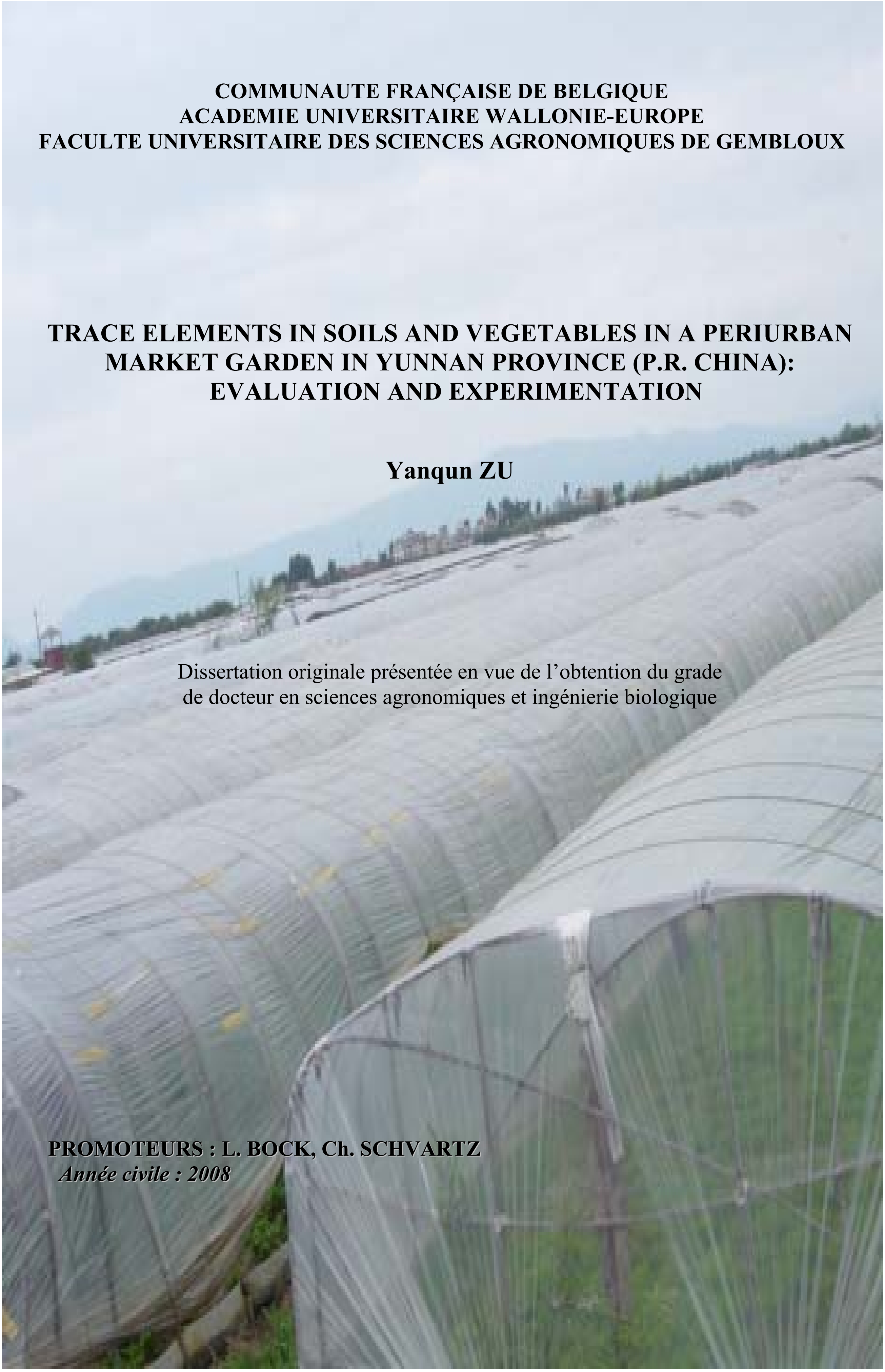

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ACADEMIE UNIVERSITAIRE WALLONIE-EUROPE
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TRACE ELEMENTS IN SOILS AND VEGETABLES IN A PERIURBAN MARKET GARDEN IN YUNNAN PROVINCE (P.R. CHINA): EVALUATION AND EXPERIMENTATION

Yanqun ZU

Dissertation originale présentée en vue de l'obtention du grade
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ZU Yanqun (2008) - Trace elements in soils and vegetables in a periurban market garden in Yunnan Province (P.R. China): evaluation and experimentation (Ph.D. Thesis). Gembloux Agricultural University, Gembloux, Belgium. 203 p., 55 tabl., 84 fig., 17 annexes

Summary

This research was conducted in order to evaluate natural trace element (TE) contents and anthropogenic contamination in soils and vegetables in Chenggong County (Yunnan Province, China). In this way, trace element contents in soils have been analysed to assess TE contamination in soils and vegetables, and transfer of TE from soil to vegetables. Agricultural practises have been proposed to amend the quality of vegetables.

We identified three geomorphopedological units: lacustrine unit, transition unit and mountain unit.

- In the mountain unit, soil texture is clay more often from the weathering of limestone and marlstone. Soil colour is red or reddish brown with acid reaction.
- In the transition unit, soil texture is loamy clay. Soil colour is red-brown with acid reaction.
- In the lacustrine unit, soil texture mainly is sandy developed from lacustrine-alluvial deposits. Soil colour is brown and is slightly acid.

Total TE contents in the topsoil are higher than usual and even Kunming Prefecture soil. TE contents indicate a high contaminated level when considered globally. Pb, Cd and Zn present however individually low contaminated levels, and Cu presents a medium contaminated level. TE contents decrease from northeast to southwest, which is consistent with the elevation gradient. Significant differences of TE contents are observed according to distance from Chenggong town in the lacustrine unit and with distance from the mountain in the transition unit. TE accumulation is usually observed along roads. TE contents in subsoil are related to soil colour, texture, parent materials and mottles. Accumulation of Pb and Zn in topsoil and of Cu and Cd in subsoil are observed.

The highest contents are observed for Pb in cauliflower, Cd in lettuce and Chinese cabbage, and Cu and Zn in pea. The order of TE accumulation in plants varies according to the plant species and organ. According to relations between TE contents in Chinese cabbage and extraction sequential fractions of TE in soils, different soil fractions are suggested as soil assessment indicators.

Lime and pig manure have been applied to modify the soil pH and to decrease the mobility of TE *in situ*. With increasing in lime rate and pH, contents of acetic-acid extractable TE fractions in soil decrease. Enrichment coefficients related to TE availability (AEC) of Pb and Cu are stable and are not changed by lime or pig manure. AEC of Cd and Zn which are high in low pH, decrease with increased pH and application rates of lime and pig manure.

When application rates of lime and pig manure increase, TE contents in Chinese cabbage decrease and biomass of Chinese cabbage increases. Application rates of lime and pig manure are recommended, but their quality should also be taken into account.

Keywords: Trace elements; Assessment; Transfer; Soils; Vegetables; Chinese cabbage; Lime; Pig manure.

ZU Yanqun (2008) - Eléments en trace dans les sols et les légumes d'une zone maraîchère périurbaine de la Province du Yunnan (RP de Chine) : évaluation et expérimentation (Thèse de doctorat en anglais). Faculté Universitaire des Sciences Agronomiques de Gembloux, Belgique. 203 p., 55 tabl., 84 fig., 17 annexes

Résumé

Cette recherche a pour objet l'étude de la teneur naturelle en éléments traces métalliques (ET) et de la contamination anthropique des sols et des productions légumières dans le Comté de Chenggong (Province du Yunnan, RP de Chine).

Pour cela, la variabilité des teneurs en fonction des conditions géomorphopédologiques a été analysée, ainsi que les transferts des ET du sol vers les végétaux. Cette approche a permis ensuite d'aborder l'évaluation de la qualité des sols et des légumes, puis de proposer des pratiques agricoles alternatives dans le but d'améliorer la qualité des légumes produits.

La zone d'étude a été divisée en 3 unités géomorphopédologiques:

- unité de montagne où les sols brun rouge à rouge résultent notamment de l'altération de calcaires et de marnes. Une texture argileuse et une réaction acide dominent.
- unité de piedmont (dite de transition) où les sols de couleur jaune clair à jaune rougeâtre résultent principalement de l'altération de grès et de shales. Une texture limono-argileuse en surface et argileuse en profondeur, ainsi qu'une réaction acide dominent.
- unité lacustre, à proximité du Dianchi Lake, dont les sols de couleur brun foncé sont essentiellement développés à partir de sédiments lacustres. Une texture sableuse domine en surface, ainsi qu'une réaction faiblement acide à neutre.

Les teneurs en ET rencontrées en surface des sols de la zone d'étude sont plus élevées que les teneurs moyennes observées dans les sols du monde ou même de la préfecture de Kunming. Evaluées séparément pour chaque ET, les teneurs rencontrées correspondent à des niveaux de contamination jugés faibles pour Pb, Cd et Zn, moyen pour Cu. Considérées simultanément, ces teneurs permettent de déterminer un indice de contamination global correspondant à un niveau de contamination élevé. Les teneurs en ET décroissent globalement du nord-est vers le sud-ouest, suivant le gradient d'altitude. Ces teneurs varient également de façon significative en fonction de l'éloignement de la montagne dans l'unité de transition et de l'éloignement de l'agglomération de Chenggong dans l'unité lacustre . Une accumulation en ET est souvent observée le long des routes. Dans le sous-sol, les teneurs en ET sont liées à la couleur, à la texture, au matériau parental, et aux marques d'altération. Les teneurs sont plus élevées en surface pour Pb et Zn, et en profondeur pour Cu et Cd.

Les teneurs les plus élevées pour Pb sont observées dans le chou-fleur, pour Cd dans la laitue et le chou chinois, pour Cu et Zn dans le pois.L'ordre d'accumulation des ET dans la plante dépend de l'espèce et de l'organe considérés. En fonction des corrélations observées entre les teneurs du chou chinois et les résultats obtenus avec différentes modalités d'extraction des ET du sol, des indicateurs d'évaluation de la qualité du sol ont été proposés.

Un amendement carbonaté et du fumier de porc ont été épandus afin de réduire in situ la mobilité des ET. L'augmentation de l'apport d'amendement carbonaté permet d'augmenter le pH du sol et de diminuer la fraction extraite avec l'acide acétique dilué (AA) pour chaque élément. Les AEC, rapports teneur dans la plante : teneur dans le sol extractible à l'AA, sont stables pour Pb et Cu et ne sont modifiés par aucun des 2 apports. Cependant, les AEC de Zn et de Cu, élevés quand le pH du sol est acide, diminuent si le pH devient plus alcalin, ainsi qu'avec les apports d'amendement carbonaté et de fumier de porc.

Quand les apports d'amendement carbonaté et de fumier de porc augmentent, les teneurs en ET du chou chinois diminuent et sa biomasse augmente. Un épandage d'amendement carbonaté est donc recommandé. Cependant la plus grande attention doit être portée à la qualité des fumiers de porcs dont les teneurs en Zn et Cu ne sont pas négligeables.

Mots clés: Eléments traces, Evaluation, Transferts, Sols, Légumes, Chou chinois, Amendement carbonaté, Fumier de porc.

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LIST OF ABBREVIATION

A: Acetic-acid extractable trace element fractions;
AEC: Available Enrichment Coefficient;
asl: Above Sea Level;
B: Hydroxyamine hydrochloride extractable trace element fractions;
BCF: Bioaccumulation Factor = (TE contents in plant)/(TE contents in soil);
BHC: Benzene Hexachloride;
C: Hydrogen peroxide and ammonium acetate extractable trace element fractions;
C_0: Nugget;
C_0+C: Sill;
CAC: Codex Alimentarius Commission;
CEC: Cation Exchange Capacity;
CK: Control;
DM: Dry Materials;
FA: Fulvic Acid;
FAO: Food and Agriculture Organization;
FM: Fresh Materials;
FPOT: First Pot experiment;
GAU: Gembloux Agricultural University;
GDP: Gross Domestic Product;
GIS: Geographical Information System;
GMO: Genetically Modified Organisms;
GPS: Global Positioning System;
H1: Topsoil
H2: Subsoil
HA: Humic Acid;
HACCP: Hazard Analysis and Critical Control Point;
L: Lacustrine unit;
L-ACd: A-fraction Cd content in the lacustrine unit;
L-ACu: A-fraction Cu content in the lacustrine unit;
L-APb: A-fraction Pb content in the lacustrine unit;
L-AvaiCd: Available Cd content in the lacustrine unit;
L-AvaiCu: Available Cu content in the lacustrine unit;
L-AvaiPb: Available Pb content in the lacustrine unit;
L-AvaiZn: Available Zn content in the lacustrine unit;
L-AZn: A-fraction Zn content in the lacustrine unit;
L-BCd: B-fraction Cd content in the lacustrine unit;
L-BCu: B-fraction Cu content in the lacustrine unit;
L-BPb: B-fraction Pb content in the lacustrine unit;
L-BZn: B-fraction Zn content in the lacustrine unit;
L-CCd: C-fraction Cd content in the lacustrine unit;
L-CCu: C-fraction Cu content in the lacustrine unit;
LCd: Cd content in the lacustrine unit;
LCEC: CEC in the lacustrine unit;
L-CPb: C-fraction Pb content in the lacustrine unit;
L-Cu: Cu content in the lacustrine unit;
L-CZn: C-fraction Zn content in the lacustrine unit;
LFD: Field experiment in the lacustrine unit;
LPb: Pb content in the lacustrine unit;
LpH: pH in the lacustrine unit;
L-Physical clay: Physical clay in the lacustrine unit;
L-PiCd: Pi of Cd in the lacustrine unit;
L-PiCu: Pi of Cu in the lacustrine unit;
L-PiPb: Pi of Pb in the lacustrine unit;
L-PiZn: Pi of Zn in the lacustrine unit;
LPOT: Pot experiment with soil from the lacustrine unit;
LSOC: SOC in the lacustrine unit;
LZn: Zn content in the lacustrine unit;
M-Physical clay: Physical clay in the mountain unit;
M: Mountain unit;
MCd: Cd content in the mountain unit;
MCEC: CEC in the mountain unit;
MCu: Cu content in the mountain unit;
MFD: Field experiment in the mountain unit;
MPb: Pb content in the mountain unit;
MpH: pH in the mountain unit;
M-PiCd: Pi of Cd in the mountain unit;
M-PiCu: Pi of Cu in the mountain unit;

M-PiPb: Pi of Pb in the mountain unit;

M-PiZn: Pi of Zn in the mountain unit;

MPOT: Pot experiment with soil from mountain unit;

MSOC: SOC in the mountain unit;

MZn: Zn content in the mountain unit;

NOS: Not suitable level;

NS: No significant results;

P: Integrative index of contamination;

P1-5: Profile No.1, 2, 3, 4 and 5;

P_1d, P_1Y: Permian system;

PCA: Principal Component Analysis;

PCBs: Polychorinated Biphenyls;

Pi: Signal index of contamination;

PSD: Particles Size Distribution;

Q: Quaternary system; Q_2: Early Pleistocene;
Q_3: Middle Pleistocene; Q_4: Holocene;
Q_4^l: lacustrine; Q^{lal}: alluvial lacustrine;

RMB: RenMinBi, Chinese currency;

RRCT: Ratio of A-fraction TE contents in Treatments to those in CK;

RTS: Ratio of trace element contents in Topsoil to those in Subsoil;

SA: Data Set of soil samples from regional approach;

SB: Data Set of soil samples responding to vegetable samples;

SD: Standard Deviation;

SE: Standard Error;

SEF: Sequential Extraction Fractions;

SOC: Soil Organic Carbon;

T: Transition unit;

T-ACd: A-fraction Cd content in the transition unit;

TPOT: Pot experiment with soil from transition unit;

TSOC: SOC in the transition unit;

TZn: Zn content in the transition unit;

WHO: World Health Organization;

X: Parameter in X axle;

Y: Parameter in Y axle;

YAU: Yunnan Agricultural University;

YR: Yellow-Red colour according Munsell charts;

T-ACu: A-fraction Cu content in the transition unit;

T-APb: A-fraction Pb content in the transition unit;

T-AvaiCd: Available Cd content in the transition unit;

T-AvaiCu: Available Cu content in the transition unit;

T-AvaiPb: Available Pb content in the transition unit;

T-AvaiZn: Available Zn content in the transition unit;

T-AZn: A-fraction Zn content in the transition unit;

T-BCd: B-fraction Cd content in the transition unit;

T-BCu: B-fraction Cu content in the transition unit;

T-BPb: B-fraction Pb content in the transition unit;

T-BZn: B-fraction Zn content in the transition unit;

T-CCd: C-fraction Cd content in the transition unit;

T-CCu: C-fraction Cu content in the transition unit;

TCd: Cd content in the transition unit;

TCEC: CEC in the transition unit;

T-CPb: C-fraction Pb content in the transition unit;

TCu: Cu content in the transition unit;

T-CZn: C-fraction Zn content in the transition unit;

TE: Trace Elements;

TFD: Field experiment in the transition unit;

Topo.: Toposequence;

Total-N: Total Nitrogen;

TPb: Pb content in the transition unit;

TpH: pH in the transition unit;

T-Physical clay: Physical clay in the transition unit;

T-Pi Cd: Pi of Cd in the transition unit;

T-Pi Cu: Pi of Cu in the transition unit;

T-Pi Pb: Pi of Pb in the transition unit;

T-Pi Zn: Pi of Zn in the transition unit;

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I: INTRODUCTION

Increasing attention being paid to the food security and ecological environmental security, sustainable agricultural development is becoming a key issue (Dudka & Miller, 1999; Chen H.M., *et al.*, 2006). There are many challenges to protection of cultivated land*, which has become a major factor affecting sustainable agricultural development and sustainable economic development in the world (Zhu G.Y., *et al.*, 2006).

The factors limiting the suitability land to be cultivated include decline of soil quantity, degradation of soil quality, soil erosion, drought, poor fertility, salinization and soil contamination (Zhao Q.G., *et al*., 2006). With the environmental concern becoming increasingly prominent, degradation of soil quality is becoming more and more prominent, especially soil contamination, such as trace element (TE) contamination. Soil TE contamination has been occurring for centuries. Widespread concern has arisen over the implications of human health problems from increasing TE contamination in soils in recent years (Mejare & Bulow, 2001; Chen H.M., 2005).

TE in soil cannot be decomposed by microbial or chemical degradation, so, total contents and eco-toxicity of TE persist in soils for a long time after introduction. These TE may affect soil ecosystem safety, agricultural product quality and human health through food chain (Dudks & Miller, 1999; Guo G.L., *et al.*, 2006). Focusing on TE contents in soil, its distribution, transformation and transferring from soil to agricultural production, the evaluation for soil TE contamination will be helpful for the sustainable use of cultivated land and the improvement of human health (Fu B.D. & Zhang X.Q., 2004).

Improvement of soil quality is a key of sustainable agriculture. There has been ever-increasing interest in developing technologies for contaminated site remediation. Remediation and purification of soil contaminated by TE include physical remediation, chemical remediation, bioremediation and phytoremediation (Baker, 1981; Zhou Q.X. & Song Y.F., 2004). But

* "Cultivated land" means lands that are used for agricultural crops, including paddy fields, upland fields, vegetables plots, as well as for mulberry fields, tea plantations and orchards.

considering the land efficiency and intensive agricultural practices, especially in periurban area, *in situ* agricultural remediation practices using exterior amendments should be a promising method for cleaning up slightly contaminated soils (Ding Y., 2000; Wang X., 1998).

In China, there is much progress, especially in agricultural production and economic development (Zhao Q.G., *et al.*, 2006). However, confronted with the Chinese demography, the availability of cultivated land is a limiting factor. Environment problems are also becoming increasingly prominent, in terms of food safety and human health. Soil contamination, especially TE contamination, has been reported in some cities, such as Beijing, Shanghai, Naijing, Shenzhen, Shenyang, Xi'an and Urumqi (Chen T.B., *et al.*, 2006; Wang Y.G., *et al.*, 2003; Zhang C.L. & Bai H.Y. 2001; Wang L.F. & Bai J.G., 1994; Ma W.X., *et al.*, 2000).

Yunnan Province is located in south-western China. Soil TE contamination has received increasing attention due to high TE background values (Duan C.Q., *et al.*, 2006).
Chenggong County is located ~20 km south-east of Kunming City, the capital of Yunnan Province and suits well to our purpose, which is to study the consequences of soil TE contents on plant quality and to find ways to improve this quality:

- ✧ It is the main base for market garden in Kunming Prefecture and thus plays a major role in vegetable supply in China.
- ✧ Three-quarters of farmland are devoted to vegetable production, which is the major source of income for this County.
- ✧ According to previous studies, its topsoil exhibits Zn, Cd and Cu contents higher than the background values for Kunming Prefecture and contents in vegetables may exceed legal standard values.
- ✧ It is possible to find out agricultural ways to decrease TE contents in vegetables and avoid severe food contamination.

By field investigation and experiments, this research aims to:

- Observe the contents and understand distribution of TE (Pb, Cd, Cu and Zn) in soils and vegetables. It is important for understanding the state of soil quality and its evolution and will be useful for predicting the soil quality evolution and to improve managements;
- Assess TE contents in soils and vegetables according to legal Chinese thresholds and collect relevant information about the severity of contamination of market garden soils by TE and subsequent risks for human health.
- Find out possible ways to decrease TE contents in vegetables and improve vegetable safety.

In general, this research aims at understanding and assessing TE contents in vegetable, and improves agricultural practises. This research will be an important reference for intensive periurban vegetable production and sustainable vegetable land use. Meanwhile, vegetable quality security and sustainable economic growth will be improved.

II: LITERATURE REVIEW

2.1. INTRODUCTION

Land demand is growing dramatically, bringing about greater pressures and challenges for protection of cultivated land in China. As cultivated land areas are progressively decreasing, their protection has become a key issue regarding sustainable development in China (Zhao Q.G., *et al.*, 2006). Cultivated land is limited by various factors, such as erosion, drought, low fertility, salinization, degradation of soil quality and soil contamination. With the development of globalization, urbanization and industrialization, environmental concern is becoming prominent, especially soil contamination (Zhou Q.X. & Song Y.F., 2004; Adriano, 2001; Majid & Argue, 2001; Mankoonga *et al.*, 2002; Bolan *et al.*, 2003).

Soil quality has been paid more attention. Appropriate land use for soils contaminated by trace elements (TE) should be decided by risk assessment of TE contents. The evaluation of soil contamination by TE is therefore a prerequisite for the development of sustainable and safe agriculture (Zhu G.Y., *et al.*, 2006; Sterckeman, *et al.*, 2004; Liaghati, *et al.*, 2003). Classical remediation includes physical, chemical and biological reactions (Baath, *et al.*, 1998; Dermatas & Meng X.G., 2003). In order to save limited cultivated land, while producing safe vegetables in periurban areas, agricultural-based remediation, including use of chemicals and crop rotation, should be recommended.

2.2. CURRENT SITUATION OF CHINA'S CULTIVATED LAND AND AGRICULTURAL PRODUCT SECURITY

2.2.1. Current situation of China's cultivated land

According to the 2nd Soil Survey of China in 1994, the total area of soil represents 8.798 $\times 10^8$ ha or 91.4% of Chinese territory. Some 2/3 could be used for agriculture, forestry and husbandry, some 1/3 is deserts or hilly regions. Areas under cultivation represents only 21.3% of the total area dedicated to agriculture and forestry, which is less than Asia (23.8%), the United States (25.7%), France (40.6%) or The United Kingdom (30.3%) (Jiang Z.D., 2004). Twelve soil orders have been recognized and the effective cultivated land area is 1.376×10^8 ha; including paddy fields (23.1% of cultivated land) and upland fields (76.9% of cultivated land).

On the one hand, according to slope degree and irrigation, four grades of cultivated land may be distinguished in China, including 1st grade (41.6%), 2nd grade (34.6%), 3rd grade (20.3%) and the remainder (3.5%), which should be used for forest. On the other hand, cultivated land also could be classified into high yield, medium yield and low yield lands in terms of quality and productivity. In China, area of high yield, medium yield and low yield lands occupies 21.5%, 37.2% and 41.3%, respectively (Lv, 2001). Pressures on cultivated land are becoming increasingly serious (Zhang Z.F. & Chen B.M., 2002).

