CHAPTER 4

BASELINE ASSESSMENT OF LEAD AND CADMIUM LEVELS IN STUDY AREA

4.1 Introduction

This chapter describes a baseline assessment of Pb and Cd levels in treated sewage, soils and existing pasture as well as soil properties of the study area where detailed experiments described in chapters 5 and 6 were eventually carried out. The purpose of the assessment was to establish characteristics of the area and use them to select portions of the area suitable for detailed experiments on Pb and Cd. This chapter also provides an assessment of the long-term total levels of accumulation of Pb and Cd in the soils, using chemical tests on soil samples from the irrigated area and non-irrigated area.

4.2 Objectives

The specific objectives of this component of the study were:

(1) to assess Pb and Cd levels in treated sewage using past chemical records
(2) to determine long-term accumulation and distribution of Pb and Cd in a sandy soil after 29 years of treated sewage disposal
(3) to establish chemical characteristics of the soil in the study area
(4) to determine the presence and levels of Pb and Cd in mixed star and kikuyu pasture grown in the area of disposal of treated sewage
(5) to investigate relationships between total concentrations of Pb and Cd in the soil and metal content in mixed star and kikuyu grass pasture.

4.3 Detailed methods and materials

4.3.1 Analysis of past records on levels of Pb and Cd in treated sewage

Available past records of chemical tests on heavy metals covered a short period of time (1991 to 1994), during which the City of Harare carried out heavy metal tests. Data on Pb and Cd levels in raw sewage, treated effluent and digested sludge were extracted and analysed statistically using
the SPSS 8.0 for Windows (www.spss.com, 1997) computer package to obtain averages and ranges that were compared with legislated limits.

4.3.2 Baseline assessment of chemical characteristics of study area

Soil sampling and testing

Soil samples were taken at least 2 months after the last irrigation. The samples were taken from portions of the control and treatment areas. Each of the portions was 200 m long and 100 m wide. The portions were sub-divided into 4 plots that were 100m long and 50 m wide. From each plot, 4 auger samples located on a grid of 6.25 m x 12.5 m were taken and corresponding horizons mixed to make a composite sample. Each horizon was 10 cm in depth. The maximum soil depth was 50 cm. Areas that had evidence of localized ponding, such as irrigation furrows were avoided. Surface litter was removed prior to soil sampling using augers. Plant debris was removed from soil samples, before they were air-dried and passed through a 0.15 mm sieve.

Soil texture was determined using the hydrometer method (Gee and Bauder, 1986). Calgon (37.5g sodium hexametaphosphate (Na$_6$O$_{18}$P$_6$) and 7.94g sodium carbonate (Na$_2$CO$_3$) dissolved in 1000 ml of water) was used to disperse the soil fractions in the soil sample. The dispersed suspension was passed through a 180-µm sieve and collected in a measuring cylinder to separate the sand from the clay and silt. The weight of the sand was measured after oven-drying it overnight. A brass plunger was used to stir the suspension. A hydrometer was used to take measurements of clay and silt after 60 seconds of inserting the plunger into the suspension. Two hours from the commencement of sedimentation, a reading representing the clay content, was taken using the hydrometer. Temperatures were measured in both cases. The hydrometer readings were corrected for temperature by adding or subtracting 0.3 units for every degree above or below 20°C, respectively. The percentage silt plus clay and clay content were corrected for hygroscopic moisture to obtain the percentages of silt and clay.

Soil pH was determined using a 1:5 soil suspension of 0.01M CaCl$_2$. A standard buffer solution (pH 7.0) of dry potassium di-hydrogen orthophosphate (KH$_2$PO$_4$) and di-sodium hydrogen orthophosphate (Na$_2$HPO$_4$) was used to calibrate the pH meter. Records of pH were made when reading on the pH meter stabilised for at least 0.1 units per 30 seconds.
Cation exchange capacity (CEC) was determined by saturating the soil with 1M CH$_3$COONH$_4$ buffered at pH 5.2. A mechanical vacuum extractor (Model LT-800-8, Concept Engineering, Inc, Nebraska, III, USA) was used for extracting exchangeable bases. Excess ammonium was washed out using ethanol (CH$_2$CH$_3$OH) and the adsorbed ammonium was determined by steam distillation and titration with sulphuric acid (H$_2$SO$_4$) in a distillation unit, Kjeltec Auto 1030 Analyser. A standard sample (Harare 5E.2) was included in every 48 samples for quality control. Where the value of the check sample was outside the expected range the whole batch was re-done.

