British Geological Survey

DFID
Department for
International Development

TECHNICAL REPORT WC/96/54
Overseas Geology Series

SOIL, GRAIN AND WATER CHEMISTRY AND HUMAN SELENIUM IMBALANCES IN ENSHI DISTRICT, HUBEI PROVINCE, CHINA

F M FORDYCE, G ZHANG, K GREEN and X LIU

Natural
Environment
Research
Council

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

DFID
Department for
International Development

British Geological Survey
TECHNICAL REPORT WC/96/54
Overseas Geology Series

SOIL, GRAIN AND WATER CHEMISTRY AND HUMAN SELENIUM IMBALANCES IN ENSHI DISTRICT, HUBEI PROVINCE, CHINA.

F M FORDYCE, G ZHANG, K GREEN AND X LIU

WITH CONTRIBUTIONS FROM

M ALLEN	BGS SAMPLE PREPARATION
M CAVE	BGS ANALYTICAL METHODS
V HARDS	BGS XRD DETERMINATIONS
B VICKERS	BGS CEC AND LOI DETERMINATIONS
L JIAXI & X LIU	IRMA ANALYTICAL METHODS

This document is an output from a project funded by the UK Department for International Development (DFID). The views expressed in this report are not necessarily those of the DFID.

DFID classification:
Sub-sector: Geoscience
Theme: Identify and ameliorate minerals-related and other geochemical toxic hazards
Project Title: Prediction and Remediation of Human Selenium Imbalances
Reference: R6227

Bibliographic reference:
Fordyce F M, Zhang G, Green K and Liu X. 1998.
Soil, Grain and Water Chemistry and Human Selenium Imbalances
in Enshi District, Hubei Province, China.
BGS Technical Report WC/96/54

Keywords: China, environmental geochemistry, human selenium imbalances

Front cover illustration: Patient from Enshi District suffering hair loss
as a result of selenium toxicity. (Photo: Prof Mao Dajun)

Keyworth, Nottingham, British Geological Survey 1998

EXECUTIVE SUMMARY

Background

Many elements which are essential to human and other animal health in small doses can be toxic if ingested in excess. Selenium (Se), a naturally occurring metalloid element is found in all natural materials on earth including rocks, soils, waters, air, plant and animal tissues. Since the early 1930's, it has been recognised that Se toxicity causes hoof disorders and hair loss in livestock. Se was also identified as an essential trace element to humans and other animals in the late 1950's. It forms a vital constituent of the biologically important enzyme glutathione peroxidase which acts as an anti-oxidant preventing cell degeneration. Se deficiency has been implicated in the aetiology of several diseases including cancer, muscular dystrophy, muscular sclerosis and cystic fibrosis. Se can be assimilated in humans through several pathways including food, drinking water and inhalation of Se-bearing particles from the atmosphere. In the majority of situations, food is the most important source of Se, as levels in water are very low. The narrow range between deficiency levels (<40 μg per day) and toxic levels in susceptible people (> 900 μg per day) makes it necessary to carefully control the amount of Se in the diet.

In China, Se deficiency has been linked to an endemic degenerative heart disease known as Keshan Disease (KD) and an endemic osteoarthropathy which causes deformity of affected joints, known as Kaschin-Beck Disease. These diseases occur in a geographic belt stretching from Heilongjiang Province in north-east China to Yunnan Province in the south-west. In the period between 1959 and 1970, peak KD incidence rates exceeded 40 per 100 000 (approximately 8500 cases per annum) with 1400 - 3000 deaths recorded each year. Incidence rates have since fallen to less than 5 per 100 000 with approximately 1000 new cases reported annually (Levander, 1986). Se toxicity (selenosis) resulting in hair and nail loss and disorders of the nervous system in the human population, has also been recorded in Enshi District, Hubei Province and in Ziyang County, Shanxi Province. China possesses one of the best epidemiological databases in the world on Se-related diseases which has been used in conjunction with geochemical data to demonstrate a significant geochemical control on human Se exposure. However, the precise geographical areas at risk and the geochemical controls on selenium availability have yet to be established.

The Study

This report outlines the results of a collaborative study undertaken by the British Geological Survey (BGS), the Institute of Rock and Mineral Analysis (IRMA), Beijing and the Enshi Public Health Department to investigate Se-related disease incidence in Enshi District, Hubei Province. The present study forms part of a British Government Department for International Development (DFID) Technology Development and Research (TDR) Project (R6227), the objectives of which are (i) to develop a methodology for delineating areas where selenium deficiency or toxicity may pose a health risk and cause health disorders and (ii) mitigate problems of natural Se imbalances by designing and implementing land-use planning, crop and dietary supplementation methods.

Epidemiological studies concentrating on the dietary intake and Se status of the local population were carried out in the Enshi area during the 1970's and 1980's in response to outbreaks of KD in the late 1960's and human selenosis in the late 1950's and early 1960's. These studies established the link between disease and the local Se environment.

Yang et al. (1983) compared levels of Se in soil, foods, drinking water and human blood, hair, nail and urine from the Enshi area with other regions of China and demonstrated that the endemic selenium intoxication of humans in Enshi was related to the occurrence of Permian Se-enriched coal-bearing strata. These comprise interbedded carbonaceous shales (known locally as "stone coal"), carbonaceous siliceous rocks, limestones and dolostones of varying carbon contents (Zheng et al., 1992). Selenium concentrations in samples from areas underlain by carbonaceous strata were up to 1000 times higher than in samples from selenium deficient areas where Keshan Disease was prevalent. Although Yang et al. (1983) speculated that the water soluble (plant available) portion of soil selenium may be influenced by a number of factors, including total soil selenium, humus and iron content and soil pH, the impact and relative importance of these geochemical factors was not quantified.

Yang et al. (1989b) evaluated the broad relationships between total soil selenium, Se in popular foods and drinking water, dietary Se-intake and a range of indicators of human Se status, including whole blood, hair, fingernail, toenail and urine for three sites with low, medium and high Se levels in Enshi District.

Unfortunately, neither of these studies provided information which permitted a detailed evaluation of the relationships between environmental Se concentrations and human Se status at the village level. In particular, they did not elucidate why some villages underlain by carbonaceous strata had several cases of Se toxicosis whereas other villages sited in apparently similar geological and geochemical environments had no recorded cases of human or animal toxicosis.

The current study was designed to address these knowledge gaps and to use the new information on geochemical controls to identify strategies which may help enhance the selenium status of residents in selenium deficient areas and reduce the risk of selenium toxicity to people living in the high selenium areas of Enshi District.

During the present study, fifteen villages from three Se environments in Enshi District were investigated. Soil, grain, drinking water and human hair samples were collected from five Low-Se-Keshan-Disease villages (LK), five High-Se-No-toxicity (HN) villages, and five High-Se-Toxicity (HT) villages. This sampling strategy was designed to establish the relationship between the human Se status of communities (represented by hair samples) and their dietary Se intake (represented by grain and drinking water samples) to the local geochemical environment characterised by cultivated soils. Where possible, soil, grain and hair samples were collected from the same farm. Grain (maize-corn) samples were collected from village grain stores therefore it was not possible to relate the grain samples directly to the soil samples.

Results

Total and water soluble (bioavailable) Se in soil, together with total Se in water, grain and hair samples indicate that Se levels in the LK villages are 17 to 690 times lower than in the HN and HT villages (Table i). Low levels of Se are associated with Jurassic siltstones and sandstones which outcrop on the north-west of Enshi District whereas high environmental Se occurs in areas underlain by Permian carbonaceous strata. These results confirm the fundamental geological control on Se distribution in Enshi District and the link between environmental Se levels and the Se status of the local population.

Table (i): Comparisons between Enshi village geometric mean values for Se in soil, grain and hair with recommended thresholds for deficient, marginal and excessive Se.

Village Code	Soil Tot Se µg/g	Soil Water Sol Se µg/g	Grain Tot Se µg/g	Hair Tot Se µg/g
Deficient *	< 0.125	<0.003	< 0.025	< 0.2
Marginal *	0.125 - 0.175	0.003 - 0.006	0.025 - 0.04	0.2 - 0.5
Mod - High *	0.175 - 3	0.006 - 0.02	0.04 - 1	0.5 - 3
Excessive *	3	0.02	1	3
LK1	0.119	0.000235	0.003	0.334
LK2	0.069	0.00021	0.001	0.345
LK3	0.118	0.000207	0.001	0.265
LK4	0.064	0.000427	0.003	0.252
LK5	0.152	0.000445	0.001	0.339
HN1	19.136	0.061	1.085	19.179
HN2	19.543	0.08	1.316	22.029
HN3	6.227	0.002	0.094	3.703
HN4	2.071	0.002	0.042	0.692
HN5	3.651	0.004	0.041	1.627
HT1	17.881	0.049	1.635	54.4
HT2	15.525	0.027	1.156	31.2
HT3	4.272	0.026	1.66	28.113
HT4	4.599	0.016	2.902	4.562
HT5	13.86	0.01	0.55	29.211

* Tan (1989) Mod = moderate Tot = total Sol = soluble

Low Selenium and Keshan Disease (LK) Villages

Geochemistry, geochemical controls and risk assessment

Within the low-Se-KD (LK) villages, Se in soil is associated with organic matter and is probably bound in organic complexes which restrict its availability to plants in the food chain. Soils with higher Fe concentrations have lower water soluble Se levels suggesting that complexing with Fe oxyhydroxides also restricts the bioavailability of Se within these villages. Selenium in grain correlates positively with Se in spring water, which may be important if spring waters are used to irrigate crops. Sulphur in soil correlates negatively with Se in grain suggesting that sulphur may inhibit the uptake of Se by plants.

The majority of the soil and grain samples in the LK villages are deficient in Se whereas most hair samples have marginal Se concentrations (Table i). The levels of Se in hair are higher than would be predicted from levels in grain and drinking water indicating that other foods containing Se must contribute significantly to the Se status of the population. The present incidence of KD in the LK villages is unknown but the results of this study suggest that the population may be at risk from Se deficiency disorders and measures may need to be taken to enhance Se levels in the diet of the local population.

Yang et al. (1989b) demonstrated that the population of a site in Enshi District characterised by relatively low environmental Se had average hair Se of 0.69 µg/g and an average daily dietary intake of 66 µg Se. An average hair Se concentration of 0.52 µg/g has been recorded for healthy adults in Glasgow (Harrison et al., 1995) which could be surmised to reflect the average selenium intake in the UK of 43 µg/day (1994 data; MAFF, 1997). No information is readily available on the current daily dietary Se intake of people in the Enshi LK villages. However, on the basis of the above, the present study has shown that the average hair Se in the LK villages is about 0.31 µg/g which implies a daily dietary intake of about 25 µg Se.

The UK Department of Health (DOH) Dietary Reference Nutrient Intake is currently set at 60 µg/day for adult women and 75 µg/day for adult men with a Lower Reference Nutrient Intake level of 40 µg/day for adults (MAFF, 1997). Average selenium intake in the UK has declined from an average of 60 µg/day in 1985 to 43 µg/day in 1994 and 33 µg/day in 1995 (MAFF, 1997). The UK Government Committee on Medical Aspects of Food and Nutrition Policy is in the process of assessing the nutritional significance of these data and have not yet made any recommendations for enhancing the dietary Se intake of the UK population. In contrast, the average dietary intake in Finland, a country which uses Se fertiliser to enhance the Se status of the population, is now approximately 80 µg/day.

Although the hair Se levels of the Enshi LK villages are low (0.31 µg/g), they are not as low as levels in the Zhangjiakou District of China (0.19 to 0.20 µg/g) where Keshan Disease is still reported. Average hair Se levels in the Enshi LK villages are higher than values recorded in Zhangjiakou villages where KD no longer occurs (0.24 µg/g) (Johnson et al., 1996).

Although the Se status of the population in the Enshi LK villages is probably below the current UK DOH Lower Reference Nutrient Intake level of 40 µg/day, the need for remedial action, through the use of Se fertilisers, for example, is not clear even though it might be recommended as a precautionary measure. Prior to such action being taken, it is recommended that a dietary survey be carried out to determine the range of Se intake of the local population. This will provide a sound basis for assessing the need for dietary Se supplementation.

Remediation strategy

Should a dietary survey confirm that the daily Se intake is indeed only 20-30 µg, then remedial action involving the use of Se fertilisers to increase grain, vegetable and farm animal Se concentrations would be recommended as a precautionary measure. The intake of organic Se in food is more natural and possibly more beneficial than using supplementation tablets containing sodium selenite, for example. Furthermore, Se tablets are probably beyond the economic means of the local population.

The relative benefits of additions of Se fertiliser to soil or foliar application direct to plants should be investigated as the results of the present study and the Zhangjiakou study (Johnson et al., 1996) strongly suggest that soil Se in low Se environments is fixed by organic matter and is therefore not readily bioavailable. As a result, the addition of Se fertiliser to soil may not increase crop Se levels. Care should be taken not to introduce Se toxicity problems into low Se areas through the use of certain phosphate fertilisers which can contain very high levels of Se.

Se rich fertiliser produced in Enshi District from the carbonaceous shale by the Enshi Coal Bureau is undergoing agronomic testing to assess the suitability of this product for remediation strategies in low Se areas. Se and other elements are extracted from the carbonaceous shale and added to commercial NPK fertiliser (Fordyce, 1996). Field trials of the Se fertiliser are being carried out by the IRMA in conjunction with Enshi Local Government and Zhangjiakou and Cixian agronomists. The results of these investigations will be reported elsewhere.

It is also recommended that the population is encouraged to supplement locally grown produce with foodstuffs from non-Se-deficient areas and to increase the level of Se-rich foods in the diet. However, it is recognised that some small-scale farmers may not have the financial resources to diversify their diets in the manner recommended.

High Selenium and Selenosis (HN and HT) Villages

Geochemistry, geochemical controls and risk assessment

In the high Se (HN and HT) villages, soil Se levels reflect the distribution of the carbonaceous strata. The highest Se levels are associated with high levels of other elements common in carbonaceous rocks, such as As, Cd, Cu, F, Hg, S, V and Zn, as well as with high levels of organic matter. The association between high Se in soils and organic matter is probably a reflection of bedrock geochemistry rather than the complexing of soil Se by secondary, biologically derived, organic matter. Se may also be held in the form of sulphide minerals, such as pyrite, associated with the carbonaceous shale in the HT villages.

The bioavailability of Se (indicated by water soluble Se) is related to soil total Se levels and pH. However, negative associations between water soluble Se with Fe and LOI suggest that Se availability may also be restricted by adsorption onto Fe oxyhydroxides and secondary, biologically derived, organic matter. Levels of total and water soluble Se in soil show marked variations between and within individual villages reflecting localised changes in lithology. The proportion of crops grown on relatively low or very high Se soils in a village may, in part, determine whether excessive Se levels affect individuals within villages. Individuals at greatest risk may be those with fields sited directly over carbonaceous shale or higher pH soils associated with limestones whereas neighbours with fields on siliceous rocks are less at risk.

On the basis of the present study, there is little evidence to suggest that the drying of maize-corn samples over carbonaceous shale fires in the HN and HT villages causes significant Se contamination of maize-corn. Tests on three grain samples washed in deionised water and 1% HCl solution indicated that only 0.0005% of the Se contained in maize-corn samples from the HN and HT villages was removed by washing. Grain samples were not therefore washed prior to analysis.

In the HN/ HT villages, grain Se, soil total Se and soil water soluble Se correlate significantly indicating the influence of soil Se levels on the amount of Se entering the food chain. In Xin Tang (HT3) and Yu Tang Ba (HT4) villages, Se levels in grain are higher than would be expected from the levels of Se in soil. It is possible that higher pH and Ca, indicating a greater dominance of limestone lithologies, make Se more available for plant uptake. Although there is no direct evidence from the present study, lower soil phosphorous concentrations in these two villages may also reduce plant growth, effectively concentrating Se in the plants.

Grain and hair Se levels correlate in the HN and HT villages confirming the link between locally grown crops and human Se status. Markedly greater concentrations of Se have been reported in vegetables than in cereal crops grown in the Enshi high Se area and it is probable that Se levels in hair are influenced by the proportions of vegetables, rice and maize-corn in the diet. The consumption of food from outside the Enshi area will also affect the Se status of the population. Estimates of dietary Se intake from the present study indicate that Se in drinking water may contribute 33% of the combined grain and water intake of Se in the HN villages.

Excessive levels of Se in hair (> 3 μg/g) were recorded in all residents sampled in the HT villages and in Luojiaba (HN1) and Bajiao (HN2). The majority of soil and grain samples in these two HN villages also contain excessive Se levels. The results of the present study suggest that the risk of human Se toxicity in Luojiaba (HN1) and Bajiao (HN2) is similar to the HT villages, even though no selenosis has ever been recorded in these two villages.

Estimates from the present study indicate that individuals may consume greater than >900 μg/day Se (toxic level, Yang & Xia, 1985) particularly if all crops are grown on Se-available soils in a village. Despite the high Se status of the local population, no incidences of selenosis have been reported in recent years in Enshi District. This suggests that the local population may have adapted to the high Se intake and that although soil, grain, water and hair samples give an indication of the potential risk of human selenosis, other factors may precipitate the onset of the disease.

Yang et al. (1983) indicated that the majority of outbreaks of human selenosis occurred in Enshi District during the early 1960's and coincided with a period of drought and rice crop failure. It is likely that the shortage of food combined with a greater proportion of vegetables and a lesser proportion of protein in the diet at this time contributed to the incidence of the disease. These factors may also explain why selenosis occurred in some villages with high environmental levels of Se and not in others.

Remediation strategy

Although no instances of selenosis have occurred in Enshi District in recent years, the results of this study suggest that the population is at risk from Se toxicity and it is recommended that the level of Se intake should be reduced in the local diet. Where possible, villagers should avoid cultivating high Se soils directly underlain by carbonaceous shale. In particular, villagers should be discouraged from growing Se-accumulating vegetables adjacent to outcrops of the carbonaceous shale. However, it is recognised that population pressure may require all land in a village to be cultivated. The local people should also be encouraged to increase the proportion of food products from outside the high Se area in their diet. Care should be taken in the HN and HT villages not to increase the levels of Se through the application of high Se-bearing phosphate fertiliser. The effects of NPK fertiliser application to the high Se soils should be tested as increased phosphate has been shown to raise the level of Se uptake by plants. Villagers should continue to be discouraged from dressing soil with coal ash and other products derived from the carbonaceous shale and with lime which may raise the soil pH making Se more bioavailable. In two of the villages studied, alternative water sources that are not associated with the carbonaceous shale have been identified. In order to lower the dietary intake of Se in the other villages, alternative water sources should be found within the village areas where possible.

Risk Mapping Methodologies

Previous investigations in China (Tan et al., 1989; Yang et al., 1983) and other areas of the world (for example, USA, Venezuela, New Zealand, South Africa, India, UK and Finland, Mayland, 1994) have shown that geochemical data for total Se determinations in soils and stream sediments can be used to delineate areas at possible risk from Se deficiency and toxicity on a regional scale. However, the results of the present study demonstrate that information on soil water soluble Se, Ca, Fe, P and organic matter contents and soil pH are required to define more clearly, specific villages and populations at risk, on the basis of geochemical data. This method of assessing risk involves a number of analyses and careful interpretation of the results. Alternatively, grain total Se levels give a good indication of the likely human Se status and it is therefore recommended that grain total Se levels provide the simplest means of assessing potential risk at the village scale. Within villages in the Enshi high- Se region, Se levels vary markedly. In order to asses the risk of Se toxicity to individuals, detailed sampling of soil and crops from specific fields would be required.

In the HN and HT villages, if it is not possible to carry out geochemical surveys and the analysis of grain or crop samples, mapping the area underlain by carbonaceous shale using local knowledge of carbonaceous shale outcrops and the amount of carbonaceous fragments in soil will identify areas at greatest risk. Equally, mapping areas where limestones occur adjacent to carbonaceous shale and a simple soil pH test can be used to indicate areas where high soil pH may increase Se bioavailability.

Recommendations for Further Investigations

Future investigations in the Enshi area should attempt to relate rock, soil, grain and human samples from the same location directly in order to confirm the very localised variations in environmental Se levels in the HN and HT villages and define agricultural risk areas within villages. An initial detailed soil geochemical study of one of the villages with widely varying soil Se levels should be carried out to evaluate the precise relationship between soil Se and geology. Further veterinary and medical studies are also required to determine the present incidence of (i) clinical and sub-clinical Se toxicity in humans and other animals; (ii) Se-deficiency disorders; and (iii) to assess the health effects of long term deficiency and exposure to high Se levels. The impact of Se inhalation from carbonaceous shale smoke and locally grown tobacco on human Se status should also be assessed.

The present study has defined more clearly the controls on Se availability in the environment of Enshi District and the relationships between environmental Se concentrations and human Se status at the village level. The results confirm the general conclusions of previous studies carried out as part of the present project in the Se-deficient Zhangjiakou area of China (Johnson et al., 1996). These results also have broader application to other Se deficient and excessive environments in China and other countries where Se-deficiency may have a negative impact on human health, such as Sri Lanka and Zaire were Se-deficiency has been implicated as a causative factor in iodine deficiency disorders (IDD).

CONTENTS

LIST OF FIGURES

LIST OF PLATES

LIST OF TABLES

ABBREVIATIONS USED IN THIS REPORT

AFS	Atomic Fluorescence Spectrometry
BGS	British Geological Survey
BSI	British Standards Institute
CAGS	Chinese Academy of Geological Sciences
CEC	Cation Exchange Capacity
DFID	Department for International Development
DOH	Department of Health
GSH-Px	Glutathione-peroxidase
HPLC	High Precision Liquid Chromatography
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IDD	Iodine deficiency disorders
IGCP	International Geological Correlation Programme
IRMA	Institute of Rock and Mineral Analysis
KD	Keshan Disease
LOD	Limit of Detection
LOI	Loss on Ignition
MAFF	Ministry of Agriculture, Fisheries and Food
MFS	Mass Fluorescence Spectrometry
NERC	Natural Environmental Research Council
NRCCRM	National Research Centre for Certified Reference Materials
TDR	Technical Development and Research
TOC	Total Organic Carbon
WHO	World Health Organisation
WRC	Water Research Council

1. INTRODUCTION

Approximately 30 of the 92 naturally occurring elements in the earth's surface are considered essential for human, animal and plant health in small doses, but can be toxic if ingested in excess. Elements can be assimilated by humans through several pathways including the food chain, drinking water and inhalation of particulates from the atmosphere. Selenium (Se) is a naturally occurring metalloid element which is essential to human and other animal health in trace amounts but is harmful in excess. The narrow range between deficiency levels (< 40 µg/day) and toxic levels in susceptible people (> 900 µg/day) (Yang & Xia, 1995) in food makes it necessary to carefully control the levels of intake by humans and other animals.

Se toxicity problems in livestock have been recorded for hundreds of years. Marco Polo reported a necrotic hoof disease in horses during travels in China in the 13th century. Similar problems were recorded in livestock in Colombia in 1560 and in South Dakota (USA) in the mid-19th century where the symptoms were termed 'alkali disease'. In 1931, this disease, which is characterised by hair and hoof loss and poor productivity, was identified as selenium toxicosis (selenosis). Localised seleniferous areas have been reported in Ireland, Israel, Australia, Russia, Venezuela, China, USA and South Africa (Mayland, 1994). In China, human selenosis was reported in Enshi District, Hubei Province and in Ziyang County, Shanxi Province during the 1960's resulting in hair and nail loss and disorders of the nervous system (Yang et al., 1983).

Se was identified as an essential trace element to other animals and humans in the late 1950's and early 1960's. It forms a vital constituent of the biologically important enzyme glutathione peroxidase (GSH-Px) which acts as an anti-oxidant preventing cell degeneration . In animals, Se deficiency has been linked to muscular weakness and muscular dystrophy but also causes reduced appetite, poor growth and reproductive capacity and embryonic deformities. These disorders are generally described as 'white muscle disease'. Se deficiency in crops and livestock have been reported in the USA, UK, Finland, Sri Lanka, New Zealand, Australia, India and Canada (Mayland, 1994).

In most non-industrial situations, Se intake into the human body is dependent on diet and is particularly related to the Se content of food as Se concentrations in water are generally very low. Relationships between low soil and crop Se and the incidence of cardiomyopathic and osteoarthropathic disorders have been recorded in various parts of China (Mayland, 1994).

Keshan Disease (KD), an endemic, degenerative heart disease thought to be attributed to Se deficiency was first described in China in 1935. Chinese scientists linked the disease to Se deficiency as it bore similarities to 'white muscle disease' in animals which occurred in the same geographic belt stretching from Heilongjiang Province in the north-east of China to Yunnan province in the south-west (Figure 1). Subsequent investigations in China demonstrated that low environmental Se in soils and crops corresponded to low Se status of the population in the belt. Further proof of the link between KD disease and Se levels was apparent when human Se supplementation trials resulted in a significant reduction in the disease incidence rate. In the period between 1959 and 1970, peak KD incidence rates exceeded 40 per 100 000 (approximately 8500 per annum) with 1400 - 3000 deaths recorded each year. Incidence rates have since fallen to less than 5 per 100 000 with approximately 1000 new cases reported annually (Levander, 1986). Kaschin-Beck disease, an endemic osteoarthropathy causing deformity of the affected joints, is also recorded in the low Se belt and Se deficiency is thought to be a contributing factor to the onset of this disease (Tan et al., 1989).

China possesses one of the best epidemiological databases in the world on Se-related diseases including information on the incidence and distribution of KD and human selenosis. This data has been used in conjunction with geochemical databases to demonstrate a significant geological control on human Se exposure. However, the precise geographical areas at risk and the geochemical controls on selenium availability have yet to be established.

The present study forms part of a British Government Department for International Development (DFID) Technical Development and Research (TDR) project to investigate methods of predicting and remediating human Se imbalances (Project R6227). During the period 1995-1996 case-studies of three regions of China with histories of Se-related human health problems were undertaken as follows:

Area 1. Zhangjiakou District, Hebei Province, situated in the north of China in the KD incidence belt (Figure 1).

Area 2. Enshi District, Hubei Province, in south-central China. Enshi District is one of two areas in China where Se toxicity problems have been identified in humans. In addition, KD is reported in the north-west corner of the District which lies within the Se deficiency belt shown in Figure 1.

Area 3. Cixian District, Hebei Province, to the south-west of Beijing is under investigation to assess the relationship between the Se status of the population and the incidence of oesophageal cancer (Figure 1).

This report outlines the results of a collaborative study of human selenium imbalances by the British Geological Survey (BGS), the Institute of Rock and Mineral Analysis (IRMA) and the Public Health Department in Enshi District. Results from the Zhangjiakou and Cixian study areas are described in detail in Johnson et al. (1996) and Appleton et al. (In Prep.) respectively.

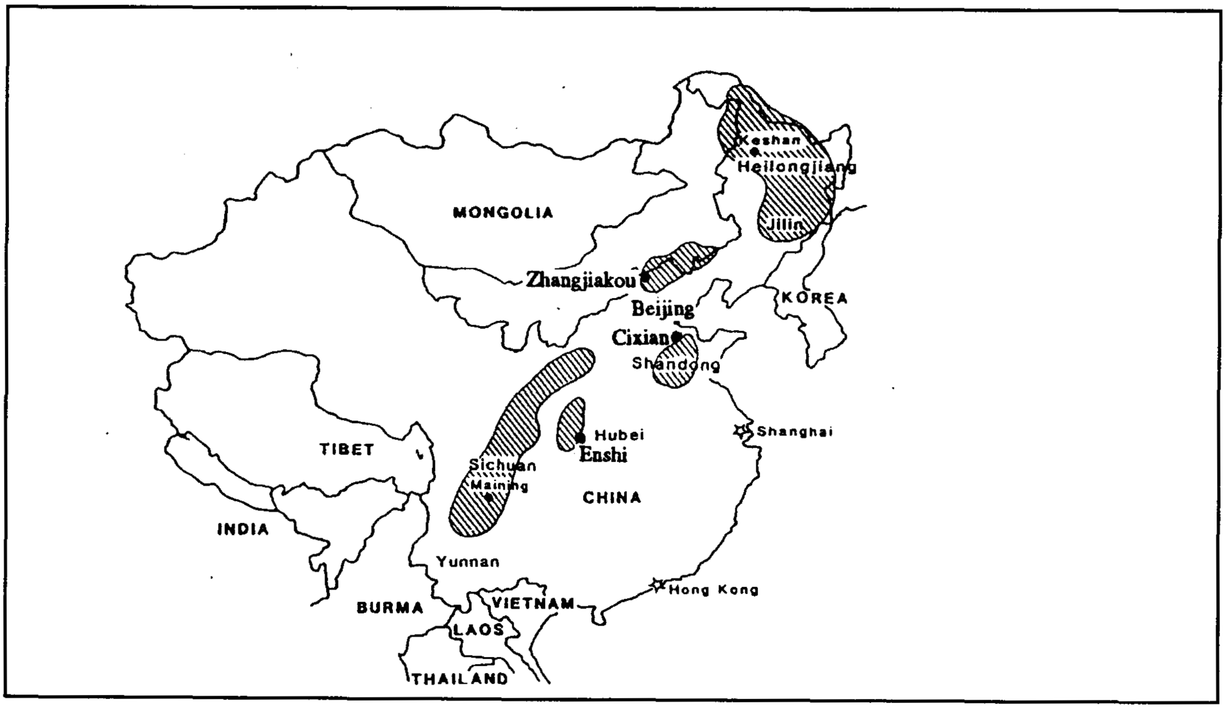


Figure 1. Location of areas under investigation in the present project and the KD incidence belt in China (modified after Crounce et al., 1983).

2. OBJECTIVES AND SCOPE OF THIS REPORT

The overall objectives of the project are to:
(i) develop a methodology for delineating areas where selenium deficiency or toxicity may pose a health risk and cause health disorders and
(ii) mitigate problems of natural Se imbalances by designing and implementing land-use planning, crop and dietary supplementation methods.

The objectives for the Enshi area in particular are as follows:
(i) establish the relationship between the human Se status of communities (represented by hair samples) and their dietary Se intake (represented by staple foodstuffs (grain) and drinking water samples) to the local geochemical environment characterised by cultivated soils.
(ii) identify criteria which may be used to define areas where there is a risk of Se-toxicity or deficiency to humans and other animals.
(iii) assess, design and implement strategies for the reduction of the toxic effects of high Se in the Enshi area.
(iv) assess the potential for developing high Se-products which may be used to ameliorate the effects of Se-deficiency in humans in other parts of China.

This report deals principally with the first three of these objectives. Objective (iv) is being addressed through agronomic trials of a high Se fertiliser manufactured from Se-carbonaceous shale and conventional NPK chemical fertiliser, the results of which will be reported elsewhere.

3. SELENIUM CHEMISTRY

Se belongs to group VIA of periodic table and has chemical and physical properties that are intermediate between metals and non-metals. The chemical behaviour of Se resembles that of sulphur and like sulphur, Se can exist in the 2^-, 0, 4^+ and 6^+ oxidation states. As a result of this complex chemistry, Se is found in all natural materials on earth including rocks, soils, waters, air, plant and animal tissues (Table 1). The main natural sources of Se in the environment are bedrock weathering, volcanic emissions and metal sulphide deposits. Anthropogenic sources of Se include coal and oil power stations and Cu processing plants.

Table 1. Se concentrations in selected materials (modified from McNeal & Balistrieri, 1989).

Material	Se (μg/g)	Material	Se(μg/g)
Earth's Crust	0.05	Lake Michigan	0.0008 - 0.01
Granite	0.01 - 0.05	Sea water	0.000009
Limestone	0.08		
Sandstone	< 0.05	USA plants	
Shale	0.06	Grasses	0.01 - 0.04
Phosphate rock	1 - 300	Clover & alfalfa	0.03 - 0.88
Soil		Barley	0.2 - 1.8
USA	< 0.1 - 4.3	Oats	0.15 - 1
England/Wales	< 0.01 - 4.7		
Seleniferous	1 - 80, < 1200	Algae	
Coal	.46 - 10.65	Marine	0.04 - 0.24
Atmospheric dust	0.05 - 10	Freshwater	< 2
River water		Whole fish	
Mississippi	0.00014	Marine	0.3 - 2
Amazon	0.00021	Freshwater	0.42 - 0.64
Colorado (alkaline)	0.01 - 0.4	Animal tissue	0.4 - 4

3.1 Geochemistry

During volcanic activity, Se escapes as high temperature volcanic gases therefore Se concentrations in volcanic rocks are generally low. The average crustal abundance of Se is 0.05 - 0.09 µg/g and average concentrations in magmatic rocks rarely exceed these values (Table 1). In sedimentary rocks, Se is associated with the clay fraction and is found in greater concentrations in shales than in limestones or sandstones. Relatively high concentrations (300 µg/g) of Se have been reported in some phosphate rocks which is particularly important because of the wide-spread use of phosphate fertilisers. Se concentrations in coal can be high relative to other rock types and typically range from 1 to 20 µg/g (Mayland et al., 1989). Se is a chalcophile element and elemental Se^0 is occasionally associated with sulphide mineralisation. More commonly, however, Se substitutes for sulphur in sulphide minerals due to the similarity in crystallography of these two elements.

3.2 Soil Chemistry

The Se concentration of most soils ranges from 0.01 - 2 µg/g (world mean 0.4 µg/g (Fergusson, 1990)) but high concentrations of up to 1200 µg/g have been reported in some seleniferous areas (Mayland et al., 1989).

The main factors controlling Se availability in soils are pH and redox conditions, Se speciation, soil texture and mineralogy, organic matter content and the presence of competitive ions. The theoretical speciation of Se in soils is shown in Figure 2. In acid and neutral soils, inorganic Se occurs as very insoluble Se^{4+} complexes of oxides and oxyhydroxides of ferric Fe. Se^{6+}, the predominant oxidation state in neutral and alkaline soils, is generally soluble, mobile and readily available for plant uptake. Se^{4+} is adsorbed onto soil particle surfaces with greater affinity than Se^{6+} and this behaviour coupled with lower solubility makes Se^{4+} less bioavailable than Se^{6+} (Mikkelsen et al., 1989). Bisbjerg & Gissel-Nielsen (1969) found that addition of Se^{6+} to soils resulted in ten times more plant uptake than addition of Se^{4+}.

Native Se (Se^0), metal Se^{2-} and Se-sulphide salts form in reduced soil conditions and the low solubility and oxidation potential of these element species make them largely unavailable to plants and animals (McNeal & Balistrieri, 1989).

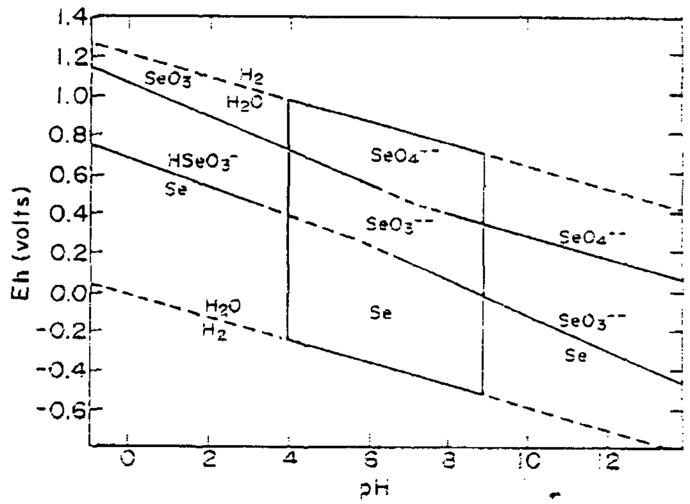


Figure 2. Eh - pH diagram of Se in soils (from Mayland et al., 1989).

Soil pH also influences the capacity of clays and ferric oxides to adsorb Se. Research has shown that Se^{4+} adsorption by clays reaches a maximum between pH 3 - 5 and decreases with increasing pH (Mikkelsen et al. 1989).

The bioavailable Se content of soil generally correlates negatively with clay content due to increased adsorption of Se onto clay minerals. Bisbjerg & Gissel-Nielsen (1969) found that Se uptake in plants grown on loamy soils was half that of plants grown on sandy soils and that vermiculite had a greater Se^{4+} adsorption capacity than montmorrilonite. However, adsorption by Fe oxides was greater than adsorption by the clay minerals tested.

Howard (1977) demonstrated that Fe exerts a major control on Se soil chemistry as both elements are affiliated under oxidising and reducing conditions. In addition, soil organic matter has a large capacity to remove Se from solution possibly as a result of fixation by organometallic complexes. Bisbjerg and Gissel-Nielsen (1969) reported ten times greater plant uptake of Se^{6+} added to mineral soils than organic rich soils.

The presence of ions such as SO_4^{2-} and PO_4^{3-} can influence Se accumulation in plants by competing with Se ions for fixation sites in the soil and plants or diluting the concentration of Se in the plants by increasing plant growth. SO_4^{2-} inhibits the uptake of Se by plants and has a greater effect on the uptake of Se^{6+} than Se^{4+}. Addition of PO_4^{3-} to soils has been shown to increase Se uptake by plants as the PO_4^{3-} ion is readily adsorbed in soils and displaces Se^{4+} from fixation sites making it more bioavailable. Conversely, increasing the levels of PO_4^{3-} in soils can dilute the Se content of vegetation by inducing increased plant growth.

Addition of $BaCl_2$ to seleniferous soils has been shown to reduce Se^{6+} uptake in plants more effectively than the addition of SO_4^{2-} probably due to the formation of $BaSeO_4$ which is barely soluble (Mikkelsen et al., 1989).

3.3 Water Chemistry

The chemical speciation of Se in water is largely dependent on the pH and redox conditions. The theoretical speciation of Se in water is shown in Figure 3. Se forms a very minor component of natural waters and rarely exceeds the World Health Organisation (WHO) limit of 10 µg/l in concentration. Waters containing 1000 µg/l Se have been recorded in seleniferous areas in Montana (Mayland et al., 1989).

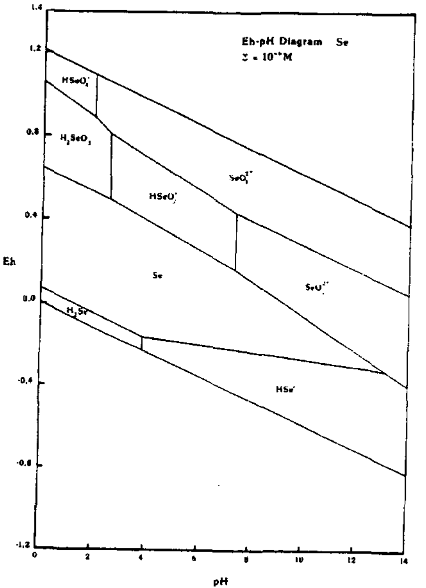


Figure 3. Eh - pH diagram of Se in waters (from McNeal & Balistrieri, 1989).

3.4 Selenium in Plants

Se is not an essential element for plant growth and Se concentrations in plants generally reflect the levels of Se in the environment. Plants are often classified according to their ability to accumulate Se when grown on seleniferous soils. Se accumulator plants can absorb > 1000 µg/g Se whereas secondary Se absorbers rarely concentrate more than 50 - 100 µg/g. The third group, which includes grains and grasses, usually accumulate less than 50 µg/g Se. Some examples of uptake of Se in different plants are given in Table 2. Much of the Se in non-accumulator plant species is found in the form of protein-bound selenomethionine whereas Se in accumulator plants is mostly water-soluble. Plants suffer Se toxicity as a result of interference with the sulphur metabolism. Exclusion of Se from the proteins of accumulator plants is thought to be the basis of Se tolerance (Mayland et al., 1989).

Se concentrations in food crops vary greatly between plant species. On average, root crops contain highest Se concentrations. Mikkelsen et al. (1989) report average concentrations of 0.407 µg/g Se in root crops from around the world whereas the concentration in field crops such as rice and wheat is 0.279 µg/g. Levels of > 3 - 5 µg/g in plants have been shown to induce Se toxicity in animals (Jump & Sabey, 1989).

Table 2. Selenium solubility in water and relative uptake in plants (from Mayland et al., 1989).

Se source	Solubility of Se in cold water†	Se added to soil	Uptake relative to added Se		
			Clover	Barley	Mustard
	g/L	mg/kg	%		
Se	i	2.5	0.005	0.02	0.07
SeO_2	i	0.5	1.0	0.9	1.2
K_2SeO_3	22.4	0.5	1.0	1.1	1.3
Na_2SeO_3	s	0.5	1.0	1.0	1.1
$BaSeO_3$	0.05	0.37	0.9	0.9	0.9
$FeSeO_3$	i	0.35	1.1	1.0	1.1
$CuSeO_3$	i	0.30	0.8	0.8	0.7
K_2SeO_4	390	0.50	24.	12.	24.
$BaSeO_4$	0.03	0.10	63.	27.	61.
$CuSeO_4$	68	0.13	53.	28.	48.

† i = insoluble, s = slightly soluble.

4. PHYSIOGRAPHY, GEOLOGY AND SOILS OF THE ENSHI AREA

Enshi District forms part of Hubei Province in central China. Enshi City lies approximately 100 km south of the Yangste River Gorges and 450 km west-south-west of the province capital Wuhan. The area of investigation lies between latitudes 29° 48' and 30° 30' N and longitudes 109° 30' and 110° E. The map produced in this report (Figure 4) is based on rough tracings of the 1: 300 000 scale Enshi District maps.

Fifteen villages were selected for the investigation based on previous studies and epidemiological records held by Enshi District Local Government. Five villages with high environmental Se and human selenosis incidence (HT), five villages with high environmental Se but no human selenosis (HN) and five villages with low environmental Se and KD incidence were chosen (LK). The villages selected lie within the counties of Enshi City, Jianshi, Lichuan and Xuan 'en (Figure 4).

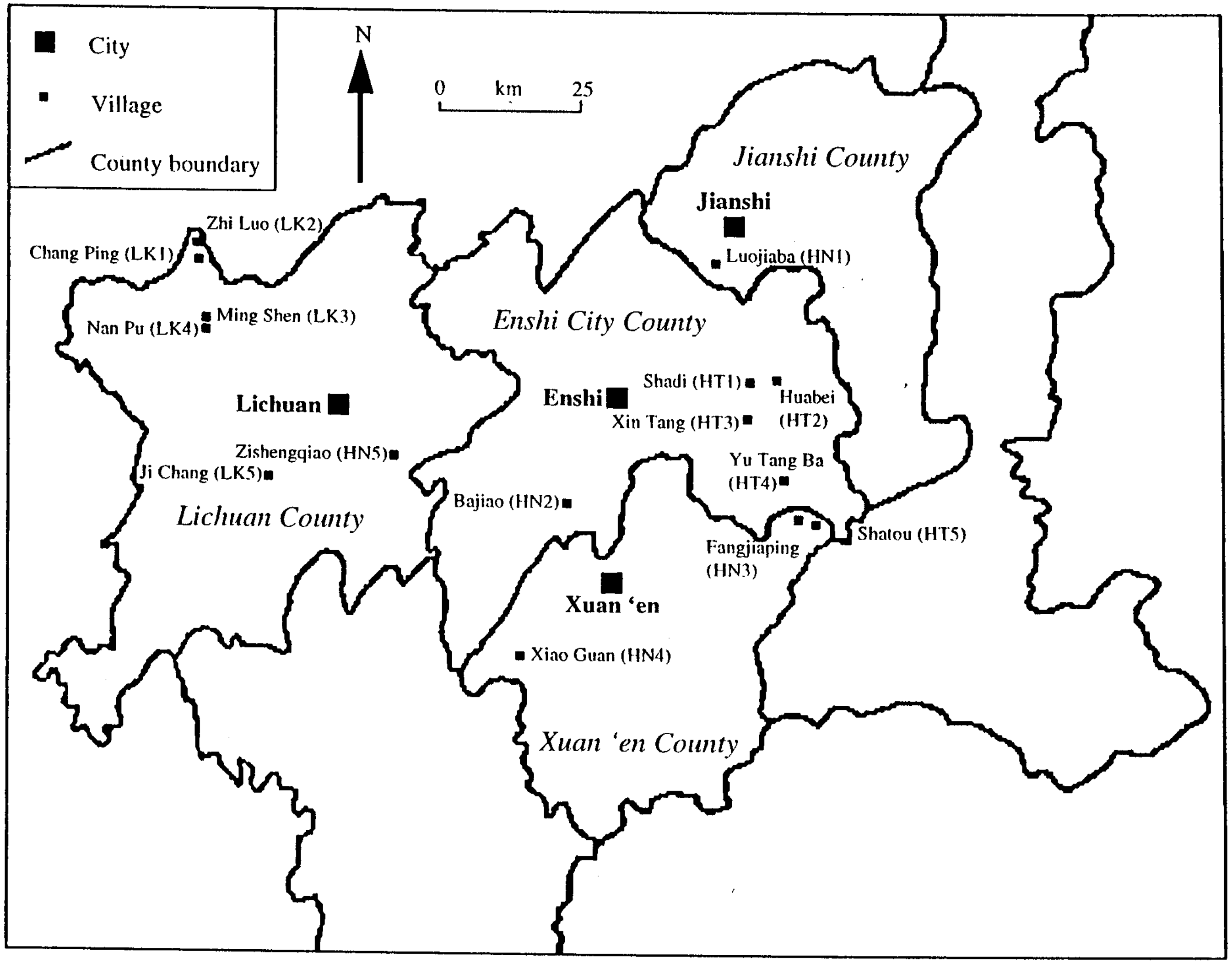


Figure 4. Sketch map of Enshi District showing the 15 villages sampled during the present study.

Throughout this report, place names are recorded as transliterations of the Chinese characters. The names of major cities appear as given in the Times Atlas of the World (Comprehensive 9th Edition, 1992) (Table 3).

Table 3. Latitude and longitude of the main cities in the counties of Enshi District sampled during the field programme.

Name	Latitude	Longitude
Enshi	30° 17' N	109° 24' E
Jianshi	30° 42' N	109° 44' E
Lichuan	30° 20' N	108° 57' E
Xuan 'en	30° 06' N	109° 23' E

The area sampled is one of the poorest parts of China and despite several tarred roads crossing the District, it remains remote due to the mountainous nature of the terrain. Although not exceptionally high (the highest village sampled was at 1400 m), the area comprises steep, densely wooded ridges dissected by deep-cut river gorges and valleys (Plate 1). The District contains several small cities but the majority of the population live in rural areas and are heavily dependent on subsistence agriculture. Rice cultivation is concentrated in valley floors whereas maize-corn, other vegetable crops and tobacco are grown on the valley sides and the steep ridges which are cleared of forest for terraced cultivation. Farmers raise three crops a year in the area which lies within the sub-tropical belt of China and therefore experiences warm wet summers and milder winters than northern China.

The study area is underlain by a sequence of sedimentary rocks ranging in age from Cambrian to Quaternary (Table 4). Studies have shown there are five high-Se formations within this sequence (Table 5), however Se toxicity only occurs in areas underlain by the Permian strata (Wang, 1993).

Se is enriched to some degree in all strata from the top of the Lower Permian Maokou Group to the Wujiaping Group of the Upper Permian (Zheng et al., 1992). These correspond to the P_1m and P_2 strata listed in Table 4. The sequence comprises carbonaceous shales and carbonaceous siliceous rocks known locally as 'stone coal' interbedded with limestones, dolostones and mudstones. Highest concentrations of Se (up to 6471 µg/g) are found in the siliceous bed at the top of the Maokou Group (P_1m) (Zheng et al., 1992).

There is some evidence to suggest that Se in these rocks is in the form of microparticles of elemental Se in association with organic carbon and that the carbon content of the rock controls the Se content (Table 6) (Zheng et al., 1992; Zheng & Yan, 1993). However, some Se is also found in the lattice of pyrite minerals. A pyrite-rich layer with elevated Se content occurs at the base of the Wujiaping Group (P_2). Two micro-crystals of Se-pyrite in these rocks were found to contain up to 5.15 - 6.68% Se (Zheng et al., 1992).

Statistical analysis of 125 rock samples from the Permian sequence (Zheng et al., 1992), demonstrated that the Se concentration correlates positively with concentrations of C, S, Si, Al, and P and negatively with Ca and Mg. Concentrations of V, Mo, As, P, F, Cd and Cr are also high in these rocks. An average F concentration of 1161 µg/g based on twelve rock samples is reported, compared to a world average of 80 µg/g.

All the villages sampled in the high Se area are underlain primarily by Permian strata (Appendix A) and in many cases villagers mine the carbonaceous shale for fuel (Plates 2 and 3). Jurassic purple sandstones and siltstones outcrop in the north-west of the

District in Lichuan County where the terrain is less rugged comprising small rounded hills surrounded by broad flat valleys. The KD belt is associated with these Jurassic sediments.

Table 4. Geological strata underlying villages sampled in Enshi District.

Geological Unit	Era	Rock Type
Q	Quaternary	Loess
K_2	Cretaceous	Quartzose sandstone and conglomerate
J_2x	Jurassic	Mudstone and feldspatic sandstone
J_2s	Jurassic	Purple silty sandstone, calcareous argillaceous silty sandstone
T_3	Triassic	Clay, sandstone, carbonaceous shale and coal layer
T_2 and T_2b	Triassic	Limestone, marl and shale
T_1j	Triassic	Dolostone, limestone and breccia
T_1	Triassic	Dolostone, oolitic limestone and breccia
P_2	Permian	Limestone, carbonaceous shale, calcareous mudstone and carbonaceous siliceous rocks
P_1m	Permian	Limestone with flints, siliceous rocks and marl
P_1q	Permian	Limestone with flints, quartzose sandstone, carbonaceous shale and siliceous rocks
P_1	Permian	Limestone, shale, siltstone and pelite
C_{1+2}	Carboniferous	Dolostone, limestone, dolomitic limestone and quartzose sandstone
D_{2+3}	Devonian	Limestone, shale and quartzose sandstone and oolitic hematite
S_2	Silurian	Quartzose fine sandstone, shale and bioclastic limestone
S_1ln^2	Silurian	Shale, sandy pelite and sandstone
S_1ln^1	Silurian	Yellow-green shale, sandstone and calcareous sandstone
S_1l	Silurian	Shale, sandy shale, and pelitic sandstone
C-O	Cambro-ordovician	Shale, limestone, dolomitic limestone and breccia

Based on translation of selected geological units from the geology map of Enshi District

Table 5. The Se content of selected Se rich strata in Enshi District.

Era	Group	Se content µg/g
Holocene		2.49
Upper Permian	Wujiaping Group	47
Lower Permian	Maokou Group	224
Ordovician	Wufeng Group	25
Cambrian	Shuijingtou Group	34.64

From Wang (1993)

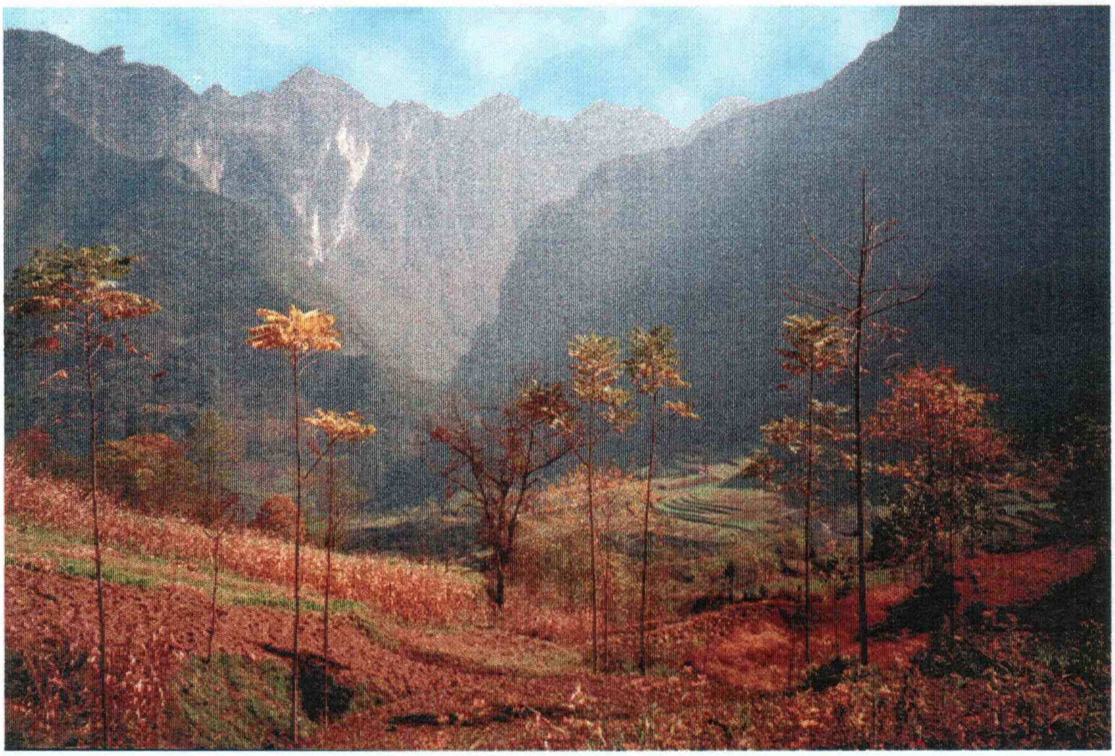


Plate 1. Typical scenery in Enshi District characterised by densely wooded ridges and deep-cut river gorges. Rice cultivation is concentrated on in valley floors whereas ridges are cleared for production of crops such as tobacco and maize-corn Top: Shatou (HT5) Bottom: Xin Tang (HT3)

Plate 2. Carbonaceous shale mine in Shatou village (HT5) typical of mines in the high Se area of Enshi District. Debris from the mine is dispersed into the adjacent terraced fields.

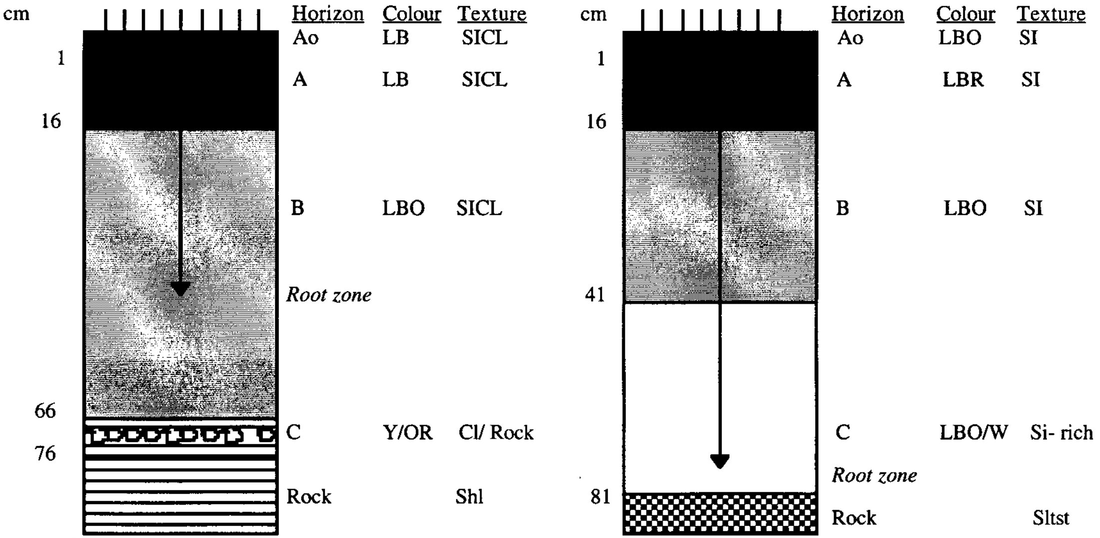
Plate 3. Debris from the carbonaceous shale mine in Shadi (HT1) collects in the valley bottom. Fields adjacent to the stream are used for maize-corn cultivation. The source of the stream is a spring issuing directly from carbonaceous shale. The acid nature of the water is indicated by the heavy orange iron precipitate in the stream bed. Villagers have been advised not to drink this water.

Table 6. The organic carbon and Se content of selected strata from the Maokou Group (P_1m) and the Wujiaping Group (P_2), Enshi District.

No of samples	Rock Type	Organic Carbon Content %	Range Se Content µg/g	Average Se Content µg/g
11	Silicate	< 5	0.29 - 110.7	24.30
11	Carbonaceous silicate	5 - 25	1.43 - 72.38	39.02
7	Carbonaceous silicate	25 - 50	64.34 - 127.4	90.66
9	Siliceous carbonaceous shale	(No data)	10.56 - 63.42	31.54
2	Carbonaceous shale	(No data)	206.8 - 280.6	243.70

From Zheng & Yan (1993)

Soils in the area are classified as yellow earths according to The Soil Atlas of China (Zhang Guangdi pers. commun.). Soils encountered during fieldwork were predominately light-brown orange silts and clays except in the north of Lichuan County where red (purple) sandy soils are derived from the Jurassic sedimentary rocks. Two soil profiles were sampled during this study, one developed on the Permian rocks of Enshi City County and the other on the Jurassic rocks of Lichuan County. Both soils consist of a narrow (1 cm) Ao horizon, with well developed A, B and C horizons (Figure 5). Soils developed on Permian rocks generally contained many shaley clasts whereas soils underlain by Jurassic sediments were relatively clast free. Soils developed over Jurassic rocks were paler, sandier and appeared to have less organic content than those in the high Se area. Grey gleyed clay soils were encountered in waterlogged rice paddies developed on both Permian and Jurassic rocks.



Carboniferous base
Xin Tang (HT3), Enshi City County

Jurassic base
Chang Ping (LK1), Lichuan County

Figure 5. Two idealised soil profiles from the Enshi sampling area.
(See Appendix B for explanation of abbreviations. Arrows indicate the depth of the root zone.)

5. PREVIOUS EPIDEMIOLOGICAL STUDIES IN ENSHI DISTRICT

Studies into the Se balance of local populations were carried out during the 1960's and 1970's by Enshi Public Health Department in response to outbreaks of Se-related diseases in the area. Between 1923 and 1988, 477 cases of human selenosis were reported (Figure 6). 338 of these cases, resulting in hair and nail loss and disorders of the nervous system, occurred between 1959 and 1963 in Shadi (HT1), Xin Tang (HT3) and Shuang He communities (Mao & Su, 1993). In Yu Tang Ba (HT4) village, Shuang He community, the population was evacuated after 82% (19 out of 23 people) of the human population suffered nail and hair loss and all livestock died from Se poisoning. During the same period, 281 selenosis cases were reported in five villages in the Shadi area. Cases of selenosis in pigs reached peak prevalence between 1979 and 1987 when 280 out of 2238 pigs were affected in Shatou (HT5) resulting in the death of 122 pigs.

Epidemiological investigations in Enshi District revealed that the selenosis occurred in areas of high environmental Se associated with the carbonaceous strata but not all villages underlain by this strata were affected. As Table 7 shows, further studies by Yang et al. (1989b) indicate that dietary intakes of Se greatly exceed the USA National Research Council recommended daily intake in the Se toxicosis area and Chinese recommended daily intakes (Yang & Xia, 1995). No human cases of Se toxicity have been reported in recent years but animals commonly suffer hoof and hair loss as a result of the high environmental Se (Mao Dajun pers. commun.).

Figure 6. Number of cases of Se toxicity in Enshi District 1923 - 1983. (From Mao & Su, 1993)

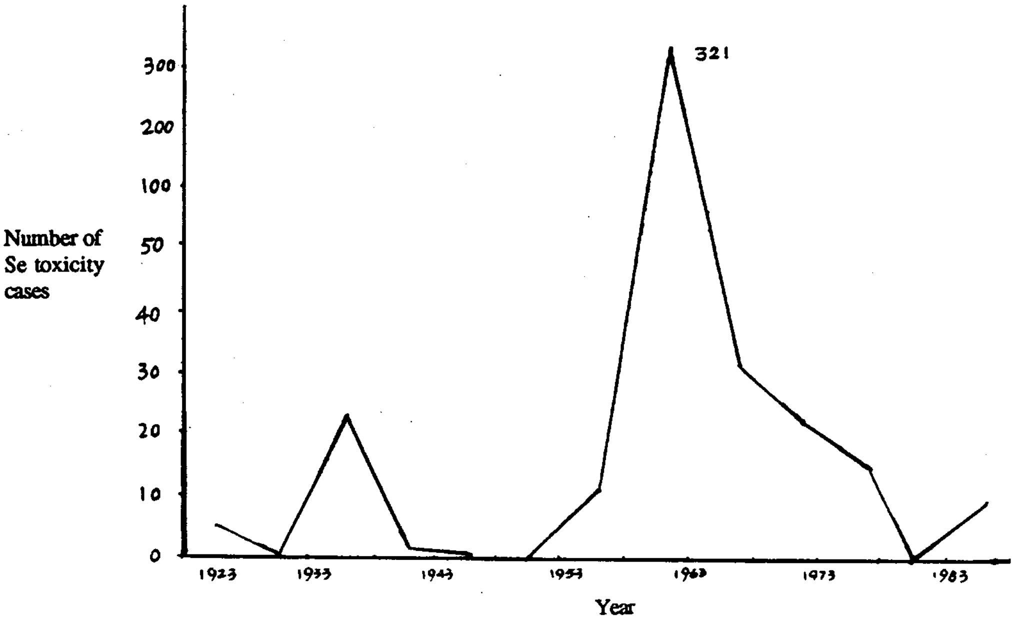


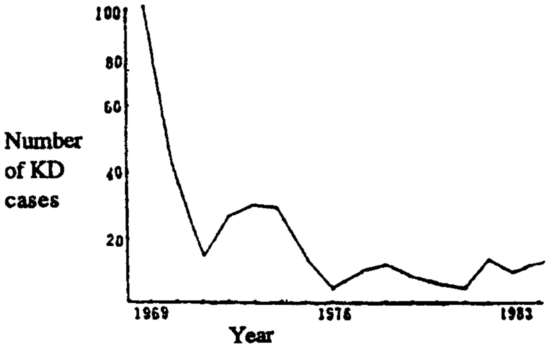
Table 7. Estimated daily dietary intake of Se in three areas of Enshi District compared to recommended intakes elsewhere.

