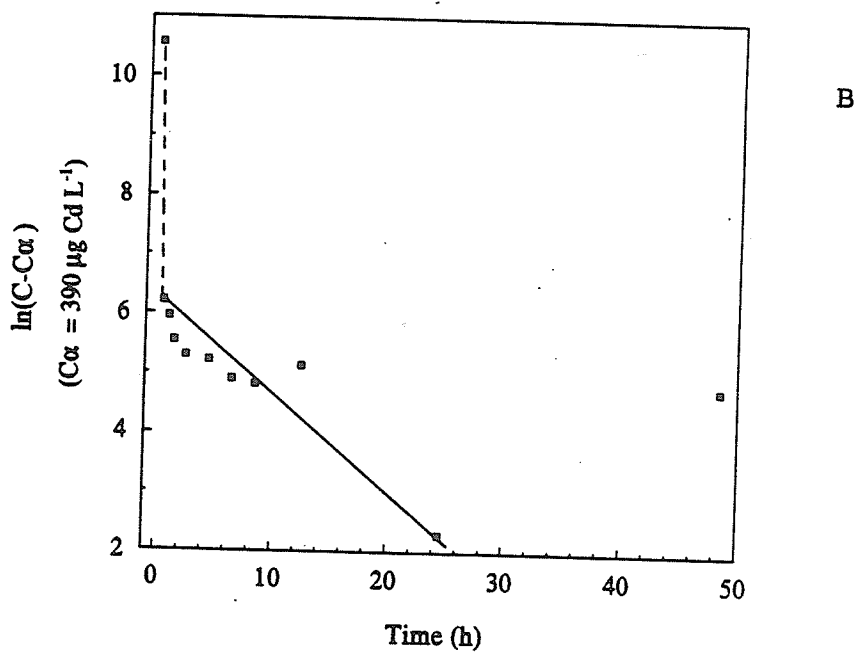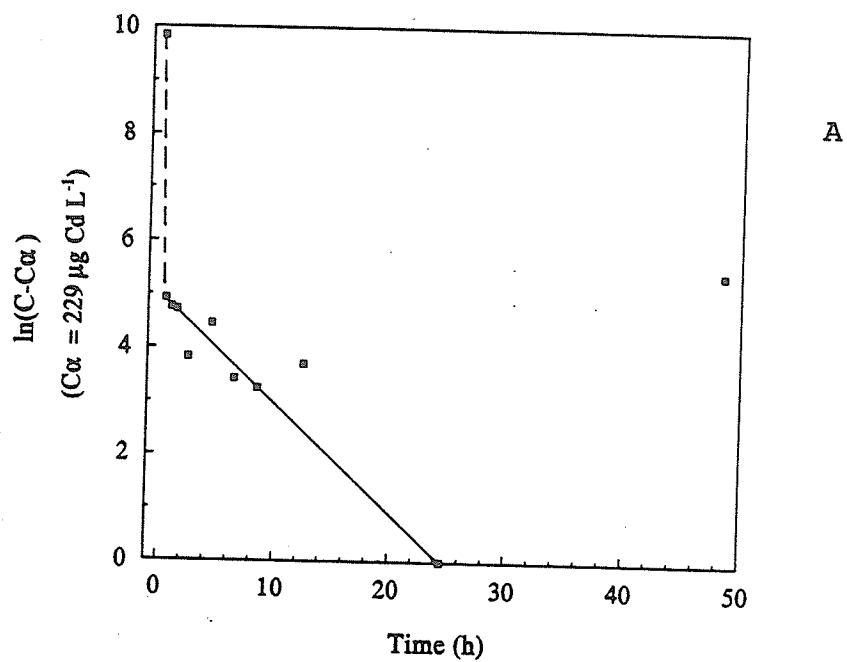Figure 3.6. First order reversible plots for the decrease in the concentration of Cd in solution by Cd treatment. A. 25 ug Cd ml$^{-1}$  B. 50 ug Cd ml$^{-1}$

the time period in which reversible first order kinetics occureds was approximately 6 h and the time period for the higher concentrations of Cd studied (25 and 50 ug ml$^{-1}$) was about 24 h. After these time intervals, the Cd concentration in solution began to increase. It was hypothesized that chelates released from microorganisms may have allowed the Cd to remain in solution. Unfortunately, however, atomic absorption measures total Cd in solution, and thus, it was not known how much Cd was present in the free inorganic or chelated forms.

The rate constants (k) or slopes, for the first order reversible reactions (solid lines) (Figs. 3.4, 3.5 and 3.6), determined from regression analysis, are presented in Table 3.21. In general, the value of k decreased with increasing initial concentration of Cd added. This means that the loss of Cd from solution was slower when higher concentrations of Cd were added.