Total heavy metals in soil were extracted with aqua regia (1:3 conc. HNO$_3$ and conc. HCl) and heated under reflux. After filtration, the extract was diluted with 2M HNO$_3$ and Pb and Cd were determined on the atomic absorption spectrometer.

Organic carbon (C) was determined by the modified Walkley and Black method (Houba et al., 1989) with additional heat applied under reflux (at 130°C). Excess Potassium dichromate (K$_2$Cr$_2$O$_7$) was used to oxidise organic C. The excess dichromate was then titrated using ferrous ammonium sulphate (Fe(NH$_4$)$_2$(SO$_4$)$_2$) to determine the amount used in oxidising organic C. A conversion factor of 1.33 was applied to organic C to determine total organic C assuming 75% recovery (Houba et al., 1989). A Total Organic Carbon (TOC) analyser was not available, hence the method described was used.

**Sampling and testing of grass**

Grass samples from the irrigated area were taken from each plot to determine the metal content. One sample, consisting of 10 sub-samples was taken from each of the 4 plots in the sewage sludge treatment. The samples were taken on a grid of 6.25 m x 10 m, within each plot.

The grass was cut at 5cm height off the ground. No grass samples were taken from the control area because the sparse and mixed grasses were different from those grown under irrigation. It was therefore not possible to compare heavy metal plant uptake between the control and the sewage sludge treatment. The samples were washed using deionised water and oven dried at 65°C to constant weight before being ground and sieved through a 0.1 mm sieve. The samples were then ashed at 550 °C for 16 hours and digested with 25% HCl and concentrated HNO$_3$. After filtration, Pb and Cd were determined using atomic absorption spectrometry.
To analyse the measured data, arithmetic means and standard deviations were calculated on clay content, pH, CEC, organic carbon, Pb and Cd for each soil horizon. Data from tests of Pb and Cd on grass was subjected to the same analysis for which means and ranges are presented. Analysis of variance was used to determine the significance of differences in means of various data. Simple correlation was used to measure the degree of association between any two soil properties, since it was important to investigate whether soil properties like CEC, organic matter, heavy metal content and soil depth were associated. Pearson’s correlation coefficients ($r^2$ values) were, therefore computed for pairs of variables, including soil depth to determine trends in the relationships of the variables and likely implications on uptake and modelling of uptake of Pb and Cd.

4.4 Results

4.4.1 Analysis of past records on levels of Pb and Cd in treated sewage

Firle Wastewater Treatment Plant utilises two types of sewage treatment technologies, namely biological trickling filtration plants and biological nutrient removal activated sludge plants. Appendix 1 summarises the treatment processes in the two technologies at Firle Treatment Works. The effluent from biological trickling filtration plants is mixed with sludge (shown as liquid digested sludge or farm compost material for farmland and humus sludge in Appendix 1) and directed to irrigate pastures. This approach serves two purposes, disposal of sludge without the need for landfill and secondary treatment of effluent through the soil, where the seepage is expected to be of acceptable quality before it gets into Manyame River. Sometimes liquid sludge on its own or effluent on its own is disposed on pastures.

Heavy metals in treated sewage

Table 4.1 presents results of an analysis of Pb and Cd levels and their prescribed limits according to the Zimbabwe Water (Wastewater and Effluent Disposal) Regulation (Zimbabwe Statutory Instrument 274, 2000). These regulations were derived from international guidelines, particularly the average recommended maximum limits that were based on United States Environmental Protection Agency guidelines for wastewater reuse enshrined in US EPA (1992) and also included in the table.
Table 4.1 shows the presence of Pb and Cd in both the effluent and digested sludge over the 4-year period. The average concentrations of the metals in effluent were within the acceptable limits for short-term irrigation. However the highest levels were above maximum recommended levels in both effluent and digested sludge.

