British Geological Survey

ODA

TECHNICAL REPORT WC/94/3
Overseas Geology Series

FINAL REPORT ON STREAM SEDIMENT, SOIL AND FORAGE CHEMISTRY AS INDICATORS OF CATTLE MINERAL STATUS IN NORTH-EAST ZIMBABWE.

F M FORDYCE, D MASARA and J D APPLETON

Natural Environment Research Council

International Division
British Geological Survey
Keyworth
Nottingham
United Kingdom NG12 5GG

British Geological Survey
TECHNICAL REPORT WC/94/3
Overseas Geology Series

FINAL REPORT ON STREAM SEDIMENT, SOIL AND FORAGE CHEMISTRY AS INDICATORS OF CATTLE MINERAL STATUS IN NORTH-EAST ZIMBABWE.

F M FORDYCE, D MASARA and J D APPLETON

A Report prepared for the Overseas Development Administration under the ODA/ BGS Technology Development and Research Programme, Project E12ES.

ODA classification:
Sub-sector: Others
Subject: Geoscience
Theme: Mineral Resources
Project title: environmental Geochemical Mapping
Reference number: R5547

Bibliographic reference:
Fordyce F M, Masara D and Appleton J D . 1994 Final Report on on Stream Sediment, Soil and Forage Chemistry as Indicators of Cattle Mineral Status in North-east Zimbabwe.
BGS Technical Report WC/94/3.

Keywords:
Zimbabwe, environmental geochemistry, trace elements, mineral status, cattle

Front cover illustration:
Typical bornhardt scenery of the Mutoko Granite, north-east Zimbabwe with cattle grazing in the foreground.

Keyworth, Nottingham, British Geological Survey, 1994

CONTENTS

LIST OF FIGURES

LIST OF TABLES

SUMMARY

Background

Undernutrition is probably the main cause of low production and reproduction rates amongst grazing livestock in many developing countries, however, mineral deficiencies and imbalances in forages undoubtedly also have a negative effect. Mineral deficiencies and excesses have been reported from most regions of the world, but the problem appears to be particularly severe in the tropics. For grazing livestock, deficiencies of Co, Cu, I, Fe, Mn, Se and Zn together with excesses of Cu, F, Mn and Mo have been recognised as detrimental to health.

As farming systems in developing countries progress and farmers are encouraged to seek higher levels of productivity from forage fed livestock, it will become increasingly important to correct for mineral deficiencies or imbalances in forage. Once the more limiting energy and protein deficiencies have been rectified, any method of identifying those areas particularly susceptible to mineral deficiencies will be of considerable value as it will permit the design and implementation of effective supplementation programmes which will lead to even higher levels of productivity.

Clinical, pathological, biochemical, soil, water, plant, animal tissue and animal fluid analyses have all been used to diagnose trace element deficiencies and excesses in animals. Apart from some notable exceptions such as goitre resulting from iodine deficiency and dental mottling and skeletal deformities associated with excess fluoride, few deficiency or toxicity syndromes induced by anomalous intakes of trace elements are distinguished by specific clinical symptoms. Diagnosis of sub-clinical cases is complicated by the fact that many of the symptoms of mild and transient mineral imbalances, such as unthriftiness, subnormal growth and reproduction, may also be caused by energy and protein deficiencies and the effects of parasites. Diagnosis of sub-clinical cases must rely on chemical and biological analyses. Screening large numbers of animals for evidence of mineral deficiency without first recognising which areas to target, would be an expensive and laborious process and would probably be subject to variations due to season, climate and physiological status of the animal at the time of sampling. Soil and forage analyses have been used by previous workers in tropical regions to identify mineral deficiencies and toxicities in grazing livestock. However, in many cases results tend to be equivocal and have to be interpreted with caution because of local variations in soil chemistry; uncertainties regarding the significance of extractable mineral concentrations in soils and variations in mineral concentrations between forage plant species and with forage maturity.

Study Objectives

Regional stream sediment geochemistry is a relatively rapid, cost-effective and reliable method of mapping the levels of elements (minerals) in the environment. This report describes the results of a study designed to assess the practical application of regional stream sediment geochemistry for mapping areas in which cattle may suffer from mineral deficiencies.

The main objectives of the study were:

1. to test the correlation between trace element distributions indicated on stream sediment geochemical maps and cattle mineral status in north-east Zimbabwe with the aim of assessing whether regional stream sediment geochemical maps can be used to identify areas where mineral deficiencies may affect cattle productivity

2. to investigate the relationship between trace element concentrations in stream sediments, soils, forage (grass and leaves) and cattle blood (serum) in order to identify which of the sample media provide a reliable guide to cattle mineral status.

The study forms part of the ODA/BGS Technology Development and Research (TDR) Programme "Environmental Geochemical Mapping" project (R5547, 91/16) which is investigating the feasibility of using regional geochemical data, including that from ODA sponsored mineral exploration surveys, for environmental studies in developing countries.

Methodology

An area of communal grazing land in north-east Zimbabwe was selected for this investigation because high quality stream sediment data already exist as a result of a previous ODA funded TC project. In addition, good collaborative links had already been established with the Zimbabwe Government Geological Survey Department and the Veterinary Services Department through various ODA TC Projects.

The study area comprises thinly populated communal lands of the Mudzi, Mutoko, Murehwa and Rushinga Districts which are farmed on a subsistence basis. Cattle form an important component of the local economy and family wealth is measured in terms of the number of cattle owned. No cattle mineral supplementation is currently practised in the area.

A variety of animal tissues and fluids including liver, bone and blood samples are commonly used to determine animal mineral status. Cattle blood (serum) was selected for this study as it is easier to collect than some of the other media. Zn was the principal trace element investigated as Zn in cattle serum is generally accepted as a reliable indicator of cattle Zn status.

It is suspected that the lack of correlation between soil, forage and animal blood compositions reported in previous studies may result, in part, from the restricted variation in environmental trace element levels in the areas investigated. An area with a wide range of Zn was therefore selected for the study and was subdivided into three regions of relatively low (<35 mg/kg), medium (35-70 mg/kg) and high (>70 mg/kg) Zn on the basis of existing stream sediment data.

Soil, grass, leaf and cattle serum samples were collected from five districts within each of the three regions to determine if the distinct variation in stream sediment Zn levels is reflected in soils and forage as well as in the cattle serum. Serum samples were collected from twenty cattle in each of the fifteen districts. Soil, grass and leaf samples were taken from up to five areas in each district that had been grazed by the cattle during the weeks preceding serum sampling. During the wet season, cattle in the study area graze and browse on a wide variety of indigenous grasses, shrubs and trees, so a representative selection of grazed and browsed species were included in the grass and leaf samples in an attempt to obtain an indication of the overall trace element levels in forage consumed by the cattle. Sampling was carried out in May 1993, at the end of the wet season. Cattle were re-sampled in May 1994 for Zn analysis as it was suspected that the 1993 samples were contaminated with Zn from the sample-tube caps. The 1994 serum samples were also analysed for Fe. Soil and forage samples were analysed for Ca, Co, Cu, Fe, Mg, Mn, P and Zn by ICP-AES following digestion in hot concentrated hydrochloric acid. Ca, Cu, Fe, Mg, P and Zn were determined in cattle serum by AAS.

The study was carried out in close collaboration with the Veterinary Research Laboratory, Harare and the Departments of Preclinical Veterinary Studies and Animal Science, University of Zimbabwe. Advice on the design and implementation of the study was provided by Mr G Freeland (ODA Senior Animal Health and Production Adviser), Dr C Livesey (Central Veterinary Laboratory), Prof. L McDowell (University of Florida), Prof. C Mills (Rowett Research Institute), Mr K Ryder (ODA Biometrics Unit, Rothamsted) and Dr N Suttle (Moredun Institute, Edinburgh).

Results and Discussion

Certain elements such as Ca, Fe, Mg, Mn, and P in soil reflect major differences in bedrock composition, being lowest over granite and grey gneiss terrains; moderate over gneissic terrains and high over meta-sedimentary rocks. Similar trends are seen in Co, Cu, and

Zn in soils and Co, Cu, Mn and Zn in stream sediments. Although bedrock composition clearly exerts the greatest influence on regional variations in trace elements, adsorption of Co, Cu, P, and Zn by secondary Fe and Mn oxides is also important in the fersiallitic soils and in stream sediments.

Relationships between variations in element concentrations in the sampling districts and sampling regions are exemplified by Zn. There is considerable variation in the distributions of Zn within each district and between districts for all sample media. At the regional level, Zn concentration in soil and forage reflects the geochemical variations in stream sediment composition. However, the variation in cattle Zn status between the districts within each region does not reflect Zn variations in forage, soil and stream sediments. Therefore, variations in element levels in cattle serum do not directly reflect environmental variations in element concentrations.

ANOVA statistical results show that despite the wide variation in Zn concentration in all sample media, stream sediment, soil and forage populations can be distinguished as three separate low, medium and high groups.However, results for serum are not significant indicating it is not possible to separate low, medium and high Zn in serum populations.

Many physiological factors control the uptake of elements by plants and animals. These factors may largely explain why the levels of elements in cattle serum do not directly reflect environmental element levels in north-east Zimbabwe. The results of this study suggest that although there is a lack of direct correlation between element levels in serum and the other media, interactions between elements in the environment may indirectly affect the mineral status of the cattle.

Statistical and spatial correlations suggest that increased levels of Zn and Cu in soils result in an increase in the levels of these elements in forage. However, ingestion of plants containing higher levels of Zn and Cu does not result in an increase in the Zn and Cu levels found in cattle serum. A probable explanation may be the antagonistic relationships between elements as they are absorbed during digestion by the cattle. Antagonistic relationships between Fe and Zn, Mn and Zn, Cu and Zn, Fe and Cu, Ca and Zn also P and Zn have been recorded in animals previously (eg. Mertz, 1987). In north-east Zimbabwe, the areas of high Zn and Cu in soils and forage correspond to areas of high Fe and Mn also. It is possible that high Fe and Mn in soil and forage is inhibiting the absorption of Zn and Cu in cattle.

Similarly, levels of P in serum and forage do not increase as levels of P in soil increase. Soils with higher P contents in north-east Zimbabwe also contain higher levels of Fe. It is possible that strong sorption of P by Fe oxides is inhibiting the availability of P to plants and cattle.

Cattle mineral studies commonly classify animal, forage and soil samples with respect to deficient, marginal and toxic element concentrations. Applying these critical levels and marginal bands to the present study, it is clear that a high proportion of cattle serum and forage samples are marginal in Zn. Discrepancies between the percentage of samples below the critical levels and marginal bands observed in previous studies are confirmed in north-east Zimbabwe. Although 26% of cattle were Cu deficient, nearly 100 % of forage samples were found to be deficient.

Conclusions

Stream sediment geochemical maps for Zn and Mn provide a reliable indication of the relative distribution of these elements in soil and forage (grass and leaves). Cu in stream sediments can be used to predict the levels of these elements in soil and grass, but less reliably in leaves. Fe in soils provides a reliable indication of levels in grass and leaves. Ca, P and Mg in soil reflect variations in the chemical composition of the underling rocks, however, this information cannot be used to predict relative concentrations of these elements in forage.

Variations in the levels of Ca, Cu, Mg, P and Zn in cattle serum do not correlate positively with variations in forage, soil and sediment samples. Fe in cattle serum correlates positively with Fe in leaves only. Therefore, it appears that it is not possible to use the concentrations of these elements in forage, soil or stream sediments directly to predict the mineral status of cattle.

The results of this study suggest that interactions and antagonistic effects between elements may significantly control the mineral status of cattle. High concentrations of Fe and Mn in soil and forage appear to inhibit the availability of P to plants and the absorption of Cu and Zn in cattle. These findings may have wide-ranging implications due to the preponderance of ferrallitic soils in many countries in tropical regions.

Although stream sediment, soil and forage geochemical maps cannot be used to predict the mineral status of grazing ruminants directly, they can serve to indicate those areas where Zn, Cu and P are likely to be low in soils and forage and those areas where higher levels of Fe (and/ or Mn) may induce low Zn, Cu and P status in cattle despite higher levels of these elements in soils and forage.

The univariate statistical approach adopted for this study is somewhat limited considering the number of possible interacting factors, between districts, regions, sample type and elements . A multivariate statistical approach to data interpretation is planned for future investigations into the relationships between elements and sample types.

It is recommended that additional studies should be carried out over a variety of geographical and geological conditions in order to confirm the findings of this study.

1. INTRODUCTION

Many developing countries suffer from poor production and reproduction rates amongst grazing livestock. In Zimbabwe, for example, the conception rate amongst female cattle in the communal areas is only 40% (Dr Hargreaves, Director of the Zimbabwe Veterinary Services Department. pers. comm.). Although undernutrition is accepted as the most limiting factor to grazing livestock production in tropical areas, mineral (trace element) deficiencies or imbalances in soils and forages have long been known to be responsible for low production and reproduction rates (McDowell et al. 1993). In South America, for example, mineral supplementation trials resulted in an increase in average calving percentages from 51% to 73% (McDowell et al. 1993). Although dietary mineral supplementation is commonly practised in developed countries, in the developing world, grazing livestock are often totally dependent on indigenous forage for their mineral intake. As farmers are encouraged to seek higher levels of productivity from forage fed livestock, it will become increasingly important to identify those areas where trace element deficiencies are negatively affecting cattle productivity to permit the design of effective supplementation programmes.

Deficiencies of Co, Cu, I, Fe, Mn, Se and Zn and excesses of Cu, F, Mn and Mo have been recognised as detrimental to the health of grazing livestock. In addition, As, Pb, Cd, Hg and Al are toxic to animals (McDowell et al., 1993).

Apart from some notable exceptions, such as the goitres of iodine deficiency and dental mottling and skeletal deformities associated with excess fluoride, few deficiency or toxicity syndromes induced by anomalous intakes of trace elements are distinguished by specific clinical symptoms. In general, effects are sub-clinical and difficult to detect without thorough investigations.The identification and assessment of areas with trace element deficiency or toxicity problems in grazing livestock has generally been executed by mapping spatial variations in soil, forage, animal tissue or fluid compositions. Soil and forage surveys generally employ high density, detailed sampling techniques in order to obtain representative results because soil chemistry can vary considerably on a local scale and because the trace element content of vegetation varies between species, ecotype and with plant maturity (McDowell et al., 1993). In addition, animal studies often require that samples are refrigerated and analysed soon after collection. In developing countries, where there is often a lack of biological and pedological information over large areas, these methods may prove too expensive and logistically impractical for reconnaissance assessment.

Stream sediment geochemical mapping may provide a practical alternative to soil, forage and animal assessment methods. It is generally accepted that stream sediment sampling is more representative and cost effective than soil or vegetation sampling for rapid reconnaissance geochemical surveys (Levinson, 1980). In addition to providing a reliable database of trace element levels in the environment, regional geochemical stream sediment data can be used for several purposes including mineral exploration and environmental studies. Previous studies in temperate regions have demonstrated that stream sediment geochemical mapping can be used to delineate areas where trace element deficiencies or excesses could prejudice animal health (Plant and Thornton, 1986; Aggett et al., 1988). Regional stream sediment geochemical data sets collected principally for mineral exploration already exist in many developing countries (Plant et al., 1988). The application of this data for animal health studies in tropical regimes have been examined in general terms (Appleton, 1992; Appleton and Greally, 1992). However, quantitative correlations between stream sediment trace element levels and livestock mineral levels have not been clearly established and no detailed investigations into these relationships in tropical regions have been carried out.

This report describes the results of a collaborative project between the BGS and the Government Veterinary Services Department, Harare designed to investigate the relationship between trace element levels in stream sediments, soils, forage and the mineral status of grazing cattle in north-east Zimbabwe. The main objective of the study was to investigate whether regional stream sediment geochemical maps can be used to identify areas where mineral deficiencies may be negatively affecting cattle productivity in developing countries.

An area of communal grazing land in north-east Zimbabwe was selected for this investigation because high quality stream sediment data already existed as a result of a previous ODA funded TC project. In addition, good collaborative links had already been established with the Zimbabwe Government Geological Survey Department and the Veterinary Services Department through various ODA TC Programmes. The study forms part of the ODA/ BGS "Environmental Geochemical Mapping" project (R5547, 91/ 16) carried out as part of the ODA Technology Development and Research (TDR) Programme.

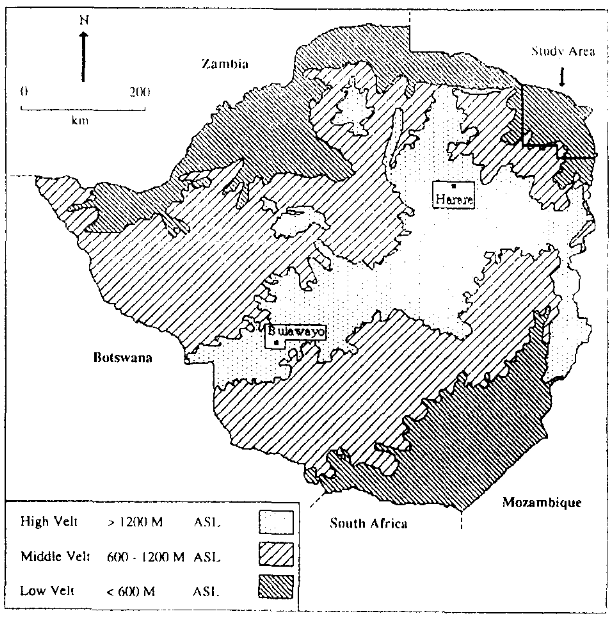


Figure 1. Simplified topographic map of Zimbabwe showing the location of the study area.

The study area (Figure 1) comprises 9000 km^2 of tropical seasonally wet terrain in the districts of Mudzi, Mutoko, Murehwa and Rushinga, north-east Zimbabwe . Annual rainfall of 600 - 800 mm occurs almost entirely in the months of November - March.

The geology of the area includes five major rock types (Figure 2) (Barton et al. 1991). In the centre of the area, the Migmatitic Gniesses include biotite and hornblende rich migmatites, mafic to felsic granulites and tonalite gneisses. The Greenstones and Grey Gniesses form a volcano-plutonic complex separated from the Migmatitic Gniesses by a major Archean tectonic break. Greenstones range in composition from basaltic andesite to dacite whereas the Grey Gniesses comprise trondhjemitic and tonalitic granitoid intrusives. In the south of the area, the Greenstone - Grey Gneiss complex is intruded by the Mutoko Granite which in turn is intruded in places by basic and ultrabasic rocks. Proterozoic metasedimentary rocks in the north of the area include leucomigmatite with horizons of mafic gneiss and garnet granulite.

Soils are mostly fersiallitic, with high Fe and Al contents (Thompson & Purves 1978). Greyish brown, coarse sands and sandy loams characterise areas underlain by granitic rocks whereas brown to reddish-brown sandy loams overlying sandy clays are more common over siliceous gneisses and schists. Reddish-brown granular clays occur over the greenstones and basic and ultrabasic intrusive rocks, such as those that intrude the Mutoko Granite in the southwest. Lithosols characterise areas of rugged terrain. Soils are acid, with pH values of 4.4 to 6.4 (Nyamapfene, 1991).

Much of the area is covered by medium to dense, mixed woodland savannah. Above 600 m the species *Julbernardia globiflora*, *Brachystegia bohemia* and *Brachystegia spiciformis* dominate whereas below 600 m, *Adansonia digitatas*, *Colophospermum mopane*, *Diopsyros*, *Terminalia*, *Combretum*, and *Commiphore* (spp) are more common (Anderson 1986a; Anderson 1986b; Brinn 1986).

The area comprises thinly populated communal lands which are farmed on a subsistence basis by small family groups. The highest population density occurs in the south-west sector of the area, especially in the relatively flat-lying area underlain by the Grey Gneisses (Barton et al. 1991; Dunkley, 1987). Cattle grazing is common within this area and water appears to be the main restricting factor for agricultural development. The Mutoko Granite in the extreme south-west of the area is characterised by more rugged terrain with extensive areas of bare rock outcrop. Habitation is restricted to valleys between the granite hills. Cattle form an important component of the local economy and family wealth is measured in terms of the number of cattle owned. In addition to the monetary revenue generated by the sale of animals, cattle provide a valuable source of milk for the family. Despite the importance of cattle for the local economy and family, no mineral supplementation is currently practised in the area.