2.2.2. Pressures on China's cultivated land

A. Area of cultivated land decreasing annually

From 1996-2004, the cultivated land area decreased obviously, by 0.77% each year (Figure 2.1). The total loss reached 1.053×10^7 ha. The average cultivated land area per capita (0.094 ha) in 2004 was 40% lower than in the world (0.25-0.3 ha). Some 20% of counties in China have only 0.053 ha per capita on average, which is lower than the limiting value (0.054 ha) defined by FAO (Zhou S.L. & Lu C.F., 2005; Zhang Q.L., *et al.*, 2005) (Figure 2.1). The loss is mainly due to construction appropriation, conversing cultivated land to forest or grass, regulation of agricultural production structure (readjustment) and natural disaster damage.

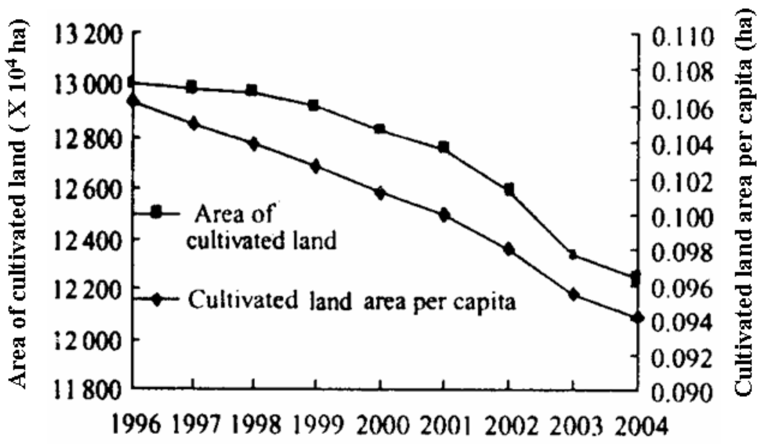


Figure 2.1: Evaluation of area of cultivated land in China and cultivated land area per capita (Zhou S.L. & Lu C.F., 2005; Zhang Q.L., *et al.*, 2005).

B. Differences in distribution of resources of cultivated land

Characteristics of cultivated land vary among regions, because of natural conditions, economic development level, human activities and management measures. Cultivated land area in the eastern part represents 94.2% of the total cultivated land of China (Zhao Q.G., *et al*., 2002; Ai J.Q., 2001). Uncultivated arable land area is only 9.88×10^4 ha, and per capita 0.0076 ha, which is mainly distributed in middle and western China.

C. Degradation of soil productivity with intensive agricultural practices

Soil quality is a key condition for soil productivity. Soil quality is influenced by natural factors and human activities. On the one hand, agricultural activities have improved soil quality, such as irrigation, soil salinization control and water logging control. On the other hand, degradation of soil quality is becoming a serious problem, such as soil erosion, nutrient deficiency and soil contamination.

Soil erosion by water and wind is identified as the main kind of degradation of soil quality at the world scale. In China, areas affected by soil erosion represent 3.65×10^8 ha, 37% of land area, and the quantity of eroded soil was 5×10^{10} t in 2004 (Zhou S.L. & Lu C.F., 2005). The loss of nutrients each year was 2.7×10^7 t OM, 5.5×10^6 t N, 6.0×10^3 t P_2O_5 and 5.0×10^6 t K_2O. The area concerned by soil erosion in 2004 was 1.34×10^7 ha in Yunnan Province, or 36.8% of the Province (Zhao Q.G., *et al.*, 2002). According to nutrient contents, some 2.29×10^7 ha of upland fields and 4.44×10^6 ha of paddy fields present organic matter (OM) deficiency. Some 2.8×10^7 ha of upland fields and 5.05×10^6 ha of paddy fields present potential nitrogen deficiency. The area of soils with P deficiency reaches 4.73×10^7 ha for upland fields and 1.99×10^7 ha for paddy fields.

D. Degradation of soil quality due to contamination

Soil contamination is caused mainly by industrial wastes, acid rain, unsuitable fertilization, transportation, pesticides and agricultural plastic films.

- ***Soil contamination caused by wastewater irrigation***

Output of wastewater is $>4 \times 10^{10}$ t each year in China. The area of wastewater irrigated land is 3.333×10^{6} ha, of which 6.67×10^{5} ha soil are contaminated, especially by Cd and Hg. Some 4×10^{4} ha are contaminated by Cd, with 130 mg/kg; and 5×10^{7} kg of grains being contaminated by Cd each year. Some 3.33×10^{4} ha are contaminated by Hg; and 1.95×10^{8} kg of grains being contaminated by Hg each year. The loss of grains each year is estimated to be 3.75×10^{9} kg due to wastewater irrigation, including 2.5×10^{9} kg of grains contaminated by TE.

- ***Soil contamination caused by industrial wastes***

The industrial solid wastes amounts to 7.2×10^{8} t each year. The total quantity of solid wastes is 8.6×10^{9} t and piled in 6×10^{4} ha of cultivated land to soil and water contamination. Some 1×10^{7} ha of cultivated soils are contaminated by industrial wastes, and lead to grain yield decrease of 1.2×10^{10} kg (Zhou S.L. & Lu C.F., 2005). On the other hand, soil acidification is becoming increasingly serious due to industrial activities. South-western and southern China are the sensitive regions to acid rain.

- ***Soil contamination caused by unsuitable application of pesticides and fertilizers***

In China, annual consumption of fertilizers, pesticides and plastic films increased from 1995 to 2003 (Figure 2.2), and generated a contamination of 8.667×10^{6} ha of cultivated soil, leading to >1 billion US dollars economic losses. Plastic films are decomposed very slowly in soil, 30% of residual plastic films accumulate in fields, resulting in soil contamination.

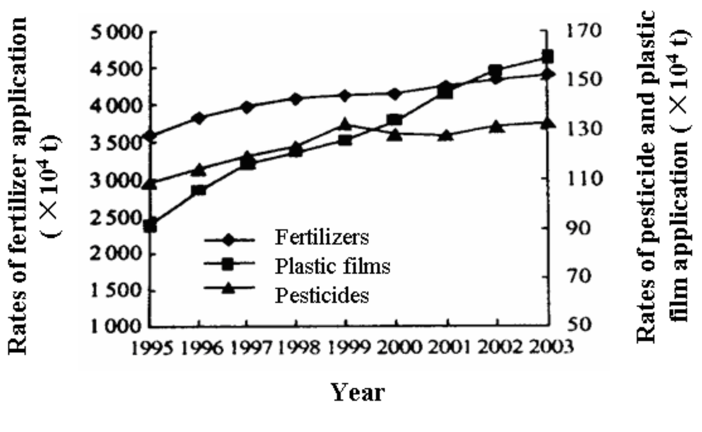


Figure 2.2: Consumption of fertilizers, pesticides and plastic films in China from 1995 to 2003 (Zhao Q.G., *et al.*, 2006).

In China, the average rate of pesticide application ranges between 2.34-14.0 kg/ha (Wu M., 2003). Some 50-60% of pesticides remain in soils; the ratio of efficiency is <30% (He L.L. & Li Y., 2003). Some 13-16 × 10^6 ha of cultivated land are contaminated by pesticides. Organic chloride is one of the important pesticide families, which was forbidden about 20 years ago, but still measured in soils and crop products. Benzene hexachloride (BHC) was tested in 99% out of all vegetable and soil samples in Guangzhou. Polychorinated biphenyls (PCBs) contents ranged between 6-151 g/kg in soil in Shenyang City (Gao X.Y., *et al.*, 2006).

- ***Current situation of soil trace element contamination in China***

According to the reports of the Ministry of Environmental Protection of China in 1999, one fifth of cultivated land is contaminated, of which 30-80% is contaminated by TE in some places, although the geological TE background levels are low. Some 25 × 10^6 ha of cultivated lands are contaminated by TE in China (Wei J.F., *et al.*, 1999; Cheng S.P., 2003).

Wastewater irrigation is very common in China, especially in the north-western, because water resources are lacking (Zhang Z.P. & Wang X.J., 1998; Nan Z.R. & Li J.J., 2001). According to the survey of the Ministry of Agriculture of China, 64.8% of wastewater irrigated lands are contaminated by TE, 46.7% at low grade, 9.7% at medium grade and 8.4% at high grade (Zhou Q.X. & Song Y.F., 2004). Wastewater irrigation has undertaken for 20 years in Zhangshi irrigation district of Shenyang City, resulting in contamination of 2500 ha of cultivated land, the Cd contents in grains being 25-35 times the standard value (0.2 mg/kg, GB5009.15) (Liao Z., 1993).

Beside wastewater irrigation, industrial emission and waste fertilization are also contributing to the primary factors influencing TE contamination in soil. TE in atmosphere from industrial emission, petrol with lead and dust-sandstorms are precipitated to soil (Cheng S.P., 2003). The amounts of Hg, Cd and Pb from atmosphere fallout into soil are 4.48, 5.79 and 347 g/ha/year, respectively (Zhang N., 2001). Fertilizing sludge in farm fields, has led to an increase of TE such as Cd, Pb, Cu and Zn, in which the mean contents of Cd in soil are 10-16 mg/kg (Guo G.L., *et al.*, 2006). In general, the main TE contamination are due to Cd, Pb, Cu and Hg contamination in soils in China. The sources are wastewater irrigation, industrial wastes, industrial emission, municipal wastes and fertilizers.

2.2.3. Current situation of agricultural product security in China

Current situation of agricultural product security

In order to ensure agricultural product security, considerable progress has been made to promote quantity and quality of agricultural products. However, contamination of agricultural products still endangers security and export. Some 21% of total grain in the world is produced in China with just 15% of the grain sowing area of the world. Thus 7% of cultivated land area in the world supports 22% of the world population. At the end of the 1990s, outputs of main agricultural products are continuing to increase. At the same time, the output of other agricultural products increased obviously, such as output of fruits and vegetables achieved 6,658 × 10^4 tonnes and 48,337 × 10^4 tonnes in 2001, respectively. China is self-sufficient in agricultural products.

On the other hand, quality of agricultural products has improved to high levels in China. Quantities with excellent grade quality of rice and wheat reach 25% and 20% of the total output according to relative standards, respectively. Some 1/3 of fruits and 20% of tea are of excellent grade quality. Pesticides and harmful substances have been effectively controlled in vegetables. In 2002, some 97.7% of vegetables samples were up to standards in Beijing, Tianjing, Shanghai and Shenzhen, according to the standards of Codex Alimentarius Commission (CAC). However, contamination of agricultural products still exists, because of environment contamination, resource deficiency and unsuitable agricultural practises. TE and pesticides transfer from soil to agricultural products. Pollutants in water and atmosphere also accumulate or deposit into agricultural products, resulting in decreased quality. Unsuitable agricultural practises, such as unsuitable pesticide spraying and fertilizer application, cause pollutant accumulation in agricultural products. Antiseptic and package materials with harmful substances also lead to decreased agricultural products quality (Bi R.T., *et al.*, 2004).

The main pollutants in agricultural products are nitrate, nitrite, TE, harmful microbes, pesticides, and plant growth regulators. The most serious contaminating pesticides exist in *Cruciferae, Solanaceae* and *Cucurbitaceous* vegetables, especially in Chinese cabbage, leeks and cucumber. TE contamination in vegetables has been paid more attention in China, especially in periurban intensive vegetable production districts (Zhang M. & Gong Z.T., 1996; Du W., *et al.*, 1999).

Current situation of trace element contamination in vegetables

Vegetable quality has been investigated in China, including effect of TE on vegetables in some areas of China. Mean contents of Pb and Cd in melon were 0.105 mg/kg and 0.005 mg/kg in Chongqing City (Chen Y.C., *et al.*, 2003), 0.074 mg/kg and 0.007 mg/kg in Shanghai City (Wang Y.G., *et al.*, 1997), and 0.317 mg/kg and 0.022 mg/kg in Baoding City (Gao X.Y., *et al.*, 2002), respectively. Some 13.3% of vegetable samples exceeded the Cd standard, and 12% of that exceeded Pb standard in Shanghai (Wang Y.G., *et al.*, 1997). Pb was the main contaminating TE in vegetables in Xi'an, 48% of vegetable samples exceeded the Pb standard (Ma W.X., *et al.*, 2000). TE contents in mustard in Nanjing were 1.41 mg/kg for Pb, 0.25 mg/kg for Cd, 5.77 mg/kg for Cu and 25.49 mg/kg for Zn, respectively (Zhang C.L. & Bai H.Y., 2001). The Hg contents in 13% of vegetables and fruits, 16% of seafood samples were higher than the standards held in Qingdao of China. Pb, Hg, Zn and Cd contents in vegetables in Shenyang exceeded standard values, while Cd, Pb and Zn contents in vegetable soil were 7.06, 3.96 and 3.87 times of soil background values (Wang L.F. & Bai J.G., 1994).

Absorption of TE by vegetables depends on many factors, such as TE characteristics, TE contents in soil and the selectivity of vegetables to TE (Xu S.P., *et al.*, 1999, Feng G.Y., *et al.*, 1993). Soil pH, soil texture, OM content and TE fractions in soil also influence TE availability for vegetables (Liu F., *et al.*, 2004; Zhou L.X. & Wong J.W.C., 2001).

Interspecific differences in accumulation ability to TE of vegetables exist (Wang L.F. & Bai J.G., 1994). Leaf vegetables easily absorb Cd and Hg, legumes Zn, Cu, Pb and As, and melons easily adsorb Cr. Mustard has the highest ability to uptake Cd, Cu and Pb, celery for Cd, Hg, As and Cr, and spinach and tarragon for Cd and Zn. String bean and potato have high BCF (Bioaccumulation factor = TE contents in plant/TE contents in soil) to Pb. The order of accumulation ability is leaf vegetables, legumes, melon vegetables, eggplant vegetables, root and stem vegetables, depend on heredity characteristics. The surfaces of leaves could also absorb pollutants from atmospheric deposition. Wang Y.G., *et al.* (1997) evaluated Cd accumulation of vegetables with BCF, showed high BCF of Cd in leaf vegetables, with high accumulation ability, such as spinach, celery and Chinese cabbage. Chinese cabbage, chilli, eggplant and radish have the highest BCF of Cd, whilst white gourd, cucumber, cabbage and tomato have the lowest Cd BCF (Chen T.M. *et al.*, 2006; Song B., *et al*., 2006). Hierarchical cluster analysis indicated that plant samples could be separated into three groups based on Pb BCF in vegetables. Round beans trellis (*Vigna unguiculata*), radish (*Raphanu*s *sativas*), Chilli (*Capsicum annuum*) and bakchoi (*Brassica chinensis*), which constituted the first group, had the highest Pb BCF. Chinese cabbage (*Brassica pekinsis*), eggplant (*Solanm* sp.), Chinese green onion, tomato (*Lycopersicon esculentum*) and cabbage (*Brassica oleracea*), have medium Pb BCF, while leaf beet (*Beta vulgaris*) and some special species vegetables have low Pb BCF. On the other hand, the TE ability to be absorbed and accumulated in vegetables is different, the order is Cr<Pb<As<Hg<Zn<Cu<Cd (Xie Z.M., *et al.*, 2006).

Interspecific and intraspecific differences in Cd uptake and accumulation of Brassica are significant. Beijing Xiaoza 55 (Chinese cabbage) has the highest shoot Cd content (61.4 mg/kg). Cd content in Hong Kong Baihua's (Chinese kale) shoot is only 18.6 mg/kg. The BCF of Xiaoza 55 (Chinese cabbage) can reach 3.07. But that of Hong Kong Baihua's (Chinese kale) and Jinqiuhong 2 is just 0.93 and 0.97, respectively. Considering the differences of accumulation ability to TE, vegetables with less accumulation ability could be planted on slightly contaminated soil, to decrease TE accumulation into the food chain, and vegetables with high accumulation ability only being planted on non-contaminated soil (Yao H.M., *et al.*, 2006).

TE in vegetable soils are mainly Cu, Zn, Pb, Cd, Cr, Hg and As, coming from pesticides, sludge, inorganic fertilizers and even organic fertilizers due to animal food and medicines with TE. Vegetable quality security still poses problems for human health in China. The main harmful substances are TE, pesticide residuals, nitrate and nitrite, which are relative to soil quality, irrigation water quality, monitoring technology and agricultural practices.

2.3. TRACE ELEMENT CONTAMINATION AND SOIL

2.3.1. Definition and sources of trace elements

- ***Concepts of trace elements***

Trace elements (TE) correspond to a group of elements, which density is >5 g cm^{-3}, and are toxic potentially to plants when the available content is in excess. TE usually in covalent compounds are highly toxic. Pb, Cd, Hg, Cr and As are the most important toxic elements.

Human beings might be exposed to metallic hazards, due to abnormally high natural contents in food or water. The use of metallic cookware increases the risk of adverse effects. With the coming of the industrial age, occupational diseases became more frequent (Adriano, 2001). Later, diseases related to industrial contaminants were recognized. Other sources of exposure include the release of V into the atmosphere from oil combustion and the release of Hg from coal combustion. Thus, while some TE are essential nutrients, they also serve as industrial and environmental hazards if the homeostatic mechanism maintaining them within physiologic limits is unbalanced. Other elements serve no biological purpose, while still others have the potential to produce environmental diseases. Disease potential of elements is related to their ability to accumulate in the body (Voegelin, *et al.*, 2003).

Toxic levels of TE (such as Cd, Pb, Zn, Cu and Hg) occur in some natural as well as agricultural soils, due to mining, smelting, some common agricultural practices (such as excessive use of fertilizers) and waste disposal practices. Nowadays, TE have become one of the major environmental hazards. TE cannot be degraded either chemically or biologically, hence they are ultimately indestructible (Mejare & Bulow, 2001).

- ***Fractions of trace elements in soil***

TE in soil may be split among five fractions, including water soluble and exchangeable, carbonate bound, iron-manganese oxide bound, organic bound and residual fractions (Tessier, *et al.*, 1979). Iron-manganese oxide bound fraction is wrapped up by iron-manganese oxides and could be released under conditions of reduction. Iron-manganese oxide bound fraction is not easily absorbed by plants, because iron-manganese oxide with huge specific surface has strong adsorptive force (Wei J.F., *et al.*, 1999). Organic bound fraction can set TE free under conditions of oxidation, due to organic matter oxidative decomposition. Different TE has different bound ability to organic matter. Residual fraction is bound to silicate mineral of quartz, clay and feldspar. So, they are stable and difficult to be absorbed by plants (Wu X.M., *et al.*, 2003a, b). Most TE exist in the residual fraction (Mo Z., *et al.*, 2002).

There are significant relationships between total TE contents and fraction contents. Relationships between total Cu, soluble Cu and exchangeable Cu were observed in 68 soils (Sauve & McBride, 1989). Total Pb influences iron-manganese oxide bound Pb, soluble Pb and exchangeable Pb fractions in 88 soils around Pb mine areas. According to the soil survey results around Wuhu Steel Factory, total TE contents had significant positive relationships with exchangeable, carbonate bound and residual fractions (Li Z., *et al.*, 2005). Meanwhile, carbonate and iron-manganese oxide bound fractions are able to transform back to exchangeable and soluble fractions with the root dissolving secretion. This process is relative to soil types, crop species and TE contents. Generally, water soluble and exchangeable fractions are the most bio-available. Fractions could change with soil pH, organic matter content and CEC.

- ***Sources of trace elements in soil***

The consequences of TE are economically important, as they can induce soil and plant contaminations from anthropogenic activities, such as mining, smelting, waste disposal, fertilizers, pesticides and wastewater irrigation, in addition to contributions from mineral weathering of parent materials. Natural metallic Cu was found and used by the ancients. Cu compounds have been used in medicine and agriculture, for example, verdigris (cupric carbonate basic) as pesticide: Bordeaux mixture (cupric hydroxycarbonate) combats mildew as a fungicide.

Cd is considered as a toxic pollutant. Agricultural soils in general are contaminated with Cd to a certain extent where P fertilizers are applied (Cakmak, *et al.* 2000), because phosphate fertilizers contain considerable amounts of Cd: 70-150 mg Cd per kg P_2O_5. Cd is produced as a by-product of Zn or Pb production. Its industrial uses include plating for other metals (iron, steel, and copper), in alloys, pigments for glass and paint and nuclear reactors as a neutron absorber and insecticides.

Pb enters the environment by escape during smelting of its sulphate ore, galena, as through use in storage batteries, pipes and conducts, solder and pewter, and especially the addition of tetraethyl Pb to petrol. Peroxide Pb, monoxide Pb, hydroxycarbonate and sulphate Pb are the principal white paint pigments. Millions of tonnes of Pb arsenate were applied for insect control in the first four decades of the 20th century. High contents in urban air have been reported in heavy automotive traffic, 38.0 μg/m^3 (natural mean content of atmospheric Pb is 0.79 μg/m^3) (Wang H.X., 2002). The natural Pb in fresh water has been estimated at ~1-10 μg/L. The natural content of Pb in soils, exclusive of areas near Pb deposits, has a range of 2-200 mg/kg, with mean of ~16 mg/kg.

The other TE also can be derived from industrial wastes, municipal domestic wastes, smelting, vehicle exhausting, pesticide and fertilizer application. In general, trace elements are distributed widely in soils, water and the atmosphere. When it is used unreasonably, is posed risks to plant and human health.

2.3.2. Distribution of trace elements in soil

Trace elements exist in different fractions in soil, some of them may move in horizontal and vertical directions; and resulting in distribution of TE within the soil. TE biological availability and harm to the environmental and ecological system are relative with TE transformation ability. Distribution of TE is linked to variability of soil characteristics, environment factors, distribution of human activities and land use. Soil characteristics are relative to geomorphology, soil formation processes and climate (Wu Y.Y. & Wang X., 1998; Zhang S., *et al.*, 1994; Koretsk, *et al.*, 2007). There are two levels of investigation, regional and local. Regional level distribution is mainly influenced by morphological factors, such as parent material, soil types and relief, whilst local level distribution is influenced by anthropogenic activities and soil characteristics (non-pedological factors).

A. Regional level distribution of trace elements in soil

The regional distribution level of TE is associated with parent materials and relief. Land use results in “island” distributions (Table 2.1). The variability of TE (Cu, Cr, Pb, Cd, Hg and As) contents was studied in central Hailun areas in Inner Mongolia (Wang J.K., *et al.*, 2003). Distribution of TE from east to west was observed, which was mainly influenced by parent materials and soil types. The variability of Cu was more significant than of Cr. “Island” distributions of Cu, Cr and Pb were significant and existed widely, especially near Hailun County town.

Table 2.1: Factors influencing the regional level distribution of trace elements in soils

Distance or Area	Trace elements	Influencing factors	References
1,000 km	Cu, Zn, Ni, Hg	Soil types, relief, land use	Wang X.J., *et al.*, 2005
45,000 km^2	Cr, Cu, As, Hg, Zn, Ni, Cd, Pb	Soil types, lithology	Navas & Machin, 2002
860 km^2	Cd,Cu,Mn, Ni, Pb, Zn	Regolithic substrates, morphogenetic characteristics, fuel combustion, solid wastes, liquid wastes	Romic & Romic, 2002
1,865 km^2	Pb, Cd, Cu, Zn, Ni, Co, Cr, Hg, As	Parent materials, soil types	Wang X.J., *et al.*, 2005
500 km^2	Cu, Ni, Zn, Cr	Parent materials, organic matter, anthropogenic input	Thuy, *et al.*, 2000
250 km^2	Pb	Tillage, traffic, vegetation	Panichayapichet, *et al.*, 2007

Land use also influences the regional distribution of TE. Distributions of Cd, Cr and Hg were isotropic, whilst Pb and As were anisotropic (1,865 km^2) in Shenzhen (Wang X.J., *et al.*, 2005). The SE-NW distribution of Cu, Co, Ni, V and As corresponded to the distribution of parent materials and soil types. Cr, Zn, Sr, Pb, Ni, Co, Cd, Mn and Cu contents in topsoil from the northern slope of Qomolangma (Everest) were linked to geochemical characteristics of different rocks (Zhang Y.L. & Wang Z.F., 2007). Distribution of TE fractions is consistent with geological distribution of brown soil in Beijing. Exchangeable and carbonate bound TE contents decreased from south to north, and east to west. While Fe-Mn oxide bound TE increased from east to west (Luo J.F., *et al.*, 1993). The distributions of fractions of TE were observed in different soil types (Liu Y.Y., *et al.*, 2006).