Source	Daily dietary intake of Se µg	Comments
Enshi Low Se area *	70.5	Male
Enshi Low Se area *	62	Female
Enshi Medium Se area *	194.7	Male
Enshi Medium Se area *	198.1	Female
Enshi High Se area *	1438	Male
Enshi High Se area *	1238.5	Female
USA National Research Council +	50 - 200	Recommended daily intake
UK Ministry of Agriculture +	80 - 200	Recommended daily intake
China†	40 - 600	Recommended daily intake

* From Yang et al. (1989b) + From Chuck (1988) † From Yang & Xia (1995)

Previous epidemiological investigations also identified an area of Se deficiency and KD, in close proximity to the high Se area (Yang et al., 1983). Keshan Disease mainly occurred in six communities in the north-west of Lichuan County. Most studies into KD disease were carried out in the late 1960's and 1970's following a high incidence (106 cases) in 1969. In total, 312 people have suffered KD in the County, an average incidence rate of 103 per 100 000. Among the 312 cases, 136 recovered, 163 died and 13 persons still suffer from the disease. Following the high incidence rates in 1969, the number of cases of KD dropped dramatically (Figure 7) (Mao et al., 1987). Children between the ages of 3 - 8 accounted for 83.4% of the total cases (Mao & Su 1993) and 80% of the children affected by the disease died (Mao Dajun pers. commun.). As yet there is no explanation why children of the 3 - 8 year old age group were particularly affected. This is in contrast to other KD areas of China, such as Zhangjiakou, where it is mainly women of child bearing age that suffer from the disease. The village of Chang Ping (LK1, Figure 4) was the worst affected with a total of 259 cases out of a population of 20368. 117 of those affected died.

Figure 7. Number of KD cases, 1969-1983 in Lichuan County (From Mao et al., 1987).



Previous investigations concentrated on Se dietary intake and the Se status of the human population in Enshi District. Levels of Se in soil, crops, drinking water and human urine, blood, nail and hair samples from the Enshi high and low Se areas were compared to samples from other areas of China. Se concentrations in these sample types in areas underlain by carbonaceous strata were up to 1000 times higher than regions where KD was prevalent (Yang et al., 1983).

Yang et al. (1989b) estimated that locally grown crops constituted 90% of the diet in the Enshi area and cereal crops (rice and maize) accounted for 65 - 85% of the Se intake indicating the importance of the local environment to Se in the food chain. However, previous investigations did not assess the geochemical controls on Se availability in soils and hence to plants. No systematic study had been carried out to evaluate the relationship between environmental Se levels, Se in staple food crops and drinking water, with human Se status. It was therefore not possible to define methods of remediating environmental and human Se imbalances on the basis of previous work.

Iodine deficiency disorders (IDD) and fluorosis are present over much of the District. Local villagers use the carbonaceous shale for fuel and the intake of F-rich smoke from burning carbonaceous shale is thought to be the main cause of fluorosis. Inhalation of Se from carbonaceous shale smoke is also thought to increase the Se loading of the local population (Mao Dajun pers. commun.).

Further details of epidemiological studies in Enshi District are given in Mao et al. (1987) and Fordyce (1996).

6. SAMPLE COLLECTION

6.1 Sampling Design

The sample collection strategy applied in the Enshi area is similar to that employed in previous studies relating environmental geochemistry to human and animal health (Fordyce et al., 1996). The fifteen villages selected for the study were coded according to the following scheme:

HT 1-5 = High Se in the environment and Se toxicity recorded
HN 1-5 = High Se in the environment but no Se toxicity recorded
LK 1-5 = Low Se in the environment and KD recorded

Samples were numbered according to a random number list (Plant, 1973) and sample details were recorded on fieldcards. Village and sample details are summarised in Appendices A-E. Where possible, samples were collected in accordance with the recommendations of the IGCP 259 Final Report (Darnley et al., 1995).

Rice and maize-corn are the main crops cultivated in the study area. At the time of sampling in November 1995 these crops had been harvested and grain samples were collected from the grain stores in each village. In several of the villages, the population supplement their food supplies with imported rice from other areas of China which is mixed with local rice in the grain stores. Since the main aim of the study was to identify environmental controls on human Se status, locally grown maize-corn was selected as the main grain sample for collection. One rice paddy soil sample from each village was collected in addition to the maize-corn soils to allow comparison between the soil chemistry of the waterlogged rice paddies and the dry conditions of the maize-corn fields. Where possible a local rice sample was collected from each village.

No evidence of Se toxicity or deficiency diseases were identified in populations sampled during the field programme. Three of the villagers sampled at Xin Tang (HT3) reported that they had lost hair in the past due to Se toxicity. In many of the high toxicity areas, 90% of the population were affected by fluorosis evident from the yellow and brown mottling of teeth. In Zhi Luo (LK2) the field team was introduced to a woman who had developed KD at the age of 3 in 1969 which had caused malformation of her heart. She reported that she was currently fit and well.

6.2 Soil Sampling

Sampling was carried out after the maize-corn had been harvested therefore many of the fields sampled had been recently ploughed and it was not possible to distinguish A and B horizon soils. Dual crop fields were common with maize-corn often grown in the same field as tea bushes. Many of the maize-corn fields had been replanted with Chinese radish or tobacco.

6.2.1 Sampling Strategy

- 5 composite soil samples were collected from each village.
- sites were selected so as to cover all the topographic aspects of arable land around the village and fields managed by different farmers.
- duplicate samples were collected from 1 in every 10 sample sites.
- near surface samples (10 - 30 cm; below A_0) were collected.
- 3 deeper samples (35 - 45 cm), one from each Se area were collected to give an indication of variation of element concentrations with depth.
- 2 soil profile samples were also collected, to examine variations with depth, one from the high Se and one from the low Se area.
- in order to carry out Se speciation studies at the BGS it was important that the soils retained their moisture content therefore the BGS soil samples were collected in plastic securitainers.

6.2.2 Collection (Plate 4)

(i) All sampling equipment (Dutch soil auger and plastic sheet) was cleaned before use.
(ii) Each composite soil sample comprised 4 sub-samples collected in the same field. Using the assembled sectional soil auger, four holes were made at the corners of a square. Where possible, this square had dimensions 20 x 20 m in accordance with IGCP 259 recommendations (Darnley et al., 1995) but many of the terraced fields in the area were smaller than this and in some cases it was only possible to separate the sub-sample holes by 3 - 5 m.
(iii) The top 10 cm organic rich layer was discarded and the deeper 10 - 20 cm sub-samples from the 4 holes were placed on the plastic sheet.
(iv) Large stones and rootlets were removed from the sample by hand and discarded.
(v) The composite sample was homogenised by lifting the corners of the plastic sheet.
(vi) The composite sample was coned and quartered to produce a split of two samples (minimum 100 g). One split was placed in a plastic securitainer (49 x 75 mm) and the other split in a 8 x 16 cm Kraft® paper bag.
(vii) The securitainer samples were transported back to the UK for analysis by the BGS and the Kraft® bag samples remained in China for analysis by the IRMA.
(viii) Duplicate soil samples were collected in the same way from four different holes in the same field as the original sample.
(ix) Deeper soils were collected from the same four holes as the original sample.
(x) Separate samples of A, B and C horizons were collected from the soil profiles.
(xi) Field descriptions of the soil samples are detailed in Appendix B.

6.3 Grain Sampling

Maize-corn is harvested and dried on the cob in the area. Cobs are bunched together and hung up to dry over carbonaceous shale fires or are hung up to dry in the air (Plates 5 and 6). The latter method is prevalent in the Se deficiency area where carbonaceous shale is less readily available. Cobs are ultimately stored in the roof space of the house which often has a slatted floor to allow air to permeate up through the corn. In the high Se area, smoke from carbonaceous shale fires in the main room of the house rises up through the slatted roof and is thought to contaminate the corn with Se (Mao Dajun pers. commun.). Locally grown rice samples were collected where possible (Plate 7).

6.3.1 *Sampling Strategy*

- 5 maize-corn samples were collected from 5 different grain stores in each village where possible.
- the grain samples were collected from villagers that farmed the fields sampled for soils where possible.
- in 7 of the 15 villages it was also possible to collect one locally grown rice sample corresponding to the rice paddy soil sample.
- a duplicate sample was collected 1 in every 10 samples.

6.3.2 *Collection* (Plate 8)

(i) The house of the farmer that worked the field sampled for soil was located.

(ii) 2 - 3 dried maize-corn cobs were selected from the grain store in the roof of the house.

(iii) The maize-corn grains were stripped off each cob by hand into a basket or sample bag.

(iv) The grain was thoroughly mixed and placed in a 13 x 13 cm white cloth sample bag.

(v) Local rice samples were usually found drying in their husks in baskets or on concrete slabs. One 13 x 13 cm cloth sample bag of rice grains was collected where possible.

(vi) On completion of the field programme, enough of the maize-corn grains were removed from the cloth sample bags to fill a grey plastic securitainer (49 x 75 mm). The securitainer samples were transported back to the UK for analysis by the BGS and the cloth bag samples remained in China for analysis by the IRMA.

(vii) On return to Beijing the husks were removed from the rice samples at the IRMA. Local villagers have rice husks removed mechanically. In the absence of a rice-dehusking machine, husks were removed at the IRMA by repeatedly beating the cloth bag of rice with a plastic hammer. The rice was then placed in a tray and taken outside to be shaken in the wind allowing the husks to be winnowed off. Ideally for this process the tray should be made of plastic, however, only metal (Zn galvanised steel) trays were available at the IRMA.

(viii) Once de-husked, the rice samples were split 50 : 50 between grey plastic (49 x 75 mm) securitainers and 8 x 13 cm paper sample bags. The securitainer samples were transported back to the UK for analysis by the BGS. The paper bag samples remained in China for analysis by the IRMA.

(ix) Field descriptions of the grain samples are detailed in Appendix C.

6.4 Water Sampling

All the villages were supplied by spring water which in many cases fed small 1 x 1 m water troughs. In the villages of Shadi (HT1) and Huabei (HT2), the population had been advised not to drink the spring water due to the high Se content. In Shadi (HT1), the villagers had been instructed to take water from another spring in an adjacent watershed. However, due to the distance of this alternative water source, villagers still occasionally used water from the Se-rich spring. In Huabei, the village had been supplied with a piped water supply from elsewhere and only used water from the Se-rich spring very rarely. In both cases, however, the Se-rich springs were sampled to determine the local hydrogeochemical environment.

6.4.1 *Sampling Strategy*

- water samples were collected from the main or only spring in each of the 15 villages sampled close to the areas where the soil and grain samples had been collected.
- duplicate samples were collected 1 in every 5 samples.

6.4.2 *Collection* (Plate 9)

(i) At each site, the following suite of water samples were collected:
- Three 30 ml filtered water samples collected in trace element free polyethylene Nalgene® bottles.
- One 100 ml filtered water sample collected by the IRMA in plastic bottles supplied by them.
- One 30 ml unfiltered water sample collected in a polystyrene Steralin® vial for pH and Eh determinations.
- One 250 ml unfiltered water sample collected in a polyethylene bottle for bicarbonate and conductivity determinations.

(ii) The 30 ml Nalgene® bottles were labelled to indicate which samples would be acidified as follows:

UA = unacidified
HA = acidified with hydrochloric acid
NA = acidified with nitric acid

(iii) Each filtered water sample was collected using a 25 ml plastic syringe and a Swinnex® filter cartridge pre-loaded with a 0.45 µm Millipore® cellulose filter. A new filter cartridge was used for each site to avoid any possible cross-contamination between sites.

(iv) At each site, the filtered water samples were collected first avoiding disturbance to sediment in the bottom of the spring-fed water reservoir.

(v) Water was drawn into the syringe which was rinsed out twice. The syringe was filled with water again and connected to the filter cartridge which was also rinsed out twice. The syringe was refilled and the sample bottle was rinsed out twice with filtered water prior to being filled. The 30 ml Nalgene® bottles were filled to the shoulder.

(vi) Both the 30 ml Steralin® vial and the 250 ml polyethylene bottle were rinsed out twice in the water reservoir. Where possible, the vial and the bottle were both submerged underwater whilst the caps were secured making sure that no air was trapped in the sample container. This minimises the degassing of HCO_3 in the samples.

(vii) Care was taken to keep all bottles and filters clean and uncontaminated by human touch.

(viii) 30 ml samples collected for trace element analysis at the BGS were acidified within 4 hours of the end of fieldwork each day. NA and HA samples were acidified by the addition of 0.3 ml (8 drops) ARISTAR grade nitric and hydrochloric acid respectively. Addition of 1% vol/vol acid reduces the pH of the samples to approximately 1.0, thus preventing adsorption of dissolved metals to the interior walls of the storage bottle and minimising post-sampling microbial activity.

(ix) Care was taken to avoid introducing contamination through the plastic dropping pipettes, each of which were stored in a plastic self-seal bag and did not come into contact with bench surfaces.

(x) Eh and pH measurements, bicarbonate and conductivity determinations were also carried out at the end of each day's sampling. Procedures are detailed in Appendix F and results are listed in Appendix D. Following the measurements, these samples were discarded and the sampling containers reused.

(xi) Two field-blank UA, HA and NA samples were made up near the start and end of fieldwork. 30 ml Nalgene® bottles were rinsed twice with filtered deionised water, filled to the shoulder with filtered deionised water and acidified in the same way as the samples. The field-blanks were numbered in the same way as the samples according to the random list.

(xii) The UA, HA and NA water samples were transported back to the UK for analysis by the BGS and the 100 ml filtered water samples remained in China for analysis by the IRMA.

6.5 Hair Sampling

Hair samples were collected from inhabitants of the 15 villages to represent the Se status of the local population. Women in particular were reluctant to take part in the study and only two women were sampled during the programme. Following the serious Se toxicity problems at Yu Tang Ba (HT4) in the early 1960's the government had moved the population off the land. One family of three persons returned to the village within the previous three months and it was only possible to obtain three hair samples at this village. In the KD area in the north of Lichuan County, it was mainly children that suffered from the disease therefore hair from children was sampled. It was not possible to collect duplicate hair samples.

6.5.1 Sampling Strategy

- hair samples were collected from 5 individuals in each village.
- where possible, individuals from different families were selected..
- where possible, individuals from farms where soils and grain samples had been collected were sampled
- individuals of a range of ages were sampled during the study, unfortunately it was not possible to include a reasonable mix of male and female subjects in the study for the reasons described above.
- age, health, disease and medication details were recorded for each individual.

6.5.2 Collection (Plate 10)

(i) With the assistance of the local guides and village headman, individuals to be sampled were identified.

(ii) Samples were collected using scissors cutting hair at the nape of the neck.

(iii) Approximately 10 g of sample was collected and placed in a small plastic self-seal bag. The bag was numbered in a similar way to the soil and grain samples using a waterproof black marker pen.

(iv) A questionnaire (in Chinese) was completed for each individual sampled. A translation of the results of these questionnaires is given in Appendix E.

(v) On return to Beijing, the hair samples were split 50 : 50 to provide a complete set of samples for both the IRMA and the BGS. Hair in the original sample bags was transported back to the UK for analysis at the BGS.

6.6 Other Samples

6.6.1 Tobacco

Following the Se toxicity problems at Yu Tang Ba (HT4) in the early 1960's the local government no longer allow the population to consume grain produced in the village. All cereal crops grown in the village are exported to be mixed with crops from elsewhere. However, grain samples from the village were collected for this study to give an indication of their Se content. A sample of tobacco leaves was collected from the village as the population do smoke the tobacco they produce. Dried tobacco leaves were collected and placed in a white cloth sample bag and then split 50 : 50 to provide samples for both the IRMA and BGS.

6.6.2 Pig Hair

Although no Se toxicity effects were reported in humans in the area sampled, at Xin Tang (HT3) and Shatou (HT5) hair loss was found in pigs suffering from Se toxicity. A sample of hair from a pig in Xin Tang (HT3) village was collected in a small plastic self-seal bag. The sample was later split 50 : 50 to provide one sample for the IRMA and one for the BGS.

Plate 5. Air drying of maize-corn cobs in the LK villages (Nan Pu, LK4).

Plate 6. Drying of maize-corn cobs over a carbonaceous shale fire in the HT villages (Shatou, HT5).

Plate 4. Soil sample collection in the Enshi area using a Dutch auger. Field observations were recorded on field data cards (Chang Ping, LK1).

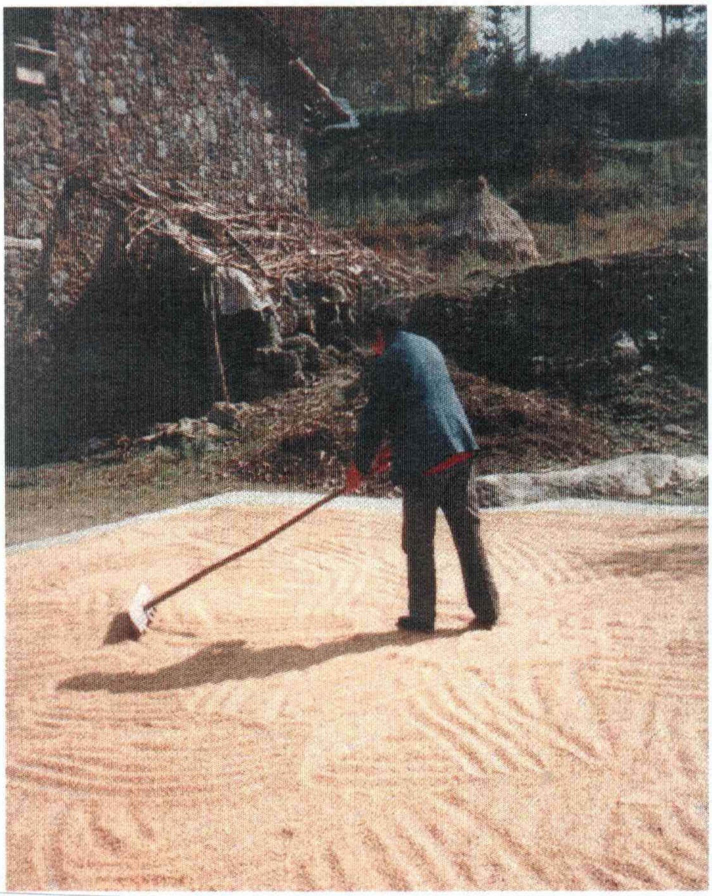


Plate 7. Drying of locally grown rice in the Enshi area. In villages where locally grown rice was being dried, rice samples were collected to compare with maize-corn samples (Zhi Luo, LK2).

Plate 8. Removal of maize-corn kernels from the cob prior to homogenisation and collection (Luojiaba, HN1).

Plate 9. Collection of 0.45 µm filtered drinking water sample from a spring issuing from carbonaceous shale (Huabei, HT2).

Plate 10. Hair sample collection from the nape of the neck (Yu Tang Ba, HT4).

7. ANALYTICAL METHODS

7.1 BGS Analysis

The soil, hair, grain and water samples collected in Enshi District were analysed for total Se content at the BGS. Water soluble Se content, loss on ignition (LOI), pH and concentrations of Ca, Cd, Cu, Mg, Mn, Mo, Fe, Mg, Pb, V and Zn were also determined in soils. In addition, soil total organic carbon (TOC) content and cation exchange capacity (CEC) were determined in 17 selected samples. Semi-quantitative XRD mineralogical analysis was carried out on two soil samples, one from the HN and one from the HT villages. Se in all samples types was determined using Atomic Fluorescence Spectrometry (AFS) whereas multi-element analysis of soil samples was based on ICP-AES techniques. In addition, Cl, NO_3, SO_4 concentrations were determined in water samples. Results below the limit of detection are reported at 2/3 the detection limit for statistical purposes.

7.1.1 Sample Preparation for ICP-AES, AFS, LOI, TOC and CEC Analysis in Soils

The BGS soil samples were separated on the basis of suspected high and low Se concentration and the low Se samples were prepared first to avoid contamination. All samples were homogenised and cone and quartered and one half was retained in the original container for reference. Samples were dried at a low temperature of 35 °C for 6 - 12 hours to avoid loss of Se through volatilisation. The soils were disaggregated to pass a 2 mm nylon sieve mesh and were ground in an agate vibrating-cup mill to < 150 µm.

7.1.2 Sample Preparation of Grain Samples for AFS Analysis

Following the initial elimination of rice husks described in section 6.3, any remaining husks were first loosened by shaking and rolling the grains in the original sample bags and were removed using a static-charged plastic ruler. Rice samples were ground in an agate vibrating-cup mill for 3 minutes. Maize-corn and tobacco samples were ground in a Waring blender at fast setting for 2 minutes.

The possible effects of Se contamination from carbonaceous shale smoke during the grain drying process employed in high Se area were assessed by washing one grain sample from each of the Se village groups prior to preparation and analysis. The samples were coned and quartered. One quarter was retained for reference, one quarter was washed twice with 1% HCl; a quarter was washed twice with deionised water and a quarter remained unwashed prior to being processed along with the other samples.

The grain samples and wash solutions were analysed for total Se content according to the methods listed in Appendix F. Results are presented in Table 8. Table 9 shows the weight of Se determined in each of the grain samples and wash solutions. The amounts of Se in the wash solutions in the LK villages, where grain is not dried over carbonaceous shale fires, are similar to the results from the HN and HT villages. Furthermore, the amount of Se present in the HCl wash solutions is not consistently greater than the amount present in the deionised water wash solutions as would be expected if the grain surfaces were contaminated with carbonaceous shale smoke.

The amount of Se in the wash solutions of the HN and HT samples as a proportion of the levels in grain is extremely small (< 0.005%) but the amount in wash solutions of the LK villages is greater (1 - 2.5%). This reflects the far lower levels of Se in grain samples from the LK villages and is not related to carbonaceous shale smoke contamination.

On the basis of these results there is little evidence to suggest carbonaceous shale smoke contamination of grain samples is a major factor in the dietary intake of Se in the HN and HT villages and the grain samples were not washed prior to analysis.

Table 8. Comparison of Se concentration in washed and unwashed grain samples and in wash solutions from the LK, HN and HT villages.

Sample Number Village Code	EN92 LK5	EN98 HN2	EN95 HT4
Unwashed Grain Se ng/g	3	4831	3742
Water washed Grain Se ng/g	5	5916	3706
HCl washed Grain Se ng/g	4	5023	3630
Deionised wash water Se ng/g	0.033	0.072	0.033
HCl wash solution Se ng/g	0.051	0.017	0.134

Table 9. Weight of Se in grain and wash waters and percentage of 'Se smoke contamination' in the LK, HN and HT villages.

Sample	Village Code	Sample Weight g	Weight of Se in sample ng	% 'Smoke Contamination' $\frac{\text{Weight of Se in wash}}{\text{Weight Se in grain}} \times 100$
EN92 Unwashed grain	LK5	25	75	
EN92 Water washed grain		25	125	1.32
EN92 HCl washed grain		25	100	2.55
EN92 Deionised water		50	1.65	
EN92 HCl wash solution		50	2.55	
EN98 Unwashed grain	HN2	22	106282	
EN98 Water washed grain		22	130152	0.00276
EN98 HCl washed grain		22	110506	0.00076
EN98 Deionised water		50	3.60	
EN98 HCl wash solution		50	0.85	
EN95 Unwashed grain	HT4	22	82324	
EN95 Water washed grain		22	81532	0.00202
EN95 HCl washed grain		22	79860	0.00838
EN95 Deionised water		50	1.65	
EN95 HCl wash solution		50	6.70	

7.1.3 Sample Preparation of Hair Samples for AFS Analysis

BGS hair samples were washed twice in deionised water and allowed to dry on clean plain paper. Once dry, the hair was cut into 2 - 4 mm lengths with a pair of clean stainless steel scissors and homogenised prior to analysis.

7.1.4 Analysis of Soil Samples by ICP-AES and AFS

Total (hydrofluoric-nitric-perchloric digestion) and water soluble Se in soil samples were determined by hydride generation AFS according to the methods detailed in Appendix F. Partial (nitric-perchloric digestion) and total (hydrofluoric-nitric-perchloric) soil Ca, Cd, Cu, Fe, Mn, Mo, Mg, Pb, V and Zn concentrations were determined by ICP-AES (Appendix F). Data quality was assured by the inclusion of international reference standards in the analytical runs and replicate analyses of selected samples. Results for Se and other elements in international standards and limits of detection (LOD) are detailed in Appendix F.

7.1.5 Analysis of Selenium in Grain, Water and Hair Samples by AFS

Sample preparation procedures for the determination of total Se content were based on a nitric-perchloric attack in grain and hair samples. Detailed methods and limits of detection for AFS analysis of grain, water and hair samples are given in Appendix F.

7.1.6 Analysis of Soil pH

Soil pH was determined on a paste (of specific consistency) of the unprepared samples to which deionised water had been added according to the British Standards Institute (BSI) method (Appendix F).

7.1.7 Analysis of LOI in Soils

Soil powders were dried at 35 ˚C before being placed in a furnace and kept at 450 °C for a minimum of four hours. Moisture and any organic matter were burnt off at this temperature and the LOI (difference in weight of the sample prior to and after heating at 450 °C) was used as an indicator of soil organic matter content. No standard reference materials were included in LOI analysis.

7.1.8 Analysis of CEC in Soils

The method used to quantify the CEC of soil samples is based on the compulsive exchange between an aqueous solution of $MgSO_4$ and a Ba soil (Bascomb, 1964). Samples were saturated with Ba supplied as $BaCl_2$ solution and any excess was removed by washing with deionised water. $MgSO_4$ solution was added to the soil and left for two hours. Mg substitutes for Ba in soil and Ba is removed as insoluble $BaSO_4$. The amount of Mg exchanged in this way was determined by titrating the excess $MgSO_4$ solution with EDTA. No standard reference materials were available for inclusion in CEC analysis but replicate analyses were determined as a check on the method (Table 10).

Table 10. Replicate CEC analysis in BGS clay reference materials.

Sample	Date						
	March 1995		June 1995	October 1996		June 1996	July 1996
HN03	43.8	43.2					44.8*
HN05	50	50.7*				50.0*	
HN08	53.6	53.8*	53.6*	54.4*	54.5*		
HN09	54.3	53.8*	54.3*				

* Based on 2.5 g of sample rather than 50 g of sample due to high initial CEC results.

7.1.9 Analysis of TOC in Soils

Determinations of TOC in soil samples was carried out using a LECO CS125 Carbon Analyser at Geolab UK Ltd. Ground samples were accurately weighed into LECO crucibles and were treated four times with hot 10% HCl solution to remove oxidised carbon. The samples were washed four times with deionised water and then dried in an oven at 60 °C prior to analysis. The instrument was calibrated with a standard LECO carbon steel ring of 0.815% carbon content. An internal claystone standard with a TOC content of 2.5% was included in the analysis.

7.1.10 Bulk Mineralogical Determinations in Soils

Details of semi-quantitative XRD analysis to determine soil bulk mineralogy are given in Appendix G.

7.1.11 Ion Chromatography determinations in Waters

Cl, NO_3 and SO_4 concentrations in water samples were determined by ion chromatography (IC) (Appendix F).

7.2 IRMA Analysis

Thirty selected soil samples underwent analysis for approximately 25 elements by ICP-AES and ICP-MS at the IRMA (Appendix H). Soil pH was also measured. Total Se in soil was determined by Molecular Fluorescence Spectrometry (MFS) and hydride generation AFS (Appendix H).

8. ERROR CONTROL AND DATA COMPARISONS

8.1 BGS Analytical Replicates

BGS analytical replicate results for ICP-AES partial soil analysis, soil water soluble Se, soil pH, grain total Se and hair total Se in general show good reproducibility of the analytical methods (Tables 11 - 15). Results near to the LOD for Mo and Pb in soil demonstrate high variability (30 - 40%, soil sample 17) indicating that results close to and below the detection limit should be treated with caution. Results for Mn in soil samples 17 and 40 (30 - 45% variation) and water soluble Se in soil sample 9 (69% variation) show high variability indicating there may be problems with the repeatability of the analytical methods for these determinants. However, the majority of determinations in all sample types are within ± 10% variation. Analytical replicate measurements were not carried out during soil total Se and water total Se analyses.

Table 11. ICP-AES partial extractant analytical replicate determinations in soil.

Sample Number	Ca µg/g	Cd µg/g	Cu µg/g	Fe µg/g	Mg µg/g	Mn µg/g	Mo µg/g	Pb µg/g	V µg/g	Zn µg/g
3	3321	4.7	45.8	29550	4085	69	15.6	17.3	328.5	112.5
3	3063	4.8	40.0	27314	3874	81	14.6	17.5	299.1	102.8
V	*6*	*1.5*	*10*	*6*	*4*	*10*	*4.7*	*0.8*	*10*	*10*
17	5449	13.6	80.3	57637	5525	348	8.1	†3.1	285.0	137.5
17	5391	13.7	80.8	51008	5543	220	4.4	†2.5	266.8	136.3
V	*0.8*	*0.5*	*0.4*	*9*	*0.2*	*30*	*40*	*20*	*4.7*	*0.6*
27	3207	†0.5	6.3	36445	8124	482	†2.5	†2.5	58.7	84.7
27	3367	†0.6	6.8	39521	8715	533	†3.0	†3.0	66.7	86.3
V	*3*	*10*	*10*	*6*	*5*	*7.1*	*10*	*10*	*10*	*1.3*
40	2769	9.8	92.5	42753	5674	335	46.5	†3.3	374.4	167.3
40	2621	9.3	86.5	40329	5299	648	51.4	†3.1	368.2	160.2
V	*4*	*3.7*	*4.7*	*4*	*5*	*45*	*10*	*4.4*	*1.2*	*3.1*
54	3341	19.5	133.0	52793	5597	1109	69.7	†3.3	816.5	222.5
54	3404	19.5	133.8	52050	5596	1106	69.9	†3.6	835.1	225.0
V	*1*	*0*	*0.4*	*1*	*0.01*	*0.2*	*0.2*	*10*	*1.6*	*0.8*
68	7581	4.8	29.4	28876	5334	729	8.8	18.0	163.2	129.0
68	7117	4.5	27.7	27604	5025	658	8.2	16.2	146.3	121.4
V	*4*	*4.6*	*4.2*	*3*	*4*	*7.2*	*5*	*10*	*10*	*4.3*
100	3698	2.2	15.8	42611	12412	355	†2.1	†2.1	64.3	87.8
100	3616	2.1	15.9	42928	12368	367	†2.2	†2.2	64.2	91.2
V	*2*	*3.3*	*0.5*	*0.5*	*0.3*	*2*	*3.3*	*3.3*	*0.1*	*2.7*

V = coefficient of variation expressed as % † results below LOD

Table 12. AFS analytical replicate determinations in soil.

Sample Number	Soil Water Sol. Se ng/g	Coefficient of Variation %
9	0.73	69
9	0.25	
15	62.9	0.45
15	63.3	
32	12.8	2
32	12.5	
56	179	5
56	193	
74	4.20	2
74	4.35	
84	46.2	2
84	45.1	
88	0.62	17
88	0.79	

Table 13. Soil pH analytical replicate determinations.

Sample Number	Soil pH	Coefficient of Variation %
7	5.34	0.7
7	5.39	
13	6.94	0.7
13	6.87	
40	4.78	1.3
40	4.87	
46	7.04	0.5
46	6.99	
55	4.80	0.7
55	4.85	
64	6.43	0.9
64	6.51	
65	6.44	0.2
65	6.46	
66	6.68	0.2
66	6.66	
68	6.87	0.3
68	6.90	
74	5.96	0.7
74	6.02	
90	6.55	0.3
90	6.52	
96	5.12	0.7
96	5.17	
99	6.47	0.5
99	6.42	

Table 14. AFS analytical replicate determinations in grain.

Sample Number	Total Se µg/g	Coefficient of Variation %
18	0.255	3.0
18	0.266	
37	1.21	6.1
37	1.32	
40	0.702	1.4
40	0.716	
52	0.197	3.5
52	0.207	
64	0.025	2.8
64	0.026	
86	0.052	5.2
86	0.056	
91	2.54	0.8
91	2.57	

Table 15. AFS analytical replicate determinations in hair.

Sample Number	Total Se µg/g	Coefficient of Variation %
14	0.177	15.9
14	0.222	
26	18.7	0.4
26	18.8	
38	36.8	6.9
38	40.6	
54	40.1	4.1
54	42.5	
58	0.240	10.4
58	0.278	
71	13.7	5.0
71	14.7	
84	6.68	8.1
84	7.49	

8.2 BGS Field Duplicates

Analytical results for BGS field duplicate soil samples are shown in Table 16. Results close to and below the detection limits for water soluble Se, partial extraction Cd, Mo and Pb show high variability (20%) and should be treated with caution. Water soluble Se results in samples 18 and 49 and 19 and 39 are highly variable (70%). ICP-AES partial results for field duplicate pairs 1, 2, 4, 5 and 7 vary considerably (20%) for one or more of the elements Ca, Cd, Cu, Fe, Mn, Mo, Pb, V, and Zn. Repeat partial extraction and ICP-AES analysis of selected samples from these field duplicate pairs was carried out to check the precision of these determinations (Tables 17 and 18).

Table 16. Results of soil field duplicate analysis.

Sample Number	Field Pair	Water Sol Se ng/g	Total Se µg/g	Ca µg/g	Cd µg/g	Cu µg/g	Fe µg/g	Mg µg/g	Mn µg/g	Mo µg/g	Pb µg/g	V µg/g	Zn µg/g	LOI %	pH	Village Code
1	1	36.9	5.15	28245	4.5	45.4	8460	4177	343	10.5	14.8	335.1	115.8	7.54	7.75	HT3
99	1	51.6	5.30	7017	3.9	38.2	25881	3877	251	10.2	16.7	301.5	98.9	6.20	*6.44	HT3
V		*23.5*	*2*	*100*	*10*	*10*	*100*	*5*	*20*	*2*	*10*	*10*	*10*	*14*	*13*	
2	2	0.37	0.171	2549	†0.5	6.3	24422	6193	250	†2.6	†2.6	47.4	6.3	5.37	5.08	LK5
92	2	0.46	0.173	2205	†0.4	5.1	21668	5589	270	†2.1	†2.1	41.4	56.7	5.15	3.97	LK5
V		*15.3*	*.8*	*10*	*20*	*10*	*8*	*7*	*5*	*20*	*20*	*10*	*100*	*3*	*17*	
5	3	0.11	.221	1008	†0.3	12.3	35696	5486	194	†1.8	†1.8	49.1	60.9	6.97	4.66	LK1
60	3	0.33	.235	807	†0.4	10.6	29942	4709	198	†2.1	†2.1	45.4	56.6	7.43	4.46	LK1
V		*70.7*	*4.3*	*20*	*20*	*10*	*10*	*10*	*10*	*10*	*10*	*10*	*10*	*5*	*3*	
18	4	123.0	11.9	5346	18.5	59.7	26140	5756	563	46.4	19.8	770.3	237.0	6.62	7.20	HN1
49	4	40.5	10.9	3995	12.8	45.2	22993	4785	497	26.3	15.8	582.4	170.9	6.56	6.67	HN1
V		*71.4*	*6.2*	*20*	*30*	*20*	*9*	*10*	*9*	*40*	*20*	*20*	*20*	*1*	*5*	
19	5	16.3	14.6	2523	8.1	85.9	49077	4914	702	26.6	19.1	358.3	147.4	8.53	6.29	HT1
39	5	20.2	17.6	2342	7.5	97.1	46063	4792	504	38.3	12.8	481.8	143.7	9.03	5.87	HT1
V		*15.1*	*13.2*	*5*	*10*	*10*	*4*	*2*	*20*	*30*	*30*	*20*	*1.8*	*4*	*5*	
20	6	1.22	0.126	2827	1.6	12.0	33308	8254	584	†2.5	†2.5	51.8	70.7	5.44	5.69	LK3
42	6	0.13	0.108	2495	1.4	9.6	28896	7128	546	†3.2	†3.2	49.6	64.8	4.77	5.62	LK3
V		*100*	*10.9*	*9*	*10*	*20*	*10*	*10*	*5*	*20*	*20*	*3*	*10*	*9*	*1*	
40	7	21.10	13.0	*2695	*9.6	*89.5	*41541	*5486	*492	*49.0	*†3.2	*371.3	*163.8	9.34	*4.82	HT5
93	7	6.34	12.1	3026	8.6	87.2	40912	5835	475	66.4	†2.5	315.1	187.8	7.73	4.10	HT5
V		*76.1*	*5.1*	*8*	*10*	*2*	*1*	*4*	*2*	*20*	*20*	*10*	*10*	*13*	*11*	
59	8	3.55	1.96	2226	2.3	42.3	36662	5435	487	†2.5	25.2	119.6	86.5	7.24	5.90	HN4
70	8	3.56	2.14	2176	2.3	43.3	37762	5258	455	†3.8	23.1	121.6	86.3	7.45	5.57	HN4
V		*0.2*	*6.2*	*2*	*0*	*2*	*2*	*2*	*5*	*30*	*10*	*1*	*0.2*	*2*	*4*	

V = coefficient of variation expressed as %   * Average of 2 analytical replicate results.   † Results below LOD

Although half the results for Pb during the first analytical run were above the limit of detection, all the results for Pb during the second set of analyses fall below the detection limit making comparison between the two sets of data difficult (Table 17).
Results for Pb should, therefore, be treated with caution. Results for Mn in samples 2, 39, 40 and 49 and for Mo in samples 40, 49 and 93 show high variability (> 20%) (Table 17) indicating there may be a problem with the analyses or partial extraction of these elements.

Differences between the concentration of Ca, Cu, Cd, V and Zn in samples 18 and 49 and V in samples 19 and 39 exhibited in the first set of results are evident in the repeat analyses (Table 18) and are therefore genuine field variations. These chemical differences between samples collected in the same field are probably due to the inhomogeneous nature of the soils in Enshi District which contain many carbonaceous and other rock fragments. Analysis of variance results show that despite these inhomogeneities, the within site variance is much less than the between site variance for each of these soil parameters confirming the robustness of the sampling method. (Appendix I).

Table 17. Repeat ICP-AES partial extractant analysis of selected soil field duplicate samples.

Anal Run	Samp No	Field Pair	Ca µg/g	Cd µg/g	Cu µg/g	Fe µg/g	Mg µg/g	Mn µg/g	Mo µg/g	Pb µg/g	V µg/g	Zn µg/g	Village Code
2	1	2	2549	†0.5	6.3	24422	6193	250.0	†2.6	†2.6	47.4	6.3	LK5
2	2	2	2232	†0.7	4.9	22269	5657	85.6	†2.0	†6.7	37.8	57.6	LK5
V			*9.4*	*20.2*	*17.7*	*6.5*	*6.4*	*69.3*	*18.4*	*62.9*	*15.9*	*100*	
18	1	4	5346	18.5	59.7	26141	5756	563	46.4	19.8	770.3	237.0	HN1
18	2	4	4951	17.0	54.4	24042	5383	519	39.3	†6.7	690.2	221.7	HN1
V			*5.4*	*6*	*6.6*	*5.9*	*4.7*	*5.8*	*11.7*	*70.1*	*7.8*	*4.7*	
19	1	5	2523	8.1	85.9	49077	4914	702	26.7	19.1	358.3	147.4	HT1
19	2	5	2426	7.6	84.2	47741	4803	650	27.3	†6.7	363.0	137.1	HT1
V			*2.8*	*4.5*	*1.4*	*2*	*1.6*	*5.4*	*1.6*	*68.2*	*0.9*	*5.1*	
39	1	5	2342	7.5	97.1	46063	4792	504	38.3	12.8	481.8	143.7	HT1
39	2	5	2287	6.8	96.2	44440	4830	690	39.5	†6.7	477.0	139.6	HT1
V			*1.7*	*6.9*	*0.7*	*2.5*	*0.6*	*22*	*2.2*	*44.5*	*0.7*	*2*	
40	1	7	2695	9.6	89.5	41541	5486	497	49.0	†3.2	371.3	170.9	HT5
40	2	7	2667	8.8	88.8	43242	5476	227	17.9	†6.3	347.8	156.9	HT5
V			*0.7*	*6.1*	*0.6*	*2.8*	*0.1*	*52.7*	*65.7*	*48.5*	*4.6*	*6*	
49	1	4	3995	12.8	45.2	22993	4785	497	26.3	15.8	582.2	170.9	HN1
49	2	4	4014	12.7	48.1	23746	4936	121	11.2	†6.5	603.5	174.9	HN1
V			*0.3*	*0.6*	*4.4*	*2.3*	*2.2*	*86*	*56.9*	*58.7*	*2.5*	*1.6*	
93	1	7	3026	8.6	87.2	40912	5835	475	66.4	†2.5	315.1	187.8	HT5
93	2	7	3027	8.4	92.6	43617	6137	463	41.8	†6.3	313.0	198.5	HT5
V			*0.02*	*1.7*	*4.2*	*4.5*	*3.6*	*1.8*	*32.2*	*61.3*	*0.5*	*3.9*	
99	1	1	7017	3.9	38.2	25881	3877	251	10.2	16.7	301.5	98.9	HT3
99	2	1	6863	4.0	37.7	25998	3829	271	9.7	†6.7	312.7	97.8	HT3
V			*1.6*	*1.8*	*0.9*	*0.3*	*0.9*	*5.4*	*3.6*	*60.7*	*2.6*	*0.8*	

V = coefficient of variation expressed as % Anal = Analytical Samp No = Sample Number
† Results below LOD

Table 18. Comparison of two partial extractant ICP-AES analysis of selected soil field duplicate samples.

Anal Run	Samp No	Field Pair	Ca µg/g	Cd µg/g	Cu µg/g	Fe µg/g	Mg µg/g	Mn µg/g	Mo µg/g	Pb µg/g	V µg/g	Zn µg/g	Village Code
1	1	1	28245	4.5	45.4	8460	4177	343	10.5	14.8	335.1	115.8	HT3
1	99	1	7017	3.9	38.2	25881	3877	251	10.2	16.7	301.5	98.9	HT3
	V		*100*	*10*	*10*	*100*	*5*	*20*	*2*	*10*	*10*	*10*	
1	1	1	28245	4.5	45.4	8460	4177	343	10.5	14.8	335.1	115.8	HT3
2	99	1	6863	4.0	37.7	25998	3892	271	9.7	†6.6	312.7	97.8	HT3
	V		*86.1*	*8.3*	*13.1*	*72*	*6.1*	*16.6*	*5.6*	*53.6*	*4.9*	*11.9*	
1	2	2	2549	†0.5	6.3	24422	6193	250	†2.6	†2.6	47.4	6.3	LK5
1	92	2	2205	†0.4	5.1	21668	5589	270	†2.1	†2.1	41.4	56.7	LK5
	V		*10*	*20*	*10*	*8*	*7*	*5*	*20*	*20*	*10*	*100*	
2	2	2	2232	†0.7	4.9	22269	5657	86	†2.0	†6.7	37.8	57.6	LK5
1	92	2	2205	†0.4	5.1	21668	5589	270	†2.1	†2.1	41.4	56.7	LK5
	V		*0.9*	*35.4*	*2.8*	*1.9*	*0.9*	*73*	*34*	*74*	*6.4*	*1.1*	
1	18	4	5346	18.5	59.7	26140	5756	563	46.4	19.8	770.3	237.0	HN1
1	49	4	3995	12.8	45.2	22993	4785	497	26.3	15.8	582.4	170.9	HN1
	V		*20*	*30*	*20*	*9*	*10*	*9*	*40*	*20*	*20*	*20*	
2	18	4	4951	17.0	54.4	24042	5383	519	39.6	†6.7	690.2	221.7	HN1
2	49	4	4014	12.7	48.1	23746	4936	121	11.2	†6.5	603.5	174.9	HN1
	V		*14.8*	*20.5*	*8.7*	*0.9*	*6.1*	*87.9*	*78.7*	*1.5*	*9.5*	*16.7*	
1	19	5	2523	8.1	85.9	49077	4914	702	26.6	19.1	358.3	147.4	HT1
1	39	5	2342	7.5	97.1	46063	4792	504	38.3	12.8	481.8	143.7	HT1
	V		*5*	*10*	*10*	*4*	*2*	*20*	*30*	*30*	*20*	*1.8*	
2	19	5	2426	7.6	84.2	47741	4803	650	27.3	†6.7	363	137.1	HT1
2	39	5	2287	6.8	96.2	44440	4830	690	39.5	†6.7	477	139.6	HT1
	V		*4.2*	*7.9*	*9.4*	*5.1*	*0.4*	*4.2*	*25.8*	*0*	*19.2*	*1.3*	
1	40	7	*2695	*9.6	*89.5	*41541	*5486	*492	*49.0	*†3.2	*371.3	*163.8	HT5
1	93	7	3026	8.6	87.2	40912	5835	475	66.4	†2.5	315.1	187.8	HT5
	V		*8*	*10*	*2*	*1*	*4*	*2*	*20*	*20*	*10*	*10*	
2	40	7	2667	8.8	88.8	43242	5476	227	17.9	†6.3	347.8	156.9	HT5
2	93	7	3027	8.4	92.6	43617	6137	463	41.8	†6.3	313.0	198.5	HT5
	V		*8.9*	*3.3*	*3*	*0.6*	*8*	*48.4*	*56.6*	*0*	*7.4*	*16.6*	

V = coefficient of variation expressed as %   Anal = Analytical   Samp No = Sample Number
* Average of 2 analytical replicate results.   † Results below LOD

Field duplicate analyses for total Se in grain samples are compatible with the exception of determinations at or below the detection limit and sample pairs 5 (sample numbers 19 and 39) and 8 (sample numbers 59 and 70) (Table 19). Samples 19 and 39 were reanalysed at the BGS and by IRMA and similar results were obtained indicating gross variation in Se concentrations between maize cobs from the same grain store (Table 19).

Reproducibility between measurements in water field duplicates is very good (< 5%) (Table 20).

Table 19. Results of AFS grain field duplicate analysis

Analytical Run	Sample Number	Field Pair	Grain Total Se µg/g	Coefficient of Variation %
1	1	1	3.19	7
1	99	1	2.88	
1	2	2	†0.002	28
1	92	2	0.003	
1	5	3	†0.0013	55
1	60	3	0.0030	
1	18	4	*0.26	22
1	49	4	0.19	
1	19	5	7.75	91
1	39	5	1.66	
2	19	5	8.6	88
2	39	5	2.0	
IRMA	19	5	7.80	92
IRMA	39	5	1.64	
1	20	6	0.0030	55
1	42	6	†0.0013	
1	40	7	*0.7090	22
1	93	7	0.5160	
1	59	8	0.026	49
1	70	8	0.054	

† Results at or below the LOD

* Average of 2 analytical replicate results

Table 20. Results of AFS water field duplicate analysis

Sample Number	Field Pair	Total Se µg/g	Eh mV	pH	Conductivity µS	Bicarbonate mg/l $CaCO_3$
5	3	0.42	364.4	6.78	513	62
60	3	0.45	386.5	6.79	510	57
V		*5*	*4.2*	*0.10*	*0.4*	*5.9*
18	4	30.3	432.6	6.98	457	172
49	4	30.2	409.6	7.00	480	175
V		*0.23*	*3.9*	*.20*	*3.5*	*1.2*
19	5	38.1	454.6	6.19	1008	38
39	5	38.1	454.9	6.17	1011	42
V		*0*	*0.05*	*0.20*	*0.2*	*7.1*

V = coefficient of variation expressed as %

8.3 Comparisons between BGS and IRMA Data

Comparisons between the BGS data and results for 30 soil samples analysed at the IRMA in general show good compatibility between analyses in the two laboratories (Figure 8). Results for Ca in sample 88, Cu in sample 48, Mn in sample 89 and Zn in sample 18 are higher in the IRMA dataset than the BGS dataset and do not fit the general trends of the data. Determinations for soil Pb range from 13 - 169 µg/g in the IRMA dataset compared with much lower values of 1.8 - 27 µg/g in the BGS dataset. In order to test whether these discrepancies were due to the different methods of extraction employed in each laboratory, repeat analysis of 10 selected samples was carried out at the BGS using the same nitric-perchloric-hydrofluoric digestion as the IRMA. Results for the initial partial extraction and the repeat total extraction are very similar for the majority of elements demonstrating that the partial extraction method did remove most elements from the soils. More V has been extracted by the total digestion method (Figure 9). Discrepancies between the IRMA and BGS datasets are therefore due to genuine sample inhomogeneities or inter-laboratory differences and not the extraction method. Results for total Pb determinations were not reported due to problems with the analytical method.

Results for total Se in selected grain and hair samples analysed by both BGS and IRMA show good agreement between results from the two laboratories (Table 21).

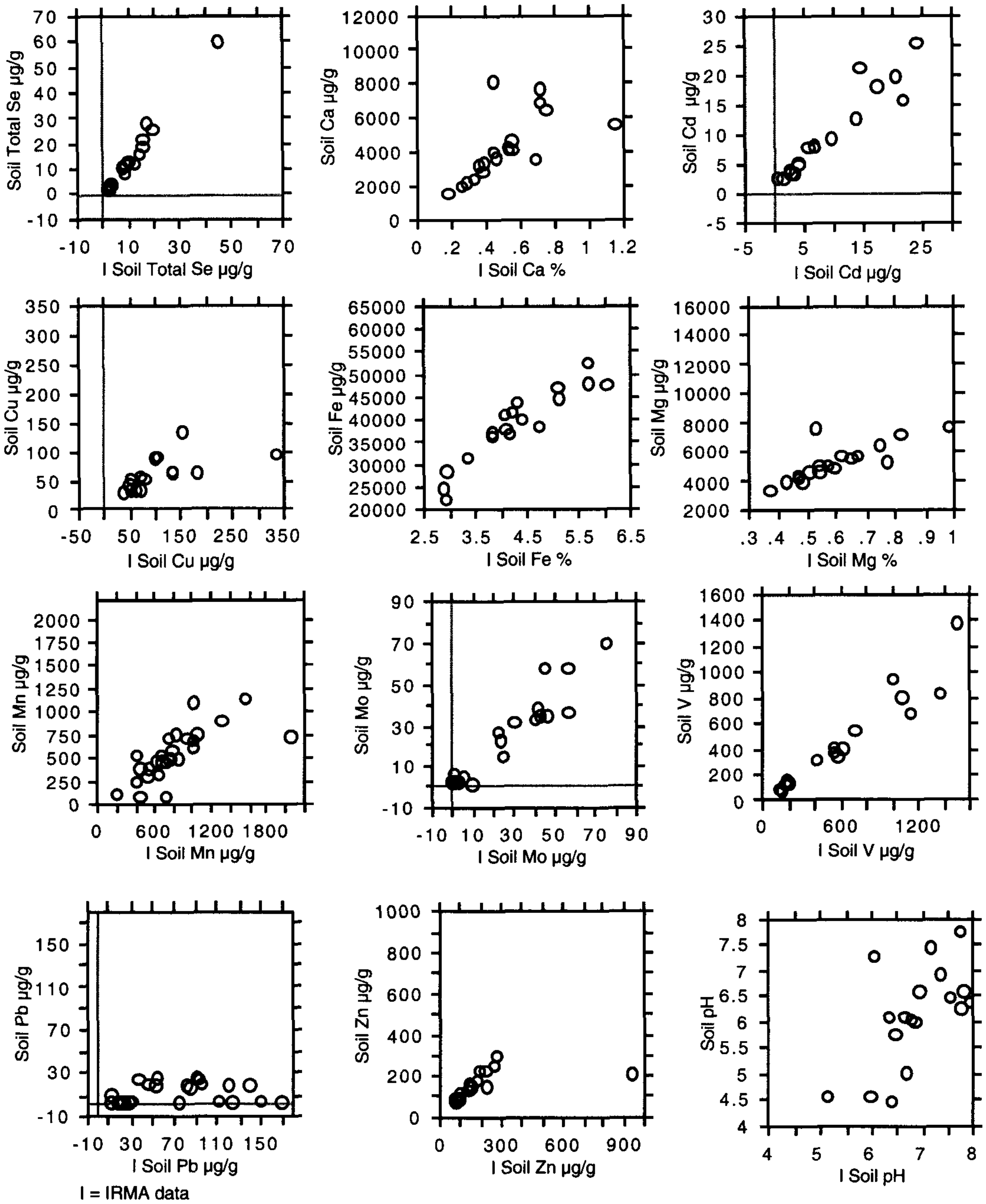
Table 21. Comparison between total Se determinations in selected grain and hair samples by the BGS and the IRMA.

Sample Type	Sample Number	BGS Total Se µg/g	IRMA Total Se µg/g
Grain	9	†0.0013	0.012
	19	7.75	7.81
	39	1.66	1.64
	83	4.47	4.85
	89	4.81	4.46
Hair	41	28.4	28.8
	48	46.7	41.7
	54	*41.3	41.5
	97	28.6	28.8

† Results below LOD

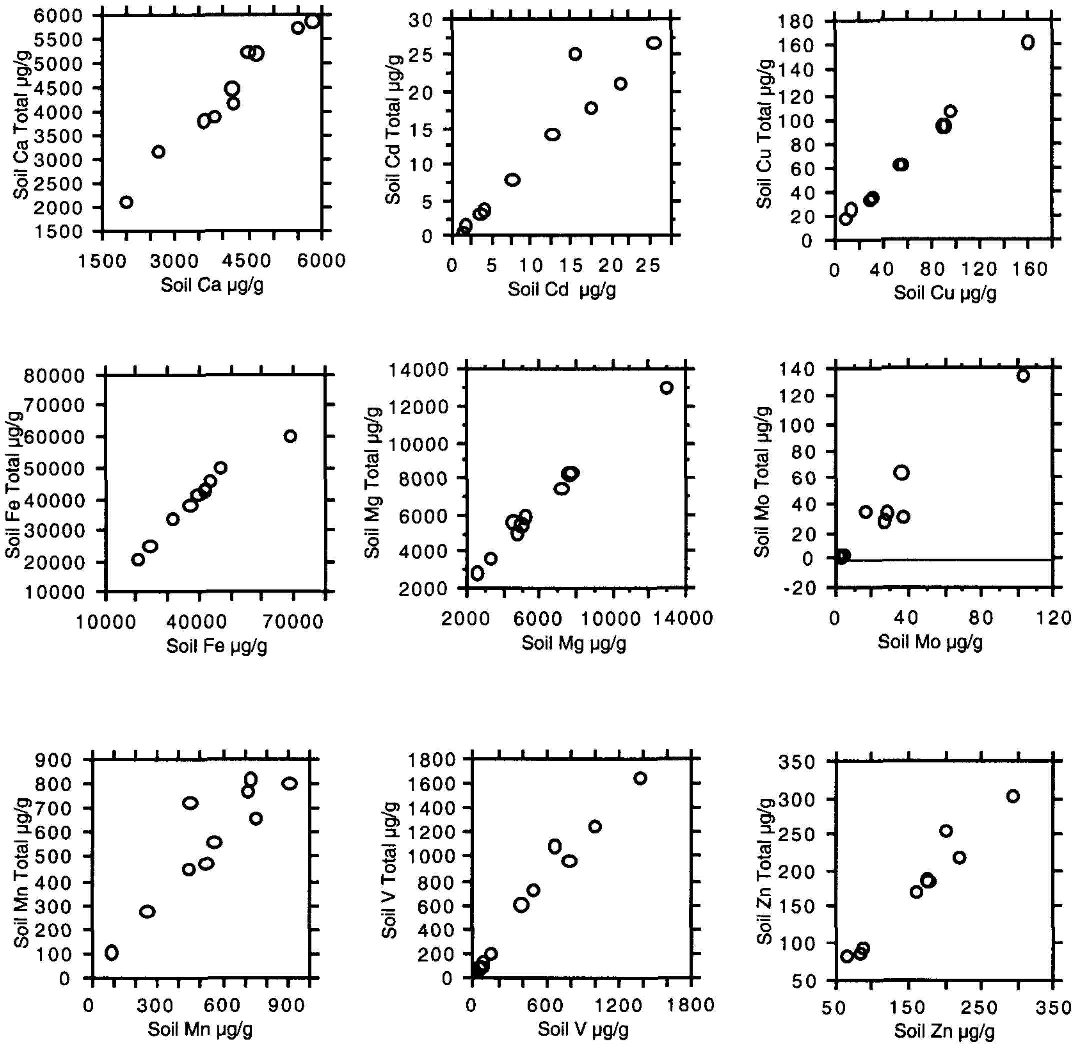
* Average of 2 analytical replicate results

The results for the analytical and field duplicates in soils and comparisons between BGS and IRMA data demonstrate the importance of error control in geochemical investigations. Due to the problems encountered with results for Pb, Mo and Mn these elements are not included in the statistical analyses presented in this report.



I = IRMA data

Figure 8. Comparisons between BGS and IRMA analytical results for soils.



Soil Zn µg/g = partial nitric perchloric digest
Soil Zn Total µg/g = total nitric perchloric hydrofluoric digest

Figure 9. Comparisons between total and partial digests of selected BGS soil samples.

8.4 Comparisons between LOI, TOC and Organic Matter in Soils

TOC was determined on a selection of samples from the three Se village groups to assess the relationship between TOC and LOI as an indicator of organic matter content. Assuming that TOC generally accounts for 58% of the organic matter in soils, the organic matter content can be calculated by multiplying the TOC values by 100/58 (Rowell, 1994).

The TOC and organic matter values determined in soil samples are shown in Figure 10. LOI correlates closely (R^2= 0.862) with TOC and organic matter in the soils but the LOI values are higher than the TOC and organic matter values (Figure 10). At most, organic matter accounts for 63% of the LOI in the Enshi soils. The disparity between organic matter content and LOI is probably due to the loss of water from clay minerals during ignition. Rowell (1994) reports that LOI can be used as an estimate of organic matter content in sandy soils but may be up to twice the organic matter content in heavy textured soils because clays and sesquioxides lose ‘structural’ water between temperatures of 100 - 500 °C.

The Enshi soils were dried at a low temperature of 35 °C to prevent loss of Se, prior to determination of LOI. LOI determinations in selected samples following drying at 100 °C indicated soil moisture contents of approximately 0.5%.

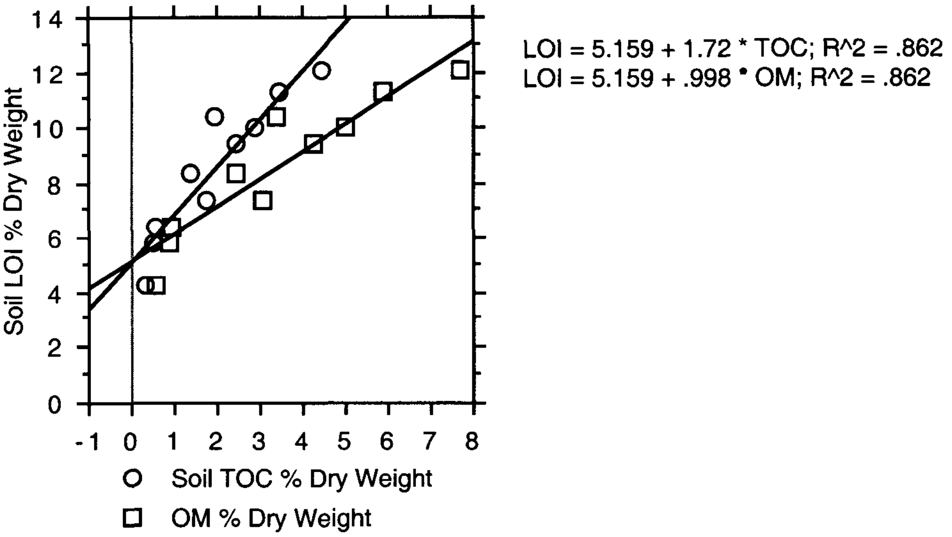


Figure 10. Comparisons between LOI, TOC and organic matter in Enshi soils.

8.5 Soil Profile Samples and Deeper Soil Samples

Selected analytical results for the two soil profiles (one from the LK and one from the HT villages (Figure 5)) and for three deeper (35 - 45 cm) soil samples from the LK, HN and HT villages are shown in Figures 11 and 12. In both soil profiles, the total Se content decreases with depth (Figure 11). In contrast, the total Se content of the HN and HT deeper soil samples is greater than the top soil samples (Figure 12).

As Fe and LOI increase, pH and soil water soluble Se decrease in the profile sample from the low Se area as expected (Figure 11). Increasing organic matter content in the soil, indicated by increasing LOI, results in more acid conditions, making Se less available. In the high Se area, water soluble Se and total Se decrease with depth whereas Fe concentrations increase (Figure 11).

Results for the top and deeper samples confirm a negative relationship between soil organic matter content and pH (Figure 12). In the HT villages, concentrations of total and water soluble Se rise as the organic matter content increases. Under acid conditions, Se in soil should be less available (McNeal & Balistrieri, 1989). It is likely that total Se exerts a greater control on water soluble Se levels than either organic matter or pH in the HT villages.

It is not possible to distinguish systematic differences in soil chemistry with depth on the basis of these few samples.