The average levels of Pb of 2.6 mg/l for digested sludge and 0.20 mg/l for effluent were below the local legislated limits for both short and long-term irrigation and US EPA (1992) limits. However the highest concentration of Pb (5.03 mg/l) was marginally higher than the recommended long-term level in sludge.

The concentration of Cd in the effluent and digested sludge was not detectable in some samples, hence it was within acceptable limits. However, the upper levels of Cd in digested sludge (0.5 mg/l) and effluent (0.03 mg/l) were 50 and 3 times the local recommended level of 0.01 mg/l, for long-term irrigation, respectively. The upper level of Cd in sludge was 10 times the level recommended for short-term irrigation. This indicates a wide range in metal content of both effluent and sludge.

### Table 4.1: Average (range) concentration (mg/l) of heavy metals in samples of digested sewage sludge and effluent (Source: Harare City Council file records, 1991-1994)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Digested sewage sludge</th>
<th>Effluent</th>
<th>Current local legislated levels in wastewater suitable for irrigation*</th>
<th>Recommended maximum concentration **</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Long term</td>
<td>Short term</td>
</tr>
<tr>
<td>Pb</td>
<td>2.6 (0.13-5.03)</td>
<td>0.20 (0.05-0.48)</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>Cd</td>
<td>ND (ND - 0.5)</td>
<td>ND (ND - 0.03)</td>
<td>0.01</td>
<td>0.05</td>
</tr>
</tbody>
</table>

ND - not detectable  

### 4.4.2 Chemical characteristics of study area

#### Type of soil, soil pH, cation exchange capacity and organic carbon

Table 4.2 presents selected soil properties of clay content, soil pH, organic carbon and CEC. The control and treatment were situated on predominantly granitic sandy soil classified as Haplic Arenosol.
Table 4.2: Selected properties of a sandy soil in the irrigated and control areas

<table>
<thead>
<tr>
<th>Sampled area</th>
<th>Soil depth (cm)</th>
<th>Clay content (%)</th>
<th>Soil pH (CaCl₂)</th>
<th>Organic carbon (%)</th>
<th>Cation exchange capacity (cmol$_{kg}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-10</td>
<td>&lt;3</td>
<td>5.4 (0.5)</td>
<td>3.3 (0.3)</td>
<td>29.3 (11.2)</td>
</tr>
<tr>
<td>Treatment</td>
<td>10-20</td>
<td>5.7 (4.7)</td>
<td>5.5 (0.6)</td>
<td>1.7 (0.5)</td>
<td>8.1 (7.9)</td>
</tr>
<tr>
<td></td>
<td>20-30</td>
<td>8.5 (4.4)</td>
<td>5.9 (0.8)</td>
<td>0.9 (0.6)</td>
<td>4.6 (3.5)</td>
</tr>
<tr>
<td></td>
<td>30-40</td>
<td>7.3 (0.6)</td>
<td>5.4 (0.2)</td>
<td>1.1 (0.2)</td>
<td>2.9 (1.0)</td>
</tr>
<tr>
<td></td>
<td>40-50</td>
<td>6.0 (1.4)</td>
<td>5.5 (0.1)</td>
<td>1.0 (0.5)</td>
<td>3.2 (1.7)</td>
</tr>
<tr>
<td>Control</td>
<td>0-10</td>
<td>6.3 (0.6)</td>
<td>4.6 (0.8)</td>
<td>1.3 (0.1)</td>
<td>1.6 (0.9)</td>
</tr>
<tr>
<td></td>
<td>10-20</td>
<td>6.0 (1.0)</td>
<td>4.4 (1.1)</td>
<td>0.9 (0.1)</td>
<td>1.5 (0.8)</td>
</tr>
<tr>
<td></td>
<td>20-30</td>
<td>5.0 (1.0)</td>
<td>4.6 (1.1)</td>
<td>1.0 (0.2)</td>
<td>1.4 (1.0)</td>
</tr>
<tr>
<td></td>
<td>30-40</td>
<td>5.7 (0.6)</td>
<td>4.5 (1.0)</td>
<td>0.9 (0.2)</td>
<td>1.4 (0.7)</td>
</tr>
<tr>
<td></td>
<td>40-50</td>
<td>10.0 (0.0)</td>
<td>4.9 (1.7)</td>
<td>0.7 (0.0)</td>
<td>1.3 (0.5)</td>
</tr>
</tbody>
</table>