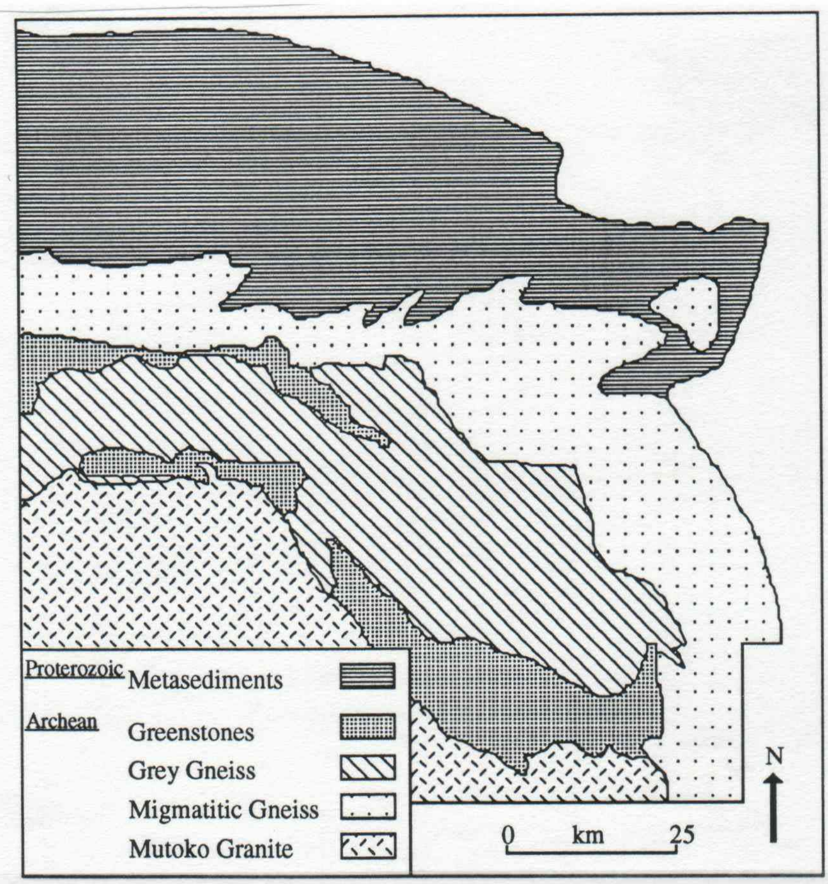
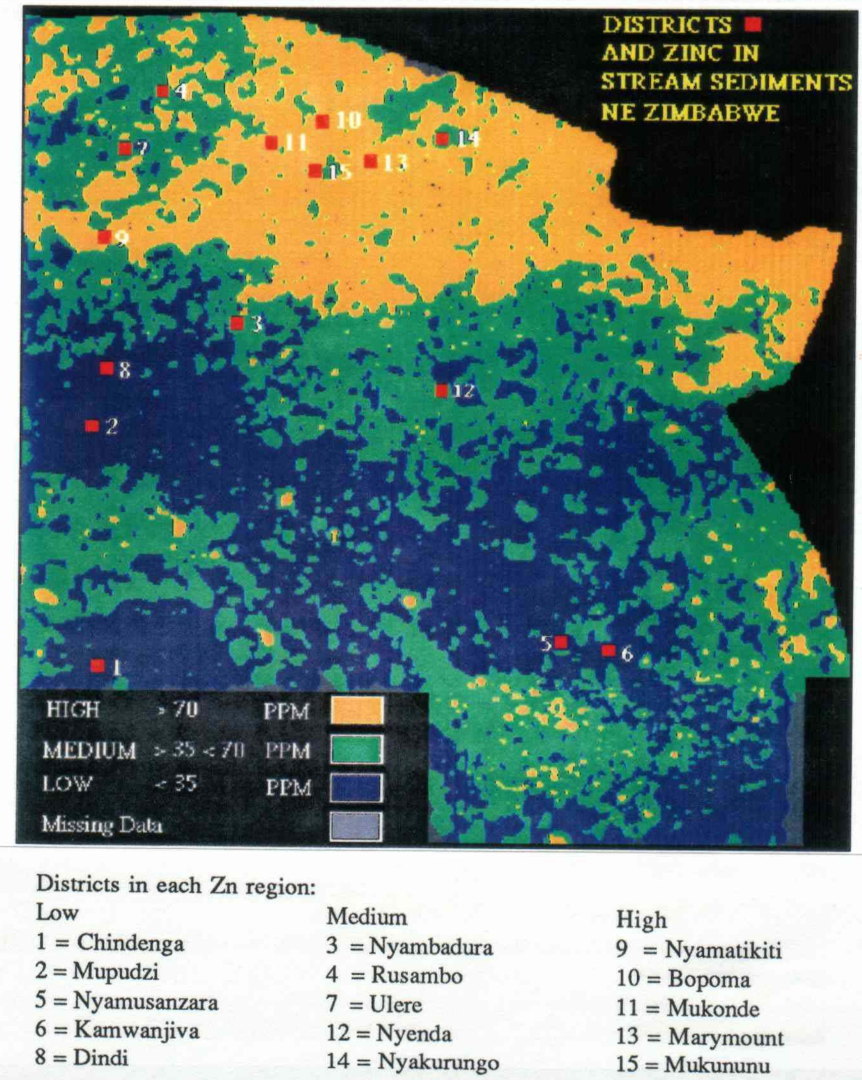


Figure 2. Simplified geological map of the north-east of Zimbabwe after Barton et al. 1991.

Figure 3. Geochemical map of Zn in stream sediments in north-east Zimbabwe showing the location of sampling districts.



Districts in each Zn region:

Low	Medium	High
1 = Chindenga	3 = Nyambadura	9 = Nyamatikiti
2 = Mupudzi	4 = Rusambo	10 = Bopoma
5 = Nyamusanzara	7 = Ulere	11 = Mukonde
6 = Kamwanjiva	12 = Nyenda	13 = Marymount
8 = Dindi	14 = Nyakurungo	15 = Mukununu

2. OBJECTIVES

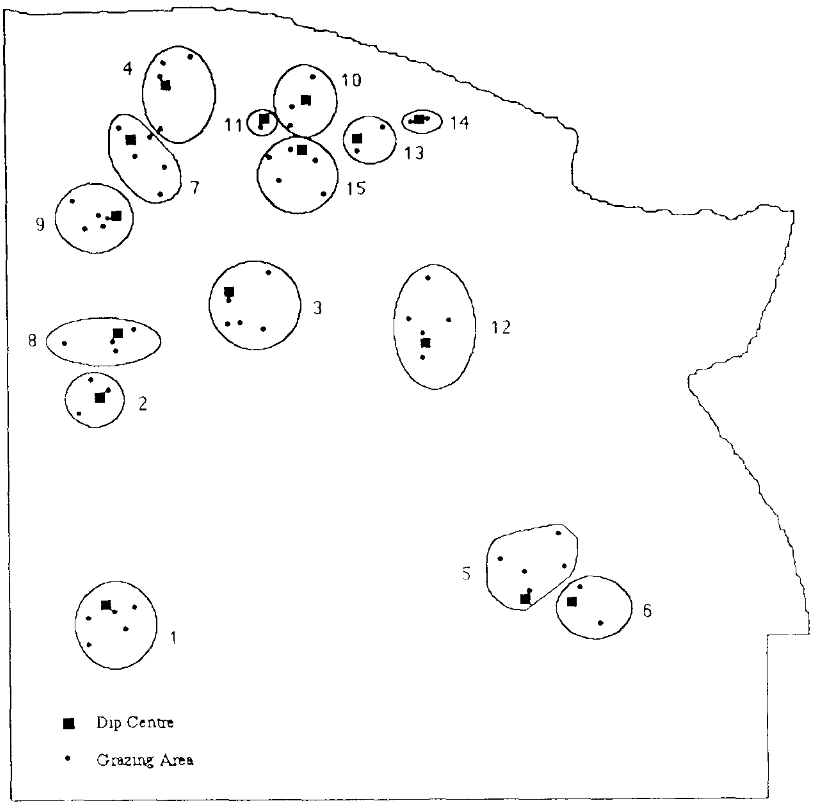
The main objectives of the study were to investigate the relationship between trace element distributions in stream sediments, soils and forage (grass and leaves) and cattle blood (serum) in order to assess (i) whether stream sediment geochemical maps can be used to identify areas where mineral deficiencies may affect cattle productivity and (ii) which of the sample media provide a reliable guide to cattle mineral status.

3. EXPERIMENTAL DESIGN

A variety of animal tissues and fluids including liver, bone and blood samples are commonly used to determine animal mineral status (McDowell et al. 1993). Cattle blood (serum) was selected for this study as it is easier to collect than some of the other media. Zn was the principal trace element investigated as Zn in cattle serum is generally accepted as a reliable indicator of cattle Zn status. Ca, Cu, Fe, Mg and P were also determined in cattle serum samples. Ca, Co, Cu, Fe, Mg, Mn, P and Se were determined in other sample media.

Previous studies (Appleton, 1992) had indicated a lack of correlation between soil, forage and animal blood compositions. It was suspected that this lack of correlation may have resulted, in part, from the restricted variation in environmental trace element levels in the areas investigated. The chosen area of north-east Zimbabwe is characterised by a wide range of Zn and was subdivided into three regions of relatively low (<35 mg/kg), medium (35-70 mg/kg) and high (>70 mg/kg) Zn, on the basis of existing stream sediment data (Figure 3). A sampling strategy was devised to test whether these geochemical differences were reflected in the other sample media.

In previous studies by McDowell and co-workers reported in Appleton (1992), CTVM (1992) and Ortiz et al. (1993), ten animals were usually sampled from each area or district. For the present study, Mr K Ryder (ODA Biometrics Unit, Rothamsted Experimental Station) recommended that twenty cattle should be sampled from five districts in each of the three Zn regions shown on the geochemical map (Figure 3). This experimental design was based on advice from Dr C Livesey (Head of Biochemistry, Central Veterinary Laboratory) and from "*Livestock Diseases Survey: A field manual for veterinarians*" (Australian Bureau of Animal Health, 1982) which suggested that data from twenty cattle in each district would provide a statistically reliable indication of cattle mineral status. The overall design of the cattle blood sampling strategy employed for north-east Zimbabwe is similar to that used in a study of cattle Se status in the USA (Stevens et al. 1985). An average of fifteen cattle were sampled from five farms located in each of three areas classified as broadly deficient, variable and toxic in soil Se.



District Number	District Name	Number of Grazing Areas	Samples Collected
1	Chindenga	5	1 soil, grass and leaf sample from each area + duplicate = 6
2	Mupudzi	3	1 soil, grass and leaf sample from each area + duplicate = 4
3	Nyambadura	5	1 soil, grass and leaf sample from each area + duplicate = 6
4	Rusambo	4	1 soil, grass and leaf sample from each area + duplicate = 5
5	Nyamusanzara	5	1 soil, grass and leaf sample from each area + duplicate = 6
6	Kamwanjiva	2	1 soil, grass and leaf sample from each area + duplicate = 3
7	Ulere	5	1 soil, grass and leaf sample from each area + duplicate = 6
8	Dindi	4	1 soil, grass and leaf sample from each area + duplicate = 5
9	Nyamatikiti	5	1 soil, grass and leaf sample from each area + duplicate = 6
10	Bopoma	3	1 soil, grass and leaf sample from each area + duplicate = 4
11	Mukonde	1	1 soil, grass and leaf sample from each area = 1
12	Nyenda	5	1 soil, grass and leaf sample from each area + duplicate = 6
13	Marymount	2	1 soil, grass and leaf sample from each area + duplicate = 3
14	Nyakurungo	2	1 soil, grass and leaf sample from each area + duplicate = 3
15	Mukununu	5	1 soil, grass and leaf sample from each area + duplicate = 6

Figure 4. Map showing the relationship of grazing areas to dip centres in each sampling district, the number of geochemical samples collected is also detailed.

Cattle in north-east Zimbabwe are brought to government-run dip centres from villages over a radius of 10 km around each centre. The most convenient way of conducting the cattle blood sampling was at the dip centres when cattle from surrounding villages were gathered together. Fifteen of the fifty-one dip centres in north-east Zimbabwe (Figure 2 in Appleton, 1993) were selected to provide cattle blood samples for five districts in each of the three Zn regions. The selection of dip centres was also constrained by the dipping schedule. Dip centres, therefore form the focal points for sampling districts (Figures 3 and 4).

Forage and soil samples were collected from the areas grazed by the twenty cattle sampled in each district. In practice, the cattle often shared grazing areas, therefore only up to five grazing areas were sampled in each district (Figure 4).

The sampling strategy is summarised in Figure 5. Sampling was carried out in April/ June 1993 over a period spanning the end of the wet season, start of the dry season. Cattle were re-sampled for Zn analysis in April/ June 1994 because it was suspected the 1993 serum samples had been contaminated with Zn from the sample-tube caps. This was confirmed by lower Zn concentrations in the 1994 serum samples.

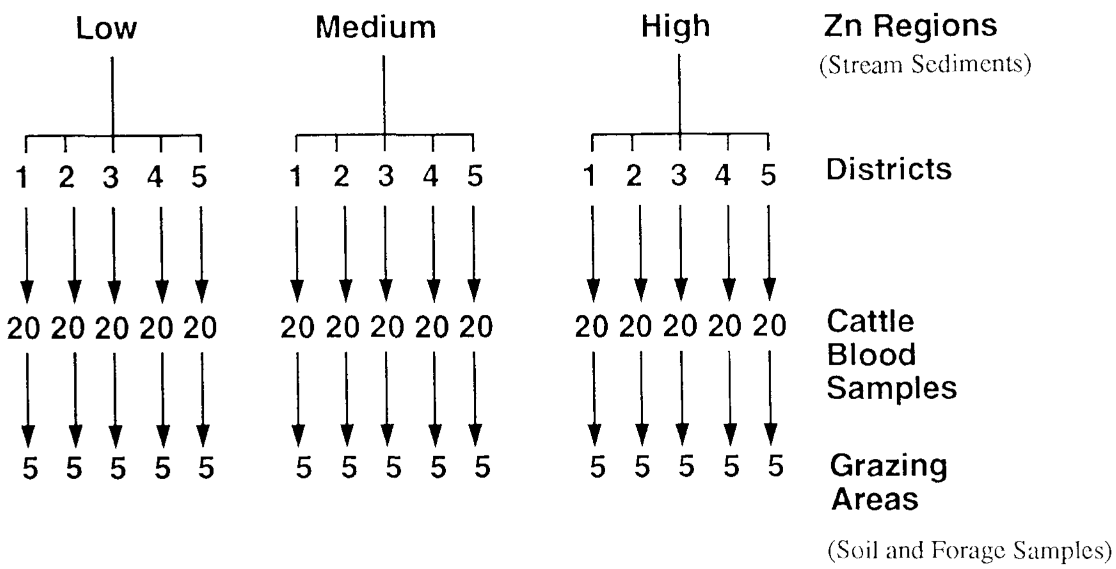


Figure 5. Summary of the experimental design employed in north-east Zimbabwe.

4. SAMPLING METHODS

4.1. Blood Sampling

Cattle blood sampling (Figure 6) was carried out by Dr Darlington Masara of the Government Veterinary Services Department with the aid of local Area Animal Health Inspectors and local Veterinary Extension Assistants. This was the first cattle blood sampling survey to be performed in the area. Cattle from the villages are penned in different kraals. One village may have several kraals and kraals contain cattle belonging to several owners. Where possible, one animal from twenty different kraals was sampled in each district. In some cases, where there were less than twenty kraals per district, more than one animal from each kraal was sampled. In these cases, cattle belonging to different owners within the same kraal were selected. Cattle were chosen at random within each kraal for sampling and were ear-tagged after sampling so that repeat sampling could be carried out at a later date. During the 1993 blood sampling programme, a total of three hundred blood samples were collected comprising twenty blood samples from each of the fifteen districts. In the 1994 re-sampling programme for Zn, it was only possible to collect 245 samples.

Blood samples from the jugular vein of the animal were collected into:

(i) 1 x 10 ml fluoride Becton and Dickenson™ vacutainer for P analysis

(ii) 1 x 10 ml Si-coated Becton and Dickenson™ vacutainer for Cu, Ca and Mg analysis

(iii) 2 x 10 ml Si-coated Becton and Dickenson™ Zn-free vacutainer for Zn and Fe analysis (1994)

Once collected, samples were stored under ice packs in cooler boxes and returned to refrigerators in Harare the same day. Serum was abstracted from the Si-coated vacutainers in the Veterinary Research Laboratory, Harare.

Information on length of ownership and supplementation history were recorded for each animal in a proforma format compatible with that being developed by Dr Monicat (French Veterinary Project at the Veterinary Research Laboratory, Harare) for the Mashonaland East Survey. None of the cattle had been given dietary supplements. The name of the owner, kraal and village were also noted for use in the forage and soil sampling programme.

4.2. Forage and Soil Sampling

Forage and soil samples were collected from the areas grazed by the cattle sampled during the blood collection programme. The intention was to collect information on grazing area locations at the blood sampling stage and to plot grazing areas on 1 : 50 000 scale maps. However, questioning the cattle herders and owners proved it would be impossible to accurately plot the position of grazing areas on 1: 50 000 maps. Therefore, each animal was identified by a village name, kraal name and the name of the owner. The names of the Veterinary Extension Assistant (VEA) and the Dip Attendant (DA) in each area were also recorded. Locating the kraals and grazing areas relied upon the local knowledge of the VEA/ DA.

Figure 7 shows the topography of the study area and a typical grazing area. Defining the size of grazing areas proved problematic as areas that initially appeared to be quite large could contain cultivated fields and large areas of mature dry grass where cattle clearly had not been grazing.Within the grazing areas cattle are commonly driven along established grazing routes, usually following rivers, or to and from dams. Therefore, the size of the actual grazing area was often significantly smaller than it appeared at first sight. The most effective method of defining areas where cattle had been grazing was as follows:

(i) Discuss the kraals to be sampled with the area VEA/ DA.
(ii) Locate the village and the kraal head-man. Discuss the sharing of grazing areas and the location and size of the grazing area.
(iii) Walk thorough the area with the kraal head-man following the route normally taken by the cattle.
(iv) Walk back through the area taking 4/5 sub-samples from areas where cattle had obviously been grazing.

Locational information was recorded on 1: 50 000 topographic maps and field cards. Samples were assigned random numbers so that no geographic relationship existed between samples with sequential numbers.

4.2.1. Forage Sampling

Forage is frequently sampled on a species specific basis due to the wide variation of trace element concentrations in different species (Fick et al. 1979). For the purposes of this study, the intention was to sample one forage species throughout the area that would represent the dietary levels of trace element available to cattle. Observation of cattle behaviour proved that this would not be practical as cattle grazed a variety of grass species and frequently browsed leaves from trees and shrubs. Professor Topps (University of Zimbabwe) recommended the following alternative method of sampling:

(i) Observe the cattle for 30 minutes noting what each animal is grazing at two minute intervals to give an indication of the proportion of grass to leaf intake.
(ii) Use this information in conjunction with the farmers' knowledge of cattle dietary habits to collect a representative grass and leaf sample.

Figure 6. Collecting cattle blood samples by jugular venipuncture into Becton and Dickenson vacutainers.

Figure 8. Grass sample (left) being cut to the height grazed (right) using stainless steel scissors.

(a)

Figure 7. Typical grazing areas in the sampling districts. A blood sample has been taken from the cow in the foreground of (b) as indicated by the red ear-tag.

Cattle blood status is generally dependant on what cattle consumed one month previously (Prof Topps, pers. comm.). One month prior to sampling, cattle in north-east Zimbabwe had been grazing indigenous forage in the grazing areas. However, the forage and soil sampling programme was conducted at the end of the maize harvest and the majority of cattle were grazing in the maize fields at the time of sampling. Therefore it was not possible to conduct Prof. Topps method of forage sampling and the following alternative strategy was adopted:

(i) Identify the grasses and trees grazed and browsed in each grazing area.
(ii) Ascertain from the kraal head-man which grasses and trees the cattle consume.
(iii) Note the range in heights of grass grazed (different species were grazed to different heights in all cases).
(iv) Hand pluck and cut with stainless steel scissors grass samples to the same height as had been grazed (Figure 8).
(v) Hand pluck leaves from shrubs and trees at the appropriate browsing height (Figure 9).
(vi) Collect a soil sample from the same sub-areas as the grass and leaf samples.

Where possible, observations on where the cattle were grazing and whether they were grazing or browsing were recorded on field proformas. The few cattle observed in the grazing areas consumed mainly grass but frequently browsed trees. Grass grazing heights ranged from ~ 1 to 100 cm. The following trees and shrubs were among those sampled: Mutowa, Mususu, Mumbumbu, Musiyo, Mumehndo, Mupngna, Mutongoro, Mupukura, Potanmzaou, Mutukute, Mupondanda, Mugaraharga and Mugoko.

Samples were collected in 30 x 22 cm cloth bags filled 1/5 or 1/4 full at each sub-sample site (depending on the number of sub-samples taken) resulting in one full bag of grass and one full bag of leaves from each grazing area. Forage samples were initially hung up to dry in their bags in the sun after collection. The drying process was completed in ovens at the Animal Science Department, University of Harare at a relatively low temperature of 60° C in order to avoid loss of volatile elements such as Se (Cave et al. 1993). Samples were dried for 16 to 40 hours, depending on their moisture content.

These sampling procedures are similar to those recommended by Fick et al. (1979).

The benefits of splitting the bulk grass and leaf samples into separate species prior to analysis was discussed with Professor McDowell (University of Florida) and with the Natural Resources Institute, Chatham. It was agreed that bulk grass and leaf samples would give an overall indication of forage mineral levels available to cattle and that sub-division of the bulk grass and leaf samples was both unnecessary and impractical.

4.2.2. Soil Sampling

A composite soil sample was collected from the same areas as the grass and leaf samples. The majority of soils in the area are light brown, dry, sandy and siliceous, derived from underlying gneisses. Soils in the south-west of the area are white and light orange in colour, very quartz-rich and derived from granite. Soil horizons are very poorly developed at depths less than 35 cm. Soils were collected at a depth of 10 - 15 cm from the grass root zone by scraping off the very top organic rich layer and breaking up the soil with a pick . The 4/5 soil sub-samples collected from each grazing area were mixed and sieved through 2 mm mesh (Figure 10). Soil colour, texture and sample depth were recorded on field cards.

4.3. Summary

In summary, a total of 300 (245 in 1994) cattle serum samples; 70 -2 mm mesh soil samples; 70 grass samples and 70 leaf samples representing 192 kraals and 56 grazing areas were collected. Duplicate soil, grass and leaf samples were collected in 14 districts, to check for within site (grazing area) variability.