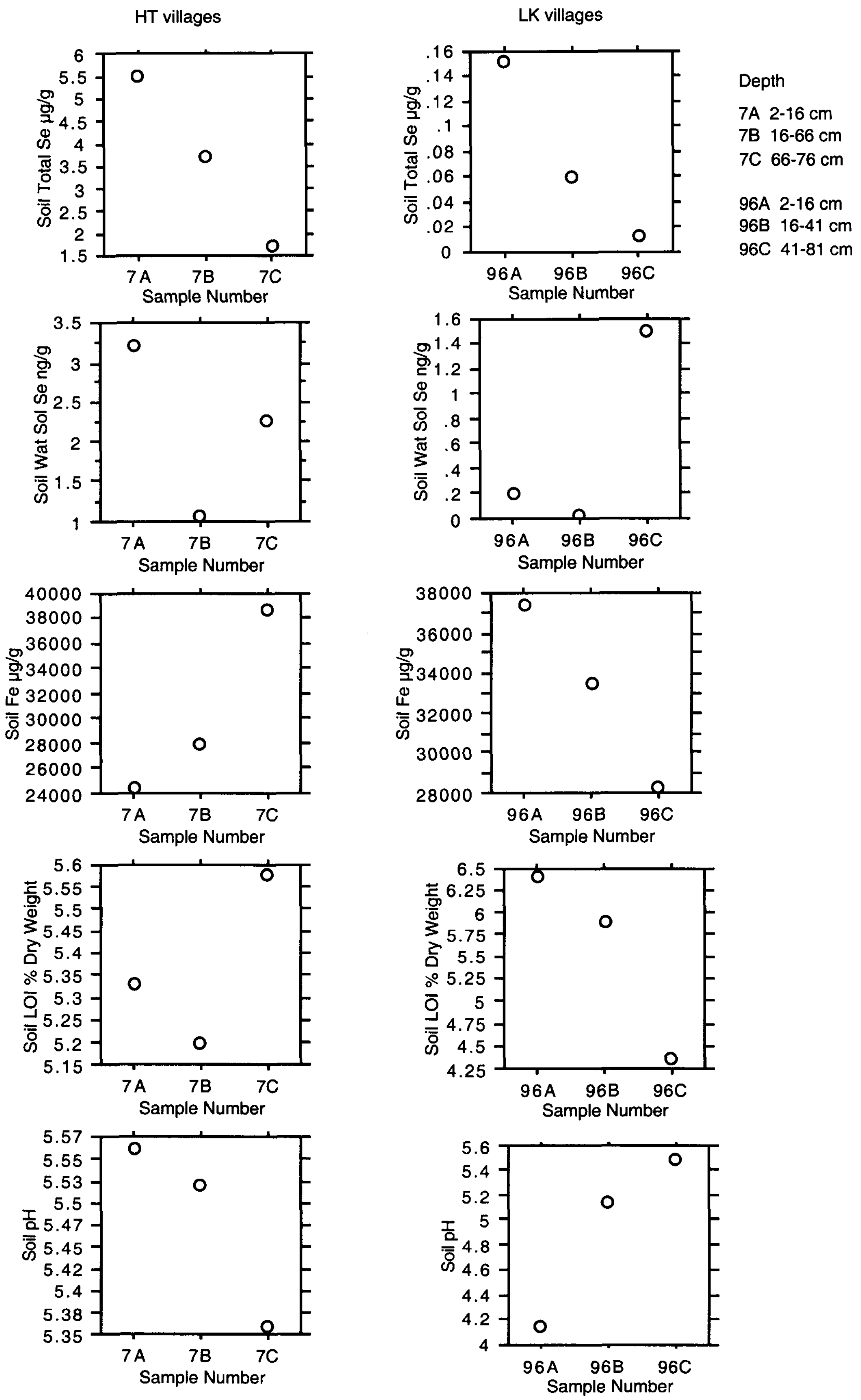


Figure 11. Selected parameters in two soil profile samples from the LK and HT villages.

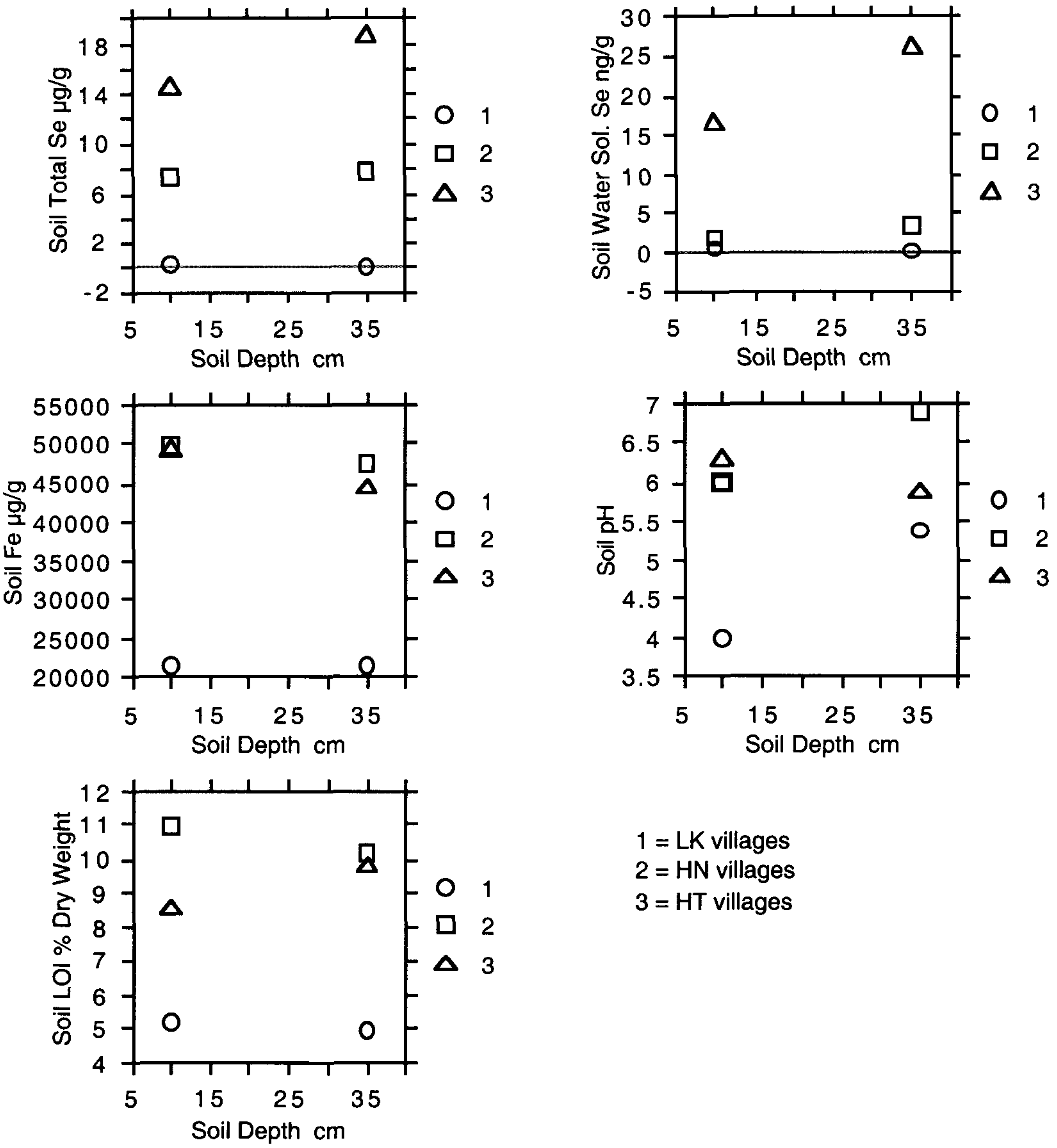


Figure 12. Selected parameters in three deeper soil samples and corresponding top soil samples in the LK, HN and HT villages.

8.6 Comparisons between Rice Paddy Soils and Maize-corn Field Soils

It has been suggested (Yang et al., 1983) that the incidence of selenosis in the 1960's was related in part to a drought which resulted in the failure of the rice crop. Villagers were forced to grow maize-corn on dry rice paddy fields. The maize-corn accumulated more Se than the rice probably as a result of the oxidation of Se^{2-} and Se^{0} to more bioavailable Se^{4+} and Se^{6+} under dry conditions (Yang et al., 1983). During the present study, ten rice paddy soils were sampled to assess the chemical characteristics of soils under the waterlogged conditions necessary for rice cultivation. No consistent difference in soil chemistry between the rice paddies and other fields is apparent in the HN and HT villages, however, in the LK villages, the paddy soils generally contain higher total Se and pH and have lower Fe and Ca than the maize-corn soils (Figure 13). Sequential extractions to assess the bioavailability of Se in rice paddy soils and maize-corn soils under wet and dry conditions are currently being conducted at the BGS.

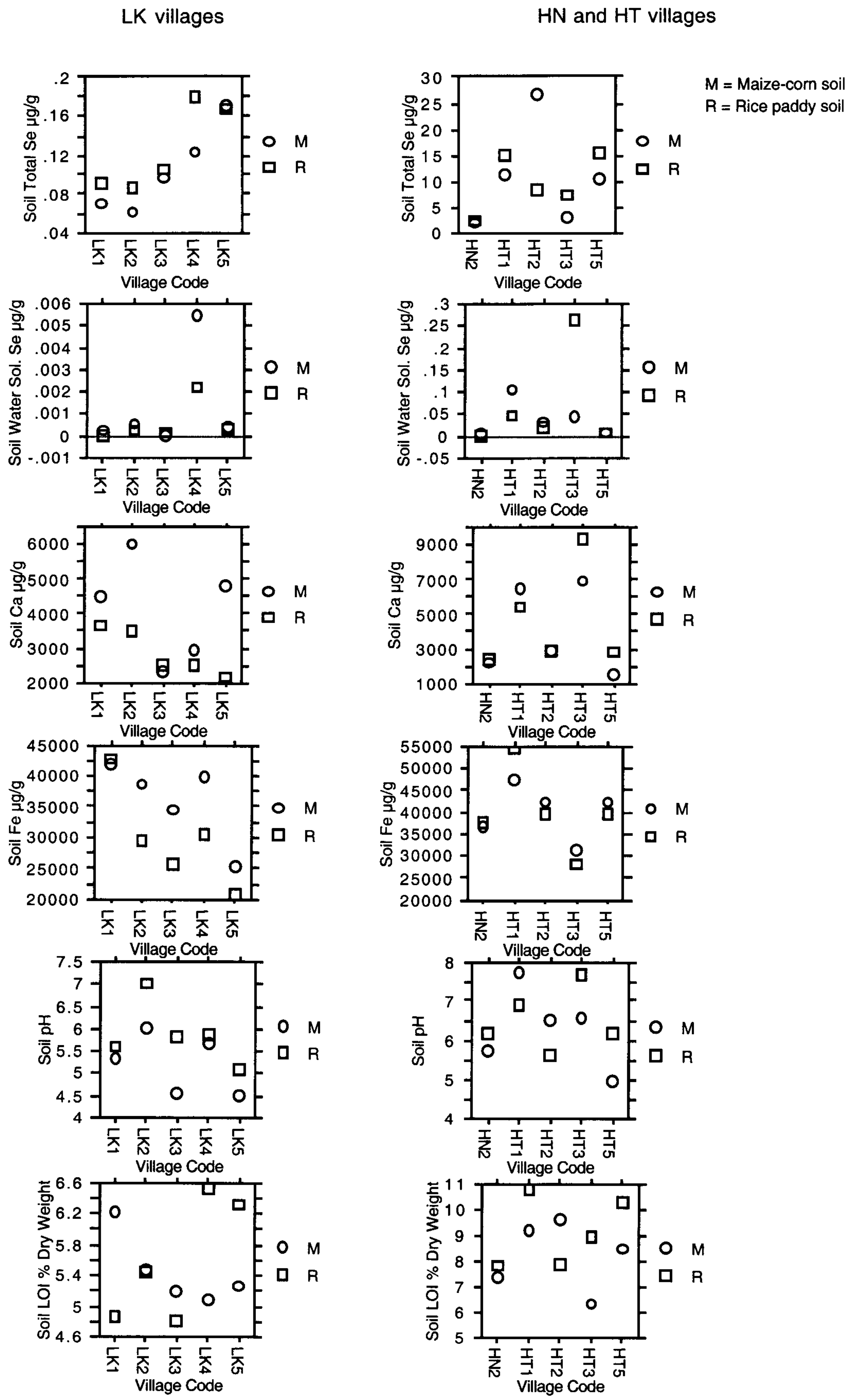


Figure 13. Comparisons between rice paddy and maize-corn field soil samples.

8.7 Comparisons between Rice and Maize-corn Samples

Maize-corn and rice samples were collected from grain stores therefore it is not possible to relate grain samples from adjacent fields for comparison of total Se levels. Results for total Se concentration in the seven rice samples and the average total Se in maize-corn samples, collected from the same villages, are presented in Figure 14.

Yang et al. (1983) reported lower levels of Se in rice than in maize-corn from the high Se area in Enshi probably reflecting differences in Se availability between wet rice paddy soils and dry maize-corn soils. In the Se toxic area, the average level of Se in rice was approximately half that of maize-corn (Table 22).

No clear relationship between the levels of total Se in maize-corn or rice in the HN and HT villages is evident from the small sample population available for comparison in the present study, however, rice contains more total Se than maize-corn in the LK villages (Figure 14) reflecting higher total Se and soil pH in the rice paddy soils (Figure 13).

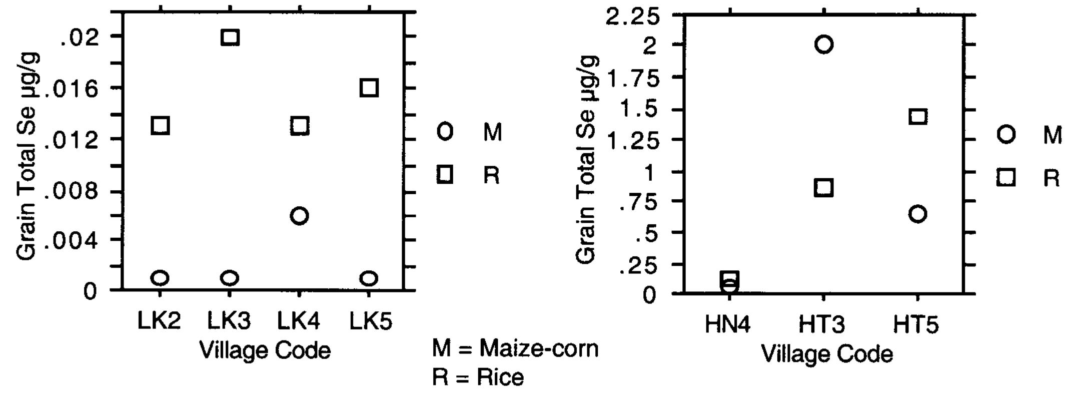


Figure 14. Comparisons between total Se content in rice and maize-corn grain samples.

Table 22. Comparisons between rice and maize-corn total Se levels in Enshi District.

Area	No. of Samples	Maize-corn Total Se µg/g Average	No. of Samples	Rice Total Se µg/g Average
Low Se*	195	0.005	49	0.007
LK†	24	0.003	4	0.015
High Se No Toxicity*	2	0.570	2	0.970
HN†	25	1.001	1	0.132
Toxic Area*	44	8.100	44	4.000
HT†	25	2.045	2	1.158

* From Yang et al., 1983 † Present study No. = Number

9. RESULTS AND DISCUSSION

9.1 Data Treatment

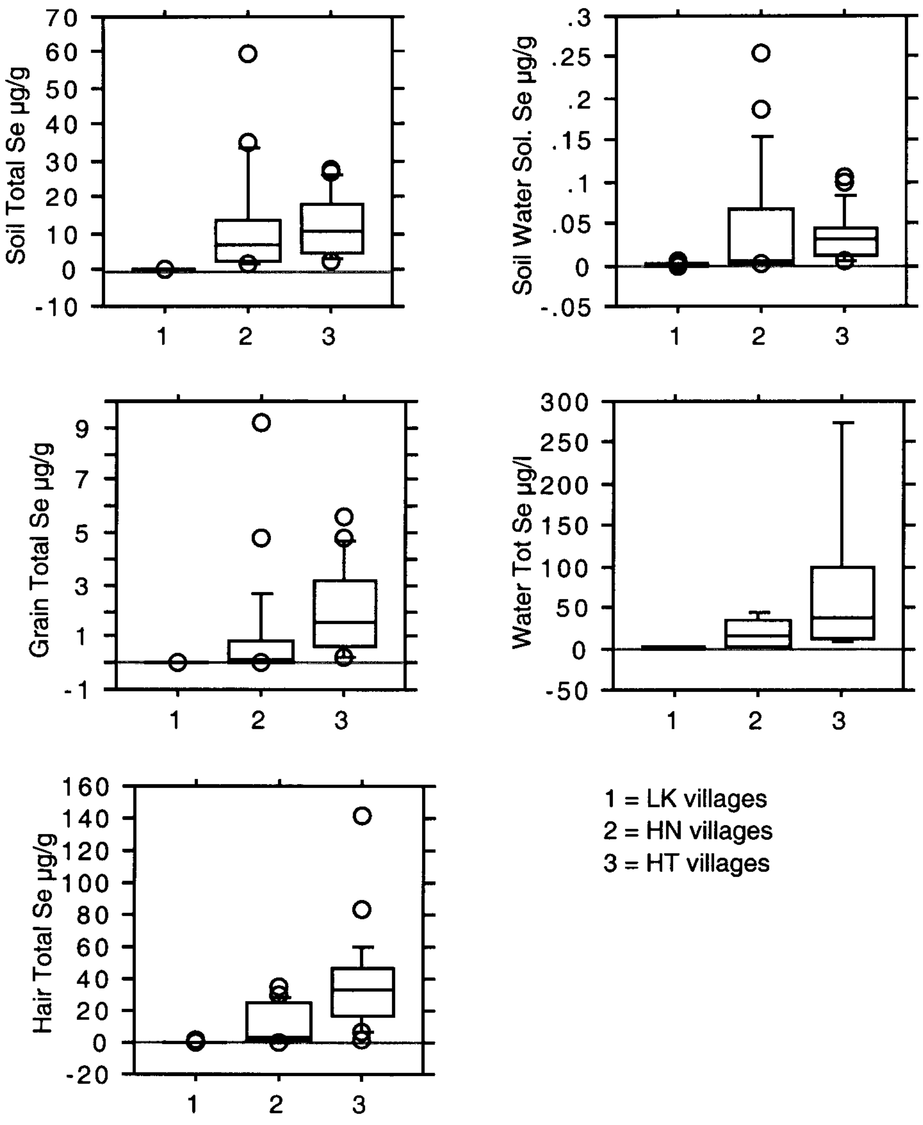
In order to carry out statistical analyses of the data, results for analytical replicates and field duplicates were averaged and rice paddy soil, deep soil, soil profile and rice grain results were removed from the datasets. Spearman Rank non-parametric correlation coefficients were calculated for statistical analysis as these are less sensitive to outlying values than product moment (Pearson) correlation coefficients. LOI is used as an indicator of organic matter content in soils. Unless otherwise stated, the results presented in the discussion refer to BGS analytical data.

9.2 Selenium Concentration in all Sample Types in the LK, HN and HT Villages

Results for Se concentrations in all sample types (Table 23) and the box and whisker plots (Figure 15) show that the Se content rises in soil, grain, water and hair samples from the LK to the HN and HT villages as expected. There is a clear association between environmental levels of Se and human Se status in the low and high Se regions. The LK, HN and HT villages and each sample type are considered in more detail to ascertain the controls on Se chemistry in the Enshi area.

Table 23. Summary of Se determinations in all sample types in the LK, HN and HT villages.

Village Group	Sample Type	Minimum Se µg/g	Maximum Se µg/g	Geometric Mean Se µg/g
LK	Soil Total	0.034	0.228	0.099
	Soil Water Soluble	0.00003	0.005	0.000288
	Grain	0.001	0.018	0.002
	Water µg/l	0.100	0. 440	0.168
	Hair	0.170	0.853	0.304
HN	Soil Total	1.494	59.4	7.06
	Soil Water Soluble	0.001	0.254	0.01
	Grain	0.017	9.175	0.198
	Water µg/l	0.460	44	7.7
	Hair	0.566	34.6	5.24
HT	Soil Total	2.736	27.5	9.46
	Soil Water Soluble	0.005	0.107	0.022
	Grain	0.182	5.6	1.38
	Water µg/l	7.3	275	32.6
	Hair	1.832	141	26.4



Number of samples in each village group = 25

Figure 15. Box and whisker plots of the 10th, 25th, 50th, 75th and 90th percentiles of Se distributions in all sample types in the LK, HN and HT villages.

9.3 Soil Chemistry

9.3.1 Results and General Description

Results of analysis of soil samples from the Enshi District are detailed in Appendix M. The distribution of elements and other parameters determined in soils in the three village groups by the BGS and the IRMA are shown in Figure 16. Results for the HN and HT villages are plotted together to allow direct comparison between these two village groups.

Spearman Rank correlation coefficients were calculated for selected BGS and IRMA soil parameters in each separate village group (Appendix J) to examine the relationships between soil chemical parameters in detail. Significant (95% confidence level) correlations in the three groups are summarised in Table 24.

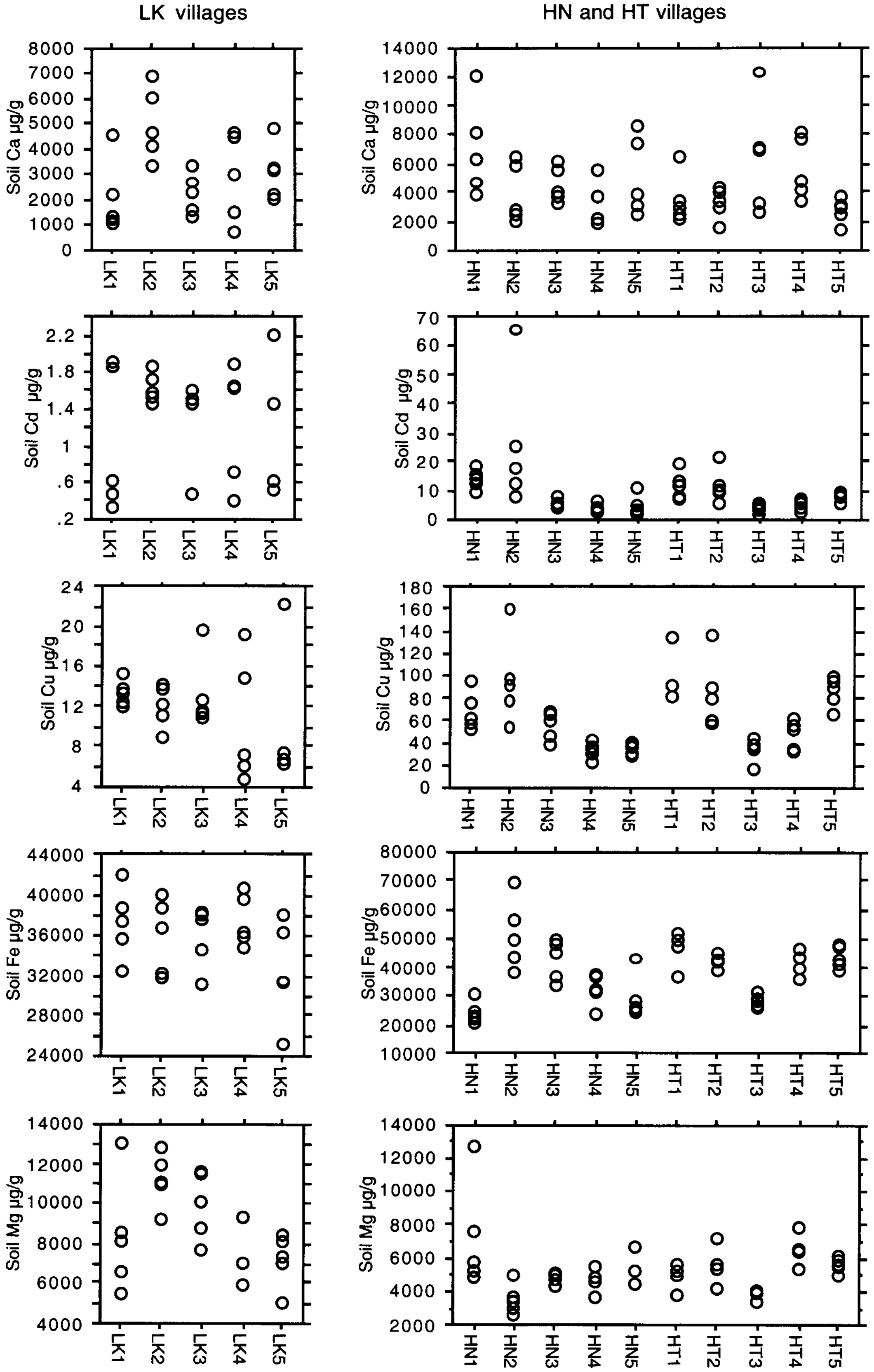


Figure 16. Selected soil chemistry parameter distributions in the LK, HN and HT villages.

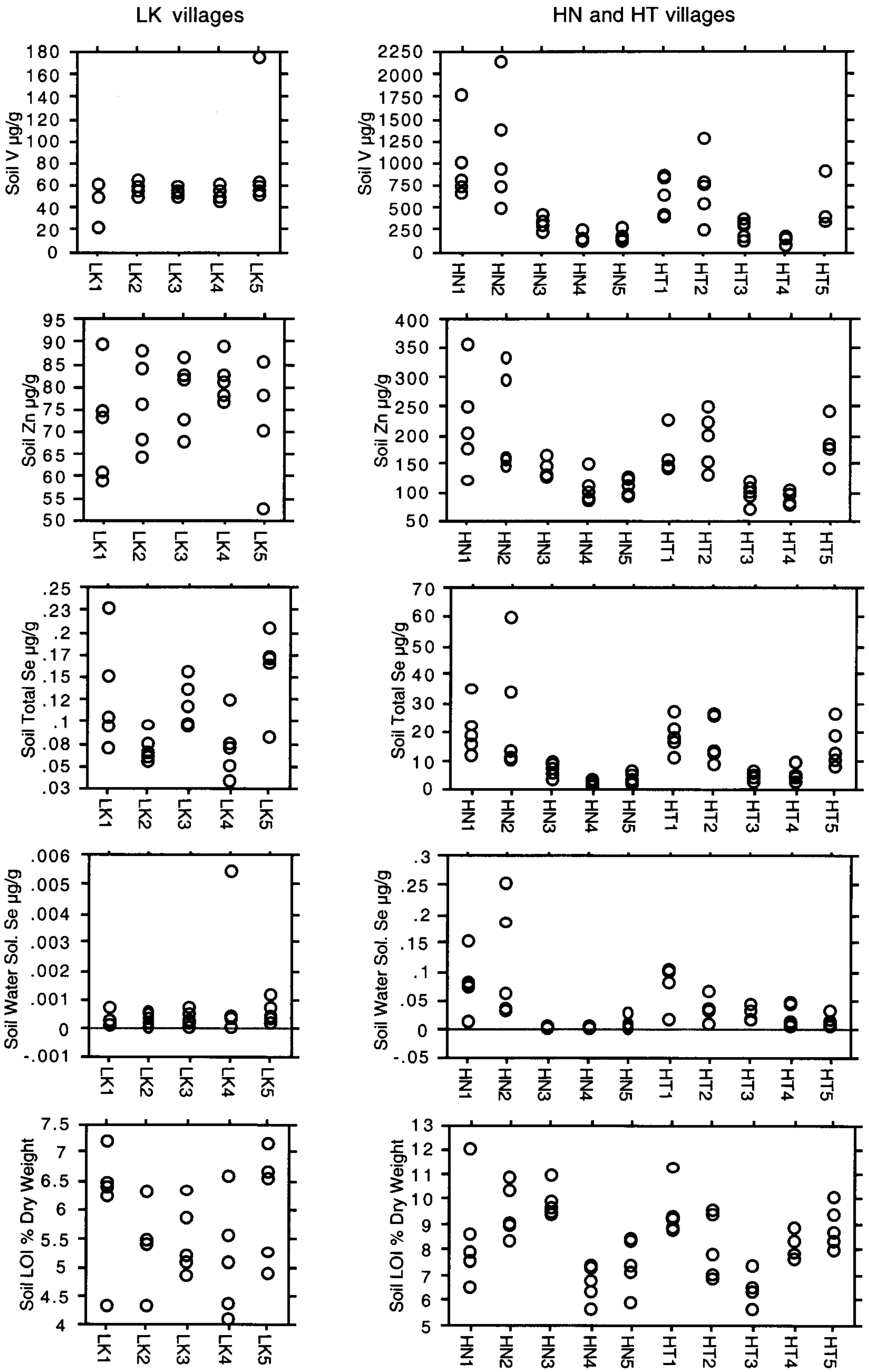
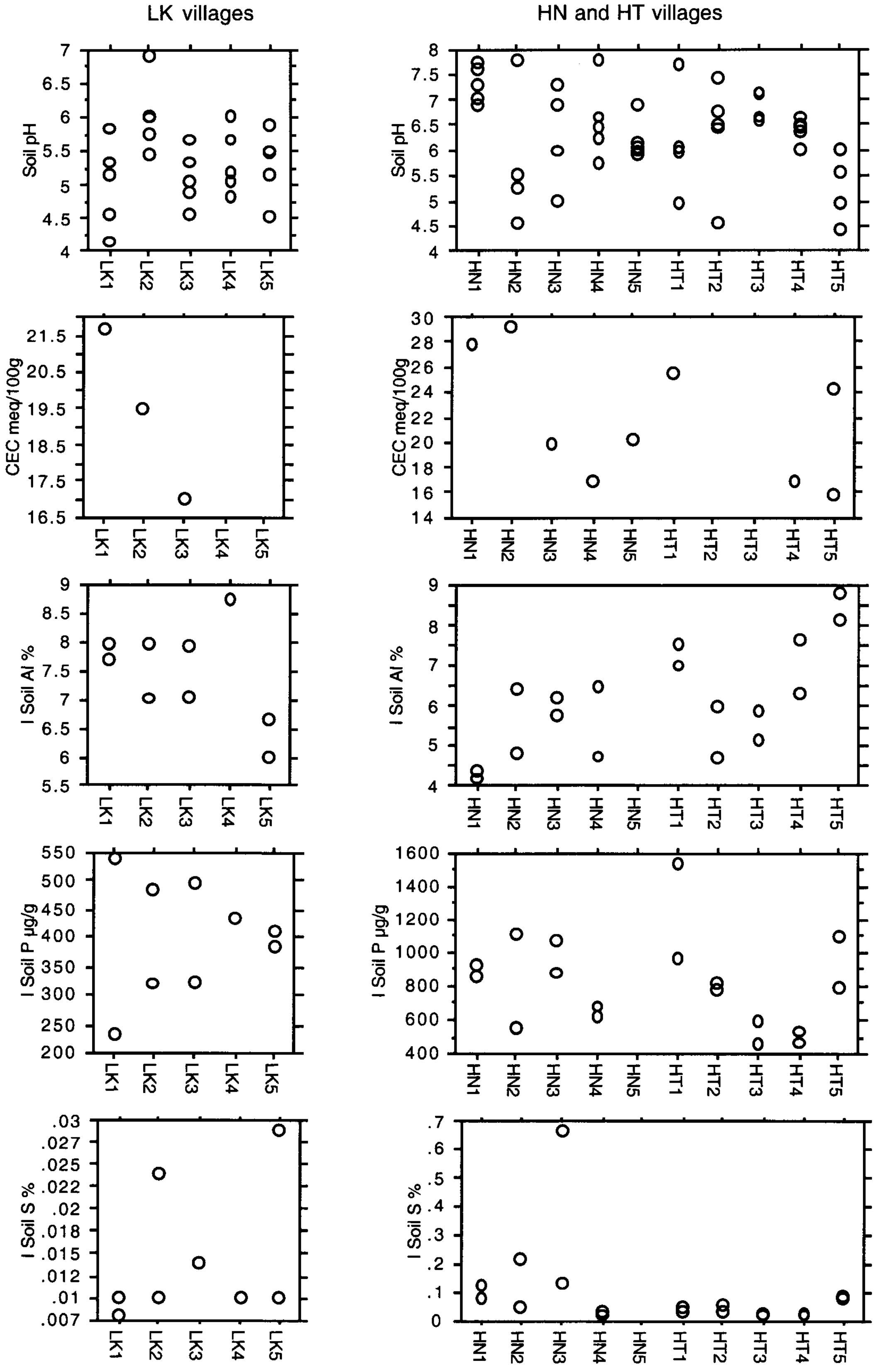


Figure 16. cont. Selected soil chemistry parameter distributions in the LK, HN and HT villages.



I = IRMA data

Figure 16. cont. Selected soil chemistry parameter distributions in the LK, HN and HT villages.

The Al and Mg content of soils is higher in the LK villages than in the high Se villages which may indicate greater dominance of feldspar and clay minerals in soils (Figure 16). Fe content does not vary greatly between the three village groups. All other elements follow the same regional trend, lowest concentrations occur in the LK villages and higher concentrations in the HN and HT villages. Soil pH, LOI and CEC are lower in the LK villages than in the in the HN and HT villages. Total and water soluble Se contents in the LK villages are, respectively, 71 - 95 and 35 - 76 times lower (geometric mean values) than in the HN and HT villages (Table 23).

These results are consistent with geological controls on soil chemistry. The LK villages are underlain by sandstone and siltstone rocks whereas the soils of the high Se villages are developed on carbonaceous strata, shales and limestones. Shales and carbonaceous rocks tend to be enriched in trace elements and organic matter content relative to other rock types (Krauskopf, 1982). The higher CEC values in the HN and HT villages probably reflect the greater organic matter content of these soils. Higher soil pH values in the HN and HT villages are indicative of the underlying carbonate rock types. It is clear from Figure 16 that soils in the LK villages are chemically distinct from soils in the HN and HT villages.

The overall geological controls in the LK and the HN and HT villages are discussed in more detail in the following sections and in Zhang et al. (In Prep.).

9.3.2 Soil Organic Matter Content (LOI) in the LK, HN and HT Villages

The total Se and Fe content of soils in the LK, HN and HT villages correlate significantly (95% confidence level) with LOI (Appendix J and Table 24). Highest total Se concentrations occur in dark brown soils in the HN and HT villages which tend to have greater LOI values indicating higher organic matter content (Figure 17). In the Zhangjiakou study area, the soils with greatest Se content contain the most organic matter which inhibits the availability of Se to plants. The highest incidence of KD occurs in the region of highest Se in soils (Johnson et al., 1996).

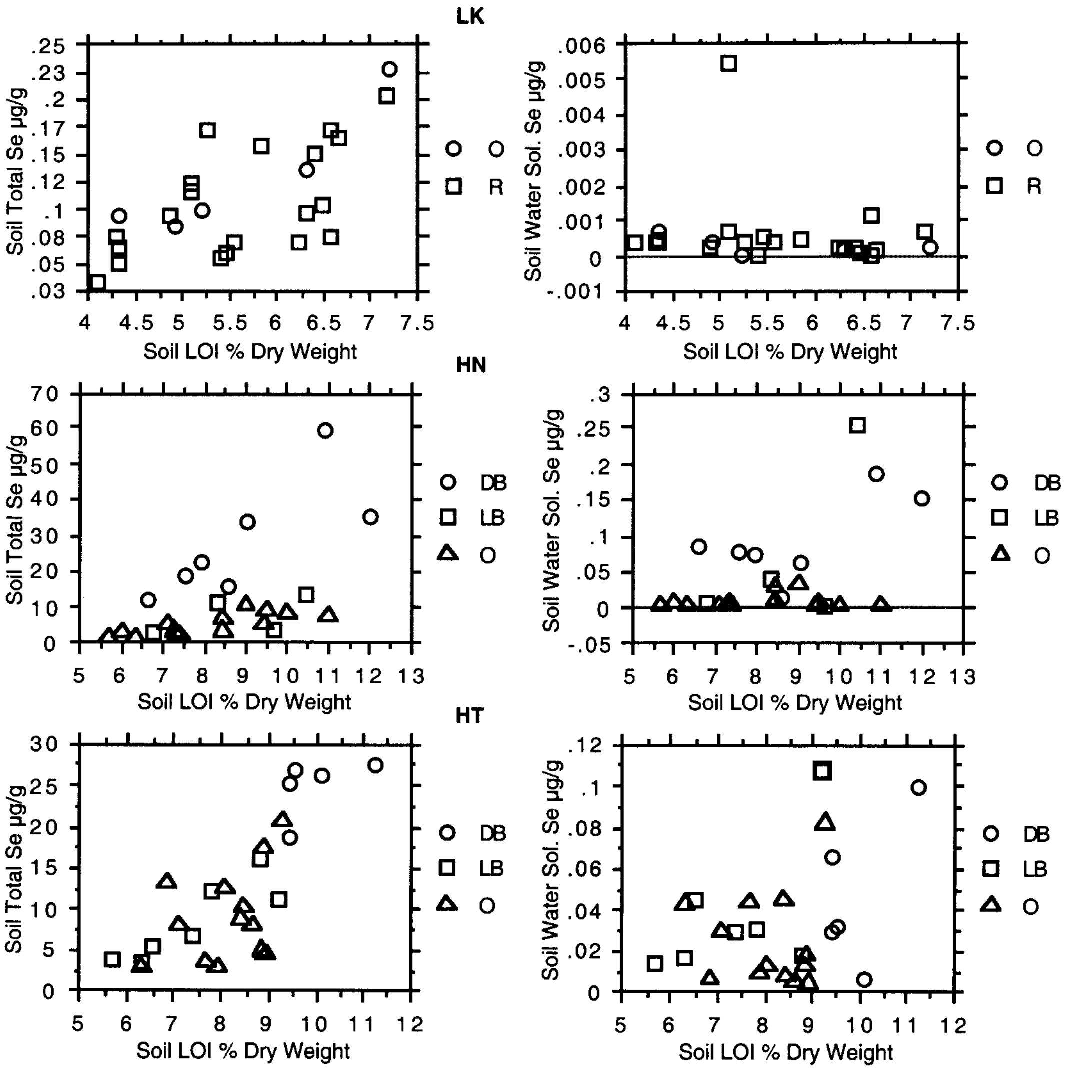
In Enshi District, despite the presence of dark brown organic rich soils in the HN and HT villages, high levels of Se are evident in grain (Figure 15) probably because the levels of Se in soils are much higher (approximately 100 times based on geometric mean values) in the Enshi area than in Zhangjiakou (Table 25).

Unlike the Zhangjiakou area, soils in the HN and HT villages of Enshi contain organic matter derived from the carbonaceous strata in addition to biological organic matter. The association between high Se in soils and LOI in the HN and HT villages is probably a reflection of carbonaceous strata geochemistry rather than the complexing of soil Se by secondary biologically derived organic matter.

Table 24. Significant (95% confidence level) Spearman Rank correlations of selected soil parameters in the LK, HN and HT villages.

Village Group	Param.	+ Correlations	Param.	- Correlations
LK	TSe -	LOI	TSe -	Ba, Ca, Cd, pH
			WSe -	Cr, Fe
	LOI -	Co, Fe, Zn	LOI -	Ca, Cd, pH
	pH -	Ca		
	Fe -	Al, As, Co, Cr , F, K , Li , Mg, Ni , Ti, V, Zn		
	Ca -	Cd, Mg		
	Mg -	As, Cr, F, Li, Ni, P, Zn		
	P -	As , Co, Cr , F, Li, V, Zn		
	Al -	Co, Cr, K, Ni, Ti, Zn		
	K -	As, Co, Cr, Na, Ni, Ti, Zn	K -	Na
			Na -	As, Ni, Zn
	Zn -	As, Co, Cr, F, Li, Ni, Ti, V		
HN/HT	TSe -	Cd, Cr, Cu, F, Fe, Hg, LOI, Ni, P, S, V, WSe, Zn	TSe -	Ba
	WSe -	Ca, Cd, Cu, Cr, F, Hg, Ni, V, Zn	WSe -	Ba
	LOI -	Al, Cd, Cr, Cu, F, Fe, Hg, Ni, S, P, Ti, V, Zn	LOI -	Ba, pH
	pH -	Ca	pH -	Al, Ti, Co, Cu, Fe
	Fe -	Al, As, Cd, Co, Cu, F, Na, P, Ti, Zn	Fe -	Ca
			Ca -	Al, Cu
	Mg -	F, K, Li, Na		
	P -	Cd, Cu, Cr, Hg, Ni, S, V, Zn	P -	Ba
	Al -	Co, F, K, Na, Ti		
	K -	Ba, Co, F, Li, Na, Ti	K -	Cr, V
	Na -	Ba, F, Ti	Na -	V
	Zn -	Cd, Cr, Cu, Hg, Ni, P, S, V	Zn -	Ba
HN	TSe -	Cd, Cr, Cu, F, Hg, LOI, Ni, WSe, V, Zn	TSe -	As, Ba, Co, K
	WSe -	Cd, Cu, Cr, Hg, Ni, V, Zn	WSe -	As, Ba, Co, K
	LOI -	Cd, Cu, Fe, P, S, Ti, V, Zn		
	pH -	Ca, Mg	pH -	Al, Fe, Na, Ti
	Fe -	Cu, Na, Ti	Fe -	Mg
	Ca -	Mg	Ca -	Al, K, Na
	P -	Cu, Hg, Ni, S, Ti, Zn		
	Al -	K, Na, Ti		
	K -	As, Ba, Co	K -	Cd, Cr, Ni, Hg, V, Zn
	Na -	S, Ti		
	Zn -	Cd, Cr, Cu, Hg, Ni, S, Ti, V	Zn -	As, Ba, Co, K
HT	TSe -	As, Cd, Cr, Cu, F, Fe, Hg, LOI, Ni, P, S, V, Zn	TSe -	Ca, Ba, pH
	WSe -	Ca, Cd, pH		
	LOI -	Al, As, Cd, Cr, Cu, F, Fe, Hg, Mg, Ni, P, S, V, Zn	LOI -	Ba
	pH -	Ca	pH -	Co, Ti
	Fe -	As, Al, Cd, Co, Cu, F, Hg, Mg, Ni, P, S, Ti, V, Zn	Fe -	Ba
	Ca -	Li	Ca -	Cu, V, Zn
	Mg -	Al, F, K , Li, Na		
	P -	As, Cd, Cr, Cu, Ni, F, Hg, S, V, Zn		
	Al -	F, K, Na, Ti		
	K -	Na		
	Na -	Ti		
	Zn -	As, Cd , Cu, Cr, F, Hg, Ni, S, V	Zn -	Ba

Param. = Parameter TSe = Total Se WSe = Water Soluble Se Correlation matrices are listed in Appendix J.



Soil Colour: DB = dark brown O = orange
LB = light brown R = red

Figure 17. Comparisons between soil LOI, soil colour and total and water soluble Se content in the LK, HN and HT villages.

Table 25. Comparisons between soil total Se levels in Enshi District and the Zhangjiakou study area.

District	Village Group	Range Total Se µg/g
Zhangjiakou*	HK	0.036 - 0.105
	MK	0.035 - 0.060
	NK	0.026 - 0.077
Enshi	LK	0.034 - 0.228
	HN	1.153 - 59.44
	HT	2.736 - 27.50

HK = High Keshan, MK = Moderate Keshan, NK = No Keshan Villages
* From Johnson et al. (1996)

9.3.3 Soil CEC in the LK, HN and HT Villages

Due to the small CEC sample population, it was not possible to determine relationships with other soil parameters in each village group. Results for the dataset as a whole are presented in Table 26. CEC correlates significantly (95% confidence level) with total Se, water soluble Se and LOI indicating that as the organic matter content of the soil rises the CEC is increased and more water soluble Se and total Se are held in the soil.

Table 26. Spearman Rank correlation coefficients for soil CEC and selected parameters in Enshi District.

	Ca	Fe	Total Se	Water Sol Se	pH	LOI
CEC	0.318	0.227	0.645	0.573	0.127	0.727

Number of samples = 11. r95% = 0.512 (Koch & Link, 1970) Sol = Soluble

9.3.4 Soil Chemistry in the LK Villages

In the LK village group, variations in the total Se content of soils between villages reflect differences in organic matter content (as shown by LOI distributions) and follow opposite trends to variations in pH (Figure 16). The stronger correlation between total Se and LOI ($r = 0.611$) than between total Se and pH ($r = -0.453$) and the lack of a significant (95% confidence level) correlation between total Se and Fe, suggest that organo-complexing of Se is a more important control on total Se chemistry than Fe concentration or pH (Table 24 and Appendix J). This concurs with the chemical controls on soil total Se chemistry in the Zhangjiakou study area (Johnson et al., 1996). Soil pH is lowered as the organic matter (and associated Se) content of soil increases as expected, hence the negative relationship between total Se and soil pH (Table 24 and Appendix J).

Soil water soluble Se concentrations in general mirror variations in pH in the LK villages (Figure 16), however, the correlation between water soluble Se and pH is not significant (95% confidence level) (Table 24 and Appendix J). Soil water soluble Se correlates negatively (95% confidence level) with Fe (Table 24 and Appendix J). This is to be expected as Se held in the form of Fe oxyhydroxides is less available for plant uptake (Mikkelsen et al., 1989).

Factor Analysis of selected soil parameters demonstrates a possible geological control on soil chemistry in the LK villages. Cu, Fe, Zn and Mg show a strong association which may reflect the chemistry of micaceous minerals in the underlying siltstone rocks. The association between these elements and LOI may also indicate adsorption of Cu and Zn onto Fe oxyhydroxides and organic matter (Table 27 and Appendix K). The second Factor includes Ca, Mg, pH, total Se and LOI. The pH of soils increases as Ca and Mg concentrations increase as expected. The positive grouping of soil total Se, LOI and V indicates that total Se and V are probably adsorbed onto organic matter. Soil Ca, Mg and pH show a negative relationship with LOI, total Se and V demonstrating that increased organic matter content reduces soil pH as expected (Table 27 and Appendix K). The third Factor comprising total Se and water soluble Se should be treated with cation as this grouping accounts for less than 10% of the total variation.

The controls on Se soil chemistry in the LK villages can be summarised at two different levels. The overall control on total Se concentrations at the regional level is geological. Soils derived from Jurassic sedimentary rocks contain low natural abundances of Se in comparison to the high Se regions of Enshi District.

Within the LK villages, total Se concentrations are controlled by the amount of organic matter in the soils whereas the water soluble Se content is dependent on soil Fe levels.

Se in the LK villages is strongly held by organic matter and complexing with Fe oxyhydroxides also restricts bioavailability.

Table 27. Summary of Factor Analysis of selected soil parameters in the LK, HN and HT villages.

Village Code	Factor	Variance %	Grouping (Factor loading > 0.300)
LK	1	32	+ Cu, + Fe, + Zn, + Mg, (+ LOI)
	2	28	+ LOI, + V, + Total Se, - Ca, - pH, (- Mg)
	3	12	+ Cd
	4	8 *	+ Water Soluble Se, (+ Total Se)
HN/HT	1	49	+ Total Se, + Cd, + V, + Water Soluble Se, + Zn, + Cu, + LOI
	2	19	+ pH, + Ca, (+ Water Soluble Se), - Fe
	3	10*	+ Mg, (+ LOI)
HN	1	50	+ Zn, + Cd, + Total Se, + V, + Water Soluble Se, + Cu, (+ LOI)
	2	23	+ pH, + Mg, + Ca, - Fe, (- LOI), (- Cu)
	3	9*	+ Ca, + LOI
HT	1	54	+ V, + Total Se, + Zn, + Cd, + Water Soluble Se, + Cu, - Mg
	2	19	+ Water Soluble Se, + pH, + Ca
	3	15	+ Mg, + Fe, + LOI, - V, (- Water Soluble Se)

Factor Analysis is listed in Appendix K. Data were log transformed to reduce the influence of outlying values prior to statistical analysis.
* Values ≤ 10 should be treated with caution ( ) Factor loading < 0.500

9.3.5 Soil Chemistry in the HN and HT Villages

The strong significant (95% - 99.9% confidence level) correlations between elements such as Cd, Cr, Cu, F, Fe, Hg, Ni, total Se, S, V and Zn in the HN/HT villages reflect carbonaceous strata geochemistry indicating that geology exerts a major control on soil chemistry in the high Se area (Table 24 and Appendix J). The significant (95% confidence level) correlations between these elements and LOI and the negative correlations with Ba or Ca (Table 24 and Appendix J), confirm that soil organic matter and trace element contents are highest when associated with the organic rich carbonaceous shales rather than the surrounding limestone lithologies. The correlations between total Se and water soluble Se are stronger with elements such as Cd, V and Zn than with LOI, Fe or pH further demonstrating the fundamental geological control on Se geochemistry in the high Se area (Appendix J and Table 24).

In the HN villages, the geological control on total Se chemistry is evidenced by the significant correlations (95% confidence level) with LOI and with other trace elements such as F, Hg, Zn and V (Appendix J and Table 24). The lack of significant (95% confidence level) correlations between total Se and other trace elements with Fe (Appendix J) may reflect the low Fe content of soils in Luojiaba (HN1) despite high concentrations of other trace elements in soils in this village (Figure 16). However, the lack of significant correlations may also indicate that Fe oxyhydroxides and sulphide minerals such as pyrite are less important in terms of soil trace element chemistry in the HN villages.

The strong (r = 0.825) correlation between water soluble Se and total Se reflects the significantly higher concentrations of total and water soluble Se levels in Luojiaba (HN1) and Bajiao (HN2) compared to the other HN villages (Figure 16). The lack of significant (95% confidence level) correlations between water soluble Se and LOI, pH and Fe demonstrate that total Se content is the major control on Se availability in the HN villages (Appendix J and Table 24).

In the HT villages, total Se correlates (95% - 99.9% confidence level) positively with other trace elements and with LOI (Appendix J and Table 24). These correlations and the negative correlations with Ca and pH (indicative of limestone) demonstrate a carbonaceous shale Se source in the HT villages as expected. Total Se correlates with both sulphur and Fe indicating that sulphide minerals may exert a significant control on Se levels in soils in the HT villages. The same relationships between sulphur and Fe are not evident in the HN villages (Table 24 and Appendix J). Se often substitutes for sulphur in sulphide minerals due to the similarity in chemistry between these two elements. High levels of Se have been recorded in pyrite (FeS_2) in the Enshi carbonaceous strata during previous studies (Zheng et al., 1992). Further investigations into the mineralogical form of Fe in these villages is required to ascertain whether Fe is held in primary mineral phases or secondary Fe oxyhydroxides.

Water soluble Se levels in the HT villages correlate significantly with pH (Table 24 and Appendix J). This is to be expected as Se^{6+}, the stable form in alkaline conditions, is more soluble than Se^{4+} (McNeal & Balistrieri, 1989).

Factor Analysis of selected soil parameters in the HN and HT villages confirms the geological association between total Se, water soluble Se and other trace elements such as Cd, Cu, V and Zn (Table 27 and Appendix K). In the HN/HT villages this association includes LOI reflecting the organic content of the carbonaceous strata.

The second Factor in the HN villages indicates an association between pH, Mg and Ca reflecting limestone geochemistry as expected. The negative relationship between these parameters and Fe, Cu and LOI probably indicates that the latter are associated with carbonaceous strata, not limestone and that Fe and Cu are adsorbed onto organic matter.

In the HT villages, the second Factor confirms the association of water soluble Se with increased pH and Ca of soils.

Although the magnitude of variation is very small (15 %), the third Factor in the HT villages indicates a negative relationship between soil water soluble Se and LOI and Fe. A negative relationship between Fe and water soluble Se is also evident from the second Factor of the HN/HT villages. These groupings suggest that Fe oxyhydroxides and secondary biologically derived organic matter may inhibit the availability of Se in soils.

These regional relationships should, however, be treated with caution as soil chemical parameters in the HN and HT villages are considerably variable. No systematic chemical differences between soils in the HN and the HT villages is apparent (Figure 16). The highest total and water soluble Se concentrations occur in Luojiaba (HN1) and Bajiao (HN2) and not in the HT villages as would be expected. Concentrations of other elements associated with the carbonaceous strata such as Cd, V and Zn are high in these two villages which, on the basis of soil chemistry, are more characteristic of the HT than the HN villages. However, within Luojiaba (HN1) and Bajiao (HN2), total and water soluble Se concentrations are highly variable (Figure 16). As Figure 18 shows, the highest total Se values in these villages correspond to high organic matter and V content indicating a carbonaceous strata source whereas highest water soluble Se values are associated with high total Se, organic matter or Fe.

The geological units underlying the HN and HT villages are the same (Appendix A). Despite the similarity in geological units, the marked variations in concentrations of elements and other soil parameters between and within individual villages are probably due to localised changes in lithology. Yang et al. (1983), noted that the distribution of Se in the carbonaceous strata is never uniform and varies from place to place and carbonaceous bed to carbonaceous bed in the Enshi area.

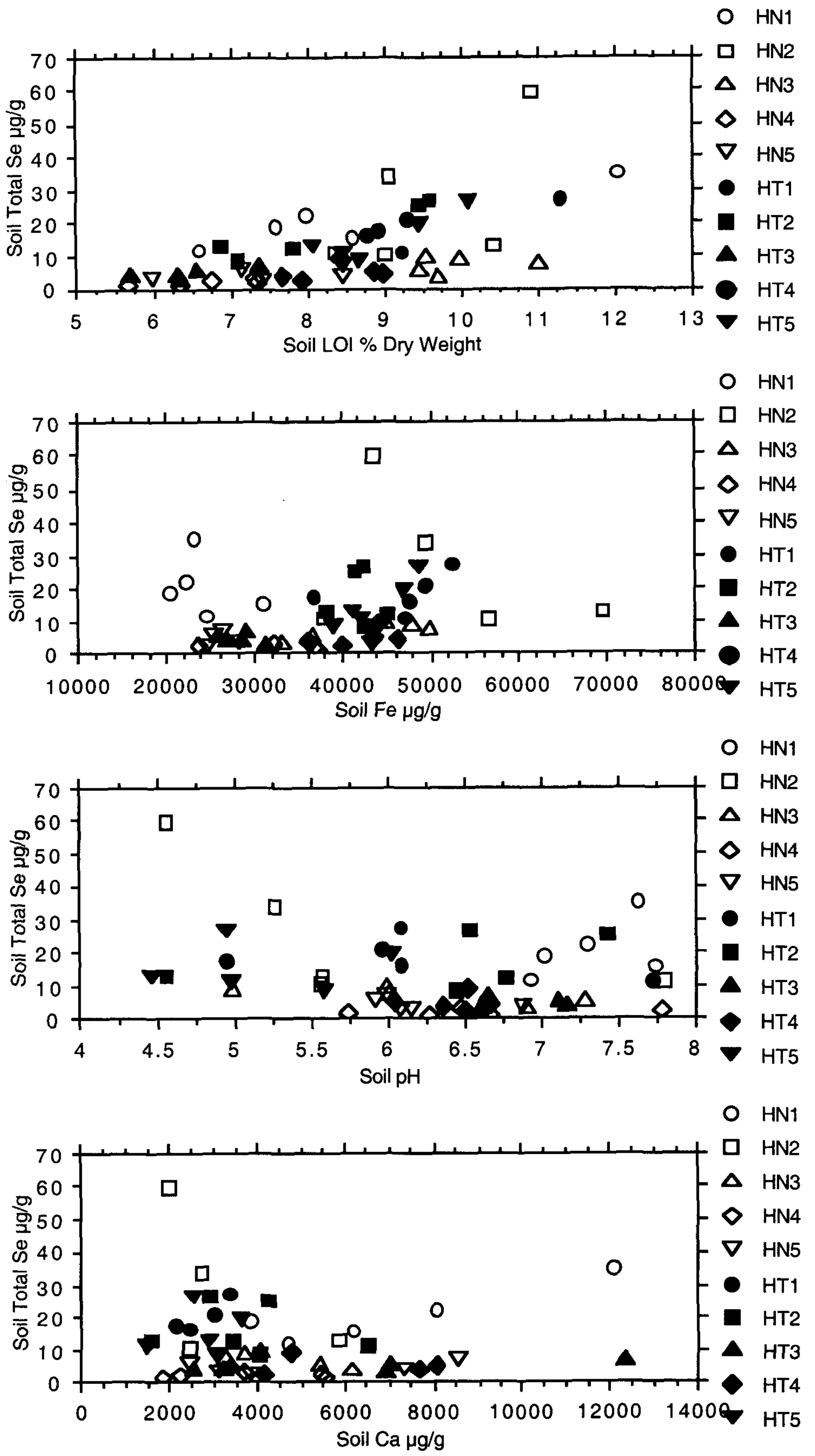


Figure 18. Soil total Se and water soluble Se compared to selected soil parameters in the HN and HT villages.

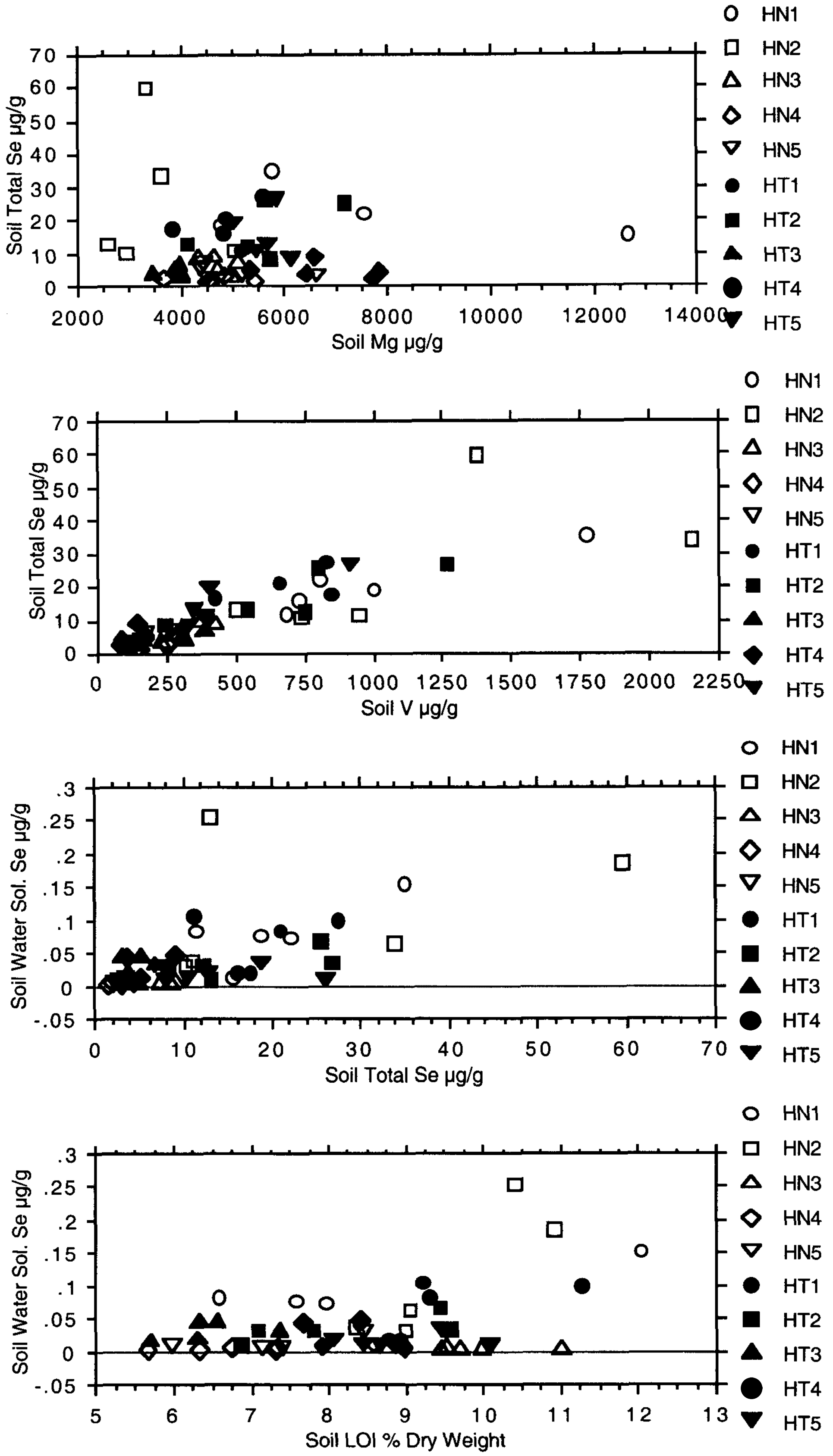


Figure 18. cont. Soil total Se and water soluble Se compared to selected soil parameters in the HN and HT villages.

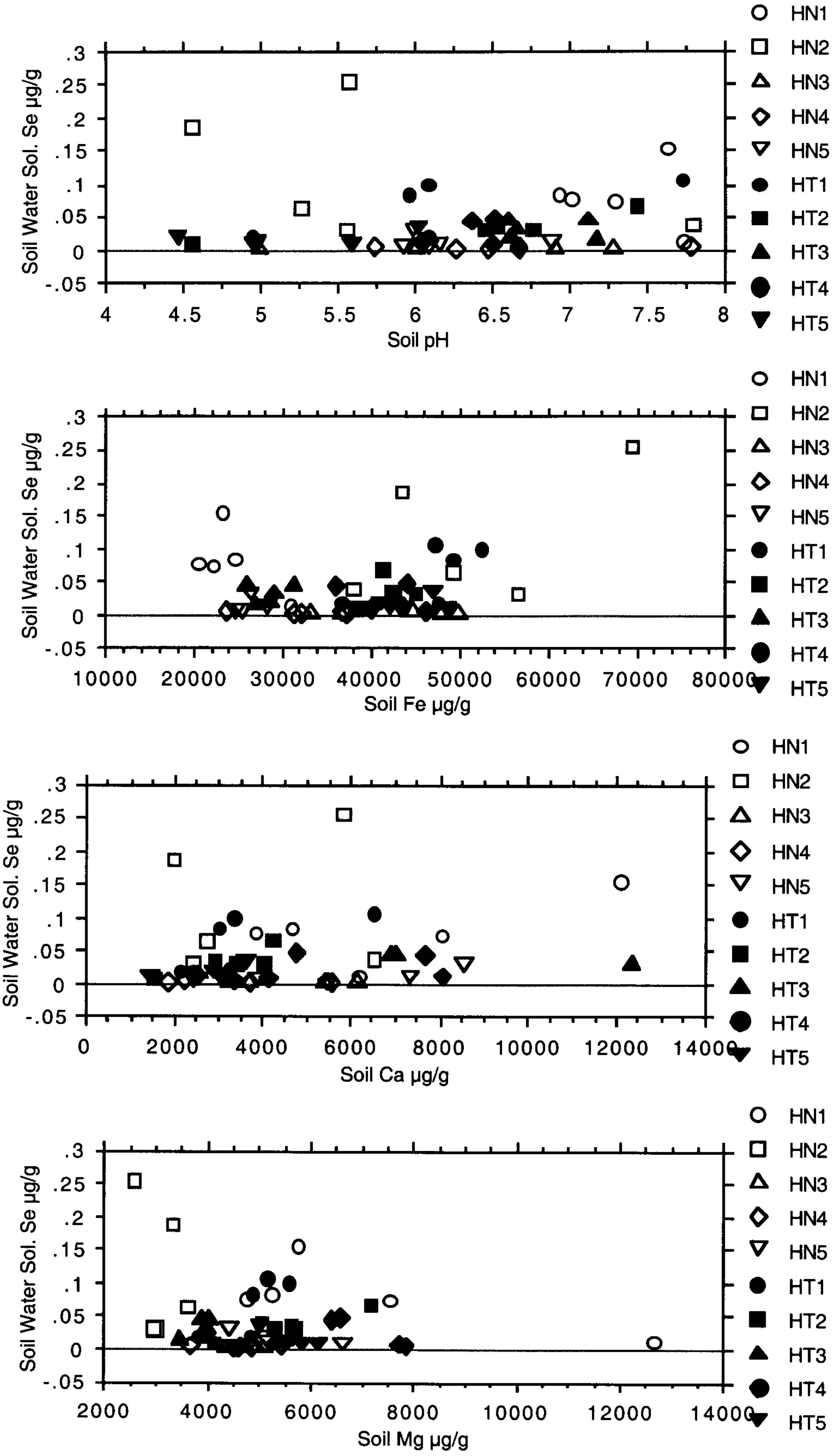


Figure 18. cont. Soil total Se and water soluble Se compared to selected soil parameters in the HN and HT villages.