Soil characteristics and waste deposits could affect TE distribution in soil. TE (Cu, Cr, Cd, Pb, Ni, Zn) distributions among the sequential extraction fractions were affected by sediment properties, such as pH (Zn), clay (Cd), readily reducible Fe oxides (Pb) and organic matter content (Cu) in sediments in the Fusaro volcanic coastal lagoon of southern Italy (Pacifico, *et al.*, 2007). Distribution of TE in vegetable soil was influenced by transportation (Pb), municipal domestic wastewater (Zn), wastewater irrigation (Zn), organic matter application (Cu) and geomorphology (Cd) in Nanjing (Zhang Q.L., *et al.*, 2005). As, Cu, Pb and Zn contents in soil around the mining and smelting area of Tharsis, Riotinto and Huelva, Iberian pyrite Belt, SW Spain varied with erosion and transportation distance (Chopin & Alloway, 2007).

Not only agricultural soils but also urban soils are consistent with soil pH, coarse particle contents, and soil organic matter. The overall contamination degree, as indicated by the contamination index calculated from the different accumulation of TE, was high for the industrial, old residential and central commercial zones in Nanjing City. Both the soil properties and TE contents exhibited a very remarkable variability. Some "islands" with extremely contaminated level might exist in some locations with emission impacts (Wu X.M., 2003a; b). Highly contaminated soils are mainly distributed in the northwest-southeast orientated areas, including most of the north, central and part of the southeast regions of Hangzhou City (Fu J.L., *et al.*, 2005). Industrial activities and age of the residential areas were the most important factors affecting TE accumulation in soils. Industrial region located at north of the city, and the main wind was from north. Pb, Cu and Zn accumulations in the residential areas were linked with coal, dust, paints and sludge (Yin J., 2000). Regional distribution of TE is linked to soil types, parent materials, relief and anthropogenic activities.

B. Local level distribution of trace elements in soil

Horizontal distribution with local level

When exogenous TE increases rapidly, the TE distribution may change significantly at local level (Uhlig, *et al.*, 2001; Van Oort, *et al.*, 2006). With wastewater irrigation, TE in wastewater will be adsorbed into soil and accumulated at field entrances, resulting in TE contents increase. So it is important to assess variation of soil quality at local level.

Distance from contamination sources and transportation also affects local TE distribution. The maximum contents of Cu and Zn occurred near Yinzhuan in 1991 and near Yangzhuan Steel Factory in 2003 in the northern industrial region of Xuzhou City, which was linked with Yinzhuan factory closing, while Yangzhuan factory had still been producing (Liu H.X. & Han B.P., 2004). Trace elements often accumulate in soil contiguous to highways, railway and tramway lines. The spread range of TE from highway was >140-150 m, and contents of TE decreased when the distance from highway increased in Ning-Han highway (Nanjing-Hanzhou) (Zhang C.L. & Bai H.Y., 1998). In steel factories, the influencing range of TE accumulation in topsoil was >300 m (Jiang L.Y., *et al.*, 2002). Remobilization of soil stored TE close to roads can cause significant environmental contamination of urban road systems and eventually stream sediments (Sutherland & Tolosa, 2001).

Vertical distribution in local level

Trace elements in soil parent materials become active and movable during soil weathering and formation. Because of vertical variation of influencing factors, TE contents in profile are different, and result in the vertical distribution. TE in transported from topsoil to subsoil through leaching, then deposits in certain layers. However, biological cycles will bring some TE back from subsoil to topsoil or TE could be adsorbed by organic matter or soil particles. Therefore, the vertical distribution of TE reflects soil formation processes and elemental cycles, indicating contamination degree with anthropogenic activities (Table 2.2).

Table 2.2: Vertical distribution types and factors influencing trace elements in soil

Types	Trace elements	Influencing factors	References
Topsoil accumulation	Cd, Co, Cu, Mn, Ni, Pb, Zn	Organic matter	Heinrich, 2007
	Pb	Organic matter	Michopoulos, *et al.*, 2005
	Cu, Zn, Ni, Hg	Soil types, climate, organic matter	Wang X.J., *et al.*, 2005
Transportation (vertical leaching)	Zn, Co, Cr, Ni, Cu, Pb	Sulphides, organic matter	Koretsky, *et al.*, 2007
	Cu, Zn, Cr, Pb, Cd, Ag	Land use	McCray, *et al.*, 2001
	Pb, Cu, Zn	Organic matter, iron oxides	Kabala & Szaeszen, 2002
	As, Pb, Mo, Hg, Cd	pH	Bellett, *et al.*, 1991
	Pb, Zn	Iron colloids, clay-iron coatings	Oort, *et al.*, 2006

- ***Accumulation in topsoil***

Accumulation of TE in topsoil widely exists in cultivated soil, which should be linked to climate, anthropogenic activities and organic matter accumulation in topsoil (Liu F., *et al.*, 2004; Heinrich, 2007). TE contents decreased with soil depth increase in Inner Mongolia (Wang X.J., *et al.*, 2005). In arid zones, the exogenous TE mainly accumulate in topsoil. On the one hand, leaching is weak, due to the dry climate and biological cycles draw up TE to topsoil. On the other hand, TE from transportation, atmospheric deposits, wastes, pesticides and fertilizers also accumulate in the topsoil. Organic matter was found as a crucial factor of Pb binding in topsoil of 25 soil profiles of forested Dystric Cambisols developed from granite and gneiss in the area of the Sudetes Mountains (SW Poland) (Kabala & Scerszen, 2002). The main layer of TE accumulation is 0-20 cm in topsoil (Zhang M. & Gong Z.T., 1996; Feng G.Y., 1993).

- ***Leaching down the profile***

Because TE have affinity with organic matter, they may move down the profile accompanying organic matter (Kabala & Scerszen, 2002). Particle size distribution also affects the vertical distribution in the profile. The varying tendency of Co, Cr and Ni contents in the profile layer was associated with the fine (<20 μm) mineral fraction, and Sn, Ti and Zn with the fine mineral fraction and organic matter, and Cd, Cu and Pb with organic matter in France (Sterckeman, *et al.*, 2004). Vertical distribution in pore water and solid phase geochemistry were investigated in urbanized minerotrophic peat sediments located in south-western Michigan, USA. Tessier extractions indicated that the total extractable quantity of all elements analysed in this study decreased with depth, and that most of the non-residual Pb, Zn, Cu, Cr, Co, Cd and U was typically associated with the organic fraction of the sediments at all depths. Non-residual Mn, in contrast, was significantly associated with carbonates in the upper 15-25 cm of the sediments, and predominantly associated with the organic fraction only in deeper sediments (Koretsky, *et al.*, 2006).

Different levels of leaching transport are found for different elements under the influence of infiltration of irrigation, or precipitation and other anthropogenic activities (Nan Z.R., *et al.*, 2000; Liu H.X. & Han B.P, 2004). Geographic setting also influences vertical TE distribution. For example, the varying of TE in profiles was less in undisturbed soils, but near Cities, TE was mainly distributed at 0-50 cm depth, because of wastewater irrigation, sludge application and atmospheric deposits in Fujian Province (Wang Y.C., *et al.*, 1996). The depth of leaching of Hg and Cd was 40 cm and Pb 20 cm. The residual fraction was the main part in topsoil and subsoil, while the exchangeable fraction was easily to move (Xiao Z., *et al.*, 2005). Cao S.P. (2004) described vertical distribution characteristics of TE contamination in soil profiles for eight landscape units in Tianjin City. The TE (As, Pb, Mo, Hg and Cd) contents varied with soil profiles. Soil profiles near the city were heavily contaminated by Cd, Hg, Cu and Pb, which were concentrated at a 0-50 cm. Wastewater irrigation, sludge application and city dust precipitation were the main causes of TE contamination. As and Mo were concentrated in the <80 cm soil layer, and deposited with Fe and Mn in this layer, because of high solubility of As and Mo with high topsoil pH.

<u>2.3.3. Factors influencing the mobility of trace elements</u>

Mobility and distribution of TE in soil mainly depend on soil morphological factors (soil parent materials, soil texture, relief and soil types) and non-pedological factors (irrigation ways, cultivation practises, fertilizer rates and pesticide rates). Besides TE contents and soil chemical characteristics, mobility of TE is influenced by soil pH, organic matter, parent materials, clay contents, rhizosphere, Eh, climate, agricultural practices and exogenous TE.

- ***Effect of soil pH on mobility of trace elements***

Soil pH is the main factor influencing the mobility and release of TE in soils, especially to explain the vertical distribution in soil profiles (Zhao R., *et al.*, 2001; Bellett, *et al.*, 1991). TE change to available fraction with decreasing pH. The adsorption and desorption of TE can be affected by pH. The mobility and availability of TE have negative relationships with soil pH (Eriksson, 1989; He & Singh, 1994). Available TE contents (soluble, exchangeable and carbonate bound contents) decrease with pH increase, and Fe-Mn oxide bound TE fraction has a significant positive relationship with soil pH (Liu X., *et al.*, 2002a; Wang X. & Zhou Q.X., 2003). When pH increases from 4.5-7.0, exchangeable Cd, Zn and Pb decreased, Fe-Mn oxide bound fraction slightly increased and OM bound and residual fractions were stable in vegetable soils (Zhang X.X., *et al.*, 2003). The effects of acidity and ion contents of acid rain on TE in acidic soils indicate that TE contents in soil solutions are controlled by the pH of acid rain and ion exchange reactions, the pH of acid rain is the main factor influencing the mobility, release and vertical leaching of TE in soils (Guo Z.H., *et al.*, 2003; Rautengarten, *et al.*, 2004).

- ***Effect of organic matter on mobility of trace elements***

Effects of organic matter (OM) on TE mobility include ion exchange adsorption and chelation. OM could change the adsorption ability of soil to TE. OM is an adsorbent, which decreases or changes the activity and transportation of TE in soil (Liu Q. & Wang Z.J., 1996; Kabala & Szersezn, 2002; Lee, *et al*., 1997; Chen N.C. & Chen H.M., 1996; Shuman & Wang J., 1997). Voegelin *et al.* (2003) regarded that organic matter may vary the activity of TE in soil, depending on adsorption of humic acid and solubility of TE-humic acid chelated substance. Organic bound Hg increased and available Hg decreased with increasing humic acid in purple soil (Hatter & Naidu, 1995). Available TE decreased significantly with organic fertilizer applied to soil (Zhang Y.L., *et al.*, 2003; Hua L., *et al.*, 1998). Carbonate bound TE contents were positively related with organic matter contents, and soluble organic matter increased the available contents and transportation of TE in soils in Hebei Province (Liu X., *et al.*, 2003).

Water soluble Cd and exchangeable Cd increased from 27-54% with 320 g/kg sphagnum peat application in soils, and Fe-Mn oxide bound Cd decreased from 19-13% (He & Singh, 1994).

Composition of organic fertilizer may be an important factor. Soluble organic matter increases the mobility and biological activity of TE, such as fulvic acids. But high molecular organic compounds (humin) adsorb TE and decrease the mobility and biological activity of TE.

Soil pH can affect organic matter constituents and oxide colloids, which will cause variability of TE fractions (Li Z.L. & Xue C.Z., 1994; Kirkham, 1977). When pH is low, the ratio of fulvic acid content in organic matter is high, resulting in TE leaching to subsoil and TE contents decreased in topsoil in Shenzhen City (Wang X.J., *et al.*, 2005). With lime application and pH increase, exchangeable and organic bound fractions of TE decreased and residual TE increased (Zhang X.X., *et al.*, 2003).

- ***Effect of particle size distribution and parent materials on mobility of trace elements***

The distribution of particle size in soil affects adsorption, mobility and transportation of TE, especially clay content in soil (Sterckeman, *et al.*, 2004; Veogelin, *et al.*, 2003). The physical and chemical adsorptions increase with clay content in soil. Physical clay (<0.01 mm) content has negative significant relationships with organic and Fe-Mn oxide bound TE in Fluvio-aquic soils (Liu X. & Liu S.Q., 2003). TE contents in different layers in profiles increase with clay content.

Parent material was the key factor controlling the distribution of TE in Tianjian City (Xu S.P., *et al.*, 1999; Cao S.P., 2004). TE in the soils derived from colluvium deposit of igneous rocks, granite rocks and sedimentary parent materials were easily to leach, and contents of TE in C layers were higher than in the A layers, because of strong weathering. The TE contents in the soils derived from alluvial parent materials were 1 - 1.5 times higher than from residual parent materials. Due to the parent material of the plain area being primarily from the nearby mountain area, separation based on particle size may be the major reason for this difference. Synthesized by parent materials, influencing factors of mobility of TE include clay content, pH and organic matter content, the order is: clay content>pH>organic matter content in soils in Inner Mongolia (Wang X.J., *et al.*, 2005).

Cultivated process, waste water irrigation, sludge application, city dust precipitation and other anthropogenic activities also are the causes for mobility and distribution of TE (Zhang Z.P. & Wang X.J., 1998; Romic & Romic, 2002; Panichayapichet, *et al.*, 2007). Although there are many models to assess TE mobility in soil, it is important to pay more attention to their transfer to the food chain, considering their effects on human health.

2.4. TRACE ELEMENTS AND THE FOOD CHAIN

A. Bioavailability and absorption of trace elements by plants

TE in soil are able to be absorbed by roots of plants, then transferred to each part of the plant, such as stem, leaves and seeds. Cu, Pb and Zn are not localized at the root surface, but are the highest within cells of the stele (the vascular bundles) in electron-dense granules (Vesk, *et al.*, 1999). The endodermis casparian strip provides a barrier to the movement of TE into the stele. Once in the leaves, however, TE is mostly in the xylem, followed by the mesophyll and then epidermal tissue. In higher plants, the greater part of TE is stored in the roots and their transport to the shoot is prevented. For example, some 86.7% of Pb in cucumber (Fodor, *et al*, 1996a) and ~98% of Pb in stinging nettle (Fodor, *et al.*, 1996b) remained in the root.

When TE are transported from root tissue to aerial tissue, they are accumulated in leaves and stems. The degree of upward translocation depends on the species of plant, the particular metal and environmental conditions (Fitzgerald, *et al.*, 2003). TE (Cu, Pb and Zn) contents in individual leaves of both *Spartina alterniflora* and *Phragmites australis* did increase greatly from new leaves to senescence leaves (Weis, *et al.*, 2003).

There are many factors which affect TE accumulation in plants. Different fractions of TE have different availability. Soluble and exchangeable TE are the most available. Eh and pH conditions can cause changes in fractions and solubility of TE, then increases in accumulation in plants. Another factor that can affect TE accumulation in plants is the presence of microbial symbionts, such as rhizosphere bacteria. Mycorrhizae (symbiotic fungi associated with roots) provides an interface between roots and soil, increase the absorptive surface area of root hairs, and are effective at assimilating TE that may be present at toxic contents in the soil in some conditions (Meharg & Carney, 2000; Khan, *et al*, 2000).

Bioavailability of TE is also affected by nutrient availability. Nitrogen may strongly influence the TE absorption in plants by changing the rhizosphere pH. NO_3^- strongly reduces uptake and TE accumulation, whereas ammonium nutrition enhances their levels in plant tissues. It has been shown that ammonium nutrition causes the net extrusion of protons and soil acidification; whereas nitrate nutrition leads to protons consumption, increasing soil pH (Krupa, *et al.*, 1997).

B. Effects on organisms

A buildup of toxic TE in the food chain results from massive quantities of TE being discharged into the environment, in which plants constitute an important link (Wiersma, *et al.*, 1986; Dudks & Miller, 1999). Although TE contents are low sometimes, TE could be transported and concentrated through the food chain, and accumulated in the human body, leading to chronic poisoning with long-term exposure.

Toxic effect of TE that have no biological function on plants exists. Plants can tolerate certain contents of potentially toxic TE, but toxicity and eventualy lethality level can be reached when TE contents exceed specific levels. For the different potentially toxic TE, there are different toxicity thresholds. TE is selectively accumulated or particularly hazardous to humans, but less to plants. Due to accumulation through the food chain, their potential toxicity to humans is great in comparison with their effects on plants. Cd is probably of most widespread concern, as it is readily accumulated from soils by plants and may thereby enter the food chain (Chen H.M., *et al.*, 2000) and accumulate in humans (Baker, 1981).

Effects of TE on growth are consistent with their effects on longevity, fertility and the viability of offspring. Toxicity includes hypertension, atherosclerosis, as well as alterations in carbohydrate, lipid metabolism, glycosuria, proteinuria, shortened longevity, reproductive abnormalities and weight loss in older persons (Varga, *et al.*, 1997; 1999). One of the toxic effects of TE is to decrease the body weight of aging human individuals. Topical exposure to certain occupational metal hazards may result in irritation of the skin and eyes or sensitization reactions, or provide an avenue of absorption, resulting in systemic toxicity. The neurological aspects of poisoning from many TE indicate that the nervous system is an important target organ with respect to metal toxicity, often this is not related to selective accumulation in the central nervous system. Cellular toxicity increases with atomic weight within Cr, Mn, Ni, Cu, Zn, Ge, Gr, As and Se groups, but decreases in V. Apart from possible human extrapolation, genetic information including for plants is vital from the standpoints of safeguarding biodiversity and ecosystem health (Wurgler & Kramer, 1992; Anderson, *et al.,* 1994).

Genetic toxicology of TE has been implicated in human cancer, birth defects and mutations (Flessel, 1977; Hartwig, 1995; Vansuyt, *et al.*, 1997). Epidemiologic studies of industrial and agricultural workers, especially from Europe, suggest that As and Ni are potent carcinogens. Skin cancer has apparently occurred in areas with high As content in water. Liver cancer is also believed to have been induced by arsenicals. Cd levels are significantly elevated in the serum, liver and kidneys of patients with bronchial carcinomas, and chronic exposure to Cr increases the incidence of lung cancer (Rossman, *et al.*, 1987).

Biodiversity index of microbes decreases with integrative index of contamination increases (Li Y., *et al.*, 1999; Yang J.L, *et al.*, 2003). The ratio of fungus/bacteria decreased in soil contaminated by Cu, Zn, Cd and Pb (Pennanen, *et al.*, 1996). Low contents of TE stimulate microbial growth, and high contents of TE cause decline of microbial biomass (Fliebbach, *et al.*, 1994). TE influences the behaviour, physiological process, heredity of organisms and biodiversity.

C. Effects on plants and crops

Soil TE affects the growth and development of plants and crops. TE stress symptoms on plant can be divided into visible and only measurable symptoms. Concerning phenology, the most usual but one of the least specific symptoms of TE toxicity is to limit growth, breeding, biomass, yield and quality.

TE influenced the absorption of other nutrient elements (Siedlecka, *et al.*, 2001). TE can affect nitrogen absorption, assimilation, transfer and metabolism. TE change bacteria activity, resulting in changes in the nitrate and ammonium contents in soil. Plasma membrane is the first place of TE action. The altered plasmalemma H^+-ATPase function would also explain the metal-induced perturbation of the uptake of nitrogen. The inhibition of TE on key enzymes of the nitrogen assimilatory pathway can alter nitrogen uptake (Zu Y.Q., *et al.*, 2008).

TE may cause apparent morphological changes in plants. One of the most usual symptoms of TE stress in the chlorosis of the leaves is due to the decrease of the chlorophyll contents (Fodor, *et al.*, 1996; Zornoza, *et al.*, 1999). Since the chlorophyll contents may fundamentally influence the functioning of the photosynthetic apparatus and thus affecting the whole plant metabolism, it is a really important factor in assessing the impact of TE stress on plants. In more serious cases (more susceptible plants or higher metal contents) necrotic spots or whole leaf necrosis appears. Cd significantly decreases shoot and root weight, shoot height, root length and tillering number in wheat genotypes, but growth inhibition is different between root and shoot, and among genotypes (Zhang G., *et al.*, 2000).

The physiological symptoms of TE toxicity include membrane permeability, water and ion uptake, transportation and translocation, transpiration, root exudation, enzyme activities, nitrogen metabolism, photosynthetic processes (electron transport, fluorescence induction, phosphorylation, CO_2 fixation), respiration, cell division and expansion, all kinds of synthetic processes and cell homeostasis.

TE adsorbed in the cell walls do not exert any effect on metabolism. It is evident that stress factors increase the activity of cell wall peroxidases and stimulate lignifications. The cell wall becomes increasingly rigid due to this process, its ability to expand. The water uptake of the cells decreases or stops and only the exchange of solutes may occur. It is also known that the proteins (α- and β-expansions) facilitate expansion of the cell wall by TE.

Free radical production due to the effect of TE can lead to lipid peroxidation and the destruction of membranes. However, plants possess numerous defensive mechanisms, so the loss of semi-permeability appears only at excessive contents. The toxic impact of TE on higher plants has numerous common features: growth inhibition, accelerated senescence and chlorosis. The common are the most general mechanism of TE stress defence, such as phytochelatin synthesis, proline accumulation and changes in activity of antioxidative enzymes (Kumar, *et al.*, 1990; Siedlecka, *et al,*. 2001). Cd can occur in free ionic state, so that it has a significantly toxic effect in plants. Cd may exert its inhibitory effect in the cells in two different ways: it may bind to specific groups on proteins and lipids inhibiting their normal function, and it may induce free radical fraction inducing oxidative stress (Stroinski, 1999).

Effects of TE on plants depend on TE contents, sensitivity of plants and plant species. Some plants are able to acclimate the negative effects of TE, resulting in specific and unspecific responses which may lead to tolerance (Wang K.R. & Gong H.Q., 2000). Plants have developed numerous mechanisms that make them maintain or restore the activity of many enzymes, thus creating a new homeostasis and to adapt to the TE stress, such as hyperaccumulators. As TE could be transferred from plant to human beings along the food chain, and will be harmful to human health, it is important to assess the agricultural production security.

2.5. ASSESSMENT

2.5.1. Assessment of agricultural products

Agricultural product security

Agricultural product security includes agricultural product quantity security and agricultural product quality security. On the one hand, quantity of agricultural product may meet the requirement of the human population. On the other hand, agricultural product should be sanitary and contamination free. Agricultural product quality security is consistent with grain safety and food safety, including quality security of plant products and animal products (grain, oil, milk, vegetables, aquatic products and mushrooms), processing products and by-products, which may meet the standards of sanitary and food security.

Agricultural technologies, such as pesticide application, fertilizer application and irrigation, have ensured quantity security of agricultural product. But unsuitable application ways of pesticides and fertilizers may lead to contamination of agricultural product; even affecting development of sustainable agriculture. Some new technologies, such as GMO technology (genetically modified organisms), ohmic heating technology and enzyme technology, could increase the output of agricultural product, improve resistance to stress and prolong crop storage time. However, changes in nutritious substances and tastes will take place unpredictably, resulting in negative effects on human health, the ecological environment and agricultural product quality. So, based on international acceptable methods, the security of new technological agricultural products should be evaluated.

Because China is largely an agricultural country, both traditional and new technologies should be used to improve sustainable agriculture and produce uncontaminated agricultural product, green food and organic food, based on their security assessment and management. Assessment of agricultural product security is based on the standards of some substances, which can ensure the quality of agricultural products and improve trade of agricultural products in the international market. Facing more strict standards of food safety and green trade, more attention has to be paid to assessment of agricultural product security in the future.