5. STREAM SEDIMENT AND ROCK DATA

Stream sediments had been collected previously from the area during an ODA funded technical co-operation project carried out by the Zimbabwe Government Geological Survey Department in collaboration with the BGS (Dunkley, 1987). -177 µm mesh sediment samples were collected at an average density of 1 per km^2. In order to make a comparison between trace element concentrations in stream sediments, soils and forage, sediment data for streams draining each grazing area were selected for the study.

Information on rock chemistry had also been collected by the Zimbabwe Government Geological Survey Department in collaboration with the BGS. Average chemical compositions for each of the major geological units in the field area were ascertained from Geological Survey reports (Barton et al. 1991).

Figure 9. Hand-plucking leaves from shrubs to the height browsed by cattle.

Figure 10. Composite soil sample sieved through 2 mm mesh.

6. ANALYTICAL METHODS

6.1. Cattle Serum

Cattle serum samples were analysed by the Veterinary Research Laboratory in Harare for Ca Mg, P and Cu in 1993. Zn and Fe in serum were determined by the Ministry of Agriculture, Fisheries and Food Veterinary Investigation Centre, Sutton Bonnington, UK in 1994.

In Harare, two sets of serum analyses were carried out by Atomic Absorption Spectrometry (AAS). Samples were diluted 1: 50 with 0.5% $SrCl_2$ for Ca and Mg and diluted 1 : 10 with distilled water and centrifuged prior to Cu analysis. Determinations for P were conducted by colorimetry. A Ciba Corning control sample and standards were run after every 20 samples for Ca, Mg and P and after every 10 samples for Cu analyses. Results for controls and standards fell within the expected range (Mr Mashanda pers commun).

Zn and Fe in serum analysis was conducted at the Veterinary Investigation Centre, Sutton Bonnington by AAS following 1: 5 dilution with de-ionised water. Results for Zn control standards are given in Table 1. Analytical precision for Zn was 11% (95% confidence level).

Table 1. AAS determinations for Zn in serum control standards, Veterinary Investigation Centre, Sutton Bonnington.

Zn µmol/l in Analytical Runs:											
1	2	3	4	5	6	7	8	9	10	11	12
14.2	14.2	14.5	13.4	12.4	14.2	13.4	13.7	14.1	13.2	12.9	15.3
14.9	14.9	15.4	14.8	14.1	14.3	15.3	15.0	15.1	14.3	14.9	15.2

6.2. Forage

Grass and leaf samples were ground to -1 mm and dry ashed at 550 °C for 8 hours and digested in hot concentrated HCl (Fick et al. 1979). Samples were analysed by ICP-AES for Ca, Mg, P, Fe, Mn, Cu and Zn. Se in grass samples was determined separately by hydride generation AAS with flow injection sample introduction (FIA/hydride generation/AAS) (Cave et al. 1993) following wet oxidation in HNO_3 - $MgNO_3$ and dissolution in 40% HCl (Standing Committee of Analysts, 1987). Detection limits for forage analyses are listed in Table 2. The effectiveness of the hydrochloric acid digestion method for forage was confirmed by the results for an international standard (Table 3).

Table 2. Limits of detection for elements determined in soil and forage.

Element	Limit of Detection (mg/kg)		
	Soil	Grass	Leaves
Mn	3.0	0.02	0.02
Fe	6.6	0.36	0.26
P	9.0	0.56	0.76
Mg	17.0	1.12	0.98
Ca	4.2	0.34	0.44
Zn	0.8	0.06	0.08
Cu	2.0	0.12	0.14
Co	3.2	nd	nd
Se	0.002	0.007	nd

BGS Analytical Geochemistry nd = not determined

Table 3. Comparison of analytical results for international rye grass standard with published data.

Sample	Mn	Fe	P	Mg	Ca	Zn	Cu
			mg/kg				
B2/81 A	86.8	190	2657	1640	7323	36.2	9.8
B2/81 B	72.8	147	2303	1380	6187	28.9	6.0
B2/81 C	78.5	166	2385	1465	6544	30.4	7.4
B2/81 D	76.1	160	2301	1447	6471	31.3	6.8
B2/81 E	9.7	170	2390	1519	6698	30.6	10.5
$\bar{x}$	78.8	167	2407	1490	6644	31.5	8.1
SD	5.2	16	146	97	422	2.8	2.0
B2/81	81.6	164	nd	nd	nd	31.5	9.6

B2/81 A - E = International Rye Grass Standard analysed 5 times.
B2/81 = Published analyses from Office of Reference Materials. (1991)
nd = no data

6.3. Soils

Soils were ground to 120 µm, and leached with hot concentrated HCl before analysis by ICP-AES for Ca, Mg, P, Fe, Mn, Co, Cu and Zn. A hydrochloric acid digestion was selected so that soil geochemical data would be directly comparable with data from the earlier reconnaissance stream sediment survey (Dunkley, 1987). Se in soils was determined separately by (FIA/hydride generation/AAS), following digestion in $HF-HNO_3-HClO_4$ and dissolution in 20% HCl (Cave et al. 1993). Results for international soil standards suggest the HCl digestion may be less effective for soils containing a significant proportion of primary minerals (GXR5, Table 4). However, since the soils in north-east Zimbabwe are fersiallitic, the HCl digestion is likely to extract elements such as Fe, Mn, Zn, Cu and Co which are contained for the most part in secondary Fe-oxides. Detection limits for soil analyses are listed in Table 2.

Table 4. Comparison of analytical results for international soil standards with published data.

Sample	Mn	Fe	P	Mg mg/kg	Ca	Zn	Cu	Co
GXR6 A	1216	62293	373	4706	1624	131.4	73.4	13.4
GXR6 B	1191	61109	356	4463	1561	131.6	71.2	12.0
GXR6 C	1316	67444	419	5063	1749	144.4	82.2	15.4
x̄	1241	63615	383	4744	1645	135.6	75.6	13.6
SD	66	3368	32	301	95	7.4	5.8	1.7
GXR6 (1)	1226	62400				144.6	78.2	18.2
GXR6 (2)	1000	56000				115.0	68.0	18.0
GXR6 (3)	1007	55800	350	6100	1800	118.0	66.0	13.8
GXR3 A	27294	205550	1119	7883	157218	211.2	15.2	48.8
GXR3 B	29362	223843	1193	8622	168974	224.8	16.6	49.6
GXR3 C	29794	219799	1191	8434	171497	238.2	18.0	52.8
x̄	28817	216397	1167	8313	165896	224.7	16.6	50.4
SD	1336	9609	42	384	7621	13.5	1.4	2.1
GXR3 (1)	24366	200500				230.0	15.4	63.4
GXR3 (2)	22500	186000				215.0	15.0	51.0
GXR3 (3)	22308	190000	1100	8100	135800	207.0	15.0	43.0
GXR5 A	211	27647	197	5822	6083	37.2	304.4	19.2
GXR5 B	209	27384	209	5731	6010	37.0	301.0	20.4
GXR5 C	274	35951	254	7565	7871	48.2	395.0	25.6
x̄	231	30327	220	6373	6655	40.8	333.5	21.7
SD	37	4872	30	1034	1054	6.4	53.3	3.4
GXR5 (1)	247	32400				46.6	374.2	27.2
GXR5 (2)	300	32000				48.0	360.0	33.0
GXR5 (3)	310	33900	310	11900	6400	49.0	354.0	30.0

GXR6 = International Soil Standard analysed three times A, B, C.
(1) = Previous analyses at the BGS
(2) = Published analyses from Allcott and Lakin. (1978)
(3) = Published analyses from Potts et al. (1992)

6.4. Stream Sediments

Cu, Co, Mn and Zn in stream sediments were analysed by AAS, following digestion in hot concentrated HCl (Dunkley, 1987).

6.5. Rocks

Rock analyses were carried out by XRF for Ca, Fe, Mg, Mn and P (Barton et al. 1991).

7. RESULTS AND DISCUSSION

Analytical results are listed in Appendices 1 - 5. Since each district is represented by different numbers of samples for each media, district average values were calculated in order to compare relationships between media. Correlation coefficients were employed to identify significant inter-element and inter-media relationships. Spearman Rank non-parametric correlation coefficients were calculated as they are less sensitive to outlying values than product moment (Pearson) correlation coefficients.

7.1. Field and Analytical Duplicates

A comparison of the results from the field duplicate samples (Figure 11 and Table 5) show that within sample-site variation is generally between ± 20 %. Within site variation is greater for forage than for soils, probably as a result of different the proportions of species in the bulk leaf and grass samples.

The average analytical precision for all elements in forage samples, expressed as the coefficient of variation is ± 16% whereas the precision for Zn in forage samples is ± 14% (Table 6). The corresponding precision values for soils are ± 12% and ± 9% respectively (Table 6).

The average of each set of replicate analyses and the average of each field duplicate pair are used in data interpretation.

7.2. Rock, Stream Sediment and Soil Geochemistry

Comparison of the Zn in stream sediments geochemical map (Figure 3) with the geological map (Figure 2) and with maps for Co, Cu and Mn in stream sediments (Appleton 1992), shows that the Greenstones are characterised by elevated levels of Co, Cu, Mn and Zn. Copper, Mn and Zn concentrations are generally high over the metasedimentary rocks, with localised high Co values. The Migmatitic Gneisses and Grey Gneisses in the centre of the area are characterised by very low levels of Co, Cu, Mn and Zn reflecting the low levels of these trace elements in the parent rocks (Barton et al. 1991) and the sandy infertile soils derived from them. Similarly low levels of Co, Cu, Mn and Zn are associated with those parts of the Mutoko Granite in the south-west of the area that are not intruded by basic rocks. The close spatial relationship between trace elements demonstrates a strong geological control on stream sediment composition (Table 7).

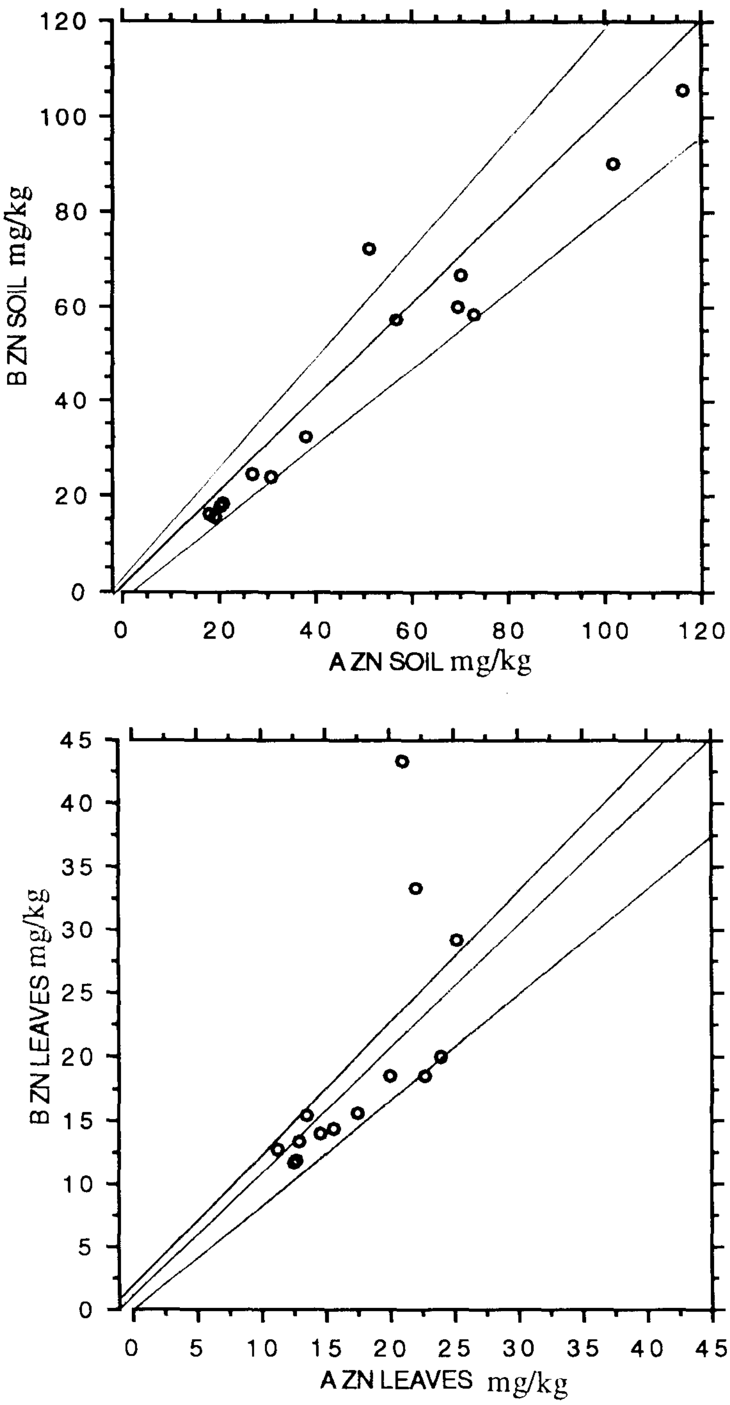


Figure 11. Graphs comparing levels of Zn in soil and leaf samples for the field duplicates A and B. Lines representing the 1:1 relationship and ± 20 % variation are shown on each graph.

Table 5. Analyitcal results for field duplicate pairs A and B.

SAMPLE NUMBER	MN SOIL	FE SOIL	P SOIL	MG SOIL	CA SOIL	ZN SOIL	CU SOIL	CO SOIL	SE SOIL
				mg/kg					
195S A	168	5711	88	1514	1200	15.4	2.6	1.6	.010
167S B	200	6770	110	1716	1133	18.8	4.0	1.6	.010
103S A	445	18426	147	3319	2011	26.4	12.8	9.2	.072
144S B	389	16214	148	3065	2241	24.6	12.2	7.0	.033
028S A	188	6854	116	2135	2038	17.6	3.8	1.6	.010
020S B	188	7104	129	1954	1601	19.8	4.2	1.6	.023
181S A	245	11053	88	2048	1960	20.4	7.3	1.6	.021
194S B	230	9991	82	1824	1944	18.1	3.1	2.5	.010
132S A	387	6745	248	610	602	17.6	5.0	1.6	.010
108S B	359	5608	185	592	534	16.0	5.4	1.6	.010
199S A	173	8208	90	1715	1351	23.8	9.8	3.6	.053
175S B	311	13080	190	2921	3792	30.6	21.1	5.3	.101
193S A	381	21236	220	5174	3525	37.8	19.6	8.0	.053
117S B	331	16679	192	3911	1937	32.4	14.4	6.8	.052
288S A	743	36217	430	7295	4142	57.2	18.4	11.2	.069
248S B	636	20696	124	6693	3534	56.6	13.8	11.2	.065
158S A	1389	66219	437	5078	2378	116.2	23.6	10.6	.133
177S B	1241	57354	502	5023	2759	105.6	23.8	11.6	.050
269S A	627	30906	452	3453	4768	60.0	14.4	7.4	.057
257S B	730	36538	463	4125	5673	69.3	15.8	9.5	.082
204S A	867	64722	324	4446	3475	51.2	42.6	18.2	.163
296S B	1197	83906	436	6736	4765	72.4	61.6	25.4	.250
266S A	843	37669	1215	6066	7636	101.4	26.0	12.8	.093
284S B	770	39469	467	4682	3773	90.2	21.2	13.0	.103
178S A	880	41393	363	2522	3326	58.1	7.4	3.2	.048
172S B	928	51655	571	3346	3584	72.6	23.6	11.8	.058
300SA	715	36237	879	5705	5741	66.6	22.0	6.0	.093
230S B	572	14830	121	7122	6546	70.0	16.6	10.6	.056

SAMPLE NUMBER	MN GRASS	FE GRASS	P GRASS	MG GRASS	CA GRASS	ZN GRASS	CU GRASS	SE GRASS
				mg/kg				
195S A	99	94	1416	1190	3964	8.5	1.0	.0442
167S B	64	675	1380	1091	3598	8.0	.9	.0373
103S A	54	127	1384	2230	5250	27.4	1.4	.0453
144S B	60	141	1098	1906	4787	27.4	1.3	.0323
028S A	71	93	1706	1499	4950	15.4	1.8	.0451
020S B	92	211	2621	1936	4818	17.6	2.1	.0525
181S A	90	150	1498	1419	5545	12.0	1.6	.0245
194S B	62	72	693	682	2708	7.2	.9	.0410
132S A	151	213	2513	1423	4335	23.1	2.1	.0552
108S B	117	196	2186	1392	6294	23.5	2.6	.1252
199S A	57	103	2653	2232	5005	18.1	1.0	.0957
175S B	44	82	2423	1932	4856	16.1	1.2	.0826
193S A	56	205	1166	1228	2824	11.5	1.3	.0429
117S B	62	172	947	1453	3951	23.4	2.3	.0551
288S A	128	280	1517	2454	5985	20.9	2.9	.0140
248S B	96	102	1471	2670	4426	27.8	3.4	.0235
158S A	65	500	1400	1647	3205	22.0	1.6	.0211
177S B	92	158	2264	1984	4901	26.6	1.8	.0443
269S A	52	145	1378	1450	3341	17.6	1.8	.0350
257S B	89	468	1457	1529	3710	18.0	1.6	.0298
204S A	96	609	626	1785	3389	19.8	2.7	.0284
296S B	107	656	817	2086	3352	28.2	2.8	.0361
266S A	130	459	1452	1590	3635	35.2	1.5	.0311
284S B	158	1231	1001	1618	4076	30.8	2.1	.0354
178S A	101	120	1401	1240	3486	13.4	1.3	.0472
172S B	111	1024	1467	944	3114	17.7	2.0	.0220
300SA	51	152	2212	2177	4102	32.7	1.7	.0455
230S B	71	793	2192	2648	3339	38.5	3.0	.0304

SAMPLE NUMBER	MN LEAVES	FE LEAVES	P LEAVES	MG LEAVES	CA LEAVES	ZN LEAVES	CU LEAVES
				mg/kg			
195S A	128	89	2005	3646	22025	11.7	4.2
167S B	138	93	2101	3637	19278	12.5	5.9
103S A	118	102	1286	3403	17671	15.5	2.3
144S B	111	122	1243	3500	18244	14.3	5.5
028S A	145	67	2242	3083	18184	12.8	2.0
020S B	230	92	1982	3274	15382	11.3	5.2
181S A	152	99	2217	3554	19203	14.7	5.4
194S B	151	115	2182	3330	17282	13.9	5.6
132S A	284	50	2240	2198	11374	12.9	5.6
108S B	301	28	2778	2486	14628	13.4	.5
199S A	170	115	2377	3927	21390	12.0	4.6
175S B	133	118	2148	4107	17894	12.8	5.1
193S A	196	167	1416	3307	16289	23.9	10.1
117S B	124	163	1513	3214	15309	20.0	9.2
288S A	132	85	1362	2522	13402	15.4	3.8
248S B	203	106	1432	2861	14478	13.5	6.5
158S A	520	230	1588	4263	12894	25.2	10.1
177S B	317	197	2018	4420	16376	29.2	14.6
269S A	146	140	1795	2924	16461	18.5	6.7
257S B	123	133	2126	2776	18665	19.9	6.3
204S A	390	108	1227	4103	17072	22.7	5.5
296S B	196	186	1313	3771	13756	18.4	6.0
266S A	187	161	2341	3374	17189	22.1	6.6
284S B	170	115	2503	3763	20753	33.4	5.4
178S A	226	444	3295	3577	20272	43.4	6.9
172S B	152	221	2661	3227	18719	21.0	4.9
300SA	89	184	1463	3266	14726	15.7	7.7
230S B	96	315	1927	5173	16464	17.6	5.5

Table 6. Replicate analyses of grass (G), leaf (L) and soil (S) samples (o = coefficient of variation %)

Sample	Mn	Fe	P	Mg mg/kg	Ca	Zn	Cu	Co
257G A	97	559	1491	1544	3801	18.2	1.9	
257G B	1057	566	1570	1667	4052	17.5	1.9	
257G C	76	429	1104	1193	2924	11.8	1.5	
257G D	103	595	1555	1602	3958	15.7	2.3	
257G E	61	193	1563	1639	3813	26.9	0.7	
o	**22**	**36**	**14**	**13**	**12**	**31.0**	**37.0**	
269G A	40	112	1028	1084	2499	15.9	0.06	
269G B	53	158	1399	1488	3451	16.9	0.16	
269G C	52	145	1335	1434	3294	20.6	0.26	
269G D	57	154	1530	1625	3728	16.6	0.28	
269G E	58	155	1596	1620	3733	18.2	0.64	
o	**14**	**13**	**16**	**15**	**15**	**10.0**	**78.0**	
204L A	404	111	1278	4345	17719	23.4	5.8	
204L B	302	83	947	3141	12800	18.2	4.4	
204L C	429	118	1360	4502	19595	24.9	5.9	
204L D	379	110	1178	3906	16449	22.1	5.3	
204L E	435	119	1371	4620	18796	24.9	6.4	
o	**14**	**14**	**14**	**15**	**16**	**12.0**	**14.0**	
296L A	209	198	1395	4020	15311	19.4	6.7	
296L B	193	183	1318	3735	13377	18.2	5.8	
296L C	194	184	1297	3736	13399	18.4	5.9	
296L D	188	180	1243	3593	12938	17.8	5.9	
296L E	185	180	1222	3562	12753	17.3	5.8	
o	**5**	**4**	**5**	**5**	**8**	**4.0**	**7.0**	
178S A	844	39186	341	2398	3233	55.6	6.4	1.6
178S B	988	46627	411	2811	3649	63.4	7.6	3.8
178S C	808	38368	337	2356	3094	55.2	8.2	4.2
o	**11**	**11**	**11**	**10**	**9**	**8.0**	**12.0**	**44.0**
238S A	773	45633	445	3531	4055	102.4	20.6	10.2
238S B	736	45048	209	3485	3698	101.8	17.6	10.2
238S C	650	38416	224	3060	3218	90.0	18.4	9.8
238S D	728	45529	609	3431	3736	104.2	22.8	9.4
238S E	504	29461	430	2232	2497	67.8	15.6	7.6
238S F	752	45397	601	3605	4050	101.8	25.2	13.2
o	**13**	**14**	**41**	**15**	**15**	**14.0**	**19.0**	**17.0**
194S A	248	10049	96	1857	1751	18.4	5.2	4.4
194S B	227	10207	75	1840	2127	19.2	1.0	1.6
194S C	215	9717	76	1776	1955	16.8	3.0	1.6
o	**7**	**3**	**14**	**2**	**10**	**7.0**	**69.0**	**64.0**
181S A	224	10066	50	1863	1927	18.6	2.8	1.6
181S B	237	10663	82	1913	2028	18.4	3.4	1.6
181S C	267	12307	96	2224	2213	21.6	3.4	1.6
o	**8**	**9**	**34**	**9**	**12**	**11.0**	**12.0**	**0.0**