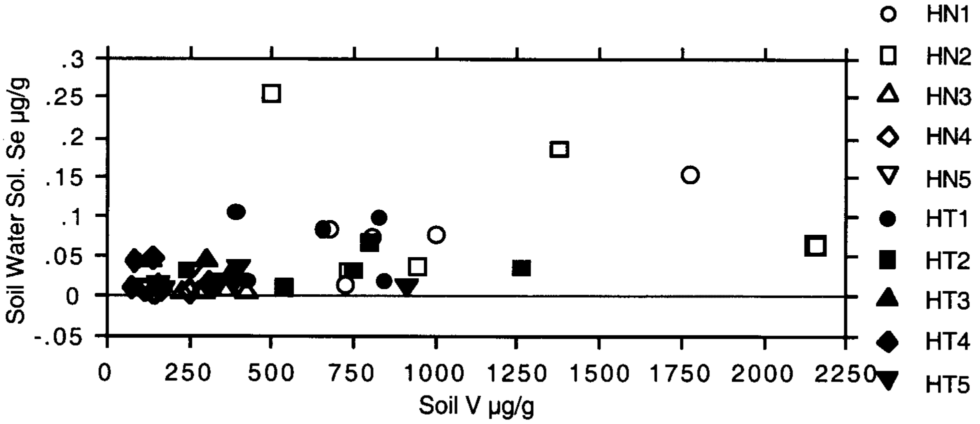


Figure 18. cont. Soil total Se and water soluble Se compared to selected soil parameters in the HN and HT villages.

In summary, geology exerts a fundamental control on Se soil chemistry in the HN and HT villages at the regional and individual village levels. Soils derived from the Permian carbonaceous strata contain high levels of total Se (1.5 - 59.5 µg/g) compared to a range of < 0.125 - 0.4 µg/g which characterises most of China (Tan, 1989).

Levels of total Se, other trace elements and organic matter in soils within villages reflect the distribution of the carbonaceous strata. There is some evidence to suggest that Se is also held in the form of sulphide minerals such as pyrite in the HT villages. The effects of recent biologically derived organic matter and Fe oxyhydroxides on total Se chemistry in soils is difficult to ascertain in the HN/HT villages as high levels of organic matter and Fe are associated with carbonaceous strata geochemistry.

The amount of water soluble Se in soils is proportional to the total Se content. In the HT villages, soil water soluble (bioavailable) Se is enhanced by pH (Ca and Mg) and depressed by Fe and LOI which perhaps reflects adsorption of Se by Fe oxyhydroxides and secondary biologically derived organic matter.

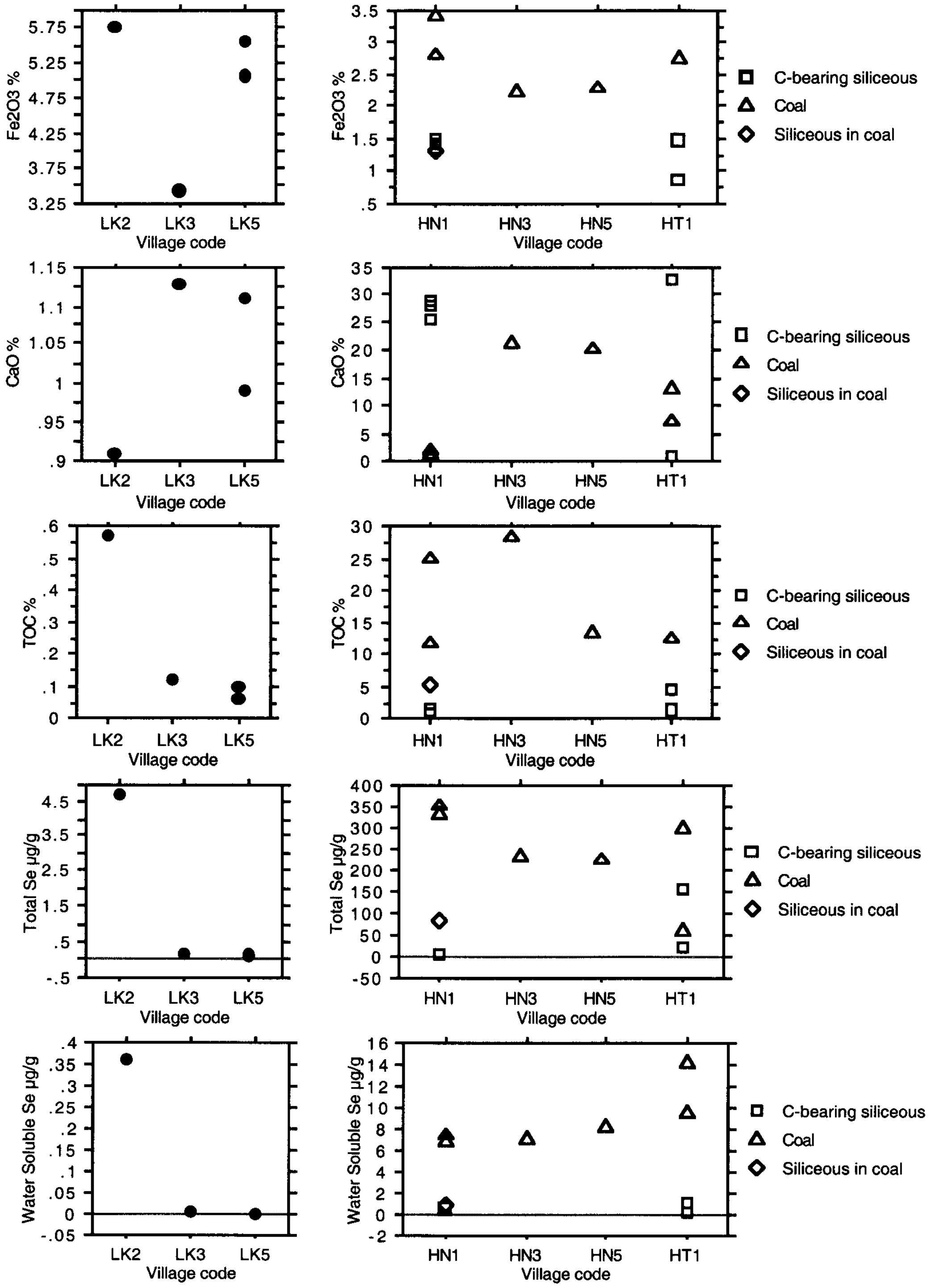
The geological units underlying villages in the HN and HT villages are similar (Appendix A), however, localised lithological variations result in significant differences in soil Se content between villages and within individual villages. These factors make geochemical distinctions between HN and HT villages difficult to determine. Both the HN and the HT villages contain soils of relatively low and very high Se content. The proportion of crops grown on each type of soil may determine whether selenosis occurs in one village and not in another.

9.3.6 Bulk XRD Semi-quantitative Analysis of Soils

Bulk XRD analysis of two soils, one from the HN and one from the HT villages, indicate that the soils are relatively immature and comprise mainly quartz with minor feldspar and mica, trace chlorite and possibly amphibole (Appendix G). No marked mineralogical differences were noted between the two soils studied.

9.4 IRMA Analysis of Enshi Rock Samples

The joint IRMA-BGS field investigations described in this report were carried out in November 1995. During a second investigation in the Enshi area carried out by the IRMA in November 1996, 16 rock samples from selected lithological units in a sub-set of the villages under investigation in the present study were analysed. Details of the analysis are described in Zhang et al. (In Prep.). Selected element concentrations in various rock types are shown in Figure 19. Marked variations in Se chemistry are apparent between different rock types collected in the same village, total Se, water soluble Se, Fe and organic matter content are all twice as high in carbonaceous strata than in the surrounding siliceous rocks. This confirms that soils derived from different lithological units within the same villages are likely to contain markedly different concentrations of Se depending on the underlying geology.



LK villages lithology = purple sandstone in each case C-bearing = carbon bearing

Rocks described in the Chinese classification as carbon-bearing siliceous and as coal contain high levels (15-34%) of CaO and are therefore impure limestones (pure calcite limestone contains 45% CaO).

Figure 19. Concentrations of selected parameters in IRMA Enshi rock samples.

9.5 Water Chemistry

9.5.1 Water Chemistry in the LK, HN and HT Villages

Results of determinations in water samples are detailed in Appendix M. Plots of water measurements show that the LK villages are distinct from the HN and HT villages (Figure 20). The LK villages are characterised by higher Cl, NO_3 and lower pH, bicarbonate concentration and conductivity than the high Se villages. Higher Cl concentrations may reflect the lake sediment origin of Jurassic sandstones in the region (Huang Huaizeng pers. commun.), whereas the higher NO_3 may be related to greater fertiliser use in the LK villages which are more intensively farmed than the high Se area. Variations in pH between the low and high Se areas reflect the greater abundance of carbonate lithologies in the HN/HT villages. There is considerable overlap between the ranges in water parameters between the HN and HT villages, however, bicarbonate concentrations are higher in the HN than the HT villages. This may reflect the greater dominance of more acid waters associated with the carbonaceous strata in the HT villages. Two of the springs sampled in the HT villages issued directly from the carbonaceous shales.

In the LK village water samples, pH and $CaCO_3$ correlate strongly as expected (95% significance level). Total Se correlates significantly (95% confidence level) with SO_4 which is to be expected if Se is associated with sulphide minerals. However, these results should be treated with caution due to the small sample population (Table 28).

The conductivity of the waters in the HN/ HT villages correlates with total Se, SO_4 and Cl whereas water pH correlates negatively with Cl, Eh and conductivity (Table 28). This suggests waters influenced by the carbonaceous strata and therefore higher in total Se and SO_4, are also higher in Cl. The pH of these waters is lower than other waters in the same area probably as a result of the oxidation of sulphide minerals. The relationship between sulphur and Se in waters confirms the association between Se and sulphur found in soils in the HT villages. The significant correlation between Cl and NO_3 in these villages, as in the LK villages, may reflect the application of KCl and nitrate fertilisers.

Table 28. Spearman Rank correlation coefficients for parameters in water.

Village Group		$CaCO_3$	SO_4	Cl	NO_3	Total Se	Eh	pH
LK								
n = 5	SO_4	0.100						
	Cl	0.200	0.400					
	NO3	0.051	0.359	0.975				
	Total Se	-0.112	0.894	0.671	0.688			
	Eh	-0.800	-0.500	-0.700	-0.564	-0.447		
	pH	1.000	0.100	0.200	0.051	-0.112	-0.800	
	Conductivity	0.800	0.500	0.700	0.564	0.447	-1.000	0.800
HN/HT								
n = 10	SO_4	0.079						
	Cl	-0.127	0.564					
	NO3	-0.486	0.231	0.717				
	Total Se	0.115	0.503	0.539	0.261			
	Eh	-0.237	-0.079	0.213	0.235	-0.061		
	pH	-0.176	-0.418	-0.564	-0.498	-0.212	-0.632	
	Conductivity	0.176	0.915	0.745	0.280	0.624	0.079	-0.576

Number of samples = 5 r95% = 0.805 Number of samples = 10 r95% = 0.549 (Koch & Link, 1970)

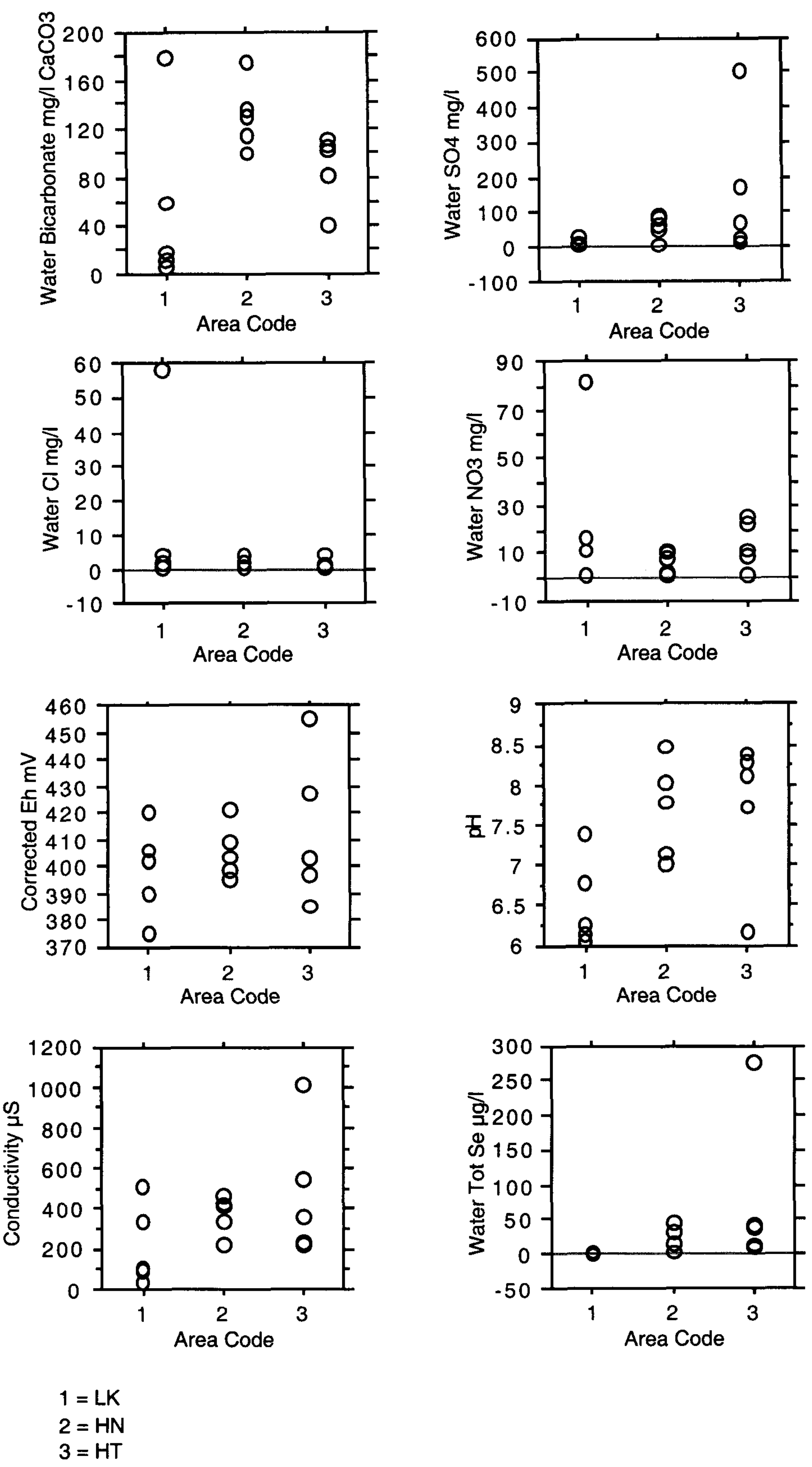
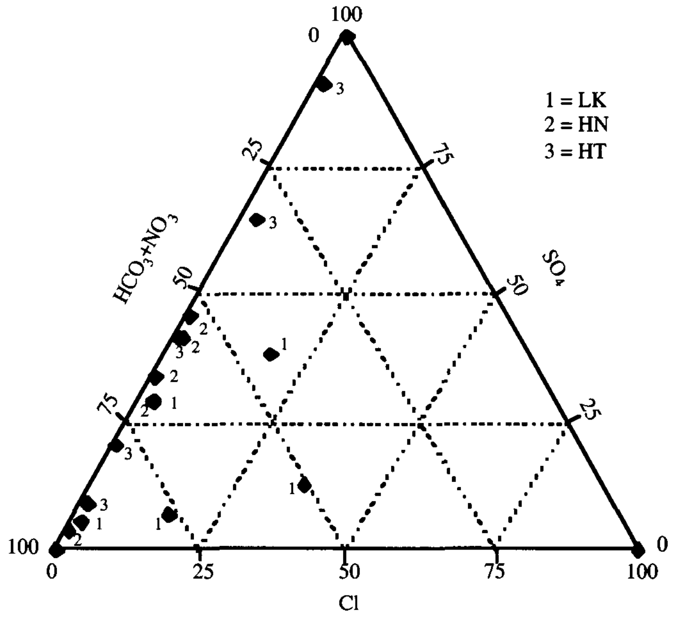


Figure 20. Water chemistry parameter distributions in the LK, HN and HT villages.

9.5.2 Anion Dominance in Enshi Waters

The majority of waters sampled in the Enshi area are < 10% dominated by Cl with the exception of three waters from the LK villages (Table 29 and Figure 21). In general, waters in the HN and HT villages are HCO_3 dominated, however, two samples from the HT villages are SO_4 dominated. In one sample from Shadi village (HT1), SO_4 accounts for 90% of the anions in solution. Villagers have been advised not to drink this water which issues directly from carbonaceous shale beds and contains a heavy Fe precipitate. Differences in anion dominance between the LK and HN/HT villages reflect regional geological variations, SO_4 and HCO_3 anions are more prevalent in waters associated with the carbonate and sulphide rich carbonaceous shales and limestones of the HN/HT villages.



Scales are % of total milli-equivalents per litre

Figure 21. Piper diagram of anion dominance in LK, HN and HT waters.

Table 29. Percentage dominance of major anions in LK, HN and HT waters.

Village Code	Sample Number	HCO_3 %	SO_4 %	Cl %	NO_3 %
LK1	5	21.7	12.5	36.5	29.4
LK2	85	92.6	5.5	1.6	0.3
LK3	73	40.4	6.7	15.8	37.1
LK4	6	15.5	37.7	17.8	29.0
LK5	63	65.2	28.9	2.4	3.6
HN1	18	66.2	28.6	2.3	2.8
HN2	94	53.4	41.2	1.2	4.2
HN3	74	54.1	45.4	0.1	0.3
HN4	52	94.0	3.9	0.4	1.7
HN5	68	60.2	33.5	0.5	5.8
HT1	19	5.7	90.3	1.0	3.1
HT2	72	30.0	64.3	2.3	3.4
HT3	1	69.1	8.8	1.3	20.7
HT4	84	79.3	20.0	0.2	0.5
HT5	93	54.2	41.1	0.5	4.2

9.6 Grain Chemistry

9.6.1 Grain Chemistry in the LK, HN and HT Villages

Concentrations of total Se in grain (maize-corn) in the LK villages are 99 to 690 times lower (geometric mean values) than concentrations in the HN and HT villages (Appendix M and Table 23) indicating the fundamental control of geology at a regional level on concentrations of Se entering the food chain in the Enshi area.

The maize-corn samples were collected from village stores therefore it is not possible to compare maize-corn and soil samples from the same field directly, as the soils sampled do not necessarily correspond to the location where the maize-corn was grown. However, the between and within village variations evident for total Se and water soluble Se in soil (Section 9.3) are reflected in the total Se content of maize-corn samples (Figure 22).

In the LK villages, maize-corn Se concentrations are more closely linked to the levels of water soluble Se in soil than soil total Se levels (Figure 22). The highest soil water soluble Se and maize-corn Se levels occur in Nan Pu (LK4).

The wide ranges in total and water soluble soil Se content noted in Luojiaba (HN1) and Bajiao (HN2), are reflected in maize-corn total Se levels for these villages confirming that localised variations in soil chemistry within villages can significantly affect the amount of Se entering the food chain (Figure 22).

In the HT villages, levels of maize-corn total Se in Xin Tang (HT3) and Yu Tang Ba (HT4) are higher than would be predicted from the levels of soil total and water soluble Se content (Figure 22). Samples from Yu Tang Ba (HT4) were collected directly from the fields therefore the higher levels of Se in these samples are not explained by carbonaceous shale smoke contamination during drying.

Levels of Cd, Cu, P, Se and V are lower in these two villages compared to the rest of the HT villages whereas soil Ca and pH are higher (Figures 16 and 22). This suggests that limestone rather than carbonaceous shale dominates the soils collected in Xin Tang (HT3) and Yu Tang Ba (HT4). Limestone and chalky fragments were recorded in all soils in each of these villages (Appendix B). Yu Tang Ba (HT4) is underlain by Permian carbonaceous strata (P_1q) and Carboniferous dolomite and limestones (C_{1+2}) (Appendix A). Although levels of total Se in soil are lower than in the other HT villages, levels of Se are high (2.7 - 8.9 µg/g) compared to most soils in China (< 0.125 - 0.4 µg/g, Tan, 1989). The combination of relatively high soil Se levels from the carbonaceous strata and high soil pH from the limestones probably accounts for the greater proportion of water soluble to total Se in soil and higher uptake of Se by maize-corn in these villages (Figure 22). Although there is no direct evidence from the present study, low levels of P in villages HT3 and HT4 may account for the disproportionate concentration of Se in grain in these two villages relative to soil Se content (Figure 16). Reduced P in soils has been shown to lessen plant growth, effectively concentrating Se in plant tissue (Mikkelsen et al., 1989).

9.6.2 Tobacco Sample

One tobacco sample collected at Yu Tang Ba (HT4) contained 9.05 µg/g total Se.

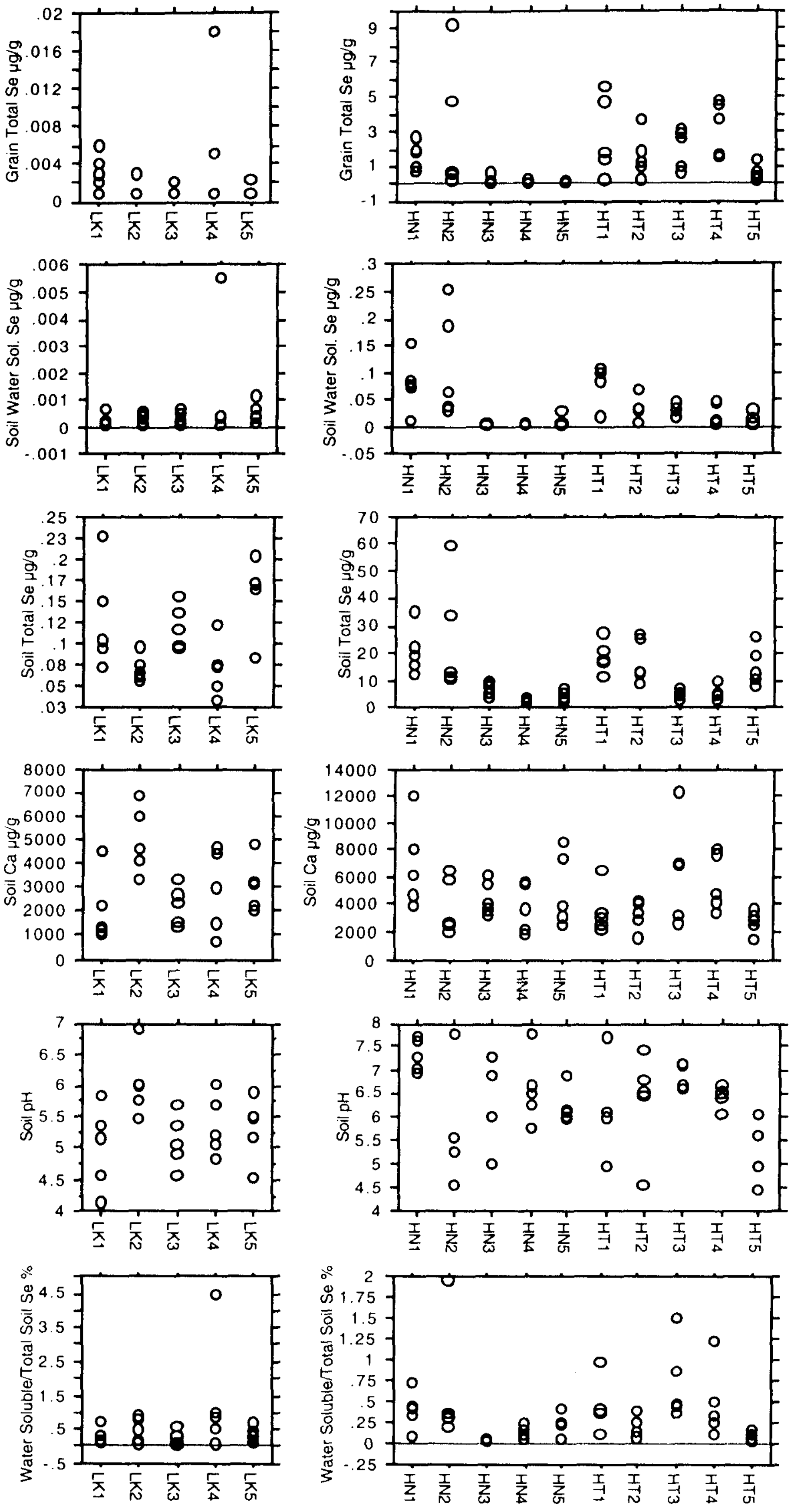


Figure 22. Total Se distributions in grain compared to selected soil parameters in the LK, HN and HT villages.

9.7 Hair Chemistry

9.7.1 *Hair Chemistry in the LK, HN and HT Villages*

Results of analysis of total Se concentrations in hair samples are detailed in Appendix M. Hair total Se concentrations are, respectively, 17 and 87 times lower (geometric mean values) in the LK villages than in the HN and HT villages indicating the strong environmental control on human Se status in the Enshi area (Table 23).

Total Se concentrations in hair vary considerably within individual HT villages reaching a maximum of 141 μg/g in Shadi (HT1) (Figure 23). Yang et al. (1983) attribute high levels (> 100 μg/g) of Se in hair to carbonaceous shale smoke contamination, however, it is not clear whether samples were washed prior to analysis. During the present study, hair samples were washed with deionised water to remove surface contaminants and yet levels of total Se between 65 to 141 μg/g were recorded suggesting these high values represent human Se status and not carbonaceous shale smoke contamination.

It was not always possible to collect grain samples from villagers whose hair had been sampled, particularly in the LK villages, and this may explain why trends in hair Se chemistry in these villages do not relate to trends in grain total Se (Figure 23).

Variations in hair total Se in the HN and HT villages correspond to variations in grain and water total Se with the exception of samples from Yu Tang Ba (HT4). The inhabitants of this village had only been resident for 3 months and did not consume grain from the village. The results for hair clearly define the lower Se status of this population indicating the link between dietary Se intake and hair Se levels (Figure 23).

Hair Se concentrations in Luojiaba (HN1) and Bajiao (HN2) are higher than in other HN villages reflecting greater concentrations of Se in soil, grain and water samples in these two villages. The levels of Se found in hair, and therefore the potential selenosis risk, in Luojiaba (HN1) and Bajiao (HN2) are comparable to levels in the HT villages. It is therefore likely that other factors have prevented the occurrence of selenosis in these villages.

9.7.2 *Comparisons between Total Selenium in Hair and other Population Parameters*

With the exception of villagers recently resident in Yu Tang Ba (HT4) all persons sampled in the HN and HT villages suffered from fluorosis (Appendix E). Only two women were sampled during the survey therefore it is not possible to determine differences in Se status with gender and no significant correlation was found between Se levels in hair and age.

9.7.3 *Pig Hair*

Although no selenosis symptoms were recorded in the local population during sampling, pigs in the HT villages were seen to suffer from hair loss as a result of Se toxicity (Mao Dajun pers. commun.). One sample of hair from a pig suffering hair loss contained 3.16 μg/g total Se. This is much lower than the concentration of 21.5 μg/g in hair from a selenosis affected pig reported by Yang et al. (1983) in the Enshi area.

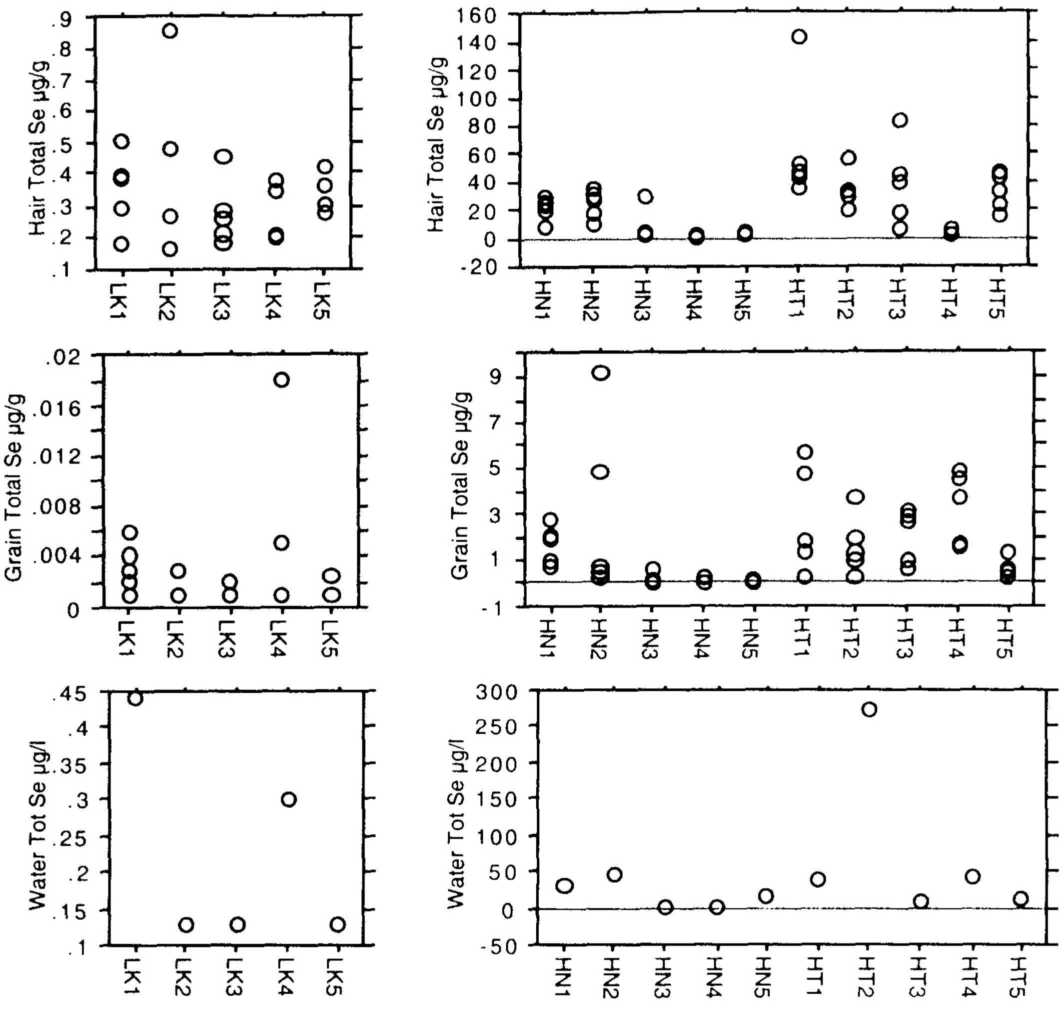


Figure 23. Total Se distributions in hair samples compared to total Se in grain and water in the LK, HN and HT villages. (Residents of HT4 do not consume locally grown grain)

9.8 Dietary Factors

It is clear from the results of the present study that levels of Se in soil, grain, water and hair samples are highly variable between HN and HT villages. High levels of Se in soil, grain, water and hair samples occur in Luojiaba (HN1) and Bajiao (HN2). Dietary factors may explain why, despite high environmental Se levels, no selenosis has been reported in these villages. Yang et al. (1983) noted that Se concentrations in vegetables were higher than in cereal crops in the high Se area. Turnip greens were particularly high in Se containing 45 000 times the average amount in other vegetables from a KD area. Although no systematic differences between rice and maize-corn chemistry were found during the present study (Section 8.7), Yang et al. (1983), reported higher levels of Se in maize-corn than in rice in the Enshi high Se area. Beilstein et al.(1991) reported 18 µg/g Se in maize-corn from Yu Tang Ba (HT4) and 3.6 µg/g Se in rice from Huabei (HT2).

Dietary data collected during a second IRMA investigation in Enshi District carried out in November 1996, indicate that HN villagers supplement locally grown rice supplies with rice from elsewhere whereas in the HT villages, the population depend solely on locally grown produce (Table 30) (Zhang et al., In Prep.). This may, in part, account for the lower levels of Se in some hair samples in the HN villages.

Table 30. Summary of main dietary components in the 15 study villages.

Village Code	Main Food Type Rice	Corn	Wheat Flour	Pork Consumption pp/pa	Source of Rice
LK1	90%	10%		25 kg	Local
LK2	90%	10%		50 kg	Local
LK3	90%	10%		25 kg	Local
LK4	90%	10%		25 kg	Local
LK5	90%	10%		20 kg	Local
HN1	60%	10%	30%	30 - 40 kg	Local and imported
HN2	90%	10%		30 - 40 kg	Local and imported
HN3	10%	90%		15 - 25 kg	Imported
HN4	100%			15 - 25 kg	Local
HN5	10%	90%		15 - 25 kg	Local and imported
HT1	50%	50%		15 - 25 kg	Local
HT2	60%	40%		15 - 25 kg	Local
HT3	90%	10%		15 - 25 kg	Local
HT4	Temporary Residents				
HT5	10%	90%		15 - 25 kg	Local

From Zhang et al. (In Prep.) pp/pa = per person per annum

Information on the proportions and amounts of different foodstuffs in the daily diet was beyond the scope of the present study and the proportion of locally grown to imported food is unknown. Therefore, it is not possible to accurately determine the average daily dietary intake of Se in the Enshi area.

However, Chen et al. (1994) in a study of the diet of 232 farming villages in Shanxi Province ascertained that the average farmer consumed approximately 340 g of staple cereal crops (corn, millet, rice, wheat flour, buckwheat and oats) per day.

Based on the assumption that the average person in the Enshi area eats 340 g of locally grown maize-corn or rice and drinks 3 l of water per day (Yang et al. 1989b), the average dietary intake from grain and water in the three village groups from the results of the present study can be can be estimated (Table 31). Levels of Se intake in the diet in Enshi reported by Yang et al.(1989b) are higher than in the present study as all dietary components were considered in the Yang et al. study (Table 31).

Results of the present study based on geometric means show that estimated dietary intake from maize-corn, rice and water in the LK villages is well below recommended daily intake levels. In the HT villages estimated Se intake from grain and water does not exceed the upper recommended daily intake level based on Chinese farmers' diets (Yang & Xia, 1995). At these levels of consumption, estimated Se intake from water is the equivalent of 10% of the total grain and water intake in the LK villages, 32% in the HN villages and 19% in the HT villages. Clearly drinking water is an important source of Se in the HN and HT villages, however, these figures do not represent proportions of the whole diet. Yang et al., 1989b, estimated that drinking water contributed a maximum of 10% of the average daily Se intake in the Enshi high Se area

Although estimated daily dietary intakes from maize-corn, rice and water based on geometric mean values in the HN and HT villages do not exceed recommended upper thresholds, it is important to consider the range in concentration in grain and drinking water samples in the Enshi area as levels of Se vary considerably within and between villages. The estimated daily dietary intakes of Se from high Se-bearing maize-corn alone in the HN and HT villages, exceed the toxicity level (900 µg/day) (Table 31). The estimated upper daily dietary Se intake based on water samples in the HT villages (825 µg/day) also approaches the toxicity level, however, this figure is based on a spring water sample in Huabei (HT2) village which is no longer used as a drinking water supply. This sample excluded, estimated daily dietary Se intakes from high-Se water still represent a significant dietary contribution (maximum 132 µg/day). These estimates demonstrate that although, on average, dietary Se intake in the HN and HT villages does not exceed recommended upper threshold levels, individuals within villages who depend on maize-corn, rice or water with a high Se content could be at risk from human selenosis especially if all their crops are cultivated on Se-available soils. Daily dietary Se intake could vary markedly, from adequate to toxic (>900 µg/day) between farmers in the same village depending on the location of crop growing areas.

These results should, however, be treated with caution as details of total dietary Se and the proportion of different foodstuffs in the diet were not obtained during the present study.

Table 31. Estimated daily dietary intake of Se from maize-corn, rice and water in the LK, HN and HT villages

Source	Village Group		
	LK	HN	HT
Maize Se µg/g (Geometric Mean (Range))	0.002 (0.001 - 0.018)	0.198 (0.017 - 9.175)	1.38 (0.18 - 5.6)
Daily Maize Consumption g (Average)	34	136*	162
Daily Se intake µg	0.068 (0.034 - 0.612)	26.9 (2.31 - 1248)	223 (29.4 - 904)
Rice Se µg/g (Geometric Mean (Range))	0.015 (0.013 - 0.20)	0.132 (0.132)	1.12 (0.88 - 1.4)
Daily Rice Consumption g (Average)	306	184*	178
Daily Se intake µg	4.59 (4 - 61)	24.2	200 (157 - 249)
Water Se µg/l (Geometric Mean (Range))	0.168 (0.1 - 0.44)	7.742 (0.46 - 44)	32.6 (7.3 - 275)
Daily Water Consumption l	3	3	3
Daily Se intake µg	0.504 (0.3 - 1.32)	23.2 (1.38 - 132)	97.8 (22 - 825)
Combined intake grain and water	5.2	74.4	521
Yang et al. (1989b) daily intake	Enshi Low Se	Enshi High Se	Enshi Toxic Se
	66.25	196.4	1338.25
Yang et al. (1989b) Se maize µg/g	0.035	0.266	1.483
Yang et al. (1989b) Se rice µg/g	0.113	0.196	1.071
Yang et al. (1989b) Se water µg/l	0.37	1.72	12.27
	Recommended daily intake µg		
USA National Research Council +	50 - 200		
UK Ministry of Agriculture +	80 - 200		
Yang & Xia (1995)	40 - 600		900 Toxic level
UK Department of Health DRNI †	40 - 60 female, 75 male		

+ From Chuck (1988) † From MAFF (1997) DRNI = Dietary Reference Nutrient Intake

* Excluding 30% wheat flour in one village imported from elsewhere

Yang et al. (1989b) demonstrated that the population of a site in Enshi District characterised by relatively low environmental Se had average hair Se of 0.69 µg/g and an average daily dietary intake of 66 µg Se. An average hair Se concentration of 0.52 µg/g has been recorded for healthy adults in Glasgow (Harrison et al., 1995) which could be surmised to reflect the average selenium intake in the UK of 43 µg/day (1994 data; MAFF, 1997).On the basis of the above, the present study has shown that the average hair Se in the Enshi LK villages is about 0.31 µg/g which implies a daily dietary intake of about 25 µg Se of which, approximately 19 µg must come from sources other than maize-corn, rice and water (Table 31).

The UK Department of Health (DOH) Dietary Reference Nutrient Intake is currently set at 60 µg/day for adult women and 75 µg/day for adult men with a Lower Reference Nutrient Intake level of 40 µg/day for adults (MAFF, 1997). Average selenium intake in the UK has declined from an average of 60 µg/day in 1985 to 43 µg/day in 1994 and 33 µg/day in 1995 (MAFF, 1997). The UK Government Committee on Medical Aspects of Food and Nutrition Policy is in the process of assessing the nutritional significance of these data and have not yet made any recommendations for enhancing the dietary Se intake of the UK population. In contrast, the average dietary intake in Finland, a country which uses Se fertilizer to enhance the Se status of the population, is now approximately 80 µg/day.

9.9 Comparison of Village Geometric Mean Results

As stated in the previous sections, it was difficult to correlate individual soil, grain and hair samples in the Enshi area as it was not possible to collect grain from the same field as the soil samples. The population in Enshi were generally reluctant to have their hair cut and hair samples were not always collected from farmers whose fields and grain stores had been sampled. Comparisons between sample types were therefore conducted on the basis of village geometric mean results. Geometric means were calculated in preference to averages as they are less influenced by outlying values (Table 32).

Significant (95% level) Spearman Rank correlations in the LK villages include grain total Se with soil Fe and water total Se (Table 33). The sources of irrigation water were not determined during the present study, however, the correlation between grain Se and water Se is interesting. If spring water or water of a similar Se composition to the spring water is used to irrigate crops, it may form a source of Se in grain. Levels of Se in water (geometric mean = 0.168 µg/l) in the LK villages are comparable to levels of water soluble Se in soils (geometric mean = 0.288 ng/g). This may also explain the higher levels of Se in rice (grown in flooded paddies) than in maize (grown in dry fields) in the LK villages (Section 8.7). Soil sulphur correlates negatively with total Se in water and grain. The negative correlation between soil sulphur and grain total Se may indicate inhibition of Se uptake in plants by sulphur in soil (Mikkelsen et al., 1989).

In the HN villages, soil water soluble Se correlates with total Se in water and hair (Table 34). Water total Se correlates with total Se in soil and hair. Estimates of dietary Se intake indicate that 33% of the total Se intake from grain and water may come from water in the HN villages (Table 31). Se in water may contribute significantly to the Se loading of the population particularly in Luojiaba (HN1) and Bajiao (HN2), where levels in water are comparable to levels found in grain in Xiao Guan (HN4) and Zishengqiao (HN5) (Table 32). Grain total Se correlates with soil total Se indicating the importance of environmental Se levels on grain Se chemistry. Hair and grain Se levels correlate demonstrating the association between dietary Se intake from staple food crops and human Se status.

Soil Ca correlates with grain total Se in the HT villages (Table 34) indicating that the presence of Ca may enhance the Se content of grain probably as a result of more alkaline soil conditions. Grain total Se correlates negatively with soil S, which, as in the LK villages, suggests that sulphur inhibits the uptake of Se. Hair and soil total Se and P also correlate in the HT villages.

The above correlations should, however, be treated with caution due to the small sample population.

In the HN/ HT villages, both soil total and water soluble Se correlate significantly (95% confidence level) with water, grain and hair total Se (Table 36). The significant correlation between grain and hair Se levels in the HN/HT villages indicates the importance of locally grown crops to the Se status of the population (Table 36 and Figure 24).

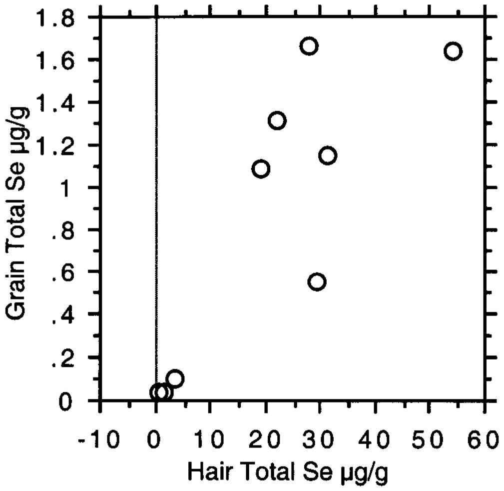


Figure 24. Village geometric mean Se concentrations in hair and grain samples in the HN/HT villages. (Results for HT4 are excluded as residents do not eat local grain)

Grain and soil water soluble Se ratios are higher in the HN and HT villages than in the LK villages confirming greater plant uptake of Se in the HN and HT villages (Table 32). Grain/soil water soluble Se ratios in the HT villages are dominated by the very high value for Yu Tang Ba village (HT4). As discussed in Section 9.6, greater availability of exchangeable Se and higher pH in soil may account for the high levels of Se in grain in this village.

High hair to grain Se ratios in the LK villages confirm that Se from sources other than maize-corn must contribute significantly to the Se status the population (Table 32).

Comparison of village geometric mean values confirms that soil chemical parameters including total and water soluble Se content are the main controlling factors in determining crop and human Se status in the Enshi area.

Table 32. Geometric mean values for selected parameters in the 15 study villages.

Village Code	Soil LOI%	Soil pH	Soil Ca µg/g	Soil Fe µg/g	I Soil P µg/g	I Soil S %	Soil Total Se µg/g	Soil Water Soluble Se µg/g	Water Total Se µg/l	Grain Total Se µg/g	Hair Total Se µg/g	Grain/ Soil Water Soluble Se %	Hair/ Grain Total Se %
LK1	6	5	1747	37105	352	0.009	0.119	0.000235	0.44	0.003	0.334	1277	11133
LK2	5.1	6	4841	35762	393	0.015	0.069	0.000210	0.1	0.001	0.345	477	34500
LK3	5.4	5.1	2110	35799	400	0.014	0.118	0.000207	0.1	0.001	0.265	483	26500
LK4	5.1	5.3	2313	37400	433	0.01	0.064	0.000427	0.3	0.003	0.252	703	8400
LK5	6	5.3	2932	32082	398	0.017	0.152	0.000445	0.1	0.001	0.339	225	33900
HN1	8.4	7.3	6407	23984	887	0.096	19.14	0.061	30.3	1.085	19.18	2367	1328
HN2	9.5	5.7	3467	50281	784	0.103	19.54	0.08	44.2	1.316	22.03	1645	1674
HN3	9.9	6.2	4363	41878	968	0.295	6.23	0.002	3.4	0.094	3.70	4700	3939
HN4	6.7	6.6	3404	31749	645	0.027	2.07	0.002	0.46	0.042	0.692	2100	1648
HN5	7.4	6.2	4500	28790	nd	nd	3.65	0.004	13.3	0.041	1.63	1025	3968
HT1	9.5	6.1	3221	46334	1219	0.04	17.88	0.049	38.1	1.635	54.4	3337	3327
HT2	8.1	6.3	3049	41826	797	0.042	15.53	0.027	275	1.156	31.2	4281	2699
HT3	6.4	6.8	5459	28203	521	0.022	4.27	0.026	7.3	1.66	28.11	6385	1694
HT4	8.3	6.4	5286	41760	503	0.021	4.6	0.016	40.4	2.902	4.56	18138	157
HT5	8.9	5.2	2592	43392	926	0.081	13.86	0.01	11.9	0.550	29.21	5500	5311

I = IRMA data nd = no data

Table 33. Spearman Rank correlation coefficients for village geometric mean values in the LK villages.

	Soil Ca	Soil Fe	Water Total Se	Hair Total Se	Grain Total Se	Soil Total Se	Soil LOI	Soil pH	Soil Water Sol Se	I Soil S
Soil Fe	-0.600									
Water Total Se	-0.671	0.783								
Hair Total Se	0.600	-0.800	-0.447							
Grain Total Se	-0.577	0.866	0.968	-0.577						
Soil Total Se	-0.200	-0.600	-0.112	0.400	-0.289					
Soil LOI	-0.474	-0.316	0.177	0.158	0.000	0.949				
Soil pH	0.975	-0.410	-0.574	0.462	-0.444	-0.410	-0.649			
Soil Water Sol Se	0.200	-0.100	0.224	0.000	0.289	0.300	0.316	0.154		
I Soil S	0.800	-0.900	-0.894	0.600	-0.866	0.300	0.000	0.667	0.200	
I Soil P	0.100	0.300	-0.224	-0.700	0.000	-0.500	-0.474	0.205	0.100	0.100

I = IRMA data Number of samples = 5 r95% = 0.805 (Koch & Link, 1970)

Table 34. Spearman Rank correlation coefficients for village geometric mean values in the HN villages.

	Soil Ca	Soil Fe	Water Total Se	Hair Total Se	Grain Total Se	Soil Total Se	Soil LOI	Soil pH	Soil Water Sol Se	I Soil S
Soil Fe	-0.700									
Water Total Se	0.400	0.100								
Hair Total Se	0.300	0.300	0.900							
Grain Total Se	0.000	0.400	0.700	0.900						
Soil Total Se	0.300	0.300	0.900	1.000	0.900					
Soil LOI	0.200	0.500	0.400	0.700	0.600	0.700				
Soil pH	0.359	-0.821	-0.359	-0.359	-0.205	-0.359	-0.462			
Soil Water Sol Se	0.308	0.051	0.975	0.821	0.667	0.821	0.205	-0.289		
I Soil S *	0.400	0.600	0.400	0.400	0.400	0.400	1.000	-0.600	0.105	
I Soil P *	0.800	0.000	0.200	0.200	0.200	0.200	0.800	0.000	-0.105	0.800

I = IRMA data Number of samples = 5 r95% = 0.805 (Koch & Link, 1970) * Number of samples = 4

Table 35. Spearman Rank correlation coefficients for village geometric mean values in the HT villages.

	Soil Ca	Soil Fe	Water Total Se	Hair Total Se	Grain Total Se	Soil Total Se	Soil LOI	Soil pH	Soil Water Sol Se	I Soil S
Soil Fe	-0.700									
Water Total Se	-0.300	0.200								
Hair Total Se	-0.500	0.800	0.200							
Grain Total Se	0.900	-0.600	0.000	*'-0.002						
Soil Total Se	-0.600	0.900	0.500	0.900	-0.500					
Soil LOI	-0.500	0.900	0.100	0.500	-0.300	0.700				
Soil pH	0.900	-0.900	-0.100	-0.600	0.800	-0.700	-0.800			
Soil Water Sol Se	0.200	0.300	0.300	0.700	0.100	0.600	0.100	0.100		
I Soil S	-0.900	0.600	0.000	0.600	-1.000	0.500	0.300	-0.800	-0.100	
I Soil P	-0.600	0.900	-0.100	0.900	-0.700	0.800	0.700	-0.800	0.400	0.700

I = IRMA data Number of samples = 5 r95% = 0.805 (Koch & Link, 1970) * 4 samples, hair results for HT4 excluded as residents do not eat local grain

Table 36. Spearman Rank correlation coefficients for village geometric mean values in the HN/HT villages.

	Soil Ca	Soil Fe	Water Total Se	Hair Total Se	Grain Total Se	Soil Total Se	Soil LOI	Soil pH	Soil Water Sol Se	I Soil S
Soil Fe	-0.709									
Water Total Se	-0.127	0.333								
Hair Total Se	-0.430	0.430	0.527							
Grain Total Se	0.358	-0.018	0.430	*0.667						
Soil Total Se	-0.139	0.479	0.648	0.612	0.358					
Soil LOI	-0.261	0.717	0.213	0.249	0.030	0.675				
Soil pH	0.693	-0.869	-0.207	-0.328	0.274	-0.316	-0.616			
Soil Water Sol Se	0.116	0.182	0.742	0.626	0.608	0.833	0.226	-0.015		
I Soil S	-0.083	0.400	0.017	-0.050	-0.517	0.617	0.736	-0.400	0.184	
I Soil P	-0.400	0.467	-0.067	0.383	-0.350	0.483	0.728	-0.483	0.059	.633

I = IRMA data Number of samples = 10 r95% = 0.549 (Koch & Link, 1970) * 9 samples, hair results for HT4 excluded as residents do not eat local grain

9.10 Comparison between the LK Villages and the Zhangjiakou Study Area

It is clear from the investigations presented in this report that the LK villages in Enshi District are distinct from the high Se area in terms of Se chemistry. The LK villages were therefore assessed in terms of the geochemical characteristics of the Zhangjiakou Keshan Disease area. Comparisons between selected data in the two areas are shown in Table 37. Soil LOI levels are similar in the two areas but soil Ca is significantly higher in the Zhangjiakou area and, accordingly, soil pH is higher. Soil Fe content is higher in the Enshi LK villages which may reflect increased chemical weathering in the warmer climatic conditions of southern China. Levels of total Se in water are higher in the Enshi area but levels of total Se in soils are similar in both areas. Hair total Se is higher in the Enshi area than the Zhangjiakou area and in both areas, levels of total Se in grain are near or below the detection limit. The results of this study (Section 9.3) and the Zhangjiakou study (Johnson et al., 1996) indicate that in low Se environments soil organic matter content is the main factor controlling Se bioavailability.

Although the hair Se levels of the Enshi LK villages are low (0.30 µg/g geometric mean value), they are not as low as levels in the Zhangjiakou District of China (0.18 to 0.19 µg/g geometric mean values) where KD is still reported. Average hair Se levels in the Enshi LK villages are higher than values recorded in Zhangjiakou villages where KD no longer occurs (0.23 µg/g geometric mean value) (Johnson et al., 1996).

Table 37. Comparisons between selected parameters in the Enshi LK villages and the Zhangjiakou study area.

	Zhangjiakou * Range	Enshi LK Range
Soil Total Se (ng/g)	43 - 263	34 - 228
Soil Water Soluble Se (ng/g)	0.030 - 2.940	0.03 - 5
Soil Ca (µg/g)	1860 - 43564	711 - 6895
Soil Fe (µg/g)	6203 - 35650	25151 - 41984
Soil LOI%	1.8 - 11.68	4.1 - 7.2
Soil pH	6.8 - 9.18	4.15 - 6.92
Water Total Se (µg/l)	0.005 - 1.15	0.1 - 0.44
Grain Total Se (ng/g)	6.7 - 86	1 - 18
Hair Total Se (ng/g)	94 - 359	170 - 853

* From Johnson et al. (1996)

9.11 Comparison of Enshi Results with Selenium Studies Elsewhere

The levels of total Se in soil in each of the three village groups recorded during the present study are similar to results (based on 5 - 6 samples) reported by Yang et al. (1989b) (Table 38). Results from the present study show a broader range in concentration probably due to the greater number of samples collected. A broader range in maize-corn Se levels and lower levels of Se in drinking water were reported by Yang et al. (1989b) compared to the present study. These differences are probably due to different sampling locations, different sizes of sample populations and different analytical techniques. Average levels of Se in hair are comparable between the two studies (Table 38).

Levels of total Se and water soluble Se in soil in the HN and HT villages are similar to seleniferous areas in India and the USA, however, the upper range in concentrations of water soluble Se in India and the USA exceeds that of the Enshi high Se area (Table 38). The geometric mean concentration of Se in maize-corn in the HT villages is 10 times higher than the average concentration of USA maize whereas levels of Se in water in the HN and HT villages are lower than those reported for seleniferous areas in South

Dakota, and Colorado, USA (Table 38). Hair samples in the HN villages are on average five times higher and, in the HT villages, 26 times higher than the levels quoted for Se concentrations in the average person (0.5 - 1 µg/g, Fergusson, 1990).

9.12 Deficient, Marginal and Excessive Levels of Selenium in Enshi District

On the basis of previous investigations into human Se imbalances carried out in China, threshold levels in various sample types indicative of low and toxic Se diseases have been defined (Tan, 1989). Applying these levels to the Enshi area, the majority of samples in all five LK villages are deficient or marginal in total soil Se, soil water soluble Se and grain total Se (Tables 39 and 40). Levels of soil water soluble Se and grain Se are, on average, one tenth of the deficiency threshold value. In contrast, the majority of hair Se values in the LK villages are marginal confirming that dietary sources other than locally grown maize-corn must contribute significantly to human Se intake. On this basis, the population in the LK villages may be at risk from Se deficiency if these other dietary sources of Se are not maintained and enhanced.

The majority of samples in nine out of ten HN and HT villages surpass the excessive threshold value for total Se in soil. Luojiaba (HN1), Bajiao (HN2), Shadi (HT1), Huabei (HT2) and Xin Tang (HT3) have a greater proportion of excessive soil water soluble Se than the other HN and HT villages (Tables 39 and 40). The remaining HN villages are marginal or deficient in soil water soluble Se and grain levels in these villages do not surpass the excessive level. Only 40% of soil water soluble Se concentrations from Yu Tang Ba (HT4) are above the excessive threshold and yet all grain samples from this village contain excessive levels of Se. Although the population of Yu Tang Ba (HT4) do not consume locally grown maize-corn and had only lived in the village for three months at the time of sampling, the Se levels in hair surpass the excessive threshold. This confirms that Se levels in hair are responsive to changes in human Se exposure and suggests that Se from locally grown vegetables and other sources affect the Se status of the population. In Shatou (HT5), the majority of Se levels in grain are not excessive whereas 100% of hair samples surpass the excessive threshold (Tables 39 and 40) indicating that Se from other sources must contribute to the Se status of the population.

Yang et al. (1989a), found no evidence of significant heart or liver damage as a result of Se toxicity in patients suffering severe nail and hair loss in Enshi District. However, increased blood clotting time indicating possible damage to the parenchymal cells of the liver; unusually low ratios of plasma-Se to red-blood-cell -Se; raised white blood cell counts; reduced blood GSH-Px levels and prevalence of chronic arthritis were recorded in subjects in the high Se area in Enshi. These effects were evident in adults and not in children under the age of 18 despite similar dietary Se intake in all age groups suggesting that long term exposure to high levels of Se is an important factor in the onset of selenosis.

Although no external clinical signs (hair and nail loss) of human selenosis were observed in Enshi District in November 1995, the results of this study suggest that the population in three of the HN and all of the HT villages are at risk from Se toxicity effects.

Table 38. Comparison between Se values in the LK, HN and HT villages and studies conducted elsewhere.

Country	Reference	Area	Comments	Total Se Soil µg/g	Water Soluble Se Soil ng/g	Se Water µg/l	Se Maize-corn µg/g	Se Hair µg/g
China	Present study	LK	Range	0.034 - 0.228	0.03 - 5	0.1 - 0.44	0.001 - 0.018	0.17 - 0.853
	Present study	LK	Geometric Mean	0.099	0.03	0.168	0.002	0.304
China	Present study	HN	Range	1.494 - 59.4	1 - 254	0.460 - 44.2	0.017 - 9.175	0.566 - 34.6
	Present study	HN	Geometric Mean	7.065	10	7.742	0.198	5.242
China	Present study	HT	Range	2.736 - 27.5	5 - 107	7.3 - 275	0.182 - 5.6	1.832 - 141
	Present study	HT	Geometric Mean	9.456	22	32.591	1.38	26.407
China	Tan et al. (1989)	KD-Belt		0.09 - 0.23			0.09 - 0.053	0.08 5- 0.379
China	Yang et al. (1989a)	Low Se area, Enshi	Husked rice and maize flour.	0.37 - 0.48		0.37	0.022 - 0.105	0.69
China	Yang et al. (1989a)	Moderate Se area, Enshi	Watkinson fluorimetric analysis	0.73 - 5.66		1.72	0.021 - 2.324	3.76
China	Yang et al. (1989a)	High Se area, Enshi	for Se	7.04 - 12.08		12.27	0.121 - 7.498	14.16
China	Yang et al. (1983)	Selenosis area, Enshi	Hair digested in sulphuric/				8.1	4.1 - 100
China	Yang et al. (1983)	High Se area, Enshi	perchloric acids + Na molybdate			54	0.57	1.9 - 8.2
China	Yang et al. (1983)	Adequate Se area	Grains digested in sulphuric/				0.036	0.36
China	Yang et al. (1983)	Low Se area	perchloric/ nitric acids				0.009	0.16
China	Yang et al. (1983)	KD Disease area	Watkinson fluorimetric analysis				0.005	0.074
China	Yang et al. (1983)	Enshi average	for Se	7.87	35		6.33	23.3
USA	Lorenz (1978)	USA						
USA	Greathouse & Craun (1979)	USA				< 1		
USA	Smith & Westfall (1937)	South Dakota	Se toxic area			50 - 300		
Australia	Fergusson (1990)	Se deficient area						
	Fergusson (1990)		Average person					0.5 - 1
Finland	Sippola & Jansson (1991)	Finland		0.005 - 1.241				
Spain	Morales et al. (1991)	Valencia				0.001 - 0.202		
China	Bai et al. (1989)	KD Belt					0.01	0.121
China	Bai et al. (1989)	Non KD area					0.035	0.230 - 0.287
China	Bai et al. (1989)	Average Chinese foods					0.035	
China	Xu & Jiang (1986)	KD Belt			0.2 - 0.8		0.021	0.072 - 0.078
China	Xu & Jiang (1986)	Non KD area			1.24 - 1.88		0.047	0.081 - 0.248
	Haygarth (1994)	Global averages		0.04		0.02		
USA	Ohlendorf & Santolo (1994)	Kesterton Reservoir	Se toxic area		50 - 390			
India	Bhattacharyya (1990)	Uttar Pradesh		0.158 - 0.710	19 - 66			
India	Bhattacharyya (1990)	Haranya	Se toxic area	1 - 19.5	50 - 620			
India	Bhattacharyya (1990)	Gujarat		0.025 - 0.606	17 - 112			
China	Ohta et al. (1990)	KD Belt	Samples washed in non-ionic					.018 - .086
China	Ohta et al. (1990)	Non KD area	detergent. Se by AFS.					0.25 - 0.87
Japan	Ohta et al. (1990)	Japan	Japanese control area					0.63 - 0.75
	McNeal & Balistreiri (1989)	Averages	Soil data from Se toxic area	1 - 1200		0.4 - 0.64		
USA	McNeal & Balistreiri (1989)	USA average		0.1 - 4.3				
UK	McNeal & Balistreiri (1989)	UK average		0.01 - 4.7				
	Mayland et al. (1989)	Most soils		0.01 - 2				
USA	Mayland et al. (1989)	Black Shale areas	Se toxic areas	1 - 10				
USA	Mikkelsen et al. (1989)	USA average					0.136	
	Hem (1985)	Stream water average				0.2		
Italy	Hem (1985)	River water				< 1		
USA	Hem (1985)	Gunnison River	Se toxic area			80		
USA	Faust & Aly (1981)	8 rivers in Colorado				1 - 400		
	Faust & Aly (1981)	Se deficient areas		0.1				
Ireland	Faust & Aly (1981)	Se toxic area		1200				
Finland	Koivestoinen & Huttunen (1985)	Finland		0.2 - 0.3				
Canada	Gibson et al. (1985)	Canada	Elderly women					0.48 - 0.66
UK	Thornton et al. (1985)	UK		0.01 - 4.66				

Table 39. Comparisons between Enshi village geometric mean values for Se in soil, grain and hair with recommended thresholds for deficient, marginal, high and excessive Se.