Assessment system of China's agricultural product security

Hazard Analysis Critical Control Point (HACCP), which began in the USA in the 1960s, was conducted throughout the world after the Codex Alimentarius Commission (CAC) of FAO/WHO recommendations in 1963. HACCP became the standards for food security all over the world. Many countries and organisms formulate standard systems for agricultural product quality, which mainly include TE levels, maximum pesticide residual levels, maximum toxin levels, maximum harmful microbe levels, food additive standards, package material standards, standards for food testing methods and food label standards. For TE, Hg, Pb, Cr, Cd, Ni, Cu, Zn, Fe, Al, As and Se are mainly considered. In China, agricultural products are classified according to three levels: non-environmental contaminated food, green food and organic food.

✧ Non-environmental contaminated food refers to agricultural products and manufactured products free from contamination and safety corresponding with manufacture standards and sanitary standards, and which are verified by provincial government. TE and pesticide contents in agricultural products are lower than standard limits.

In 2006 “The Code of Primary Products Quality Security” was promulgated and put into practice, which urged agricultural product quality. <The Farmland Environmental Quality Evaluation Standards for Edible Agricultural Products> (HJ332-2006) has been put into practice on 1 February 2006. Trade standards for non-environmental contaminated food and national standards for agricultural product quality are promulgated by the Ministry of Agriculture (China), at the same time, which is the base of verification of agricultural product quality.

National standards for agricultural product quality include manufacturing environment standards and quality standards. Manufacturing environment standards for agricultural products (GB/T18407-2001) involve four national standard specifications, i.e. safety qualification for agricultural product - environmental requirements for origin of non-environmental contaminated vegetables (GB18407.1-2001), fruits (GB18407.2-2001), meat of livestock and poultry (GB18407.3-2001) and aquatic products (GB18407.4-2001). Quality standards for agricultural products (GB18406-2001) also include four national standard specifications. They are safety qualifications for agricultural products, requirements for non-environmental contaminated vegetables (GB18406.1-2001), fruits (GB18406.2-2001), meat of livestock and poultry (GB18406.3-2001) and aquatic products (GB18406.4-2001).

✧ “Green food” refers to food with free from contamination, safe of excellent quality and high nutritional value, which is verified by the China Green Food Development Centre, the “green food” standard is also promulgated by the Ministry of Agriculture (China), including A level and AA level. In the A level of “green food”, it is permitted to apply chemical materials in the manufacturing process. In the AA level of "green food", it is not permitted to apply any chemical substances, such as pesticides, inorganic fertilizers, animal food additives or food additives. Green food projects were put into practice in China in 1990, and carried forward to the international market in 1997. But AA level of green food still has some differences with organic food. Standard systems for green food includes environmental quality standards, general standards for food production and management, standards for pesticides, fertilizers, chemical hormones and additives, standards for product quality, general standards for food labelling and documents for product management.

The basic requirements for production area of green agricultural products and manufacture products are no direct contamination sources from industries, upstream and windward. Crops, livestock and poultry, aquatic products and food processing should correspond with green food operation procedures. Agricultural product quality should meet national standards for green food. Packing appearance should correspond with general standards for the labelling of foods.

✧ Organic food refers to agricultural products and processing products corresponding with organic producing standards and verification by the China Organic Food Certification Centre. Any chemical substances, such as pesticides, fertilizers, hormones, plant growth adjusters and food additives, cannot be applied.

2.5.2. Assessment of vegetable and crop quality security

A. China's vegetable quality security

The planting area of vegetables is 1,300 × 10^4 ha each year, and the total output is 4.05 × 10^9 tonnes in China. Vegetable quality is becoming increasingly important for human health and more attention must be paid to vegetable quality security. The main problems concerning vegetable quality in China include:

➢ Environmental problems lead to vegetable contamination, from atmospheric, irrigation water and soil sources. In China, most vegetable areas are located in periurban areas. SO_2, HF, nitrogen oxides and Cl_2 are discharged by vehicles, deposited on agricultural soil and vegetable surfaces, and cause soil and vegetable contamination. Industry wastewater and municipal wastewater with F^-, Pb and Hg flow directly on vegetable land. Municipal domestic waste contaminated by TE is piled near vegetable land.

- Pesticides are frequently applied to vegetables. So, pesticide residues are very serious. In the world, the ratio of insecticides, fungicides, herbicides and others are 28, 19, 48 and 5%, respectively. But in China, the ratios are 72, 11, 15 and 2%, respectively. About 35% of insecticides are acute poison in the market in China, such as organo-phosphorus insecticides (Chen H.M., *et al.*, 2006). The tolerance of disease to fungicides increases with climate change and intensive agricultural operations. The times of pesticide application increases from 5 to 30 each growth period. The loss of vegetables which were contaminated by pesticides achieved 10 billion dollars in China in the last 10 years (He L.L. and Li Y., 2003).
- Inorganic fertilizers are applied unsuitably, resulting in decreased vegetable quality. Especially, contents of nitrate and nitrite are over standard limits in vegetables. Nitrate contents of 27% of vegetables samples were over the standard limit in Guangdong Province (Luo X.M. & Zhu B., 2003). Nitrate is accumulated in different parts of vegetables.
- Standard systems are not perfect, and are not always consistent with international standards.

B. Assessment of China's vegetable quality security

Assessment of vegetable quality depends on three levels, including harmful substance contents, nutritious substance contents and outward appearance. Corresponding to soil quality standards, the standard systems of agricultural products and vegetables are Chinese food hygiene standards, <Safety Qualification for Non-environmental contaminated Vegetables> (GB18406.1-2001), <Maximum Standards for Green Food > (for example, Chinese cabbage group, NY/T 654-2002) and <Maximum Levels of Contaminants in Food> (GB 2762-2005).

In order to ensure agricultural product security, Chinese food hygiene standards were proposed by the Chinese Centre for Disease Control and Prevention in 1994, in which TE standards for vegetables are included. The maximum levels for vegetables have been proposed in 2005 in China (Table 2.3) (<Maximum Levels of Contaminants in Foods> (GB 2762-2005)).

About <Safety Qualification for Non-environmental Contaminated Vegetables> (GB18406.1-2001), the maximum levels for TE are consistent with Chinese food hygiene standards for As, Hg, Cd, Pb and Cr (Table 2.3). Considering the different accumulation of TE in different vegetables, there are food sanitation standards for each group of vegetables, such as Chinese cabbage, which is the same as that for non-environmental contaminated vegetables, except for Cr (Table 2.3). Comparing with the European standard (REG (EU) N^{o} 466/2001), the standard values of Pb and Cd for vegetables are the same as maximum levels of GB 2762-2005.

Table 2.3: Chinese food hygiene standards for TE in vegetables

Element	China national food sanitation standards		Maximum levels (mg/kg FM)
	Standards (mg/kg FM)	Reference	Standards and reference
As≤	0.5	<Tolerance Limit of Arsenic in Foods> (GB 4810-94)	0.5 (GB4810-84); 0.05[a] (GB 2762-2005)
Hg≤	0.01	< Tolerance Limit of Mercury in Foods > (GB 2762-94)	0.01 (GB2762-81)
Cd≤	0.05	< Tolerance Limit of Cadmium in Foods > (GB 15021-1994)	0.05 (GB238-84); 0.05[d],0.1[e],0.2[f] (GB 2762-2005)
Pb≤	0.2	< Tolerance Limit of Lead in Foods > (GB 14935-94)	0.2 (GB14935-94); 0.1[b] , 0.3[c] (GB 2762-2005)
Cr≤	0.5	< Tolerance Limit of Chromium in Foods> (GB 14961-94)	
Cu≤	10.0	< Tolerance Limit of Copper in Foods > (GB 15199-94)	10 (GB15199-94)
Zn≤	20.0	< Tolerance Limit of Zinc in Foods> (GB 13106-91)	20 (GB13106-94)

a: inorganic As content; b: vegetables except stem vegetables and leaf vegetables; c: stem vegetables and leaf vegetables; d: vegetables except e and f; e: root-stem vegetables; f: leaf vegetables, celery and mushrooms;

As for green vegetables, there are different maximum levels for each group of vegetables, such as Chinese cabbage, eggplant and tomato. Maximum levels of TE for green food, understanding the Chinese cabbage group, are shown in Table 2.4.

Table 2.4: The maximum levels (mg/kg FM) for TE in vegetables in China

Element	Non-environmental contaminated Food		Green food
	Vegetables (GB18406.1-2001)	Chinese cabbage (NY 5003-2001)	Chinese cabbage (NY/T 654-2002)
As	≤0.5	≤0.5	≤0.2
Hg	≤0.01	≤0.01	≤0.01
Cd	≤0.05	≤0.05	≤0.05
Pb	≤0.2	≤0.2	≤0.1
Cr	≤0.5		

In general, vegetable quality security is a requirement of international markets and customers, and is a guarantee for human health. The development of vegetable production in China depends on the development of non-environmental contaminated vegetables, green vegetables and organic vegetables, improved by new technologies of fertilizer application and vegetable disease control, monitoring, controlling and management.

2.5.3. Assessment of soil quality

Soil quality refers to the suitability of soil to be used and its adequacy to other environmental functional factors, especially the health of human beings and other organisms, and economic development. Soil quality assessment depends on land use, ecological systems, geological context, soil types and soil characteristics.

For management in sustainable agriculture, assessment of soil quality is very important. Assessment of the current situation of soil quality includes background value surveys, contamination assessment and "soil health" assessment*. Assessment of environmental effects refers to the effect of soil contamination on other environmental functional factors. Prediction assessment is to evaluate change tendency of soil quality, in order to control and abate soil contamination. Risk assessment is to evaluate the potential danger of pollutants to human health. However, assessment of soil quality should be based on standard values of soil quality. It is important to establish suitable soil quality standards and soil health quality standards with legal

* "Soil health" is an assessment of the ability of a soil to meet its range of ecosystem functions as appropriate to its environment.

efficacy. Soil quality standard parameters are relative to yields of crops, enzyme activities, microbe quantity, pollutant contents and other environmental parameters.

In China, <Environmental Quality Standard for Soils> (GB 15618-1996) was put into practice on March, 1996 (Table 2.5). The evaluation system involves <Environmental Quality Standard for Soils>, <Farmland Environmental Quality Evaluation Standards for Edible Agricultural Products> (HJ332-2006) (Table 2.6) and <Environmental Quality Evaluation Standards for Farmland of Greenhouses Vegetables Products> (HJ333-2006) (Table 2.6). There are three levels of vegetable soil quality linked to three levels of environmental quality evaluation standards, i. e. <Safety Qualification for Agricultural Product-Environmental Requirements for Origin of Non-environmental Contaminated Vegetables> (GB18407.1-2001) (Table 2.7), <Environmental Technical Terms for Green Food Production Area> (NY/T 391-2000) (Table 2.8) and <Technical Norm on Organic Food> (HJ/T 80-2001).

Table 2.5: China national standards for soil environmental quality of total TE contents (GB15618-1996) (mg/kg)

Grade		As	Hg	Cd	Pb	Cr	Cu	Ni	Zn
1st Grade		15	0.15	0.2	35	90	35	40	100
2nd Grade	pH <6.5	40	0.3	0.3	250	150	50	40	200
	6.5-7.5	30	0.5	0.3	300	200	100	50	250
	pH>7.5	25	1.0	0.6	350	250	100	60	300
3rd Grade	pH>6.5	40	1.5	1.0	500	300	400	200	500

Table 2.6: Maximum levels of total TE contents for vegetable soils (HJ332-2006) and vegetable soil in greenhouses (HJ333-2006) (mg/kg)

Element*	pH<6.5	pH 6.5-7.5	pH>7.5
Cd≤	0.3	0.3	0.4
Hg≤	0.25	0.30	0.35
As≤	30	25	20
Pb≤	50	50	50
Cr≤	250/150**	300/200**	350/250**
Cu≤	50	100	100
Zn≤	200	250	300
Ni≤	40	50	60

*Standards are suitable to soil with CEC>5 cmol/kg. If CEC5 ≤ cmol /kg, standards should be divided by 2;

**Standards in HJ333 - 2006.

Table 2.7: Maximum levels of total TE contents for soil of non-environmental contaminated vegetables (GB/T 18407.1-2001) (mg/kg)

Element	pH<6.5	pH 6.5-7.5	pH>7.5
Hg≤	0.3	0.5	1.0
As≤	40	30	25
Pb≤	100	150	150
Cd≤	0.3	0.3	0.6
Cr^{6+}≤	150	200	250

Table 2.8: Maximum levels of total TE contents for soil of green vegetables production area (NY/T 391-2000) (mg/kg)

Element	Upland fields			Paddy fields		
	pH <6.5	pH 6.5-7.5	pH >7.5	pH <6.5	pH 6.5-7.5	pH >7.5
Cd≤	0.3	0.3	0.4	0.3	0.3	0.4
Hg≤	0.25	0.3	0.35	0.3	0.4	0.4
As≤	25	20	20	20	20	15
Pb≤	50	50	50	50	50	50
Cr≤	120	120	120	120	120	120
Cu≤	50	60	60	50	60	60

<Technical norm on organic food > (HJ/T80-2001) is used for organic vegetable production. But there are no soil TE standards proposed for organic vegetable production. In order to assess the comprehensive contamination degree of TE, the signal index (Pi) and integrative index (P) of contamination could be used (GB 2762-2005) (Table 2.9) (Liu F.Z., 2001; Wang Y.G., *et al.*, 2001).

Table 2.9: Standard grades of single index and integrative index for soil contaminated by trace elements (GB 15618-1996; Huang G.F. & Wu Q.T., 2000; Liu F.Z., 2007)

Grade	Pi	P			Contamination condition
1	Pi ≤1.0	P≤1.0	P^a≤0.85	P^b ≤0.7	No contamination
2	1.0<Pi ≤2.0	1.0<P≤2.0	0.85< P^a ≤1.71	0.7< P^b ≤1.4	Low grade contamination (low contaminated level)
3	2.0<Pi ≤3.0	2.0<P≤3.0	1.71< P^a ≤2.56	1.4< P^b ≤2.1	Medium grade contamination (medium contaminated level)
4	Pi >3.0	P≤3.0	P^a ≤2.56	P^b >2.1	High grade contamination (high contaminated level)

$P=[(P'^2i+P^2max)/2]^{1/2}$, P'i: the mean Pi; Pmax: the maximum of Pi; Pi: the signal index of contamination.

If Ci≤Xs, Pi=Ci/Si (Xs is the 1st grade standard value), Ci is the analysis content, and Si is the standard value; If Xs<Ci≤Xm, Ci/Si=1+(Ci-Xs)/(Xm-Xs)(Xm is the 2nd grade standard value); If Xm<Ci≤Xh, Ci/Si=2+(Ci-Xm)/(Xh-Xm) (Xh is the 3rd grade standard value); If Ci>Xh, Ci/Si=3+(Ci-Xh)/(Xh-Xm).

Huang G.F. & Wu Q.T. (2000) modified the value of P (Table 2.9, P^a), and suggested that for green food production area, the Nationa1 Soil Environmenta1 Quality Standard (GB156l8 - 1996) is used as the soil quality assessment standards, in replace background values.

Liu F.Z. (2007) proposed that two stages of evaluation for TE contamination in soil, i.e. evaluation for farmland soil TE contamination and evaluation for soil of agricultural production area.

- Evaluation for farmland soil TE contamination is based on background values, showing the accumulation of TE. The methods include single index (Pi) evaluation and integrative index (P^b) evaluation (Table 2.9).
- Evaluation for soil of agricultural production area is based on maximum standard levels for available TE in soil, which is linked to relationships between TE contents in soil and in food parts of vegetables, and the suitability of soil for vegetables.

2.6. EFFECTS OF AGRONOMIC PRACTISES ON THE MOBILITY OF TRACE ELEMENTS

In order to control soil TE contamination, prevention should be recommended at the beginning. Firstly, contamination sources should be controlled and suitably managed. Wastewater irrigation and sludge applications should be careful and cautious. Fertilizers and pesticides containing TE should be forbidden or limited. Secondly, assessment of soil environmental capacity[†] to pollutants is necessary to prevent soil TE contamination. Finally, control measures should be taken into account, which include physical remediation, chemical remediation, bioremediation and phytoremediation.

Physical remediation includes “exchanging soil” technology, “covering clean soil” technology, “turning over soil” technology and “diluting soil” technology. Those technologies are expensive, and suitable only for small areas. Chemical remediation mainly includes soil leaching, flushing/washing and soil amelioration. Soil buffer capacity and effect of self purification are

[†] TE content expressed in kg/ha

improved through lime, phosphate, furnace slag and organic matter application. *In situ* fixation of TE using exterior amendments is a promising technology for cleaning up contaminated soils (Zhou Q.X. & Song Y.F., 2004; Guo G.L., *et al.*, 2006). *In situ* application of soil additives modifying the physicochemical properties of the contaminating TE bound with the development of biological communities and plants is a very useful alternative remediation method, based on risk reduction and time and cost efficiency (Diels, *et al.*, 2002).

Bioremediation refers to microbes and animals which could decrease TE contents in soil and fix them through activities, adsorption and precipitation. Phytoremediation is relative to plants which extract TE from soil and clean up soil. On the one hand, hyperaccumulators could extract TE from soil effectively, especially in high grade contaminated soil and mining areas. On the other hand, non-food plant instead of food crops could decrease TE in the food chain in medium or low grade contaminated soil.

Periurban areas, special belts including urbanization, industrialization and agriculture, have developed markedly in China. With the rapid development of the economy and human activities, soil contamination has become more serious. in this place. Status of soil contamination and its eco-environmental impacts should be considered. Corresponding strategies to control the mobility of TE in soil *in situ* should be taken.

A. Availability of fixing additives

Fixing additives are suitable for low level contaminated soil, which fix TE and decrease the TE bioavailability. In the fixation processes, cation exchange, adsorption and precipitation are the main phenomena that can activate the primary mechanism of TE immobilization. However it is unable to decrease total TE contents, or decrease TE contents to safe levels for human health in highly contaminated soil. The typical fixation agents include alkaline amendments, phosphates, organic manure and industrial co-products based synthetics (Guo G.L., *et al.*, 2006; Wang W.J., *et al.*, 2006).

- ***Alkaline amendment application***

Low pH is accompanied by increased bioavailability of TE and soil calcium deficiency. So, to increase the pH of soil is an effective way for acid soils. Alkaline amendments, including limestone ($CaCO_3$ 95-98%), lime (CaO), alkaline furnace and basic slag, are the typical amendments used for *in situ* immobilization. There are used to decrease the TE contents in soil solution, TE extractability, metal mobility and leaching ability, increase transformation of soluble TE to residual fraction, and finally decrease TE contents in plant tissues (Bolan *et al.*, 2003; Guo G.L., *et al.*, 2006).

Quicklime (CaO) is put into soil resulting in large pH increases (Dermatas & Meng X.G., 2003). Al toxicity could be eliminated, and activity of microbes and availability of phosphate are improved with lime application. Meanwhile, pathogenic bacteria, insect eggs and weeds will be killed, and clubroot could be prevented from radish and Chinese cabbage due to lime alkalinity.

Lime application is regarded as useful practice for controlling TE transfer from soil to plant (Chen N.C. & Chen H.M., 1996; Xia H.P., 1997; Mathur, *et al.*, 1991). Lime improves carbonate and hydroxide precipitates and decreases TE availability. When pH increases, Cd bound with clay and oxides (Wen Y.M., 1999), and most water-soluble Cd enters into the solid phase. Residual and oxide bound Cd increases with lime application (Liao M., *et al.*, 1998). Cd Bioavailability was decreased by pH>6 (Liao M, *et al.*, 1999). There were negative relationships between pH and Cd and Zn bioavailability (He & Singh, 1994). Rate of lime application is relative to initial soil types.

The mechanism for pH influencing availability of TE is as follows:

- With increasing pH, negative charges on the surface of clay mineral, hydrated oxides and organic matter increase and TE contents in soil decrease.
- With increasing pH, the stability of chelates of TE-organic matter increases.
- With increasing pH, specific adsorption of oxides to TE is enhanced.
- With increasing pH, hydroxide precipitates are easily formed.

- ***Organic additive application***

Organic additives could improve soil structure and combine with TE to decrease bioavailability of TE as a slow release nutrient source. Most organic additives are from farmyard manure, poultry manure, sewage sludge, domestic refuse and straw (Suran, *et al,*, 1998; Guo G.L., *et al.*, 2006). Available Cd can decrease by 40% with organic fertilizer application (Zhang Y.L., *et al.*, 2003). Bark and sawdust are effective because of their high tannin contents. The polyhydroxy groups of tannin are considered as the active sites in the adsorption process of TE (Vazquez, *et al.*, 1994; Suran, *et al.*, 1998).

The mechanism for organic matter influencing TE availability lies in:

- Humus in organic fertilizer combines with TE to form stable chelate (metal-HA complex) (HA: humic acid), especially humin.
- There is dilution of organic fertilizer to decrease TE contents in soil.
- Some elements in organic fertilizer have antagonism with TE.
- Organic fertilizer improves plant growth and affects TE adsorption.

Soluble organic matter in organic fertilizer could increase available TE contents in soil, for example metal-FA (FA: fulvic acid) complex (Zu Y.Q., *et al.*, 2003; Weng L.P., *et al.*, 2002). S*phagnum peat* was used as organic fertilizer in sandy soil, soluble Cd and exchangeable Cd increased from 27-54% and Fe-Mn oxide bound Cd decreased from 19-13%, respectively (He & Singh, 1993). Application of organic fertilizer containing excess TE should be forbidden.

- ***Other fixing additive***

There are interactions between TE and nutrient elements (N, P, K, Fe, Ca and Mg). On the one hand, TE influence nutrient elements absorbed by plants. On the other hand, nutrient element application will also decrease absorption and TE stress on plants (An Z.Z., *et al.*, 2002; Serrano, 1990; Zu YQ, *et al.*, 2008). NH_4^+-N could cause H^+ exosmosises and soil acidification in the rhizosphere, while NO_3^--N causes H^+ absorption and pH increase in soil. So, NO_3^--N fertilizer applied will restrain absorption of Pb, Zn, Mn and Cu by plants (Cox & Reisenauer, 1997; Tills & Alloway, 1981; Kumar, *et al.*, 1990; Weber, *et al.*, 1991).

Interactions between P and TE were observed (Zimdahl & Foster, 1976; Karblane, 1994). Phosphate fertilizer decreased Cd content by 41% in potato and ryegrass, which includes $CaHPO_3$, $Ca(H_2PO_3)_2$, K_2HPO_4, H_3PO_4 and $(NH_4)HPO_4$ (Karblene, 1994; He & Singh, 1982). Fe and TE also have interactions. Fe deficiency in soil could cause increases in Cd, Cu, Co, Cr, Ni, Mn and Zn contents in plants (Misra & Romani, 1991; Siedlecka & Baszyn'ski, 1993; Ouzounidou, 1995; Schmidt, *et al.*, 1997; Lagriffoul, *et al.*, 1998). Cd absorbed by ryegrass could be restrained by Ca, Mn and Zn (Jarris, 1976), and Mn caused decreases in Cd absorption (Harrison, *et al.*, 1983).

B. Decrease in accumulation of trace elements by crop rotation with vegetables

Crop rotation is a useful measure in agricultural production practice. To tackle TE contamination in soil, especially in intensive agricultural areas, it has an important role and excellent effects. Trees, flowers, grass and cash crops are chosen to plant in low TE contaminated soil, and shoots of sorghum and corn could be used to produce alcohol and press for plant fibre (Ding Y., 2000; Wang X., 1998). Wang K.R. & Gong H.Q. (2000) proposed a strategy of agro-ecological regulation and safe utilization in farmland contaminated by Cd, which used Cd-tolerant cash crops to replace sensitive crops, bound with agricultural remediation practises. Some plants have strong physiological resistance to Cd, such as *Brassica napus, Arachis hypogaea,* and *Saccharum offrunarum*. Meanwhile, Cd contents in oil and sugar are low and have little effect on their edible quality, so, it is possible to cultivate these crops in some slightly Cd contaminated farmlands. But the straw and remains of oil crops and sugarcane residue should be treated as pollutants, as they are not suitable as manure or stock food.