Table 6. continued

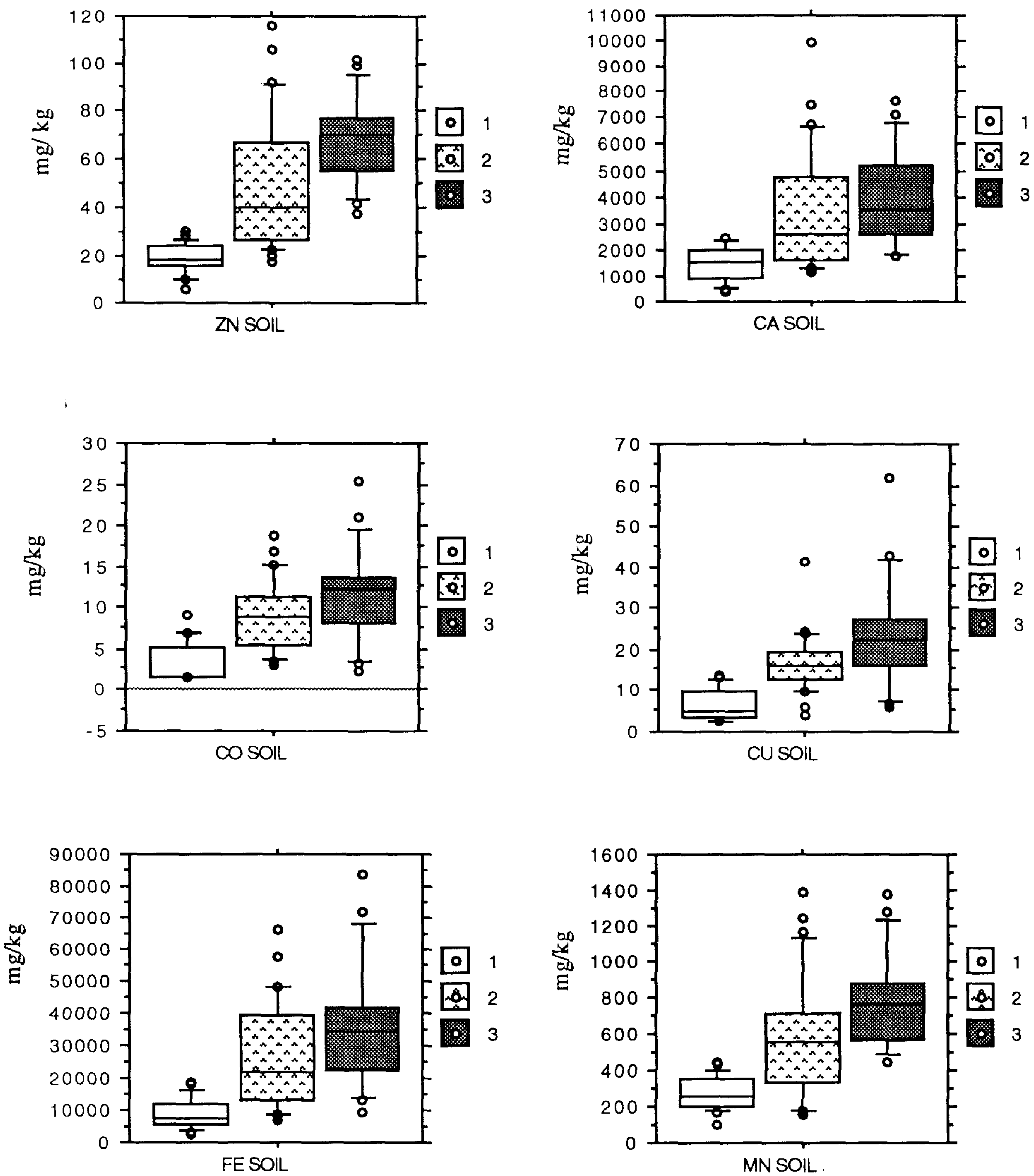
Sample	Mn	Fe	P	Mg mg/kg	Ca	Zn	Cu	Co
257S A	782	38904	502	4410	5980	74.4	17.0	10.4
257S B	709	35741	441	4049	5694	67.0	14.6	8.8
257S C	699	34968	444	3915	5344	66.4	15.8	9.2
o	**6**	**6**	**7**	**6**	**6**	**6**	**8**	**9**
223S A	719	52079	297	7278	5804	60.2	20.6	15.8
223S B	653	46837	281	6832	5122	56.4	19.6	14.8
223S C	649	46329	275	6690	5126	55.4	19.4	15.2
o	**6**	**7**	**4**	**4**	**7**	**4**	**3.0**	**3.0**
243S A	558	39337	113	7908	1408	36.8	15.0	15.2
243S B	567	39390	156	7965	1566	37.2	14.6	14.2
243S C	557	38494	162	7845	1687	46.0	15.6	16.4
o	**1**	**1**	**19**	**1**	**9**	**13.0**	**3.0**	**7.0**
195S A	180	6092	97.6	1624	1256	15.8	4.4	1.6
195S B	156	5391	79.6	1393	1289	14.4	1.0	1.6
195S C	168	5651	88.2	1525	1055	16.0	2.4	1.6
o	**7**	**6**	**10**	**8**	**11**	**6**	**66.0**	**0.0**
250S A	399	23584	233	3997	1434	36.4	18.8	11.0
250S B	395	23165	199	3884	1351	35.0	14.4	8.0
250S C	326	19354	180	3249	1123	29.6	14.2	9.0
o	**11**	**11**	**13**	**11**	**12**	**11.0**	**16.0**	**16.0**
254S A	681	41008	501	4399	6559	86.6	19.2	10.6
254S B	744	45492	547	4849	7055	97.6	20.6	10.0
254S C	705	42939	527	4512	6568	90.0	19.0	10.6
o	**4**	**5**	**4**	**5**	**4**	**6.0**	**4.0**	**3.0**
218S A	527	28313	161	7079	3718	34.4	27.6	14.2
218S B	539	29082	155	7339	4180	58.6	26.4	13.6
218S C	507	27396	156	6817	3628	32.8	26.0	13.6
o	**3**	**3**	**2**	**4**	**8**	**3**	**3**	**3**
175S A	361	15144	209	3337	4322	32.6	24.0	5.8
175S B	344	14549	222	3292	4279	36.6	23.6	6.4
175S C	228	9548	141	2135	2775	22.6	15.6	3.6
o	**23**	**23**	**23**	**23**	**23**	**24**	**22**	**28**
209S A	1229	69488	179	2097	1860	68.2	6.4	3.6
209S B	1385	78774	226	2353	2109	80.4	6.0	1.0
209S C	1204	67039	191	2090	1825	67.2	5.0	1.0
o	**8**	**9**	**12**	**7**	**8**	**10.0**	**12.0**	**51.0**

Table 7. Comparison of average element concentrations in rocks, sediments and soils in north-east Zimbabwe.

Sample Media	Element	Average Element Composition in Rock Type (mg/kg)		
		Mutoko Granite and Grey Gneiss*	Migmatitic Gneiss	Metasedimentary
Rock	Ca	15700	32200	35100
	Fe	13200	40100	66300
	Mg	3860	17100	13800
	Mn	290	840	1300
	P	290	700	800
	No of samples	22	16	37
Sediments	Co	6	10	12
	Cu	11	20	22
	Zn	28	34	86
	Mn	381	436	975
	No of samples	34	50	101
Soils	Ca	1293	2189	3649
	Fe	8314	14718	36870
	Mg	1644	3356	4480
	Mn	249	321	800
	P	115	159	381
	Co	3	7	11
	Cu	6	14	20
	Zn	18	27	66
	No of samples	15	14	27

Average rock compositions calculated from data in Barton et al. (1991).
* No grazing areas were underlain by greenstones therefore average rock data do not include analyses of greenstones.

Unfortunately, no rock trace element data are available for direct comparison with trace elements in stream sediments and soils. However, the trends in the major element chemistry of rocks are reflected in the stream sediment trace element geochemistry (Table 7). Similarly the major element chemistry of soils generally reflects bedrock chemistry especially for Ca, Fe and Mn (Table 7).The trace and major element chemistry of soils correlates closely with stream sediment geochemistry (Table 8 and Figure 12) confirming the dominant influence of bedrock composition on regional variation in both these sample media. Adsorption of trace elements by secondary Fe and Mn oxides also influences the trace element content of soils as indicated by the strong correlations between Mn, Fe, Co, Cu, P and Zn in soils (Table 8).



1 = low Zn in stream sediment region

2 = medium Zn in stream sediment region

3 = high Zn in stream sediment region

Figure 12. Box and whisker plots of the 10th, 25th, 50th, 75th and 90th percentiles of element distributions in soils split into the three Zn regions.

Table 8.Spearman Rank correlation matrix based on average values of elements in stream sediments and soils for the 15 districts.

	Co Soil	Cu Soil	Fe Soil	Mg Soil	Mn Soil	P Soil	Zn Soil	Co Sed	Cu Sed	Mn Sed	Zn Sed
Ca Soil	.821	.643	.671	.896	.750	.639	.814	.553	.715	.557	.725
Co Soil		.793	.686	.929	.696	.521	.743	.713	.765	.564	.646
Cu Soil			.786	.718	.711	.607	.689	.627	.722	.632	.675
Fe Soil				.643	.936	.825	.896	.458	.543	.796	.786
Mg Soil					.675	.507	.721	.647	.803	.489	.614
Mn Soil						.825	.957	.415	.465	.821	.814
P Soil							.861	.416	.468	.829	.757
Zn Soil								.468	.511	.782	.796
Co Sed									.854	.517	.670
Cu Sed										.518	.706
Mn Sed											.921
Zn Sed											

r 95% = 0.457; r 99% = 0.612; r 99.95% = 0.780 (Koch & Link 1970)
Sed = Sediment

7.3. Cattle Serum, Forage, Soil and Stream Sediment Chemistry

7.3.1 Zinc

The distributions of Zn within each district and between districts vary considerably for all sample media (Figure 13). Concentrations of Zn in sediment, soil, leaves and grass from districts in the low Zn region generally have lower Zn concentrations than samples from districts in the medium or high Zn regions. However, within each region there is no consistent relationship between district Zn concentrations in sediment, soil, leaves and grass. There is no apparent relationship between Zn in sediment, soil and forage and Zn in serum at the district level.

At the regional level, there are statistically significant differences between the regions for Zn in sediment, soil, grass and leaves but not in cattle serum (Table 9). Zn concentrations in soil and forage reflect the geochemical trend from low to high Zn in stream sediments (Figure 14). In grass and leaves, more overlap occurs between the concentration ranges for the low, medium and high Zn regions. In contrast to the other sample media, the ranges for Zn in cattle serum are approximately the same in the three regions. These observations are reiterated in Table 10 which shows there are significant (95 % confidence level) correlations between district average values for Zn in grass, leaves, soils and sediments but no significant correlations between Zn in serum and the other sample media. Therefore, at both the district and regional levels, cattle serum Zn does not directly reflect environmental Zn concentration.

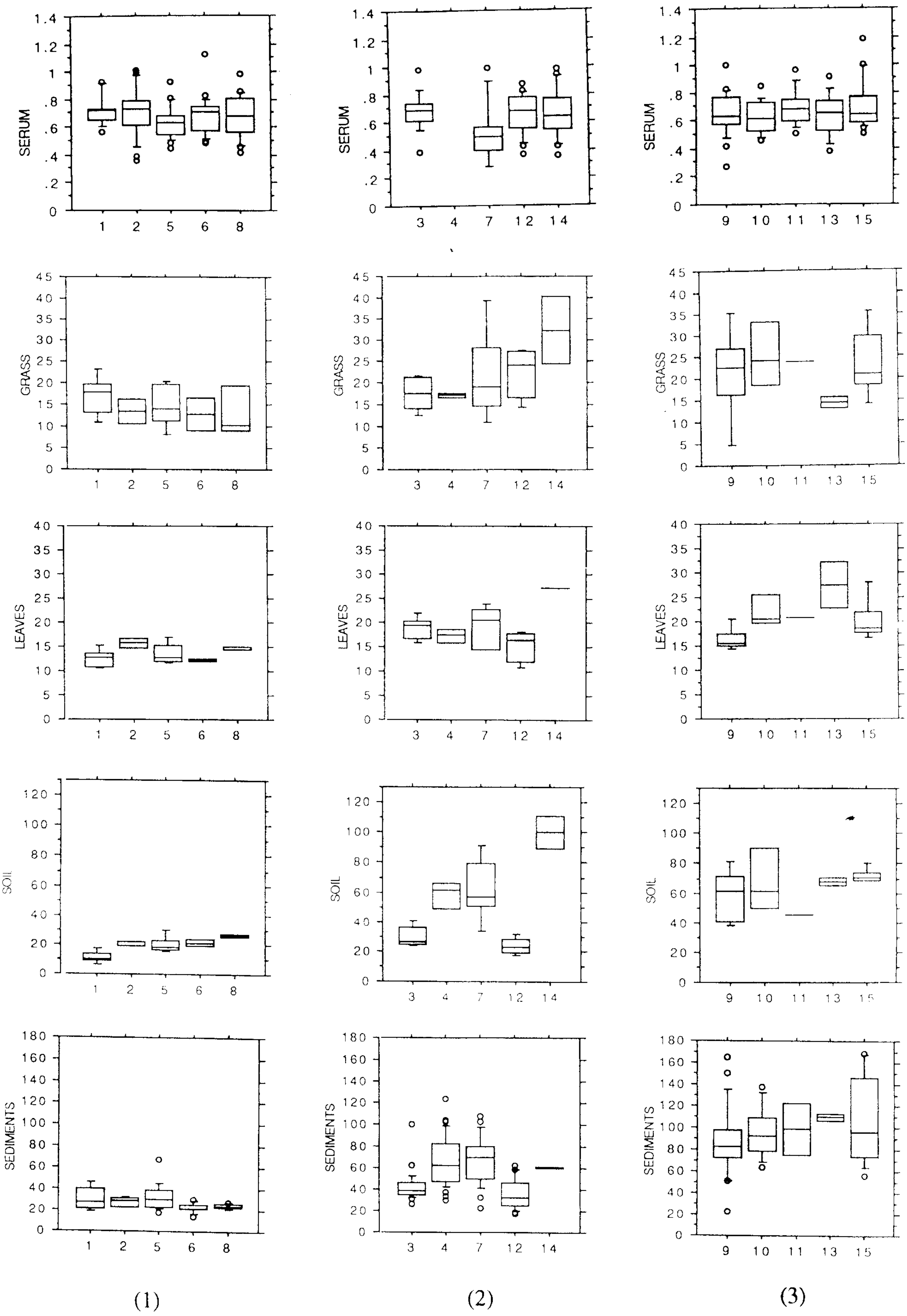


Figure 13. Box and whisker plots of the 10th, 25th, 50th, 75th and 90th percentiles of Zn distributions in each sample media for districts (1 to 15) in the low (1), medium (2) and high (3) Zn regions. Circles indicate values < 10th and > 90th percentiles. Zn concentrations in mg/kg except serum (mg/l) (No cattle serum data are available for district number 4).

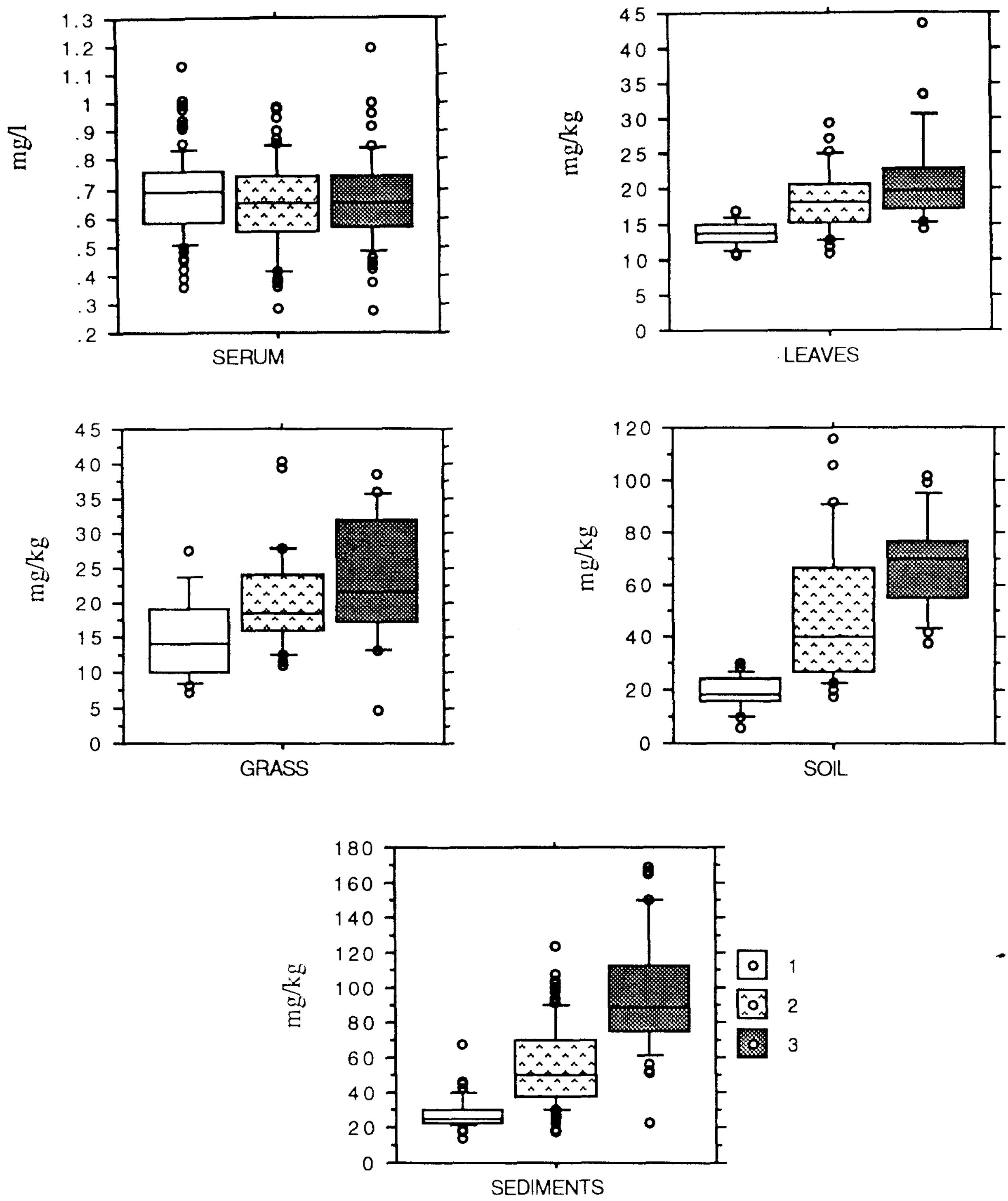


Figure 14. Box and whisker plots of the 10th, 25th, 50th, 75th and 90th percentile of Zn distributions in each sample media for the low (1), medium (2) and high (3) Zn regions. Circles indicate values < 10th and > 90th percentiles.

Table 9. Analysis of variance statistical probability test for three distinct low, medium and high populations in all media using results for Zn.

ANOVA	F-value	P-value
Zn sediment vs. Zn region		
224 Samples	119.370	< 0.001
15 District mean values	45.939	< 0.001
Zn soil vs. Zn region		
56 Samples	29.662	< 0.001
15 District mean values	6.754	0.0108
Zn grass vs. Zn region		
56 Samples	5.429	0.0072
15 District mean values	5.343	0.0219
Zn leaves vs. Zn region		
56 Samples	13.254	< 0.001
15 District mean values	6.612	0.0116
Zn serum vs. Zn region		
245 Samples	1.424	0.2428
15 District mean values	1.691	0.2289

Table 10. Spearman Rank correlation table based on average values of Zn in serum, grass, soil and leaves for the 15 districts with other elements in various media.