Village Code	Soil Tot Se µg/g	Soil Water Sol Se µg/g	Grain Tot Se µg/g	Hair Tot Se µg/g
Deficient *	< 0.125	<0.003	< 0.025	< 0.2
Marginal *	0.125 - 0.175	0.003 - 0.006	0.025 - 0.04	0.2 - 0.5
Mod - High *	0.175 - 3	0.006 - 0.02	0.04 - 1	0.5 - 3
Excessive *	3	0.02	1	3
LK1	0.119	0.000235	0.003	0.334
LK2	0.069	0.00021	0.001	0.345
LK3	0.118	0.000207	0.001	0.265
LK4	0.064	0.000427	0.003	0.252
LK5	0.152	0.000445	0.001	0.339
HN1	19.136	0.061	1.085	19.179
HN2	19.543	0.08	1.316	22.029
HN3	6.227	0.002	0.094	3.703
HN4	2.071	0.002	0.042	0.692
HN5	3.651	0.004	0.041	1.627
HT1	17.881	0.049	1.635	54.4
HT2	15.525	0.027	1.156	31.2
HT3	4.272	0.026	1.66	28.113
HT4	4.599	0.016	2.902	4.562
HT5	13.86	0.01	0.55	29.211

* Tan (1989) Tot = total Mod = moderate Sol = soluble

Table 40. Percentage of deficient, marginal and excessive Se concentrations in soil, grain and hair samples in the 15 study villages.

Village	% of deficient samples				% of marginal samples				% of excessive samples			
Code	TSe Soil	WSe Soil	TSe Grain	TSe Hair	TSe Soil	WSe Soil	TSe Grain	TSe Hair	TSe Soil	WSe Soil	TSe Grain	TSe Hair
LK1	60	100	100	20	20			60				
LK2	100	100	100	20				60				
LK3	60	100	80	20	40			80				
LK4	100	80	100	20		20		80				
LK5	20	100	100		60			100				
HN1									100	80	100	100
HN2									100	100	60	100
HN3		80				20	20		100			40
HN4		60	20			20	60		40			
HN5		20	20				20		80	20		20
HT1									100	60	80	100
HT2									100	80	80	100
HT3									100	60	80	100
HT4						20			100	40	100	67
HT5						40			100	20	20	100

TSe = Total Se WSe = Water Soluble Se

9.13 Controls on Selenium Chemistry and Se-related Disease in Enshi District

As discussed in the previous sections, Se availability in the environment and the food chain and human Se status are controlled by a number of factors. In soils, the main factors affecting Se availability to the food chain include geology, the pH and Eh conditions, organic matter and clay content and the concentrations of Fe, P and sulphur (McNeal & Balistrieri, 1989). The factors affecting Se in the environment and the human population of Enshi are summarised below.

9.13.1 Geology

At the regional level, geology exerts a fundamental control on environmental Se levels in Enshi District. The geographic distribution of Jurassic purple sandstones and siltstones containing low levels of Se and Permian age carbonaceous strata and limestone sequences associated with high Se concentrations result in a significant difference in soil, water and grain chemistry between the LK and HN/HT villages. These environmental differences are reflected in and have marked effects upon the human population such that communities which are marginal or deficient in Se (LK) occur within 20 km of communities whose Se status exceeds recommended excessive threshold values (HN/HT).

At the village level, localised geochemical variations in Permian carbonaceous and limestone strata result in significant differences in soil chemistry both between and within individual villages. High soil total Se levels reflect carbonaceous strata geochemistry. The proportion of crops grown on very high Se soils developed directly over carbonaceous beds relative to lower Se soils associated with surrounding siliceous rocks and limestones, may, in part, explain the occurrence of human selenosis problems in some villages underlain by carbonaceous strata (HT) and not in others (HN).

9.13.2 Total Selenium in Soil

Soil total Se concentrations in the LK villages are 95 times lower (geometric mean values) than levels in the HN and HT villages. However, soil total Se concentrations are not consistently lower in the HN than the HT villages as would be expected. Soil total Se concentrations are a major control on soil water soluble Se levels in the HN villages and to a lesser extent in the HT villages (Spearman Rank correlations, Table 27 and Appendix J). The levels of total Se in soil in the HN/HT villages are reflected in soil water soluble Se and in grain, water and hair total Se levels (Spearman Rank Correlations, Table 36).

9.13.3 Water Soluble Selenium in Soil

Soil water soluble Se levels are 76 times lower (geometric mean values) in the LK villages than the HN/HT villages, however, highest soil water soluble Se levels occur in the HN and not in the HT villages as expected. Soil water soluble Se in the HN/HT villages is primarily controlled by geological variations, and within individual villages, levels can vary from excessive to marginal or deficient (Table 40). The marked variations in soil water soluble Se chemistry at the village level in the LK, HN and HT villages are reflected in the broad range of Se concentrations in grain (Figure 22). However, uptake of Se by grain in HT3 and HT4 villages is higher than would be predicted from soil water soluble Se levels and is probably influenced by other factors such as higher soil Ca and pH. (Figure 22).

9.13.4 Organic Matter in Soil

Soil organic matter exerts a major control on Se soil chemistry in the Enshi area. In the LK villages, Se in soils is probably bound in organic matter complexes (Spearman Rank correlations, Appendix J). In the HN/HT villages, high total concentrations of trace elements including Se are associated with high levels of organic matter in soils developed over carbonaceous strata (Spearman Rank correlations, Appendix J; Factor

Analysis, Appendix K). Soils in these villages contain many carbonaceous fragments and this relationship reflects carbonaceous strata geochemistry. There is some evidence to suggest that secondary plant derived organic matter inhibits the availability of Se in the HN/HT villages but this is a less important association than the relationship between organic matter and Se in carbonaceous strata (Factor Analysis, Appendix K).

9.13.5 Soil pH

Soil pH is higher in the HN/HT villages than the LK villages reflecting the dominance of carbonate lithologies in the high Se area. Soil pH is less important in determining Se availability in the LK villages than soil Fe content (Spearman Rank correlations, Appendix J). Soil pH exerts an important control on levels of water soluble Se in HT villages (Spearman Rank correlations, Appendix J; Factor Analysis, Appendix K) which, in part, enhances the uptake of Se by grain (Figure 22).

9.13.6 Soil Iron, Phosphorous and Sulphur Content

The presence of Fe in soils in the LK villages appears to reduce the amount of bioavailable Se probably as a result of complexing into Fe oxyhydroxides (Spearman Rank correlations, Appendix J). In the HT villages, Fe, P and sulphur are associated with total Se reflecting carbonaceous strata geochemistry (Spearman Rank correlations, Appendix J). The association between Fe, sulphur and total Se in the HT villages probably indicates the presence of Se-bearing sulphide minerals such as pyrite. This association is not apparent in the HN villages (Spearman Rank correlations, Appendix J). Factor Analysis (Appendix K) indicates that Fe inhibits the availability of Se in the HT villages probably due to complexing with Fe oxyhydroxides. Although there is no direct evidence from the present study, lower levels of P in villages HT3 and HT4 may account for the disproportionate concentration of Se in grain in these two villages relative to soil Se content. Reduced levels of P in soils have been shown to retard plant growth and concentrate Se in plants (Mikkelsen et al., 1989). Slower plant growth may effectively concentrate the levels of Se in grain from these two villages (Figures 16 and 22). In the LK and HT villages greater soil sulphur corresponds to lower grain Se levels (Spearman Rank correlations, Tables 33 and 35) confirming results elsewhere that sulphur competes with Se during plant mineral uptake from soil (Mikkelsen et al, 1989).

9.13.7 Soil Clay Content

Clay minerals in soil can inhibit the availability of Se due to adsorption (Mikkelsen, et al., 1989). There is no evidence in the current study to indicate the effects of clay minerals on soil Se chemistry.

9.13.8 Selenium in Grain

Levels of Se in grain in the LK villages are 690 times lower (geometric mean values) than levels in the HN/ HT villages. Grain Se concentrations vary from excessive to marginal in the HN/HT villages reflecting differences in soil chemistry. The proportion of high Se grain grown in a village may, in part, determine the occurrence of human selenosis (Table 40). No information on the amount of grain consumed in the Enshi area was obtained during the present study, however, Yang et al. (1989b) estimated that approximately 70% of Se intake in the Enshi area was from local cereal crops. It can therefore be assumed that Se in grain forms a significant component of the human Se intake Enshi. In the HN/HT villages, the link between grain and human Se status is apparent. Se levels in grain correlate with Se levels in hair with the exception of Yu Tang Ba (HT4) village where the population did not consume local grain (Figure 23 and Table 36).

9.13.9 Selenium in Water

Levels of Se in water in the LK villages are 194 times lower than in the HN/HT villages. In the HN/HT villages seven of the ten water samples exceed the WHO guideline level of 10 µg/l. At these high concentrations, drinking water undoubtedly contributes to the Se intake of the local population. Levels of Se in water in some HN and HT villages are comparable to levels of Se in grain from some HN villages (Table 32) and dietary estimates indicate that Se in water accounts for 33% of daily Se intake from grain and water combined in the HN villages (Table 31).

9.13.10 Selenium in Hair

Se levels in hair give a good indication of human Se status in the Enshi area. Levels of Se in hair in the LK villages are 87 times lower (geometric mean values) than in the HN/HT villages. The majority of the population in the LK villages are marginal or deficient in Se whereas excessive levels of hair Se are recorded in the HN/HT villages. Levels of hair Se are close to or below the excessive threshold in the HN villages with the exception of Luojiaba (HN1) and Bajiao (HN2). On the basis of the results of the present study, these two villages are at risk from Se toxicity problems, although no selenosis has been recorded in the past.

9.13.11 Dietary Factors

In the LK villages, average grain Se concentrations are one tenth of the recommended deficiency level, however, most villagers have marginal Se status (Table 40). It is clear that food sources other than grain contribute significant amounts of Se to the diet in these villages. Although not quantified during the present study, factors such as the consumption of rice from other regions of China will undoubtedly affect human Se levels. A lower dietary intake of vegetables and greater proportion of rice rather than maize-corn in the diet may also lower the Se status of the population as previous studies (Yang et al, 1983) have shown Se concentrations to increase from rice < maize-corn < vegetables grown in the Enshi high Se area.

9.13.12 Other Factors

The results of this study suggest that the majority of the population investigated in Enshi District are at risk from Se-related diseases (Table 40). However, no human selenosis cases have been reported in the District for several years and the occurrence of KD in the LK villages is, at present unknown. This suggests that the local population may have adapted to the high and low Se intakes present in the different environments and that the historical occurrences of clinical effects related to Se imbalances were caused by other factors. The outbreaks of human selenosis in Enshi during the late 1950's and early 1960's coincided with low rainfall (Table 41) and the failure of the rice crop (Yang et al., 1983). The crop failure had serious implications for the dietary intake and health of the local population with less food available and higher dependence on vegetables and maize. These factors may have lead to the outbreaks of selenosis in the Enshi area. Yang et al. (1983) also cite the decrease in protein intake during this time as a factor increasing human susceptibility to excessive Se levels. The practice of treating soil with carbonaceous shale ash and liming soil, thus increasing soil pH, may also have contributed to the availability of Se in the high Se area. The local population have been advised to avoid these soil applications (Yang et al., 1983). In the LK villages, it is likely that improved communications and increased availability of foodstuffs from other regions of China have enhanced the Se status of the population so that the high prevalences of KD in the late 1960's no longer occur.

Table 41. Annual precipitation range and average values in Enshi District

County	Survey Years	Max. Value mm/y	Year	Min. Value mm/y	Year	Average Value mm/y
Lichuan	1952 - 1984	1466.1	1976	987.7	1959	1327.9
Enshi City	1959 - 1984	1681.9	1967	1105	1959	1441.8
Jianshi	1956 - 1984	1569.9	1963	1093.5	1966	1425.3
Badong	1952 - 1984	2173.6	1968	782.2	1976	1424.9
Xuan 'en	1952 - 1984	1703.3	1975	1166.7	1959	1501.1

Max. = maximum Min. = Minimum mm/y = mm/year

From Zhang Guangdi pers. commun.

10. RISK ASSESSMENT AND REMEDIATION

10.1 Risk Assessment

Previous investigations in China and other areas of the world have shown that geochemical data for total Se determinations in soils and stream sediments can be used to delineate areas at possible risk from Se deficiency and toxicity on a regional scale. However, the results of the present study have shown that information on soil water soluble Se, Ca, Fe, P and organic matter contents and soil pH are required to define more clearly, specific villages and populations at risk, on the basis of geochemical data. This method of assessing risk involves a number of analyses and careful interpretation of the results. Alternatively, this study has shown that grain total Se levels give a good indication of the likely human Se status and **it is therefore recommended** that grain total Se levels provide the simplest means of assessing potential risk at the village and field scale.

In the HN and HT villages of Enshi District, if it is not possible to carry out geochemical surveys and the analysis of grain or crop samples, mapping the area underlain by carbonaceous strata using local knowledge of carbonaceous shale outcrops and the amount of carbonaceous fragments in soil will identify areas at greatest risk. Equally, mapping limestones adjacent to carbonaceous strata and a simple soil pH test can be used to indicate areas where high soil pH may increase Se bioavailability.

Whilst environmental sample types can be used to predict the likely areas at risk from disease, this does not imply that the disease will occur. Other factors and external pressures such as shortage of food, general health of the population, length of exposure and proportion of certain foods in the diet all contribute to the occurrence of Se-related disease.

In the high Se area in Enshi, localised geological variations within villages result in marked differences in soil and grain Se levels making the proportion of crops grown on carbonaceous strata soils an important consideration in assessing risk at the individual village level.

10.2 Remediation in the LK Villages

Although the Se status of the population in the Enshi LK villages is probably below the current UK DOH Lower Reference Nutrient Intake level of 40 µg/day, the need for remedial action, through the use of Se fertilisers, for example, is not clear even though it might be recommended as a precautionary measure. Prior to such action being taken, **it is recommended** that a dietary survey be carried out to determine the range of Se intake of the population in the Enshi LK area. This will provide a sound basis for assessing the need for dietary Se supplementation. Should a dietary survey confirm that the daily Se intake is indeed only 20-30 µg, then several options for remedial action are available as follows:

10.2.1 Selenium Supplementation Tablets

Dietary supplements have been used successfully in parts of China to alleviate the effects of KD disease (Tan et al., 1989). However, the average cost of an annual supply of Se tablets in China is 400 yuan whereas the average annual rural farm wage is 300 - 400 yuan (Ge Xiaoli pers. commun.). Se supplementation tablets are therefore beyond the means of most rural populations making it necessary for government institutions to provide the supplements. The intake of organic Se in food is more natural and perhaps more beneficial than the use of supplementary tablets containing sodium selenite, for example. In the longer term, it is better to enhance the natural level of Se intake through foodstuffs by methods such as Se fertiliser application.

10.2.2 Soil Application of Selenium Fertilisers

The application of Se salts to soil can raise the level of Se in crops. Addition of 70g of Se as $NaSeO_4$ per hectare was sufficient to remove Se deficiencies from New Zealand pastures (Bisbjerg & Gissel-Nielsen, 1969). Studies into the effectiveness of application of various forms of Se to soils have shown the following sequence of availability: $CuSeO_4$ > $BaSeO_4$ > $NaSeO_4$ > selenite salts > elemental Se. Addition of selenate salts to soil resulted in 20 - 50 times plant tissue Se levels than addition of selenite salts (Gissel-Nielsen & Bisbjerg, 1970). Se applications should, however, be made with care to avoid creating Se toxicity problems in plants and soil due to the large variation in plant uptake between different forms of Se. Additions of Se^{6+} in particular should be made with caution as this form is highly water soluble and available to plants (Mikkelsen et al., 1989).

Several studies have shown that although Se concentrations in crops initially rise following fertiliser application, they decline in subsequent crops grown on the same soil due to rapid fixation of Se in the soil (Mikkelsen et al., 1989). Van Dorst & Peterson (1984) demonstrated the importance of factors such as soil pH and organic matter content in determining Se fertiliser availability. At pH 4.5, selenate added to soil was quickly immobilised but at pH 7, selenate remained mobile. Up to 40% of the soluble Se in this experiment was converted to organic Se.

Se rich fertiliser produced in Enshi District from the carbonaceous shale by the Enshi Coal Bureau is undergoing chemical testing to assess the suitability of this product for remediation strategies in low Se areas. Se and other elements are extracted from the carbonaceous shale and added to commercial NPK fertiliser (Fordyce, 1996). Field trials of the Se fertiliser are being carried out by the IRMA in conjunction with Enshi Local Government and Zhangjiakou and Cixian agronomists. Farmers already use NPK fertilisers in the area.

Soil Se fertiliser application to alleviate crop Se deficiencies in the KD areas of China should, however, be considered with caution. Organic complexing of Se in soil has been shown to significantly reduce the availability of Se in the Zhangjiakou study area (Johnson et al., 1996) and is an important control on Se availability in the LK villages in the present study. Direct application to soil in low Se environments may prove inefficient as Se is fixed to soil organic matter. At the same time, care should be taken to ensure that the concentration and speciation of Se in the fertiliser does not result in Se toxicity problems.

10.2.3 Foliar Application of Selenium Fertilisers

Direct application of Se to plant foliage has been shown to be more efficient than soil applications as the problem of Se immobilisation in the soil is avoided. Studies have shown that plant tissue Se concentrations were five times higher following foliar spraying of Se than when applied to soil (Watkinson & Davies, 1967). In general, Se^{6+} is more readily taken up by the plant than Se^{4+} and spraying late in the season results in higher Se concentrations due to greater leaf cover and slower plant growth (Mikkelsen et al., 1989). Factors such as local humidity and time between spraying and rainfall events can give variable results from this method and recoveries are poor (4.2 - 8.1% of Se added) (Haygarth, 1994). In KD areas in China, however, this method may avoid the problem of Se fixation by organic matter in soil.

10.2.4 Increasing Dietary Sources of Se

Increasing the proportion of food from elsewhere or the amount of Se rich food such as fish in the diet will enhance the Se status of the LK population. As the improvements in communication and transport evident in China over the last 10 years continue, greater integration and availability of food supplies should reduce the risk of KD disease. It is recognised, however, that small-scale farmers may not have the financial resources to diversify their diets in the manner recommended.

10.3 Remediation in the HN/HT Villages

10.3.1 Soil Applications

Some measures to reduce the amount of Se in soil in the high Se areas in Enshi have already been implemented. Following studies into the occurrence of selenosis in the 1970's and early 1980's, the local population were advised to discontinue the practice of dressing soil with burnt coal ash and with lime (Mao Dajun pers. commun.).

NPK fertilisers are used in the villages to enhance crop yields. Conflicting evidence has been reported in previous studies on the effects of plant Se uptake following addition of P fertilisers to soils. The majority of investigations have shown that P and Se^{4+} may react competitively for fixation sites in the soil. When PO_4 or PO_3 are added to soil they are more readily adsorbed onto fixation sites and displace Se making it more bioavailable hence levels of Se in plants increase (Mikkelsen et al., 1989). However, some studies have demonstrated a decrease in plant Se levels following P application probably as a result of Se dilution in the plant due to enhanced plant growth rates (Mikkelsen et al., 1989). P fertilisers can also contain significant levels of Se. Kabata-Pendias & Pendias (1984) reported levels of 0.5 - 25 µg/g Se in various fertilisers whereas Senesi et al. (1979), found 10 - 13.25 µg/g Se in ammonium nitrate and triple superphosphate preparations but no Se in ammonium sulphate, calcium nitrate, urea, calcium cyanamide, superphosphate, potassium sulphate, NP and NPK compounds. Some rock phosphates can contain up to 200 µg/g Se (Mayland et al., 1989).

Fertilisers should be applied with caution in the high Se area of Enshi District to ensure that the fertilisers used are Se-free and do not contribute to the Se loading of soil. Care should also be taken to prevent an increase in the availability of Se following P application by exchange of P for Se in soil fixation sites. Further investigations are required into the forms and controls of Se in soil in the high Se area and the effects of the application of fertilisers and other soil conditioning agents on plant Se uptake.

10.3.2 Crop Restrictions

This study has demonstrated that within individual villages in the Enshi high Se area, soil chemistry can vary considerably depending on the local lithology. Excessive or deficient levels of Se in soil can occur in the same village. Careful farming of these soils could therefore significantly reduce the Se intake of the local population. Villagers should be advised, where possible, to avoid growing crops on fields directly underlain by carbonaceous strata and, in particular, should be dissuaded from cultivating Se accumulating vegetables such as turnips on carbonaceous strata soils. It is recognised, however, that this may not be a practical option if population pressure requires use of all cultivated land in a village.

10.3.3 Dietary Controls

The mixing of foodstuffs grown outside the high Se area and local produce is already taking place within Enshi District. Villagers should be encouraged to incorporate food from outside the region into their diet and to reduce the consumption of locally grown vegetables containing high Se. In two of the villages studied, alternative water sources that are not associated with the carbonaceous strata have been identified. In order to lower the dietary intake of Se in the other villages, alternative water sources should be found within the village areas where possible.

10.4 Future Investigations

In addition to testing the use of soil applications and fertilisers, future investigations in the Enshi area should attempt to relate rock, soil, grain and human samples from the same location directly to confirm the very localised variations in environmental Se levels in the HN and HT villages and determine agricultural risk areas within villages. An initial detailed soil geochemical study of one of the villages with widely varying soil Se levels should be carried out to evaluate the detailed relationship between soil Se and geology. Further veterinary and medical studies are also required to define the present incidence of human and other animal selenosis and Se-deficiency disorders in the District and to assess the health affects of long term deficiency and exposure to high Se levels. The impact of Se inhalation from carbonaceous shale smoke and locally grown tobacco in the local population should also be assessed.

The present study has defined more clearly the controls on Se availability in the environment in Enshi District and the relationships between environmental Se levels and human Se status. These results have broader application to other Se deficient and excessive environments in China and the rest of the world.

11. CONCLUSIONS

1. Previous work during the 1970's and 1980's established that the occurrence of human selenosis problems and the incidence of Se-deficiency related Keshan Disease (KD) in Enshi District were linked to the local Se environment (Yang et al., 1983). High environmental Se occurs in areas underlain by Permian carbonaceous strata whereas Se deficiency is associated with Jurassic siltstones and sandstones. However, previous investigations concentrated on the dietary intake and Se status of the local population and did not assess the geochemical controls on Se availability in soils and hence to plants. No systematic study had been carried out to evaluate the relationship between environmental Se levels, Se in staple food crops and drinking water, with human Se status. It was therefore not possible to define methods of remediating environmental and human Se imbalances on the basis of previous work.

2. During the present study, five low environmental Se and KD incidence (LK), five high environmental Se and no selenosis (HN) and five high environmental Se and selenosis incidence (HT) villages in Enshi District were sampled. This experimental design proved successful in determining chemical differences in the environment (demonstrated by soil, staple foodstuffs (grain) and water samples) and the Se status of the human population (shown by hair samples) in the three village groups.

3. BGS analytical replicate results showed good reproducibility of analytical methods for ICP-AES determinations in soil samples and AFS selenium determinations in soil, water, grain and hair samples. Field duplicate results for waters showed good representivity of these samples. Results for soil and grain samples showed more variability due to natural inhomogeneities in the Enshi environment but ANOVA statistics confirmed the robustness of the field sampling methods. Comparisons between BGS and IRMA analysis for soil samples showed good agreement between the two laboratories for most elements.

4. There is little evidence to suggest that the drying of maize-corn samples over carbonaceous shale fires in the HN and HT villages causes significant Se contamination of maize-corn. Tests on three grain samples washed in deionised water and 1% HCl solution concluded that only 0.0005% of the Se contained in maize-corn samples from the HN and HT villages was removed by washing. Grain samples were not therefore washed prior to analysis.

5. Soil LOI and TOC show good agreement, but the LOI values are higher than TOC values due to the loss of structural water from clays and sesquioxides during the ignition process. Although LOI values do not represent the organic

matter content of soils directly in the Enshi area, LOI values give an indication of the relative organic matter content of the soil.

6. Two soil profiles, three deeper (35 - 45 cm) soil samples and ten rice paddy soils were collected during the present study for comparison with other soils. No systematic changes in soil chemistry with depth or between rice paddy soils and other soils were apparent from the HN and HT villages. However, the rice paddy soils from the LK villages generally contained higher total Se concentrations and pH and lower Fe and Ca levels than other soils. Further studies involving sequential extractions to assess the bioavailability of Se in rice paddy soils are being conducted at the BGS.

7. Several villages import rice from other areas of China to supplement local supplies therefore only seven locally grown rice samples were collected. On the basis of this small sample population was not possible to distinguish systematic differences between rice and maize-corn chemistry. However, the four rice samples collected in the LK villages contained higher levels of Se than maize-corn samples, reflecting higher Se in the rice paddy soils.

8. The HN and HT villages soils have a higher organic content than the LK villages. Total Se contents in soil show a strong correlation with organic matter and soil colour for the whole dataset. Highest organic matter and Se concentrations occur in dark brown soils associated with the carbonaceous strata. Despite the high organic matter content in the HN and HT villages, high levels of Se are found in grain samples. This is in contrast to the Zhangjiakou study area where high soil organic matter content inhibits the uptake of Se into the food chain (Johnson et al., 1996). Levels of Se in soil are approximately 100 times higher (geometric mean values) in the HN and HT villages than in the Zhangjiakou field area and this, in part, may account for the lesser effect of soil organic matter on grain Se levels in these villages. Unlike the Zhangjiakou area, soils in the HN and HT villages of Enshi contain organic matter derived from the carbonaceous strata. The association between high Se in soils and organic matter in the HN and HT villages is probably a reflection of carbonaceous strata geochemistry rather than the complexing of soil Se by secondary biologically derived organic matter.

9. The main control on soil trace element and Se distribution in Enshi District is geology. The majority of trace elements and other soil parameters (pH, organic matter and CEC) are higher over the carbonaceous and limestone rocks of the HN and HT villages than the sandstones of the LK villages. Se concentrations in soil, grain, water and hair samples in the LK villages are 690 times lower (geometric mean values) than in the HN and HT villages.

10. Estimates from the present study indicate that individuals in HN and HT villages may consume greater than >900 µg/day (toxic level, Yang & Xia, 1985) Se particularly if all crops are grown on Se-available soils in a village. Results from the present study also show that only one tenth of the recommended daily dietary intake of Se is provided by grain and drinking water in the LK villages.

LK Villages

11. Within the LK villages, Se is associated with organic matter (Spearman Rank correlations) and is probably bound in organic complexes which restrict availability to plants in the food chain. Soils with higher iron (Fe) concentrations have lower water soluble Se levels (Spearman Rank correlations) suggesting that complexing with Fe oxyhydroxides also restricts bioavailability within these villages. The levels of Se in hair are higher than would be predicted from levels in grain and drinking water samples indicating that other foods

containing Se (such as fish) must contribute significantly to the Se status of the population.

12. The majority of the soil and grain samples in the LK villages are deficient in Se whereas most hair samples have marginal Se concentrations. The present incidence of KD disease in the LK villages is unknown but the results of this study suggest that the population may be at risk from Se deficiency disorders.

13. In the LK villages, **it is recommended** that a dietary survey be carried out to determine the range of Se intake of the population in the Enshi LK villages. This will provide a sound basis for assessing the need for dietary Se supplementation. Should a dietary survey confirm that the levels of Se in the diet are insufficient, then dietary Se intake should be supplemented by the use of Se fertiliser. Se intake from foodstuffs is in a more natural form and may be more beneficial than the provision of Se supplementation tablets. The relative benefits of Se fertiliser application to soil or foliar application direct to plants should be investigated as the results of the present study and the Zhangjiakou study (Johnson et al., 1996) strongly suggest that soil Se in low Se environments is fixed by organic matter and is therefore not readily bioavailable. As a result, the addition of Se fertiliser to soil may not increase crop Se levels. Care should be taken not to introduce Se toxicity problems into low Se areas through the use of certain P fertilisers which can contain very high levels of Se. It is also recommended that the population is encouraged to supplement locally grown produce with foodstuffs from non-Se-deficient areas and to increase the level of Se rich foods in the diet where possible. However, it is recognised that some small-scale farmers may not have the financial resources to diversify their diets in the manner recommended.

14. Se rich fertiliser produced in Enshi District from the carbonaceous shale by the Enshi Coal Bureau is undergoing agronomic testing to assess the suitability of this product for remediation strategies in low Se areas. Se and other elements are extracted from the carbonaceous shale and added to commercial NPK fertiliser (Fordyce, 1996). Field trials of the Se fertiliser are being carried out by the IRMA in conjunction with Enshi Local Government and Zhangjiakou and Cixian agronomists.

HN and HT Villages

15. Within the HN and HT villages, soil Se levels reflect the distribution of the carbonaceous strata. The highest Se levels are associated with high levels of other elements common in carbonaceous rocks, such as As, Cd, Cu, F, Hg, S, V and Zn, also with high levels of organic matter (Spearman Rank correlations). Se may also be held in the form of sulphide minerals such as pyrite in the HT villages (Spearman Rank correlations). The bioavailability of Se (indicated by water soluble Se) in these villages is related to soil total Se levels and pH (Spearman Rank correlations and Factor Analysis). Negative associations between water soluble Se with Fe and LOI (Factor Analysis) suggest that to some extent Se availability may be restricted by adsorption onto Fe oxyhydroxides and secondary biologically derived organic matter. Levels of Se in grain increase as the water soluble Se content of the soil increases in the HN/HT villages. However, levels of Se in grain are higher than would be predicted from soil chemistry, in Xin Tang (HT3) and Yu Tang Ba (HT4) villages. It is possible that higher Ca and pH indicating a greater dominance of limestone lithologies make Se more available for plant uptake. Although there is no direct evidence from the present study, lower soil phosphorous concentrations in these two villages may also reduce plant growth, effectively concentrating Se in the plants.

16. Localised lithological changes result in considerable variations in Se levels in all sample types at the individual village level. Villages can contain both deficient and excessive levels of Se in soil and grain making the assessment of Se toxicity risk difficult. The proportion of crops grown on relatively low or very high Se soils in an individual village may, in part, determine which individuals within villages are at risk. Individuals at highest risk may be those with fields sited directly over carbonaceous strata or areas where limestones increase the availability of Se whereas neighbours with adjacent fields on surrounding siliceous rocks are less at risk.

17. As a result of the inhomogeneous nature of the geology and soils in the HN and HT villages, there is considerable overlap between Se levels in all sample types in the these two villages and the highest soil and grain Se concentrations actually occur in HN and not HT villages as would be expected.

18. In the HN/HT villages, grain and hair Se levels correlate demonstrating a link between locally grown crops and human Se status. However, other dietary factors probably affect the levels of Se in hair. Yang et al. (1983) reported lower levels of Se in rice than in maize-corn and markedly greater concentrations in vegetables than in cereal crops grown in the Enshi high Se area. Se levels in hair are, therefore, probably influenced by the proportions of vegetables, rice and maize-corn in the diet. The consumption of food from outside the Enshi area will also affect the Se status of the population. Estimates of daily dietary intake from grain and water in the present study indicate that drinking water may contribute 33% of the combined grain and water Se intake in HN villages.

19. Excessive levels of Se in hair were recorded in all residents sampled in the HT villages and in Luojiaba (HN1) and Bajiao (HN2). The majority of soil and grain samples in these HN villages also contain excessive Se levels. The results of the present study suggest that the risk of human Se toxicity problems in Luojiaba (HN1) and Bajiao (HN2) is similar to the HT villages, however, no selenosis has ever been recorded in these two villages. Furthermore, despite the high levels of Se found in the HN/HT population, no incidences of selenosis have been reported in recent years in Enshi District. This suggests that the local population may have adapted to the high Se intake and that although soil, grain, water and hair samples give an indication of the potential risk of human Se toxicity problems, other factors may precipitate the onset of human selenosis.

20. Yang et al., (1983) indicated that the worst outbreaks of human selenosis occurred in Enshi District during the early 1960's and coincided with a period of drought and rice crop failure. It is likely that the shortage of food, greater proportion of vegetables and lesser proportion of protein in the diet at this time contributed to the incidence of the disease (Yang et al., 1983). These factors may also explain why selenosis occurred in some villages with high environmental levels of Se and not in others.

21. Although no instances of selenosis have occurred in Enshi District in recent years, the results of this study suggest that the population are still at risk from Se toxicity and it is recommended that the level of Se intake should be reduced in the local population if possible.

22. In the HN and HT villages, **it is recommended** that where possible villagers should avoid cultivating high Se soils directly underlain by carbonaceous strata. In particular, villagers should be discouraged from growing vegetables (especially turnips) adjacent to outcrops of the carbonaceous strata. However, it is recognised that population pressure may require all land in a village to be cultivated. The local population should also be encouraged to reduce the

proportion of high Se foods in the diet and to increase the percentage of produce from outside the high Se area. Care should be taken in the HN and HT villages not to increase the levels of Se further by application of high Se-bearing phosphate fertiliser. The addition of fertilisers to soils in the high Se area should be tested as increased P has been shown to raise the level of plant Se uptake from soil. Villagers should continue to be discouraged from dressing soil with coal ash and other products derived from the carbonaceous strata and with lime which increases soil pH making Se more bioavailable. In two of the villages studied, alternative water sources that are not associated with the carbonaceous strata have been identified. In order to lower the dietary intake of Se in the other villages, alternative water sources should be found within the village areas where possible.

23. In addition to testing the use of fertilisers, **it is recommended** that future investigations in the Enshi area should attempt to relate rock, soil, grain and human samples from the same location directly, to confirm the very localised variations in environmental Se levels in the HN and HT villages and determine agricultural risk areas within villages. An initial detailed soil geochemical study of one of the villages with widely varying soil Se levels should be carried out to evaluate the precise relationship between soil Se and geology.

24. Further veterinary and medical studies are also required to define the present incidence of human and other animal selenosis and Se-deficiency disorders in the District and to assess the health affects of long term deficiency and exposure to high Se levels. Further studies should also assess the impact of Se inhalation from carbonaceous shale smoke and locally grown tobacco in the local population.

25. The present study has defined more clearly the controls on Se availability in the environment in Enshi District and the relationships between environmental Se levels and human Se status. These results also have broader application to other Se deficient and excessive environments in China and other countries where Se-deficiency may have a negative impact on human health, such as Sri Lanka and Zaire where Se-deficiency has been implicated as a causative factor in iodine deficiency disorders (IDD).

12. ACKNOWLEDGMENTS

The authors extend grateful thanks for the excellent assistance provided during fieldwork by all members of the field sampling team (Appendix L) and to staff of the IRMA and the BGS during the completion of this report. Dr Li, Prof Mao Dajun and Dr Su Hongcan and all members of the Public Heath Department and Enshi Local Government at District, County and Community level are thanked for the excellent arrangements they made during fieldwork, for the epidemiological information provided to the project and for their enthusiastic participation. The project has been carried out under the guidance of Prof Li Jiaxi, Prof Huang Huaizeng and Liu Xiaoduan (IRMA) and by Dr Don Appleton (BGS) who are thanked for their constructive comments and suggestions. The support of Prof Li Jiaxi, and staff at the IRMA, particularly Ms Ge Xiaoli, Prof Luo Daihong and Ms Zhang Qiling, is very gratefully acknowledged.

Analytical work at the BGS was carried out by Mrs Kay Green and Mr Simon Burden under the guidance of Dr Mark Cave following sample preparation supervised by Mr Mark Allen. Bulk soil XRD mineralogical determinations were provided by Dr Vickie Hards and soil LOI and CEC determinations by Mrs Barbara Vickers. Analytical work at the IRMA was carried out under supervision by Mr Liu Xinping and Mrs Yin Pinjun.

Dr Chris Johnson (BGS) is also thanked for providing information on the Zhangjiakou study area.

Finally, very grateful thanks are extended to all the residents of Enshi District who agreed to take part in this study.

The BGS contribution to this project has been made possible with funding from the United Kingdom Department for International Development (Project R6227).

13. REFERENCES

Appleton J D, Zhang Q, Green K & Liu X. In Prep. An Evaluation of the Relationships between Environmental Concentrations of Se and Oesophageal Cancer in the Cixian Area, Hebei Province, China. British Geological Survey Overseas Geology Series Technical Report.

Bai N, Zhang K & Du M. 1989. A study on selenium-health database in China. Environmental Sciences (China). 11. pp 65-72.

Bascomb C L. 1964. Rapid method for the determination of cation exchange capacity of calcareous and non-calcareous soils. Journal of the Science of Food and Agriculture. 15. pp 821-823.

Bhattacharyya A K. 1990. Environmental problems associated with distribution of selenium in Indian soils and plants. In: Environmental Life Elements and Health. Tan J, Peterson P J, Li R & Wang W (eds). Science Press Beijing. pp 65-74.

Beilstein M A, Whanger P D & Yang G Q. 1991. Chemical forms of selenium in corn and rice grown in a high selenium area of China. Biomed. Environ. Sci. Vol. 4 (4). pp 392-398.

Bisbjerg B & Gissel-Nielsen G. 1969. The uptake of applied Se by agricultural plants. 1. The influence of soil type and plant species. Plant Soil. 31. pp 563-565.

Chuck W. 1988. Selenium and Human Health with Particular Reference to Keshan and Kaschin-Beck Disease in China. MSc. Thesis. Imperial College London.

Chen F, Cole P, Lifan W, Zhibao M & Trapido E J. 1994. Estimates of trace element intakes in Chinese farmers. Community and International Nutrition. American Institute of Nutrition. pp 196-201.

Crounce R G, Pories W J, Bray J T & Mauger R L. 1983. Geochemistry and man: health and disease. 1. Essential elements. In: Applied Environmental Geochemistry. Thornton I. (ed). Academic Press London.

Darnley A G, Bjorklund A, Bolviken B, Gustavsson N, Koval P V, Plant J A, Steenfelt A, Tauchid M & Xie X. 1995. A Global Geochemical Database for Environmental and Resource Management. Recommendations for International Geochemical Mapping. Final Report of IGCP Project 259. Earth Sciences 19, UNESCO, Paris.

Faust S D & Aly O M. 1981. Chemistry of Natural Waters. Ann Arbor Science. Michigan.

Fergusson J E. 1990. The Heavy Elements: Chemistry Environmental Impact and Health. Pergamon Press. Oxford.

Fordyce F M. 1996. Report of Field Visit and Initial Data from Investigations into the Predication and Remediation of Human Se Imbalances in Enshi District, Hubei Province, China 8-26 November 1995. British Geological Survey Overseas Geology Series Technical Report WC/96/7R.

Fordyce F M, Masara D & Appleton J D. 1996. Stream sediment soil and forage chemistry as indicators of cattle mineral status in north-east Zimbabwe. In: Appleton J D, Fuge R & McCall G J H. (eds). Environmental Geochemistry and Health. Geological Society Special Publication. 113. pp 23-38.

Gibson R S, Martinex O B & MacDonald A C. 1985. The Zn Cu and Se status of a selected sample of non-institutionalised elderly Canadian women. In: Trace Elements in Man and Animals. Mills C F, Bremner I and Chesters J K. (eds). Commonwealth Agricultural Bureau. 5. pp 789-791.

Gissel-Nielsen G & Bisbjerg B. 1970. The uptake of applied Se by agricultural plants. 2. The utilisation of various Se compounds. Plant Soil. 32. 382-396.

Greathouse D G & Craun G F.1979. In: Trace Substances in Environmental Health. Hemphill D D. (ed). University of Missouri Press. Columbia. p 31.

Haygarth P M. 1994. Global importance and global cycling of Se. In: Selenium in the Environment. Frankenberger W T & Benson S (eds). Marcel Dekker Inc. New York . pp 1-28.

Harrison I & Littlejohn D. 1995. Determination of selenium in human hair and nail by electrothermal atomic absorption spectrometry. Journal of Analytical Atomic Spectrometry. Vol. 10. pp 215-219.

Hem J D. 1985. Study and Interpretation of the Chemical Characteristics of Natural Water. USGS Water Supply Paper. 2254.

Howard J H. 1977. Geochemistry of Se: formation of ferroselite and selenium behaviour in the vicinity of oxidising sulphide and uranium deposits. Geochim. Cosmochim. Acta. 41. pp 1665-1678.

Johnson C C, Ge X, Green K & Liu X. 1996. Studies of Se Distribution in Soil, Grain Drinking Water and Human Hair Samples from the Keshan Disease Belt of Zhangjiakou District, Hebei Province, China. British Geological Survey Overseas Geology Series Technical Report WC/96/52.

Jump R K & Sabey B R.1989. Soil test extractants for predicting Se in plants. In: Selenium in Agriculture and the Environment. Jacobs L W. (ed). SSSA Special Publication 23. pp 95-105

Kabata-Pendias A & Pendias H. 1984. Trace Elements in Soils and Plants. CRC Press. Boca Raton, Fl.

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

Koivistoinen P & Huttunen J. 1985. Selenium deficiency in Finnish food and nutrition research strategy measures. In: Trace Elements in Man and Animals. Mills C F, Bremner I and Chesters J K. (eds). Commonwealth Agricultural Bureau. 5. pp 425-929.

Krauskopf K B.1982. Introduction to Geochemistry. McGraw-Hill Book Company London.

Levander O A. 1986. Selenium. In: Trace Elements in Human and Animal Nutrition. Mertz W. (ed). Academic Press Inc. London. pp 209-266

Lorenz K. 1978. Cereal Chemistry. 55. p 287.

MAFF. 1997. Dietary intake of Se. Food Surveillance Information Sheet. No. 126. Ministry of Agriculture, Fisheries and Food.

Mao D, Gong Z & Liu J. 1987. The features of keshan disease in Lichuan County, Hubei Province. Environmental Science Publication of China. 76. pp 76-78.

Mao D & Su H. 1993. Endemic investigation of Se toxicity in Enshi. Chinese Endemic Disease Magazine. 9. No. 5.

Mayland H F. 1994. Selenium in plant and animal nutrition. In: Selenium in the Environment. Frankenberger W T & Benson S (eds). Marcel Dekker Inc. New York. pp 29-46.

Mayland H F, James L F, Panter K E & Sonderegger J L. 1989. Selenium in seleniferous environments. In: Selenium in Agriculture and the Environment. Jacobs L W. (ed). SSSA Special Publication 23. pp 15-5.

McNeal J M & Balistrieri L S. 1989. Geochemistry and occurrence of selenium: an overview. In: Selenium in Agriculture and the Environment. Jacobs L W. (ed). SSSA Special Publication 23. pp 1-14.

Mikkelsen R L, Page A L, & Bingham F T. 1989. Factors affecting selenium accumulation by agricultural crops. In: Selenium in Agriculture and the Environment. Jacobs L W. (ed). SSSA Special Publication 23. pp 65-94.

Morales M, Vitoria A, Alegria A, Llopis A & Brines J. 1991. Cadmium and selenium concentrations in drinking water in the Valencian community. In: Human and Animal Health in Relation to Circulation Processes of Selenium and Cadmium. Lag J. (ed). The Norwegian Academy of Science and Letters. pp 55-65.

Ohlendorf H M & Santolo G M. 1994. Kesterton Reservoir - Past Present and Future. In: Selenium in the Environment. Frankenberger W T & Benson S (eds). Marcel Dekker Inc. New York. pp 1-28.

Ohta Y, Nakano A, Matsumoto M & Li F. 199. Content of essential trace elements in hair from children lived in Keshan Disease district in China. In: Environmental Life Elements and Health. Tan J, Peterson P J, Li R & Wang W.(eds). Science Press Beijing. pp 158-16.

Plant J A. 1973. A random numbering system for geochemical samples. Transactions of the Institute of Mining and Metallurgy. B82. pp 63-66.

Rowell D L.1994. Soil Science: Methods and Applications. Longman Scientific and Technical. UK.

Senesi N, Polemio M & Lorusso L. 1979. Commun. Soil Sci. Plant Anal. 10. p 1109.

Sippola J & Jansson H. 1991. Experience with selenium intermixture in commercial fertilisers in Finland. In: Human and Animal Health in Relation to Circulation Processes of Selenium and Cadmium. Lag J. (ed). The Norwegian Academy of Science and Letters. pp 191-199.

Smith M I & Westfall B B. 1937. Public Health Report. 52. p 1375.

Tan J. (ed). 1989. The Atlas of Endemic Diseases and Their Environments in the People's Republic of China. Science Press. Beijing.

Tan J, Zhu W & Li R. 1989. Chemical endemic diseases and their impact on population in China. Environmental Sciences (China). 11. pp 107-114.

The Times Atlas of the World. 1992. Comprehensive 9th Edition.

Thornton I, Smith C & Van Dorst S. 1985. Selenium in the soil-plant system in relation to livestock nutrition. In: Trace Elements in Man and Animals. Mills C F, Bremner I & Chesters J K. Commonwealth Agricultural Bureau. 5. pp 853-855.

Van Dorst S H & Peterson P J. 1984. Selenium speciation in the soil solution and its relevance to plant uptake. Journal of the Science of Food and Agriculture. 35. pp 610-605.

Wang H. 1993. Geological Setting, Controlling Factors and Orientation Study of Se Minerogenetic Prospectivity Area in Enshi Autonomous Prefecture, Se Resource and Comprehensive Utilisation. Chinese Science and Technology Publishing House.

Watkinson J H & Davies E B. 1967. Uptake of native and applied Se by pasture species. 4. Relative uptake through foliage and roots by white clover and browntop. Distribution of Se in white clover. New Zealand Journal of Agricultural Research. 10. pp 122-133.

Xu G & Jiang Y. 1986. Se and the prevalence of Keshan and Kaschin-Beck diseases in China. In: Proceedings of the First International Symposium on Geochemistry and Health. Thornton I. (ed). Science Reviews Ltd. Northwood. pp 192-205.

Yang G, Wang S, Zhou R & Sun S. 1983. Endemic selenium intoxication of humans in China. American Journal of Clinical Nutrition. 37. pp 872-881.

Yang G, Yin S, Zhou R, Gu L, Yan B, Lui Y & Liu Y. 1989a. Studies of Safe and Maximal Daily Dietary Selenium Intake in a Seleniferous Area in China. Part 2. Journal of Trace Element Electrolytes Health and Disease. 3. pp 123-129.

Yang G, Zhou R, Yin S, Gu L, Yan B, Liu Y, Liu Y & Li X. 1989b. Studies of Safe and Maximal Daily Dietary Selenium Intake in a Seleniferous Area in China. Part 1. Journal of Trace Element Electrolytes Health and Disease. 3. pp 77-87.

Yang G & Xia M. 1995. Studies on human dietary requirements and safe range of dietary intakes of selenium in China and their application to the prevention of related endemic diseases. Biomedical and Environmental Sciences. 8. pp 187-201.

Zhang G, Ge X, Zhang Q, Liu X, Luo D & Fordyce F M. In Prep. The Geological and Geochemical Environmental Background and the Distribution of Se-related Diseases in Enshi District, Hubei Province, China. Institute of Rock and Mineral Analysis-British Geological Survey Technical Report.

Zheng B, Hong Y, Zhao W, Zhou H, Xia W, Su H, Mao D, Yan L & Thornton I. 1992. The Se-rich carbonaceous siliceous rock and endemic selenosis in south-west Hubei, China. Chinese Science Bulletin. 37. 2. pp 1725-1729.

Zheng B & Yan L. 1993. The Se resource in southwestern Hubei Province, China and its exploration strategy. Journal of Natural Resources (China) 8. No.3.

APPENDIX A: SUMMARY DATA FOR THE 15 STUDY VILLAGES

Village Code	Village Name	County	Pop.	% Selenosis	% KD	% Fluorosis	Geology*	Remoteness	Number of Soil Samples	Number of Grain Samples	Number of Water Samples	Number of Hair Samples	Date Sampled
HT1	Shadi	Enshi City	787	None	None	90	P_1m P_2 P_1q C_{1+2}	4	8	6	2	5	13/11/95
HT2	Huabei	Enshi City	1410	None	None	90	P_1m P_2 T_1d	4	6	5	1	5	13/11/95
HT3	Xin Tang	Enshi City	1036	None	None	90	P_1m P_2 P_1q T_1d	4	10	7	1	6	14/11/95
HT4	Yu Tang Ba	Enshi City	3	None	None	None	P_1m P_1q C_{1+2}	5	5	5	1	3	14/11/95
HT5	Shatou	Xuan 'en	840	None	None	90	P_1m P_2 P_1q T_1d	5	7	7	1	5	15/11/95
HN1	Loujiaba	Jianshi	2760	None	None	100	P_1m P_2 T_1d	1	6	7	2	5	12/11/95
HN2	Bajiao	Enshi City	1700	None	None	100	P_1q D_{2+3}	3	5	5	1	5	12/11/95
HN3	Fangjiaping	Xuan 'en	1460	None	None	90	P_1m P_2 P_1q T_1d	4	7	5	1	5	15/11/95
HN4	Xiao Guan	Xuan 'en	2100	None	None	Unknown	P_1m P_2 P_1q	2	7	7	1	3	16/11/95
HN5	Zishengqiao	Lichuan	400	None	None	Unknown	P_1m P_2 P_1q	2	5	5	1	5	18/11/95
LK1	Chang Ping	Lichuan	2280	None	Unknown	None	J_2s	2	9	6	2	5	17/11/95
LK2	Zhi Luo	Lichuan	2843	None	Unknown	None	J_2s	2	6	6	1	5	17/11/95
LK3	Ming Shen	Lichuan	726	None	Unknown	None	J_2s	2	7	6	1	5	17/11/95
LK4	Nan Pu	Lichuan	1672	None	Unknown	None	J_2s	2	6	6	1	5	17/11/95
LK5	Ji Chang	Lichuan	2100	None	Unknown	None	J_2x	2	7	6	1	5	18/11/95

D_{2+3} = Devonian limestone, shale and quartzite
C_{1+2} = Carboniferous limestone and carboniferous siliceous rocks
P_1q, P_1m and P_2 = Permian limestone, siliceous rocks, carboniferous shale and mudstone
T_1d = Triassic shale and calcareous mudstone
J_2s and J_2x = Jurassic purple sandstone
* See Table 4 for stratigraphic sequence

Pop. = population
1 = least remote
5 = most remote

APPENDIX B: SOIL SAMPLE LISTS AND SUMMARY FIELD DATA

a) Listed by village name

Samp. No.	Date Sampled	Village Name	Code	Depth Top(cm)	Depth Base(cm)	Soil Colour	Soil Texture	Landuse	Topography	Sample Spacing(m)	Soil Sample Notes
18	12/11/95	Luojiaba	HN1	20	30	DB	SICL	Radish field	Mod. slope	20 x 10	200m 165° from doctor's house. At base of 20° terrace slope. Clst + chlky clasts.
49	12/11/95	Luojiaba	HN1	20	30	DB	SICL	Radish field	Mod. slope	20 x 10	Duplicate of 18.
46	12/11/95	Luojiaba	HN1	20	30	DB	SICL	Radish field	Flat	20 x 10	500m 165° from doctor's house. In valley between terraces. Clst + shl clasts.
41	12/11/95	Luojiaba	HN1	10	20	DB	SICL	Tea field	10° slope	20 x 20	400m 180° from doctor's house. In valley on 20° terrace slope . Clst, sst + shl clasts.
32	12/11/95	Luojiaba	HN1	10	20	DB	SICL	Cabbage field	20° slope	10 x 15	200m 180° from doctor's house. On 20° terrace slope. Clst, lst + shl clasts. Sandy or. patches.
45	12/11/95	Luojiaba	HN1	20	30	DB	CLSI	Cabbage field	20° slope	10 x 10	10m 000° from doctor's house. On 20° terrace slope. Few clst + shl clasts.
94	12/11/95	Bajiao	HN2	10	20	LB	CL	Cabbage field	Flat	10 x 7	30m 070° from coal mine. On 50° terrace slope. Clst, shl + sst clasts.
98	12/11/95	Bajiao	HN2	20	30	LBO	SICL	Ploughed field	Flat	10 x 10	50m 300° from coal mine. On 50° terrace slope. Clst, sst and or. Fe-rich chlky clasts.
56	12/11/95	Bajiao	HN2	10	30	DB	SICL	Ploughed field	Flat	15 x 20	80m 280° from coal mine. On 50° terrace slope. Clst + sst clasts.
15	12/11/95	Bajiao	HN2	10	20	DBO	SICL	Ploughed field	Flat	7 x 10	180m 260° from coal mine. On 50° terrace slope. Shl + clst clasts. Mixture db. silt + or. clay.
26	12/11/95	Bajiao	HN2	10	20	LB	SICL	Tea field	30° slope	10 x 7	150m 240° from school. Beside track at top of terrace. Shl, clst + chlky clasts.
19	13/11/95	Shadi	HT1	10	20	LB	SICL	Ploughed field	20° slope	5 x 5	40m 274° from valley head farmhouse. In valley. Shl, clst and or. sst clasts.
39	13/11/95	Shadi	HT1	10	20	LB	SICL	Ploughed field	20° slope	5 x 5	Duplicate of 19.
28	13/11/95	Shadi	HT1	35	45	LB	SICL	Ploughed field	20° slope	5 x 5	Deeper soil from same holes as 19.
54	13/11/95	Shadi	HT1	10	20	DB	SICL	Maize field	50° slope	5 x 10	200m 274° from valley head farmhouse. On valley side. Clst, shl, sst + yel./or. chlky clasts.
62	13/11/95	Shadi	HT1	10	20	LBO	SICL	Ploughed field	45° slope	20 x 20	250m 310° from valley head farmhouse. Base of valley terr. Clst, shl, sst + or. chlky clasts.
80	13/11/95	Shadi	HT1	10	20	LBO	SICL	Radish field	Flat	15 x 15	350m 280° from valley head farmhouse. On banks of stream in valley floor. Clst + shl clasts.
16	13/11/95	Shadi	HT1	10	20	LB	SICL	Ploughed field	Flat	10 x 10	500m 292° from valley head farmhouse. 1st terrace above stream. Clst + shl clasts.
17	13/11/95	Shadi	HT1	10	20	GR	CL	Rice paddy	Flat	20 x 20	520m 292° from valley head farmhouse. 1st terr abve stm. Clst + or. chlky clasts. Not flooded.
72	13/11/95	Huabei	HT2	10	20	LBO	CLSI	Cabbage field	10-40° slope	20 x 20	200m 180° from main street. Base of terr on bank of stm. 50 m 210° from bridge. Shl clasts.
65	13/11/95	Huabei	HT2	10	20	LBO	CLSI	Radish field	Flat	20 x 20	900m 160° from main street. Base of 1st terrace below house. Shl + chlky clasts.
37	13/11/95	Huabei	HT2	10	20	DB	CLSI	Ploughed field	Flat	20 x 20	300m 020° from main street. Base of 10 m shl outcrop. Beside road. Shl + sst clasts.
4	13/11/95	Huabei	HT2	10	20	LB	CLSI	Radish field	20° slope	20 x 20	450m 020° from main street. On 20° terrace below road. Shl + sst clasts.
90	13/11/95	Huabei	HT2	10	20	DB	CLSI	Radish field	Flat	20 x 20	600m 320° from main street. On 20° terrace slope. Shl + orange chlky clasts.
69	13/11/95	Huabei	HT2	10	20	LBO	CL	Rice paddy	Flat	20 x 20	700m 340° from main street. Valley top. Gr. shl + or. chlky clasts at 20cm. Not flooded.
1	14/11/95	Xin Tang	HT3	5 to 10	15	LB	CLSI	Radish field	Flat	10 x 15	600m 060° from N end village centre. Beside road. Clst, shl, chlky + or. sst clasts.
99	14/11/95	Xin Tang	HT3	5 to 10	15	LB	CLSI	Radish field	Flat	10 x 15	Duplicate of 1. Stony layer at 15 cm hence shallower samples. Clay + sst increase at 13cm.
3	14/11/95	Xin Tang	HT3	10	20	LBGR	SICL	Ploughed field	Flat	20 x 20	1000m 070° from N end village centre. 1st terr above stm in valley. Shl, clst + lst clasts.
38	14/11/95	Xin Tang	HT3	10	20	LB	SICL	Maize field	45° slope	20 x 20	1350m 045° from N end village centre. 1st terr above stm + road. Few shl, lst + clst clasts.
91	14/11/95	Xin Tang	HT3	10	20	LB	SICL	Ploughed field	10° slope	20 x 20	1900m 080° from N end village centre. 1st terr below road. Shl, lst, chlky + or. sst clasts.
67	14/11/95	Xin Tang	HT3	10	20	LBO	SICL	Maize field	Flat	5 x 15	500m 026° from N end village centre. On 20° terrace slope. Lst, clst + shl clasts. Or. patches.
7	14/11/95	Xin Tang	HT3	2	70	LB	SICL	Soil bank	Vertical		1100m 062° from N end village centre. Soil profile.
34	14/11/95	Xin Tang	HT3	10	20	GR	CL	Rice paddy	Flat	20 x 20	470m 020° from N end village centre. On 20° terrace slope. Orange patches. Flooded.
89	14/11/95	Yu Tang Ba	HT4	10	20	LBO	SICL	Maize field	Flat	15 x 20	500m 100° from farmhouse. Base of E valley side. Clst + orange chlky clasts.
83	14/11/95	Yu Tang Ba	HT4	10	20	LBO	SICL	Maize field	Flat	20 x 20	450m 100° from farmhouse. On stm floodplain in valley floor. Shl, clst + or./wh. chlky clasts.
95	14/11/95	Yu Tang Ba	HT4	10	20	LBO	SICL	Maize field	5° slope	20 x 20	400m 090° from farmhouse. On W-side of valley floor. Clst + or./white chlky clasts.
21	14/11/95	Yu Tang Ba	HT4	10	20	LBO	SICL	Tobco + rdsh	10° slope	20 x 20	50m 020° from farmhouse. Field below farmhouse. Clst, shl + white chlky clasts.
84	14/11/95	Yu Tang Ba	HT4	10	20	LBO	SICL	Maize field	10° slope	15 x 20	40m 135° from farmhouse. 1st terrace below farmhouse. Shl, clst + or./white chlky clasts.

Samp. No.	Date Sampled	Village Name	Code	Depth Top(cm)	Depth Base(cm)	Soil Colour	Soil Texture	Landuse	Topography	Sample Spacing(m)	Soil Sample Notes
90	13/11/95	Huabei	HT2	10	20	DB	CLSI	Radish field	Flat	20 x 20	600m 320° from main street. On 20° terrace slope. Shl + orange chlky clasts.
91	14/11/95	Xin Tang	HT3	10	20	LB	SICL	Ploughed field	10° slope	20 x 20	1900m 080° from N end village centre. 1st terr below road. Shl, lst, chlky + or. sst clasts.
92	18/11/95	Ji Chang	LK5	10	20	LBR	SISA	Radish field	Flat	10 x 15	100m 140° from white house on W-side road. On alluvium in valley. Shl, sst + sltst clasts.
93	15/11/95	Shatuo	HT5	10	20	LBO	SICL	Maize field	Flat	20 x 4	70m 090° from top house. On 30° terrace slope below house. Clst, shl, lst + or./wh. chlky clasts.
94	12/11/95	Bajiao	HN2	10	20	LB	CL	Cabbage field	Flat	10 x 7	30m 070° from coal mine. On 50° terrace slope. Clst, shl + sst clasts.
95	14/11/95	Yu Tang Ba	HT4	10	20	LBO	SICL	Maize field	5° slope	20 x 20	400m 090° from farmhouse. On W-side of valley floor. Clst + or./white chlky clasts.
96	17/11/95	Chang Ping	LK1	10	20	LBR	SISA	Ploughed field	20° slope	5 x 4	550m 320° from E end main street. On 20° terrace slope. Shl, sst + sltst clasts.
97	15/11/95	Fangjiaping	HN3	10	20	LBO	CLSI	Radish field	5° slope	20 x 20	300m 260° from S-most house. Shl, clst, or. shl + white chlky clasts.
98	12/11/95	Bajiao	HN2	20	30	LBO	SICL	Ploughed field	Flat	10 x 10	50m 300° from coal mine. On 50° terrace slope. Clst, sst and or. Fe-rich chlky clasts.
99	14/11/95	Xin Tang	HT3	5 to 10	15	LB	CLSI	Radish field	Flat	10 x 15	Duplicate of 1. Stony layer at 15 cm hence shallower samples. Clay + sst increase at 13cm.
100	17/11/95	Chang Ping	LK1	10	20	LBR/GR	CL/SI	Rice paddy	Flat	10 x 10	650m 345° from E end main street. 1st + 4th hole in flooded area. 2nd and 3rd hole in dry area.
96B/C	17/11/95	Chang Ping	LK1	15	80	LBW	SISA	Soil bank	Vertical		550m 320° from E end main street. Soil profile.