Fibre crops, such as *Gossypium hirsutum, Hibiscus cannabinus, Boehmerium nivea* and *Morus alba,* are resistant to Cd contaminated soil to different degrees. There are basically no unfavourable effects of Cd contaminated soil on the products of fibre crops. Moreover, there is hardly any Cd entering the food chain through these crops. Cd content of soil decreased by 27.6% after 5 years when ramie（*Boehmeria nivea* (L.) Gaud.）grew in Cd 100 mg/kg soil（Lin K.F., 1996）. Therefore, considering the strategy of agro-ecological regulation and safe-and-efficient utilization of Cd contaminated farmlands, these fibre crops should replace those sensitive crops in contaminated regions.

Vegetable rotation has obvious effects for low TE contaminated soil. Vegetables are divided among three levels according to BCF for Cd, i.e. low accumulation vegetables (BCF <1.5, cucumber, China bean, cauliflower, kale, white gourd), medium accumulation vegetables (BCF <4.5, lettuce, potato, radish, green onion, onion, and tomato) and high accumulation vegetables (BCF >4.5, spinach, celery, Chinese cabbage). In highly contaminated areas, low accumulation vegetables should be chosen; in medium grade contaminated area, vegetables should be chosen with low and medium accumulation. Cabbage and cauliflower planted in Spring, tomato, cucumber and China bean in Summer, kale, cauliflower, cucumber and China bean in Autumn in the Shanghai suburban area decreased Cd contents in vegetables by ~68% compared to Cd contents in vegetables prior to this rotation (Wang Y.G., *et al.*, 1997).

To some extent, low percentage of soluble parts and unstable transformation of TE in soils result in difficulty in fixation of TE. I*n situ* fixation with exterior amendments within low TE contents in soils may offer a promising option, especially for the low contaminated level derived from agricultural sources. Possible release of metal ions from fixed contexts under environmental stresses, such as acidic flows, temperature fluctuation and accelerated weathering processes, could be simulated in a kinetic way, which should obtain the detailed information for environmental risk assessment.

2.7. CONCLUSIONS

Total cultivated land area in China only occupies 15.1% of land area. Soil erosion, drought, nutrient deficiency, salinization and soil contamination lead to degradation of cultivated land. The main TE contamination is due to Cd, Pb, Cu and Hg contamination in soil in China. The sources of soil TE include wastewater irrigation, industrial wastes, industrial emissions, municipal waste, phosphate fertilizers and organic fertilizers linked to animal food and medicines with TE.

TE have become one of the major environmental hazards which cannot be degraded chemically or biologically, hence, they are ultimately indestructible. In the following sections, five fractions of TE in soil will be distinguished: water soluble and exchangeable, carbonate bound, iron-manganese oxide bound, organic bound and residual fractions. Mobility of TE in soil (horizontally and vertically) depends mainly on soil morphological factors (soil parent materials, soil texture, relief and soil types) and non-pedological factors (irrigation, cultivated practises, fertilizers and pesticides).

Organisms may absorb TE and suffer toxic effects of TE accumulation. TE influences the behaviour, physiological process, heredity of organisms and biodiversity. TE transfer from soil to vegetables and crops, then affect crop growth, breeding, biomass, yield and quality. Effects of TE on plants depend on TE contents, plant sensitivity and plant species. Some plants have developed numerous mechanisms to maintain or restore the activity of enzymes, then to create a new homeostasis and adapt to TE stress, such as hyperaccumulators.

Considering sustainable cultivated land use and food security, assessment of agricultural products and soil quality is necessary. The evaluation system of agricultural products involves environmental quality standards for soils, edible agricultural products and farmland of greenhouse vegetable product. There are three levels of vegetable soil quality which are linked to three levels of environmental quality evaluation standards, which are environmental requirements for the origin of non-environmental contaminated vegetables, environmental technical terms for green food production areas and technical norms for organic food.

Physical remediation, chemical remediation, bioremediation and phytoremediation are the main remediation mechanisms for soil contaminated by TE. Fixing additive application and crop rotation measures, belonging to *in situ* fixation techniques in low TE contaminated soil, are consistent with intensive agricultural districts with limited cultivated land, especially in periurban areas.

III: GENERAL METHODOLOGY

3.1. INTRODUCTION

The research area is located in Chenggong County, which is one of the most important vegetable production areas in Yunnan Province (the south-western border Province of China). There are special natural conditions, soil types, land uses, soil pressures and vegetable production situations in the research area.

In order to investigate soil TE contamination in the research area, the methodology is consistent with soil types, relief and vegetable production practises. Aims of this chapter are:

1) Introduce the basic information of the research area.

2) Explain the methodology.

3) Present the analytical methods used.

3.2. GENERAL DESCRIPTION

3.2.1. General description of Yunnan Province

Yunnan is located on the south-western border of China, covers an area of 3,832.1 × 10^4 ha and lies between 21°8’32’’ and 29°15’8’’ North and 97°31’39’’ and 106°11’47’’ East (Figure 3.1).

Figure 3.1: Map of China

(Source: http://www.perso.wanadoo.fr/cruells/chine/index-cartes.html).

Generally, northwest Yunnan is connected with the Qinghai-Tibet Plateau and strongly influenced by Himalayas in their late development. The Yunnan crust has been expressing very intense mobility and strong earthquakes still occasionally occur in Yunnan. The climate of Yunnan Province is mild, features small differences in temperature during the year, has only two obvious differentiated seasons, resulting from the alternate influence of the tropical summer monsoon and air masses from the Qinghai-Tibet plateau. Over 70 % of annual rain falls during the rainy season, from June to October, whereas rain can be very scarce during the dry season. From southern to north-western ends of the Province, seven mesoclimatic zones exist (Table 3.1).

Table 3.1: Main features of the seven mesoclimatic zones in Yunnan Province

(Source: Yunnan Province Planting Areas, 1992)

Climatic zones	Coldest month temperature range (^oC)		Days with temperature > 10 ^oC	Cumulative temperature (> 10 ^oC)	Harvest frequency (times)
	Mean value	Lowest value			
North tropics	>15	>3	>360	>7,500	3 / year
South subtropics	10 - 15	0 - 3	320 - 360	6,000 - 7,500	3 / year
Middle subtropics	8 - 10	- 3 - 0	280 - 320	5,000 - 6,000	5 / 2 years
North subtropics	**6 - 8**	**- 5 - - 3**	**220 - 280**	**4,200 - 5,000**	**2 / year**
South temperate	1 - 6	- 8 - - 5	160 - 220	3,200 - 4,200	2 / year
Middle temperate	0 - 2	- 10 - - 8	100 - 160	1,600 - 3,000	3 / 2 years
Plateau climate	<0	<-10	<100	<1,600	1 / year

The Province average elevation is 2,000 m, whereas the Meily Snow Mountain peaks at 6,740 m, the elevation in Hekou (near the Vietnamese border) is 76 m. Yunnan Province is mainly formed of mountainous areas, only 6% of the total area is considered as flat. From a geomorphological viewpoint, three great geomorphological units can be distinguished in Yunnan Province, which are the eastern Karst Plateau, Central Red Plateau and Western Hengduanshan Mountain (extension of Qinghai-Tibet Plateau) (Figure 3.2).

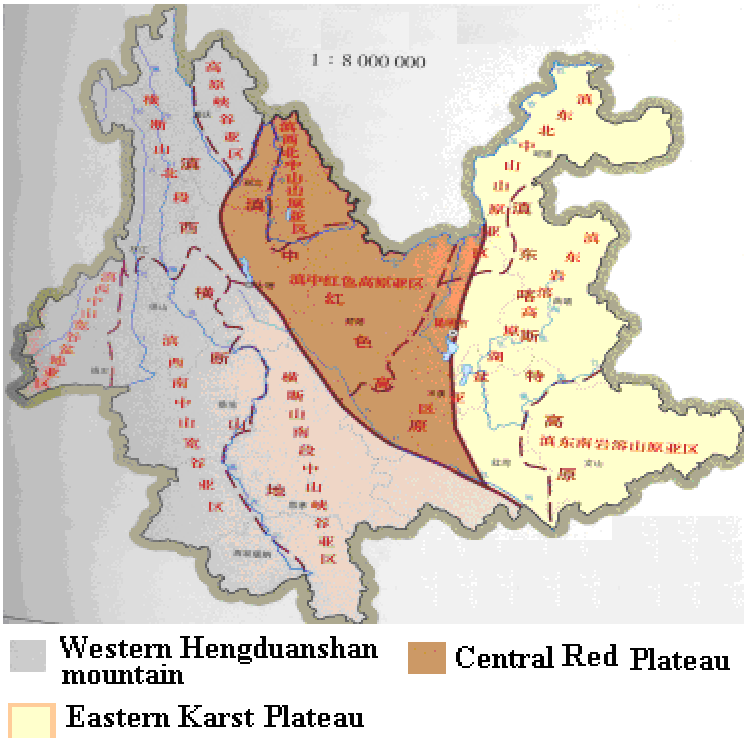


Figure 3.2: The three geomorphological units in Yunnan Province

(Source: Booklet of Yunnan Map, 2002).

Yunnan is largely endowed with mineral and biological resources, it is called the: “kingdom of non-ferrous metals”, “natural garden” and “kingdom of plants”. The total population is 44,830,000 inhabitants (2006). About 85% of the population lives in rural area and about one half is concentrated in basin areas.

- ***Yunnan soils***

The total area of soil is 3,522.9 × 10^4 ha in Yunnan Province (Figure 3.3). Red soils are the most widespread, accounting for 32.2% of the total area. Red soils show a patchy distribution all over the Province. Laterite soils are mainly encountered in southern areas ≤1,200-1,500 m. Purple soils (14.1%) are mainly distributed in the central region, alternating with red soils. Lateritic red soils (14.6%) become predominant up to an elevation of 2,300 m. Yellow soils increase with altitude, as a result of the combination of high precipitation and low temperature. In the region between 2,500-3,000 m altitude, brown soils dominate, whereas in the north and north-western high mountains (>3,500 m elevation), the main soils are dark brown earths and grass marshland. Purple shale exists from the Mesozoic Era (as parent material) at elevations <2,300 m (Figure 3.4).

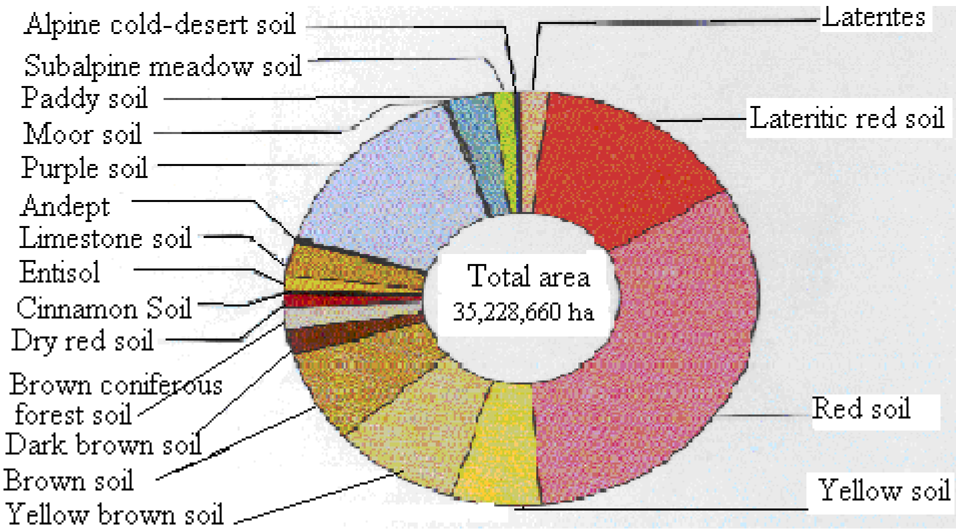


Figure 3.3: The soil types of Yunnan Province (Source: Zhao Q.G., *et al.*, 2006).

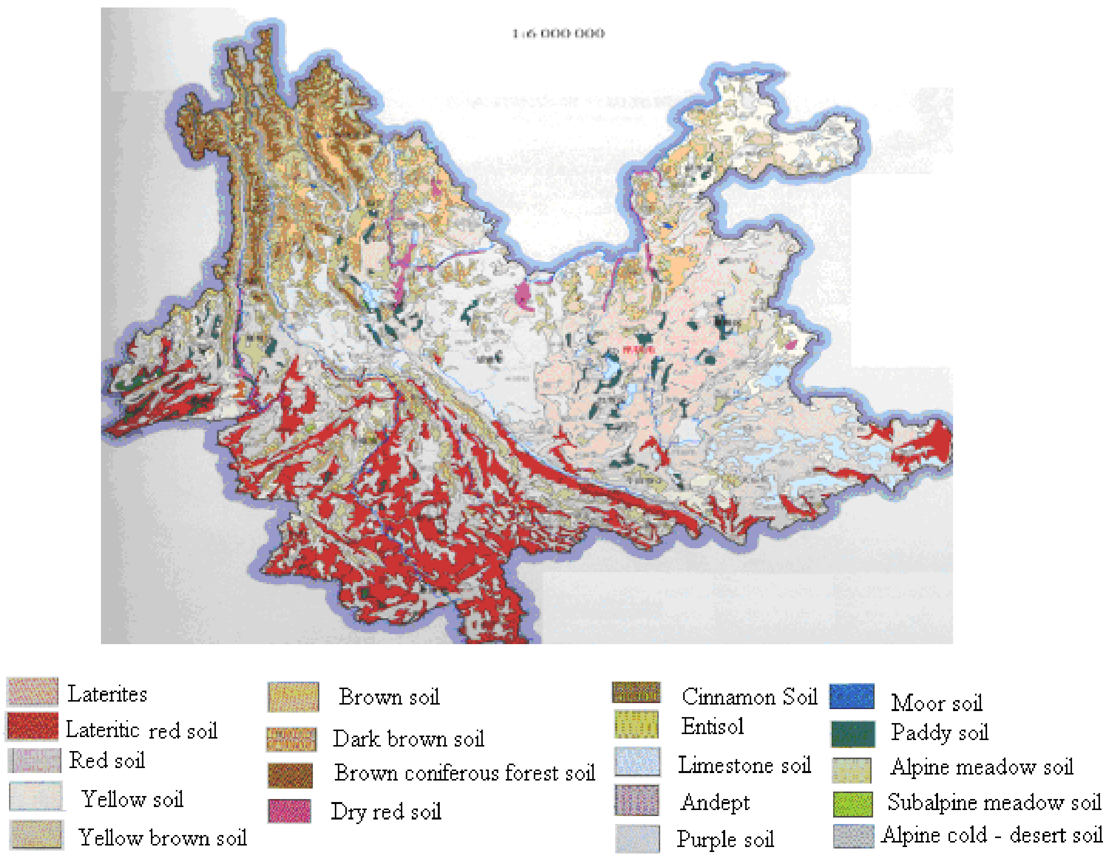


Figure 3.4: The distribution of soil types in Yunnan Province

(Source: Zhao Q.G., *et al.,* 2006).

● ***Cultivated land in Yunnan Province***

The total cultivated land is 633.97 × 10^4 ha (16.5% of the total Province area), including paddy fields (138.21 × 10^4 ha) and uplands (468.85 × 10^4 ha) in 2000 (Figure 3.5). The sloping upland is the most common land. Area of cultivated land with slope degree <2° is 72.38 × 10^4 ha, or 11.6% of the total area. There are 47.6% (306.83 × 10^4 ha) of cultivated land with slopes >15° (Figure 3.6).

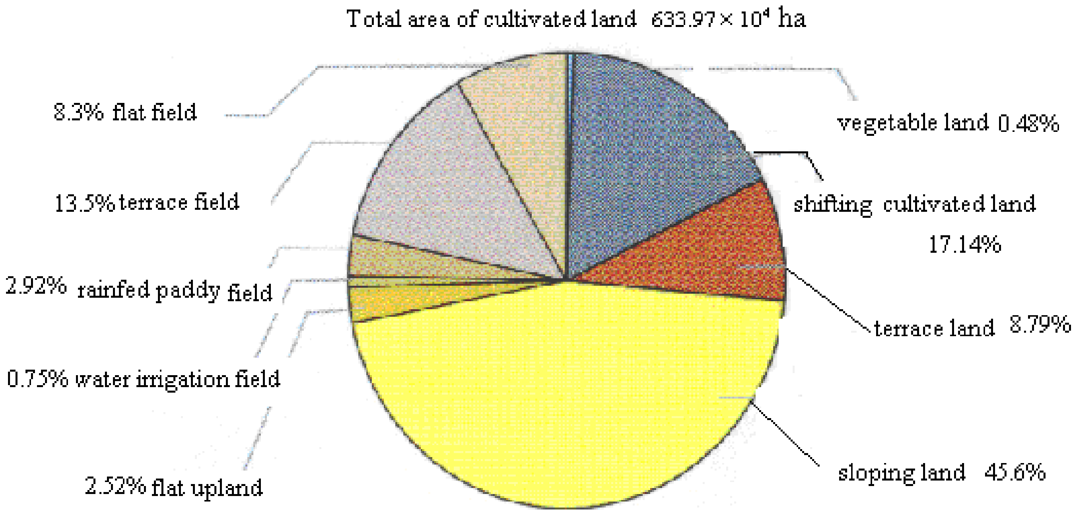


Figure 3.5: The distribution of percentage of different types of cultivated land to total cultivated land area in Yunnan Province (Source: Zhao Q.G., *et al.*, 2006).

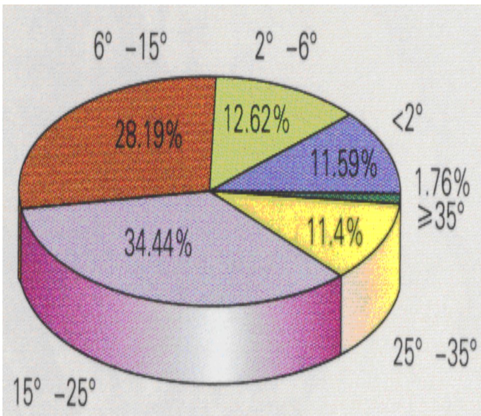


Figure 3.6: The distribution of percentage of cultivated land area with different slope degree to total cultivated land area in Yunnan Province (Source: Zhao Q.G., *et al.*, 2006).

● ***The importance of agriculture in Yunnan Province***

Agriculture is of prime importance for the Yunnan economy. Some 80% of the total population depend upon agricultural incomes. In 2006, the total gross domestic product (GDP) was 4,001.87

× 10^9 Yuan (RMB) (1€=10.09 Yuan, 1$=6.83 Yuan, August 2008), and total agricultural product value was 751.15 × 10^9 Yuan (RMB). The total area under crops in 2004 was 5,539,963 ha (Figure 3.7). Food crops refer to cereals, pulses and tubers, which are predominant (Figure 3.8). The major food crop is rice. The main rice planting areas are in Central Yunnan (24-26º N latitude) which, with 36% of the plantation area, produces 41% of the Provincial output, featuring an average yield of 10,500-12,000 kg/ha, with an increase from 1950-1995, and gentle decrease in 2000. Then, area and yield, corn is widely distributed (76-2,900 m altitude). Wheat is mainly grown in Central Yunnan, at elevations ranging from 1,000-2,500 m.

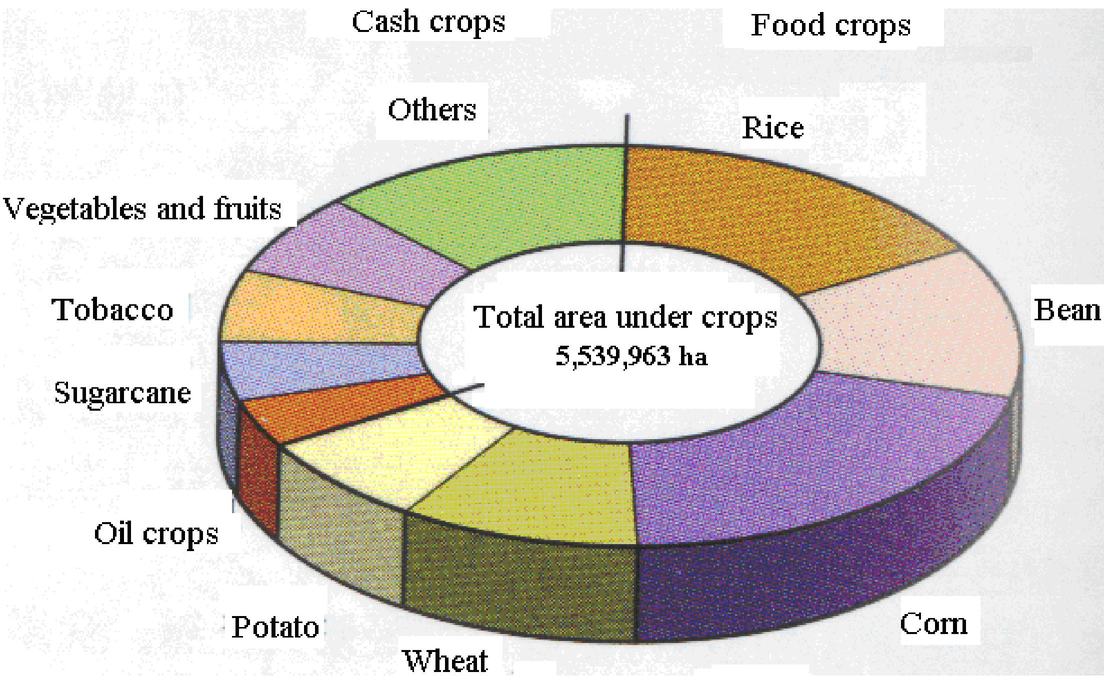


Figure 3.7: The distribution of areas under different crops in Yunnan Province

(Source: Zhao Q.G., *et al*., 2006).

Cash crops have been introduced gradually into farming systems. Rapid development is observed in rubber, tea, sugarcane and tobacco (Figure 3.8). Vegetables are becoming increasingly important in Yunnan Province, due to the dominant position of geological, climate and species resources. In 2006, the area of vegetables was 52.2 × 10^4 ha, output 1,031 × 10^4 tonnes, and income 115 × 10^9 Yuan (RMB) (15.3% of total agricultural product value).

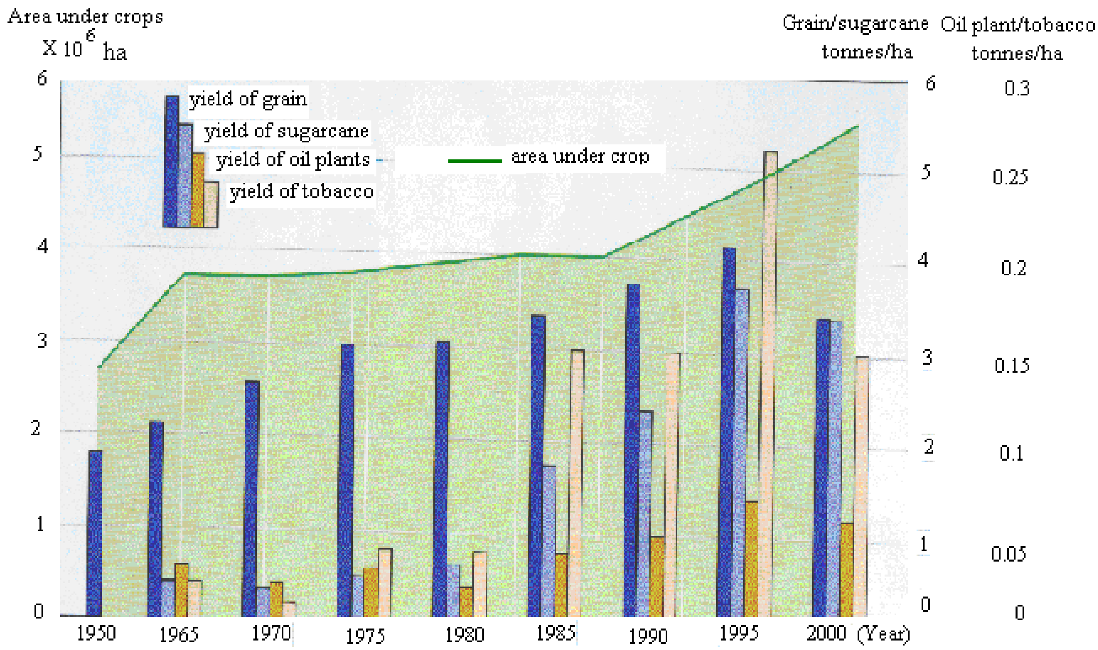


Figure 3.8: The area and yield of main crops from 1950-2000 in Yunnan Province

(Source: Zhao Q.G., *et al.*, 2006).