	Zn Serum	Zn Grass	Zn Leaves	Zn Soil
Zn Grass	-.200			
Zn Leaves	-.293	.575		
Zn Soil	.392	.732	.886	
Zn Sed	-.359	.600	.836	.796
Cu Grass	.150	.461	.300	.271
Cu Leaves	-.117	.521	.793	.654
Cu Soil	-.112	.586	.725	.689
Fe Grass	-.299	.511	.843	.775
Fe Leaves	-.112	.357	.764	.618
Fe Soil	-.392	.621	.857	.896
Mn Grass	-.035	.214	.411	.214
Mn Leaves	- 273	.368	.735	.175
Mn Soil	-.366	.632	.893	.957
Ca Leaves	-.350	-.461	-.909	-.186
Ca Soil	-.442	.582	.625	.814
P Soil	-.317	.807	.825	.861

r 95% = 0.457; r 99% = 0.612; r 99.95% = 0.780 (Koch & Link 1970)
Sed = Sediment

Many biological factors such as the species-type and state-of-maturity of plants, and the age and gender of animals, exert significant controls on the uptake of major and trace elements by living organisms (Mertz, 1987). In addition, infection and vaccination are known to enhance Cu and deplete Zn in cattle serum. A large number of serum samples were collected in this study to minimise the effects of biological factors on district means. Despite this precaution, these biological factors may largely explain why the levels of Zn in cattle serum do not directly reflect environmental Zn in northeast Zimbabwe. Another explanation for the lack of correlation between cattle serum Zn and forage Zn may be the uncertain contribution of individual grass and browse species and the proportion of grass and browse material in the dietary intake of cattle in this study.

Although statistical correlations do not prove a causal relationship, the strong spatial and statistical correlations between sediment, soil and forage Zn suggest that increased levels of Zn in soils result in increased uptake of Zn by plants. However, ingestion of plants containing higher levels of Zn does not result in an increase in the Zn levels found in cattle serum. In fact, Zn in serum appears to decrease slightly as Zn in forage increases (Table 10).

One possible explanation may be the antagonistic relationships present between elements as they are absorbed during digestion by the cattle. Fe and Zn are known to have an antagonistic relationship during absorption in humans (Mertz, 1987; Sandstrom et al. 1985) and in rats (Quarterman, 1985). Antagonistic relationships between Mn, Fe and Zn have been reported in humans (Christophersen, 1994). (Lebdosoekojo, et al. 1980) suggest that high levels of Fe and Mn may interfere with the metabolism of other trace elements in cattle. Several clinical studies in animals and humans have identified a mutually antagonistic relationship between Cu and Zn (Mertz 1987). In northeast Zimbabwe, the area of high Zn in soils and forage coincides with high Cu, Fe and Mn in soils and forage (Tables 8 and 10), therefore it is possible that uptake of these elements is inhibiting the absorption of Zn in cattle.

Serum P and Ca levels are low (Table 16) and it is probable that cattle in north-east Zimbabwe are reabsorbing their skeletal reserves of P and Ca. During this process, Zn is also reabsorbed from the skeleton. The levels of Zn in serum may not depend on dietary intake alone but may be enhanced by reabsorbed skeletal Zn (C Mills pers commun.).

Zn concentrations in serum tend to decrease slightly as the Ca content of leaves and soil and the P content of soil increase (Table 10). This could be due, in part, to the reabsorption process described above. In addition, high Ca and P ingestion have been shown to reduce Zn absorption in humans, pigs and poultry but these relationships are less clear in cattle (Mertz 1987).

7.3.2. Copper

There are significant correlations between district average values for Cu in sediment and soil (Table 8) and between Cu in soil and leaves (Table 11) . However, Cu in serum exhibits no correlation with Cu in soil, grass or leaves (Table 11) or average forage (Figure 15). Therefore although there is some evidence to suggest that higher levels of Cu in the environment are taken up by vegetation, these higher levels are not reflected in the Cu content of serum. Similar results are reported by McDowell (1976) who found that the Cu content of soils and forage did not correlate with the Cu status of cattle. Evidence from the present study suggests that, as with Zn, this lack of correlation may partly reflect antagonistic relationships between elements during uptake.

Table 11. Spearman Rank correlation table based on average values of Cu in serum, grass and leaves for the 15 districts with other elements in various media.

	Cu Serum	Cu Grass	Cu Leaves
Cu Grass	-.195		
Cu Leaves	.032	.446	
Cu Soil	.009	.371	.696
Cu Sed	-.019	.452	.374
Zn Grass	-.496	.461	.521
Zn Leaves	-.356	.300	.793
Zn Soil	-.347	.271	.645
Zn Sed	-.489	-.398	.500
Mn Grass	-.593	.204	.354
Mn Leaves	-.675	.464	.139
Mn Soil	-.340	.204	.614
Mn Sed	-.640	.504	.543
Fe Grass	-.381	.329	.657
Fe Leaves	-.349	.189	.486
Fe Soil	-.277	.336	.629

r 95% = 0.457; r 99% = 0.612; r 99.95% = 0.780 (Koch & Link 1970)
Sed = Sediment

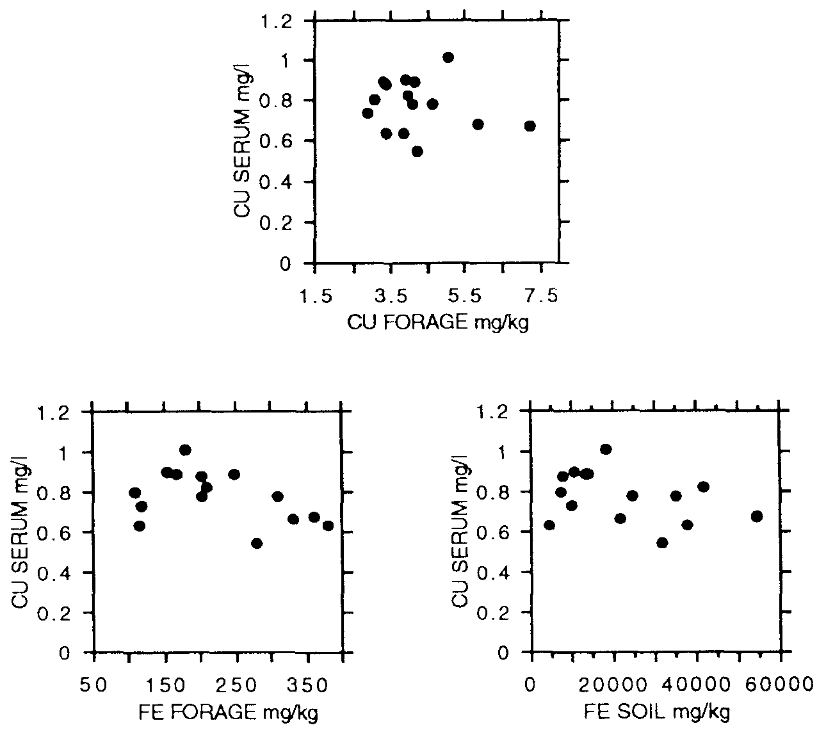


Figure 15. Plots of district average values of Cu in serum versus Cu in forage, Fe in forage and Fe in soil. Average forage values represent the average of grass and leaf compositions for each district.

Media		Country	Ca	Mg	P	Fe	Mn	Co	Cu	Zn
Serum	*a*	Zimbabwe	80	23	45	1.332	nd	nd	0.8	0.7
mg/l	*b*	Swaziland	na	na	39	na	na	na	na	na
	h	Malawi	76	na	56	na	na	na	0.3	na
	d	Indonesia	na	na	na	na	na	na	0.6	0.8
	e	Bolivia	112	18	70	na	na	na	0.9	1.0
	f	Bolivia	80	21	67	na	na	na	0.6	1.1
Forage	*a*	* Zimbabwe	4409	1713	1444	234	109	nd	1.9	19.0
mg/kg		†	16189	3575	1750	165	179	nd	6.1	17.0
	b	Swaziland	4050	1500	5500	224	86	na	5.6	9.0
	c	Guatemala	3100	1850	2500	520	92	0.4	14.0	32.5
	d	Indonesia	na	na	na	742	88	0.3	9.3	5.0
	e	Bolivia	4400	1850	1900	170	390	0.5	5.2	24.0
	f	Bolivia	2100	1600	1500	134	133	0.2	5.9	30.0
	g	Colombia	1300	1550	1300	563	143	0.1	1.8	13.5
	g	Brazil	5050	2550	5000	238	145	0.1	4.0	26.5
Soil ‡	*a*	Zimbabwe	2807	3653	251	23537	517	8.1	15.4	43.1
mg/kg	*b*	Swaziland	524	191	12	na	4	na	1.0	1.1
	c	Guatemala	1860	387	10	52	59	na	2.4	5.8
	d	Indonesia	na	na	na	98	24	na	1.6	4.6
	e	Bolivia	648	204	4	115	17	na	0.5	3.0
	f	Bolivia	192	34	1.2	24	0.3	na	0.3	1.3

a = present study *c* = Tejada et al. (1985) *e* = McDowell et al. (1982) *g* = Miles et al. (1989)
b = Ogwang, (1988) *d* = Prabowo et al. (1991) *f* = Peducassé et al. (1983) *h* = Mtimuni et al. (1983)
nd = not determined na = not available
* Mean concentrations for grass samples† Mean concentrations for leaf samples
‡ Soils were digested with hot concentrated HCl in the present study whereas published results from Guatemala, Indonesia, Bolivia and the USA are for partial extraction with 0.05 N HCL + 0.025 N H_2SO_4. Soil data for Swaziland are for partial extraction with ammonium acetate.

Table 12. Average element values in serum, forage and soils from the present study compared to studies from other areas of mineral deficiency in grazing ruminants.

The most significant negative correlations are between serum Cu and (i) Mn in stream sediment, grass and leaves and (ii) Zn in stream sediment and grass (Table 11). In addition the correlations between Cu in serum and Fe in soil and forage are slightly negative (Figure 15). These negative relationships suggest that Zn, Mn and possibly Fe ingested in forage and soil may be inhibiting the absorption of Cu in cattle. Clinical trials have demonstrated that high levels of dietary Zn reduce Cu absorption in rats, pigs and sheep although the relationship in cattle is less clear (Mertz 1987). The inhibitory affects of dietary Fe on Cu absorption are well documented (Mertz 1987). For example, Humphries et al. (1985) found dietary intakes of 350 mg/kg of Fe in forage were sufficient to significantly reduce the Cu content of the liver in young calves. Russell et al. (1985) demonstrated that Fe ingested from soil has a negative effect on Cu absorption in sheep. Up to 25 % of the Fe content of soils can be extracted during simulated digestion in sheep (Brebner et al. 1985). Since the level of Fe in soils is 100 times the content of forage in northeast Zimbabwe (Table 12), ingestion of high Fe soils may exert a greater inhibitory effect on Cu uptake than Fe in forage.

7.3.3. Calcium and Magnesium

Ca and Mg in soils correlate closely with all the other elements in soils as a result of the strong influence of bedrock geochemical variations (Table 8). Ca and Mg in soils do not correlate significantly with Ca and Mg in forage or serum samples (Table 13). Increased uptake of these elements by plants and animals as a result of higher levels in soils is not evident.

Table 13. Spearman Rank correlation table based on average values of Ca in serum, grass and leaves and Mg in serum for the 15 districts with other elements in various media.

	Ca Grass	Ca Leaves	Ca Soil	P Grass	P Leaves	Mg Grass	Mg Leaves
Ca Serum	-.279	-.039	-.093	-.461	-.007	-.254	.321
Ca Grass		-.207	.136	.257	-.218	.446	.089
Ca Leaves			-.209	-.096	.543	-.286	-.479
Mg Serum	-.157	.389	.043	.318	.625	-296	-.282

r 95% = 0.457; r 99% = 0.612; r 99.95% = 0.780 (Koch & Link 1970)
Sed = Sediment

7.3.4. Phosphorous

P in serum does not correlate significantly with P in any of the other sample media (Table 14). Although there is a strong positive correlation between Fe and P in soil, strong sorption of P by Fe oxides in soils normally reduces the availability of P to plants. This may explain why P in forage and cattle serum does not increase with P in soils; indeed P in serum tends to decrease slightly as Fe in soil and forage increases (Table 14 and Figure 16). This suggests that elevated levels of Fe in soil and forage may cause P deficiency in cattle. Additional significant relationships between P and other elements are mentioned in previous sections.

Table 14. Spearman Rank correlation table based on average values of P in serum for the 15 districts with other elements in various media.

	P Soil	P Grass	P Leaves	Fe Soil	Fe Grass	Fe Leaves
P Serum	-.079	-.025	.243	-.311	-.343	-.321

r 95% = 0.457; r 99% = 0.612; r 99.95% = 0.780 (Koch & Link 1970)
Sed = Sediment

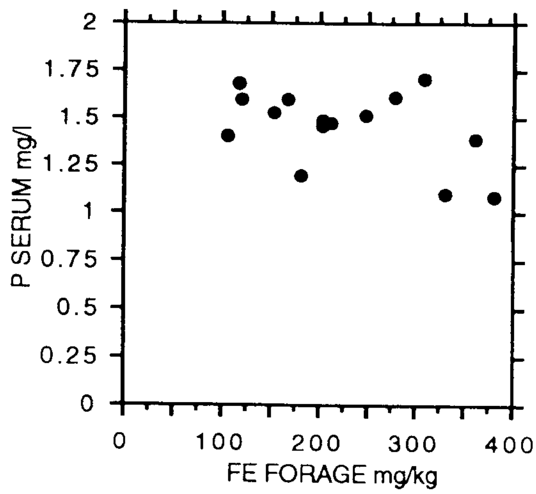


Figure 16. Plot of district average values of P in serum versus Fe in forage. Average forage values represent the average of grass and leaf compositions for each district.

7.3.5. Iron and Manganese

In addition to the relationships discussed above, significant correlations exist between Fe in soil with grass and leaves (Table 15) and Mn in sediment with soil (Table 8), grass and leaves (Table 15). This demonstrates that Fe and Mn in sediments and soils can be used as indicators of levels of these elements in forage. It is possible, however, that soil contamination of forage samples may influence the relationship between low, medium and high regions because of the high ratio between soil/ forage Fe content. Under these circumstances grass Fe values would show a stronger correlation with soil Fe than leaves as grass samples are likely to contain more soil than leaves. Since the correlations between Fe in grass and soil and Fe in leaves and soil are similar, soil contamination is not thought to be a significant factor. Furthermore, trends observed in forage comparisons for Mn, Cu and Zn indicate that soil contamination has little influence on the results.

There is a significant (95%) correlation between Fe in cattle serum and Fe in leaves but cattle serum Fe does not correlate with levels of Fe in the other sample types (Table 15). Despite an increase in the Fe content of soil and forage between the low and medium Zn region, the average Fe content of serum decreases between the low Zn region and the medium Zn region. The serum Fe concentrations rise in the high Zn region (Table 16). Reasons why the Fe content of serum decrease in the medium Zn region are unclear. It is possible that the difference in Fe concentration in forage between the low and medium Zn regions (150 mg/kg - 200 mg/kg) is not enough to result in an increase in serum Fe levels. Humphries et al. (1985) reported levels of plasma Fe in calves fed a diet containing various concentrations of Fe. It is evident from this study that although the dietary input of Fe was increased by the same amount each time (250 mg/kg), this did not always correspond to an increase in plasma Fe.

The normal range for Fe in cattle serum is between 1.42-1.82 mg/l. Many of the cattle in north-east Zimbabwe have Fe levels below this despite adequate levels of Fe in forage (> 30 mg/kg). High dietary intake of Fe would not necessarily be reflected in Fe serum levels and it is still possible that Fe may be interfering with the metabolism of Zn and Cu (C Mills and N Suttle pers commun). No indicators of cattle mineral status were obtained for Mn.

Table 15. Spearman Rank correlation table based on average values of Fe in serum, grass, leaves and soil for the 15 districts with Mn in various media and Zn in serum.

	Fe Grass	Fe Leaves	Fe Soil	Mn Leaves	Mn Soil	Mn Sed	Zn Serum
Fe Serum	.039	.484	-.049	-.256	.017	.171	.295
Fe Grass		.428	.743	.346	.828	.825	
Fe Leaves			.671	.089	.628	.632	
Fe Soil				.314	.936	.796	
Mn Grass				.578	.246	.486	
Mn Leaves					.225	.493	

r 95% = 0.457; r 99% = 0.612; r 99.95% = 0.780 (Koch & Link 1970)
Sed = Sediment

7.3.6. Selenium

In contrast to the strong correlations noted between other trace elements in soils (Table 8), Se distributions in soil only correlate significantly with distributions of Cu, Co and P (Table 16). There is no significant correlation between Se levels in soil and grass (Table 16). This may be because Se in soil is less available to plants and animals in areas of low pH such as north-east Zimbabwe therefore although soils may be high in Se these levels are not reflected in grasses (Davies, 1980).

Table 16. Mean values for elements in serum samples from the 15 sampling districts.

District No.	Zn Region	Ca mg/l	Cu mg/l	Fe mg/l	Mg mg/l	P mg/l	Zn mg/l
1	1	83.0	0.637	1.315	21.6	52.0	0.717
2	1	84.8	0.899	1.581	22.5	47.3	0.707
5	1	86.3	0.876	1.23	21.0	37.1	0.635
6	1	76.0	0.795	1.134	23.3	46.9	0.686
8	1	80.0	0.894	1.411	24.3	45.8	0.685
3	2	78.0	1.01	1.255	23.1	43.3	0.678
4	2	81.8	0.894	•	22.1	45.1	•
7	2	85.5	0.782	1.226	25.0	49.4	0.527
12	2	81.5	0.733	1.352	21.2	45.6	0.655
14	2	78.3	0.682	1.178	23.2	53.0	0.66
9	3	55.1	0.817	1.286	22.3	34.0	0.66
10	3	79.2	0.779	1.378	21.9	49.7	0.628
11	3	85.6	0.667	1.399	23.7	33.4	0.688
13	3	84.7	0.63	1.492	22.9	43.0	0.636
15	3	81.7	0.539	1.409	22.2	50.0	0.704

1 = low Zn 2 = medium Zn 3 = high Zn . = no data

Table 17. Spearman Rank correlation table based on the average values of Se in grass and soil for the 15 districts with other elements in soil.

	Se grass	Se Soil
Se soil	-.011	
Mn soil	-.586	.408
Fe soil	-.582	.431
Mg soil	-.564	.434
Cu soil	-.546	.536
Zn soil	-.529	-.377
Co soil	-.482	.481
P soil	-.261	.601

7.4. Deficiency Levels

Table 12 shows the average element concentrations in cattle serum, forage and soil from the present study compared with published data from other parts of the world where deficiencies in cattle serum, forage and soils have been recorded. Cattle mineral status studies commonly classify animal, forage and soil samples with respect to deficient, marginal and toxic element concentrations (McDowell et al. 1993). Samples below the critical level are termed deficient. The use of marginal bands acknowledges the uncertainty of predicting the precise level at which deficiency is induced. Applying the critical levels and marginal bands used in the published studies (Table 17) to the data from northeast Zimbabwe, it is clear that a high proportion of cattle serum and forage samples are marginal in Zn (Table 18).

Discrepancies between the percentage of samples below the critical levels and marginal bands in serum, forage and soil have been observed in previous studies (References from Table 12). This is confirmed by the present study in which only 26 % of the cattle are Cu deficient whereas nearly 100 % of forage samples are below the critical concentration (Table 18).

Table 18. Deficiency critical levels and marginal bands for elements in serum, forage and soil.

Media	Element	Critical Value Deficient	Marginal Band
Serum mg/l	Ca *	< 80	
	Mg		< 10 - 20
	P *	< 45	
	Cu	< 0.65	
	Zn		< 0.6 - 0.8
	Fe +		< 1.42
Forage mg/kg	Ca	< 3000	
	Mg	< 2000	
	P	< 2500	
	Co	< 0.1	
	Cu	< 10	
	Fe	< 30	
	Mn		< 30 - 40
	Zn	< 30	

All values taken from McDowell et al. (1993)
except * = Peducassé et al. (1983)
+ = C. Mills pers commun

Table 19. Percentages of north-east Zimbabwe serum and forage samples with elements below critical levels and marginal bands.

	% Deficient						% Marginal			
	Ca	Mg	P	Cu	Fe	Zn	Mg	Mn	Zn	Fe
Serum	47	-	55	26	nd	-	17	nd	86	62
Grass	10	77	94	100	0	92	-	6	-	-
Leaves	0	2	88	98	0	100	-	0	-	-

marginal = < 20 mg/l Mg serum; < 0.8 mg/l Zn serum; <1.2 mg/l Fe serum; < 40 mg/kg Mn forage
nd = no data

8. CONCLUSIONS

1. Stream sediment geochemical maps for Zn and Mn provide a reliable indication of the relative distribution of these elements in soil and forage (grass and leaves). Cu in stream sediments can be used to predict the levels of these elements in soil and grass, but less reliably in leaves. Fe in soils provides a reliable indication of levels in grass and leaves. Although hot hydrochloric acid extractable Ca, P and Mg in soil reflect variations in the chemical composition of the underling rocks, this information cannot be used to predict relative concentrations of these elements in forage.

2. Variations in the levels of Ca, Cu, Mg, P and Zn in cattle serum do not correlate positively with variations in forage, soil and sediment samples. Fe in serum correlates with Fe in leaves only.Therefore, it appears that it is not possible to use the concentrations of these elements in forage, soil or stream sediments directly to predict the Zn status of cattle at either the district or regional level.

3. The lack of direct relationship between cattle mineral status and forage status is undoubtedly due in part to physiological factors. Direct relationships between forage and cattle may also be obscured because of the uncertain contribution of grass and leaf species to dietary intake in this study.