From the equilibrium concentrations of Cd in solution (C$\alpha$) obtained in the kinetic part of the study, it is possible to calculate the amount of Cd adsorbed at the point of equilibrium, i.e. B$\alpha$, when the rate of or amount of adsorption is equal to that of desorption or release (Table 3.21). The amount of Cd adsorbed increased as the concentration of Cd added increased (Table 3.21). A logarithmic plot of the

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Table 3.21. Concentration of Cd in solution and Cd
adsorbed at equilibrium  and the rate
constant for the first order reversible
kinetic reactions from the addition of
$Cd(NO_3)_2$ to sewage sludge.

| $Cd(NO_3)_2$ (ug Cd $ml^{-1}$) | Equilibrium Concentration of Cd ($C\alpha$) (ug $ml^{-1}$) | Rate Constant | Concentration of Cd Adsorbed at Equilibrium ($B\alpha$) (ug $ml^{-1}$) |
|---|---|---|---|
| 5 | 59 | -0.521 | 276 |
| 10 | 111 | -0.305 | 584 |
| 15 | 179 | -0.452 | 841 |
| 20 | 204 | -0.173 | 1136 |
| 25 | 229 | -0.185 | 1314 |
| 50 | 390 | -0.137 | 2720 |

logarithmic plot of the equilibrium values (Freundlich adsorption isotherm) also shows that the amount of Cd adsorbed is directly related to the concentration of Cd in solution (Fig. 3.7).

As a corollary, it can be said that due to its active (i.e. adsorption-desorption) nature, SS can be both a sink and a source of Cd. The data in the second and fourth columns of Table 3.21 show that, if equilibrium is reached, the amount of Cd remaining in solution is greater when the amount adsorbed is higher (although the percentage of Cd in solution is constant relative to the initial concentration). The fate of free and adsorbed Cd as well as other metals when the SS is mixed with soil should be the subject of further study. It would, no doubt, be influenced by reactions with soil components and the changes that occur from SS during decomposition (Audette, 1993).
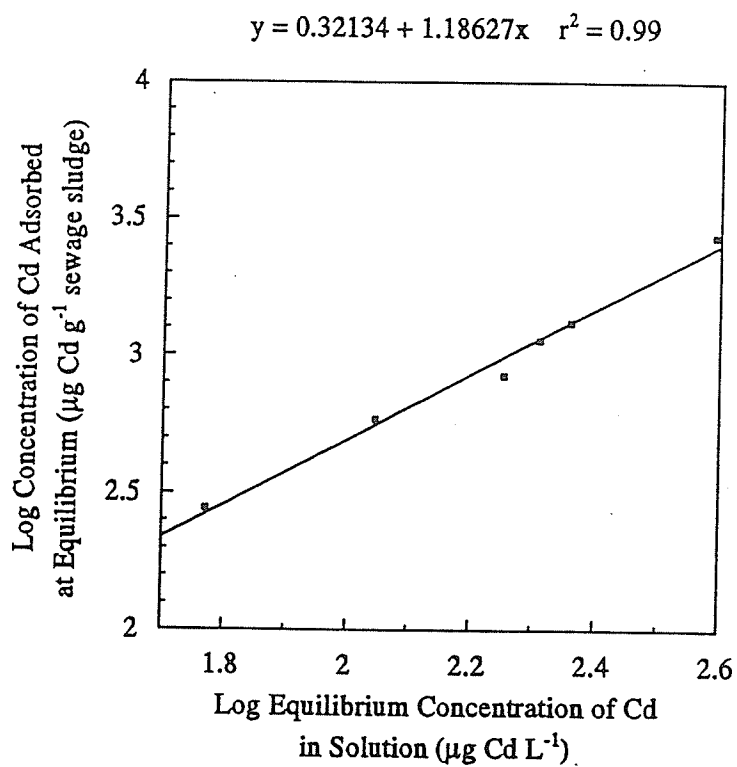
$$y = 0.32134 + 1.18627x \quad r^2 = 0.99$$



Figure 3.7. Freundlich Adsorption Isotherm of the adsorption of cadmium by freeze-dried sewage sludge.

## 4. CONCLUSION

The results of this thesis indicate that the application of SS
to agricultural land has little impact on the growth or Cd
content of wheat for SS rates of up to 200 t ha$^{-1}$. Even under
extreme environmental conditions that may induce Cd
bioavailability such as flooding or acidification, the growth
of the wheat was not detrimentally affected nor the uptake of
Cd enhanced. Only the direct application of inorganic Cd to
the soil caused unacceptable levels of Cd in grain and straw
tissue but still did not affect yield. It is well documented,
however, that inorganic sources of Cd are far more readily
bioavailable than organic sources.

Cadmium in SS is not readily released from the SS due to its
carbonate and oxide content. However, once present in the
soil, the soil's organo-mineral fraction plays an important
role in tying up Cd that is released by the SS. It was shown
that Cd is held by bidentate bonding on Fe oxides commonly
present in soil. This Cd is not readily released. Over time
this Cd may become increasingly less available as it is
occluded by the oxides.

Even the SS itself acts as a barrier to large amounts of Cd
becoming bioavailable over time. Sewage sludge displays a
great ability to remove soluble Cd from solution. The

adsorption of Cd by SS involved at least two steps; an initial fast reaction (within 30 minutes) and then a slower reaction which followed first order kinetics. Eventually an equilibrium was established between adsorbed Cd and Cd remaining in solution.

It can be concluded, therefore, that with respect to Cd the application of SS to Red River clay or Lakeland clay loam soil for grain production, at rates of 56 t ha$^{-1}$ established by the City of Winnipeg, is a safe method for its disposal.

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