(standard deviation)

The soil consisted of a sandy top layer (0-30 cm) overlying a sandy-loam subsoil (30-50 cm). It was generally acidic with the pH of the sewage sludge and effluent irrigated soils being on average 1 pH unit higher than the corresponding horizon in the control. The very low CEC and organic C levels were consistent with sandy soils. However addition of sewage sludge and effluent resulted in a 2.6-fold and 15.5-fold increase in organic carbon and CEC, respectively in the 0-20 cm soil layers, when compared to corresponding horizons in the control.

**Total concentrations of Pb and Cd in soils**

Table 4.3 presents the average total concentrations of Pb and Cd in the soil profile of the irrigated and the control areas for every 10cm soil depth. Throughout the soil profiles of both the control and the irrigated areas, Pb and Cd were present. The average levels of Pb and Cd within the 0-50 cm profile of the control were 18.4 mg/kg Pb and 0.40 mg/kg Cd, respectively. The average levels of the metals in the area of disposal were 55.5 mg/kg Pb and 0.65 mg/kg Cd. Therefore the level of accumulation over the 29 years were 37.1 mg/kg Pb and 0.25 mg/kg Cd.

The mean profile concentrations of Pb of 55.46 mg/kg and Cd, 0.65 mg/kg were 3.0 and 1.6 times the mean profile levels in the control, respectively. Accumulation of the two metals predominantly occurred within the 0-20 cm horizons, particularly in the 0-10cm horizons. In the 0-10 cm horizon of the irrigated area, Pb and Cd were 11.6 and 3.2 times the levels in the 0-10 cm horizon of the control, respectively. Otherwise the background levels in the 30-50 cm horizons of the control were largely similar to the levels in the area of disposal.
Analysis of variance showed that metal levels in the treatment were significantly \((p \leq 0.01)\) higher than in the control. The mean levels of the metals in the top 0-20 cm in the irrigated area were significantly \((p \leq 0.05)\) higher than the levels in the 20-50 cm and also significantly higher \((p \leq 0.05)\) than the levels in the 0-20 cm of the control.

**Table 4.3: Average total soil metal concentrations in horizons of soil profile of irrigated and control areas**

<table>
<thead>
<tr>
<th>Sampled area</th>
<th>Soil depth (cm)</th>
<th>Total metal concentration (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pb</td>
</tr>
<tr>
<td>Treatment</td>
<td>0-10</td>
<td>186.31 (120.92)</td>
</tr>
<tr>
<td></td>
<td>10-20</td>
<td>33.32 (26.61)</td>
</tr>
<tr>
<td></td>
<td>20-30</td>
<td>22.03 (5.70)</td>
</tr>
<tr>
<td></td>
<td>30-40</td>
<td>18.71 (5.01)</td>
</tr>
<tr>
<td></td>
<td>40-50</td>
<td>17.00 (9.92)</td>
</tr>
<tr>
<td>Control</td>
<td>0-10</td>
<td>16.00 (1.63)</td>
</tr>
<tr>
<td></td>
<td>10-20</td>
<td>24.00 (13.47)</td>
</tr>
<tr>
<td></td>
<td>20-30</td>
<td>19.00 (7.39)</td>
</tr>
<tr>
<td></td>
<td>30-40</td>
<td>15.50 (1.00)</td>
</tr>
<tr>
<td></td>
<td>40-50</td>
<td>17.33 (1.15)</td>
</tr>
</tbody>
</table>

\(()\) standard deviation

Comparison of mean levels of metals in the 20-50 cm soil horizons showed that there were no significant differences within the horizons in both the control and the treatment. Total metal concentrations of the soil horizons correlated well with depth in the irrigated areas \((r^2 = -0.76\) for Pb and 0.89 for Cd) and poorly in the control \((r^2 = -0.27\) for Pb and -0.09 for Cd).