4. The results of this study suggest that interactions and antagonistic effects between elements may significantly control the mineral status of cattle. High concentrations of Fe and Mn in soil and forage appear to inhibit the availability of P to plants and the

absorption of Cu and Zn in cattle. These findings may have wide-ranging implications due to the preponderance of ferrallitic soils in many countries in tropical regions.

5. Although stream sediment, soil and forage geochemical maps cannot be used to predict the mineral status of grazing ruminants directly, they can serve to indicate those areas where Zn, Cu and P are likely to be low in soils and forage and those areas where higher levels of Fe (and/ or Mn) may induce low Zn, Cu and P status in cattle despite higher levels of these elements in soils and forage.

6. Discrepancies between the percentage of deficient serum and percentage of deficient forage samples found in previous studies are also apparent in northeast Zimbabwe. This suggests that the critical levels used to determine deficiency in forage may require further investigation.

7. The univariate statistical approach adopted for this study is somewhat limited considering the number of possible interacting factors, between districts, regions, media type and elements . A multivariate statistical approach to data interpretation is planned for future investigations into the relationships between elements and sample media.

8. It is recommended that additional studies should be carried out over a variety of geographical and geological conditions in order to confirm the findings of this study.

9. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the enthusiastic response of Dr Ushewokunse-Obatolu (Assistant Director, Veterinary Services Department, Harare) to the project. Sincere thanks are due to Dr P. Gamble, Ms M. Simpson, Mr C. Mashanda, Mr Ngwebvu and Dr E. Anderson (Veterinary Services Department, Harare) for invaluable laboratory and logistical support and advice. Sincere thanks are also due to Dr N. Ndiweni (Department of Preclinical Veterinary Science, University of Zimbabwe) and Prof.J Topps (Department of Animal Science, University of Zimbabwe) for additional preparation and analysis of samples and for expert advice. Gratitude is extended to Dr P. Pitfield, Dr P. Lowenstein, Dr M. Armstrong, Dr P. Fey and Mr S. Ncube (Geological Survey Department, Harare) for the provision of a British High Commission vehicle, field equipment, logistical support and valuable guidance. Invaluable field assistance for the geochemical sampling programme was provided by Mr R Mbofana (Geological Survey Department, Harare). In addition, the authors gratefully acknowledge the excellent field assistance provided by Mr Nyoni and Mr Mudafi (Veterinary Services Office, Rushinga); Mr Nyatanga, Mr Madimutsa, Mr Gumbo and Mr Muranzi (Veterinary Services Office, Mutoko); Mr Kaweluka (Veterinary Service Office, Murehwa) and Mr R Mavhura and Mr A Mbofana (Rushinga). Thanks are extended to Mr Nkomo (Rushinga Tsetse Station) and Mr Gurongo (Kotwa Tsetse Station) for use of the tsetse stations as field bases. Thanks are also due to Dr A Hunt (MAFF Veterinary Inspection Centre, Sutton Bonnington) for valuable advice on the analysis of serum samples.

The authors gratefully acknowledge the advice on the sampling programme provided by Mr G. Freeland (ODA Senior Animal Health Adviser), Dr C. Livesey (Head of Biochemistry, Central Veterinary Laboratory, England), Prof. L McDowell (Animal Science Department, University of Florida). Prof. C. Mills (Rowett Research Institute, Aberdeen), Mr K. Ryder (ODA Biometrics Unit, Rothamsted) and Dr N.Suttle (Moredun Institute, Edinburgh).

This report is published with permission from the Director of Veterinary Services, Harare and the Director of the British Geological Survey.

10. REFERENCES

Aggett, P J, Mills, C F, Plant, J A, Simpson, P R, Stevenson, A, Dingwall-Fordyce, I and Halliday, C F. 1988. A study of environmental geochemistry and health in northeast Scotland. In: Thornton, I. (ed) Geochemistry and Health. Proceedings of the Second International Symposium. Science Reviews Ltd, Northwood. 81-91.

Allcott, G H and Lakin, H W. 1978. Tabulation of Geochemical Data Furnished by 109 Laboratories for Six Geochemical Exploration Reference Samples. Open File Report 78-163. United States Department of the Interior Geological Survey.

Anderson, I. 1986a. Communal Land Physical Resource Inventory Mudzi District. Chemistry and Soil Research Institute, Zimbabwe. Soils Report No. A519.

Anderson, I. 1986b. Communal Land Physical Resource Inventory Darwin District. Chemistry and Soil Research Institute, Zimbabwe. Soils Report No. A529.

Appleton, J D. 1992. Review of the Use of Regional Geochemical Maps for Identifying Areas where Mineral Deficiencies or Excesses may Affect Cattle Productivity in Tropical Countries. British Geological Survey Technical Report WC/92/24.

Appleton, J D. 1993. Environmental Geochemistry Project: Report on a Visit to Zimbabwe 17 - 26 February 1993. British Geological Survey Technical Report WC/93/12/R.

Appleton, J D and Greally, K. 1992. Environmental Geochemistry R&D Project : A comparison of the Trace Element Geochemistry of Drainage Sediments and Soils in Eastern Bolivia. British Geological Survey Technical Report WC/92/67.

Australian Bureau of Animal Health. 1982. Livestock Diseases Survey : A field manual for veterinarians.

Barton, C M, Cairney, J N, Crow, M J, Dunkley P N and Simango, S. 1991. The Geology of the Country Around Rushinga and Nyampanda. Zimbabwe Geological Survey Bulletin No. 92.

Brebner, J, Thornton, I, McDonald, P and Suttle, N F. 1985. The release of trace elements from soil under conditions of simulated rumenal and abomasal digestion. In: Mills, C F, Bremner, I and Chesters, J K. (eds) Trace Elements in Man and Animals - TEMA 5. Commonwealth Agricultural Bureaux, Slough, 850-852.

Brinn, P J. 1986. Communal Land Physical Resource Inventory Rushinga District. Chemistry and Soil Research Institute, Zimbabwe. Soils Report No. A518.

Cave, M, Reeder, S and Blackwell, P A. 1993. Analytical Methodology for the Determination of Selenium in Environmental Samples by Hydride Generation Atomic Absorption Analysis with Flow Injection Sample Introduction. British Geological Survey Technical Report WC/93/6.

Centre for Tropical Veterinary Medicine (CTVM), Edinburgh University. 1992. Report on the Mineral Status of Animals in Some Tropical Countries and Their Relationship to Drainage Geochemical Maps of Minerals in those Countries. British Geological Survey Technical Report WC/92/60.

Christophersen, O A. 1994. Some aspects of the biogeochemical behaviour of Mn as compared to other elments. In: Lag, J. (ed) Geomedical Problems related to Al, Fe and Mn. The Norwegian Academy of Sciences and Letters, Oslo, 85-99.

Davies, B E. (ed) 1980. Applied Soil Trace Elements. John Wiley and Sons. Chichester.

Dunkley, P N. 1987. A Regional Geochemical Survey of the Country Between Rushinga and Nyampanda, North-east Zimbabwe. British Geological Survey Overseas Directorate Open File Report. MP/87/16.

Fick, K R, McDowell, L R, Miles, P H, Wilkinson, N S, Funk, J D, Conrad, J H. 1979. Methods of Mineral Analysis for Plant and Animal Tissues. University of Florida.

Humphries, W R, Bremner, I. and Phillippo, M. 1985. The influence of dietary iron on copper metablosim in the calf. In: Mills, C. F., Bremner, I. and Chesters, J K. (eds) Trace Elements in Man and Animals - TEMA 5. Commonwealth Agricultural Bureaux, Slough, 371-373.

Koch, G S and Link, R F. 1970. Statistical Analysis of Geological Data. John Wiley and Sons. New York.

Lebdosoekojo, S, Ammerman, C B, Raun, N S, Gomez, J and Litell, R C. 1980. Mineral nutrition of beef cattle grazing native pastures on the eastern plains of Colombia. Journal of Animal Science, 51, 1249-1260.

Levinson, A A. 1980. Introduction to Exploration Geochemistry. Applied Publishing Ltd.

Wilmette.

McDowell, L R. 1976. Mineral Deficiencies and Toxicities and Their Effects on Beef Production in Developing Countries. In: Smith, A. J. (ed) Beef Cattle Production in Developing Countries. University of Edinburgh Press, Edinburgh, 216

McDowell, L R, Bauer, B, Gaido, E, Koger, M, Loosli, J K and Conrad, J H. 1982. Mineral supplementation of beef cattle in the Bolivian tropics. Journal of Animal Science. Vol. 55 No. 4. pp 964-970.

McDowell, L R, Conrad, J H and Hembry, F G. 1993. Minerals for Grazing Ruminants in Tropical Regions. Second Edition. University of Florida.

Mertz, W. (ed) 1987. Trace Elements in Human and Animal Nutrition. Academic Press Inc. London.

Miles, W H, McDowell, L R and Raun, N S. 1989. More complete mineral supplements key technology for tropical America. In: World Animal Review. Vol. 1. Pope, L S and Moore, P. eds. Agriservices Foundation, Clovis, California.

Mtimuni, J P, Conrad, J H and McDowell, L R. 1983. Effect of season on mineral concentrations on beef cattle in Malawi. S. Afr. J. Anim. Sci. Vol. 13. No. 1. pp 1-2.

Nyamapfene, K. 1991. Soils of Zimbabwe. Nehanda Publishers. Harare.

Office of Reference Materials. 1991. Certified Reference Materials. Issue No. 2. Laboratory of the Government Chemist. London.

Ogwang, B H. 1988. The mineral status of soil, forage and cattle tissues in the middleveld of Swaziland. Expl. Agric. Vol . 24. pp 177 - 182.

Oritz, J, Peducasse, A C and Appleton, J D. 1993 Review of Mineral Status of Cattle in Eastern Bolivia. British Geological Survey Technical report WC/93/1.

Peducasse, A C, McDowell, L R, Parra, L, Wilkins, J V, Martin, F G, Loosli, J K and Conrad, J H. 1983. Mineral status of grazing beef cattle in the tropics of Bolivia. Trop. Anim. Prod. Vol 8. pp 118-130.

Plant, J A and Thornton, I. 1986. Geochemistry and health in the United Kingdom. In:

Thornton, I . (ed.) Proceedings of the First International Symposium on Geochemistry and Health. Science Reviews Ltd. Northwood. pp 5-16.

Potts, P J, Tindle, A G and Webb, P C. 1992. Geochemical Reference Material Compositions. CRC Press. London.

Prabowo, A, McDowell, L R, Wilkinson, N S, Wilcox, C J and Conrad, J H. 1991. Mineral status of grazing cattle in South Sulawesi, Indonesia: 2: Microminerals. AJAS. Vol. 4. No 2. pp 121-130.

Quarterman, J. 1985. The role of intestinal mucus on metal absorption. In: Mills, C F, Bremner, I. & Chesters, J K. (eds) Trace Elements in Man and Animals - TEMA 5. Commonwealth Agricultural Bureaux, Slough, 400-401.

Russell, K, Brebner, J, Thornton, I. & Suttle, N F. 1985. The influence of soil ingestion on the intake of potentially toxic metals and absorption of essential trace elements by grazing livestock. In: Mills, C. F., Bremner, I. & Chesters, J K. (eds) Trace Elements in Man and Animals - TEMA 5. Commonwealth Agricultural Bureaux, Slough, 847-849.

Sandstrom, B, Davidsson, L, Cederblad, A and Lonnerdal, B. 1985. Effects of inorganic iron on the absorption of zinc from a test solution and a composite meal. In: Mills, C F, Bremner, I and Chesters, J K. (eds) Trace Elements in Man and Animals - TEMA 5. Commonwealth Agricultural Bureaux, Slough, 414-415.

Standing Committee of Analysts. 1987. Methods for Determination of Metals in Soils, Sediments and Sewage Sludge and Plants by Hydrochloric-nitric Acid Digestion. HMSO. London.

Stevens, J B,Olson, W G, Kraemer, R and Arcgambeau, J. 1985. Serum selenium concentrations and glutathione peroxidase activities in cattle forages of various selenium concentrations. Am. J. Vet. Res. Vol 46. No 7. pp 1556-1560.

Tejada, R, McDowell, L R, Martin, F G and Conrad, J H. 1985. Mineral element analyses of various tropical forages in Guatemala and their relationship to soil concentrations. Nutrition Reports International. Vol. 32. No. 2. pp 313-323.

Thomson, J G and Purves, W D. 1978. A Guide to the Soils of Rhodesia. Rhodesian Journal of Agriculture. Technical Handbook No. 3.

APPENDIX 1. Results of cattle serum analyses by AAS and colorimetry.

Sample Number	Zn Serum (1994)	Fe Serum (1994)	Cu Serum	Mg Serum mg/l	P Serum	Ca Serum	District	Zn Region
C1920	0.712	1.095	0.854	24.494	48.313	94.344	1	1
C1905	•	•	0.343	21.384	50.791	83.162	1	1
C1908	0.732	1.134	0.645	19.246	45.836	79.475	1	1
C1914	0.725	0.788	0.545	19.756	55.127	73.062	1	1
C1917	•	•	0.355	20.995	52.649	78.593	1	1
C1913	0.654	1.726	0.476	26.657	59.772	74.505	1	1
C1904	0.719	1.229	0.447	18.128	35.615	63.003	1	1
C1903	0.647	1.52	0.809	20.388	67.205	84.965	1	1
C1907	•	•	0.659	19.003	39.951	79.515	1	1
C1916	0.693	1.419	0.427	21.676	68.134	89.334	1	1
C1902	0.922	1.073	0.44	22.137	49.552	99.834	1	1
C1901	•	•	0.854	21.019	65.037	92.821	1	1
C1906	0.614	1.508	0.794	23.328	44.906	85.206	1	1
C1910	•	•	0.723	18.711	43.048	80.517	1	1
C1911	•	•	0.886	22.478	54.817	76.469	1	1
C1919	•	•	0.734	23.279	49.552	83.963	1	1
C1918	•	•	0.371	23.207	65.037	70.417	1	1
C1909	0.719	1.212	0.816	23.036	41.5	93.101	1	1
C1912	0.562	1.866	0.922	23.571	61.011	88.492	1	1
C1915	0.908	1.212	0.647	20.339	42.739	88.452	1	1
M2513	0.359	1.352	0.788	20.801	49.552	88.132	2	1
M2507	•	•	1.09	22.55	30.97	82.961	2	1
M2520	0.797	1.095	0.959	19.877	26.944	109.814	2	1
M2519	0.732	1.274	0.849	18.225	44.906	85.166	2	1
M2502	•	•	1.229	26.268	44.906	107.529	2	1
M2511	•	•	0.995	24.713	42.429	75.948	2	1
M2527	0.739	1.598	•	•	•	•	2	1
M2512	0.941	1.592	1.025	21.967	50.481	74.184	2	1
M2515	0.627	1.866	1.023	22.793	54.817	76.589	2	1
M2517	0.712	1.291	0.629	20.436	51.72	84.965	2	1
M2522	1.007	1.687	•	•	•	•	2	1
M2503	•	•	0.994	24.665	61.321	71.379	2	1
M2526	0.791	1.391	•	•	•	•	2	1
M2505	•	•	0.799	24.3	45.216	96.788	2	1
M2516	0.542	1.475	0.679	23.279	43.977	79.996	2	1
M2518	•	•	0.831	21.992	52.959	70.617	2	1
M2508	•	•	0.966	19.902	32.519	67.211	2	1
M2523	0.993	1.592	•	•	•	•	2	1
M2525	0.608	1.743	•	•	•	•	2	1
M2510	0.693	1.514	0.691	25.005	46.145	81.96	2	1
M2504	•	•	0.625	20.023	72.16	94.384	2	1
M2506	0.601	2.201	1.034	21.068	48.003	85.727	2	1
M2501	0.725	1.754	1.078	25.588	42.119	78.272	2	1
M2514	0.392	1.514	0.934	22.235	50.481	96.788	2	1
M2521	0.765	1.654	•	•	•	•	2	1
M2509	0.654	2.073	0.764	24.081	54.507	87.049	2	1
M2524	0.752	1.542	•	•	•	•	2	1

Sample Number	Zn Serum (1994)	Fe Serum (1994)	Cu Serum	Mg Serum mg/l	P Serum	Ca Serum	District	Zn Region
M2528	0.607	1.413	•	•	•	•	•	•
N2810	0.601	0.832	0.675	21.943	38.712	82.16	3	2
N2814	0.98	1.134	1.085	19.076	20.44	76.91	3	2
N2805	•	•	0.861	20.776	42.119	76.268	3	2
N2801	0.706	1.385	1.007	19.732	53.888	76.749	3	2
N2812	0.386	1.179	1.437	18.395	26.634	81.599	3	2
N2811	0.797	1.134	1.676	20.728	22.298	85.967	3	2
N2806	0.739	1.196	1.009	24.835	29.421	91.097	3	2
N2824	0.745	1.279	•	•	•	•	3	2
N2826	0.778	1.179	•	•	•	•	3	2
N2823	0.699	1.212	•	•	•	•	3	2
N2822	0.739	1.207	•	•	•	•	3	2
N2825	0.641	1.514	•	•	•	•	3	2
N2817	0.588	1.168	0.865	20.096	40.88	81.519	3	2
N2807	0.621	1.324	0.942	23.935	34.067	77.631	3	2
N2818	0.745	1.369	1.174	19.27	39.642	94.544	3	2
N2808	0.686	1.57	0.975	23.352	31.589	90.857	3	2
N2804	•	•	0.986	19.464	54.817	104.083	3	2
N2820	0.614	1.263	0.97	21.433	45.526	92.821	3	2
N2809	•	•	0.817	22.575	40.88	86.889	3	2
N2802	0.667	1.229	1.064	21.627	40.88	88.372	3	2
N2819	0.686	1.43	0.821	20.388	32.209	92.179	3	2
N2815	•	•	1.032	22.429	36.545	91.698	3	2
N2816	•	•	0.933	20.12	47.074	88.893	3	2
N2803	•	•	0.961	23.765	33.448	86.929	3	2
N2813	0.68	1.246	0.903	15.965	31.899	79.675	3	2
R3920	•	•	0.91	22.235	48.003	76.268	4	2
R3912	•	•	0.511	30.035	50.791	73.263	4	2
R3909	•	•	1.282	23.401	42.119	74.866	4	2
R3911	•	•	0.923	18.565	40.261	76.709	4	2
R3908	•	•	0.805	25.102	38.712	66.85	4	2
R3904	•	•	1.232	24.13	45.526	69.736	4	2
R3916	•	•	1.034	24.543	52.03	78.553	4	2
R3918	•	•	0.831	25.831	33.448	64.646	4	2
R3915	•	•	0.621	21.724	47.694	62.281	4	2
R3917	•	•	0.969	25.588	43.977	90.777	4	2
R3905	•	•	0.628	23.693	50.171	62.602	4	2
R3903	•	•	0	26.608	49.242	87.41	4	2
R3906	•	•	1.059	22.016	43.977	85.166	4	2
R3902	•	•	1.19	25.952	57.914	91.658	4	2
R3907	•	•	1.111	20.218	43.358	72.581	4	2
R3913	•	•	0.836	24.008	58.533	71.579	4	2
R3919	•	•	0.783	18.298	67.515	66.61	4	2
R3901	•	•	1.546	23.765	•	78.914	4	2
R3914	•	•	0.69	20.023	37.783	80.717	4	2
R3910	•	•	0.911	21.36	39.642	88.933	4	2
N1025	0.549	0.726	•	•	•	•	5	1

Sample Number	Zn Serum (1994)	Fe Serum (1994)	Cu Serum	Mg Serum mg/l	P Serum	Ca Serum	District	Zn Region
N1032	0.68	0.899	•	•	•	•	5	1
N1014	•	•	0.769	21.384	49.242	84.444	5	1
N1015	•	•	0.841	22.866	•	79.595	5	1
N1019	•	•	0.767	22.769	39.642	86.609	5	1
N1009	•	•	1.129	24.64	40.571	73.182	5	1
N1001	0.686	1.324	1.171	24.883	48.623	86.689	5	1
N1013	•	•	0.798	22.648	39.642	73.784	5	1
N1029	0.673	0.844	•	•	•	•	5	1
N1030	0.706	1.475	•	•	•	•	5	1
N1022	0.451	1.156	•	•	•	•	5	1
N1031	0.627	1.469	•	•	•	•	5	1
N1016	•	•	0.765	23.838	56.365	81.96	5	1
N1020	•	•	0.916	24.737	38.712	84.164	5	1
N1034	0.771	1.369	•	•	•	•	5	1
N1033	0.549	1.006	•	•	•	•	5	1
N1012	•	•	0.881	23.158	44.287	79.835	5	1
N1003	•	•	1.104	23.304	43.668	79.795	5	1
N1010	•	•	0.661	27.046	41.19	73.102	5	1
N1005	•	•	0.762	24.373	55.746	71.579	5	1
N1006	•	•	0.795	27.338	43.048	84.965	5	1
N1038	0.627	1.397	•	•	•	•	5	1
N1007	•	•	0.863	23.012	43.358	80.276	5	1
N1035	0.928	1.464	•	•	•	•	5	1
N1002	•	•	0.831	26.293	41.5	87.21	5	1
N1028	0.641	1.19	•	•	•	•	5	1
N1027	0.575	1.542	•	•	•	•	5	1
N1026	0.484	1.179	•	•	•	•	5	1
N1021	0.588	1.564	•	•	•	•	5	1
N1023	0.641	1.246	•	•	•	•	5	1
N1011	•	•	1.026	23.62	44.906	89.494	5	1
N1024	0.536	1.011	•	•	•	•	5	1
N1037	0.536	1.223	•	•	•	•	5	1
N1017	•	•	0.629	24.057	51.72	71.619	5	1
N1004	•	•	0.91	26.924	44.906	77.872	5	1
N1036	0.81	1.279	•	•	•	•	5	1
N1018	•	•	0.833	23.012	52.649	74.665	5	1
N1008	•	•	1.061	26.171	51.41	80.797	5	1
K0531	0.824	1.341	•	•	•	•	6	1
K0501	0.693	1.251	0.706	22.235	51.41	86.849	6	1
K0506	0.686	0.905	0.757	23.158	41.5	74.545	6	1
K0504	•	•	0.758	21.651	43.977	74.745	6	1
K0518	0.758	1.235	0.859	22.307	48.933	76.789	6	1
K0532	0.758	1.045	•	•	•	•	6	1
K0515	0.647	1.045	0.849	31.031	41.19	82.16	6	1
K0507	0.516	1.173	1.061	25.078	32.519	69.135	6	1
K0509	•	•	0.841	24.106	34.996	85.326	6	1
K0525	0.797	1.151	•	•	•	•	6	1