For explanation of abbreviations see section a)

b) Listed by sample number

Samp. No.	Date Sampled	Village Name	Code	Depth Top(cm)	Depth Base(cm)	Soil Colour	Soil Texture	Landuse	Topography	Sample Spacing(m)	Soil Sample Notes
1	14/11/95	Xin Tang	HT3	5 to 10	15	LB	CLSI	Radish field	Flat	10 x 15	600m 060° from N end village centre. Beside road. Clst, shl, chlky + or. sst clasts.
2	18/11/95	Ji Chang	LK5	10	20	LBR	SISA	Radish field	Flat	10 x 15	Duplicate of 92. Few clst clasts.
3	14/11/95	Xin Tang	HT3	10	20	LBGR	SICL	Ploughed field	Flat	20 x 20	1000m 070° from N end village centre. 1st terr above stm in valley. Shl, clst + lst clasts.
4	13/11/95	Huabei	HT2	10	20	LB	CLSI	Radish field	20° slope	20 x 20	450m 020° from main street. On 20° terrace below road. Shl + sst clasts.
5	17/11/95	Chang Ping	LK1	10	20	LBO	CLSI	Radish field	Flat	7 x 10	500m 030° from E end main street. On flat terrace. No clasts in sample. Sst + shl clasts in field.
6	17/11/95	Nan Pu	LK4	10	20	LBR	SI	Radish field	40° slope	10 x 20	500m 340° from large house on E-side road. Slope below sltst outcrop. Sltst, shl + sst clasts.
7	14/11/95	Xin Tang	HT3	2	70	LB	SICL	Soil bank	Vertical		1100m 062° from N end village centre. Soil profile.
8	17/11/95	Chang Ping	LK1	10	20	LBR	CLSI	Radish field	20° slope	5 x 4	500m 023° from E end main street. Top of terraced valley. Shl, sst + sltst clasts.
9	17/11/95	Zhi Luo	LK2	10	20	LBR	CLSI	Ploughed field	45° slope	20 x 20	500m 015° from S-most houses. On 1st terrace N of road. Sltst outcrop. Shl, sltst + sst clasts.
11	18/11/95	Ji Chang	LK5	10	20	LBR	SISA	Rice paddy	Flat	10 x 15	90m 135° from wh. hse on W-side road. On alluvium in valley. Sst, sltst + shl clasts. Not flooded.
12	17/11/95	Nan Pu	LK4	10	20	GR	CL	Rice paddy	Flat	20 x 20	480m 340° from large house on E-side road. In valley floor. Sltst, shl + sst clasts. Flooded.
13	15/11/95	Fangjiaping	HN3	10	20	LB	CLSI	Tobacco field	5° slope	20 x 20	50m 050° from S-most house. On 20° terrace slope. White chlky clasts.
14	17/11/95	Nan Pu	LK4	10	20	LBR/O	SISA	Cabbage field	Flat	6 x 6	100m 300° from large house on E-side road. On valley floor. Many sltst clasts in bottom 3 cm.
15	12/11/95	Bajiao	HN2	10	20	DBO	SICL	Ploughed field	Flat	7 x 10	180m 260° from coal mine. On 50° terrace slope. Shl + clst clasts. Mixture db. silt + or. clay.
16	13/11/95	Shadi	HT1	10	20	LB	SICL	Ploughed field	Flat	10 x 10	500m 292° from valley head farmhouse. 1st terrace above stream. Clst + shl clasts.
17	13/11/95	Shadi	HT1	10	20	GR	CL	Rice paddy	Flat	20 x 20	520m 292° from valley head farmhouse. 1st terr abve stm. Clst + or. chlky clasts. Not flooded.
18	12/11/95	Luojiaba	HN1	20	30	DB	SICL	Radish field	Mod. slope	20 x 10	200m 165° from doctor's house. At base of 20° terrace slope. Clst + chlky clasts.
19	13/11/95	Shadi	HT1	10	20	LB	SICL	Ploughed field	20° slope	5 x 5	40m 274° from valley head farmhouse. In valley. Shl, clst and or. sst clasts.
20	17/11/95	Ming Shen	LK3	10	20	LBO/R	SISA	Maize field	50° slope	5 x 5	Duplicate of 42. Increase orange colour in bottom 2 cm.
21	14/11/95	Yu Tang Ba	HT4	10	20	LBO	SICL	Tobco + rdsh	10° slope	20 x 20	50m 020° from farmhouse. Field below farmhouse. Clst, shl + white chlky clasts.
23	15/11/95	Fangjiaping	HN3	10	20	LBO	CLSI	Radish field	10° slope	10 x 10	150m 320° from N end main street. Shl, clst, + white chlky clasts.
24	17/11/95	Zhi Luo	LK2	10	20	LBR	SISA	Ploughed field	40°slope	20 x 4	100m 355° from S houses. On 50° terrace slope. Few sst, sltst + shl clasts.
25	17/11/95	Chang Ping	LK1	10	20	LBR	SISA	Tea field	3° slope	3 x 3	600m 345° from E end main street. 1st terrace above road. Few sltst, sst + shl clasts.
26	12/11/95	Bajiao	HN2	10	20	LB	SICL	Tea field	30° slope	10 x 7	150m 240° from school. Beside track at top of terrace. Shl, clst + chlky clasts.
27	18/11/95	Ji Chang	LK5	10	20	LBO/R	SICL	Radish field	5° slope	10 x 7	20m 000° from white house on W-side road. Base of main valley. Sltst, sst + shl clasts.
28	13/11/95	Shadi	HT1	35	45	LB	SICL	Ploughed field	20° slope	5 x 5	Deeper soil from same holes as 19.
29	17/11/95	Ming Shen	LK3	10	20	LBO	SISA	Radish field	3° slope	5 x 10	400m 130° from petrol station. Top of ravine. Few sst, sltst + shl clasts.
30	18/11/95	Ji Chang	LK5	35	45	LBR	SICL	Radish field	Flat	10 x 15	Deeper soil. Same holes as 92.
31	18/11/95	Ji Chang	LK5	10	20	LBR	SICL	Pear + rdsh	10° slope	10 x 15	200m 210° from white house on W-side road. On hillside. Sltst, sst + shl clasts. Or. sandy.
32	12/11/95	Luojiaba	HN1	10	20	DB	SICL	Cabbage field	20° slope	10 x 15	200m 180° from doctor's house. On 20° terrace slope. Clst, lst + shl clasts. Sandy or. patches.
33	17/11/95	Zhi Luo	LK2	10	20	LBR	SICL	Rice paddy	Flat	10 x 10	750m 010° from S-most houses. On terrace below road. Moist not flooded.
34	14/11/95	Xin Tang	HT3	10	20	GR	CL	Rice paddy	Flat	20 x 20	470m 020° from N end village centre. On 20° terrace slope. Orange patches. Flooded.
35	15/11/95	Shatuo	HT5	10	20	GR	CL	Rice paddy	Flat	20 x 4	700m 150° from top house. On 40° terr slope. Dk. gr. + or. sandy. Much organics. Not flooded.
36	15/11/95	Fangjiaping	HN3	35	45	LBO	SICL	Radish field	10° slope	10 x 10	Deeper soil from same holes as 23. One hole only 30 cm deep due to stony layer.
37	13/11/95	Huabei	HT2	10	20	DB	CLSI	Ploughed field	Flat	20 x 20	300m 020° from main street. Base of 10 m shl outcrop. Beside road. Shl + sst clasts.
38	14/11/95	Xin Tang	HT3	10	20	LB	SICL	Maize field	45° slope	20 x 20	1350m 045° from N end village centre. 1st terr above stm + road. Few shl, lst + clst clasts.
39	13/11/95	Shadi	HT1	10	20	LB	SICL	Ploughed field	20° slope	5 x 5	Duplicate of 19.
40	15/11/95	Shatuo	HT5	10	20	LBO	SICL	Maize field	Flat	20 x 4	Duplicate of 93. Or./wh. chlky clasts are in bottom 5 cm.
41	12/11/95	Luojiaba	HN1	10	20	DB	SICL	Tea field	10° slope	20 x 20	400m 180° from doctor's house. In valley on 20° terrace slope . Clst, sst + shl clasts.
42	17/11/95	Ming Shen	LK3	10	20	LBO	SISA	Maize field	50° slope	5 x 5	200m 040° from petrol station. 1st terrace above valley floor. Few sltst, lst, sst + shl clasts.
43	17/11/95	Ming Shen	LK3	10	20	LBO	SISA	Rice paddy	Flat	7 x 2	150m 085° from petrol station. On 30° terrace slope. Few sst, sltst + shl clasts. Not flooded.
44	17/11/95	Ming Shen	LK3	10	20	LBR	CLSI	Radish field	Flat	10 x 10	250m 120° from petrol station. Top of terrace. Few sst, sltst + shl clasts.

Samp. No.	Date Sampled	Village Name	Code	Depth Top(cm)	Depth Base(cm)	Soil Colour	Soil Texture	Landuse	Topography	Sample Spacing(m)	Soil Sample Notes
45	12/11/95	Luojiaba	HN1	20	30	DB	CLSI	Cabbage field	20° slope	10 x 10	10m 000° from doctor's house. On 20° terrace slope. Few clst + shl clasts.
46	12/11/95	Luojiaba	HN1	20	30	DB	SICL	Radish field	Flat	20 x 10	500m 165° from doctor's house. In valley between terraces. Clst + shl clasts.
47	17/11/95	Chang Ping	LK1	10	20	LBO	SISA	Radish field	20° slope	5 x 6	600m 330° from E end main street. On hummock W of road. Sltst, + shl clasts. Sandy or. patches.
48	15/11/95	Shatuo	HT5	10	20	DB	CLSI	Radish field	5° slope	20 x 20	600m 290° from top house. 1st terrace above stream, opposite coal mine. Clst + or. shl clasts.
49	12/11/95	Luojiaba	HN1	20	30	DB	SICL	Radish field	Mod. slope	20 x 10	Duplicate of 18.
50	17/11/95	Zhi Luo	LK2	10	20	LBR	CLSI	Winter wheat	45° slope	5 x 5	750m 040° from S-most houses. On terrace above road. Few sltst, sst + shl clasts. Sst outcrop.
51	15/11/95	Fangjiaping	HN3	10	20	LBO	CLSI	Radish field	3° slope	15 x 20	100m 270° from S-most house. On 20° terrace slope. Clst + white chlky clasts.
52	16/11/95	Xiao Guan	HN4	10	20	LB	CLSI	Rdsh + tea	Flat	10 x 7	20m 003° from house 2km N reservoir. On 1st terr above house. Lst, clst, wh. chlky + shl clasts.
53	18/11/95	Ji Chang	LK5	10	20	LBO	SISA	Radish field	5° slope	4 x 10	200m 260° from white hse on W-side road. Base of side valley. Sltst, sst + shl clasts. Or. sandy.
54	13/11/95	Shadi	HT1	10	20	DB	SICL	Maize field	50° slope	5 x 10	200m 274° from valley head farmhouse. On valley side. Clst, shl, sst + yel./or. chlky clasts.
55	17/11/95	Nan Pu	LK4	10	20	LBR	CLSI	Maize field	10° slope	10 x 10	100m 040° from large house on E-side road. On 10° terrace. Few sst, sltst + shl clasts.
56	12/11/95	Bajiao	HN2	10	30	DB	SICL	Ploughed field	Flat	15 x 20	80m 280° from coal mine. On 50° terrace slope. Clst + sst clasts.
57	15/11/95	Shatuo	HT5	8	18	LBO	CLSI	Maize field	40° slope	10 x 3	700m 150° from top house. On 40° terrace slope. Shl, clst, lst + orange shl clasts.
58	17/11/95	Ming Shen	LK3	10	20	LBR	CLSI	Radish field	10° slope	10 x 20	200m 070° from petrol station. On 10° terrace slope in side valley. Sst, sltst + shl clasts.
59	16/11/95	Xiao Guan	HN4	10	20	LBO	SICL	Tea field	Flat	5 x 20	Duplicate of 70. Increase in orange colour in bottom 2 cm.
60	17/11/95	Chang Ping	LK1	10	20	LBO	CLSI	Radish field	Flat	7 x 10	Duplicate of 5. Few shl clasts.
61	15/11/95	Shatuo	HT5	10	20	DB	CLSI	Maize field	Flat	20 x 20 (line)	860m 165° from top house. On 20° terr slope at base of clst tip. Clst + or. shl clasts.
62	13/11/95	Shadi	HT1	10	20	LBO	SICL	Ploughed field	45° slope	20 x 20	250m 310° from valley head farmhouse. Base of valley terr. Clst, shl, sst + or. chlky clasts.
63	18/11/95	Ji Chang	LK5	10	20	LBR	SISA	Pear + rdsh	5° slope	10 x 20	150m 190° from white house on W-side road. On terrace slope. Few sltst, sst + shl clasts.
64	16/11/95	Xiao Guan	HN4	10	20	LBO	SICL	Maize field	30° slope	10 x 10	200m 280° from house 2km N reservoir. On 40° terrace slope. Clst, lst shl clasts. Clst quarry.
65	13/11/95	Huabei	HT2	10	20	LBO	CLSI	Radish field	Flat	20 x 20	900m 160° from main street. Base of 1st terrace below house. Shl + chlky clasts.
66	16/11/95	Xiao Guan	HN4	10	20	LBO	SICL	Radish field	30° slope	20 x 10	1000m 080° from N end reservoir. 1st terr on E valley side. Shl, clst + lst clasts. Clst quarry.
67	14/11/95	Xin Tang	HT3	10	20	LBO	SICL	Maize field	Flat	5 x 15	500m 026° from N end village centre. On 20° terrace slope. Lst, clst + shl clasts. Or. patches.
68	18/11/95	Zishengqiao	HN5	10	20	LBO	CLSI	Winter wheat	Flat	15 x 20	5m 050° from main street. Base of 20° terrace slope. Shl, clst, sltst + lst clasts.
69	13/11/95	Huabei	HT2	10	20	LBO	CL	Rice paddy	Flat	20 x 20	700m 340° from main street. Valley top. Gr. shl + or. chlky clasts at 20cm. Not flooded.
70	16/11/95	Xiao Guan	HN4	10	20	LBO	SICL	Tea field	Flat	5 x 20	60m 060° from N end reservoir. On alluvial valley floor. Few clst + shl clasts.
71	15/11/95	Shatuo	HT5	10	20	LBO	SICL	Maize field	30° slope	20 x 20	500m 120° from top house. On 30° terrace slope below houses. Clst, shl + orange chlky clasts.
72	13/11/95	Huabei	HT2	10	20	LBO	CLSI	Cabbage field	10-40° slope	20 x 20	200m 180° from main street. Base of terr on bank of stm. 50 m 210° from bridge. Shl clasts.
73	17/11/95	Ming Shen	LK3	10	20	LBO	CLSI	Maize field	50° slope	4 x 10	300m 085° from petrol station. 1st terrace above valley floor. Few sst , sltst + shl clasts.
74	15/11/95	Fangjiaping	HN3	10	20	LBO	CLSI	Ploughed field	5° slope	15 x 10	500m 345° from N end main street. On 40° terrace slope. Shl, clst + white chlky clasts.
76	18/11/95	Zishengqiao	HN5	10	20	LBO	SICL	Ploughed field	5° slope	20 x 20	300m 090° from main street. On 10° terrace slope. Shl, clst, sltst, lst + or./wh. chlky clasts.
77	17/11/95	Zhi Luo	LK2	10	20	LBR	SISA	Radish field	5° slope	4 x 6	500m 005° from S-most houses. On 30° terrace slope. Few sst, sltst + shl clasts
78	18/11/95	Zishengqiao	HN5	10	20	LBO	CLSI	Ploughed field	5° slope	20 x 20	150m 080° from main street. On 20° terrace slope. Shl, clst, sltst + lst clasts.
79	16/11/95	Xiao Guan	HN4	10	20	LBO	SICL	Rice paddy	Flat	20 x 15	50m 055° from N end reservoir. On alluvial valley floor. Shl + clst clasts. Moist not flooded.
80	13/11/95	Shadi	HT1	10	20	LBO	SICL	Radish field	Flat	15 x 15	350m 280° from valley head farmhouse. On banks of stream in valley floor. Clst + shl clasts.
81	18/11/95	Zishengqiao	HN5	10	20	LBO	SICL	Radish field	20° slope	7 x 20	250m 090° from main street. On 20° terrace slope. Shl, clst, sltst, lst + chlky clasts.
82	17/11/95	Nan Pu	LK4	10	20	LBR	CLSI	Pear + cbbge	Flat	5 x 5	100m 080° from large house on E-side road. Base of steep bank. Few sst, sltst + shl clasts.
83	14/11/95	Yu Tang Ba	HT4	10	20	LBO	SICL	Maize field	Flat	20 x 20	450m 100° from farmhouse. On stm floodplain in valley floor. Shl, clst + or./wh. chlky clasts.
84	14/11/95	Yu Tang Ba	HT4	10	20	LBO	SICL	Maize field	10° slope	15 x 20	40m 135° from farmhouse. 1st terrace below farmhouse. Shl, clst + or./white chlky clasts.
85	17/11/95	Zhi Luo	LK2	10	20	LBR	CL	Radish field	10° slope	5 x 5	500m 360° from S-most houses. On 30° terrace below road. Few sltst, sst + shl clasts.
86	18/11/95	Zishengqiao	HN5	10	20	LBO	SI	Ploughed field	5° slope	20 x 20	150m 085° from main street. On 20° terrace slope. Shl, clst, sltst + lst clasts.
87	17/11/95	Nan Pu	LK4	10	20	LBR/O	SA	Cabbage field	60° slope	10 x 20	150m 325° from large house on E-side road. Steep bank below sst outcrop. Sst + sltst clasts.
88	16/11/95	Xiao Guan	HN4	10	20	LBO	CLSI	Radish field	10° slope	10 x 10	500m 070° from N end reservoir. Base of 1st terr below road. Shl, lst + white chlky clasts.
89	14/11/95	Yu Tang Ba	HT4	10	20	LBO	SICL	Maize field	Flat	15 x 20	500m 100° from farmhouse. Base of E valley side. Clst + orange chlky clasts.

Samp. No.	Date Sampled	Village Name	Code	Depth Top(cm)	Depth Base(cm)	Soil Colour	Soil Texture	Landuse	Topography	Sample Spacing(m)	Soil Sample Notes
93	15/11/95	Shatuo	HT5	10	20	LBO	SICL	Maize field	Flat	20 x 4	70m 090° from top house. On 30° terrace slope below house. Clst, shl, lst + or./wh. chlky clasts.
40	15/11/95	Shatuo	HT5	10	20	LBO	SICL	Maize field	Flat	20 x 4	Duplicate of 93. Or./wh. chlky clasts are in bottom 5 cm.
71	15/11/95	Shatuo	HT5	10	20	LBO	SICL	Maize field	30° slope	20 x 20	500m 120° from top house. On 30° terrace slope below houses. Clst, shl + orange chlky clasts.
57	15/11/95	Shatuo	HT5	8	18	LBO	CLSI	Maize field	40° slope	10 x 3	700m 150° from top house. On 40° terrace slope. Shl, clst, lst + orange shl clasts.
61	15/11/95	Shatuo	HT5	10	20	DB	CLSI	Maize field	Flat	20 x 20 (line)	860m 165° from top house. On 20° terr slope at base of clst tip. Clst + or. shl clasts.
48	15/11/95	Shatuo	HT5	10	20	DB	CLSI	Radish field	5° slope	20 x 20	600m 290° from top house. 1st terrace above stream, opposite coal mine. Clst + or. shl clasts.
35	15/11/95	Shatuo	HT5	10	20	GR	CL	Rice paddy	Flat	20 x 4	700m 150° from top house. On 40° terr slope. Dk. gr. + or. sandy. Much organics. Not flooded.
13	15/11/95	Fangjiaping	HN3	10	20	LB	CLSI	Tobacco field	5° slope	20 x 20	50m 050° from S-most house. On 20° terrace slope. White chlky clasts.
51	15/11/95	Fangjiaping	HN3	10	20	LBO	CLSI	Radish field	3° slope	15 x 20	100m 270° from S-most house. On 20° terrace slope. Clst + white chlky clasts.
97	15/11/95	Fangjiaping	HN3	10	20	LBO	CLSI	Radish field	5° slope	20 x 20	300m 260° from S-most house. Shl, clst, or. shl + white chlky clasts.
74	15/11/95	Fangjiaping	HN3	10	20	LBO	CLSI	Ploughed field	5° slope	15 x 10	500m 345° from N end main street. On 40° terrace slope. Shl, clst + white chlky clasts.
23	15/11/95	Fangjiaping	HN3	10	20	LBO	CLSI	Radish field	10° slope	10 x 10	150m 320° from N end main street. Shl, clst, + white chlky clasts.
36	15/11/95	Fangjiaping	HN3	35	45	LBO	SICL	Radish field	10° slope	10 x 10	Deeper soil from same holes as 23. One hole only 30 cm deep due to stony layer.
70	16/11/95	Xiao Guan	HN4	10	20	LBO	SICL	Tea field	Flat	5 x 20	60m 060° from N end reservoir. On alluvial valley floor. Few clst + shl clasts.
59	16/11/95	Xiao Guan	HN4	10	20	LBO	SICL	Tea field	Flat	5 x 20	Duplicate of 70. Increase in orange colour in bottom 2 cm.
88	16/11/95	Xiao Guan	HN4	10	20	LBO	CLSI	Radish field	10° slope	10 x 10	500m 070° from N end reservoir. Base of 1st terr below road. Shl, lst + white chlky clasts.
66	16/11/95	Xiao Guan	HN4	10	20	LBO	SICL	Radish field	30° slope	20 x 10	1000m 080° from N end reservoir. 1st terr on E valley side. Shl, clst + lst clasts. Clst quarry.
64	16/11/95	Xiao Guan	HN4	10	20	LBO	SICL	Maize field	30° slope	10 x 10	200m 280° from house 2km N reservoir. On 40° terrace slope. Clst, lst shl clasts. Clst quarry.
52	16/11/95	Xiao Guan	HN4	10	20	LB	CLSI	Rdsh + tea	Flat	10 x 7	20m 003° from house 2km N reservoir. On 1st terr above house. Lst, clst, wh. chlky + shl clasts.
79	16/11/95	Xiao Guan	HN4	10	20	LBO	SICL	Rice paddy	Flat	20 x 15	50m 055° from N end reservoir. On alluvial valley floor. Shl + clst clasts. Moist not flooded.
5	17/11/95	Chang Ping	LK1	10	20	LBO	CLSI	Radish field	Flat	7 x 10	500m 030° from E end main street. On flat terrace. No clasts in sample. Sst + shl clasts in field.
60	17/11/95	Chang Ping	LK1	10	20	LBO	CLSI	Radish field	Flat	7 x 10	Duplicate of 5. Few shl clasts.
8	17/11/95	Chang Ping	LK1	10	20	LBR	CLSI	Radish field	20° slope	5 x 4	500m 023° from E end main street. Top of terraced valley. Shl, sst + sltst clasts.
96	17/11/95	Chang Ping	LK1	10	20	LBR	SISA	Ploughed field	20° slope	5 x 4	550m 320° from E end main street. On 20° terrace slope. Shl, sst + sltst clasts.
96B/C	17/11/95	Chang Ping	LK1	15	80	LBW	SISA	Soil bank	Vertical		550m 320° from E end main street. Soil profile.
25	17/11/95	Chang Ping	LK1	10	20	LBR	SISA	Tea field	3° slope	3 x 3	600m 345° from E end main street. 1st terrace above road. Few sltst, sst + shl clasts.
47	17/11/95	Chang Ping	LK1	10	20	LBO	SISA	Radish field	20° slope	5 x 6	600m 330° from E end main street. On hummock W of road. Sltst, + shl clasts. Sandy or. patches.
100	17/11/95	Chang Ping	LK1	10	20	LBR/GR	CL/SI	Rice paddy	Flat	10 x 10	650m 345° from E end main street. 1st + 4th hole in flooded area. 2nd and 3rd hole in dry area.
24	17/11/95	Zhi Luo	LK2	10	20	LBR	SISA	Ploughed field	40°slope	20 x 4	100m 355° from S houses. On 50° terrace slope. Few sst, sltst + shl clasts.
77	17/11/95	Zhi Luo	LK2	10	20	LBR	SISA	Radish field	5° slope	4 x 6	500m 005° from S-most houses. On 30° terrace slope. Few sst, sltst + shl clasts
9	17/11/95	Zhi Luo	LK2	10	20	LBR	CLSI	Ploughed field	45° slope	20 x 20	500m 015° from S-most houses. On 1st terrace N of road. Sltst outcrop. Shl, sltst + sst clasts.
85	17/11/95	Zhi Luo	LK2	10	20	LBR	CL	Radish field	10° slope	5 x 5	500m 360° from S-most houses. On 30° terrace below road. Few sltst, sst + shl clasts.
50	17/11/95	Zhi Luo	LK2	10	20	LBR	CLSI	Winter wheat	45° slope	5 x 5	750m 040° from S-most houses. On terrace above road. Few sltst, sst + shl clasts. Sst outcrop.
33	17/11/95	Zhi Luo	LK2	10	20	LBR	SICL	Rice paddy	Flat	10 x 10	750m 010° from S-most houses. On terrace below road. Moist not flooded.
42	17/11/95	Ming Shen	LK3	10	20	LBO	SISA	Maize field	50° slope	5 x 5	200m 040° from petrol station. 1st terrace above valley floor. Few sltst, lst, sst + shl clasts.
20	17/11/95	Ming Shen	LK3	10	20	LBO/R	SISA	Maize field	50° slope	5 x 5	Duplicate of 42. Increase orange colour in bottom 2 cm.
58	17/11/95	Ming Shen	LK3	10	20	LBR	CLSI	Radish field	10° slope	10 x 20	200m 070° from petrol station. On 10° terrace slope in side valley. Sst, sltst + shl clasts.
44	17/11/95	Ming Shen	LK3	10	20	LBR	CLSI	Radish field	Flat	10 x 10	250m 120° from petrol station. Top of terrace. Few sst, sltst + shl clasts.
29	17/11/95	Ming Shen	LK3	10	20	LBO	SISA	Radish field	3° slope	5 x 10	400m 130° from petrol station. Top of ravine. Few sst, sltst + shl clasts.
73	17/11/95	Ming Shen	LK3	10	20	LBO	CLSI	Maize field	50° slope	4 x 10	300m 085° from petrol station. 1st terrace above valley floor. Few sst , sltst + shl clasts.
43	17/11/95	Ming Shen	LK3	10	20	LBO	SISA	Rice paddy	Flat	7 x 2	150m 085° from petrol station. On 30° terrace slope. Few sst, sltst + shl clasts. Not flooded.
82	17/11/95	Nan Pu	LK4	10	20	LBR	CLSI	Pear + cbbge	Flat	5 x 5	100m 080° from large house on E-side road. Base of steep bank. Few sst, sltst + shl clasts.

Samp. No.	Date Sampled	Village Name	Code	Depth Top(cm)	Depth Base(cm)	Soil Colour	Soil Texture	Landuse	Topography	Sample Spacing(m)	Soil Sample Notes
55	17/11/95	Nan Pu	LK4	10	20	LBR	CLSI	Maize field	10° slope	10 x 10	100m 040° from large house on E-side road. On 10° terrace. Few sst, sltst + shl clasts.
14	17/11/95	Nan Pu	LK4	10	20	LBR/O	SISA	Cabbage field	Flat	6 x 6	100m 300° from large house on E-side road. On valley floor. Many sltst clasts in bottom 3 cm.
87	17/11/95	Nan Pu	LK4	10	20	LBR/O	SA	Cabbage field	60° slope	10 x 20	150m 325° from large house on E-side road. Steep bank below sst outcrop. Sst + sltst clasts.
6	17/11/95	Nan Pu	LK4	10	20	LBR	SI	Radish field	40° slope	10 x 20	500m 340° from large house on E-side road. Slope below sltst outcrop. Sltst, shl + sst clasts.
12	17/11/95	Nan Pu	LK4	10	20	GR	CL	Rice paddy	Flat	20 x 20	480m 340° from large house on E-side road. In valley floor. Sltst, shl + sst clasts. Flooded.
92	18/11/95	Ji Chang	LK5	10	20	LBR	SISA	Radish field	Flat	10 x 15	100m 140° from white house on W-side road. On alluvium in valley. Shl, sst + sltst clasts.
2	18/11/95	Ji Chang	LK5	10	20	LBR	SISA	Radish field	Flat	10 x 15	Duplicate of 92. Few clst clasts.
63	18/11/95	Ji Chang	LK5	10	20	LBR	SISA	Pear + rdsh	5° slope	10 x 20	150m 190° from white house on W-side road. On terrace slope. Few sltst, sst + shl clasts.
31	18/11/95	Ji Chang	LK5	10	20	LBR	SICL	Pear + rdsh	10° slope	10 x 15	200m 210° from white house on W-side road. On hillside. Sltst, sst + shl clasts. Or. sandy.
53	18/11/95	Ji Chang	LK5	10	20	LBO	SISA	Radish field	5° slope	4 x 10	200m 260° from white hse on W-side road. Base of side valley. Sltst, sst + shl clasts. Or. sandy.
27	18/11/95	Ji Chang	LK5	10	20	LBO/R	SICL	Radish field	5° slope	10 x 7	20m 000° from white house on W-side road. Base of main valley. Sltst, sst + shl clasts.
30	18/11/95	Ji Chang	LK5	35	45	LBR	SICL	Radish field	Flat	10 x 15	Deeper soil. Same holes as 92.
11	18/11/95	Ji Chang	LK5	10	20	LBR	SISA	Rice paddy	Flat	10 x 15	90m 135° from wh. hse on W-side road. On alluvium in valley. Sst, sltst + shl clasts. Not flooded.
76	18/11/95	Zishenqiao	HN5	10	20	LBO	SICL	Ploughed field	5° slope	20 x 20	300m 090° from main street. On 10° terrace slope. Shl, clst, sltst, lst + or./wh. chlky clasts.
81	18/11/95	Zishenqiao	HN5	10	20	LBO	SICL	Radish field	20° slope	7 x 20	250m 090° from main street. On 20° terrace slope. Shl, clst, sltst, lst + chlky clasts.
86	18/11/95	Zishenqiao	HN5	10	20	LBO	SI	Ploughed field	5° slope	20 x 20	150m 085° from main street. On 20° terrace slope. Shl, clst, sltst + lst clasts.
78	18/11/95	Zishenqiao	HN5	10	20	LBO	CLSI	Ploughed field	5° slope	20 x 20	150m 080° from main street. On 20° terrace slope. Shl, clst, sltst + lst clasts.
68	18/11/95	Zishenqiao	HN5	10	20	LBO	CLSI	Winter wheat	Flat	15 x 20	5m 050° from main street. Base of 20° terrace slope. Shl, clst, sltst + lst clasts.

clst = carbonaceous shale
shl = shale
chlky=chalky
sst = sandstone
sltst = siltstone
yel. /Y = yellow
wh./W = white
gr./GR= grey
dk./DK = dark
LB = light brown

DBO = dark brown orange
LBO = light brown orange
LBGR = light brown grey
LBW = light brown white
LBO/R = light brown orange/red
LBR/O = light brown red/ orange
LBR/GR = light brown red/ grey
LBR = light brown red
db. /DB = dark brown
or./0 = orange

CL = clay
SI = silt
SA = sand
CLSI = clay silt
SICL = silty clay
SISA = silty sand
SASI = sandy silt
terr = terrace
stm = stream

hse = house
N = north
S = south
E = east
W = west
rdsh = radish
tobco = tobacco
cabbge = cabbage
abve = above

APPENDIX C: GRAIN SAMPLE LISTS AND SUMMARY FIELD DATA

a) Listed by village name

Samp. No.	Date Sampled	Village Name	Code	Landuse	Grain Type	Grain Sample Notes
18	12/11/95	Luojiaba	HN1	Radish field	Maize-corn	Carbonaceous shale outcrops in fields.
49	12/11/95	Luojiaba	HN1	Radish field	Maize-corn	Duplicate of 18.
46	12/11/95	Luojiaba	HN1	Radish field	Maize-corn	Luojiaba villagers mine and burn carbonaceous shale.
41	12/11/95	Luojiaba	HN1	Tea field	Maize-corn	
32	12/11/95	Luojiaba	HN1	Cabbage field	Maize-corn	
45	12/11/95	Luojiaba	HN1	Cabbage field	Maize-corn	
94	12/11/95	Bajiao	HN2	Cabbage field	Maize-corn	Bajiao villagers mine and burn carbonaceous shale.
98	12/11/95	Bajiao	HN2	Ploughed field	Maize-corn	
56	12/11/95	Bajiao	HN2	Ploughed field	Maize-corn	
15	12/11/95	Bajiao	HN2	Ploughed field	Maize-corn	
26	12/11/95	Bajiao	HN2	Tea field	Maize-corn	
19	13/11/95	Shadi	HT1	Ploughed field	Maize-corn	Shadi villagers mine and burn carbonaceous shale.
39	13/11/95	Shadi	HT1	Ploughed field	Maize-corn	Duplicate of 19.
54	13/11/95	Shadi	HT1	Maize field	Maize-corn	
62	13/11/95	Shadi	HT1	Ploughed field	Maize-corn	
80	13/11/95	Shadi	HT1	Radish field	Maize-corn	
16	13/11/95	Shadi	HT1	Ploughed field	Maize-corn	
72	13/11/95	Huabei	HT2	Cabbage field	Maize-corn	Huabei villagers mine and burn carbonaceous shale.
65	13/11/95	Huabei	HT2	Radish field	Maize-corn	Farmer no longer feeds pigs maize-corn as they lost their trotters due to Se toxicity.
37	13/11/95	Huabei	HT2	Ploughed field	Maize-corn	Farmer's pigs suffer hair loss and have red skin due to Se toxicity.
4	13/11/95	Huabei	HT2	Radish field	Maize-corn	
90	13/11/95	Huabei	HT2	Radish field	Maize-corn	
1	14/11/95	Xin Tang	HT3	Radish field	Maize-corn	Xin Tang villagers mine and burn carbonaceous shale.
99	14/11/95	Xin Tang	HT3	Radish field	Maize-corn	Duplicate of 1.
3	14/11/95	Xin Tang	HT3	Ploughed field	Maize-corn	
38	14/11/95	Xin Tang	HT3	Maize field	Maize-corn	Farmer's pig suffers hair loss due to Se toxicity.
91	14/11/95	Xin Tang	HT3	Ploughed field	Maize-corn	
67	14/11/95	Xin Tang	HT3	Maize field	Maize-corn	
34	14/11/95	Xin Tang	HT3	Rice paddy	Rice	

Samp. No.	Date Sampled	Village Name	Code	Landuse	Grain Type	Grain Sample Notes
89	14/11/95	Yu Tang Ba	HT4	Maize field	Maize-corn	Collected in field.
83	14/11/95	Yu Tang Ba	HT4	Maize field	Maize-corn	Collected in field.
95	14/11/95	Yu Tang Ba	HT4	Maize field	Maize-corn	Collected in field.
21	14/11/95	Yu Tang Ba	HT4	Tobco + rdsh	Maize-corn	
84	14/11/95	Yu Tang Ba	HT4	Maize field	Maize-corn	Tobacco sample also collected.
93	15/11/95	Shatuo	HT5	Maize field	Maize-corn	Shatou villagers mine and burn carbonaceous shale.
40	15/11/95	Shatuo	HT5	Maize field	Maize-corn	Duplicate of 93.
71	15/11/95	Shatuo	HT5	Maize field	Maize-corn	
57	15/11/95	Shatuo	HT5	Maize field	Maize-corn	
61	15/11/95	Shatuo	HT5	Maize field	Maize-corn	Farmer's pigs have lost hair in the past due to Se toxicity.
48	15/11/95	Shatuo	HT5	Radish field	Maize-corn	Much altered Fe and S rich coal slag in fields in valley.
35	15/11/95	Shatuo	HT5	Rice paddy	Rice	
13	15/11/95	Fangjiaping	HN3	Tobacco field	Maize-corn	Fangjiaping villagers mine and burn carbonaceous shale.
51	15/11/95	Fangjiaping	HN3	Radish field	Maize-corn	
97	15/11/95	Fangjiaping	HN3	Radish field	Maize-corn	
74	15/11/95	Fangjiaping	HN3	Ploughed field	Maize-corn	Farm is below coal mining slag tip.
23	15/11/95	Fangjiaping	HN3	Radish field	Maize-corn	
70	16/11/95	Xiao Guan	HN4	Tea field	Maize-corn	Xiao Guan villagers mine and burn carbonaceous shale.
59	16/11/95	Xiao Guan	HN4	Tea field	Maize-corn	Duplicate of 70.
88	16/11/95	Xiao Guan	HN4	Radish field	Maize-corn	Limestone and carbonaceous shale outcrop in field.
66	16/11/95	Xiao Guan	HN4	Radish field	Maize-corn	
64	16/11/95	Xiao Guan	HN4	Maize field	Maize-corn	
52	16/11/95	Xiao Guan	HN4	Rdsh + tea	Maize-corn	
79	16/11/95	Xiao Guan	HN4	Rice paddy	Rice	
5	17/11/95	Chang Ping	LK1	Radish field	Maize-corn	
60	17/11/95	Chang Ping	LK1	Radish field	Maize-corn	Duplicate of 5.
8	17/11/95	Chang Ping	LK1	Radish field	Maize-corn	
96	17/11/95	Chang Ping	LK1	Ploughed field	Maize-corn	
25	17/11/95	Chang Ping	LK1	Tea field	Maize-corn	
47	17/11/95	Chang Ping	LK1	Radish field	Maize-corn	
24	17/11/95	Zhi Luo	LK2	Ploughed field	Maize-corn	
77	17/11/95	Zhi Luo	LK2	Radish field	Maize-corn	

Samp. No.	Date Sampled	Village Name	Code	Landuse	Grain Type	Grain Sample Notes
9	17/11/95	Zhi Luo	LK2	Ploughed field	Maize-corn	
85	17/11/95	Zhi Luo	LK2	Radish field	Maize-corn	
50	17/11/95	Zhi Luo	LK2	Winter wheat	Maize-corn	
33	17/11/95	Zhi Luo	LK2	Rice paddy	Rice	
42	17/11/95	Ming Shen	LK3	Maize field	Maize-corn	
20	17/11/95	Ming Shen	LK3	Maize field	Maize-corn	Duplicate of 42.
58	17/11/95	Ming Shen	LK3	Radish field	Maize-corn	
44	17/11/95	Ming Shen	LK3	Radish field	Maize-corn	
29	17/11/95	Ming Shen	LK3	Radish field	Maize-corn	
43	17/11/95	Ming Shen	LK3	Rice paddy	Rice	
82	17/11/95	Nan Pu	LK4	Pear + cbbge	Maize-corn	
55	17/11/95	Nan Pu	LK4	Maize field	Maize-corn	
14	17/11/95	Nan Pu	LK4	Cabbage field	Maize-corn	
87	17/11/95	Nan Pu	LK4	Cabbage field	Maize-corn	
6	17/11/95	Nan Pu	LK4	Radish field	Maize-corn	
12	17/11/95	Nan Pu	LK4	Rice paddy	Rice	
92	18/11/95	Ji Chang	LK5	Radish field	Maize-corn	
2	18/11/95	Ji Chang	LK5	Radish field	Maize-corn	Duplicate of 92.
63	18/11/95	Ji Chang	LK5	Pear + rdsh	Maize-corn	
31	18/11/95	Ji Chang	LK5	Pear + rdsh	Maize-corn	
53	18/11/95	Ji Chang	LK5	Radish field	Maize-corn	
27	18/11/95	Ji Chang	LK5	Radish field	Maize-corn	
11	18/11/95	Ji Chang	LK5	Rice paddy	Rice	
76	18/11/95	Zishengqiao	HN5	Ploughed field	Maize-corn	Zishengqiao villagers mine and burn carbonaceous shale.
81	18/11/95	Zishengqiao	HN5	Radish field	Maize-corn	
86	18/11/95	Zishengqiao	HN5	Ploughed field	Maize-corn	
78	18/11/95	Zishengqiao	HN5	Ploughed field	Maize-corn	
68	18/11/95	Zishengqiao	HN5	Winter wheat	Maize-corn	

tobco = tobacco rdsh = radish cbbge = cabbage

b) Listed by sample number

Samp. No.	Date Sampled	Village Name	Code	Landuse	Grain Type	Grain Sample Notes
1	14/11/95	Xin Tang	HT3	Radish field	Maize-corn	Xin Tang villagers mine and burn carbonaceous shale.
2	18/11/95	Ji Chang	LK5	Radish field	Maize-corn	Duplicate of 92.
3	14/11/95	Xin Tang	HT3	Ploughed field	Maize-corn	
4	13/11/95	Huabei	HT2	Radish field	Maize-corn	
5	17/11/95	Chang Ping	LK1	Radish field	Maize-corn	
6	17/11/95	Nan Pu	LK4	Radish field	Maize-corn	
8	17/11/95	Chang Ping	LK1	Radish field	Maize-corn	
9	17/11/95	Zhi Luo	LK2	Ploughed field	Maize-corn	
11	18/11/95	Ji Chang	LK5	Rice paddy	Rice	
12	17/11/95	Nan Pu	LK4	Rice paddy	Rice	
13	15/11/95	Fangjiaping	HN3	Tobacco field	Maize-corn	Fangjiaping villagers mine and burn carbonaceous shale.
14	17/11/95	Nan Pu	LK4	Cabbage field	Maize-corn	
15	12/11/95	Bajiao	HN2	Ploughed field	Maize-corn	
16	13/11/95	Shadi	HT1	Ploughed field	Maize-corn	
18	12/11/95	Luojiaba	HN1	Radish field	Maize-corn	Carbonaceous shale outcrops in fields.
19	13/11/95	Shadi	HT1	Ploughed field	Maize-corn	Shadi villagers mine and burn carbonaceous shale.
20	17/11/95	Ming Shen	LK3	Maize field	Maize-corn	Duplicate of 42.
21	14/11/95	Yu Tang Ba	HT4	Tobco + rdsh	Maize-corn	
23	15/11/95	Fangjiaping	HN3	Radish field	Maize-corn	
24	17/11/95	Zhi Luo	LK2	Ploughed field	Maize-corn	
25	17/11/95	Chang Ping	LK1	Tea field	Maize-corn	
26	12/11/95	Bajiao	HN2	Tea field	Maize-corn	
27	18/11/95	Ji Chang	LK5	Radish field	Maize-corn	
29	17/11/95	Ming Shen	LK3	Radish field	Maize-corn	
31	18/11/95	Ji Chang	LK5	Pear + rdsh	Maize-corn	
32	12/11/95	Luojiaba	HN1	Cabbage field	Maize-corn	
33	17/11/95	Zhi Luo	LK2	Rice paddy	Rice	
34	14/11/95	Xin Tang	HT3	Rice paddy	Rice	
35	15/11/95	Shatuo	HT5	Rice paddy	Rice	
37	13/11/95	Huabei	HT2	Ploughed field	Maize-corn	Farmer's pigs suffer hair loss and have red skin due to Se toxicity.

Samp. No.	Date Sampled	Village Name	Code	Landuse	Grain Type	Grain Sample Notes
38	14/11/95	Xin Tang	HT3	Maize field	Maize-corn	Farmer's pig suffers hair loss due to Se toxicity.
39	13/11/95	Shadi	HT1	Ploughed field	Maize-corn	Duplicate of 19.
40	15/11/95	Shatuo	HT5	Maize field	Maize-corn	Duplicate of 93.
41	12/11/95	Luojiaba	HN1	Tea field	Maize-corn	
42	17/11/95	Ming Shen	LK3	Maize field	Maize-corn	
43	17/11/95	Ming Shen	LK3	Rice paddy	Rice	
44	17/11/95	Ming Shen	LK3	Radish field	Maize-corn	
45	12/11/95	Luojiaba	HN1	Cabbage field	Maize-corn	
46	12/11/95	Luojiaba	HN1	Radish field	Maize-corn	Luojiaba villagers mine and burn carbonaceous shale.
47	17/11/95	Chang Ping	LK1	Radish field	Maize-corn	
48	15/11/95	Shatuo	HT5	Radish field	Maize-corn	Much altered Fe and S rich coal slag in fields in valley.
49	12/11/95	Luojiaba	HN1	Radish field	Maize-corn	Duplicate of 18.
50	17/11/95	Zhi Luo	LK2	Winter wheat	Maize-corn	
51	15/11/95	Fangjiaping	HN3	Radish field	Maize-corn	
52	16/11/95	Xiao Guan	HN4	Rdsh + tea	Maize-corn	
53	18/11/95	Ji Chang	LK5	Radish field	Maize-corn	
54	13/11/95	Shadi	HT1	Maize field	Maize-corn	
55	17/11/95	Nan Pu	LK4	Maize field	Maize-corn	
56	12/11/95	Bajiao	HN2	Ploughed field	Maize-corn	
57	15/11/95	Shatuo	HT5	Maize field	Maize-corn	
58	17/11/95	Ming Shen	LK3	Radish field	Maize-corn	
59	16/11/95	Xiao Guan	HN4	Tea field	Maize-corn	Duplicate of 70.
60	17/11/95	Chang Ping	LK1	Radish field	Maize-corn	Duplicate of 5.
61	15/11/95	Shatuo	HT5	Maize field	Maize-corn	Farmer's pigs have lost hair in the past due to Se toxicity.
62	13/11/95	Shadi	HT1	Ploughed field	Maize-corn	
63	18/11/95	Ji Chang	LK5	Pear + rdsh	Maize-corn	
64	16/11/95	Xiao Guan	HN4	Maize field	Maize-corn	
65	13/11/95	Huabei	HT2	Radish field	Maize-corn	Farmer no longer feeds pigs maize-corn as they lost their trotters due to Se toxicity.
66	16/11/95	Xiao Guan	HN4	Radish field	Maize-corn	
67	14/11/95	Xin Tang	HT3	Maize field	Maize-corn	
68	18/11/95	Zishengqiao	HN5	Winter wheat	Maize-corn	
70	16/11/95	Xiao Guan	HN4	Tea field	Maize-corn	Xiao Guan villagers mine and burn carbonaceous shale.

Samp. No.	Date Sampled	Village Name	Code	Landuse	Grain Type	Grain Sample Notes
71	15/11/95	Shatuo	HT5	Maize field	Maize-corn	
72	13/11/95	Huabei	HT2	Cabbage field	Maize-corn	Huabei villagers mine and burn carbonaceous shale.
74	15/11/95	Fangjiaping	HN3	Ploughed field	Maize-corn	Farm is below coal mining slag tip.
76	18/11/95	Zishengqiao	HN5	Ploughed field	Maize-corn	Zishengqiao villagers mine and burn carbonaceous shale.
77	17/11/95	Zhi Luo	LK2	Radish field	Maize-corn	
78	18/11/95	Zishengqiao	HN5	Ploughed field	Maize-corn	
79	16/11/95	Xiao Guan	HN4	Rice paddy	Rice	
80	13/11/95	Shadi	HT1	Radish field	Maize-corn	
81	18/11/95	Zishengqiao	HN5	Radish field	Maize-corn	
82	17/11/95	Nan Pu	LK4	Pear + cbbge	Maize-corn	
83	14/11/95	Yu Tang Ba	HT4	Maize field	Maize-corn	Collected in field.
84	14/11/95	Yu Tang Ba	HT4	Maize field	Maize-corn	Tobacco sample also collected.
85	17/11/95	Zhi Luo	LK2	Radish field	Maize-corn	
86	18/11/95	Zishengqiao	HN5	Ploughed field	Maize-corn	
87	17/11/95	Nan Pu	LK4	Cabbage field	Maize-corn	
88	16/11/95	Xiao Guan	HN4	Radish field	Maize-corn	Limestone and carbonaceous shale outcrop in field.
89	14/11/95	Yu Tang Ba	HT4	Maize field	Maize-corn	Collected in field.
90	13/11/95	Huabei	HT2	Radish field	Maize-corn	
91	14/11/95	Xin Tang	HT3	Ploughed field	Maize-corn	
92	18/11/95	Ji Chang	LK5	Radish field	Maize-corn	
93	15/11/95	Shatuo	HT5	Maize field	Maize-corn	Shatou villagers mine and burn carbonaceous shale.
94	12/11/95	Bajiao	HN2	Cabbage field	Maize-corn	Bajiao villagers mine and burn carbonaceous shale.
95	14/11/95	Yu Tang Ba	HT4	Maize field	Maize-corn	Collected in field.
96	17/11/95	Chang Ping	LK1	Ploughed field	Maize-corn	
97	15/11/95	Fangjiaping	HN3	Radish field	Maize-corn	
98	12/11/95	Bajiao	HN2	Ploughed field	Maize-corn	
99	14/11/95	Xin Tang	HT3	Radish field	Maize-corn	Duplicate of 1.

tobco = tobacco rdsh = radish cbbge = cabbage

APPENDIX D: WATER SAMPLE LISTS AND SUMMARY FIELD DATA

a) Listed by village name

Samp. No.	Date Sampled	Village Name	Village Code	Water Source	Sample Temp°C	Field Eh(mV)	Corrected Eh(mV)	pH	Conductivity (µS)	Total Alkalinity (mg/lCaCO3)	Water Sample Notes
18	12/11/95	Luojiaba	HN1	Spring 500m 017° from doctors house.	22.4	231	432.6	6.98	457	172	
49	12/11/95	Luojiaba	HN1	Duplicate of 18.	22.4	208	409.6	7.00	480	175	
94	12/11/95	Bajiao	HN2	Spring 200m 270° from school.	21.0	206	409	7.13	427	135	
19	13/11/95	Shadi	HT1	Spring 40m 274° from farmhouse at valley head.	19.4	250	454.6	6.19	1008	38	Spring feeds into stream with heavy orange Fe ppt.
39	13/11/95	Shadi	HT1	Duplicate of 19.	19.1	250	454.9	6.17	1011	42	Villagers have alternative water supply.
72	13/11/95	Huabei	HT2	Spring 10m 180° from main street.	18.7	180	385.3	8.28	550	102	Villagers have alternative piped water supply.
1	14/11/95	Xin Tang	HT3	Spring 1300m 75° from N end village centre.	12.3	216	427.7	7.73	221	82	
84	14/11/95	Yu Tang Ba	HT4	Stream 50m 30° from farmhouse.	10.3	189	402.7	8.40	228	105	Drinking water trib. clear, main stm cloudy.
93	15/11/95	Shatuo	HT5	Spring 50m 110° from top house.	17.5	190	396.5	8.10	354	111	Streams in valley have heavy orange Fe ppt.
74	15/11/95	Fangjiaping	HN3	Spring 480m 345° from main street.	17.7	192	398.3	8.03	406	129	Spring drains hillside covered in coal mining slag.
52	16/11/95	Xiao Guan	HN4	Spring 200m 180° from house 2km N reservoir.	14.6	194	403.4	8.48	219	100	
5	17/11/95	Chang Ping	LK1	Spring 10m 180° from main street.	14.6	155	364.4	6.78	513	62	Water has high particulate content.
60	17/11/95	Chang Ping	LK1	Duplicate of 5.	14.5	177	386.5	6.79	510	57	
85	17/11/95	Zhi Luo	LK2	Spring 530m 360° from S-most houses.	14.2	180	389.8	7.39	338	178	
73	17/11/95	Ming Shen	LK3	Spring 300m 87° from petrol station.	14.7	192	401.3	6.25	96	18	
6	17/11/95	Nan Pu	LK4	Spring 300m 270° from large house on E-side road.	14.9	197	406.1	6.06	86	5.9	
63	18/11/95	Ji Chang	LK5	Spring 150m 190° from white house on W-side road	15.9	212	420.1	6.15	35	11.9	
68	18/11/95	Zishengqiao	HN5	Spring 7m 045° from 1st house above main street.	16.0	187	395	7.79	333	114	

stm = stream trib. = tributary ppt = precipitate

b) Listed by sample number

Samp. No.	Date Sampled	Village Name	Village Code	Water Source	Sample Temp°C	Field Eh(mV)	Corrected Eh(mV)	pH	Conductivity (µS)	Total Alkalinity (mg/lCaCO3)	Water Sample Notes
1	14/11/95	Xin Tang	HT3	Spring 1300m 75° from N end village centre.	12.3	216	427.7	7.73	221	82	
5	17/11/95	Chang Ping	LK1	Spring 10m 180° from main street.	14.6	155	364.4	6.78	513	62	Water has high particulate content.
6	17/11/95	Nan Pu	LK4	Spring 300m 270° from large house on E-side road.	14.9	197	406.1	6.06	86	5.9	
18	12/11/95	Luojiaba	HN1	Spring 500m 017° from doctors house.	22.4	231	432.6	6.98	457	172	
19	13/11/95	Shadi	HT1	Spring 40m 274° from farmhouse at valley head.	19.4	250	454.6	6.19	1008	38	Spring feeds into stream with heavy orange Fe ppt.
39	13/11/95	Shadi	HT1	Duplicate of 19.	19.1	250	454.9	6.17	1011	42	Villagers have alternative water supply.
49	12/11/95	Luojiaba	HN1	Duplicate of 18.	22.4	208	409.6	7.00	480	175	
52	16/11/95	Xiao Guan	HN4	Spring 200m 180° from house 2km N reservoir.	14.6	194	403.4	8.48	219	100	
60	17/11/95	Chang Ping	LK1	Duplicate of 5.	14.5	177	386.5	6.79	510	57	
63	18/11/95	Ji Chang	LK5	Spring 150m 190° from white house on W-side road.	15.9	212	420.1	6.15	35	11.9	
68	18/11/95	Zishengqiao	HN5	Spring 7m 045° from 1st house above main street.	16.0	187	395	7.79	333	114	
72	13/11/95	Huabei	HT2	Spring 10m 180° from main street.	18.7	180	385.3	8.28	550	102	Villagers have alternative piped water supply.
73	17/11/95	Ming Shen	LK3	Spring 300m 87° from petrol station.	14.7	192	401.3	6.25	96	18	
74	15/11/95	Fangjiaping	HN3	Spring 480m 345° from main street.	17.7	192	398.3	8.03	406	129	Spring drains hillside covered in coal mining slag.
84	14/11/95	Yu Tang Ba	HT4	Stream 50m 30° from farmhouse.	10.3	189	402.7	8.40	228	105	Drinking water trib. clear, main stm cloudy.
85	17/11/95	Zhi Luo	LK2	Spring 530m 360° from S-most houses.	14.2	180	389.8	7.39	338	178	
93	15/11/95	Shatuo	HT5	Spring 50m 110° from top house.	17.5	190	396.5	8.10	354	111	Streams in valley have heavy orange Fe ppt.
94	12/11/95	Bajiao	HN2	Spring 200m 270° from school.	21.0	206	409	7.13	427	135	

stm = stream

trib. = tributary

ppt = precipitate

APPENDIX E: HAIR SAMPLE LISTS AND SUMMARY FIELD DATA

a) Listed by village name

Samp. No.	Date Sampled	Village Name	Code	Gender	Age	Health	Medication	Main Food	Hair Sample Notes
18	12/11/95	Luojiaba	HN1	Male	27	Good. Fluorosis	None	Maize-corn + rice	
46	12/11/95	Luojiaba	HN1	Male	34	Good. Fluorosis	None	Maize-corn + rice	
41	12/11/95	Luojiaba	HN1	Male	28	Good. Fluorosis	None	Maize-corn + rice	
32	12/11/95	Luojiaba	HN1	Male	30	Good. Fluorosis	None	Maize-corn + rice	
45	12/11/95	Luojiaba	HN1	Male	33	Good. Fluorosis	None	Maize-corn + rice	
94	12/11/95	Bajiao	HN2	Male	35	Good. Fluorosis	None	Maize-corn + rice	
98	12/11/95	Bajiao	HN2	Female	13	Good. Fluorosis	None	Maize-corn + rice	
56	12/11/95	Bajiao	HN2	Male	49	Good. Fluorosis	None	Maize-corn + rice	
15	12/11/95	Bajiao	HN2	Male	43	Good. Fluorosis	None	Maize-corn + rice	
26	12/11/95	Bajiao	HN2	Male	42	Good. Fluorosis	None	Maize-corn + rice	
19	13/11/95	Shadi	HT1	Male	17	Good. Fluorosis	None	Maize-corn + rice	
16	13/11/95	Shadi	HT1	Male	42	Good. Fluorosis	None	Maize-corn + rice	
54	13/11/95	Shadi	HT1	Male	53	Good. Fluorosis	None	Maize-corn + rice	
62	13/11/95	Shadi	HT1	Male	21	Good. Fluorosis	None	Maize-corn + rice	
80	13/11/95	Shadi	HT1	Male	48	Good. Fluorosis	None	Maize-corn + rice	
72	13/11/95	Huabei	HT2	Male	24	Good. Fluorosis	None	Maize-corn + rice	
65	13/11/95	Huabei	HT2	Male	47	Good. Fluorosis	None	Maize-corn + rice	
37	13/11/95	Huabei	HT2	Male	48	Good. Fluorosis	None	Maize-corn + rice	
4	13/11/95	Huabei	HT2	Male	13	Good. Fluorosis	None	Maize-corn + rice	
90	13/11/95	Huabei	HT2	Male	28	Good. Fluorosis	None	Maize-corn + rice	
1	14/11/95	Xin Tang	HT3	Male	45	Good. Fluorosis	None	Maize-corn + rice	
3	14/11/95	Xin Tang	HT3	Male	29	Good. Fluorosis	None	Maize-corn + rice	Has lost hair in the past due to Se toxicity.
38	14/11/95	Xin Tang	HT3	Male	40	Good. Fluorosis	None	Maize-corn + rice	Lost hair in 1962 due to Se toxicity. Pig hair also collected.
91	14/11/95	Xin Tang	HT3	Male	66	Good. Fluorosis	None	Maize-corn + rice	Lost hair in 1962 due to Se toxicity.
67	14/11/95	Xin Tang	HT3	Male	29	Good. Fluorosis	None	Maize-corn + rice	
89	14/11/95	Yu Tang Ba	HT4	Male	47	Good	None	Imported maize-corn + rice	Temporary resident of 2 months.
83	14/11/95	Yu Tang Ba	HT4	Female	68	Good	None	Imported maize-corn + rice	Resident of 2 years.
21	14/11/95	Yu Tang Ba	HT4	Male	69	Good	None	Imported maize-corn + rice	Resident of 2 years.
93	15/11/95	Shatuo	HT5	Male	36	Good. Fluorosis	None	Maize-corn + rice	

Samp. No.	Date Sampled	Village Name	Code	Gender	Age	Health	Medication	Main Food	Hair Sample Notes
71	15/11/95	Shatuo	HT5	Male	31	Good. Fluorosis	None	Maize-corn + rice	
57	15/11/95	Shatuo	HT5	Male	21	Good. Fluorosis	None	Maize-corn + rice	
61	15/11/95	Shatuo	HT5	Male	15	Good. Fluorosis	None	Maize-corn + rice	
48	15/11/95	Shatuo	HT5	Male	21	Good. Fluorosis	None	Maize-corn + rice	
13	15/11/95	Fangjiaping	HN3	Male	27	Good. Fluorosis	None	Maize-corn + rice	
51	15/11/95	Fangjiaping	HN3	Male	33	Good. Fluorosis	None	Maize-corn + rice	
97	15/11/95	Fangjiaping	HN3	Male	27	Good. Fluorosis	None	Maize-corn + rice	
74	15/11/95	Fangjiaping	HN3	Male	36	Good. Fluorosis	None	Maize-corn + rice	
23	15/11/95	Fangjiaping	HN3	Male	19	Good. Fluorosis	None	Maize-corn + rice	
70	16/11/95	Xiao Guan	HN4	Male	25	Good. Fluorosis	None	Maize-corn + rice	
88	16/11/95	Xiao Guan	HN4	Male	27	Good. Fluorosis	None	Maize-corn + rice	
66	16/11/95	Xiao Guan	HN4	Male	28	Good. Fluorosis	None	Maize-corn + rice	
5	17/11/95	Chang Ping	LK1	Male	10	Good	None	Maize-corn + rice	
8	17/11/95	Chang Ping	LK1	Male	11	Good	None	Maize-corn + rice	
96	17/11/95	Chang Ping	LK1	Male	10	Good	None	Maize-corn + rice	
25	17/11/95	Chang Ping	LK1	Male	9	Good	None	Maize-corn + rice	
47	17/11/95	Chang Ping	LK1	Male	9	Good	None	Maize-corn + rice	
24	17/11/95	Zhi Luo	LK2	Male	12	Good	None	Maize-corn + rice	
77	17/11/95	Zhi Luo	LK2	Male	14	Good	None	Maize-corn + rice	
9	17/11/95	Zhi Luo	LK2	Male	13	Good	None	Maize-corn + rice	
85	17/11/95	Zhi Luo	LK2	Male	14	Good	None	Maize-corn + rice	
50	17/11/95	Zhi Luo	LK2	Male	13	Good	None	Maize-corn + rice	
42	17/11/95	Ming Shen	LK3	Male	8	Good	None	Maize-corn + rice	
58	17/11/95	Ming Shen	LK3	Male	6	Good	None	Maize-corn + rice	
44	17/11/95	Ming Shen	LK3	Male	10	Good	None	Maize-corn + rice	
29	17/11/95	Ming Shen	LK3	Male	10	Good	None	Maize-corn + rice	
73	17/11/95	Ming Shen	LK3	Male	10	Good	None	Maize-corn + rice	
82	17/11/95	Nan Pu	LK4	Male	9	Good	None	Maize-corn + rice	
55	17/11/95	Nan Pu	LK4	Male	9	Good	None	Maize-corn + rice	
14	17/11/95	Nan Pu	LK4	Male	7	Good	None	Maize-corn + rice	
87	17/11/95	Nan Pu	LK4	Male	8	Good	None	Maize-corn + rice	
6	17/11/95	Nan Pu	LK4	Male	7	Good	None	Maize-corn + rice	

Samp. No.	Date Sampled	Village Name	Code	Gender	Age	Health	Medication	Main Food	Hair Sample Notes
92	18/11/95	Ji Chang	LK5	Male	12	Good	None	Maize-corn + rice	
63	18/11/95	Ji Chang	LK5	Male	20	Good	None	Maize-corn + rice	
31	18/11/95	Ji Chang	LK5	Male	19	Good	None	Maize-corn + rice	
53	18/11/95	Ji Chang	LK5	Male	14	Good	None	Maize-corn + rice	
27	18/11/95	Ji Chang	LK5	Male	13	Good	None	Maize-corn + rice	
76	18/11/95	Zishengqiao	HN5	Male	45	Good	None	Maize-corn + rice	
81	18/11/95	Zishengqiao	HN5	Male	39	Good	None	Maize-corn + rice	
86	18/11/95	Zishengqiao	HN5	Male	39	Good	None	Maize-corn + rice	
78	18/11/95	Zishengqiao	HN5	Male	28	Good	None	Maize-corn + rice	
68	18/11/95	Zishengqiao	HN5	Male	8	Good	None	Maize-corn + rice	

b) Listed by sample number

Samp. No.	Date Sampled	Village Name	Code	Gender	Age	Health	Diesase	% Pop	Medication	Main Food	Hair Sample Notes
1	14/11/95	Xin Tang	HT3	Male	45	Good	Fluorosis	90	None	Maize-corn + rice	
3	14/11/95	Xin Tang	HT3	Male	29	Good	Fluorosis		None	Maize-corn + rice	Has lost hair in the past due to Se toxicity.
4	13/11/95	Huabei	HT2	Male	13	Good	Fluorosis		None	Maize-corn + rice	
5	17/11/95	Chang Ping	LK1	Male	10	Good			None	Maize-corn + rice	
6	17/11/95	Nan Pu	LK4	Male	7	Good			None	Maize-corn + rice	
8	17/11/95	Chang Ping	LK1	Male	11	Good			None	Maize-corn + rice	
9	17/11/95	Zhi Luo	LK2	Male	13	Good			None	Maize-corn + rice	
13	15/11/95	Fangjiaping	HN3	Male	27	Good	Fluorosis	90	None	Maize-corn + rice	
14	17/11/95	Nan Pu	LK4	Male	7	Good			None	Maize-corn + rice	
15	12/11/95	Bajiao	HN2	Male	43	Good	Fluorosis		None	Maize-corn + rice	
16	13/11/95	Shadi	HT1	Male	42	Good	Fluorosis		None	Maize-corn + rice	
18	12/11/95	Luojiaba	HN1	Male	27	Good	Fluorosis	100	None	Maize-corn + rice	
19	13/11/95	Shadi	HT1	Male	17	Good	Fluorosis	90	None	Maize-corn + rice	
21	14/11/95	Yu Tang Ba	HT4	Male	69	Good			None	Imported maize-corn + rice	Resident of 2 years.
23	15/11/95	Fangjiaping	HN3	Male	19	Good	Fluorosis		None	Maize-corn + rice	
24	17/11/95	Zhi Luo	LK2	Male	12	Good			None	Maize-corn + rice	
25	17/11/95	Chang Ping	LK1	Male	9	Good			None	Maize-corn + rice	
26	12/11/95	Bajiao	HN2	Male	42	Good	Fluorosis		None	Maize-corn + rice	
27	18/11/95	Ji Chang	LK5	Male	13	Good			None	Maize-corn + rice	
29	17/11/95	Ming Shen	LK3	Male	10	Good			None	Maize-corn + rice	
31	18/11/95	Ji Chang	LK5	Male	19	Good			None	Maize-corn + rice	
32	12/11/95	Luojiaba	HN1	Male	30	Good	Fluorosis		None	Maize-corn + rice	
37	13/11/95	Huabei	HT2	Male	48	Good	Fluorosis		None	Maize-corn + rice	
38	14/11/95	Xin Tang	HT3	Male	40	Good	Fluorosis		None	Maize-corn + rice	Lost hair in 1962 due to Se toxicity. Pig hair also collected.
41	12/11/95	Luojiaba	HN1	Male	28	Good	Fluorosis		None	Maize-corn + rice	
42	17/11/95	Ming Shen	LK3	Male	8	Good			None	Maize-corn + rice	
44	17/11/95	Ming Shen	LK3	Male	10	Good			None	Maize-corn + rice	
45	12/11/95	Luojiaba	HN1	Male	33	Good	Fluorosis		None	Maize-corn + rice	
46	12/11/95	Luojiaba	HN1	Male	34	Good	Fluorosis		None	Maize-corn + rice	
47	17/11/95	Chang Ping	LK1	Male	9	Good			None	Maize-corn + rice	

Samp. No.	Date Sampled	Village Name	Code	Gender	Age	Health	Diesase	% Pop	Medication	Main Food	Hair Sample Notes
48	15/11/95	Shatuo	HT5	Male	21	Good	Fluorosis		None	Maize-corn + rice	
50	17/11/95	Zhi Luo	LK2	Male	13	Good			None	Maize-corn + rice	
51	15/11/95	Fangjiaping	HN3	Male	33	Good	Fluorosis		None	Maize-corn + rice	
53	18/11/95	Ji Chang	LK5	Male	14	Good			None	Maize-corn + rice	
54	13/11/95	Shadi	HT1	Male	53	Good	Fluorosis		None	Maize-corn + rice	
55	17/11/95	Nan Pu	LK4	Male	9	Good			None	Maize-corn + rice	
56	12/11/95	Bajiao	HN2	Male	49	Good	Fluorosis		None	Maize-corn + rice	
57	15/11/95	Shatuo	HT5	Male	21	Good	Fluorosis		None	Maize-corn + rice	
58	17/11/95	Ming Shen	LK3	Male	6	Good			None	Maize-corn + rice	
61	15/11/95	Shatuo	HT5	Male	15	Good	Fluorosis		None	Maize-corn + rice	
62	13/11/95	Shadi	HT1	Male	21	Good	Fluorosis		None	Maize-corn + rice	
63	18/11/95	Ji Chang	LK5	Male	20	Good			None	Maize-corn + rice	
65	13/11/95	Huabei	HT2	Male	47	Good	Fluorosis		None	Maize-corn + rice	
66	16/11/95	Xiao Guan	HN4	Male	28	Good	Fluorosis		None	Maize-corn + rice	
67	14/11/95	Xin Tang	HT3	Male	29	Good	Fluorosis		None	Maize-corn + rice	
68	18/11/95	Zishengqiao	HN5	Male	8	Good			None	Maize-corn + rice	
70	16/11/95	Xiao Guan	HN4	Male	25	Good	Fluorosis	Unknown	None	Maize-corn + rice	
71	15/11/95	Shatuo	HT5	Male	31	Good	Fluorosis		None	Maize-corn + rice	
72	13/11/95	Huabei	HT2	Male	24	Good	Fluorosis	90	None	Maize-corn + rice	
73	17/11/95	Ming Shen	LK3	Male	10	Good			None	Maize-corn + rice	
74	15/11/95	Fangjiaping	HN3	Male	36	Good	Fluorosis		None	Maize-corn + rice	
76	18/11/95	Zishengqiao	HN5	Male	45	Good			None	Maize-corn + rice	
77	17/11/95	Zhi Luo	LK2	Male	14	Good			None	Maize-corn + rice	
78	18/11/95	Zishengqiao	HN5	Male	28	Good			None	Maize-corn + rice	
80	13/11/95	Shadi	HT1	Male	48	Good	Fluorosis		None	Maize-corn + rice	
81	18/11/95	Zishengqiao	HN5	Male	39	Good			None	Maize-corn + rice	
82	17/11/95	Nan Pu	LK4	Male	9	Good			None	Maize-corn + rice	
83	14/11/95	Yu Tang Ba	HT4	Female	68	Good			None	Imported maize-corn + rice	Resident of 2 years.
85	17/11/95	Zhi Luo	LK2	Male	14	Good			None	Maize-corn + rice	
86	18/11/95	Zishengqiao	HN5	Male	39	Good			None	Maize-corn + rice	
87	17/11/95	Nan Pu	LK4	Male	8	Good			None	Maize-corn + rice	
88	16/11/95	Xiao Guan	HN4	Male	27	Good	Fluorosis		None	Maize-corn + rice	

Samp. No.	Date Sampled	Village Name	Code	Gender	Age	Health	Diesase	% Pop	Medication	Main Food	Hair Sample Notes
89	14/11/95	Yu Tang Ba	HT4	Male	47	Good			None	Imported maize-corn + rice	Temporary resident of 2 months.
90	13/11/95	Huabei	HT2	Male	28	Good	Fluorosis		None	Maize-corn + rice	
91	14/11/95	Xin Tang	HT3	Male	66	Good	Fluorosis		None	Maize-corn + rice	Lost hair in 1962 due to Se toxicity.
92	18/11/95	Ji Chang	LK5	Male	12	Good			None	Maize-corn + rice	
93	15/11/95	Shatuo	HT5	Male	36	Good	Fluorosis	90	None	Maize-corn + rice	
94	12/11/95	Bajiao	HN2	Male	35	Good	Fluorosis	100	None	Maize-corn + rice	
96	17/11/95	Chang Ping	LK1	Male	10	Good			None	Maize-corn + rice	
97	15/11/95	Fangjiaping	HN3	Male	27	Good	Fluorosis		None	Maize-corn + rice	
98	12/11/95	Bajiao	HN2	Female	13	Good	Fluorosis		None	Maize-corn + rice	

APPENDIX F. BGS ANALYTICAL METHODS

F.1. Determination of Selenium by Hydride Generation Atomic Fluorescence Spectroscopy

F.1.1 Instrumentation

Measurements are made on a P.S. Analytical Excalibur™ Atomic Fluorescence Detector. The vapour generation system used is a P.S. Analytical-hydride system with a Type B gas/ liquid separator.