**Correlation of soil parameters and total metal concentrations**

The pH correlated poorly with depth since \(r^2\) values for the irrigated area and control area were 0.08 and 0.59 respectively compared to an \(r^2\) critical value of 0.87. The correlation of the pH of the soil and total metal concentration along the soil horizons was weak in both the irrigated and the control areas for both Pb \((r^2 = -0.44\) in both cases) and Cd \((r^2 = 0.35\) in the irrigated area and 0.30 in the control area).

The clay content of the soils correlated strongly with total concentrations of both Pb and Cd in the irrigated area \((r^2 = -0.85\) for Pb and -0.87 for Cd) but relatively weakly in Pb of the control \((r^2 = 0.05)\). In the case of Cd correlation was strong in both cases \((r^2 = -0.87\) in the irrigated area and 0.75 in the control area).
Cation exchange capacity correlated strongly with total concentrations in the irrigated area ($r^2 = 0.99$ for Pb and 0.97 for Cd). It however correlated weakly with total concentrations in the control ($r^2 = 0.12$ for Pb and 0.04 for Cd). Organic C strongly correlated with total metal concentrations in the irrigated area ($r^2 = 0.97$ for both Pb and Cd) but weakly with total metal concentrations in the control ($r^2 = 0.25$ for Pb and 0.34 for Cd).

**Concentrations of Pb and Cd in soils and grasses**

Table 4.4 presents the average total Pb and Cd concentrations in the 0-20 cm soil horizon and in grass from sub-sampling areas within the irrigated area. Mixed star and kikuyu grasses took up Pb and Cd. Cadmium was not detected in some samples. Using the Student’ t-test showed that there was no significant difference in mean soil levels of Pb and Cd on sub-sampling points 1 and 4 and in levels of Cd in the corresponding grasses. However soil Pb levels at these points were significantly ($p \leq 0.05$) higher than on sub-sampling points 2 and 3 and the level for sub-sampling point 3 was significantly ($p \leq 0.05$) higher than at sub-sampling point 2. The Pb level of grass at sampling point 1 was significantly ($p \leq 0.05$) higher than on sub-sampling points 2 to 4. Sub-sampling point 2 had a significantly ($p \leq 0.05$) higher Cd level than the rest.

There was very weak correlation between total soil concentration of Pb and levels in the grass ($r^2 = 0.39$). Similarly, weak correlation coefficients were obtained using log$_{10}$-transformed total soil concentration and log$_{10}$-transformed concentration of the metals in grass.

**Table 4.4: Average total metal levels (mg/kg) in 0-20 cm soil depth and mixed grass**

<table>
<thead>
<tr>
<th>Sub-sampling points</th>
<th>Soil Pb</th>
<th>Soil Cd</th>
<th>Grass Pb</th>
<th>Grass Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>148.65 (15.32)</td>
<td>0.66 (0.09)</td>
<td>1.50 (0.04)</td>
<td>ND</td>
</tr>
<tr>
<td>2</td>
<td>17.0 (11.31)</td>
<td>1.21 (0.11)</td>
<td>1.01 (0.02)</td>
<td>1.2 (0.03)</td>
</tr>
<tr>
<td>3</td>
<td>88.91 (8.22)</td>
<td>ND</td>
<td>1.21 (0.11)</td>
<td>0.17 (0.02)</td>
</tr>
<tr>
<td>4</td>
<td>167.54 (17.68)</td>
<td>0.95 (0.08)</td>
<td>1.0 (0.03)</td>
<td>ND</td>
</tr>
</tbody>
</table>

() standard deviation
4.5 DISCUSSION

4.5.1 Analysis of past records on levels of Pb and Cd in treated sewage

A comparison of mean levels of Pb and Cd in the treated wastewaters and legislated limits, suggested that no hazard should be expected from the two metals. However, the upper limits of Cd in treated sludge and effluent were 50 and 3 times the local legislated level of 0.01 mg/l, respectively. The limitations in the data, described below and the probability that higher levels of the metals could be discharged into the treatment system and onto the pasturelands, implied that Pb and Cd hazard could not be ruled out on the basis of the data analysed in this component of the study. This notion is supported by the fact that the upper levels of the metals in treated water were very high, particularly in the case of Cd.