Sample Number	Zn Serum (1994)	Fe Serum (1994)	Cu Serum	Mg Serum mg/l	P Serum	Ca Serum	District	Zn Region
K0502	0.536	1.017	0.769	23.45	50.481	85.126	6	1
K0533	0.562	1.246	•	•	•	•	6	1
K0512	0.719	0.916	0.76	22.113	46.765	71.86	6	1
K0516	•	•	0.884	18.881	48.313	88.252	6	1
K0510	0.582	1.313	0.635	23.984	46.145	79.475	6	1
K0519	•	•	0.902	20.072	26.944	81.158	6	1
K0521	0.739	1.168	•	•	•	•	6	1
K0529	0.719	1.33	•	•	•	•	6	1
K0528	1.131	1.184	•	•	•	•	6	1
K0527	0.745	1.168	•	•	•	•	6	1
K0530	0.497	1.112	•	•	•	•	6	1
K0513	•	•	0.817	17.885	48.313	78.433	6	1
K0522	0.739	1.196	•	•	•	•	6	1
K0524	0.673	1.291	•	•	•	•	6	1
K0511	0.484	1.101	0.512	27.921	45.526	70.297	6	1
K0508	•	•	0.981	23.668	28.802	73.944	6	1
K0514	•	•	0.794	24.203	46.765	79.314	6	1
K0517	0.529	0.709	0.814	22.526	62.25	77.27	6	1
K0503	•	•	0.464	19.513	37.164	70.818	6	1
K0523	0.758	1.106	•	•	•	•	6	1
K0526	0.739	1.034	•	•	•	•	6	1
K0505	0.634	1.173	1.008	24.64	40.261	72.501	6	1
K0520	•	•	0.732	23.061	43.668	81.318	6	1
U3824	0.987	1.352	•	•	•	•	7	2
U3811	0.562	1.609	0.828	23.474	39.022	81.719	7	2
U3818	•	•	0.745	20.29	46.145	78.954	7	2
U3803	•	•	0.701	20.023	42.739	68.012	7	2
U3808	•	•	0.731	21.7	47.694	80.196	7	2
U3809	•	•	0.685	23.717	59.462	97.069	7	2
U3813	0.497	1.425	1.019	24.494	35.615	84.003	7	2
U3816	•	•	0.587	17.569	44.287	79.034	7	2
U3812	0.503	0.994	1.233	22.866	49.242	91.618	7	2
U3817	0.438	1.101	0.619	21.263	70.612	76.148	7	2
U3810	•	•	0.912	25.272	43.358	74.826	7	2
U3814	•	•	0.702	22.842	57.294	81.158	7	2
U3807	0.412	1.011	0.686	19.999	48.313	79.395	7	2
U3820	•	•	0.708	22.186	44.597	80.597	7	2
U3821	0.281	0.961	•	•	•	•	7	2
U3806	0.556	1.341	0.669	24.81	43.977	75.467	7	2
U3825	0.856	1.542	•	•	•	•	7	2
U3822	0.281	0.844	•	•	•	•	7	2
U3804	•	•	0.675	19.902	32.828	84.164	7	2
U3819	•	•	1.448	23.62	46.145	91.378	7	2
U3805	•	•	0.578	19.732	39.951	68.253	7	2
U3823	0.392	1.05	•	•	•	•	7	2
U3801	•	•	0.878	22.259	36.545	83.723	7	2
U3802	•	•	0.451	23.012	31.28	86.729	7	2

Sample Number	Zn Serum (1994)	Fe Serum (1994)	Cu Serum	Mg Serum mg/l	P Serum	Ca Serum	District	Zn Region
U3815	0.562	1.486	0.781	22.429	42.429	93.181	7	2
D2612	•	•	0.999	24.713	39.022	96.307	8	1
D2635	0.51	1.274	•	•	•	•	8	1
D2621	0.647	1.279	•	•	•	•	8	1
D2619	•	•	0.804	24.64	57.914	84.444	8	1
D2627	0.83	1.447	•	•	•	•	8	1
D2630	0.98	1.598	•	•	•	•	8	1
D2605	0.83	1.475	0.875	23.62	52.339	79.515	8	1
D2609	•	•	1.006	26.706	53.578	84.003	8	1
D2616	•	•	0.776	27.265	43.977	84.645	8	1
D2613	•	•	1.124	19.537	•	78.954	8	1
D2611	•	•	0.739	27.872	57.294	98.071	8	1
D2604	0.614	1.654	1.176	27.459	39.951	86.047	8	1
D2610	•	•	0.935	27.289	39.642	89.454	8	1
D2607	•	•	0.764	24.737	48.313	92.059	8	1
D2625	0.824	1.33	•	•	•	•	8	1
D2622	0.484	1.397	•	•	•	•	8	1
D2631	0.856	1.453	•	•	•	•	8	1
D2623	0.458	1.173	•	•	•	•	8	1
D2606	•	•	0.972	25.758	55.127	87.089	8	1
D2603	•	•	1.099	22.769	56.675	95.025	8	1
D2615	•	•	0.605	25.223	49.242	89.855	8	1
D2617	•	•	0.773	26.22	60.082	83.723	8	1
D2633	0.556	1.43	•	•	•	•	8	1
D2632	0.654	1.313	•	•	•	•	8	1
D2634	0.765	1.531	•	•	•	•	8	1
D2626	0.575	1.525	•	•	•	•	8	1
D2608	0.712	1.296	1.032	26.463	47.384	92.019	8	1
D2624	0.791	1.559	•	•	•	•	8	1
D2628	0.771	1.374	•	•	•	•	8	1
D2614	0.418	1.302	0.746	25.321	51.41	79.314	8	1
D2602	•	•	0.914	21.36	47.074	75.547	8	1
D2629	0.797	1.307	•	•	•	•	8	1
D2620	•	•	0.85	25.685	57.294	88.091	8	1
D2618	0.627	1.508	0.863	25.369	58.224	77.992	8	1
D2601	•	•	0.827	22.283	24.466	68.453	8	1
N3719	•	•	0.912	21.141	28.802	80.637	9	3
N3715	•	•	0.654	24.179	50.171	94.183	9	3
N3712	0.686	1.425	0.979	19.367	40.571	77.19	9	3
N3701	•	•	0.806	23.425	37.474	77.351	9	3
N3721	0.614	2.084	•	•	•	•	9	3
N3717	•	•	0.79	19.95	52.649	80.717	9	3
N3720	•	•	1.038	24.179	40.571	77.07	9	3
N3718	0.732	1.268	0.604	23.644	45.526	77.07	9	3
N3723	0.765	1.011	•	•	•	•	9	3
N3708	•	•	0.476	18.444	41.19	81.238	9	3
N3710	•	•	0.887	19.95	55.127	73.303	9	3

Sample Number	Zn Serum (1994)	Fe Serum (1994)	Cu Serum	Mg Serum mg/l	P Serum	Ca Serum	District	Zn Region
N3709	•	•	0.79	22.162	39.642	86.288	9	3
N3729	0.817	1.207	•	•	•	•	9	3
N3727	0.275	1.201	•	•	•	•	9	3
N3731	0.627	1.212	•	•	•	•	9	3
N3725	0.765	0.95	•	•	•	•	9	3
N3713	•	•	0.974	23.911	43.668	81.879	9	3
N3714	0.595	1.57	0.74	19.902	65.037	84.725	9	3
N3711	0.556	1.246	0.702	19.173	•	80.717	9	3
N3730	0.569	1.162	•	•	•	•	9	3
N3702	•	•	1.158	19.148	46.765	75.467	9	3
N3724	1	1.352	•	•	•	•	9	3
N3707	•	•	0.702	18.055	51.72	84.845	9	3
N3728	0.765	1.235	•	•	•	•	9	3
N3722	0.608	1.24	•	•	•	•	9	3
N3704	0.627	1.341	0.953	20.582	44.287	86.168	9	3
N3716	0.418	1.173	0.636	24.13	38.403	76.91	9	3
N3706	0.569	1.106	0.706	17.302	47.074	80.076	9	3
N3726	0.824	1.028	•	•	•	•	9	3
N3703	•	•	0.901	21.846	52.339	78.072	9	3
N3705	0.739	1.626	0.922	23.595	44.906	95.826	9	3
B4612	•	•	0.554	23.182	50.481	76.108	10	3
B4617	0.732	1.369	0.773	23.668	42.429	82.12	10	3
B4601	0.725	1.732	0.906	22.915	•	84.565	10	3
B4615	0.484	0.816	0.731	23.231	60.701	89.214	10	3
B4606	0.614	1.33	0.86	19.975	48.003	59.155	10	3
B4613	•	•	0.843	24.713	46.765	81.038	10	3
B4620	0.673	1.229	0.68	23.377	51.41	70.177	10	3
B4614	•	•	0.662	21.87	155.16	76.549	10	3
B4611	•	•	0.714	23.911	53.888	90.095	10	3
B4607	•	•	0.782	19.294	51.72	68.413	10	3
B4619	0.719	1.212	0.887	23.765	38.403	79.675	10	3
B4609	•	•	0.787	24.203	43.048	43.244	10	3
B4610	0.458	1.453	0.603	24.008	40.571	86.568	10	3
B4608	0.562	1.302	0.677	23.984	58.843	79.755	10	3
B4602	0.595	1.246	0.969	26.414	38.403	78.473	10	3
B4605	0.732	1.531	0.777	25.952	53.888	79.835	10	3
B4604	0.49	1.201	0.841	22.842	48.933	74.705	10	3
B4603	•	•	0.752	23.474	30.97	78.152	10	3
B4618	0.843	1.732	0.77	21.724	47.694	92.26	10	3
B4616	0.542	1.76	1.019	21.408	45.216	95.265	10	3
M4325	0.693	1.061	•	•	•	•	11	3
M4326	0.725	1.341	•	•	•	•	11	3
M4306	•	•	0.61	21.141	33.757	59.476	11	3
M4307	•	•	0.947	20.874	42.119	78.072	11	3
M4303	0.569	0.905	0.674	25.612	32.519	62.361	11	3
M4324	0.967	1.469	•	•	•	•	11	3
M4304	•	•	0.597	20.776	34.996	59.636	11	3

Sample Number	Zn Serum (1994)	Fe Serum (1994)	Cu Serum	Mg Serum mg/l	P Serum	Ca Serum	District	Zn Region
M4311	•	•	0.671	24.883	32.209	57.071	11	3
M4305	•	•	0.721	22.259	30.351	52.222	11	3
M4310	0.758	•	0.556	22.623	34.377	40.759	11	3
M4315	•	•	0.366	30.618	40.571	41.481	11	3
M4318	•	•	0.583	21.53	35.306	51.781	11	3
M4323	0.732	1.994	•	•	•	•	11	3
M4301	0.595	1.464	0.855	21.408	39.022	52.662	11	3
M4313	•	•	0.895	18.006	26.944	47.773	11	3
M4316	•	•	0.6	22.599	26.015	67.491	11	3
M4317	0.582	0.927	0.696	26.098	33.757	48.494	11	3
M4314	•	•	0.606	20.266	24.466	55.628	11	3
M4322	0.627	1.547	•	•	•	•	11	3
M4308	0.85	1.212	0.595	19.294	29.731	57.792	11	3
M4319	•	•	0.454	24.276	39.332	41.681	11	3
M4320	•	•	0.6	22.648	40.88	53.023	11	3
M4312	0.595	1.335	0.894	19.003	33.138	62.201	11	3
M4309	0.66	2.145	0.73	19.464	38.712	53.424	11	3
M4321	0.503	1.385	•	•	•	•	11	3
M4302	•	•	0.691	21.87	31.899	58.875	11	3
N0924	0.373	1.19	•	•	•	•	12	2
N0916	•	•	0.573	22.137	45.526	70.658	12	2
N0926	0.778	1.101	•	•	•	•	12	2
N0925	0.556	1.112	•	•	•	•	12	2
N0908	•	•	0.95	22.453	41.5	80.236	12	2
N0904	•	•	0.693	23.644	58.843	84.605	12	2
N0915	•	•	0.549	20.388	53.888	76.83	12	2
N0914	0.49	1.687	0.612	21.408	50.171	93.702	12	2
N0919	•	•	0.825	22.04	52.03	79.916	12	2
N0918	•	•	0.768	23.522	46.765	71.219	12	2
N0903	•	•	0.745	24.713	42.119	76.549	12	2
N0906	•	•	1.09	24.446	49.242	86.889	12	2
N0922	0.634	1.33	•	•	•	•	12	2
N0929	0.778	0.927	•	•	•	•	12	2
N0921	0.68	1.341	•	•	•	•	12	2
N0928	0.654	1.313	•	•	•	•	12	2
N0909	•	•	0.974	21.87	37.164	75.226	12	2
N0901	•	•	0.859	20.752	65.347	81.919	12	2
N0938	0.824	•	•	•	•	•	12	2
N0911	•	•	0.651	22.356	35.306	67.612	12	2
N0932	0.732	1.547	•	•	•	•	12	2
N0910	0.503	1.939	0.901	17.86	55.127	87.851	12	2
N0920	•	•	0.603	19.027	62.25	83.122	12	2
N0913	•	•	0.629	20.218	51.41	80.677	12	2
N0902	•	•	0.62	28.431	48.313	75.868	12	2
N0936	0.693	•	•	•	•	•	12	2
N0934	0.81	•	•	•	•	•	12	2
N0933	0.556	•	•	•	•	•	12	2

Sample Number	Zn Serum (1994)	Fe Serum (1994)	Cu Serum	Mg Serum mg/l	P Serum	Ca Serum	District	Zn Region
N0935	0.542	•	•	•	•	•	12	2
N0923	0.425	1.475	•	•	•	•	12	2
N0917	•	•	0.571	18.201	47.694	85.326	12	2
N0927	0.693	1.475	•	•	•	•	12	2
N0931	0.876	1.034	•	•	•	•	12	2
N0937	0.588	•	•	•	•	•	12	2
N0912	•	•	0.643	21.992	47.694	73.263	12	2
N0930	0.771	1.464	•	•	•	•	12	2
N0905	•	•	0.689	20.606	52.959	73.984	12	2
N0907	•	•	0.711	21.676	50.171	77.791	12	2
M4716	•	•	0.587	23.863	35.925	96.508	13	3
M4730	0.627	1.721	•	•	•	•	13	3
M4705	0.595	1.318	0.668	22.04	28.492	87.971	13	3
M4709	0.379	0.855	0.685	23.498	38.403	78.673	13	3
M4718	•	•	0.75	29.962	27.873	87.41	13	3
M4703	•	•	0.886	23.474	32.519	91.218	13	3
M4719	•	•	0.57	21.943	40.571	91.458	13	3
M4724	0.739	1.615	•	•	•	•	13	3
M4732	0.915	1.274	•	•	•	•	13	3
M4728	0.647	1.743	•	•	•	•	13	3
M4714	0.444	1.782	0.64	24.13	35.615	86.969	13	3
M4706	•	•	0	25.296	29.421	90.697	13	3
M4731	0.784	1.659	•	•	•	•	13	3
M4702	0.425	1.212	0.773	21.433	18.892	78.833	13	3
M4713	•	•	0.576	24.057	38.403	92.059	13	3
M4712	•	•	0.342	28.358	30.041	69.215	13	3
M4707	•	•	0.671	23.377	27.254	83.362	13	3
M4701	0.425	0.866	0.759	18.201	40.261	86.849	13	3
M4733	0.686	1.531	•	•	•	•	13	3
M4727	0.784	1.553	•	•	•	•	13	3
M4725	0.739	1.48	•	•	•	•	13	3
M4723	0.66	1.626	•	•	•	•	13	3
M4726	0.582	1.43	•	•	•	•	13	3
M4715	0.699	1.486	0.617	26.317	41.5	82.801	13	3
M4708	0.549	2.045	0.739	24.543	37.783	79.475	13	3
M4722	0.915	1.682	•	•	•	•	13	3
M4717	•	•	0.734	19.853	40.88	93.502	13	3
M4729	0.758	1.687	•	•	•	•	13	3
M4711	•	•	0.449	23.522	23.847	77.19	13	3
M4704	•	•	0.707	26.949	27.873	90.095	13	3
M4721	0.673	1.223	•	•	•	•	13	3
M4710	0.529	1.631	0.758	19.489	31.28	86.248	13	3
M4720	0.438	1.413	0.694	23.693	41.19	81.919	13	3
N4919	•	•	0.504	22.478	41.81	84.444	14	2
N4914	0.948	1.028	0.691	23.401	61.63	89.695	14	2
N4921	0.804	1.318	•	•	•	•	14	2
N4911	0.608	1.229	0.645	22.866	48.623	92.059	14	2

Sample Number	Zn Serum (1994)	Fe Serum (1994)	Cu Serum	Mg Serum mg/l	P Serum	Ca Serum	District	Zn Region
N4918	0.765	1.179	0.614	22.648	53.578	87.25	14	2
N4907	0.654	2.145	0.781	25.345	45.526	85.767	14	2
N4908	0.712	0.777	0.663	25.758	36.235	87.651	14	2
N4920	0.484	1.38	0.495	22.988	49.862	73.062	14	2
N4912	0.98	1.777	0.67	21.457	43.668	76.228	14	2
N4902	0.359	1.034	0.518	28.698	26.634	104.483	14	2
N4913	0.902	1.045	0.842	22.55	56.675	82.681	14	2
N4906	0.438	1.145	0.594	20.606	34.996	74.906	14	2
N4909	0.614	1.587	0.835	19.877	34.996	84.965	14	2
N4901	0.549	0.575	0.809	24.592	45.216	82.12	14	2
N4905	0.431	0.972	0.72	24.422	18.582	88.612	14	2
N4903	0.68	0.911	0.731	23.061	31.899	82.24	14	2
N4915	0.712	1.279	0.743	17.302	54.197	87.25	14	2
N4916	0.614	0.726	0.769	21.311	55.436	78.793	14	2
N4910	•	•	0.729	21.7	42.429	88.773	14	2
N4917	0.621	1.095	0.709	24.203	45.216	76.91	14	2
N4904	•	•	0.586	22.891	31.28	86.969	14	2
M4523	0.627	1.687	•	•	•	•	15	3
M4501	•	•	0.841	23.109	43.048	83.603	15	3
M4510	•	•	0.445	21.603	42.119	75.667	15	3
M4514	•	•	0.492	20.169	52.03	80.958	15	3
M4533	0.647	0.888	•	•	•	•	15	3
M4527	0.601	1.391	•	•	•	•	15	3
M4509	•	•	0.6	27.824	52.339	89.013	15	3
M4518	•	•	0.556	19.076	60.391	82.44	15	3
M4507	•	•	0.482	22.793	42.119	73.142	15	3
M4508	•	•	0.482	23.644	56.985	83.683	15	3
M4506	•	•	0.485	26.317	72.78	86.368	15	3
M4529	0.503	1.531	•	•	•	•	15	3
M4517	•	•	0.456	21.117	34.996	80.757	15	3
M4516	•	•	0.522	24.081	49.552	94.223	15	3
M4515	•	•	0.647	21.943	56.985	81.599	15	3
M4525	0.582	1.777	•	•	•	•	15	3
M4539	0.562	1.709	•	•	•	•	15	3
M4519	•	•	0.44	19.659	33.757	78.833	15	3
M4534	1.19	1.268	•	•	•	•	15	3
M4536	0.739	1.62	•	•	•	•	15	3
M4511	•	•	0.566	23.863	42.739	79.194	15	3
M4512	•	•	0.519	20.266	52.649	86.609	15	3
M4505	•	•	0.531	18.517	79.593	64.005	15	3
M4538	0.608	1.81	•	•	•	•	15	3
M4502	•	•	0.521	23.668	48.313	97.71	15	3
M4526	0.778	1.804	•	•	•	•	15	3
M4504	•	•	0.599	20.679	39.951	70.337	15	3
M4524	0.556	1.637	•	•	•	•	15	3
M4520	•	•	0.413	19.78	43.668	83.563	15	3
M4531	1	1.855	•	•	•	•	15	3

Sample Number	Zn Serum (1994)	Fe Serum (1994)	Cu Serum	Mg Serum mg/l	P Serum	Ca Serum	District	Zn Region
M4513	•	•	0.575	22.745	43.668	87.731	15	3
M4528	0.549	1.81	•	•	•	•	15	3
M4535	0.765	1.413	•	•	•	•	15	3
M4530	0.634	1.933	•	•	•	•	15	3
M4537	0.693	1.581	•	•	•	•	15	3
M4522	0.68	1.827	•	•	•	•	15	3
M4503	•	•	0.616	22.915	54.507	74.745	15	3
M4532	0.967	1.983	•	•	•	•	•	•

APPENDIX 2. Results of grass analyses by ICP-AES and FIA/AAS.