● ***Pressures on Yunnan soil***

Decrease in cultivated land surface is the greatest challenge for the soil resources of Yunnan Province, because of soil erosion, mud-rock flow, slip and soil contamination. The area of soil affected by erosion is 141,334 ha, or 36.9% of the total land area (Zhao Q.G., *et al.*, 2006). Some 83.45×10^4 ha of agricultural land are annually damaged by mud-rock flow and slip. Soil contamination also is a very serious pressure in Yunnan Province, due to domestic waste, pesticides, fertilizers, wastewater and plastic film residues (Liu H.J., *et al.*, 2006). Industrial activities are allowed by the natural resources in non-ferrous metals. Pesticides and fertilizers are applied unsuitably, causing pesticide residues, nitrate/nitrite and TE contaminations. Pesticides are used on 75-120 kg/ha each year in the main vegetable areas in Yunnan Province. In 2000, 54.2% of vegetable samples contained pesticide residues in Kunming market, 22.6% in 2003 (Duan C.Q., *et al.*, 2006).

Increasingly attention has been paid to soil TE contaminations. In south-east Yunnan Province, soil with high background values of TE should be avoided for planting vegetables. Because vegetable production is always near cities and towns, TE from industrial wastes, municipal domestic refuse and wastewater also cause soil contamination in Yunnan Province.

High background values of trace elements

As shown in Tables 3.2 and 3.3, the soil background values are quite high in Yunnan, especially in Kunming Prefecture, compared to that in China, even in the world. On average in Kunming, contents of Pb, Cu, Zn and Cd are higher than in the rest of China. Contents of Pb in topsoil (A layer) are higher than in parent materials (C layer).

The high background values are relative to mineral resources, which are abundant in Yunnan Province. The mineral main resources are Cu, Fe, Pb, Zn and P. For example, there is a distribution belt of Cu mines from north-west to south-east, resulting in high Cu contents in soil. Pb/Zn mines are distributed widely in Yunnan Province, causing high Pb, Zn and Cd contents in soil.

Table 3.2: Background values (mg/kg) of TE in soil (A layer) and parent materials (C layer) in Yunnan Province (Source: Duan C.Q., *et al.*, 2006)

Element	A layer		C layer
	Range	Mean	
Pb	2.2 - 108.2	44.8	40.1
Cd	0.003 - 1.059	0.241	0.243
Cu	3.5 - 145.6	49.2	49.1
Zn	0.4 - 211.6	95.0	103.6
As	0.6 - 64.8	18.9	21.2
Cr	1.0 - 160.0	78.4	87.3
Hg	0.003 - 0.150	0.054	0.080
Ni	0.4 - 104.2	45.2	58.4

Table 3.3: TE contents (mg/kg) in soils (Source: Duan C.Q., *et al.*, 2006)

Element	World Soils		China soils		Yunnan soils		Kunming soils
	Range	Mean	Range	Mean	Range	Mean	Mean
Pb	2 - 300	35.0	1.5 - 52.1	24.0	2.2 - 108.2	37.9	43.3
Cd	0.010 - 2.000	0.060	0.001 - 0.460	0.070	0.075 - 0.331	0.116	0.177
Cu	2 - 250	20.0	7.3 - 55.1	20.0	3.5 - 145.6	34.0	44.6
Zn	1 - 900	40.0	5.0 - 143.8	74.4	0.4 - 211.6	77.7	99.2

Anthropogenic sources of trace elements

Contents of TE are different among soil types in Yunnan Province (Table 3.4). TE contents in soil are increasing in some regions (Wang H.S., *et al*., 2006; Zha T. & Li Z.Y., 2003). It seems that agricultural soils contaminated by TE suffer from the use of contaminated water for irrigation. These pesticides often contain with TE as active materials, for example, Zn-based (Zineb, Mancozeb) or Cu-based ($CuSO_4$). Some 26,000-30,000 tonnes of pesticides are used each year, in which 40% of pesticides are applied on vegetables in Yunnan Province.

Table 3.4: Mean contents (mg/kg) of Pb, Cd, Cu and Zn in Yunnan soils in 1996

(Source: Wang H.S., *et al*., 2006)

Soil	Pb	Cd	Cu	Zn
Mean	52.8	1.430	38.7	89.8
Red soil	50.3	1.510	50.6	92.3
Paddy soil	62.1	1.430	37.8	87.2
Alluvial soil	39.6	1.070	49.3	98.4

The use of phosphate fertilizers and other materials contaminated by TE were also observed (Table 3.5). For instance, the mean contents of TE in rock phosphate are 3.8 mg/kg for Cd, 242.1 mg/kg for Pb, 54.2 mg/kg for Cu and 225.3 mg/kg for Zn (Hua Z.Z. & Duan Q.Z., 2001). Cd contents in phosphate mines in China are 0.1-571 mg/kg (mainly 0.2-2.5 mg/kg) and correspond to a medium level (Lu R.S., 1998). However, it represents a small part of the total quantity of phosphate fertilizers used by farmers, compared to calcium superphosphate [$Ca(H_2PO_4)_2 \cdot H_2O$], fused calcium magnesium phosphate [α-$Ca_3 (PO_4)_2 \cdot H_2O$] and $CaH_4(PO_4)_2 \cdot H_2O$. Average amounts of phosphate fertilizers are ~ 40 kg/ha/year in Yunnan, 260 kg//ha/year in Kunming Prefecture, ~438 kg/ha/year around Dianchi Lake.

Table 3.5: TE contents (mg/kg) in agricultural materials (Source: Wang H.X., 2002)

Element	Solid wastes	Farmyard manure	Phosphate fertilizers	Nitrogen fertilizers	Lime	Pesticides	Urban sludge	Ash
Cd	0.010 - 100	0.100 - 0.800	0.100 - 190	0.050 - 8.500	0 - 0.040	-	<1 - 3,410	0.200 - 14
Cu	13 - 3,580	2 - 172	1 - 300	-	2 - 125	-	50 - 8,000	45 - 616
Pb	1.3 - 2,240	0.4 - 27	4 - 1,000	2 - 120	20 - 1,250	11 - 26	2 - 7,000	3.1 - 241
Zn	82 - 5,894	15 - 566	50 - 1,450	1 - 42	10 - 450	-	91 - 49,000	14 - 406

Facing these pressures, measures should be taken to maintain safe agricultural production and guarantee human health.

3.2.2. Description of the research area: Chenggong County

3.2.2.1 Natural conditions

Chenggong County is located to the south-east of Kunming City, which is located in the middle of the Yunnan Province. Dianchi Lake is next to the west border line of Chenggong County (Figure 3.9).

Figure 3.9: Location of Chenggong County and the research area

(Source: Map Collection of Yunnan Province of China, original scale: 1:550,000).

Chenggong County covers 4.79 × 10^4 ha, which lies between 25^o 59’ 32’’-24^o 24’ 0’’ N and 102^o 59’ 15’’-102^o 45’ 30’’ E. The total soil area is 33,236 ha. Agricultural production has been untaken for ~2,000 years. The main agricultural crops are rice, fruits, vegetables and flowers.

The climate belongs to the north-subtropical climate zone, which has the features of the tropical monsoon. Over 70% of annual rain fall during the rainy season, running from June to October. As a result, rainfall can be very scarce during the dry season from November to May. There are small differences in temperature during the year. The average temperature is 14.7 ^{o}C annually, with the coldest mean temperature of 7.8 ^{o}C in January, and the warmest mean temperature of 19.8 ^{o}C in July. The average temperature of east mountain areas is 1.7 ^{o}C lower than in the lacustrine plains. Total precipitation is 778 mm annually, and the highest rainfall is 152 mm in August, whilst the lowest rainfall is ~10 mm in January. According to the situation, the rainfall in the mountain areas is more than in the lacustrine plains.

Evaporation is 2,129 mm annually, which is 2.7 times higher than precipitation. The average relative humidity is 74% and the lowest relative humidity is 63%, in Spring. The average wind speed is 2.7 m/s, which is mainly from the south-west. The highest speed wind is ~20 m/s in March. The average sunshine time is 2,194 hours annually.

3.2.2.2. Geomorphology, Geology and Pedology

- ***Geomorphology***

The general orientation of relief is EN-WS in Chenggong County. The eastern and the northern areas are middle-mountain areas, which are transition or hilly land, and the western area is the lakeside, forming a relief gradient from the north-east to south-west. Elevation ranges from 1,775 m-2,820 m in Chenggong County. There are three geomorphological units (Poncin, 2003) (Figure 3.10):

- Lacustrine unit, which is the main agricultural area from 1,775 m-1,900 m elevation, next to Dianchi Lake.
- Transition unit, which is flat, but has some isolated hills with 1,900 m-2,300 m elevation. The vegetation is fruit trees and vegetables.

- Middle mountain unit, which is the main forestry and husbandry area with 2,300 m-2,820 m elevation.

● ***Geology***

Strata of Chenggong County and the research area

The strata in Yunnan are developed completely. There are exposed strata from Proterozoic Era to the Quaternary Period, except the Archaeozoic Era. The degrees of stratigraphic development being different in each area, groups being complex and useful sedimentary minerals are abundant (Yunnan Bureau of Geology and Mineral Resources, 1990).

There are many strata in Chenggong County from Palaeozoic to Cainozic era, and the distribution of Palaeozoic era stratum is the most frequent in the east Liangwanshan Mountain area, including limestone of Sinian, sandstone, shale and siltstones of Cambrianage, Devonian-Carboniferous calcareous rock, Permian limestone and basalt (Figure 3.10). In hilly land area, the most important stratum is Tertiary dark-grey argillaceous sandstones and conglomerate. In south-western Jian Mountain and some isolated mountains, the main strata are Sinian limestone, Cambrian sandstones, and Carboniferous-Permian limestone and basalt. There are Quaternary sands and gravels, calcium clay, slime, and peat covering the Tertiary strata.

Geology of the research area

Strata of the research area include the Cambrian system（$Є_1C$), Permian system (P_1d, P_1Y) and Quaternary system (Q) (Figure 3.10). Between the lacustrine area and the transition area, there are some isolated hills from the Cambrian system. The main constituent rocks are shale and quartz sandstone mixed with some argillaceous siltstone.

The Permian system is located on the eastern mountain area named Bailongtan Mountain, including P_1d and P_1Y units. The P_1d unit is composed of quartz sandstone, argillites and siltstone mixed with dolomite and limestone. The P_1Y unit is carbonate stone and dolomite mixed with limestone.

The Quaternary system (Q) is distributed in lacustrine and transition units. Lacustrine unit is Q_4 (Holocene) including Q_4^{l} (lacustrine) and Q^{lal} (alluvial lacustrine). The lithological composition is yellow-gravel, clay, silt and coarse sand mixed with peat-mud, slime and turf. It is a typical lacustrine deposit. Q^{lal} (alluvial lacustrine) is composed of colourful gravel and clay-silt. The upper layer belongs to lacustrine deposits and the lower layer belongs to alluvial deposits. The transition unit has Q_2 (Early Pleistocene), Q_3 (Middle Pleistocene) and Q_4 (Holocene). The lithology is composed of sand and gravel with an 0.8 m layer of red soil.

Soil-forming parent materials

The soil types come from five groups of parent materials in the research area (Yunnan Bureau of Geology and Mineral Resources, 1990):

- Soils from lacustrine sediments distributed in lacustrine and transition units, correspond to the main farming area. Lacustrine sediments are part of the Quaternary system. At the end of the Tertiary and early Quaternary, the eastern land raised and the Dianchi Lake basin subsided, resulting in the soil gradually de-swamping. Sediments are composed of clay, silt and fine sand; their main distribution area is along the Dianchi lakeside.
- Lacustrine sediments - alluvial mixed deposits are distributed in the transition area with elevation from 1,887-1,900 m. They consist of clay, silt and fine sand, but the particle size is a little larger than in the lacustrine materials. The texture is heavy loam and light clay.
- Soils from diluvium deposits are the main upland soils with red or light red colours. They can keep water and nutrients very well. Sometimes, small iron-manganese concretion particles can be found in these soils. Diluvium deposits include gravel, sand and clay on hill sides. It is the main area of fruits and vegetable production.
- Soils from sandstone and shale weathering are distributed in the transition unit. The features are less organic matter, abundant silt, high water permeability with acid reaction and yellow-red or light yellow colour.
- Soils from carbonate limestone and marlstone weathering can be found in the mountain unit. They have clay texture, lower nutrient contents with acid reaction and red or red-brown colour. Residual-slope deposits are distributed in this area, which accumulate on footslopes after the weathering of parent materials.

Legend:

- Quaternary: lacustrine deposit; slope deposit ; sand clay
- Permian: dolomite + basalt
- Permian: dolomite
- Carboniferous: mud stone with calcic podzol + sandy stone
- Permian: dolomite + mudstone
- Cambrian: shale with interbedded sandstone
- Lakes

Figure 3.10: Geological map of the research area, Chenggong County (Source: Department of Soil and Land Resources of Yunnan Province, original scale: 1:50,000, 1991).

- ***Pedology***

Soil types

In Chenggong County, there are five soil groups, which are brown soil, red soil, purple soil, alluvial soil and paddy soil (Yunnan Bureau of Geology and Mineral Resources, 1990). Meanwhile, 10 subgroups and 18 soil genus are observed (Table 3.6). Red soil is the most familiar soil group, with 25,174 ha, or 75.74% of the total soil area. The second one is paddy soil, with 5,210 ha (15.68% of the total soil area). Then purple soil, brown soil and alluvial soil are 2,157 ha (6.49%), 358 ha (1.08%) and 337 ha (1.01%), respectively. In the research area, the soil groups are mainly red soil, alluvial soil and paddy soil.

Table 3.6: Soil classification of Chenggong County

(Source: Yearbook of Chenggong County, 2004)

Soil order	Soil great group	Subgroup	Area (ha)
Alfisol	Brown soil	Brown earth	358
Ferralsol	Red soil	Brown red soil	1,849
		Red earth	23,325
Entisol	Alluvial soil	Alluvial soil with dark colour	241
		Alluvial soil with light colour	96
	Purple soil	Purple earth	2,157
Anthrosol	Paddy soil	Submergic paddy soil	1,402
		Hydragric paddy soil	2,885
		Gleyic paddy soil	580
		Swamp paddy soil	343

Lateral distribution of soil

Soil types change with elevation in Chenggong County. The paddy soil is distributed from 1,887-2,300 m. Red soil is distributed from 2,300-2,600 m elevation, the subgroup is the brown red soil and red earth is the transition type from brown to red in the limestone mountain area. Then brown soil is distributed in cold mountain areas between 2,600-2,800 m elevation (Figure 3.11).

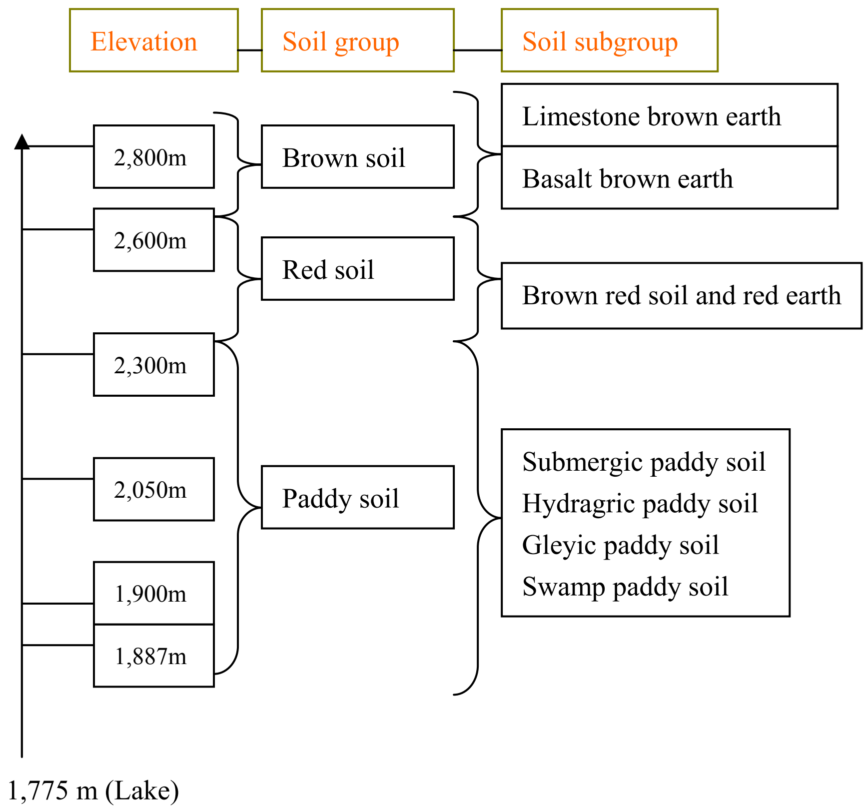


Figure 3.11: The lateral distribution of soil in Chenggong County

(Source: Kunming Soil Investigation Office, 1984).

3.2.2.3 Land use and problems

● ***Description of land use***

Out of the total land area in Chenggong County, mountain, transition and lacustrine areas are 49.5, 33.1 and 17.4%, respectively. The population was 158,085 in 2003 with 125,181 (79.19%) in rural areas, whilst average cultivated land area was ~0.03 ha/person. The areas of food crops were 1,706.67 ha and total yield in 2003 was 9,080 t, including wheat, broad beans, peas, sweet potatoes, rice, corn and others (Table 3.7) (Yearbook of Chenggong County, 2004).

Table 3.7: Areas of food crops in 2003 (Source: Yearbook of Chenggong County, 2004)

Crops	Areas (ha)	% of total areas
Rice	200	11.8
Corn	667	39.1
Sweet potato	347	20.3
Pea	100	5.8
Broad bean	57	3.3
Wheat	69.7	4.1
Bean	66. 7	3.8
Other food crops	233.3	13.7

Four geographical areas are classified according to land use types in Chenggong County, which are:

- Food crop-vegetable area is in the lacustrine unit on paddy soil and alluvial soil. This unit is located on the west of the Kunming-Luoyang Road, and near Dianchi Lake, at 1,887-1,900 m elevation. The area is 7,700 ha or 17% of the total area. The multiple crop index and yield are high, and irrigation is convenient. Presently, crops are vegetables and flowers.
- Fruit-the food crop area is in the transition unit on red soil. This unit is located east of Kunming-Luoyang Road, at 1,900-2,050 m elevation. The area is 15,400 ha or 34% of the total area. The relief is flat and the slope 4-8^{o}. Irrigation is difficult. The yield is lower than in the lacustrine unit, and presently the main crops are wheat, corn, beans and vegetables.
- Forest-food crop - husbandry is in the mountain unit on red soil and purple soil. The elevation is 2,050-2,300 m. The temperature and yield are low. This unit is more suitable for forest than for agriculture. The main crops are potatoes, corn, wheat and rape.
- Forest-husbandry area is in the mountain unit on brown soil. The relief is high with abrupt slopes at 2,300-2,820 m elevation, resulting in a cold climate. The main crops are potatoes, rape and buckwheat.

With the development of agriculture, vegetables and flowers are planted in the main agricultural production area, especially in the lacustrine unit. In 2003, the area of vegetables was 10,333 ha, flowers 167 ha and fruit 5,533 ha (Table 3.8). Over 60 species of vegetables and flowers are grown, the main vegetables being Chinese cabbage, salad, celery, chilli and sweat pea. The main fruits are pear, apple and peach (Table 3.8).

Table 3.8: Areas of vegetables, flowers and fruits in 2003

(Source: Yearbook of Chenggong County, 2004)

Plants	Areas (ha)	Economic income ($\times 10^9$ Yuan RMB*)	Main species	Areas (ha)
Vegetables	10,333	2.87	Chinese cabbage	1,400
			Salad	1,467
			Celery	1,500
			Chilli	627
			Sweat Pea	640
			Cauliflower	1,040
Flowers	1,667	2.26	Rose	407
			Carnation	345
			Lily	41
Fruits	5,533	0.23	Pear	979
			Apple	377
			Peach	503

*Yuan RMB: Chinese currency money unit (1€=10.09 Yuan, 1$=6.83 Yuan, August 2008).

- ***Main land use problems***

The main land use problems in Chenggong County are:

- Areas of cultivated land are decreasing every year, due to city development and soil erosion.
- Soil fertility and pH of some soils are low, resulting in low production levels.
- Soil contamination is becoming increasingly serious, and soil quality is influenced by water and air contamination.

Attention has been paid to soil contamination in Yunnan Province (Hua Z.Z. & Duan Q.Z., 2001). The ranges of total TE contents in soil were 27.18-265.78 mg/kg for Pb, 0.30-1.25 mg/kg for Cd and 13.89-171.68 mg/kg for Cu, in Dianchi Lake watershed (Vegetable Office of Chenggong County, 2001) (Table 3.9). Cd contents in Dayu and Daying villages were higher than the background value of Kunming Prefecture. In 1999, samples from three villages out of five showed Zn and Cu contents above the background values of Kunming Prefecture.

Table 3.9: Total TE contents in soil of Chenggong County

(Source: Vegetable Office of Chenggong County, 2001)

Village	Year	Contents (mg/kg)			
		Pb	Cd	Cu	Zn
Dayu	1998	25.9	0.380	175	112
	1999	23.3	0.080	91.1	92.2
Haiyan	1998	28.5	0.076	45.5	76.8
	1999	35.3	0.096	38	98.7
Daying	1998	29.8	0.267	155	99.5
	1999	31.7	0.205	145	111
Maizi	1999	34.4	0.098	86.4	118
Wanxicong	1999	23.9	0.089	182	139
Background values in Kunming Prefecture		43.3	0.177	44.6	99.2

Considering the situation of vegetable production and soil TE contamination in Chenggong County, it should be important to understand the sources of TE and assess the degree of TE contamination in soils and vegetables, then to improve the quality and sustainable vegetable production in Chenggong County.

3.3. PRESENTATION OF THE METHODOLOGY

In this study, information was collected through field survey and laboratory analysis, processed and expressed using a Geographical Information System (GIS) and statistical analyses. A geomorphopedological approach has been used, which links the soil characteristics of each map unit with geology (rocks as soil parent material) and geomorphology (relief forms). Conceptual models of information data structure are shown in Figure 3.12. The outline conceptual framework of this study is shown in Table 3.10.