The data used in this analysis was scanty. Considering that on-the-spot or grab samples were taken once every two months, it was not possible to determine the distribution of the levels within each 2 month period, let alone the variation within the intervening period or within a production cycle. Junkins et al (1983) recommended hourly sampling programs during some production cycles and non-production cycles in order to capture variations in organic loading, including detection of peak organic loads. Therefore it was not possible to ascertain the distribution of the concentrations of the metals with respect to the upper or lower values, on the basis of the data obtained from the City of Harare. If the systems tended to operate close to the upper limit, the scenario presented considerable Pb and Cd hazard. Hofwegen and Veenstra (1995) noted that a 50% increase in total soil Cd from 0.5 mg/kg to 0.82 mg/kg caused a large increase in Cd content in brown rice from 0.08 to 1 mg/kg (1200%).

The wide range of metal concentrations in both the effluent and digested sludge (Table 4.1) implied large variations in levels of pollutants in raw sewage from the sources. This variation could be a result of varying levels of dilution of the pollutants from sources or increases and decreases of activities causing pollution at the sources or intermittent high levels of pollution. Besides dilution, most variation in pollutant concentrations could be attributed to industrial pollution since domestic pollution would not be expected to vary so widely. The variability in strength and character of influent wastewater (which can cause organic shock loads to biological treatment systems) is experienced by most treatment systems and is related to industrial and commercial operation schedules, which tend to vary (Junkins et al 1983).
There was insufficient disposal data on treated sewage application. The lack of data on the proportions of mixes of sludge and effluent implied that the actual concentrations of the metals in the mixture of effluent and sludge were unknown. The levels shown in Table 4.1 however suggest that the concentration of the mixed effluent and sludge disposed on pastures was somewhere in between the concentrations of the two. This implied that based on the 1991-1994 data, treated sewage disposed on pastures had 0.20-2.60 mg/l Pb and <0.0-0.5 mg/l Cd, leaving open the possibility of irrigation water having a concentration that could be higher than recommended levels.

The fact that Harare City Council sometimes irrigated the land using effluent only or sludge only or a mixture of the two also added uncertainty regarding heavy metal loading on the soils. In addition the lack of proper irrigation schedules implied that some areas could receive more water than others, suggesting that some areas could be exposed to higher metal concentrations from the irrigation water if their irrigation coincided with a period when high loads were received by the treatment plant.

4.5.2 Pb and Cd accumulation in soils

Variations of total soil metal concentrations between irrigated and control areas

The higher levels of total Pb and Cd obtained in the soil profile of the irrigated area indicate accumulation when compared with levels in profile of the control area. The average background level of Pb of 18.4 mg/kg in the control area and the average soil profile Pb level of 55.5 mg/kg in the irrigated area indicate accumulation of 37.1 mg/kg (1.3 mg/kg/year) in the soil over 29 years. Both soils fell within the 10 mg/kg to 70 mg/kg background levels of Pb for normal soils (Johannesson, 2002). Accumulation in the top soil layers translates to an average increase of 5.7 mg/kg per year in the top 10 cm and 0.3 mg/kg per year in the 10-20 cm depth.

The mean profile levels of Cd of 0.65 mg/kg obtained in the irrigated area against a background level of 0.40 mg/kg in the control area indicates accumulation of 0.25 mg/kg in 29 years or 0.01 mg/kg/year in the irrigated area. Cadmium has been reported to be less than 1 mg/kg (Alloway, 1995), 0.2 mg/kg (WHO, 1993) and 0.1-0.4 mg/kg (Johannesson, 2002) in normal soils.
Therefore the level obtained in this study was in agreement with levels quoted in these references. McGrath and Loveland (1992) observed total Cd concentrations of 0.2 to 1.7 mg/kg in agricultural soils in England and Wales, while Alloway (1995) reported up to 100 mg/kg Cd in agricultural soils subjected to high application of phosphate fertilisers.