F.1.2 Theory

Selenium is analysed in a three stage process:

1. Selenium, in solution, is reduced to its 4^+ oxidation state using a combination of KBr + HCl at 80°C.

2. Gaseous selenium hydride is formed by reaction with sodium borohydride.

3. The hydride is atomised in a flame cell and determined by Atomic Fluorescence Spectroscopy (AFS).

Selenium hydride and hydrogen are formed in a continuous flow system by mixing the acidified sample with sodium borohydride. This gas liquid mixture is passed into a gas liquid separator where the gaseous selenium hydride and hydrogen are swept out of the mixture with Ar into a flame cell, and the gases are burnt as an air hydrogen flame. Within the flame, the selenium hydride is dissociated and Se atoms are formed. The atoms are excited by light emission from a Se hollow cathode lamp. The fluorescence emission is measured non-dispersively in a direction at right angles to the excitation source using a photomultiplier tube.

In atomic fluorescence, an intense light source, of a wavelength characteristic to the element of interest, is used to excite ground state atoms of the element through radiative absorption transitions. When these selectively excited atoms decay, the light emitted gives a measure of the element concentration. The intensity of the fluorescence emission is proportional to the element concentration.

F.1.3 Analytical Method

An acid carrier of 4 M HCl is required to produce sufficient hydrogen to sustain the atomisation flame. Therefore all samples are prepared in a 4 M acid matrix.

The reductant solution is prepared from 15 g $NaBH_4$ with 4 g sodium hydroxide (to stabilise the solution) made up to 1000 ml with deionised water.

Potassium bromide solution (50% w/v) is prepared using a reagent (50 g made up to 100 ml with de-ionised water).

At least four standards are prepared, using serial dilution from 1000 µg/g standard solution in 1% HCl, covering the range expected in the samples. A Se^{6+} standard is also prepared to check the efficiency of the reduction.

All standards, samples and check samples are reduced to ensure that all the selenium is in the form Se^{4+}. This is achieved by acidifying the samples and standards to match the acid concentration in the carrier and adding potassium bromide to make the samples 2% w/v KBr. The solutions are heated in loosely capped plastic containers at approximately 80°C for 30-40 minutes and left to cool for at least 30 minutes before analysis. Samples are analysed within 48 hours of reduction.

Data are captured by computer and concentrations calculated based on a calibration curve created by running known standards before and during each run.

F.1.4 Sample Preparation for Analysis of Water

Water samples are received preserved with 1% v/v HCl after filtration through 0.45 μm filters. Apart from the acidification and reduction procedure described in Section F1.3 no further preparation of the samples is carried out prior to analysis.

F.1.5 Sample Preparation for Analysis of Soil

0.1 g of soil is weighed into a uniquely labelled 15 ml PTFE test tube to which 1.0 ml of HF, 0.8 ml of concentrated HNO_3 and 0.4 ml of concentrated $HClO_4$ is added. The tubes are placed on a programmable heating block and are heated for three hours at 100°C, one hour at 140°C and ten hours at 190°C. Following digestion, the dry residue is dissolved in 4 M HCl at 50°C for one hour followed by the reduction procedure described in Section F1.3. Acid blanks and Water Research Council (WRC) Aquacheck reference samples are prepared with each batch of samples.

F.1.6 Sample Preparation for Analysis of Hair and Grain

0.1 g of grain or hair is weighed into a uniquely labelled 15 ml glass test tube to which 2.0 ml of concentrated HNO_3 and 0.4 ml of concentrated $HClO_4$ is added. The tubes are placed on a programmable heating block and are heated for one hour at 50°C, one hour at 85°C, two hours at 105°C, two hours at 125°C and eight hours at 200°C. Following digestion, the dry residue is dissolved in 4 M HCl at 50°C for 1 hour followed by the reduction procedure described in Section F1.3. Acid blanks and standard reference materials are prepared with each batch of samples.

F.1.7 Sample Preparation for Analysis of Water Soluble Element Concentrations in Soil

3 g of soil is weighed into a uniquely labelled 15 ml glass test tube into which 15 ml of deionised water is pipetted. The tubes are placed on a programmable heating block and are heated for 1 hour at 110°C. Following the hot water extraction, the samples are cooled, mixed on a vortex mixer and centrifuged. 10 ml of the supernatant liquid is collected to undergo the reduction method described in Section F1.3.

F.1.8 Data Quality

Se determinations in international reference materials from the Aquacheck scheme (WRC) UK, The National Research Centre for Certified Reference Materials (NRCCRM), China and the European Commission, Belgium (BCR) are summarised in Tables A-D. In general there is good agreement between the analytical results and the certified reference values.

The limits of detection (LOD) for the determination of Se in the various sample types by AFS are listed in Table E. LOD can vary depending on the sample matrix, the dilution required to give sufficient volume of solution for analysis, the current sensitivity of the instrument, the calibration range used and the level of Se found in the blank. The LOD quoted in Table E refer specifically to the Enshi analyses.

Table A. Total Se concentrations in international soil and stream sediment reference materials determined by AFS.

Reference material	Average Se µg/g	Number of Analyses	Standard Deviation	Reference Value µg/g
NRCCRM Stream sediment				
GBW07312	0.251	6*	0.007	0.25
WRC Aquacheck Soil				
Distribution 89	515	2		540
Distribution 97	855	2		880

* Based on Enshi and Cixian analyses

Table B. Total Se concentrations in international vegetation reference material determined by AFS.

Reference material	Average Se µg/g	Number of Analyses	Standard Deviation	Reference Value µg/g
NRCCRM Tea				
GBW08505	0.037	5*	0.006	0.041

* Based on Enshi and Cixian analyses

Table C. Total Se concentrations in national water reference materials determined by AFS.

Reference material	Average Se µg/l	Number of Analysis	Standard Deviation	Reference Value µg/l
WRC Aquacheck Water				
Distribution 89	6.26	6	0.15	6.3
Distribution 93	2.57	6	0.14	2.1
Distribution 101	4.26	7	0.21	4.2
Distribution 105	4.46	5	0.19	4.1

Table D. Total Se concentrations in international hair reference material determined by AFS.

Reference material	Average Se µg/g	Number of Analysis	Standard Deviation	Reference Value µg/g
BCR Hair				
BCR397	1.837	15*	0.392	2

* Based on Enshi, Cixian and Zhangjiakou analyses

Table E. AFS limits of detection for Se in various sample types

Sample Type	Se LOD ng/g
Soil	15
Soil Water Soluble Se	0.04
Grain	2
Water	0.2
Hair	10

Based on Enshi analyses

F.2 Determination of Major Cations and Trace Elements in Soils by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

F.2.1 Instrumentation

The ICP-spectrometer used to carry out this work is a Perkin-Elmer Plasma II sequential scanning system with twin 1 m vacuum monochromators. Monochromator A has a 3600 line/mm grating and wavelength range of 160-400 nm. The second monochromator (B) has a 1800 line/mm grating and wavelength range of 160-800 nm. The monochromator gratings, plasma power, plasma gas flows, plasma viewing height, 50-position auto-sampler and nebuliser peristaltic pump are all under computer control.

F.2.2 Theory

The nebulised sample is swept into the central channel of the inductively coupled plasma in a stream of argon carrier gas. On introduction to the plasma, the sample undergoes desolvation, evaporation, atomisation/ionisation and excitation. The atoms or ions decay from their excited state through radiative energy transitions, emitting light of specific energies (or wavelengths). The light emission from the plasma is separated into its component wavelengths by a monochromator, and a photomultiplier tube at the exit slit of the monochromator quantifies the light intensity at specific wavelengths. The intensity of the light emitted at the characteristic wavelength for a particular element is proportional to the amount of the element in the sample being sprayed into the plasma. The instrument is calibrated against standards containing known amounts of the elements to be analysed.

F.2.3 Analytical Method

Major and trace metals (Ca, Cd, Cu, Fe, Mg, Mn, Mo, Pb, V and Zn) are determined directly by ICP-AES. Analysis is carried out on approximately 10-15 ml of sample acidified to 1-5% with respect to HNO_3 depending on the sample preparation. The instrument is standardised every 10 samples and quality control checks are run every 20 samples. The control standards are always analysed at the end of the run to check for drift. Reported measurements are based on the average of three replicate analyses. Mixed standards, made up in the same acid matrix as the samples, are prepared from certified 1000 mg/l single element stock solutions.

F.2.4 Sample Preparation for Partial Acid Digestion of Soils

0.1 g of soil is weighed into a uniquely labelled 15 ml glass test tube to which 0.8 ml of concentrated HNO_3 and 0.4 ml of concentrated $HClO_4$ is added. The tubes are placed on a programmable heating block and are heated for three hours at 100°C, one hour at 140°C and ten hours at 190°C. One ml of 50% v/v HNO_3 is added to the dry residue remaining after the digestion, and heated for 30 minutes at 50°C to bring the sample into solution. On cooling, the solutions are finally made up to 10 ml with deionised water and decanted into polystyrene screw top storage tubes. Acid blanks and standard reference materials are prepared with each batch of samples.

F.2.5 Sample Preparation for Total Acid Digestion of Soils

0.1 g of soil is weighed into a uniquely labelled 15 ml PTFE test tube to which 1.0 ml of HF, 0.8 ml of concentrated HNO_3 and 0.4 ml of concentrated $HClO_4$ is added. The tubes are placed on a programmable heating block and heated for three hours at 100°C, one hour at 140°C and ten hours at 190°C. One ml of 50% v/v HNO_3 is added to the dry residue remaining after the digestion, and heated for 30 minutes at 50°C to bring the sample into solution. On cooling, the solutions are finally made up to 10 ml with deionised water and decanted into polystyrene screw top storage tubes. Acid blank samples and standard reference materials are prepared with each batch of samples.

F.2.6 Data Quality

A summary of the results found for three NRCCRM standard materials (two soils and one stream sediment) taken through the partial acid extraction procedure are shown in Table F. In general the extraction gave repeatable values which had a low bias compared to the certified value. Since this is a partial not a total digestion, low values are to be expected.

ICP-AES limits of detection are listed in Table G.

Table F. Partial extraction analysis of international soil and stream sediment reference materials by ICP-AES.

	GBW07312 Stream sediment			GBW07402 Soil			GBW07402 Soil		
	Average Value µg/g	Standard Deviation (n=3)	Certified Value µg/g	Average Value µg/g	Standard Deviation (n=3)	Certified Value µg/g	Average Value µg/g	Standard Deviation (n=3)	Certified Value µg/g
Ca	7795	622	8290	14966	158	16867	223	17	679
Cd	5.6	0.3	4	1.1	0.2	0.1	4.3	0.5	0.5
Cu	1236	48	1230	13	1	16	141	2	144
Fe	33832	2126	34132	23817	314	24620	73555	2385	88267
Mg	2268	161	2834	5832	78	6272	3136	81	3679
Mn	817	12	1400	407	37	510	911	91	1360
Mo	5.6	0.4	8.4	<10		1.0	<10	15.9	4.6
Pb	250	6	285	10	1	20	577	26	552
V	34	1	47	43	2	62	117	1	166
Zn	525	50	498	38	3	42	520	9	494

Table G. ICP-AES limits of detection for Enshi soil analyses.

Element	LOD µg/g
Ca	5
Cd	0.8
Cu	0.5
Fe	2
Mg	10
Mn	0.1
Mo	4
Pb	4
V	1
Zn	0.5

F.3 Field Water Chemistry Methods

A detailed list of field water chemistry equipment is given in Fordyce (1996).

F.3.1 pH and Temperature

1. Remove the protective cap from the pH electrode and check that no air bubbles are trapped in the bulb at the end of the electrode. If air is present in the bulb, shake the electrode like a thermometer to remove the air. Connect the electrode and the temperature probe to the portable pH/Eh meter. Rinse the electrode and probe thoroughly with deionised water and dry them.

2. Switch on the meter holding the on/off button for a few seconds until the LCD display appears.

3. To calibrate the meter press the CAL button. The meter is now expecting the 4.01 calibration buffer solution. The first buffer solution measured during calibration is usually 7.01 therefore use the up arrow button to flick through the buffer solution options until 7.01 is selected. The meter is now ready to begin the calibration.

4. Place the pH electrode and the temperature probe in the first buffer (7.01) and wait for the reading to stabilise. The meter initially indicates that the reading is NOT READY and will flash a READY signal when the reading has stabilised. Once the READY signal has appeared and the reading is stable press the CFM (confirm) button. Record the pH and temperature readings.

5. The meter automatically expects the second buffer solution. Use the up and down arrow buttons to flick through the buffer solution options until the correct solution is selected (usually 4.01 for acid samples or 1.01 for alkaline samples). The meter is now ready to continue the calibration.

6. Rinse the electrode and temperature probe thoroughly in deionised water and dry them. Place the electrode and probe in the second buffer solution and wait for the READY signal before pressing the CFM (confirm) button. Note the pH reading. The calibration is now complete and the meter automatically switches to pH measurement mode.

7. To check the calibration, rinse the electrode and probe in deionised water, dry and return to the first buffer solution. The reading should stabilised around 7.01.

8. Rinse the electrode and temperature probe thoroughly in deionised water and dry them before measuring the first sample. Rinse the electrode and probe with some of the sample water in-between measuring each sample.

9. Store the pH electrode with the protective cap containing pH electrode storage solution over the end. Do not allow it to dry out. Care must be taken to avoid damage to the bulb at the end of the electrode.

10. If the electrode performance is not satisfactory on calibration try shaking it to remove any air from the bulb.

F.3.2 Redox Potential

1. Remove the protective cap from the redox (Eh) electrode and uncover the filling hole. Fill the electrode using Orion filling solution 90-00-11 to just below the filling hole. Empty the solution to waste by pushing the cap and body together and refill with solution ensuring that no bubbles are trapped around the electrode base. Connect the electrode and the temperature probe to the pH/Eh meter. Rinse the electrode and probe in deionised water and dry them.

2. Switch on the meter holding the on/off button for a few seconds until the LCD display appears.

3. Select the redox measurement function by pressing the RANGE button, mV will appear on the display.

4. To check the electrode performance place the electrode and probe in Zobelles solution. The value should settle between 200 and 250 mV, depending on the temperature.

5. Rinse the electrode and temperature probe thoroughly in deionised water and dry them before measuring the first sample. Rinse the electrode and probe with some of the sample water in-between measuring each sample.

6. The readings obtained require correction to redox potential relative to the standard hydrogen electrode according to the formula:

   Corrected Eh = Measured Eh + (224 - Temperature °C)

7. Prior to storage the electrode should be emptied and rinsed with deionised water. Store the electrode dry with the protective cap in place. A small amount of electrode storage solution should be added to the cap before storage.

F.3.3 Total Alkalinity

1. Select a sulphuric acid cartridge 1.6N or 0.16N according to the expected alkalinity of the samples.

2. Fit the cartridge to the hand held digital titrator and push the titrator piston down until it meets the top of the cartridge. Remove the cap from the cartridge and fit a feeder straw into the end of the cartridge. Wind the large wheel on the titrator until all the air is removed from the cartridge and the straw and a drop of acid leaves the end of the straw. Wipe the end of the straw to remove excess acid. Reset the titrator scale to zero by winding the small wheel to the left of the scale forwards.

3. Rinse the measuring cylinder and conical flask with deionised water prior to rinsing them with a small amount of the first sample. Using the measuring cylinder, measure 100 ml of the first sample into the conical flask.

4. Make sure the lid is securely tightened on the sample bottle in-between each stage of the measurements to reduce degassing of the samples.

5. Add a few (two) drops of bromocresol green indicator using a small pipette.

6. Add the acid using the large wheel on the titrator until the solution changes from blue to green-yellow and note the reading on the titrator scale when this occurs.

7. When the 0.16N cartridge is used the readings should be multiplied by 0.1.

8. The reading is the total alkalinity expressed as mg/l $CaCO_3$.

9. The titrator should be reset to zero and the conical flask and measuring cylinder rinsed in a small amount of the next sample prior to the next measurement.

10. Titrations should be carried out as quickly as possible to reduce degassing effects.

F.3.4 Conductivity

1. Remove the plastic cover from the conductivity probe and rinse the probe and the cover in deionised water. Dry the probe and the cover and replace the cover. Connect the conductivity probe to the conductivity meter.

2. Switch on the meter and place the probe in the 12.88 mS. calibration buffer solution making sure the solution covers the probe up to the join between the probe and the cover. The holes in the cover must be immersed in the solution.

3. Shake the probe in the solution to remove any air bubbles trapped between the probe and the cover. This is important as the probe measures conductivity in the volume of <u>liquid</u> defined by the cover therefore <u>air</u> trapped in the cover will affect the readings.

4. Press the CAL button and the 1413 µS indicator will be lit on the LCD display. Press the BUF button to change to the 12.88 mS calibration.

5. When the reading is stable and the calibration is within +/- 15% of the ideal value the BUF indicator on the display stops flashing and the CON indicator appears on the display. When the CON indicator appears press the CFM (confirm) button. The meter is now calibrated and will automatically return to measurement mode. To quit from calibration mode at any time press the CAL button.

6. Remove the plastic cover from the probe, rinse with deionised water and dry the probe and the cover prior to measuring each sample. Remember to cover the probe with sample up to the join between the cover and the probe and to remove air by shaking the probe.

7. The probe and cover should be rinsed in deionised water and dried before storage.

8. If the meter is difficult to calibrate try shaking the probe to remove air trapped under the cover.

F. 4 Determination of Major and Trace Anions by Ion Chromatography

Instrumentation

The ion chromatography system used for the anion analysis is a Dionex 2000i fitted with an auto sampler. An integral conductivity detection module and an additional on-line Philips PU4110 UV/VIS detector are used for analyte detection. The data were processed using a Dionex advanced computer interface and AI-450 data capture and manipulation software loaded onto a Dell personal computer

Theory

When a solvent containing dissolved anions is passed through a column of anion exchange resin, the progress of the anions through the column are retarded with respect to the solvent. Different anions are retained by different degrees according to their size and charge. The conductivities of the separated anions eluted from the column are detected as transient peaks and quantification may be achieved by comparing the peak area or peak height of the samples to those of known standards. For measurements to be accurate, the high background conductivity of the eluent is removed using chemical suppression. This relies on the exchange of sodium and hydrogen ions across a membrane to convert the sodium carbonate and sodium bicarbonate eluent to weakly conducting carbonic acid, and the weakly conducting anionic salts of the sample to more conductive anionic acids.

Analytical Method

Major and trace anions (Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, $S_2O_3^{2-}$ and Br) are determined using approximately 1 ml of unpreserved sample by ion chromatography. The instrument is calibrated at the start of the run and recalibrated after not more than 33 samples. Quality control check samples are analysed with each calibration and bracket the analytical samples. The analysis follows a pre-programmed schedule and the data are collected by the software with peaks identified by retention time. Quantitation is performed by comparing peak areas against a quadratic calibration curve based on the peak areas of standards over an appropriate concentration range. All raw data are stored on the computer's hard drive and can, if required, be re-integrated, for example using different standards.

The method is limited by the number of exchange sites available within the column. With the injection loop and column used in this study, solutions with total anion concentrations of up to 500 mg/l can be analysed; above this the column becomes overloaded, causing poor peak shapes, variable retention times and thus unreliable results. To overcome this problem, more concentrated solutions are diluted. Dilution is also used to bring the analyte concentration within the concentration range covered by the standards and to reduce sample viscosity.

F.5 Soil pH Methodology

(Based on British Standards Institute methods)

Equipment:

1. Orion pH meter equipped with a combination pH electrode
2. 50 ml glass beakers
3. Stirring rod

Reagents:

1. Standard buffer solution: pH 4.00 and pH 7.00
2. Deionised water

Procedure:

1. Calibrate the pH meter using the buffer solutions

2. Weigh out approximately 10 g of the sample and add approximately 5 ml of deionised water to the sample without stirring. Allow the sample to wet by capillary action and add more water as necessary to saturate the sample (no pooling of water or dry sample).

3. Stir the sample with the rod to form a thin paste adding more water or sample to keep the sample at saturation point. The paste should slide off the rod easily.

4. Carefully place the pH electrode into the paste and agitate to ensure contact between the paste and the electrode. Exercise care not to scratch the electrode.

5. Record pH reading.

APPENDIX G: REPORT ON BULK SOIL MINERALOGY IN TWO SELECTED SAMPLES.

BRITISH GEOLOGICAL SURVEY

Mineralogy and Petrology Group

Short Report No. MPSR/96/38R

X-ray diffraction analysis of five soil samples from China

V L Hards

INTRODUCTION

Five soil samples from China were supplied for X-ray diffraction (XRD) analysis by Dr. J. D. Appleton, Geochemistry Group, BGS. The methods employed and results obtained are outlined below.

LABORATORY METHODS

A representative, ~3g, sub-sample of each sample supplied was micronised under acetone for 10 minutes to ensure a fine and uniform particle size, and dried at 55°C. The resultant powders were then back-loaded into a standard aluminium sample holders.

XRD analysis was carried out using a Phillips PW1700 series diffractometer using Co-Kα radiation and operating at 45kV and 40mA. The mounted powders were scanned over the range 3-50 °2θ, at a scanning speed of 0.9 °2θ/minute. Diffraction data were analysed using Phillips APD1700 software coupled to a JCPDS database running on a DEC Micro Vax 2000 micro-computer system.

RESULTS

The results of semi-quantitative XRD analyses are summarised in Table 1 (overleaf). All of the soils show broadly similar mineralogy. All are dominantly composed of quartz, with minor amounts of calcite, dolomite, feldspar (either albite or albite and orthoclase) and mica. Trace amounts of gypsum, chlorite, smectite and ?amphibole were also detected.

Table 1. Summary of semi-quantitative XRD analyses

Sample	Major	Minor	Trace
C 14	Quartz	Calcite	Albite, orthoclase, mica, gypsum
C 15	Quartz	Dolomite	Albite, mica, chlorite, ?smectite
EN 78	Quartz	Albite, orthoclase, mica,	Chlorite, ?amphibole
EN 84	Quartz	Albite, orthoclase, mica	Chlorite
ZJ 44	Quartz	Albite, orthoclase, calcite	Dolomite, mica, chlorite, ?smectite

CONCLUSIONS

The presence of ferro-magnesian (Chlorite, ?amphibole) and feldspar minerals would seem to suggest that the samples are relatively immature soils.

In order to facilitate identification of any clay mineral species present, it is suggested that fine (<2μm) fractions are isolated and oriented mount XRD analysis is carried out.

APPENDIX H: IRMA ANALYTICAL METHODS

Determination of Selenium by Hydride Generation Atomic Fluorescence Spectrophotometer

LI Jiaxi Liu Xinping Liu Xiaoduan

APPARATUS AND OPERATING CONDITIONS

1. XGY-1011 Atomic Fluorescence Spectrophotometer
2. A VEKY-AF Hollow-Cathode Lamp of Selenium
   Lamp current: 100 mA
3. ZJ10-Auto-adding liquid equipment
4. Atomization Temperature: 800 ℃
5. Oven height: 6 mm
6. Carrier gas(Argon) flow rate: 1.2 L/min.
7. Reductant solution(0.8% KBH_4) flow rate: 1.2 ml/s.

REAGENTS

All chemicals are of extrapure grade, unless otherwise stated. Doubly distilled water is usede throughout for preparing solutions.

1. A selenium stock solution, 100 ug/ml, is prepared by dissolving 0.1405 g of SeO_2(analytical reagent grade, Beijing Chemical Ltd. China) in 20 ml of 4 mol/L HCI and diluting to 1000 ml with water.
2. The standard solution of selenium are prepared from the stock solution by serial diluting with 0.1 mol/L HCI.
3. Reductant solution is prepared by dissolving 8.0 g of analytical reagent grade KBH_4 in 200 ml of 1% KOH solution, the solution is filtered using vaccum filtration through a 0.45 um Millipore filter. Finaly, the solution is diluted to 1000 ml with water.
4. Collecting reagent is prepared by mixing 20 g of MgO and 80 g of Na_2CO_3 thoroughly.
5. Activated carbon(spectral reagent grade, Shanghai Chemical Ltd. China)

PREPARATION OF CALIBRATION GRAPH

Volumes of standard selenium solution covering the range 0.000- 1.000 ug of Se are transfered into 20-ml test tubes, 6 ml of concentrated HCI is added, and each solution is diluted to 20 ml with water. Take 2.0 ml of the solution into hydride generator to determine the fluorescence intensity of selenium.

PROCEDURE

1. Sample Preparation for Analysis of Soil Samples

Weigh 1.000 g of soil sample into a oxide of alumina crucible and add 0.15g A.C, mix thoroughly with a metal spatula or rod. Then cover 0.5 g of MgO and

1.5 g of collecting reagent carefully in that order. Put the crucible in a Mv oven, increase the oven tempereture from the room tempereture to 750 ℃ and hold at 750 ℃ for 45 min. Cool, then transfer the fusion block into a 50-ml Teflon beaker. Add 30 ml of water , put it on a hot-plate. Hold boiling for 25 min. Cool, transfer the solution into a 25-ml test tube and dilute to the scale with water.Take 10 ml of the above solution into a 20-ml test tube, add 6.5 ml of concentrated HCI, dilute to the scale with water. Put the tube into a water-bath at 70 ℃ for 40 min. in order to reduce Se(VI) to Se(IV). Take 2.0 ml of the solution into hydride generator to analyse selenium. Three sample blanks and three standard reference materials are prepared with each batch of samples.

2. Sample Preparation for Analysis of Hair and Grain Samples

Up to 0.1-0.5 g of sample is weighed into a 50-ml glass beaker, 10 ml of concentrated HNO_3 and 2 ml of concentrated $HCIO_4$ are added, then the beaker is covered with a watch-glass and placed on a hot-plate. the heating is stopped when dense white fumes of perchloric acid appeared. When the beaker is cooled to the room tempereture, 10 ml of 30%(v/v) HCI is added, the beaker is set in a water-bath at 70 ℃ for 40 min. in order to reduce Se(VI) to Se(IV). Transfer the solution into a 20-ml test tube and dilute to the scale with 30%(v/v) HCI. Take 2.0 ml of the solution into hydride generater to analyse selenium. Three sample blank and three standard reference materials are prepared with each batch of samples.

3. Sample Preparation for Analysis of Water samples

Take 20 ml of water sample into a 50-ml glass beaker, add 10 ml of concentrated HNO_3 and 2 ml of concentrated $HCIO_4$. Then the beaker is covered with a watch-glass and placed on a hot-plate. The hating is stopped when dense white fumse of perchloric acid appeares. When the beaker is cooled to the room temperature, 10 ml of 30%(v/v) HCI is added, then the beaker is set in a water-bath at 70 ℃ for 40 min.in order to reduce Se(VI) to Se(IV). Transfer the solution into a 20-ml test tube and dilute to the scale with 30%(v/v) HCI . Take 2.0 ml of the solution into hidride generater to analyse selenium. Three sample blank and three standard reference materials are prepared with each batch of samples.

Determination of Selenium
by Molecular Fluorescence Spectrophotometer

Li Jiaxi Liu Xinping Liu Xiaoduan

APPARATUS AND OPERATING CONDITIONS

1. HITACHI 650--40 Fluorescence Spectrophotometer
2. Xenon Lamp Power Supplier
3. HITACHI 056 Recorder
4. Excitation Wavelength: 380 nm Ex. Slit: 5 nm
   Emission Wavelength: 520 nm Em. Slit: 5 nm

REAGENTS

All chemicals are extrapure grade, unless otherwise stated. Doubly distilled water is used throughout for preparing solutions.

1. A selenium stock solution, 100 ug/ml, is prepared by dissolving 0.1405g SeO_2 (analytical reagent grade, Beijing Chemical Ltd. China) in 20 ml of 4 mol/L HCI and diluting to 1000 ml with water.
2. The standard solutions of selenium is prepared from the stock solution by serial dilution with 0.1 mol/L HCI.
3. 0.1% DAN (2,3-diaminophthalene) solution is prepared by dissolving 0.1g of DAN (2,3-diaminophthalene) in 100 ml of 0.1 mol/L HCI, and puried by cyclohexane at least 3 times, stored at a refrigerator.
4. Mixture solution is prepared by dissolving 9.3g of EDTA (disodium salt) and 2.0g of $NH_2OH.HCI$ in 200 ml of water and finally diluting to 500 ml with water.

PREPARATION OF CALIBRATION GRAPH

Volumes of standard selenium solution covering the range 0.000--1.000 ug of Se are transferred into 25-ml glass test tubes, each solution is diluted to 10 ml with water the pH is then adjusted to 1.5 with 7 mol/L ammonium hydroxide. 4 ml of mixture solution and 1.0 ml of 0.1% DNA solution are added in that order. After mixing, the tubes are set in a water-bath at 60 ℃ for 30 min. When the tubes is cooled to room temperature, 5.0 ml of cyclohexane is added, vigorously shaken for 1 min., then Se-DAN(4,5-benzopiaselenol) is extracted into cyclohexane. After layer is separated, the fluorescence intensity is measured at an excitation wavelength of 380 nm and an emission wavelength of 520 nm using a HITACHI 650-40 Fluorescence Spectrophotometer.

PROCEDURE

1. Sample Preparation for Analysis of Hair and Grain Samples

Up to 0.1--0.5g of soil is weighed into a 50-ml glass beaker, 10 ml of concentrated HNO_3 and 2 ml of concentrated $HClO_4$ are added, then the beaker is covered with a watch-class and placed on a hot-plate. The heating is stopped when dense white fumes of perchloric acid appears(baking must be avoided). When the beaker is cooled to the room temperature, 5 ml of 4 mol/L HCI is added. the beaker is set in a water-bath at 70 ℃ for 40 min. in order to reduce Se(VI) to Se(IV). Transfer the solution into a 25-ml test tube for subsequent analysis as described under the " PREPARATION OF CALIBRATION GRAPH " . Three sample blanks and three standard reference materials are prepared with each batch of samples.

2. Sample Preparation for Analysis of Soils

Up to 0.1--0.5 g of soil is weighed into a 50-ml Teflon beaker, 15 ml of concentrated HNO_3 and 3 ml of concentrated $HClO_4$ are added. The beaker is set on a hot-plate and heated until the brown fumes appears. Cool to the room temperature add 5 ml of concentrated HF, continue to heat until the dense white fumes of perchloric acid appears(baking must be avoided). After the beaker is cooled, 5 ml of 4 mol/L CHI is added, then the beaker is set in a water-bath at 70 ℃ for 40 min. in order to reduce Se(VI) to Se(IV). Transfer the solution into a 25-ml test tube for subsequent analysis as described under the " PREPARATION OF CALIBRATION GRAPH " Three sample blanks and three standard reference materials are prepared with each batch of samples.

3. Sample Preparation for Analysis of Water Samples

Take 20 ml of water sample into a 50-ml glass beaker, add 10 ml of concentrated HNO_3 and 2 ml of concentrated $HClO_4$. Then the beaker is covered with a watch-glass and set on a hot-plate. The heating is stopped when dense white fumes of perchloric acid appears. After the beaker is cooled to the room temperature, 5 ml 4 mol/L HCI is added, the beaker is set in a water-bath at 70 ℃ for 40 min. in order to reduce Se(VI) to Se(IV). Transfer the solution into a 25-ml test tube for subsequent analysis as described under the " PREPARATION OF CALIBRATION GRAPH " . Three sample blanks and three standard reference materials are prepared with each batch of samples.

MULTIELEMENTS ANALYSIS
IN SOIL SAMPLES BY ICP-AES

APPARATUS AND OPERATING CONDITIONS

1. Jarrell-Ash Mark III 1160 ICP-Spectrometer
2. Jarrell-Ash 2500 ICP-Generator
3. Jarrell-Ash Atomizer
4. Ar Flow Rate: Cooling Gas 17 L/min.
   Atomizing Gas 0.4 L/min.
5. Viewing Height: 17 mm
6. Integrating Time: 7 s
7. Solution Intake Rate: 3 ml/min.

STANDARD SOLUTIONS

1. Stock standard solutions are prepared by spectral grade metals or their compounds.

2. Standard solutions are prepared from the stock standard solution by appropriate dilution. The solutions are adjusted to 10% aqua regia solutions.

STD 1	10% aqua regia solution(including all elements)	0.01 ug/ml
STD 2	AI	500
	Fe, Ca, Mg, K,	250
	Ti, Na	100
STD 3	Ba, Bi, Co, Mn, Pb, Sr, Zn	10
STD 4	Be, Li, Ni, Mo	10
STD 5	Cd, Cr, Cu, P	10

CALIBRATION

Before samples are analyzed a calibration should be performed using the standard solutions that bracket the anticipated concentration range of the samples.

PROCEDURE

Weigh 0.1000 g of soil sample to a PTFE beaker, add 3 ml of HCI and 2 ml of HNO_3. The beaker is placed in a programmable heating plate and is heated at 110 C for 1.5 h. Then cool, add 3 ml of HF and 1 ml of $HCIO_4$, cover a lid, hold for 16 h without heating. Then, heat at 130 C for 2 h, take off the lid, continue to heat at 150 C until no perchloric white fume appears. Add 1.5 ml of HCI(1+1) and 0.5 ml HNO_3(1+1) to dissolve the dry residue. Transfer the solution into a 10-ml tube, dilute to the scale with water. Mix and store for subsequent analysis.

For analysis by ICP-MS an additional dilute is required.

Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analysis should be performed as soon as possible after the completed preparation.

Determination of Various Forms of Selenium in Water Samples by Molecular Fluorescence Spectrophotometer

Li Jiaxi Liu Xinping Liu Xiaoduan

APPARATUS AND OPERATING CONDITIONS

1. HITACHI 650--40 Fluorescence Spectrophotometer
2. Xenon Lamp Power Supplier
3. HITACHI 056 Recorder
4. Excitation Wavelength: 380 nm Ex. Slit: 5 nm
   Emission Wavelength: 520 nm Em. Slit: 5 nm

REAGENTS

All chemicals are extrapure grade, unless otherwise stated. Doubly distilled water is used throughout for preparing solutions.

1. A selenium stock solution, 100 ug/ml, is prepared by dissolving 0.1405g SeO_2 (analytical reagent grade, Beijing Chemical Ltd. China) in 20 ml of 4 mol/L HCI and diluting to 1000 ml with water.
2. The standard solutions of selenium is prepared from the stock solution by serial dilution with 0.1 mol/L HCI.
3. 0.1% DAN (2,3-diaminophthalene) solution is prepared by dissolving 0.1g of DAN (2,3-diaminophthalene) in 100 ml of 0.1 mol/L HCI, and puried by cyclohexane at least 3 times, stored at a refrigerator.
4. Mixture solution is prepared by dissolving 9.3g of EDTA (disodium salt) and 2.0g of $NH_2OH.HCI$ in 200 ml of water and finally diluting to 500 ml with water.

PREPARATION OF CALIBRATION GRAPH

Volumes of standard selenium solution covering the range 0.000--1.000 ug of Se are transferred into 25-ml glass test tubes, each solution is diluted to 10 ml with water the pH is then adjusted to 1.5 with 7 mol/L ammonium hydroxide. 4 ml of mixture solution and 1.0 ml of 0.1% DNA solution are added in that order. After mixing, the tubes are set in a water-bath at 60 ℃ for 30 min. When the tubes is cooled to room temperature, 5.0 ml of cyclohexane is added, vigorously shaken for 1 min., then Se-DAN(4,5-benzopiaselenol) is extracted into cyclohexane. After layer is separated, the fluorescence intensity is measured at an excitation wavelength of 380 nm and an emission wavelength of 520 nm using a HITACHI 650-40 Fluorescence Spectrophotometer.

PROCEDURE

1. Sample Preparation for Analysis of Total Se

Take 20 ml of water sample into a 50-ml glass beaker, add 10 ml of concentrated HNO_3 and 2 ml of concentrated $HClO_4$. Then the beaker is covered with a watch-glass and set on a hot-plate. The heating is stopped when dense white fumes of perchloric acid appears. After the beaker is cooled to the room temperature, 5 ml 4 mol/L HCI is added, the beaker is set in a water-bath at 70 ℃ for 40 min. in order to reduce Se(VI) to Se(IV). Transfer the solution into a 25-ml test tube for subsequent analysis as described under the " PREPARATION OF CALIBRATION GRAPH ". Three sample blanks and three standard reference materials are prepared with each batch of samples.

2. Sample Preparation for Analysis of Se(IV)
Take 10 ml of water sample into a 25-ml test tube for analysis as described under the " PREPARATION OF CALIBRATION GRAPH " . Sample blanks and standard reference are prepared with each batch of saples.

3. Sample Preparation for Analysis of Se(VI) + Se(IV)
Take 10 ml of water sample into a 25-ml test tube , add 4 ml of concentrated HCI. Put the tube in a water-bath at 70 C for 40 min. in order to reduce Se(VI) to Se(IV). The subsequent analysis steps are the same as described under the " PREPARATION OF CALIBRATION GRAPH ". Sample blanks and standard reference materials are prepared with each batch of samples.

4. Calculate the content of Se(VI)
$\mathrm{Se(VI)} = \mathrm{Se}_{tot} - \mathrm{Se(VI)}$

5.Calculate the content of Organic Se
Organic $\mathrm{Se} = \mathrm{Se}_{tot} - \mathrm{Se(VI)} - \mathrm{Se(IV)}$

Determination of Varioues Forms of Selenium in Water Samples by Hydride Generation Atomic Fluorescence Spectrophotometer

Li Jiaxi Liu Xinping Liuxiaoduan

APPARATUS AND OPERATING CONDITIONS

1. XGY-1011 Atomic Fluorescence Spectrophotometer
2. A VEKY-AF Hollow-Cathode Lamp of Selenium
   Lamp current: 100 mA
3. ZJ10-Auto-adding liquid equipment
4. Atomization Temperature: 800 ℃
5. Oven highth: 6 mm
6. Carrier gas(Argon) flow rate: 1.2 L/min.
7. Reductant solution(0.8% KBH_4) flow rate: 1.2 ml/s.

REAGENTS

All chemicals are of extrapure grade, unless otherwise stated. Doubly distilled water is used throughout for preparing solutions.

1. A selenium stock solution, 100 ug/ml, is prepared by dissolving 0.1405 g of SeO_2(analytical reagent grade, Beijing Chemical Ltd. China) in 20 ml of 4 mol/L HCI and diluting to 1000 ml with water.
2. The standard solution of selenium is prepared from the stock solution by serial diluting with 0.1 mol/L HCI.
3. Reductant solution is prepared by dissolving 8.0 g of analytical reagent grade KBH_4 in 200 ml of 1% KOH solution, the solution is filtered using vacuum filtration through a 0.45 um Millipore filter. Finally, the solution is diluted to 1000 ml with water.

PREPARATION OF CALIBRATION GRAPH

Volumes of standard selenium solution covering the range 0.000- 1.000 ug of Se are transferred into 20-ml test tubes, 6 ml of concentrated HCI is added, and each solution is diluted to 20 ml with water. Take 2.0 ml of the solution into hydride generator to determine the fluorescence intensity of selenium.

PROCEDURE

1. Sample Preparation for Analysis of Total Se

Take 20 ml of water sample into a 50-ml glass beaker, add 10 ml of concentrated HNO_3 and 2 ml of concentrated $HCIO_4$. Then the beaker is covered with a watch-glass and placed on a hot-plate. The hating is stopped when dense white fumes of perchloric acid appears. When the beaker is cooled to the room temperature, 10 ml of 30%(v/v) HCI is added, then the beaker is set in a water-bath at 70 ℃ for 40 min. in order to reduce Se(VI) to Se(IV). Transfer the solution into a 20-ml test tube and dilute to the scale with 30%(v/v) HCI . Take 2.0 ml of the solution into hidride generator to analyze selenium. Three sample blanks and three standard reference materials are prepared with each batch of samples.

2. Sample Preparation for Analysis of Se(IV)
Take 15 ml of water sample into a 25-ml test tube, add 7.5 ml concentrated HCI, dilute to the scale with doubly distilled water. Take 2.0 ml of the solution to analyze selenium. Sample blanks and standard reference materials are prepared with each batch of samples.

3. Sample Preparation for Analysis of Se(VI) + Se(IV)
Take 15 ml of water sample into a 25-ml test tube, add 7.5 ml concentrated HCI, dilute to the scale with doubly distilled water. Put the tube a water-bath at 70 C for 40 min. in order to reduce Se(VI) to Se(IV).Take 2.0 ml of the solution to analyze selenium. Sample blanks and standard reference materials are prepared with each batch of samples.

4. Calculate the content of Se(VI)
Se(VI) = $\mathrm{Se}_{t\,to}$- Se(IV)

5. Calculate the content of Organic Se
Organic Se = $\mathrm{Se}_{t\,to}$- Se(VI) - Se(IV)

APPENDIX I: CLASSICAL EXPERIMENTAL APPROACH ANOVA FOR SOIL CHEMISTRY PARAMETERS

Dependent Variable: Total Se

Due To	Sum of Squares	Deg Fre	Mean Square	F-stat	Signif	Var. Comp.	% of Varience	
Main Effects	584.328	7	83.475	122.923	0.0000	42.077		
Field Duplicate Pair	584.328	7	83.475	122.923	0.0000	41.39813571	98.3861	B
Explained	584.328	7	83.475	122.923	0.0000			
Error	5.433	8	0.679			0.679	1.6139	W
Total	589.760	15	39.317					

Dependent Variable: Ca

Due To	Sum of Squares	Deg Fre	Mean Square	F-stat	Signif	Var. Comp.	% of Varience	
Main Effects	14917873.714	6	2486312.286	15.547	0.0010	1323119.857		
Field Duplicate Pair	14917873.714	6	2486312.286	15.547	0.0010	1163192.429	87.9129	B
Explained	14917873.714	6	2486312.286	15.547	0.0010			
Error	1119492.000	7	159927.429			159927.429	12.0871	W
Total	16037365.714	13	1233643.516					

Dependent Variable: Cd

Due To	Sum of Squares	Deg Fre	Mean Square	F-stat	Signif	Var. Comp.	% of Varience	
Main Effects	400.699	7	57.243	26.726	0.0001	29.692		
Field Duplicate Pair	400.699	7	57.243	26.726	0.0001	27.55044643	92.7864	B
Explained	400.699	7	57.243	26.726	0.0001			
Error	17.135	8	2.142			2.142	7.2136	W
Total	417.834	15	27.856					

Dependent Variable: Cu

Due To	Sum of Squares	Deg Fre	Mean Square	F-stat	Signif	Var. Comp.	% of Varience	
Main Effects	15846.194	7	2263.742	89.673	0.0000	1144.493		
Field Duplicate Pair	15846.194	7	2263.742	89.673	0.0000	1119.248839	97.7943	B
Explained	15846.194	7	2263.742	89.673	0.0000			
Error	201.955	8	25.244			25.244	2.2057	W
Total	16048.149	15	1069.877					

Dependent Variable: Fe

Due To	Sum of Squares	Deg Fre	Mean Square	F-stat	Signif	Var. Comp.	% of Varience	
Main Effects	930900322.429	6	155150053.738	26.898	0.0002	80459034.798		
Field Duplicate Pair	930900322.429	6	155150053.738	26.898	0.0002	74691018.94	92.8311	B
Explained	930900322.429	6	155150053.738	26.898	0.0002			
Error	40376111.000	7	5768015.857			5768015.857	7.1689	W
Total	971276433.429	13	74713571.802					

Dependent Variable: Mg

Due To	Sum of Squares	Deg Fre	Mean Square	F-stat	Signif	Var. Comp.	% of Varience	
Main Effects	15604755.750	7	2229250.821	10.377	0.0018	1222040.286		
Field Duplicate Pair	15604755.750	7	2229250.821	10.377	0.0018	1007210.536	82.4204	B
Explained	15604755.750	7	2229250.821	10.377	0.0018			
Error	1718638.000	8	214829.750			214829.750	17.5796	W
Total	17323393.750	15	1154892.917					

Dependent Variable: V

Due To	Sum of Squares	Deg Fre	Mean Square	F-stat	Signif	Var. Comp.	% of Varience	
Main Effects	727663.774	7	103951.968	30.293	0.0000	53691.752		
Field Duplicate Pair	727663.774	7	103951.968	30.293	0.0000	50260.21545	93.6088	B
Explained	727663.774	7	103951.968	30.293	0.0000			
Error	27452.295	8	3431.537			3431.537	6.3912	W
Total	755116.069	15	50341.071					

Dependent Variable: Zn

Due To	Sum of Squares	Deg Fre	Mean Square	F-stat	Signif	Var. Comp.	% of Varience	
Main Effects	51113.629	7	7301.947	14.906	0.0005	3895.911		
Field Duplicate Pair	51113.629	7	7301.947	14.906	0.0005	3406.035714	87.4259	B
Explained	51113.629	7	7301.947	14.906	0.0005			
Error	3919.005	8	489.876			489.876	12.5741	W
Total	55032.634	15	3668.842					

Dependent Variable: LOI

Due To	Sum of Squares	Deg Fre	Mean Square	F-stat	Signif	Var. Comp.	% of Varience	
Main Effects	24.950	7	3.564	10.572	0.0017	1.951		
Field Duplicate Pair	24.950	7	3.564	10.572	0.0017	1.613552679	82.7167	B
Explained	24.950	7	3.564	10.572	0.0017			
Error	2.697	8	0.337			0.337	17.2833	W
Total	27.647	15	1.843					

B = Between-site varience W = Within-site varience

APPENDIX J: SPEARMAN RANK CORRELATION COEFFICIENTS FOR SELECTED SOIL PARAMETERS IN THE LK, HN AND HT VILLAGES

Spearman Rank correlation coefficients for BGS and selected IRMA parameters in soils in the LK villages.