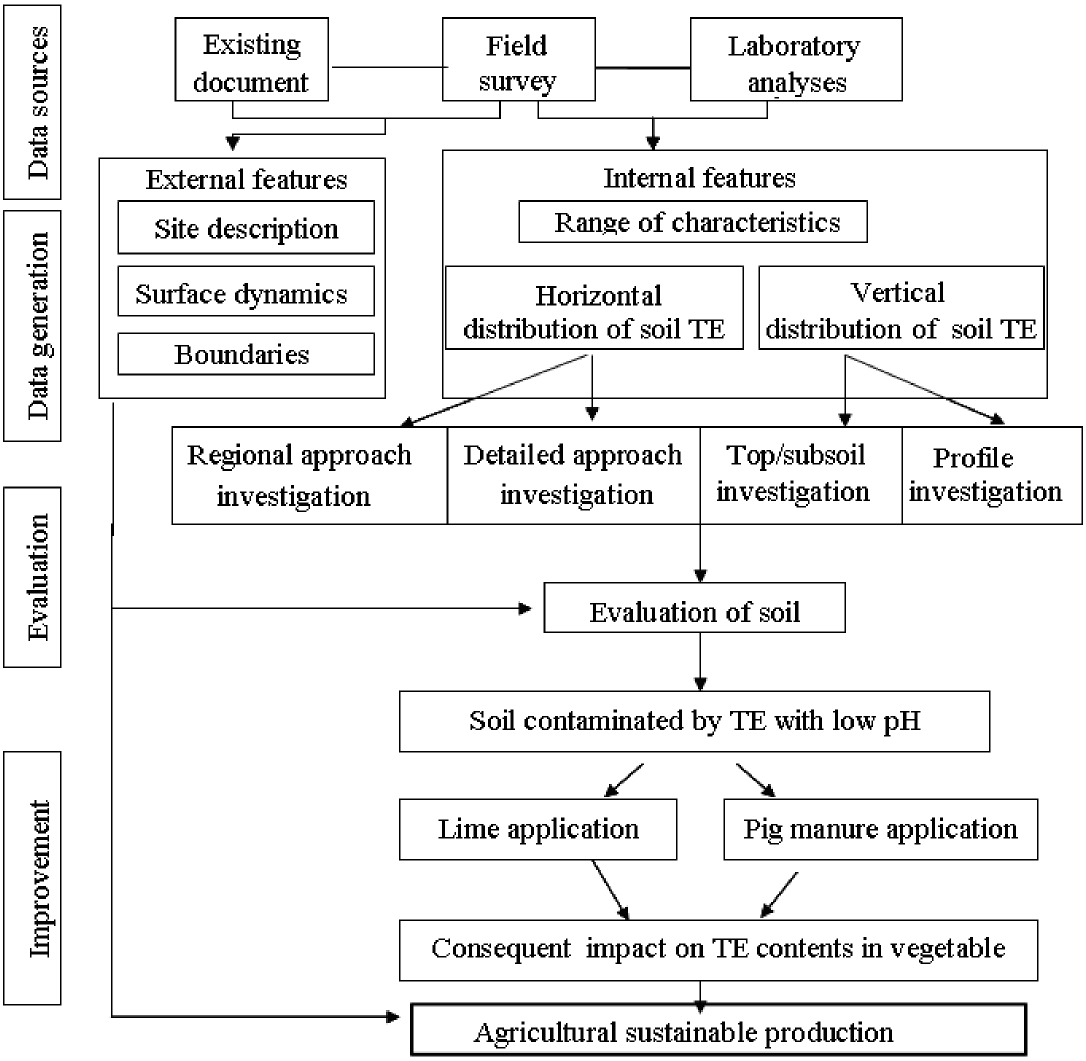


Figure 3.12: Conceptual model of information data structure.

Table 3.10: General description of framework

Scale			Tasks
Field surveys	Horizontal distribution	Regional approach	Analysis of 130 plots for overview of soil contaminated by TE (56 km^2)
		Detailed approach	Variability analysis of intra-unit and intra-plot/greenhouse to address the problems of soil with TE variation (0.5-1 km^2 and 5 × 5 greenhouses)
	Vertical distribution	Top/subsoil	Detailed analysis in 32 pairs of plots (extracted from 130 plots) to assess contamination and natural background values
		Profile	Analysis of 5 profiles for soil characteristics at vertical scale
Experiments	Pot		Choice of soils from the three units for pot experiments in order to decrease TE contents in Chinese cabbage
	Field		Choice of plots/greenhouse from the three units for field experiments in order to decrease TE contents in Chinese cabbage

3.3.1. Existing documents

There are few accurate and recent soil documents in Chenggong County, including one set of Topographical maps from 1976 (Figure 3.13), a Geological Map at 1:50,000 scale from 1991 (Figure 3.10), and Satellite Imagery from February 2004 (Figure 3.14).

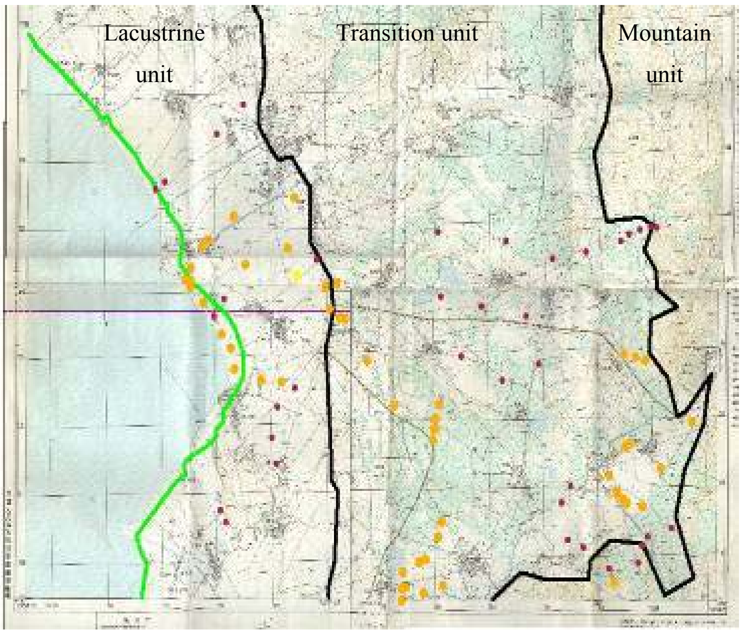


Figure 3.13: Topographical Map (Source: Department of Survey and Map of Yunnan Province, Original scale: 1:25,000, 1976).

Figure 3.14: Satellite Imagery (Source: Department of Survey and Map of Yunnan Province, Original scale: 1:50,000, 2004).

3.3.2. Field survey

A series of field surveys were conducted to collect geological, geomorphological and pedological information in 2004-2006 (Plate 3.1). To match and synthesize the information from different documents, these documents had to be placed into the same co-ordinate system. In surveys, the positions were determined with a portable GPS (Global Positioning System) (Magellan, US) (10 m accuracy); the co-ordinates of some points (e.g. main paths, roads) were taken in Chenggong County to georeference the topographical and geological maps.

Plate 3.1: Field survey in Chenggong County.

Geological survey: lithology and geomorphology

On the basis of the Geological Map of Chenggong County (Figure 3.10), a lithological survey was carried out in 2004 by Professor Daniel Lacroix and Dr Gilles Colinet from Gembloux Agricultural University. The main lithological formation were identified and some rock samples taken for further observation. Based on the original topographical map (Figure 3.13) and aerial photos examined under the stereoscope, the field check was conducted. Altitude was recorded at additional positions using a portable GPS.

Pedological survey

The scope, intensity and scale of the pedological survey were decided based on data required and the purposes of the evaluation. The aims of the survey are to define land qualities in terms of TE (Pb, Cd, Cu and Zn) and effect factors. In this study, soil surveys were carried out through horizontal (regional and detailed) and vertical approaches.

A. Augering along toposequences

Hand augering down to 80-120 cm where possible, was conducted along 17 toposequences in 2004-2006 (Figure 4.1, Plate 3.2). Six toposequences along Dianchi Lake are expressed as Toposequences 1-6. Nine toposequences in transition unit are expressed as Toposequences 7-15. Both toposequences 16 and 17 illustrate the mountain unit. Field observations for soil volumes included texture by hand analysis, colour (Munsell charts), stoniness and pH with a test kit. Soil samples of 130 topsoil and 32 pairs top/subsoil samples were collected for laboratory analysis. Chemical properties (pH, physical clay, SOC, Total-N, CEC) and TE contents (Pb, Cd, Cu, Zn) were analysed at Gembloux Agricultural University (GAU) and Yunnan Agricultural University (YAU).

Plate 3.2: Augering in the field.

B. Detailed observations

In order to better assess the effects of agricultural practises at detailed scales, two sites for detailed investigation were selected, the representatively of which was assessed by augerings (Figure 4.1, Figure 3.15, Figure 3.16). One site was selected in the lacustrine unit and the other in the transition unit. As the land is covered by greenhouses, the size of these greenhouses was taken into account to decide the sampling locations.

The analysis of variability was organized in two steps:

- Step 1: variability within 1 km^2. Survey area (1 km^2) in the lacustrine unit is chosen between four villages (Jianwei, Gucheng, Kele, Shibei) (Figure 4.1).Variability at this detailed scale was analysed by a composite sampling, with 100 points in a 1000 × 1000 m surface along a grid of 100 × 100 m fitted to the size of the greenhouses (according to their size, 3 greenhouses × 20-22 greenhouses) in the lacustrine unit. Samples were collected in the greenhouse in the 100 grids (Figure 3.15). For the transition unit, the number of samples (7 × 7 = 49) and the area (700 × 700 m, 0.49 km^2) were chosen according to the relief between two villages (Yuhua, Xiazhuan) (Figure 3.16, Figure 4.1).
- Step 2: variability within one grid. Analysis of the variability within 1 greenhouse and among five greenhouses close together, from which 25 samples were collected by 5 samples in each greenhouse. The results are available for both places.

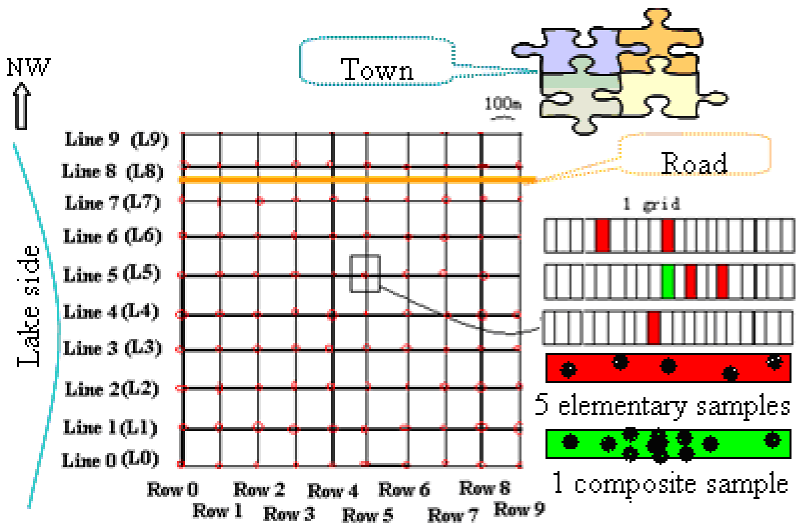


Figure 3.15: The location of soil samples of the detailed approach in the lacustrine unit.

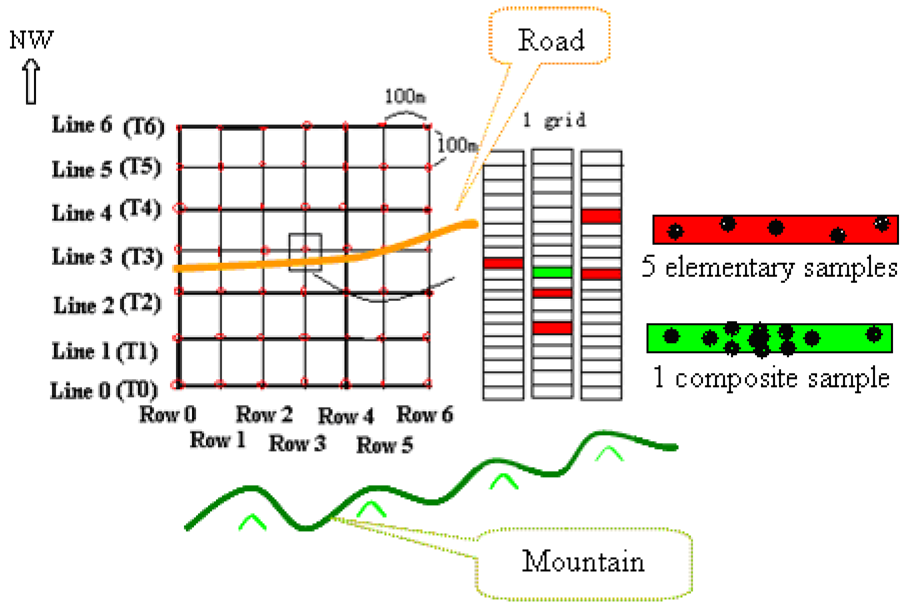


Figure 3.16: The location of soil samples of the detailed approach in the transition unit.

<u>C. 32 pairs of top/subsoil sample observation</u>

Topsoil and subsoil pairs consist of the first horizon of the soil and the horizon ranging between 60-80 cm. When the horizon at this depth is too different from the surface horizon, samples from the same parental material were taken. Some 32 pairs of top/subsoil samples were analysed in order to evaluate vertical differences in soil characteristics, TE contents, natural background values and the origin of contamination. The topsoil of the primary 32 top/subsoil pair samples is included in the 130 topsoil samples.

D. Soil profile description

Based on the results of augering descriptions and field observations, five main soil types were selected and soil profiles were described in detail, including two profiles (P1, P2) in the lacustrine unit and three (P3, P4, P5) in the transition unit (Figure 4.1).

3.4. METHODS

Soil sampling

On the basis of the soil identification and methodology described in Section 3.3, the soil sampling strategy is summarized in Table 3.11. Soil augering and soil profile samples were collected from different horizons. Topsoil samples for regional approach were collected from 0-15 cm depth, which is an elementary sample. Topsoil samples for the detailed approaches were also collected from 0-15 cm depth, composite topsoil samples; each of them being composed of nine sub-samples taken at random from a 10 × 10 m area in the centre of plot and two samples from two opposite sides of the plot. Top/subsoil pair samples were collected from 0-15 cm and 60-80 cm. One kg samples taken from these collective sites were air-dried.

Table 3.11: Summary of soil sampling strategy

Soil sampling	Depth (cm)	Sampling Method	Numbers	Analysis Laboratory
Regional topsoil	0 - 15	Elementary sample	130	GAU, YAU
Subsoil	60 - 80	Elementary sample	32	GAU,YAU
Profile	0 - 80 (- 185)	Elementary sample	5	GAU, YAU
Detailed approach	0 - 15	Composite sample	149 (100+49)	YAU
Greenhouse topsoil	0 - 15	Composite sample	50 (25 + 25)	YAU

Soil preparation

Gembloux Agricultural University

Air-dried samples were gently broken up in a porcelain mortar and passed through a 2.0 mm sieve for soil property and available TE content analysis. A sub-sample was then crushed to 0.25 mm in the same mortar for carbon content and total TE content analyses.

Yunnan Agricultural University

The method was the same as GAU, except for size fraction <1.0 mm used in Chinese methods instead of <2.0 mm.

Laboratory soil analysis methods

Laboratory work was jointly carried out at Gembloux Agricultural University (GAU) and Yunnan Agricultural University (YAU). Therefore sub-samples were transported to these two laboratories. Soil pH, soil organic carbon (SOC), total nitrogen (T-N), CEC, physical clay (<0.01 mm), total TE contents (Pb, Cd, Cu, Zn), sequential extraction fraction (SEF) TE contents (Pb, Cd, Cu, Zn) and available TE contents (Pb, Cd, Cu, Zn) were analysed (Table 3.12). The analysis procedures are described in details in Annex 3.1.

Table 3.12: Summary of soil analysis methods

Parameter	Analysis procedures		Numbers of analysed samples
	GAU	YAU	
pH water	2/5 soil suspension (2 mm)[(a)] Extraction: water (2 h shaking) Centrifugation (10 min) Measurement: pH potentiometer	2/5 soil suspension (1 mm) Extraction: water (10 min) Measurement: Whatman pH meter	130 (regional topsoil)
CEC	Metson method (2 mm) Saturation: NH_4OAC 1N pH 7 (2 h shaking) Centrifugation (10 min) Supernatant: NaOH replace NH_4^+ Measurement: titrate with HCI	$BaCl_2$ method (1 mm) Saturation: $BaCl_2$ 1 N pH 7 (2 h shaking) Centrifugation (20 min) Supernatant: H_2SO_4 replace Cl^- Measurement: titrate with NaOH	88 (regional topsoil)
SOC	Springer - Klee method (0.25 mm) Oxidant: $K_2Cr_2O_7 + H_2SO_4$ Measurement: titrate the excess of oxidant with Mohr's salt	Walkley - Black method (0.25 mm) Oxidant: $K_2Cr_2O_7 + H_2SO_4$ Measurement: titrate the excess of oxidant with Fe_2SO_4	130 (regional topsoil)
Physical clay		<0.01 mm physical clay <0.001 mm clay Pre-treatment: Na OH 0.5 M (15 min) (1 mm) Measurement: hydrometer	88 (regional topsoil)
T-N	Macro - Kjeldahl method (0.25 mm) Mineralization: Na_2SO_4.Se + H_2SO_4 Distillation: alkaline condition and trapped with H_3BO_3 Measurement: titrate $(NH_4)_3BO_3$ with HCI		130 (regional topsoil)
Total TE content	Aqua regia method (0.25 mm) Extraction: Aqua regia Measurement: AAS*	Aqua regia - $HCIO_4$ method (0.25 mm) Extraction: Aqua regia - $HCIO_4$ Measurement: AAS	130 + 32 (All soil samples)
SEF**TE content		Tessier method (1 mm) Extraction; acetic acid + hydroxyl ammonium chloride + hydrogen peroxide-ammonium acetate Measurement: AAS	21 (Chinese cabbage soil)
Available TE	EDTA method (2 mm) Extraction: EDTA (0.02 N) + NH_4OAc (Ammonium acetate 0.5 N), 1 h shaking Measurement: AAS		21 (Chinese cabbage soil)

AAS*: Atomic Absorption Spectrophotometer; SEF**: sequential extraction fraction

Plant sampling and laboratory analysis methods

These methods are described in Section 5.3.

Pot and field Experiments

Designs of pot and field Experiments are described in Section 6.3.

3.5. DISCUSSION AND CONCLUSIONS

Chenggong County is one of most important vegetable and flower production areas in Yunnan Province. Geomorphological units, soil types and land use history in the research area influence the soil sampling strategies.

First, soil toposequences and the regional approach of soil sampling are based on the relief in the research area, subdivided into mountain, transition and lacustrine units, as identified by topographic maps and augering observation. This sampling strategy of the regional approach was taken in 2004 and 2006. Because of the development of Kunming City, some fields located in mountain and transition units being under construction in 2005, some sampling sites moved to lacustrine and transition units which still remained under vegetable production in 2006. With the further development of Kunming City, more attention should be paid to those fields due to the more intensive vegetable production and potential threats from municipal wastes.

Then, in order to understand the source of TE, it is necessary to trace the charge of background values in subsoil and profiles of different soil types. Two aspects should be considered, including the site of pair sampling and the depth of subsoil sampling. The sites of pairs and profiles were decided according to the augering observations, soil types, the geomorphological units and the new city location.

The depth of subsoil sampling was different in lacustrine and transition units due to the underground water level and soil formation process. In the lacustrine unit, the underground water level is <1 m, and the closer to Dianchi Lake, the higher the level. The subsoil sampling was the layer just above the underground water level, to avoid the effect of water on TE transformation. But it may be not enough to reflect the background value. In the transition unit, soils were deeper and the samples were mainly taken at 60-80 cm depth, without necessarily reaching the parent material. This strategy should be difficult for estimating the effect of the background values on TE contents, although it still could be used for understanding the potential effects of background values and transportation behaviour.

For the detailed approach, two sites are chosen in lacustrine and transition units, which correspond to the new city development and the new distribution of vegetable production. In the lacustrine unit, the detailed approach site concerns four villages close to the Chenggong town, making the typical representative for anthropogenic effects. The situation existed in the transition unit which is between two villages close to the mountain, making the representative for anthropogenic and diluvium deposit effects.

IV: NATURAL TRACE ELEMENT CONTENTS AND ANTHROPOGENIC CONTAMINATION OF SOILS

4.1. INTRODUCTION

Trace elements (TE) have become one of the major environmental hazards, which are not chemically or biologically degraded (Adriano, 2001). Definitions and sources of TE have been described in Section 2.3, including factors influencing TE mobility.

This chapter assesses natural TE contents and anthropogenic contamination in soil. TE in subsoil are investigated to assess pedological background values, and TE in topsoil to trace anthropogenic effects. Influencing factors of TE variability are also included in this section.

4.2. MATERIALS AND METHODS

4.2.1. Summary methods

Based on geomorphological investigations, the soil sampling strategy involved 130 topsoil samples distributed along 17 toposequences, 199 topsoil samples from two systematic detailed surveys and two greenhouse-scale samplings, 32 top/subsoil pairs and 5 profiles (Table 4.1a). Laboratory parameters included total TE contents and soil properties (pH, clay content, SOC, T-N and CEC), according to GAU or YAU procedures (Section 3.3, Annex 3.1, Table 4.1b).

Table 4.1: Soil sampling strategy

Table 4.1a: Soil sampling numbers

<table>
<tr><th>Soil sampling strategy</th><th>Sampling</th><th>Numbers</th><th>Total numbers</th></tr>
<tr><td rowspan="2">Regional approach</td><td rowspan="2">Topsoil samples (elementary)</td><td>17 toposequences</td><td rowspan="2">130</td></tr>
<tr><td>General observation</td></tr>
<tr><td rowspan="2">Detailed approach</td><td rowspan="2">Grid topsoil samples (composite)</td><td>L*=100</td><td rowspan="2">149</td></tr>
<tr><td>T**=49</td></tr>
<tr><td rowspan="2">Greenhouses</td><td rowspan="2">Topsoil samples (elementary)</td><td>L=25</td><td rowspan="2">50</td></tr>
<tr><td>T=25</td></tr>
<tr><td rowspan="2">Top/subsoil pairs</td><td rowspan="2">Top/subsoil samples (elementary)</td><td>Topsoil: 32</td><td rowspan="2">64</td></tr>
<tr><td>Subsoil: 32</td></tr>
</table>

*Lacustrine unit; ** Transition unit.

Table 4.1b: Numbers of soil samples analysed in GAU and YAU

Soil sampling strategy	Parameter	GAU	YAU
Regional approach	Total contents of Pb, Cu and Zn	88	42*
	Total contents of Cd	0	130
	pH, SOC, T-N	88	42*
	Physical clay contents	0	88
	CEC	0	88
Detailed approach	Total contents of TE	0	149
Greenhouses	Total contents of TE	0	50
Top/subsoil pairs	Total contents of TE	64	

*Data not used for analysis in this thesis.

The data were analysed with descriptive statistics (Excel 2003). T-tests were carried out ($P<0.05$ or $P<0.01$ level) using SPSS and DPS v6.55. The regression analysis and principal component analysis (PCA) are used for models of TE contents with variable soil and other factors by SPSS and XLSTAT at $P <0.05$ or $P <0.01$ level. Boxplots of data distribution were analysed with STATISTICA 6.0. Geostatistical analysis of point information and mapping were performed with Surfer 8 (Golden software surfer academic version 8.0) and Geo-ATATer. In case of absence of spatial continuity, interpolation was realized according to Shepard's method of inverse power distance.

4.2.2. Comparative analysis of data from Gembloux Agricultural University and Yunnan Agricultural University

In order to check if these two data sets can be merged, 48 topsoil samples analysed in both laboratories were chosen to compare mean pH, SOC and total TE results (Table 4.2).

Table 4.2: Data (mean ± SD) based on methods in laboratories of GAU and YAU

Parameter	GAU	YAU
pH	5.8 ± 0. 9	6.1 ± 0.9 *
SOC (%)	2.12 ± 0.76	2.48 ± 0.89*
Pb (mg/kg)	48.66 ± 9.54	43.89 ± 8.27 **
Cd (mg/kg)	0.10 ± 0.18	0.64 ± 0.12**
Cu (mg/kg)	133.21 ± 60.44	107.44 ± 44.65 *
Zn (mg/kg)	122.11 ± 36.78	117.77 ± 25.41

* and ** mean significant difference with $P<0.05$ and $P<0.01$ with T-tests, n=48.

It appears that means are significantly different for pH, SOC, Pb, Cd and Cu contents between the two data sets with T-tests analysis. A part of explanation could be the different definition about fine-earth size between GAU and YAU. Although the difference in percentage between particle size of 2 and 1 mm is <5% (Annex 4.1), on the basis of lower standard deviation (SD), we have decided to select 88 sample data sets (pH, SOC, Pb, Cu and Zn contents) only from GAU. Nevertheless, as GAU, Cd results are often below the detection limit, we have also selected a 130 sample data set of Cd from YAU.