The preceding arguments confirm that the observed levels of all metals in the control area were the base levels for an unpolluted soil. The fact that the two areas were just adjacent eliminates the possibility of other sources of pollution, such as air pollution, being responsible for the increase in metal concentration in the soils. Therefore the metals that were identified in treated sewage led to a rise in the levels of the metals in the sandy soil.

The higher pH in the irrigated area (Table 4.3) was attributed to the alkalisation effect of basic cations contained in sewage sludge and effluent. While some variations in metal levels are expected due to inherent differences in soil chemistry between one sampling point and another, the large variation in metal levels between sampling points was attributed to poor water application and distribution associated with the flood disposal system.

In this study, the total metal concentrations of the Pb and Cd were strongly and positively correlated to clay content, CEC and organic matter, but weakly correlated to pH in the sewage-irrigated soil. In contrast the total metal concentrations of Pb and Cd in the control were generally weakly correlated to clay content, CEC and organic matter but more strongly correlated to pH. This confirms the influence of organic matter on soil parameters, including total metal content of soils and suggests that high levels of organic matter is associated with high levels of total metal content and vice versa. Since organic matter is largely retained in the topsoil (Birley and Lock, 2001), its correlation with CEC and total metal content along the soil profile suggests that where a soil receives treated sewage, the extent of exposure of plant roots to metal ions depends on level of organic matter and distribution of plant roots along the soil profile. This has implications on plant metal uptake as discussed below.
Distribution of metal concentrations along soil depth

There was a large variation of total metal concentration with depth. The top 20cm of the soil and in particular the top 10cm had relatively higher metal concentrations than the lower horizons in the irrigated area. Since Pb and Cd levels within the 30-50 cm horizons of the control and the area of disposal were similar and the 0-20 cm horizons of the irrigated area had much higher levels than the control, it can be argued that the metals were largely immobile.

Considering that the top 20cm had far less clay than the lower horizons, the high CEC could be attributed to the high organic matter content of these layers, rather than the clay content. The results suggest that organic matter held Pb and Cd in the top layers, making them immobile, and thereby confirming their high affinity to organic matter (McGrath and Lane, 1989). This is also confirmed by the high correlation between the metal levels and organic C ($r^2 = 0.97$). This outcome suggests that the metals accumulated in the top horizons where grass roots were expected to grow.

The variation of total metal concentration with depth presents a potentially large source of error in relating soil concentrations to acceptable limits and to plant concentrations as well as in modeling soil-plant uptake. This is so if one considers that the depth interval at which various plants in different environments obtain water and nutrients and the relative density of feeder roots at different depths are unknown (US Department of Energy, 1998). When the average profile content of Pb of 55.5 mg/kg is compared with 87 mg/kg stated by Johannesson (2002) as the lower limit at which basic soil processes, such as microbial activity, are affected, Pb problems would not be expected. However the opposite is true if the 109.8 mg/kg in the 0-20 cm depth is considered. Similarly, the average level of Cd of 1.0 mg/kg in the 0-20cm horizon would be regarded as being too high for a soil, considering that it is equal to the recommended sludge directive limit of 1 mg/kg (EEC, 1986) for use of sewage in agriculture. However, the average soil profile concentration of 0.65 mg/kg would be considered more acceptable.

Total soil concentration versus recommended guidelines

The maximum permissible concentrations of Pb in soil under grass, stated by different authorities are: 300 mg/kg (Department of Environment, 1989), 100 mg/kg (Ross et al., 1992) and 150 mg/kg Birley (2001). A comparison of the results shown in Table 4.3 and these maximum
permissible limits suggests that the levels obtained in this study would be acceptable according to Department of Environment (1989) but unacceptable according to Ross et al (1992).