	I Al	I K	I Na	I F	I S	I Ti	I P	I Ba	I Co	I Cr	I Li	I Ni	I As	I Hg	Total Se	LOI	pH	Water Sol Se	Ca	Cd	Cu	Fe	Mg	V
I K	0.678																							
I Na	-0.351	-0.683																						
I F	0.193	0.561	-0.276																					
I S	-0.299	-0.114	0.157	0.263																				
I Ti	0.921	0.667	-0.333	0.301	-0.105																			
I P	0.569	0.567	-0.283	0.644	-0.061	0.517																		
I Ba	0.527	0.333	0.200	0.050	-0.315	0.383	0.433																	
I Co	0.735	0.611	-0.577	0.319	-0.329	0.828	0.301	0.100																
I Cr	0.790	0.661	-0.301	0.601	-0.044	0.879	0.661	0.176	0.748															
I Li	0.427	0.483	-0.067	0.720	-0.166	0.550	0.583	0.117	0.527	0.828														
I Ni	0.703	0.800	-0.667	0.619	-0.297	0.733	0.517	0.117	0.895	0.812	0.683													
I As	0.443	0.756	-0.588	0.730	-0.163	0.487	0.698	-0.042	0.532	0.751	0.790	0.790												
I Hg	0.344	0.000	0.411	0.138	0.431	0.548	0.274	0.137	0.138	0.550	0.411	0.000	0.069											
Total Se	-0.544	-0.267	-0.350	0.050	0.324	-0.550	-0.333	-0.750	-0.201	-0.410	-0.417	-0.117	-0.109	-0.548										
LOI	0.410	-0.033	-0.367	-0.142	-0.280	0.417	-0.050	-0.283	0.678	0.335	0.050	0.450	0.050	0.000	0.611									
pH	0.151	0.233	0.383	0.243	-0.026	0.250	0.400	0.467	-0.100	0.326	0.550	-0.017	0.311	0.548	-0.453	-0.355								
Water Sol Se	-0.472	-0.034	-0.162	-0.176	-0.004	-0.393	-0.539	-0.017	-0.116	-0.605	-0.462	-0.188	-0.349	-0.562	0.139	-0.265	0.126							
Ca	-0.126	-0.217	0.550	0.427	0.376	-0.067	0.450	0.400	-0.326	0.050	0.217	-0.233	-0.092	0.411	-0.513	-0.607	0.598	0.094						
Cd	-0.192	-0.167	0.367	0.669	0.411	-0.100	0.417	0.083	-0.167	0.167	0.383	0.000	0.109	0.274	-0.358	-0.537	0.240	0.159	0.685					
Cu	0.393	0.067	-0.017	0.176	0.393	0.333	0.400	0.367	0.109	0.192	-0.183	0.067	-0.185	0.274	0.100	-0.020	-0.329	-0.163	-0.004	0.211				
Fe	0.603	0.633	-0.500	0.603	-0.297	0.583	0.433	-0.050	0.753	0.795	0.733	0.917	0.773	0.000	-0.101	0.412	0.007	-0.388	-0.182	0.103	0.158			
Mg	0.452	0.533	-0.133	0.745	-0.192	0.517	0.533	0.083	0.544	0.820	0.967	0.750	0.798	0.274	-0.299	-0.059	0.303	-0.253	0.388	0.292	-0.035	0.462		
V	-0.151	0.033	0.017	0.770	0.437	-0.067	0.583	-0.017	-0.092	0.209	0.350	0.133	0.319	0.137	0.207	0.228	-0.128	-0.077	0.210	0.443	0.157	0.361	0.218	
Zn	0.720	0.817	-0.700	0.628	-0.297	0.700	0.650	0.100	0.803	0.828	0.683	0.967	0.874	0.000	-0.150	0.372	0.060	-0.147	-0.032	0.032	-0.182	0.770	0.507	0.462
No. of Samples	9	9	9	9	9	9	9	9	9	9	9	9	9	9	25	25	25	25	25	25	25	25	25	25

Number of samples = 9 r95% = 0.582 Number of samples = 25 r95% = 0.337 (Koch & Link, 1970) I = IRMA Data

Spearman Rank correlation coefficients for BGS and selected IRMA parameters in soils in the HN villages

	I Al	I K	I Na	I F	I S	I Ti	I P	I Ba	I Co	I Cr	I Li	I Ni	I As	I Hg	Total Se	LOI	pH	Water Sol Se	Ca	Cd	Cu	Fe	Mg	V
I K	0.738																							
I Na	0.675	0.602																						
I F	-0.143	-0.571	0.012																					
I S	0.214	-0.071	0.675	0.405																				
I Ti	0.786	0.429	0.724	0.167	0.690																			
I P	0.214	-0.167	0.577	0.548	0.881	0.619																		
I Ba	0.571	0.952	0.442	-0.738	-0.262	0.167	-0.333																	
I Co	0.381	0.857	0.589	-0.595	-0.024	0.119	-0.143	0.905																
I Cr	-0.357	-0.857	-0.209	0.738	0.476	0.071	0.500	-0.952	-0.857															
I Li	0.293	-0.146	-0.063	0.317	-0.146	0.000	0.171	-0.122	-0.268	0.171														
I Ni	-0.143	-0.643	0.172	0.762	0.738	0.286	0.810	-0.762	-0.571	0.881	0.293													
I As	0.268	0.756	0.302	-0.756	-0.342	-0.073	-0.366	0.854	0.805	-0.878	-0.350	-0.781												
I Hg	-0.193	-0.651	0.149	0.892	0.663	0.217	0.771	-0.783	-0.566	0.855	0.284	0.964	-0.765											
Total Se	-0.214	-0.762	-0.098	0.714	0.548	0.167	0.571	-0.857	-0.762	0.952	0.342	0.929	-0.927	0.868										
LOI	0.476	0.071	0.577	0.429	0.810	0.881	0.643	-0.214	-0.167	0.429	-0.171	0.524	-0.366	0.482	0.602									
pH	-0.738	-0.452	-0.737	-0.190	-0.405	-0.714	-0.548	-0.262	-0.214	0.095	-0.171	-0.143	-0.268	-0.181	-0.012	-0.251								
Water Sol Se	-0.119	-0.690	-0.086	0.595	0.429	0.095	0.476	-0.738	-0.690	0.857	0.537	0.857	-0.854	0.771	0.825	0.319	0.029							
Ca	-0.857	-0.500	-0.749	-0.119	-0.333	-0.690	-0.429	-0.333	-0.238	0.119	-0.366	-0.119	-0.220	-0.120	0.204	0.196	0.613	0.238						
Cd	-0.333	-0.833	-0.184	0.643	0.524	0.095	0.548	-0.905	-0.810	0.976	0.220	0.905	-0.878	0.831	0.894	0.459	0.029	0.821	0.298					
Cu	0.190	-0.238	0.442	0.524	0.929	0.714	0.857	-0.452	-0.310	0.643	-0.024	0.810	-0.586	0.723	0.847	0.688	-0.257	0.673	0.012	0.753				
Fe	0.548	0.524	0.675	-0.214	0.524	0.738	0.262	0.333	0.333	-0.143	-0.561	-0.071	0.342	-0.133	0.034	0.405	-0.636	-0.033	-0.402	0.082	0.433			
Mg	-0.381	-0.190	-0.393	0.119	-0.357	-0.548	-0.286	-0.048	0.048	-0.095	0.366	-0.048	-0.268	0.012	-0.019	-0.155	0.606	0.000	0.370	-0.031	-0.102	-0.389		
V	-0.238	-0.738	-0.258	0.571	0.405	0.167	0.310	-0.857	-0.857	0.929	0.049	0.714	-0.854	0.651	0.950	0.558	0.063	0.760	0.192	0.874	0.804	0.069	-0.102	
Zn	-0.286	-0.762	-0.037	0.619	0.643	0.167	0.690	-0.833	-0.690	0.929	0.220	0.952	-0.805	0.868	0.807	0.447	-0.024	0.623	0.050	0.880	0.752	0.207	0.016	0.790
No. of Samples	8	8	8	8	8	8	8	8	8	8	8	8	8	8	25	25	25	25	25	25	25	25	25	25

Number of samples = 8 r95% = 0.621 Number of samples = 25 r95% = 0.337 (Koch & Link, 1970) I = IRMA Data

Spearman Rank correlation coefficients for selected BGS and IRMA parameters in soils in the HT villages

	I Al	I K	I Na	I F	I S	I Ti	I P	I Ba	I Co	I Cr	I Li	I Ni	I As	I Hg	Total Se	LOI	pH	Water Sol Se	Ca	Cd	Cu	Fe	Mg	V
I K	0.855																							
I Na	0.853	0.755																						
I F	0.565	0.462	0.431																					
I S	0.543	0.268	0.346	0.606																				
I Ti	0.770	0.467	0.571	0.207	0.378																			
I P	0.455	0.127	0.153	0.729	0.799	0.479																		
I Ba	0.188	0.382	0.436	-0.432	-0.506	0.115	-0.709																	
I Co	0.248	0.297	-0.129	0.134	0.146	0.309	0.297	-0.127																
I Cr	0.103	-0.152	-0.172	0.610	0.743	0.024	0.833	-0.924	0.134															
I Li	0.006	0.383	0.025	0.311	-0.165	-0.426	-0.195	0.274	0.195	-0.210														
I Ni	0.382	0.139	0.043	0.559	0.860	0.309	0.818	-0.758	0.188	0.888	-0.298													
I As	0.128	0.018	-0.130	0.644	0.683	0.000	0.807	-0.826	0.422	0.865	0.046	0.734												
I Hg	0.042	-0.212	-0.166	0.632	0.726	-0.042	0.806	-0.927	0.030	0.985	-0.188	0.842	0.844											
Total Se	0.127	-0.103	-0.092	0.638	0.665	0.091	0.842	-0.927	0.067	0.942	-0.280	0.842	0.862	0.939										
LOI	0.588	0.442	0.350	0.942	0.695	0.358	0.867	-0.576	0.236	0.717	0.116	0.733	0.752	0.709	0.746									
pH	-0.450	-0.243	-0.271	-0.034	-0.523	-0.559	-0.419	0.122	-0.602	-0.235	0.387	-0.371	-0.414	-0.146	-0.341	-0.227								
Water Sol Se	0.042	0.127	-0.055	0.432	0.104	-0.067	0.382	-0.345	-0.224	0.322	0.243	0.273	0.330	0.321	0.257	0.165	0.417							
Ca	0.030	0.309	0.215	0.146	-0.305	-0.285	-0.273	0.442	-0.370	-0.377	0.687	-0.430	-0.275	-0.345	-0.448	-0.166	0.546	0.471						
Cd	0.297	0.103	0.031	0.669	0.793	0.176	0.770	-0.794	0.115	0.875	-0.182	0.939	0.734	0.879	0.806	0.710	-0.088	0.408	-0.172					
Cu	0.321	0.006	0.080	0.596	0.701	0.370	0.891	-0.818	0.103	0.869	-0.456	0.855	0.771	0.842	0.925	0.844	-0.330	0.198	-0.428	0.837				
Fe	0.588	0.333	0.301	0.833	0.683	0.552	0.927	-0.600	0.382	0.705	-0.103	0.733	0.734	0.685	0.612	0.768	-0.207	0.189	-0.161	0.718	0.742			
Mg	0.552	0.794	0.558	0.681	0.201	0.030	0.115	0.176	0.236	-0.024	0.705	0.055	0.220	-0.006	0.032	0.409	-0.065	-0.092	0.133	0.240	0.179	0.388		
V	-0.091	-0.285	-0.362	0.480	0.610	-0.042	0.770	-0.988	0.200	0.942	-0.243	0.818	0.881	0.939	0.915	0.635	-0.255	0.143	-0.489	0.723	0.841	0.442	-0.155	
Zn	0.248	0.042	-0.067	0.584	0.835	0.115	0.794	-0.830	0.164	0.948	-0.195	0.976	0.807	0.915	0.902	0.665	-0.299	0.138	-0.456	0.840	0.895	0.563	0.139	0.892
No. of Samples	10	10	10	10	10	10	10	10	10	10	10	10	10	10	25	25	25	25	25	25	25	25	25	25

Number of samples = 10 r95% = 0.549 Number of samples = 25 r95% = 0.337 (Koch & Link, 1970) I = IRMA Data

Spearman Rank correlation coefficients for BGS and selected IRMA parameters in soils in the HN and HT villages

	I Al	I K	I Na	I F	I S	I Ti	I P	I Ba	I Co	I Cr	I Li	I Ni	I As	I Hg	Total Se	LOI	pH	Water Sol Se	Ca	Cd	Cu	Fe	Mg	V
I K	0.858																							
I Na	0.820	0.777																						
I F	0.534	0.477	0.472																					
I S	0.034	-0.179	0.088	0.082																				
I Ti	0.820	0.548	0.664	0.396	0.119																			
I P	0.234	-0.066	0.116	0.342	0.759	0.340																		
I Ba	0.386	0.591	0.506	-0.226	-0.474	0.210	-0.621																	
I Co	0.498	0.544	0.350	0.262	-0.205	0.334	0.023	0.398																
I Cr	-0.193	-0.445	-0.332	0.300	0.639	-0.069	0.686	-0.918	-0.422															
I Li	0.215	0.418	0.034	0.376	-0.260	-0.046	-0.237	0.196	0.273	-0.163														
I Ni	0.049	-0.224	-0.080	0.395	0.719	0.143	0.814	-0.787	-0.194	0.913	-0.138													
I As	0.019	0.111	-0.115	-0.088	0.115	-0.271	0.302	-0.114	0.395	0.021	-0.042	0.044												
I Hg	0.004	-0.243	-0.111	0.508	0.631	0.001	0.785	-0.844	-0.187	0.895	-0.065	0.925	0.167											
Total Se	0.112	-0.182	-0.007	0.586	0.580	0.216	0.740	-0.814	-0.180	0.891	-0.059	0.899	-0.030	0.923										
LOI	0.443	0.243	0.361	0.442	0.691	0.459	0.752	-0.409	0.092	0.503	-0.079	0.571	0.228	0.570	0.612									
pH	-0.446	-0.203	-0.283	-0.016	-0.300	-0.493	-0.371	-0.110	-0.493	0.084	0.111	-0.118	-0.317	-0.075	-0.171	-0.235								
Water Sol Se	-0.018	-0.106	-0.101	0.440	0.189	0.112	0.319	-0.533	-0.398	0.643	0.305	0.604	-0.385	0.544	0.660	0.222	0.159							
Ca	-0.410	-0.038	-0.124	-0.099	-0.138	-0.389	-0.319	0.117	-0.353	-0.124	0.122	-0.249	-0.216	-0.295	-0.160	0.000	0.600	0.239						
Cd	-0.053	-0.275	-0.152	0.337	0.646	0.003	0.631	-0.803	-0.339	0.922	-0.062	0.893	-0.025	0.834	0.845	0.520	-0.022	0.686	0.053					
Cu	0.383	0.062	0.269	0.547	0.633	0.430	0.841	-0.604	0.039	0.710	-0.254	0.822	0.156	0.833	0.868	0.708	-0.326	0.477	-0.285	0.781				
Fe	0.595	0.371	0.478	0.405	0.396	0.554	0.626	-0.177	0.418	0.202	-0.202	0.317	0.467	0.359	0.350	0.575	-0.509	0.126	-0.362	0.331	0.642			
Mg	0.245	0.520	0.279	0.536	-0.016	-0.084	-0.065	0.101	0.177	0.001	0.492	0.049	-0.030	0.071	0.095	0.138	0.222	0.024	0.163	0.157	0.178	0.072		
V	-0.288	-0.510	-0.425	0.163	0.607	-0.121	0.608	-0.920	-0.419	0.946	-0.219	0.794	0.091	0.795	0.910	0.532	-0.068	0.548	-0.150	0.807	0.765	0.228	-0.090	
Zn	-0.077	-0.335	-0.198	0.354	0.720	0.005	0.738	-0.837	-0.299	0.954	-0.084	0.967	0.024	0.927	0.817	0.517	-0.157	0.408	-0.219	0.854	0.805	0.366	0.123	0.825
No. of Samples	18	18	18	18	18	18	18	18	18	18	18	18	18	18	50	50	50	50	50	50	50	50	50	50

Number of samples = 18 r95% = 0.400 Number of samples = 50 r95% = 0.235 (Koch & Link, 1970) I = IRMA Data

APPENDIX K: FACTOR ANALYSIS OF SELECTED SOIL PARAMETERS IN THE LK, HN AND HT VILLAGES

LK Villages

Factor Analysis Summary

Number of Variables	11
Est. Number of Factors	5
Number of Factors	4
Number of Cases	25
Number Missing	0
Degrees of Freedom	65
Bartlett's Chi Square	•
P-Value	•

Factor Extraction Method: Principal Components
Extraction Rule: Method Default
Transformation Method: Orthotran/Varimax
The correlation matrix is singular.

Eigenvalues

	Magnitude	Variance Prop.
Value 1	3.473	.316
Value 2	3.135	.285
Value 3	1.267	.115
Value 4	.921	.084
Value 5	.771	.070

Oblique Solution Primary Pattern Matrix

	Factor 1	Factor 2	Factor 3	Factor 4
Tot Se	-.026	.685	.298	.487
LOI	.455	.729	.126	.154
pH	.172	-.720	-.248	.157
WSol Se	-.005	-.136	-.025	.931
Ca	-.100	-.873	.083	.088
Cd	-.003	.001	.949	.011
Cu	.948	.101	.012	-.028
Fe	.948	.101	.012	-.028
Mg	.720	-.497	.230	-.047
V	-.195	.690	-.249	-.200
Zn	.905	-.057	-.174	.079

HN Villages

Factor Analysis Summary

Number of Variables	11
Est. Number of Factors	5
Number of Factors	3
Number of Cases	25
Number Missing	0
Degrees of Freedom	65
Bartlett's Chi Square	340.701
P-Value	<.0001

Factor Extraction Method: Principal Components
Extraction Rule: Method Default
Transformation Method: Orthotran/Varimax

Eigenvalues

	Magnitude	Variance Prop.
Value 1	5.468	.497
Value 2	2.539	.231
Value 3	1.011	.092
Value 4	.805	.073
Value 5	.433	.039

Oblique Solution Primary Pattern Matrix

	Factor 1	Factor 2	Factor 3
Tot Se	.927	-.026	.113
LOI	.312	-.377	.694
pH	-.088	.860	.224
WSol Se	.842	.046	.081
Ca	.002	.547	.744
Cd	.956	.001	-.041
Cu	.753	-.326	.226
Fe	.038	-.839	.119
Mg	.120	.756	-.113
V	.922	.045	.087
Zn	.963	.099	-.224

HT Villages

Factor Analysis Summary

Number of Variables	11
Est. Number of Factors	5
Number of Factors	3
Number of Cases	25
Number Missing	0
Degrees of Freedom	65
Bartlett's Chi Square	364.180
P-Value	<.0001

Factor Extraction Method: Principal Components
Extraction Rule: Method Default
Transformation Method: Orthotran/Varimax

Eigenvalues

	Magnitude	Variance Prop.
Value 1	5.939	.540
Value 2	2.080	.189
Value 3	1.619	.147
Value 4	.436	.040
Value 5	.347	.032

Oblique Solution Primary Pattern Matrix

	Factor 1	Factor 2	Factor 3
Tot Se	1.117	-.012	-.210
LOI	.271	.072	.726
pH	-.037	.872	.073
WSol Se	.841	.953	-.336
Ca	-.257	.807	.182
Cd	.882	.276	.162
Cu	.789	-.036	.209
Fe	.011	-.065	.909
Mg	-.892	-.022	1.439
V	1.376	-.020	-.679
Zn	1.025	-.077	-.135

HN/HT Villages

Factor Analysis Summary

Number of Variables	11
Est. Number of Factors	5
Number of Factors	3
Number of Cases	50
Number Missing	0
Degrees of Freedom	65
Bartlett's Chi Square	555.112
P-Value	<.0001

Factor Extraction Method: Principal Components
Extraction Rule: Method Default
Transformation Method: Orthotran/Varimax

Eigenvalues

	Magnitude	Variance Prop.
Value 1	5.344	.486
Value 2	2.057	.187
Value 3	1.156	.105
Value 4	.910	.083
Value 5	.557	.051

Oblique Solution Primary Pattern Matrix

	Factor 1	Factor 2	Factor 3
Tot Se	.950	-.029	-.007
LOI	.588	-.180	.372
pH	.005	.867	.227
WSol Se	.836	.385	-.229
Ca	.151	.836	.173
Cd	.950	.103	.008
Cu	.785	-.284	.217
Fe	.162	-.686	.262
Mg	-.056	.230	.884
V	.944	.063	-.174
Zn	.822	-.075	.134

APPENDIX L: DETAILS OF FIELD SAMPLING TEAM

Main Sampling Team

Prof Zhang Guangdi, Project Manager	Institute of Rock and Mineral Analysis Chinese Academy of Geological Sciences Baiwanzhuang Road 26 Beijing 100037 China Tel: 0086 10 68311133 Fax: 0086 10 68320365
Ms Ge Xiaoli, Geochemist	"
Prof Mao Dajun, Research Fellow	Institute of Epidemic Prevention Department of Public Health Enshi
Dr Su Hongcan, Director	"
Mr Zhang Xianying, Driver	"
Ms Fiona Fordyce, Geochemist	British Geological Survey Keyworth Nottingham NG12 5GG UK Tel: 0044 (0)1159 363221 Fax: 0044 (0)1159 363329 Email: f.fordyce@BGS.ac.uk

Sampling of Luojiaba
Guide: Mr Hu, Village Doctor, Luojiaba
Soil sampling: Prof Zhang, Dr Su and Ms Fordyce
Grain sampling: Prof Mao and Ms Ge
Water sampling: Ms Ge and Ms Fordyce
Hair sampling: Prof Mao and Ms Ge

Sampling of Bajiao
Arrangements: Mr Wu Ben Chao, Vice Mayor, Enshi City
Guide: Mr Wang, Director, Bajiao Community
Soil sampling: Prof Zhang, Dr Su and Ms Fordyce
Grain sampling: Ms Ge
Water sampling: Ms Ge and Ms Fordyce
Hair sampling: Prof Mao with local hair dresser

Sampling of Shadi
Arrangements: Mr Wu Ben Chao; Mr Huang, Director, Shadi Community; Mr Faj, Deputy Director of Shadi Community and Mr He, Secretary of Shadi Community.
Guides: Mr Wu Ben Chao and Mr Faj
Soil sampling: Prof Zhang, Dr Su, Ms Ge and Ms Fordyce and Mr Wu
Grain sampling: Ms Ge and Mr Faj
Water sampling: Ms Ge and Ms Fordyce
Hair sampling: Prof Mao and Mr Faj with local hair dresser

Sampling of Huabei
Arrangements: Mr Wu Ben Chao; Mr Huang, Director, Shadi Community; Mr Faj, Deputy Director of Shadi Community and Mr He, Secretary of Shadi Community.
Guides: Mr Wu Ben Chao, Mr Faj and local officials from Huabei village

Soil sampling: Prof Zhang, Dr Su, Ms Fordyce and Mr Wu
Grain sampling: Ms Ge, Mr Wu and Mr Faj
Water sampling: Ms Ge and Ms Fordyce
Hair sampling: Prof Mao, Ms Ge and Mr Faj with local hair dresser

Sampling of Xin Tang

Arrangements: Mr Zhang, Director, Xin Tang Community and Mr Huang, Secretary, Xin Tang Community.
Guide: Mr Huang
Soil sampling: Prof Zhang, Dr Su, Ms Fordyce and Mr Zhang
Grain sampling: Ms Ge and Mr Zhang
Water sampling: Ms Ge and Ms Fordyce
Hair sampling: Prof Mao with local hair dresser

Sampling of Yu Tang Ba

Arrangements: Mr Xu, Director, Shuang He Community
and Guide
Soil sampling: Prof Zhang, Dr Su and Ms Fordyce
Grain sampling: Ms Ge and Mr Xu
Water sampling: Ms Ge and Ms Fordyce
Hair sampling: Prof Mao, Ms Ge with local hair dresser

Sampling of Shatou

Arrangements: Mr Luo, Secretary of Shunmuying Community
and Guide
Soil sampling: Prof Zhang, Dr Su, Ms Ge, Ms Fordyce and Mr Luo
Grain sampling: Ms Ge and Mr Luo
Water sampling: Ms Ge and Ms Fordyce
Hair sampling: Prof Mao with local hair dresser

Sampling of Fangjiaping

Arrangements: Mr Luo and local officials from Fangjiaping village
and Guides
Soil sampling: Prof Zhang, Dr Su, Ms Ge and Ms Fordyce
Grain sampling: Ms Ge and Mr Luo
Water sampling: Ms Ge and Ms Fordyce
Hair sampling: Prof Mao and Ms Ge with local hair dresser

Sampling of Xiao Guan

Arrangements: Mr Cheng, Director, Xuan 'en County
Guide: Mr Yu, Xuan 'en County Government Office
Soil sampling: Dr Su, Ms Ge and Ms Fordyce
Grain sampling: Prof Mao and Ms Ge
Water sampling: Ms Ge and Ms Fordyce
Hair sampling: Prof Mao and Prof Zhang with local hair dresser

Sampling of Chang Ping

Arrangements: Director of Public Health, Lichuan County
Guides: Mr Cheng, Director of the Public Hospital, Mou Dao
Mr Cheng, Public Health Department, Lichuan County
Soil sampling: Prof Zhang, Dr Su, Ms Ge, Ms Fordyce and Mr Cheng
Grain sampling: Ms Ge and Mr Cheng
Water sampling: Ms Ge, Ms Fordyce and Mr Cheng
Hair sampling: Prof Mao and Mr Cheng with local hair dresser

Sampling of Zhi Luo

Arrangements: Director of Public Health, Lichuan County
Guides: Mr Cheng, Director of the Public Hospital, Mou Dao

Mr Cheng, Public Health Department, Lichuan County
Soil sampling: Prof Zhang, Dr Su, Ms Ge, Ms Fordyce and Mr Cheng
Grain sampling: Ms Ge, Prof Mao and Mr Cheng
Water sampling: Ms Ge and Ms Fordyce
Hair sampling: Prof Mao and Mr Cheng with local hair dresser

Sampling of Ming Shen
Arrangements: Director of Public Health, Lichuan County
Guides: Mr Cheng, Director of the Public Hospital, Mou Dao
Mr Cheng, Public Health Department, Lichuan County
Soil sampling: Dr Su, Ms Ge, Ms Fordyce and Mr Cheng
Grain sampling: Ms Ge and Mr Cheng
Water sampling: Ms Ge and Ms Fordyce
Hair sampling: Prof Mao, Prof Zhang and Mr Cheng with local hair dresser

Sampling of Nan Pu
Arrangements: Director of Public Health, Lichuan County
Guides: Mr Cheng, Director of the Public Hospital, Mou Dao
Mr Cheng, Public Health Department, Lichuan County
Soil sampling: Prof Zhang, Dr Su, Ms Ge, Ms Fordyce and Mr Cheng
Grain sampling: Prof Zhang and Ms Ge
Water sampling: Ms Ge and Ms Fordyce
Hair sampling: Prof Mao, Prof Zhang and Mr Cheng with local hair dresser

Sampling of Ji Chang
Arrangements: Director of Public Health, Lichuan County
Guides: Mr Cheng, Public Health Department, Lichuan County
Headman of Ji Chang village
Soil sampling: Prof Zhang, Dr Su, Ms Ge, Ms Fordyce and Mr Cheng
Grain sampling: Ms Ge and Mr Cheng
Water sampling: Ms Ge and Ms Fordyce
Hair sampling: Prof Mao with local hair dresser

Sampling of Zishengqiao
Arrangements: Director of Public Health, Lichuan County
Guide: Mr Cheng, Public Health Department, Lichuan County
Soil sampling: Prof Zhang, Dr Su, Ms Ge, Ms Fordyce and Mr Cheng
Grain sampling: Ms Ge and Mr Cheng
Water sampling: Ms Ge and Ms Fordyce
Hair sampling: Prof Mao with local hair dresser

APPENDIX M: LISTING OF ANALYTICAL RESULTS

DATA LISTING FOR BGS SOIL SAMPLES

Sample Number	Total Se µg/g	Water Soluble Se ng/g	Ca µg/g	Cd µg/g	Cu µg/g	Fe µg/g	Mg µg/g	Mn µg/g	Mo µg/g	Pb µg/g	V µg/g	Zn µg/g	LOI %	pH	TOC %	CEC meq/ 100g	Village Code
1/99	5.225	44.250	7017	3.9	38.2	25881	3877	251	10.2	16.7	302	99	6.6	7.11			HT3
2/92	0.172	0.420	4783	2.2	22.2	25152	5035	251	6.4	9.7	174	53	5.3	4.53			LK5
3	3.728	17.100	3192	4.8	42.9	28432	3980	75	15.1	17.4	314	108	6.3	6.61			HT3
4	12.258	31.000	3391	11.5	78.1	44894	5284	915	24.2	21.8	752	198	7.8	6.76			HT2
5/60	0.228	0.220	1008	0.3	12.3	35696	5486	194	1.8	1.8	49	61	7.2	4.56			LK1
6	0.050	0.410	4475	1.6	6.0	35857	9266	528	3.0	3.0	55	81	4.4	5.19			LK4
7A	5.50	3.200	852	1.5	29.4	24454	3190	236	33.0	3.5	262.5	66.2	5.33	5.56			HT3
7B	3.72	1.060	888	1.4	23.7	28071	3711	207	23.5	3.3	182.4	67.9	5.20	5.52			HT3
7C	1.69	2.250	481	0.6	6.2	38634	5749	55	6.2	2.9	36.3	74.8	5.58	5.36			HT3
8	0.105	0.110	1305	0.5	13.3	38812	8065	357	2.3	2.3	48	73	6.5	5.84			LK1
9	0.065	0.490	4144	1.5	8.9	31857	9151	455	3.0	3.1	50	64	4.3	5.74			LK2
11	0.168	0.300	2162	0.6	5.5	20781	5515	257	2.9	2.9	43	57	6.3	5.10	1.49	12.2	LK5
12	0.180	2.200	2523	0.5	11.3	30661	5769	421	2.3	2.3	51	68	6.5	5.86	1.24	15.0	LK4
13	3.447	0.990	6111	4.8	38.0	33086	4948	1065	8.5	20.1	230	128	9.7	6.90			HN3
14	0.123	5.480	2967	1.9	14.7	39611	7006	822	2.3	2.3	62	78	5.1	5.66			LK4
15	33.765	63.100	2746	65.8	96.0	49394	3635	248	135.7	15.0	2154	336	9.0	5.26			HN2
16	11.262	107.000	6508	12.8	82.2	47186	5173	624	22.3	3.0	391	148	9.2	7.72			HT1
17	14.955	45.900	5420	13.6	80.6	54323	5534	284	6.2	2.8	276	137	10.7	6.90			HT1
18/49	11.400	81.750	4671	15.6	52.5	24567	5271	530	36.3	17.8	676	204	6.6	6.94			HN1
19/39	16.100	18.250	2433	7.8	91.5	47570	4853	603	32.5	16.0	420	146	8.8	6.08			HT1
20/42	0.117	0.680	2661	1.5	10.8	31102	7691	565	2.8	2.8	51	68	5.1	5.66			LK3
21	4.451	4.610	3362	5.2	61.5	46259	7839	576	4.0	3.1	163	104	9.0	6.67			HT4
23	7.270	1.910	3236	5.3	64.4	49816	5095	1155	22.5	22.4	298	166	11.0	6.00			HN3
24	0.096	0.150	3362	1.7	13.7	40110	11954	472	3.6	3.6	64	84	6.3	5.45			LK2
25	0.071	0.210	4497	1.9	13.6	41985	12981	442	2.8	3.5	61	90	6.2	5.32			LK1
26	10.800	37.900	6490	12.3	52.6	37886	5037	390	57.7	3.4	948	148	8.4	7.79			HN2
27	0.165	0.150	3287	0.6	6.6	37983	8420	508	2.8	2.8	63	86	6.7	5.88			LK5
28	18.512	26.200	2674	7.9	97.6	44193	4635	872	44.4	17.0	478.4	151.1	9.79	5.88			HT1
29	0.136	0.150	1562	1.5	11.3	38322	11478	411	3.2	3.2	60	82	6.3	5.06			LK3
30	0.127	0.027	2019	0.6	4.4	21577	5270	255	3.0	3.0	43.0	53.5	4.96	5.39			LK5
31	0.171	1.150	2206	0.5	7.4	31399	7304	429	2.6	2.6	54	78	6.6	5.46			LK5
32	15.467	12.650	6158	13.6	95.3	30798	12682	846	23.5	27.1	729	358	8.6	7.74			HN1
33	0.086	0.230	3480	1.4	10.9	29310	8511	386	3.5	3.5	53	65	5.4	7.01			LK2
34	7.429	261.000	9284	4.1	35.9	28345	4182	117	8.4	18.0	167	101	9.0	7.71	1.96	14.4	HT3
35	15.330	7.380	2787	33.9	92.6	39539	5872	247	38.9	24.2	390	414	10.3	6.16			HT5
36	7.700	3.270	4622	5.4	61.3	47424	5149	1229	26.8	2.5	295.2	168.0	10.22	6.91			HN3
37	25.411	65.700	4225	21.3	89.4	41465	7170	748	37.7	24.6	795	221	9.4	7.43			HT2
38	3.782	13.300	2551	1.9	17.2	26763	3474	562	5.8	16.2	160	69	5.7	7.16			HT3
40/93	12.550	13.720	2861	9.1	88.3	41227	5661	484	57.7	2.8	343	176	8.1	4.46			HT5
41	22.080	71.900	8069	18.0	62.0	22100	7532	539	34.2	18.4	804	251	8.0	7.29			HN1
43	0.106	0.160	2482	0.7	11.9	25499	6812	495	3.5	3.5	51	56	4.8	5.84			LK3
44	0.156	0.520	1297	1.5	11.2	37590	10109	473	3.0	3.1	54	83	5.9	4.88	0.52	17.0	LK3
45	35.003	153.000	12107	8.8	75.6	23246	5757	293	48.9	12.9	1775	121	12.0	7.63	4.45	27.9	HN1
46	18.830	76.900	3841	12.6	57.5	20418	4765	260	28.9	11.3	999	176	7.6	7.02			HN1
47	0.093	0.670	2258	1.8	15.3	32361	6621	395	3.5	3.5	51	59	4.3	5.15			LK1
48	18.671	30.200	3601	7.7	94.7	46920	5006	716	26.9	2.2	396	175	9.4	6.02	2.46	24.3	HT5
50	0.074	0.340	6895	1.6	11.1	32173	11020	448	2.7	2.7	50	68	4.3	6.92	0.31	19.5	LK2
51	4.885	1.380	5394	4.5	44.8	36423	4710	1100	13.8	18.0	285	131	9.4	7.28			HN3
52	2.833	6.690	5462	3.7	32.5	23726	3653	340	4.6	20.4	247	112	6.8	7.78			HN4
53	0.083	0.350	3135	1.5	6.2	31280	6936	389	2.6	2.6	52	70	4.9	5.50			LK5
54	27.504	98.900	3373	19.5	133.4	52422	5597	1108	69.8	3.4	826	224	11.3	6.08	3.41	25.5	HT1
55	0.074	0.050	711	0.7	7.2	40608	6965	358	3.5	3.5	62	89	6.6	4.83			LK4
56	59.438	186.000	1998	25.5	90.9	43617	3335	96	102.9	3.0	1377	295	10.9	4.56			HN2
57	10.400	7.520	1464	8.4	77.5	42192	5457	848	34.3	22.1	386	185	8.4	4.97			HT5
58	0.094	0.240	3334	1.6	12.5	37993	11621	581	3.3	3.3	59	86	4.9	5.34			LK3
59/70	2.050	3.550	2226	2.3	42.3	36662	5435	487	2.5	25.2	120	87	7.3	5.73	1.45	16.9	HN4
61	26.050	5.820	2523	8.8	97.7	48547	5853	607	66.3	23.1	912	241	10.1	4.95			HT5
62	20.800	81.700	3027	11.5	91.9	49443	4874	936	37.2	18.0	653	157	9.3	5.96			HT1
63	0.204	0.690	1993	0.6	6.6	36224	8082	448	3.0	3.0	60	85	7.2	5.18			LK5
64	2.925	2.940	3693	6.7	36.7	32027	4815	874	3.1	19.0	247	149	7.3	6.47			HN4
65	8.177	30.400	4029	9.0	59.8	42475	5721	969	9.7	19.8	243	131	7.1	6.45			HT2
66	1.500	0.950	1837	2.4	22.1	31120	4503	135	2.5	18.3	141	101	5.7	6.67			HN4
67	2.887	43.300	6881	3.5	32.9	31171	4009	84	1.5	19.4	134	93	6.3	6.60			HT3
68	3.512	7.240	7349	4.7	28.5	28240	5180	694	8.5	17.1	155	125	8.5	6.88			HN5
69	8.214	20.800	2945	3.1	78.3	39454	5891	369	11.1	22.7	470	198	7.9	5.66	1.60	15.8	HT2
71	8.078	5.540	3074	5.6	65.0	38828	6137	811	29.5	20.6	332	139	8.7	5.58			HT5
72	13.238	7.080	1577	5.0	56.7	38253	4143	705	34.7	23.6	543	153	6.9	4.55			HT2
73	0.097	0.026	2325	0.5	19.5	34542	8745	672	2.3	2.3	55	72	5.2	4.55			LK3
74	9.015	4.270	4037	8.0	65.9	44711	4631	1137	31.4	19.3	364	149	9.5	5.99			HN3

Sample Number	Total Se µg/g	Water Soluble Se ng/g	Ca µg/g	Cd µg/g	Cu µg/g	Fe µg/g	Mg µg/g	Mn µg/g	Mo µg/g	Pb µg/g	V µg/g	Zn µg/g	LOI %	pH	TOC %	CEC meq/ 100g	Village Code
76	6.796	28.100	8575	10.7	39.9	26268	4403	905	17.1	18.5	269	127	8.4	5.99			HN5
77	0.056	0.026	4599	1.9	14.1	36777	10989	470	2.5	2.5	58	76	5.4	6.01			LK2
78	2.123	0.750	3846	2.0	30.4	24492	4495	674	5.9	17.3	135	92	7.4	6.09	1.78	20.2	HN5
79	2.351	2.120	2405	2.5	47.0	37497	5463	431	2.7	23.8	130	90	7.8	6.18			HN4
80	17.588	17.900	2146	7.3	81.1	36705	3816	709	32.3	1.8	844	140	8.9	4.95			HT1
81	2.622	6.500	3115	2.8	38.7	43198	6613	638	5.2	2.6	127	113	6.0	6.15			HN5
82	0.070	0.370	1501	0.4	19.1	36478	5957	328	2.5	2.5	49	82	5.5	5.05			LK4
83	3.700	44.900	7703	2.4	33.4	36053	6425	703	3.4	3.4	87	76	7.7	6.36			HT4
84	8.945	45.650	4773	7.0	55.8	44017	6583	137	2.5	2.5	143	106	8.4	6.52	1.40	16.8	HT4
85	0.061	0.540	6020	1.5	12.1	38692	12837	583	3.5	3.5	54	88	5.5	6.02			LK2
86	4.885	1.570	2444	3.2	36.9	25204	4390	501	11.2	18.6	174	94	7.1	5.91			HN5
87	0.034	0.340	4676	1.6	4.7	34782	7013	454	1.9	1.9	45	77	4.1	6.03			LK4
88	1.494	0.710	5546	3.5	30.6	37212	4603	905	4.5	22.7	148	90	6.3	6.27			HN4
89	2.736	8.930	4149	4.0	32.3	39795	7726	730	2.2	19.2	78	83	7.9	6.50			HT4
90	26.747	32.700	2894	10.0	136.6	42320	5645	697	35.6	26.3	1269	248	9.6	6.53			HT2
91	6.691	29.400	12336	5.9	34.8	29069	3940	533	14.9	14.5	380	119	7.4	6.65			HT3
94	12.981	254.000	5820	17.7	160.0	69444	2585	458	16.4	3.1	503	161	10.4	5.57	1.94	29.3	HN2
95	5.102	12.900	8051	6.6	51.3	43474	5341	727	5.7	2.9	164	95	8.9	6.04			HT4
96A	0.151	0.210	1218	0.6	12.0	37366	8540	303	3.1	3.1	22	74	6.4	4.15	0.54	21.7	LK1
96B	0.059	0.027	1506	0.5	12.6	33451	8131	339	3.5	3.5	41.6	68.1	5.90	5.14	0.22	22.9	LK1
96C	0.014	1.490	2635	0.5	13.3	28246	8775	391	2.5	2.5	27.3	64.2	4.35	5.49	0.06	23.8	LK1
97	8.481	2.680	3673	4.0	60.6	47991	4340	756	22.7	17.9	421	131	10.0	4.99	2.90	19.9	HN3
98	10.100	29.500	2419	7.9	77.5	56701	2978	301	38.5	2.7	737	158	9.0	5.55			HN2
100	0.092	0.026	3657	2.2	15.9	42770	12390	361	2.2	2.2	64	90	4.9	5.61			LK1

DATA LISTING FOR BGS GRAIN SAMPLES

Sample Number	Se µg/g	Grain Type	Village Name	Village Code
1/99	3.035	Maize-corn	Xin Tang	HT3
2/92	0.002	Maize-corn	Ji Chang	LK5
3	0.626	Maize-corn	Xin Tang	HT3
4	1.887	Maize-corn	Huabei	HT2
5/60	0.002	Maize-corn	Chang Ping	LK1
6	0.001	Maize-corn	Nan Pu	LK4
8	0.004	Maize-corn	Chang Ping	LK1
9	0.001	Maize-corn	Zhi Luo	LK2
11	0.016	Rice	Ji Chang	LK5
12	0.013	Rice	Nan Pu	LK4
13	0.082	Maize-corn	Fangjiaping	HN3
14	0.018	Maize-corn	Nan Pu	LK4
15	9.175	Maize-corn	Bajiao	HN2
16	5.600	Maize-corn	Shadi	HT1
18/49	0.225	Maize-corn	Luojiaba	HN1
19/39	4.705	Maize-corn	Shadi	HT1
20/42	0.002	Maize-corn	Ming Shen	LK3
21	1.536	Maize-corn	Yu Tang Ba	HT4
23	0.072	Maize-corn	Fangjiaping	HN3
24	0.001	Maize-corn	Zhi Luo	LK2
25	0.001	Maize-corn	Chang Ping	LK1
26	0.763	Maize-corn	Bajiao	HN2
27	0.001	Maize-corn	Ji Chang	LK5
29	0.001	Maize-corn	Ming Shen	LK3
31	0.001	Maize-corn	Ji Chang	LK5
32	1.808	Maize-corn	Luojiaba	HN1
33	0.013	Rice	Zhi Luo	LK2
34	0.877	Rice	Xin Tang	HT3
35	1.439	Rice	Shatuo	HT5
37	1.265	Maize-corn	Huabei	HT2
38	0.901	Maize-corn	Xin Tang	HT3
40/93	0.613	Maize-corn	Shatuo	HT5
41	2.664	Maize-corn	Luojiaba	HN1
43	0.020	Rice	Ming Shen	LK3
44	0.001	Maize-corn	Ming Shen	LK3
45	1.970	Maize-corn	Luojiaba	HN1
46	0.703	Maize-corn	Luojiaba	HN1
47	0.003	Maize-corn	Chang Ping	LK1
48	0.619	Maize-corn	Shatuo	HT5
50	0.001	Maize-corn	Zhi Luo	LK2
51	0.025	Maize-corn	Fangjiaping	HN3
52	0.202	Maize-corn	Xiao Guan	HN4
53	0.001	Maize-corn	Ji Chang	LK5
54	1.765	Maize-corn	Shadi	HT1
55	0.001	Maize-corn	Nan Pu	LK4
56	0.563	Maize-corn	Bajiao	HN2
57	0.409	Maize-corn	Shatuo	HT5
58	0.001	Maize-corn	Ming Shen	LK3
59/70	0.040	Maize-corn	Xiao Guan	HN4
61	1.363	Maize-corn	Shatuo	HT5

Sample Number	Se µg/g	Grain Type	Village Name	Village Code
62	1.383	Maize-corn	Shadi	HT1
63	0.001	Maize-corn	Ji Chang	LK5
64	0.026	Maize-corn	Xiao Guan	HN4
65	0.959	Maize-corn	Huabei	HT2
66	0.021	Maize-corn	Xiao Guan	HN4
67	2.879	Maize-corn	Xin Tang	HT3
68	0.074	Maize-corn	Zishengqiao	HN5
71	0.239	Maize-corn	Shatuo	HT5
72	0.242	Maize-corn	Huabei	HT2
74	0.662	Maize-corn	Fangjiaping	HN3
76	0.017	Maize-corn	Zishengqiao	HN5
77	0.001	Maize-corn	Zhi Luo	LK2
78	0.041	Maize-corn	Zishengqiao	HN5
79	0.132	Rice	Xiao Guan	HN4
80	0.182	Maize-corn	Shadi	HT1
81	0.041	Maize-corn	Zishengqiao	HN5
82	0.005	Maize-corn	Nan Pu	LK4
83	4.467	Maize-corn	Yu Tang Ba	HT4
84	1.696	Maize-corn	Yu Tang Ba	HT4
85	0.003	Maize-corn	Zhi Luo	LK2
86	0.054	Maize-corn	Zishengqiao	HN5
87	0.005	Maize-corn	Nan Pu	LK4
88	0.029	Maize-corn	Xiao Guan	HN4
89	4.810	Maize-corn	Yu Tang Ba	HT4
90	3.721	Maize-corn	Huabei	HT2
91	2.555	Maize-corn	Xin Tang	HT3
92	0.003	Maize-corn	Ji Chang	LK5
94	0.210	Maize-corn	Bajiao	HN2
95	3.680	Maize-corn	Yu Tang Ba	HT4
96	0.006	Maize-corn	Chang Ping	LK1
97	0.076	Maize-corn	Fangjiaping	HN3
98	4.760	Maize-corn	Bajiao	HN2

DATA LISTING FOR BGS WATER SAMPLES

Sample Number	Total Se µg/l	Cl µg/l	SO4 µg/l	NO3 µg/l	Sample Temp°C	Corrected Eh(mV)	pH	Conductivity (µS)	Bicarbonate (mg/lCaCO3)	Village Code	Village Name
1	7.3	0.91	8.23	25.0	12.3	427.7	7.73	221	82	HT3	Xin Tang
5	0.42	57.9	26.8	82.2	14.6	364.4	6.78	513	62	LK1	Chang Ping
6	0.3	3.94	11.3	11.2	14.9	406.1	6.06	86	5.9	LK4	Nan Pu
10	0.1	0.07	0.07	0.07							Blank Water
18	30.3	3.49	58.9	7.41	22.4	432.6	6.98	457	172	HN1	Luojiaba
19	38.1	3.97	494	22.4	19.4	454.6	6.19	1008	38	HT1	Shadi
39	38.1	3.92	512	22.3	19.1	454.9	6.17	1011	42	HT1	Shadi
49	30.2	3.52	59.1	7.65	22.4	409.6	7.00	480	175	HN1	Luojiaba
52	0.46	0.23	3.30	1.83	14.6	403.4	8.48	219	100	HN4	Xiao Guan
60	0.45	58.2	27.0	81.3	14.5	386.5	6.79	510	57	LK1	Chang Ping
63	0.1	0.25	4.15	0.07	15.9	420.1	6.15	35	11.9	LK5	Ji Chang
68	13.3	0.52	49.9	11.2	16.0	395	7.79	333	114	HN5	Zishengqiao
72	275	4.56	172	11.7	18.7	385.3	8.28	550	102	HT2	Huabei
73	0.1	4.09	2.35	16.8	14.7	401.3	6.25	96	18	LK3	Ming Shen
74	3.4	0.20	85.2	0.07	17.7	398.3	8.03	406	129	HN3	Fangjiaping
75	0.1	0.17	0.11	0.07							Blank Water
84	40.4	0.13	20.9	0.07	10.3	402.7	8.40	228	105	HT4	Yu Tang Ba
85	0.1	2.31	8.96	5811	14.2	389.8	7.39	338	178	LK2	Zhi Luo
93	11.9	0.60	66.3	8.76	17.5	396.5	8.10	354	111	HT5	Shatuo
94	44.2	1.79	82.1	10.7	21.0	409	7.13	427	135	HN2	Bajiao

DATA LISTING FOR BGS HAIR SAMPLES

Sample Number	Total Se µg/g	Gender	Age	Village Name	Village Code
1	15.95	Male	45	Xin Tang	HT3
3	7.47	Male	29	Xin Tang	HT3
4	27.72	Male	13	Huabei	HT2
5	0.51	Male	10	Chang Ping	LK1
6	0.20	Male	7	Nan Pu	LK4
8	0.40	Male	11	Chang Ping	LK1
9	0.26	Male	13	Zhi Luo	LK2
13	1.55	Male	27	Fangjiaping	HN3
14	0.20	Male	7	Nan Pu	LK4
15	26.79	Male	43	Bajiao	HN2
16	140.99	Male	42	Shadi	HT1
18	22.63	Male	27	Luojiaba	HN1
19	51.40	Male	17	Shadi	HT1
21	7.32	Male	69	Yu Tang Ba	HT4
23	3.92	Male	19	Fangjiaping	HN3
24	0.85	Male	12	Zhi Luo	LK2
25	0.39	Male	9	Chang Ping	LK1
26	18.75	Male	42	Bajiao	HN2
27	0.36	Male	13	Ji Chang	LK5
29	0.21	Male	10	Ming Shen	LK3
31	0.36	Male	19	Ji Chang	LK5
32	25.08	Male	30	Luojiaba	HN1
37	54.71	Male	48	Huabei	HT2
38	38.70	Male	40	Xin Tang	HT3
41	28.41	Male	28	Luojiaba	HN1
42	0.46	Male	8	Ming Shen	LK3
44	0.28	Male	10	Ming Shen	LK3
45	19.83	Male	33	Luojiaba	HN1
46	8.12	Male	34	Luojiaba	HN1
47	0.29	Male	9	Chang Ping	LK1
48	46.72	Male	21	Shatuo	HT5
50	0.26	Male	13	Zhi Luo	LK2
51	2.48	Male	33	Fangjiaping	HN3
53	0.28	Male	14	Ji Chang	LK5
54	41.30	Male	53	Shadi	HT1
55	0.34	Male	9	Nan Pu	LK4
56	29.67	Male	49	Bajiao	HN2
57	22.50	Male	21	Shatuo	HT5
58	0.26	Male	6	Ming Shen	LK3
61	42.58	Male	15	Shatuo	HT5
62	34.76	Male	21	Shadi	HT1
63	0.42	Male	20	Ji Chang	LK5
65	29.82	Male	47	Huabei	HT2
66	0.70	Male	28	Xiao Guan	HN4
67	83.43	Male	29	Xin Tang	HT3
68	1.80	Male	8	Zishengqiao	HN5
70	0.57	Male	25	Xiao Guan	HN4
71	14.20	Male	31	Shatuo	HT5
72	19.44	Male	24	Huabei	HT2

Sample Number	Total Se µg/g	Gender	Age	Village Name	Village Code
73	0.19	Male	10	Ming Shen	LK3
74	1.61	Male	36	Fangjiaping	HN3
76	2.65	Male	45	Zishengqiao	HN5
77	0.17	Male	14	Zhi Luo	LK2
78	1.20	Male	28	Zishengqiao	HN5
80	45.98	Male	48	Shadi	HT1
81	1.54	Male	39	Zishengqiao	HN5
82	0.20	Male	9	Nan Pu	LK4
84	7.09	Female	68	Yu Tang Ba	HT4
85	0.48	Male	14	Zhi Luo	LK2
86	1.30	Male	39	Zishengqiao	HN5
87	0.37	Male	8	Nan Pu	LK4
88	0.84	Male	27	Xiao Guan	HN4
89	1.83	Male	47	Yu Tang Ba	HT4
90	33.58	Male	28	Huabei	HT2
91	45.65	Male	66	Xin Tang	HT3
92	0.30	Male	12	Ji Chang	LK5
93	33.46	Male	36	Shatuo	HT5
94	34.59	Male	35	Bajiao	HN2
96	0.18	Male	10	Chang Ping	LK1
97	28.65	Male	27	Fangjiaping	HN3
98	10.07	Female	13	Bajiao	HN2

DATA LISTING FOR IRMA SOIL SAMPLES

	EN18	EN41	EN56	EN26	EN19	EN54
	276721	276722	276723	276724	276725	276726
Al(%)	4.37	4.20	6.39	4.84	7.02	7.54
Fe(%)	2.88	2.91	4.31	4.11	6.05	5.68
Ca(%)	0.56	0.44	0.25	0.75	0.33	0.39
Mg(%)	0.77	0.53	0.37	0.54	0.59	0.62
K (%)	0.91	0.83	0.97	0.98	1.31	1.54
Na(%)	0.19	0.18	0.23	0.18	0.34	0.23
F (%)	0.107	0.162	0.123	0.096	0.173	0.188
S (%)	0.077	0.12	0.22	0.048	0.034	0.048
Ti	3585.00	4326.00	7581.00	5054.00	7697.00	6827.00
Mn	662.30	409.50	197.20	447.60	1015.00	1015.00
P	851.70	924.20	1107.00	554.90	971.30	1529.00
Ba	200.70	159.40	175.70	228.30	206.50	191.00
Be	1.99	1.45	<1.00	1.78	4.34	5.59
Co	13.25	9.06	8.88	9.94	21.46	35.44
Cr	486.40	551.30	595.20	334.80	196.20	493.80
Cu	79.05	183.00	100.30	54.92	104.00	152.80
Ga	33.48	27.28	44.29	32.25	31.30	49.08
Li	37.82	37.17	39.27	36.68	34.59	41.37
Ni	151.20	155:70	157.30	69.30	100.80	216.20
Pb	119.80	140.40	169.40	110.70	85.00	150.20
Sr	75.52	107.90	190.90	108.60	66.78	88.02
Th	10.18	6.17	8.27	9.48	10.55	4.63
V	1143.00	1083.00	1517.00	1004.00	551.90	1384.00
Zn	937.30	269.30	276.50	143.80	231.30	224.70
Bi	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00
Cd	21.91	17.23	24.01	13.84	6.51	20.66
Ta	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00
Zr	71.93	122.30	249.40	118.80	250.30	354.00
Mo	57.0	46.5	78.8	57.0	40.6	75.0
Se	9.17	16.0	44.6	8.10	14.3	17.4
As	14	9.0	11	13	13	16
Hg	0.19	0.21	0.21	0.09	0.16	0.28
pH	7.37	6.06	5.15	7.74	6.37	6.67

SOIL P 2

	EN72	EN37	EN03	EN67	EN89	EN83
	276727	276728	276729	276730	276731	276732
Al(%)	4.68	6.01	5.17	5.86	7.68	6.30
Fe(%)	4.71	4.19	2.96	3.37	4.40	3.85
Ca(%)	0.18	0.53	0.36	0.72	0.55	0.72
Mg(%)	0.47	0.82	0.43	0.48	0.98	0.75
K (%)	0.80	1.32	0.94	1.26	1.84	1.57
Na(%)	0.16	0.25	0.23	0.23	0.54	0.45
F (%)	0.125	0.278	0.088	0.119	0.181	0.148
S (%)	0.034	0.053	0.019	0.026	0.024	0.019
Ti	4135.00	3954.00	5630.00	6419.00	6531.00	6236.00
Mn	762.90	841.70	740.30	438.10	2065.00	1014.00
P	774.50	820.70	461.10	588.30	538.80	470.00
Ba	194.80	193.30	248.70	319.80	472.00	378.80
Be	2.16	2.93	2.07	2.13	1.65	1.95
Co	25.89	16.60	14.28	19.20	23.53	19.31
Cr	251.60	391.60	146.10	115.00	81.85	74.41
Cu	71.65	101.40	51.73	53.27	70.99	60.35
Ga	30.50	33.29	21.08	24.78	29.29	18.50
Li	39.27	68.65	34.59	47.18	72.21	50.41
Ni	85.39	127.30	63.86	48.56	35.59	33.58
Pb	94.12	90.27	54.14	45.73	46.53	31.24
Sr	49.97	74.81	62.14	76.38	82.27	71.63
Th	12.89	12.02	12.41	15.67	14.24	12.90
V	710.80	1086.00	408.80	206.20	151.20	126.80
Zn	148.30	197.60	106.40	97.92	102.20	80.19
Bi	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00
Cd	4.14	14.58	4.22	3.44	2.54	1.45
Ta	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00
Zr	81.48	110.70	166.40	113.60	106.60	106.70
Mo	43.2	42.0	25.0	10.0	2.4	2.7
Se	10.4	19.7	3.57	2.67	2.58	3.03
As	15	15	10	11	11	12
Hg	0.17	0.46	0.09	0.07	0.04	0.03
pH	5.99	7.19	6.95	7.82	7.54	7.93

SOIL

P 3

	EN93	EN48	EN97	EN94	EN70	EN88
	276733	276734	276735	276736	276737	276738
Al(%)	8.80	8.11	5.75	6.24	6.48	4.73
Fe(%)	4.06	5.10	5.69	5.14	4.18	3.85
Ca(%)	0.38	0.69	0.46	0.44	0.29	1.15
Mg(%)	0.67	0.57	0.47	0.54	0.65	0.51
K (%)	1.85	1.47	1.05	1.15	1.54	0.99
Na(%)	0.56	0.60	0.30	0.32	0.23	0.18
F (%)	0.167	0.188	0.114	0.086	0.104	0.066
S (%)	0.086	0.077	0.13	0.67	0.034	0.022
Ti	7170.00	7070.00	6095.00	6116.00	5790.00	4035.00
Mn	767.80	966.70	1056.00	1577.00	846.40	1316.00
P	783.50	1095.00	883.10	1062.00	674.80	617.30
Ba	278.30	247.90	244.60	275.70	325.90	248.50
Be	4.47	6.47	3.65	3.11	1.96	2.19
Co	22.31	17.59	18.21	22.88	21.53	16.84
Cr	195.50	262.40	186.60	182.60	96.75	118.30
Cu	102.90	333.70	135.20	133.70	50.30	37.39
Ga	33.18	34.84	24.08	30.22	25.02	20.76
Li	37.81	36.04	31.02	36.68	47.35	36.67
Ni	133.10	107.40	71.43	92.57	37.93	36.81
Pb	123.30	74.66	82.13	95.16	55.15	37.15
Sr	84.14	94.22	62.66	96.23	78.60	82.38
Th	12.67	9.03	11.07	12.56	15.79	11.23
V	584.20	625.50	543.70	546.60	171.70	199.40
Zn	181.90	180.90	134.50	153.90	93.19	84.19
Bi	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00
Cd	9.59	5.74	2.54	6.55	<1.00	2.69
Ta	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00
Zr	415.40	301.50	162.30	162.10	112.30	77.57
Mo	46.0	22.8	24.5	30.5	3.6	5.5
Se	12.31	15.69	8.64	10.07	2.39	1.59
As	13	14	15	15	15	17
Hg	0.13	0.20	0.12	0.10	0.09	0.05
pH	6.39	6.78	6.69	6.86	6.47	7.77

SOIL

	EN96	EN25	EN77	EN09	EN58	EN44
	276739	276740	276741	276742	276743	276744
Al(%)	7.69	7.96	7.96	7.03	7.93	7.06
Fe(%)	3.60	4.16	4.13	3.29	4.16	3.99
Ca(%)	0.29	0.57	0.73	0.65	0.41	0.18
Mg(%)	0.93	1.38	1.27	0.99	1.24	1.06
K (%)	1.76	2.59	2.24	2.02	3.02	2.72
Na(%)	1.06	0.81	1.28	1.66	0.65	0.38
F (%)	0.041	0.070	0.063	0.056	0.074	0.066
S (%)	0.010	0.008	0.024	0.010	0.014	0.014
Ti	4372.00	4633.00	4800.00	3936.00	4466.00	4494.00
Mn	522.20	692.20	691.80	730.50	800.30	631.30
P	231.20	536.90	483.60	319.20	494.60	322.60
Ba	428.50	501.80	497.90	508.30	478.80	316.60
Be	1.41	2.24	2.34	1.51	2.64	2.06
Co	14.79	16.06	14.86	11.93	13.51	16.10
Cr	63.55	78.44	80.48	48.68	74.36	71.69
Cu	23.52	26.83	28.12	18.73	23.72	21.26
Ga	28.18	33.75	30.55	27.97	30.80	29.81
Li	34.25	53.14	47.50	35.70	47.15	40.40
Ni	25.21	37.85	29.82	24.37	31.03	33.06
Pb	21.02	20.46	28.61	18.46	29.02	23.21
Sr	131.20	110.90	166.30	190.40	87.32	62.92
Th	9.93	12.93	12.43	7.97	15.52	8.37
V	91.23	101.60	108.20	73.41	104.40	88.86
Zn	76.02	95.64	89.67	69.72	93.71	89.52
Bi	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00
Cd	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Ta	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00
Zr	83.30	89.44	99.13	76.56	86.43	87.50
Mo	1.2	1.3	<0.5	0.8	0.6	<0.5
Se	0.087	0.080	0.074	0.088	0.10	0.164
As	2.4	6.0	4.2	2.4	6.6	5.6
Hg	<0.01	<0.01	0.01	<0.01	<0.01	<0.01
pH	5.74	5.87	5.79	6.27	6.45	5.91

SOIL P 5

	EN82 276745	EN12 276746	EN92 276747	EN53 276748	EN96SAB 276749	EN96SC 276750
Al(%)	8.74	6.64	5.98	6.66	7.35	7.17
Fe(%)	4.02	3.28	2.39	3.17	3.95	3.01
Ca(%)	0.24	0.30	0.31	0.39	0.22	0.52
Mg(%)	0.72	0.67	0.61	0.79	0.91	0.96
K (%)	2.94	1.78	1.75	1.81	2.09	1.62
Na(%)	0.50	0.73	1.07	1.04	0.63	1.80
F (%)	0.053	0.063	0.059	0.053	0.064	0.066
S (%)	0.010	0.024	0.029	0.010	0.014	0.012
Ti	4689.00	4540.00	3484.00	3725.00	4716.00	3216.00
Mn	649.40	721.50	402.60	548.20	445.30	631.60
P	433.10	371.30	385.40	411.20	300.60	227.80
Ba	537.70	445.10	459.40	453.00	399.10	536.00
Be	2.57	2.43	1.64	1.63	1.91	1.93
Co	15.21	13.21	9.47	10.76	14.61	14.76
Cr	66.23	58.15	48.00	49.35	63.53	42.56
Cu	33.04	48.50	17.70	17.76	22.95	23.86
Ga	32.81	21.35	23.64	25.94	22.93	20.23
Li	33.74	36.84	32.16	35.38	35.37	27.13
Ni	30.18	25.02	19.57	23.52	25.91	22.41
Pb	13.14	14.68	<13.00	13.53	21.82	13.49
Sr	65.74	76.94	89.38	99.23	85.71	230.30
Th	13.14	6.05	<3.00	7.95	6.55	8.56
V	102.10	88.37	63.73	77.08	94.76	65.66
Zn	92.69	168.50	63.90	76.29	81.27	71.93
Bi	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00
Cd	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Ta	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00
Zr	116.20	102.30	89.01	95.56	95.99	62.41
Mo	0.8	0.6	0.8	<0.5	0.6	0.6
Se	0.87	0.188	0.185	0.102	0.136	0.048
As	3.7	5.0	1.9	4.2	3.0	0.8
Hg	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
pH	6.19	6.10	6.02	6.35	5.41	6.06

SOIL

	EN07SA 276751	EN07SB 276752	EN07SC 276753
Al(%)	4.01	5.67	6.70
Fe(%)	2.95	2.67	3.40
Ca(%)	0.10	0.11	0.07
Mg(%)	0.35	0.45	0.50
K (%)	0.69	0.91	1.06
Na(%)	0.12	0.12	0.06
F (%)	0.086	0.114	0.192
S (%)	0.022	0.012	<0.001
Ti	4489.00	5055.00	4579.00
Mn	441.10	329.30	63.24
P	401.10	372.00	489.70
Ba	165.80	189.90	111.20
Be	2.01	2.84	3.98
Co	16.46	8.24	2.44
Cr	106.10	66.21	31.04
Cu	41.45	39.15	14.20
Ga	18.03	26.60	38.13
Li	25.67	25.35	20.51
Ni	48.18	28.75	19.82
Pb	93.63	54.08	42.85
Sr	37.97	42.61	29.20
Th	5.43	7.37	<3.00
V	369.90	169.20	70.39
Zn	71.75	74.10	72.28
Bi	<10.00	<10.00	<10.00
Cd	<1.00	<1.00	<1.00
Ta	<10.00	<10.00	<10.00
Zr	125.40	402.30	652.50
Mo	33.5	18.5	8.9
Se	5.99	2.88	2.31
As	13	8.6	4.0
Hg	0.07	0.03	0.01
pH	5.74	5.85	5.80

ANNEX ANALYTICAL COMPARISONS

As a check on the AFS analytical methods used to determine Se concentrations in the present study, subsets of soil, grain and hair samples were selected for total Se analysis by XRF (soil and grain) at the BGS and for Neutron Activation Analysis (NAA) (grain and hair) at the Centre for Environmental Technology, Imperial College, Silwood Park.

Soil Se values determined by AFS and XRF show good comparison between the results (Figure A.1). However, AFS results for Se in grain are approximately 76% lower than those determined by XRF or NAA (Figures A.2 and A.3). There is good agreement between total Se levels in grain determined by XRF and NAA which use a similar calibration (Figure A.4). The differences between these methods and AFS are probably due to different calibration methods. Although the AFS results are lower, the trends in total Se composition are the same. AFS results for total Se in hair are lower than NAA results (Figure A.5). This again may be due to different calibrations and although there is a difference in the values for the samples, trends in Se concentration between samples are the same.

Figure A.1

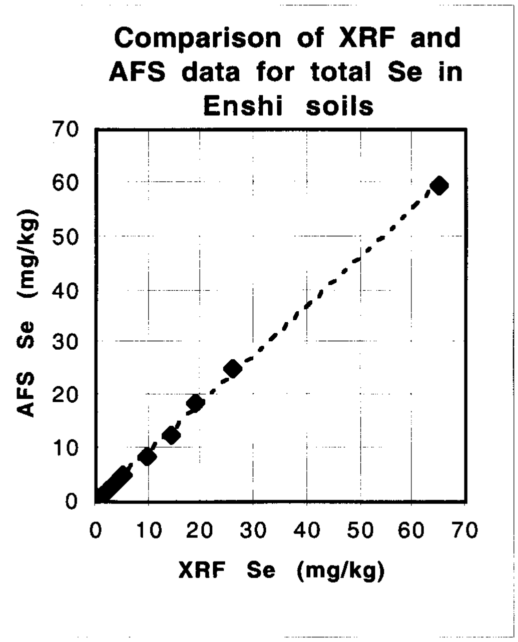


Figure A.2

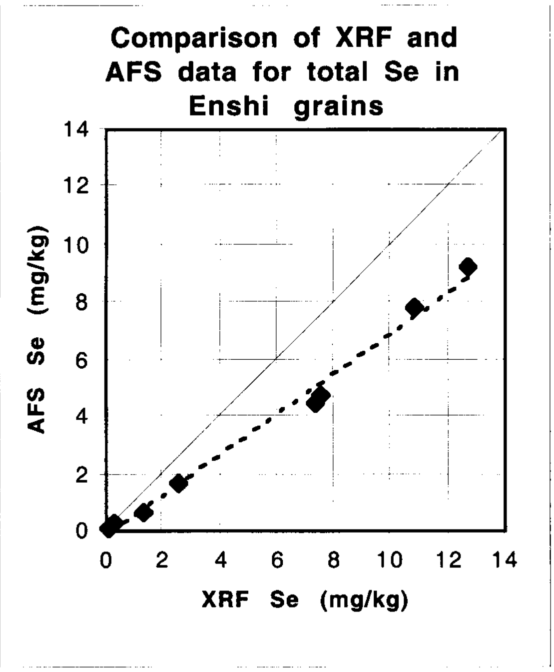


Figure A.3

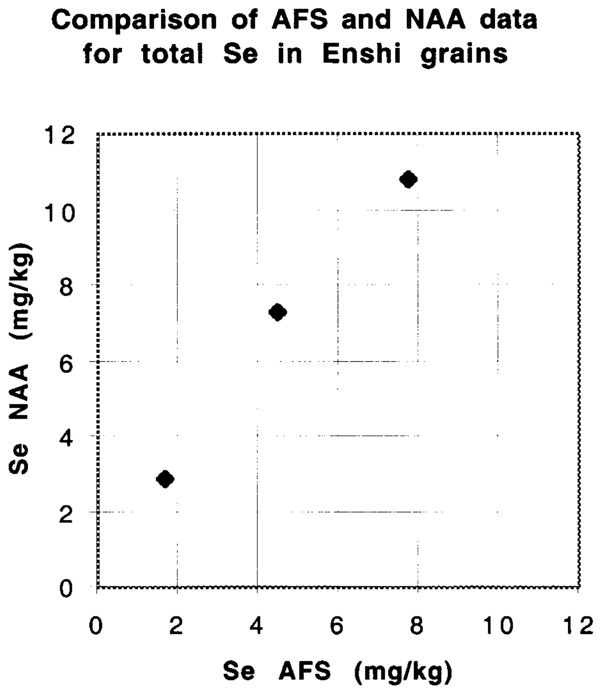


Figure A.4

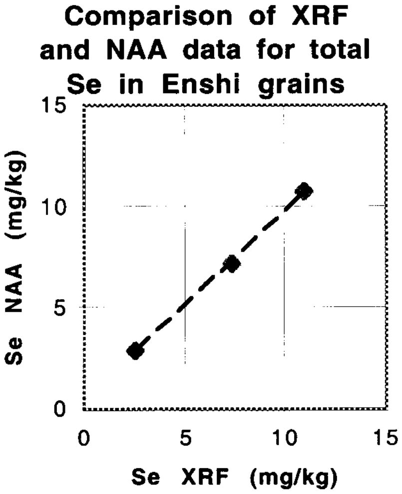


Figure A.5