Sample No	Mn Grass	Fe Grass	P Grass	Mg Grass	Ca Grass	Zn Grass	Cu Grass	Se Grass	District	Zn Region
				mg/kg						
150S	122	125	1909	1018	4319	18.4	1.3	.0441	1	1
179S	204	122	1357	776	3464	10.8	1.5	.0814	1	1
149S	170	132	1442	1452	4549	17.7	1.6	.0406	1	1
132S/ 108S	134	205	2349	1407	5314	23.3	2.4	.0902	1	1
163S	298	175	1360	1439	5314	14.1	1.7		1	1
194S/ 181S	76	111	1095	1051	4127	9.6	1.2	.0328	2	1
151S	156	272	1183	1422	4525	13.3	1.4	.0298	2	1
157S	88	172	801	1568	3411	17.2	1.2	.0589	2	1
193S/ 117S	59	189	1057	1340	3388	17.4	1.8	.0490	3	2
106S	103	203	1214	2940	7910	21.7	3.8	.0742	3	2
188S	45	178	994	1662	3271	21.2	2.6	.0515	3	2
159S	58	93	1165	1394	3193	12.4	1.0	.0348	3	2
135S	109	196	1148	2824	7795	14.4	3.3	.0539	3	2
223S	122	423	1357	1694	3771	17.1	2.7	.0535	4	2
243S	62	629	1131	1374	4434	15.9	1.1	.0344	4	2
269S/ 257S	71	307	1417	1490	3525	17.8	1.7	.0324	4	2
229S	51	44	1667	1740	6516	17.0	1.0	.0339	4	2
160S	104	413	2089	1737	4917	20.3	2.7	.1068	5	1
195S/167S	82	385	1398	1141	3781	8.2	1.0	.0408	5	1
190S	92	150	1361	1799	3734	12.1	1.0	.0292	5	1
110S	103	174	2075	1554	4004	19.5	2.3	.0527	5	1
140S	83	104	1091	2201	3510	14.0	1.6	.0226	5	1
191S	78	91	1335	992	4710	9.0	1.4	.0748	6	1
020S/ 028S	81	152	2163	1717	4884	16.5	2.0	.0488	6	1
250S	104	119	1399	3371	10207	39.2	4.6	.0320	7	2
248S/ 288S	112	191	1494	2562	5206	24.3	3.2	.0188	7	2
203S	153	296	1217	1671	4115	10.9	1.1	.0235	7	2
254S	233	133	1138	1489	4555	16.1	1.5	.0338	7	2
294S	93	584	1267	1719	3592	19.0	1.7	.0206	7	2
103S/ 144S	57	134	1241	2068	5018	27.4	1.4	.0388	8	1
187S	49	159	1233	1297	2747	9.3	1.2	.0205	8	1
130S	49	91	1012	1026	4549	8.8	1.0	.0295	8	1
165S	67	122	1557	2214	6566	11.2	2.0	.0318	8	1
239S	73	96	894	1679	4956	35.4	3.5	.0193	9	3
281S	97	197	592	1447	2246	22.6	2.7	.0279	9	3
263S	40	86	1335	1813	4218	20.3	1.9	.0688	9	3
218S	21	20	228	653	1306	4.7	.7	.0315	9	3
204S/ 296S	102	632	721	1935	3370	24.0	2.7	.0323	9	3
238S	79	68	2634	1908	5398	36.1	.9	.0329	10	3
224S	59	51	1532	1801	6356	16.6	1.3	.0650	10	3
266S/ 284S	102	632	721	1935	3370	24.0	2.7	.0323	10	3
200S	447	444	2180	2345	6748	23.9	5.3	.0621	11	3
199S/ 175S	50	92	2538	2082	4931	17.1	1.1	.0892	12	2
116S	112	144	2117	1554	4117	27.5	1.4	.0305	12	2
112S	71	118	1089	2908	2205	27.3	1.9	.0368	12	2
242S	84	67	1329	1843	3231	14.5	.8	.0334	12	2
118S	66	53	1619	1344	2926	24.0	1.5	.0517	12	2
178S/ 172S	106	572	1434	1092	3300	15.5	1.6	.0346	13	3
123S	433	242	1793	1105	2847	13.1	1.3	.0435	13	3
119S	193	980	3302	2206	5310	40.3	2.4	.0410	14	2
177S/ 158S	78	329	1832	1815	4053	24.3	1.7	.0327	14	2
209S	132	229	1001	1453	3998	20.8	1.5	.0221	15	3
213S	28	192	1240	1313	2634	14.0	1.5	.0393	15	3
258S	110	280	1015	2281	3953	27.7	1.5	.0263	15	3
300S/ 230S	61	472	2202	2413	3720	35.6	2.3	.0379	15	3
265S	105	228	1792	1864	6808	19.9	3.0	.0844	15	3

APPENDIX 3. Results of leaf analyses by ICP-AES.

Sample No.	Mn Leaves	Fe Leaves	P leaves	Mg Leaves	Ca Leaves	Zn Leaves	Cu Leaves	District	Zn Region
				mg/kg					
150S	264	83	2218	2314	14405	10.5	5.9	1	1
179S	149	81	1410	1708	9514	10.9	5.6	1	1
149S	336	90	2088	2525	16978	15.2	6.3	1	1
132S/ 108S	292	39	2509	2342	13001	13.1	3.1	1	1
163S	250	101	1286	2385	12394	12.8	5.8	1	1
194S/ 181S	152	107	2200	3442	18243	14.3	5.5	2	1
151S	125	144	1634	2851	19366	15.7	8.3	2	1
157S	185	197	1442	4332	15166	17.0	6.9	2	1
193S/ 117S	160	165	1465	3261	15799	22.0	9.6	3	2
106S	94	159	1249	3891	17031	19.6	7.3	3	2
188S	72	293	1206	3987	15639	19.8	6.2	3	2
159S	88	137	2085	4789	16842	15.7	5.7	3	2
135S	95	189	1414	4046	15911	16.9	8.0	3	2
223S	131	114	1691	3249	13679	18.0	7.0	4	2
243S	79	73	1651	2310	10645	16.9	6.9	4	2
269S/ 257S	134	136	1960	2850	17563	19.2	6.5	4	2
229S	107	171	1913	3269	19417	15.0	5.6	4	2
160S	177	203	1871	2797	19153	14.8	7.5	5	1
195S/167S	133	91	2053	3641	20652	12.1	5.0	5	1
190S	171	167	1702	3607	17199	12.9	5.0	5	1
110S	143	179	2493	3235	18437	16.9	5.2	5	1
140S	148	87	1084	4033	15892	11.8	3.2	5	1
191S	135	87	1866	2838	21582	12.5	5.8	6	1
020S/ 028S	188	79	2112	3179	16783	12.1	3.6	6	1
250S	436	135	1166	3331	13276	24.0	9.4	7	2
248S/ 288S	167	95	1397	2692	13940	14.4	5.2	7	2
203S	90	210	2016	3475	14288	20.7	6.7	7	2
254S	101	112	1246	2321	11721	14.5	6.0	7	2
294S	126	285	1624	3123	19218	22.5	8.0	7	2
103S/ 144S	115	112	1264	3451	17957	14.9	3.9	8	1
187S	79	521	1803	3455	16303	15.3	6.1	8	1
130S	229	99	1533	3158	19946	14.1	5.3	8	1
165S	87	195	2522	3359	17403	14.8	7.2	8	1
239S	181	147	1373	3579	15395	16.6	5.7	9	3
281S	469	231	1313	3723	12827	14.5	4.9	9	3
263S	115	79	2001	3678	17555	15.5	5.1	9	3
218S	64	106	990	4579	15174	15.3	5.5	9	3
204S/ 296S	293	147	1270	3937	15414	20.6	5.8	9	3
238S	135	237	2689	3012	19013	27.1	8.2	10	3
224S	65	147	1918	3343	15100	19.4	7.0	10	3
266S/ 284S	293	147	1270	3937	15414	20.6	5.8	10	3
200S	284	216	1444	3155	13659	20.9	9.2	11	3
199S/ 175S	152	117	2262	4017	19642	12.4	4.8	12	2
116S	181	148	1663	3229	14079	17.9	4.7	12	2
112S	134	219	1907	4980	17305	10.8	4.9	12	2
242S	98	148	1431	3201	17667	16.4	3.9	12	2
118S	130	111	1528	3642	18276	17.9	3.8	12	2
178S/ 172S	189	332	2978	3402	19496	32.2	5.9	13	3
123S	160	234	2810	2942	14480	22.8	6.5	13	3
119S	307	106	1606	3209	12518	27.3	4.7	14	2
177S/ 158S	419	213	1803	4342	14635	27.2	12.3	14	2
209S	344	174	1000	3702	14265	18.5	4.6	15	3
213S	93	218	1910	3084	18703	20.0	6.4	15	3
258S	402	302	1886	3358	14413	28.1	6.2	15	3
300S/ 230S	92	249	1695	4219	15595	16.6	6.6	15	3
265S	164	281	2080	3482	20628	18.1	7.7	15	3

APPENDIX 4. Results of soil analyses by ICP-AES.

Sample No.	Mn Soil	Fe Soil	P Soil	Mg Soil	Ca Soil	Zn Soil	Cu Soil	Co Soil	Se Soil	District	Zn Region
				mg/kg							
150S	178	2772	124	360	349	9.8	2.6	1.6	.023	1	1
179S	208	4087	25	325	481	10.2	2.8	1.6	.028	1	1
149S	196	4941	173	499	700	13.0	2.2	1.6	.010	1	1
132S/ 108S	373	6176	216	601	568	16.8	5.2	1.6	.010	1	1
163S	98	3256	73	297	579	6.2	4.8	1.6	.010	1	1
194S/ 181S	238	10522	85	1936	1952	19.2	5.2	2.1	.015	2	1
151S	274	12362	131	2002	1596	22.0	10.4	5.4	.041	2	1
157S	395	15788	85	2447	1202	18.4	8.2	4.8	.036	2	1
193S/ 117S	356	18957	206	4543	2731	35.1	17.0	7.4	.053	3	2
106S	355	16726	123	2952	1748	23.6	16.4	7.2	.309	3	2
188S	559	29733	236	5015	4197	40.8	41.2	13.6	.094	3	2
159S	331	13258	171	3144	2380	24.8	13.6	5.4	.028	3	2
135S	201	12942	152	3593	1571	26.6	10.2	5.4	.022	3	2
223S	674	48415	284	6933	5351	57.3	19.9	15.3	.085	4	2
243S	561	39074	144	7906	1554	40.0	15.1	15.3	.076	4	2
269S/ 257S	678	33722	457	3789	5220	64.6	15.1	8.4	.069	4	2
229S	670	9460	160	7213	9925	66.6	24.2	18.8	.107	4	2
160S	360	8481	120	1313	1722	15.0	6.6	1.6	.025	5	1
195S/167S	184	6241	99	1615	1167	17.1	3.3	1.6	.010	5	1
190S	222	7453	143	2440	1462	20.2	9.0	3.6	.029	5	1
110S	264	11304	164	3200	1857	29.6	4.0	1.6	.038	5	1
140S	223	10009	95	2671	1153	17.8	3.0	3.4	.052	5	1
191S	274	7860	104	1526	1342	23.4	13.2	6.0	.010	6	1
020S/ 028S	188	6979	123	2044	1820	18.7	4.0	1.6	.016	6	1
250S	374	22034	204	3710	1303	33.7	15.8	9.3	.093	7	2
248S/ 288S	690	28457	277	6994	3838	56.9	16.1	11.2	.067	7	2
203S	658	35575	740	5119	7505	75.6	19.0	10.2	.068	7	2
254S	710	43146	525	4587	6727	91.4	19.6	10.4	.088	7	2
294S	834	43230	454	3492	5411	56.2	10.0	7.8	.066	7	2
103S/ 144S	417	17320	147	3192	2126	25.5	12.5	8.1	.053	8	1
187S	264	5076	49	3664	2398	24.2	5.2	4.6	.033	8	1
130S	431	18794	168	2743	2418	28.2	13.6	6.8	.053	8	1
165S	322	12121	173	3898	2460	26.6	10.0	5.8	.047	8	1
239S	689	30314	287	3738	2434	68.6	21.2	9.0	.093	9	3
281S	768	42964	382	6232	1722	81.2	41.4	14.2	.180	9	3
263S	447	21399	197	5591	2763	37.8	24.2	12.8	.070	9	3
218S	524	28264	157	7078	3842	41.9	26.7	13.8	.054	9	3
204S/ 296S	1032	74314	380	5591	4120	61.8	52.1	21.8	.207	9	3
238S	529	23820	266	3671	2912	45.6	15.2	7.9	.109	10	3
224S	785	38996	854	7035	7104	99.2	32.4	12.8	.113	10	3
266S/ 284S	1032	74314	380	5591	4120	61.8	52.1	21.8	.207	10	3
200S	450	21708	298	2703	2052	45.4	13.4	8.2	.091	11	3
199S/ 175S	242	10644	140	2318	2572	27.2	15.4	4.4	.077	12	2
116S	155	8464	151	2431	1118	22.2	3.8	3.0	.010	12	2
112S	311	19807	133	4145	1272	19.8	12.8	16.8	.105	12	2
242S	337	16482	212	3670	2248	31.8	15.8	8.6	.049	12	2
118S	177	7126	112	1663	1228	17.6	5.6	3.4	.031	12	2
178S/ 172S	904	46524	467	2934	3455	65.3	15.5	7.5	.053	13	3
123S	1381	32246	444	1376	1749	70.6	6.8	3.8	.071	13	3
119S	1170	40454	416	1782	1580	89.8	10.2	4.2	.102	14	2
177S/ 158S	1315	61787	470	5050	2569	110.9	23.7	11.1	.092	14	2
209S	1272	71767	199	2180	1931	71.9	5.8	2.3	•	15	3
213S	571	13100	177	5625	5061	68.4	18.2	11.4	.047	15	3
258S	692	9205	102	4378	3102	70.8	27.6	21.0	.072	15	3
300S/ 230S	643	25533	500	6413	6144	68.3	19.3	8.3	.074	15	3
265S	776	32562	879	7637	5291	80.0	23.2	13.4	.070	15	3

APPENDIX 5. Results of stream sediment analyses by AAS.

Sample Number	Mn Sediment	Zn Sediment	Cu Sediment	Co Sediment	District	Zn Region
		mg/kg				
2947	320	19	6	4	1	1
2990	290	27	4	4	1	1
11005	490	38	10	7	1	1
11142	760	22	6	7	1	1
11019	730	46	16	8	1	1
1812	500	22	12	7	2	1
1949	280	29	8	5	2	1
2000	450	33	15	9	2	1
1880	200	22	6	6	2	1
10627	490	31	11	8	2	1
4453	560	42	8	8	3	2
4644	410	37	27	13	3	2
4635	650	50	48	17	3	2
4656	850	43	58	15	3	2
4600	500	37	22	9	3	2
4981	770	100	45	17	3	2
4990	240	26	14	4	3	2
4648	340	38	35	6	3	2
4602	640	31	21	12	3	2
4517	310	46	9	8	3	2
4530	470	36	24	12	3	2
4587	910	48	30	11	3	2
12363	610	41	20	10	3	2
4042	760	33	13	7	3	2
4111	740	53	38	16	3	2
4979	370	39	19	9	3	2
4029	500	38	16	9	3	2
4195	420	49	10	7	3	2
4452	270	34	17	8	3	2
4589	560	34	37	12	3	2
4313	780	63	30	19	3	2
4581	720	44	47	13	3	2
4236	450	33	18	11	3	2
4735	660	35	14	10	3	2
4924	550	40	24	12	3	2
522	500	51	12	9	4	2
383	1330	46	43	12	4	2
557	830	98	19	11	4	2
440	620	34	13	10	4	2
463	1000	104	26	16	4	2
346	650	83	17	10	4	2
150	560	46	17	10	4	2
379	550	53	13	8	4	2
331	1380	124	28	20	4	2
419	720	51	19	16	4	2
539	370	49	10	5	4	2
328	550	66	20	13	4	2
332	710	65	15	12	4	2
472	680	61	15	10	4	2
504	690	83	14	12	4	2
439	780	73	14	10	4	2
456	510	46	18	11	4	2
654	670	75	14	11	4	2
429	640	55	19	11	4	2
199	640	47	22	10	4	2
447	940	102	22	14	4	2
425	1080	79	15	11	4	2
695	1110	74	10	9	4	2
680	600	57	14	9	4	2

Sample Number	Mn Sediment	Zn Sediment	Cu Sediment	Co Sediment	District	Zn Region
		mg/kg				
338	610	44	16	10	4	2
22169	870	86	16	16	4	2
376	530	63	11	8	4	2
22170	1040	85	20	22	4	2
147	1050	94	27	18	4	2
101	470	38	24	9	4	2
457	440	30	6	4	4	2
22168	940	49	24	15	4	2
7781	660	67	30	14	5	1
8316	310	33	18	8	5	1
8402	330	27	4	6	5	1
7900	680	39	29	15	5	1
8409	850	36	35	23	5	1
8381	320	30	34	8	5	1
7737	210	18	6	3	5	1
7576	900	43	41	24	5	1
8195	280	32	7	6	5	1
8363	360	45	11	8	5	1
7992	310	21	27	6	5	1
8043	130	23	4	3	5	1
7823	240	29	12	5	5	1
8073	240	22	9	4	5	1
7828	260	23	3	5	5	1
7660	170	22	5	3	6	1
7542	190	25	5	3	6	1
7922	260	25	6	5	6	1
8014	240	25	6	4	6	1
7998	180	21	7	3	6	1
8231	190	14	12	4	6	1
8008	220	25	9	5	6	1
7773	240	27	7	5	6	1
7969	200	19	5	3	6	1
7940	290	30	6	4	6	1
22157	1440	50	14	10	7	2
175	900	70	19	13	7	2
164	870	78	25	19	7	2
30	820	67	19	14	7	2
22161	1280	89	26	18	7	2
22132	450	32	15	9	7	2
22073	1540	68	12	10	7	2
57	750	47	16	18	7	2
22109	770	68	12	8	7	2
96	610	41	16	8	7	2
3	850	70	67	16	7	2
62	760	76	24	14	7	2
22064	1060	52	14	10	7	2
117	1170	98	29	11	7	2
1	430	23	13	5	7	2
58	500	50	12	8	7	2
60	810	70	31	17	7	2
93	610	46	26	15	7	2
138	930	91	18	9	7	2
100	810	78	16	8	7	2
22156	750	49	15	13	7	2
22025	970	107	23	11	7	2
22119	1180	103	21	12	7	2
56	970	86	26	14	7	2
22100	590	78	18	7	7	2
1922	300	23	9	5	8	1

Sample Number	Mn Sediment	Zn Sediment	Cu Sediment	Co Sediment	District	Zn Region
		mg/kg				
1095	400	24	12	5	8	1
1473	390	27	34	11	8	1
1520	400	21	23	10	8	1
1049	430	26	14	8	8	1
10703	220	21	7	3	8	1
2011	300	23	8	5	8	1
1446	300	24	19	8	8	1
1937	210	28	20	8	8	1
641	950	87	10	7	9	3
689	890	77	21	9	9	3
478	720	91	27	13	9	3
690	1090	69	18	10	9	3
494	720	75	13	7	9	3
499	890	76	40	21	9	3
613	1410	85	47	23	9	3
667	1050	98	27	17	9	3
489	960	79	27	15	9	3
497	250	22	10	7	9	3
479	1380	165	15	8	9	3
343	1350	98	51	27	9	3
371	820	99	61	24	9	3
344	1140	100	24	13	9	3
374	1560	150	36	17	9	3
370	800	72	20	11	9	3
679	1010	52	28	20	9	3
368	730	51	26	13	9	3
3726	1210	138	50	20	10	3
3932	820	79	26	14	10	3
3612	1070	119	38	21	10	3
3957	800	95	24	13	10	3
3952	890	91	29	17	10	3
3856	840	78	21	14	10	3
3756	680	64	16	11	10	3
3592	960	98	22	11	10	3
3019	1150	122	29	18	11	3
3003	850	75	22	13	11	3
7183	400	36	25	9	12	2
13262	210	26	10	6	12	2
13384	450	47	18	10	12	2
13491	250	25	8	6	12	2
13382	200	23	8	5	12	2
13403	290	29	10	6	12	2
12098	625	45	30	25	12	2
13448	170	19	9	6	12	2
4314	760	62	40	44	12	2
13338	1120	51	15	13	12	2
7432	400	39	10	8	12	2
4759	520	59	41	38	12	2
13520	220	27	4	4	12	2
7019	370	33	11	6	12	2
13359	480	32	23	8	12	2
13495	250	17	10	6	12	2
3168	1380	106	7	3	13	3
3157	1040	113	21	12	13	3
3113	1070	60	19	10	14	2
6185	900	61	12	7	14	2
3086	1030	77	22	10	15	3
3026	530	56	22	11	15	3
3021	1680	150	14	7	15	3

Sample Number	Mn Sediment	Zn Sediment	Cu Sediment	Co Sediment	District	Zn Region
		mg/kg				
3156	1450	142	11	4	15	3
3199	890	78	35	11	15	3
3073	840	67	21	13	15	3
3163	1150	82	27	10	15	3
3002	1130	70	26	13	15	3
3584	910	169	38	16	15	3
3529	1750	166	20	12	15	3
3049	910	110	36	13	15	3
3188	760	133	45	16	15	3