The disparities in the guidelines quoted here and other international literature emanate from the different climatic, soil and crop conditions under which they were determined. Indeed most of these guidelines do not specify the soil type and the organic content on which the heavy metal sorption depends (Christensen 1989b). In addition they often do not specify the type of crop or soil depth they apply to, both of which are important factors when considering the possibility of plant uptake of the metals.

**Heavy metal content in mixed grasses**

Table 4.4 shows that the mixture of kikuyu and star grasses accumulated large quantities of Cd and small amounts Pb compared to recommended limits. The average Pb level of 1.2 mg/kg in grass was below the 10mg/kg tolerance level for agronomic crops (Seaker, 1991) and 40 mg/kg recommended for pasture grass (U.K Statutory Instrument No. 1412, 1995). However, the fact that Cd uptake varied from non-detectable to a level of 1.2 mg/kg indicates a potential for the pasture grass to take up levels beyond the 1 mg/kg recommended for pasture for grazing animals (U.K Statutory Instrument No. 1412, 1995).

**Correlation of total soil metal content and metal content in mixed grasses**

A comparison of mean total soil concentration of Pb and concentration of Pb in grass shows that there was a weak correlation between the two ($r^2 = -0.03–0.4$). This can partly be explained by the fact plant uptake of metals is normally related to the bio-available metal concentration in the soil (Nyamangara and Mzezewa, 1999). Organic matter, pH and CEC are the most important factors that control the availability of heavy metals in the soils (Forbes et al, 1976).

**4.5.3 Implications of findings**

The findings of this component of the study could not be used to confirm or rule out the hazard Pb and Cd contamination in soils and grasses due to a number of reasons. Although the average level of Pb in the grass was relatively low (1.2 mg/kg), this did not necessarily confirm low uptake of the metal by star or kikuyu grasses since the assessment was done on mixed kikuyu and
star grass. Similarly, although grass accumulated up to 1.2 mg/kg of Cd this did not confirm high uptake by star grass or kikuyu grasses for the same reason. The concentrations of Pb and Cd relative to their total levels in the soil and levels in the grass left questions relating to whether they interacted in the soil leading to increased or reduced uptake of one or the other or both. Bak and Jensen (1998) noted that uptake of metals by plants could be antagonistic, synergistic or additive.

The strong correlations between total soil concentration of Pb and Cd and soil properties of CEC, clay content and organic matter confirms findings of previous research work on soils amended with wastewater or sludge. While correlation provides an idea of the pattern distribution of the metals within the soil profile the lack of information on distribution of plant roots within the profile complicates selection of the soil depth on which to relate soil concentrations and plant concentrations of metals.

The accumulation of up to 1.2 mg/kg Cd in mixed kikuyu and star grasses against a total soil concentration of Cd of 0.65 mg/kg (35% less than 1 mg/kg recommended) confirmed the risk of relying on total metal concentration for purposes of predicting hazard to animals. Roberts et al (1994) reported restricted growth in livers and kidneys of animals grazing on pasture exposed to total soil Cd concentrations lower than the recommended sludge directive limit of 1 mg/kg (EEC, 1986). The high Cd content of grass in this part of the study confirmed Bak and Jensen (1998)'s observations that plants did not assimilate metals in direct proportion to total soil concentrations. The weak correlation coefficients between total soil metal content and metal content of grass were also consistent with Bak and Jensen (1998)'s observations. Indeed, Carson and Bazzaz (1977) noted that plant uptake relationships to total soil concentrations were only valid within a narrow range of chemical concentrations in the relatively non-toxic range. The data in this component of the study was not sufficient to define such a range for the sandy soil and mixed kikuyu and star grasses.

These findings suggested that the use of bio-available metal concentrations in the soil levels of metal uptake by plants should be accorded more attention in research. Highiri (1973) and US Department of Energy (1998) noted that if bio-available soil metal concentrations were to be used to improve reliability of critical metal limits in soils, they would have to be related to the plant species, since plant uptake of Pb and Cd were observed to vary with plant species.
Given the unanswered questions that emanated from the findings of this component of the study, it was considered logical to run an experiment under controlled conditions, using one of the grasses, star grass, to clarify the issues.