4.3. RESULTS

4.3.1. Soil survey and soil identification

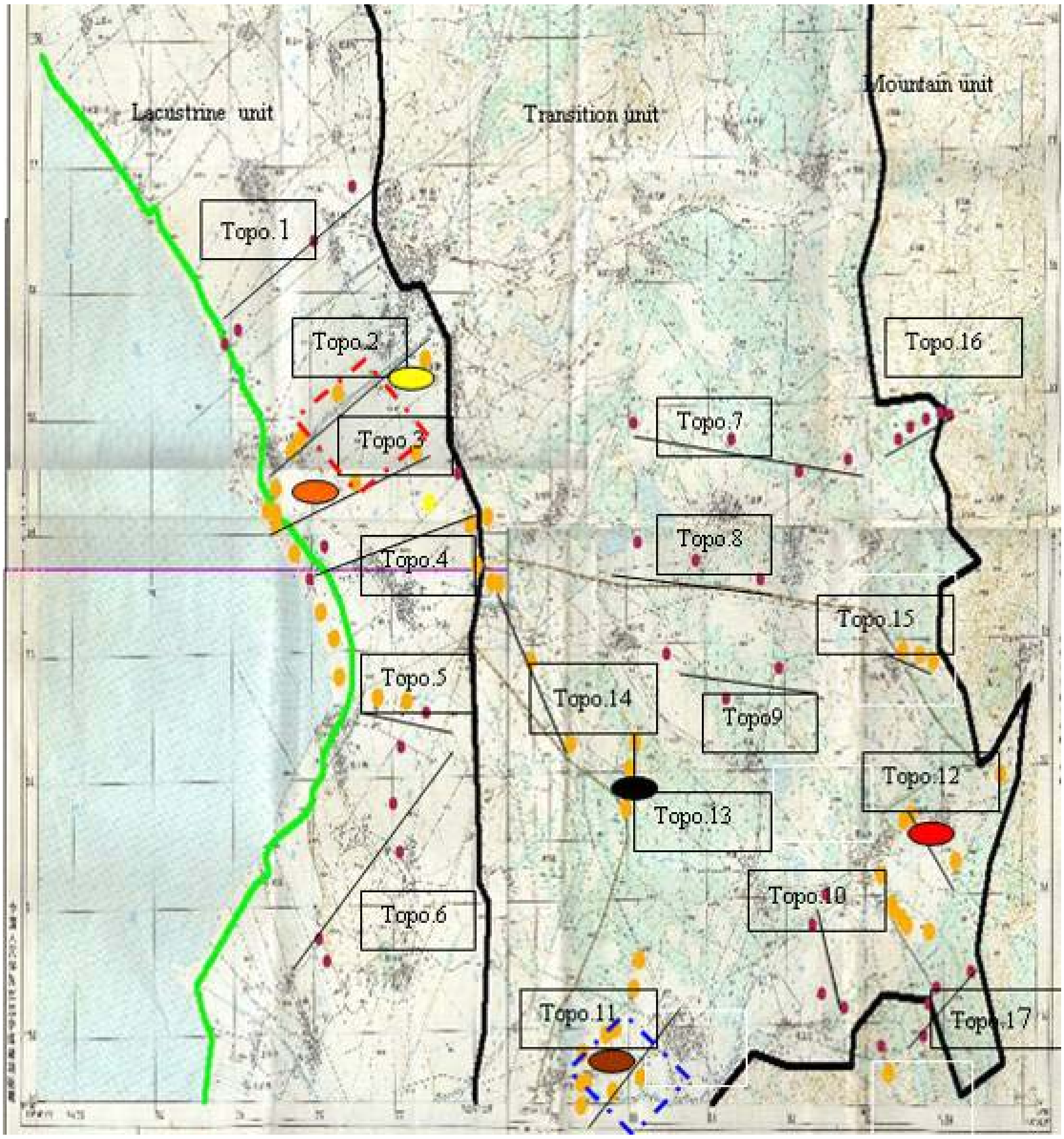
4.3.1.1. Topsoil augering description

In the research area, three geomorphical units: lacustrine unit, transition unit and mountain unit, have been identified and characterized by soil augering observations along 17 toposequences (Figures 4.1, 4.2-see the end of IV).

A. Lacustrine unit

The six toposequences (1-6) of the lacustrine unit are presented in Figure 4.1. They are located near Dianchi Lake where soils are developed from lacustrine and alluvium deposits, according to parent materials belonging to Q_4^{l} (lacustrine with yellow-gravel, clay, silt and coarse sand mixed with peat-mud, slime and turf) and Q^{lal} (alluvial lacustrine-colourful gravel and clay-silt).

The augerings and general observations are shown in Annex 4.2. Five toposequences (1-5) parallel to each other are laid down from the border of the transition unit across the lacustrine deposits, and to Dianchi Lake. Samples No. 18 and 19 of toposequence 1, sample No. 29 of toposequence 2 and samples No. 21 and 22 of toposequence 3 were taken near Dianchi Lake. The depth to groundwater was only 30-60 cm. The texture of toposequences 1-5 was sandy clay, loam or loamy clay, according to observations. The soil colour was brown or dark red. Stoniness was <15%, while lithology of the stones was sandstone.



Samples in lacustrine unit: **Topo.1**: 16, 17, 18, 19; **Topo.2**: 29, 31, 32; **Topo.3**: 20, 21, 22; **Topo.4**: 28, 40, 42; **Topo.5**: 39, 41, 43; **Topo.6**: 23, 24, 25, 26, 27;

Samples in transition unit: **Topo.7**: 82, 83, 84, 85; **Topo.8**: 86, 87, 88; **Topo.9:** 79, 80, 81; **Topo.10**: 74, 75, 76, 77, 78; **Topo.11**: 100, 101, 102, 103; **Topo.12**: 109, 110, 113; **Topo.13**: 89, 90, 104, 105; **Topo.14**: 106, 107, 108, 114; **Topo.15**: 127, 128, 129;

Samples in mountain unit border: **Topo.16**: 122, 123, 124, 125, 126; **Topo.17**: 118, 119, 120, 121;

Detailed approach site in lacustrine unit — Detailed approach site in transition

Profiles: P1 P2 P3 P4 P5

Figure 4.1: The location of pedological observations in Chenggong County.

Toposequence 6 was orientated from northeast to southwest across a hill with sample No. 25, and No. 27 on the foot-slope. Main rocks of the isolated hill were shale and quartz-rich sandstone mixed with some argillaceous siltstone (Figure 4.3). The soil colour is brown; the stoniness is <15% with some sandstone fragments.

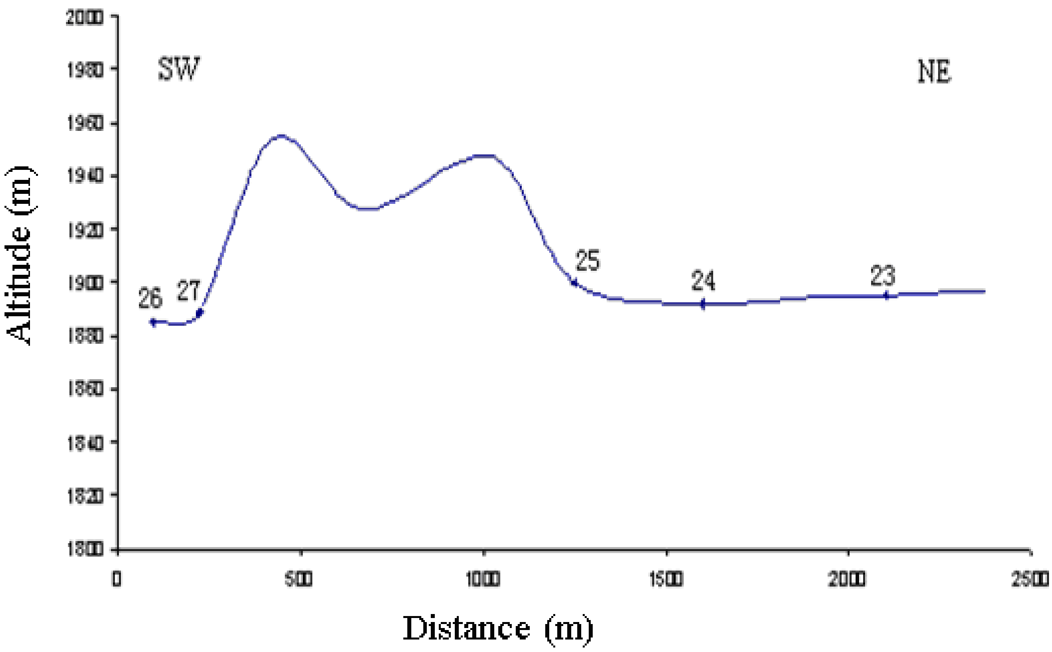


Figure 4.3: Relief of toposequence 6.

The particle size distribution (PSD) of topsoil in lacustrine unit is shown in Table 4.3. The texture was loam more often according to measurements, even if the clay fraction ranged between 23.4-44.3%, and the sand fraction was >30%.

Table 4.3: Particle size distribution of topsoil and texture according FAO (2006)

Unit	Sample No.	Percentages of particle (%)			FAO texture
		Clay (<0.002mm)	Silt (0.002-0.05mm)	Sand (0.05-2mm)	
Lacustrine	17	44.3	24.4	31.3	Clay
	18	26.3	14.5	59.2	Sandy clay loam
	22	23.4	36.3	40.3	Loam
Transition	75	71.6	22.6	5.8	Heavy clay
	76	76.0	8.1	15.9	Heavy clay
	77	51.6	32.7	15.7	Clay
	79	52.8	23.4	23.8	Clay
	84	57.7	23.3	19.0	Clay
	85	42.4	22.5	35.1	Clay
Mountain	122	76.7	17.0	6.3	Heavy clay
	123	68.7	17.8	13.5	Heavy clay
	125	81.0	6.7	12.3	Heavy clay

B. Transition Unit

The nine toposequences (7-15) have been surveyed according to the relief in the transition unit (Figure 4.1). This unit makes the transition between the lacustrine unit and the mountain unit. Augerings and general observations of toposequences 7-15 are shown in Annex 4.2. Soils are formed on diluvium deposits. The parent materials in toposequences 7 and 9 belong to Q_2, in toposequence 10 to Q_3. The Holocene Q_4, which characterizes toposequences 8 and 10, is composed of sands and gravels.

Toposequences 7 and 8 and toposequences 9 and 10 were, respectively, located on the northern and the southern side of the main road (Chenggong-Yiliang) (Figure 4.1). Soil sample No. 88 of toposequence 8 was characterized by an abundance of redox features. Samples usually presented a loamy clay texture. For example, the texture of samples No. 74, No. 77, No. 78 of toposequence 10 was loamy clay, of sample No. 76 sandy clay texture, and of sample No. 75 clay texture according to observation (Figure 4.4). The soil colour was brown or dark red. Stoniness was <15% and the lithology of stones was sandstone.

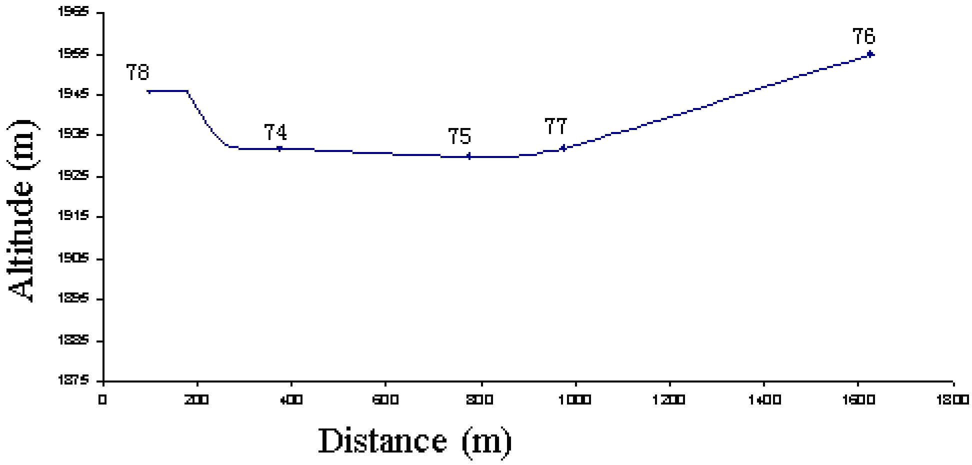


Figure 4.4: Relief of toposequence 10.

The soil texture in toposequences 11-15 is loam and clay according to observations. The soil colour was usually brown. The PSD of soils is shown in Tables 4.3. The soils present high amounts of clay. According to measurements and the FAO classification, all soils belong to clay or heavy clay textural classes.

C. Mountain unit

The two toposequences (16 and 17) in the mountain unit are described (Figure 4.1). Toposequence 16 was chosen to represent soils developing from limestone and marlstone, and toposequence 17 for soils from diluvium deposits. The rocks about toposequence 16 belong to the Permian system, (P_1d) unit composed of quartz-rich sandstone, clayite, siltstone mixed with dolomite and limestone, and P_1Y unit of carbonate stones and dolomite mixed with limestone. Rocks in toposequence 17 belong to Early Pleistocene (Q_2) or Middle Pleistocene (Q_3). This unit was composed of diluvium (gravel, coarse sand, silt and clay) and diluvium-alluvium deposits (gravelly loam, clay-silt and some roots of plants).

Toposequence 16 was located between the Bailongtan Mountain (2075 m above sea leave (asl)) and an isolated hill (1961 m asl) (Figure 4.5). The augering observations of toposequence 16 are shown in Annex 4.2. The colour of the five soil samples was dark reddish brown except, sample

No.122 with bright reddish brown. All samples present clay texture according to observation and <15% of stones (except sample No. 126).

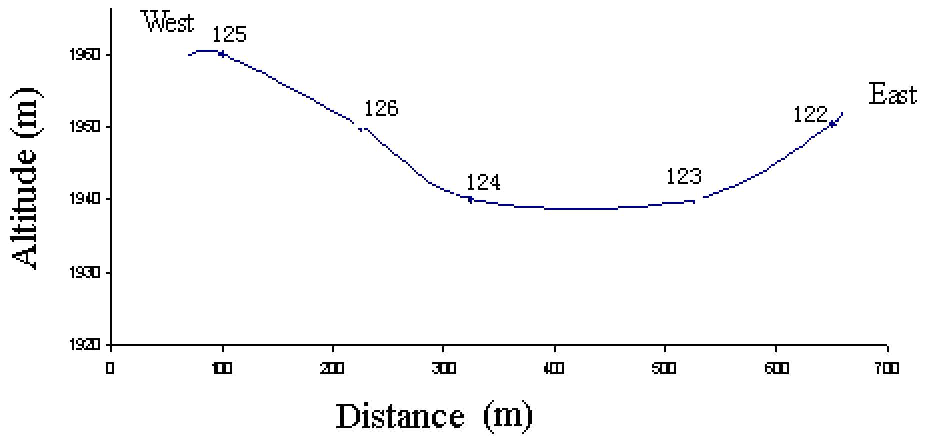


Figure 4.5: Relief of toposequence 16.

Toposequence 17 is located between Xiaojianshan Mountain (2049 m asl) and another isolated hill (1996 m asl), and the auguering features are shown in Annex 4.2. The colour of four samples was reddish brown, except sample No. 121 with dark red. No. 120 and No. 121 present sandy clay texture, while No. 119 was loamy clay and No.118 was clay texture according to observations. Table 4.3 shows PSD in mountain unit. The clay fraction is often the most important. The clay content in toposequence 16 was higher than in toposequence 17. The texture of toposequence 16 was heavy clay, according to measurements and the FAO classification.

4.3.1.2. Pedogeochemical background and soil profile description

Some 32 pairs of top/subsoil samples have been chosen for comparison as follows: 8 pairs in the lacustrine unit, 21 pairs in the transition unit and 3 pairs in the mountain unit (Annex 4.1, Table 4.4).

In the lacustrine unit, texture of samples No. 22 and 29 varied from loam in topsoil to sand in subsoil, because of the proximity of Dianchi Lake. Texture of other samples varies from loam or sandy clay in topsoil to clay in subsoil, except for samples No. 17 and 18 being sandy clay in both horizons. Subsoil Texture is clay and sandy clay more often according to observations. The colour of subsoil is usually brown and darker than in topsoil.

In the transition unit, texture varied from loam or loamy clay mainly in topsoil to clay in subsoil, except for toposequence 10, in which texture of sample No. 75 (foot of hill) and No. 76 (hilltop) varies from clay and sand clay to loamy clay according to observations. The colour changed from brown in topsoil to reddish brown, or remains brown in the subsoil. However, colour of samples No. 77, 85, 89 and 105 on slope was similar both in topsoil and subsoil. The texture in mountain unit is mainly clay on top and subsoil according to observations. The colour was reddish brown in both horizons.

Table 4.4: Basic information for 32 pairs of top/subsoil samples in the research area

Unit	No.	Colour (Munsell chart)		Texture		Unit	No.	Colour (Munsell chart)		Texture	
		Topsoil	Subsoil	Topsoil	Subsoil			Topsoil	Subsoil	Topsoil	Subsoil
Lacustrine	17	10YR3/3	10YR3/2	Sandy clay	Sandy clay	Transition	90	7.5YR4/4	7.5YR3/2	Clay	Clay
	18	5YR4/4	5YR3/1	Sandy clay	Sandy clay		100	5YR4/4	2.5YR4/4	Loam	Clay
	20	10YR4/3	10YR5/4	Loamy clay	Clay		101	7.5YR4/4	7.5YR4/4	Loam	Clay
	22	7.5YR3/4	10YR4/6	Sandy clay	Clay		102	10YR4/3	2.5YR4/2	Clay	Clay
	23	10YR4/4	10YR4/1	Loamy clay	Clay		105	5YR5/6	5YR5/6	Clay	Clay
	29	5YR3/6	5YR4/4	Loam	Sandy Silt		109	5YR4/8	2.5YR3/6	Loam/clay	Clay
	45	7.5YR5/4	10YR4/4	Loam	Clay		110	7.5YR4/4	5YR4/4	Loam	Clay
	46	5YR4/4	10YR3/3	Loam	Sandy		113	7.5YR5/6	5YR3/6	Loam	Clayish loam
Transition	75	10YR3/4	5YR3/4	Clay	Loamy clay		115	7.5YR4/4	5YR4/6	Loam	Clay
	76	5YR4/8	2.5YR3/6	Sandy clay	Loamy clay		127	7.5YR4/4	7.5YR3/4	Loam	Clayish loam
	77	10YR4/4	10YR4/4	Loamy clay	Clay		128	7.5YR4/4	10YR4/4	Loamy clay	Loamy clay
	79	5YR3/6	7.5YR4/6	Loamy clay	Clay		129	2.5YR4/4	5YR4/4	Clay	Clay
	81	10YR4/4	5YR4/4	Loamy clay	Loamy clay		130	5YR4/6	5YR3/4	Loamy clay	Clay
	84	5YR3/6	2.5YR3/6	Loamy clay	Clay	Moun tain	122	2.5YR4/6	2.5YR7/2	Clay	Sandy clay
	85	10YR4/4	10YR5/4	Loamy clay	Sandy clay		123	2.5YR3/6	2.5YR3/6	Clay	Clay
	89	5YR3/4	5YR3/4	Clay	Clay		125	2.5YR3/6	2.5YR3/6	Clay	Clay

Five profiles have been described, P1 and P2 in the lacustrine unit, while P3, P4 and P5 in the transition unit (Figure 4.1, Table 4.5). Soil texture in P1, P3 and P4 was clay in all profile horizons. Texture in P2 varied from clay to clay loam and sandy clay, showing high clay content in horizon 1-17 cm and high sand content in <66 cm horizon, suggesting three different soil parent materials. Texture of soils in P5 was clay, except for the 117-126 cm horizon, with 0.3% clay content and 84.5% silt content.

The soil colour in P1 and P2 was brown and darker, while soil colour in P3 and P4 was brown and varies, becoming brighter with increased depth. Soil colour in P5 is brown more often, except for horizon 117-126 cm (brown).

Table 4.5: Basic information for the five profiles in Chenggong County

Profile	Latitude	Longitude	Altitude (m)	Horizon (cm)	Soil colour (Munsell charts)	Percentages of clay, silt and sand (%)		
P1	24º52’54’’	102º47’30’’	1888	0 - 15 (30)	7.5YR5/4	51.9	28.8	19.3
				15 (30) - 40	7.5YR4/4	52.4	27.5	20.1
				40 - 80	10YR4/4	54	28.2	17.8
P2	24º52’10’’	102º46’49’’	1887	0 - 8 (17)	5YR4/4	54.9	25.8	19.3
				8 (18) - 33	5YR4/4			
				33 - 43 (46)	5YR4/6	17.8	55.8	26.4
				43 (46) -53 (66)	7.5YR5/6			
				53 (66) -80 (87)	7.5YR4/6	18.8	16.3	64.9
				80 (87) - 120	10YR3/3	22.5	19.8	57.7
P3	24º50’06’’	102º49’14’’	1923	0 - 16 (23)	7.5YR4/4	56.4	33.8	9.8
				16 (23) -33 (44)	7.5YR4/4			
				33 (44) -60 (67)	5YR4/4	53.5	37.8	8.7
				60 (67) - 100	5YR4/6	49	40.4	10.6
P4	24º51’46’’	102º51’34’’	1944	0 - 20 (23)	7.5YR4/4	55.8	29	15.2
				20 (23) -35 (40)	7.5YR4/4	57.5	34.8	7.7
				35 (40) - 64 (74)	5YR4/4	51.6	36.2	12.2
				64 (74) - 83 (95)	5YR3/6	76	18	6
P5	24º51’21’’	102º49’20’’	1925	0 - 12 (14)	5YR5/6	52.7	27.7	19.6
				12 (14) -105 (117)	2.5YR4/6	45.5	27.7	26.9
				105 (117) -113 (126)	7.5YR3/4	0.3	84.3	15.4
				113 (126) -167 (185)	5YR3/2	56.8	32.1	11.2

4.3.1.3. Description of soil chemical properties

Soil pH

According to the results of topsoil investigation in 2004 and 2006, pH ranged from 4.1-7.8 and the mean pH is 6.2 (Figure 4.2). The pH of 62.5% of samples is <6.5 (Figure 4.6, Annex 4.2). Comparing the geomorphical units, the mean value (6.8) in the lacustrine unit is higher than in the other two units. The mean pH in the transition and mountain units is 5.8 and 6.3, respectively (Figure 4.6).

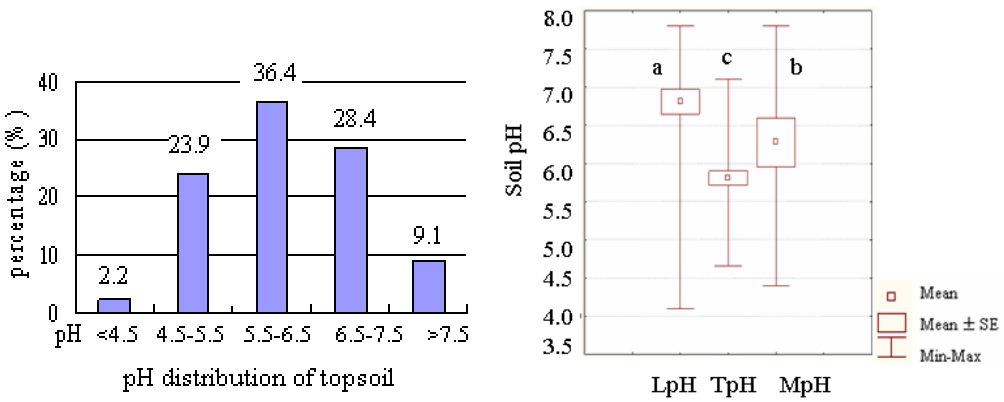


Figure 4.6: pH distributions of topsoil samples in the research area and the three units

(L: lacustrine unit; T: Transition unit; M: Mountain unit).

Considering the relief, pH of samples No. 26 and 27 of toposequence 6, located on the western side of a hill close to Dianchi Lake, was higher than that of the other three samples located on the eastern side of this hill (Figure 4.7). The pH of samples increased from top (sample No. 76 and 78) to foot (sample No. 74) of the hill along the slope in toposequence 10, and was less different in toposequence 16.

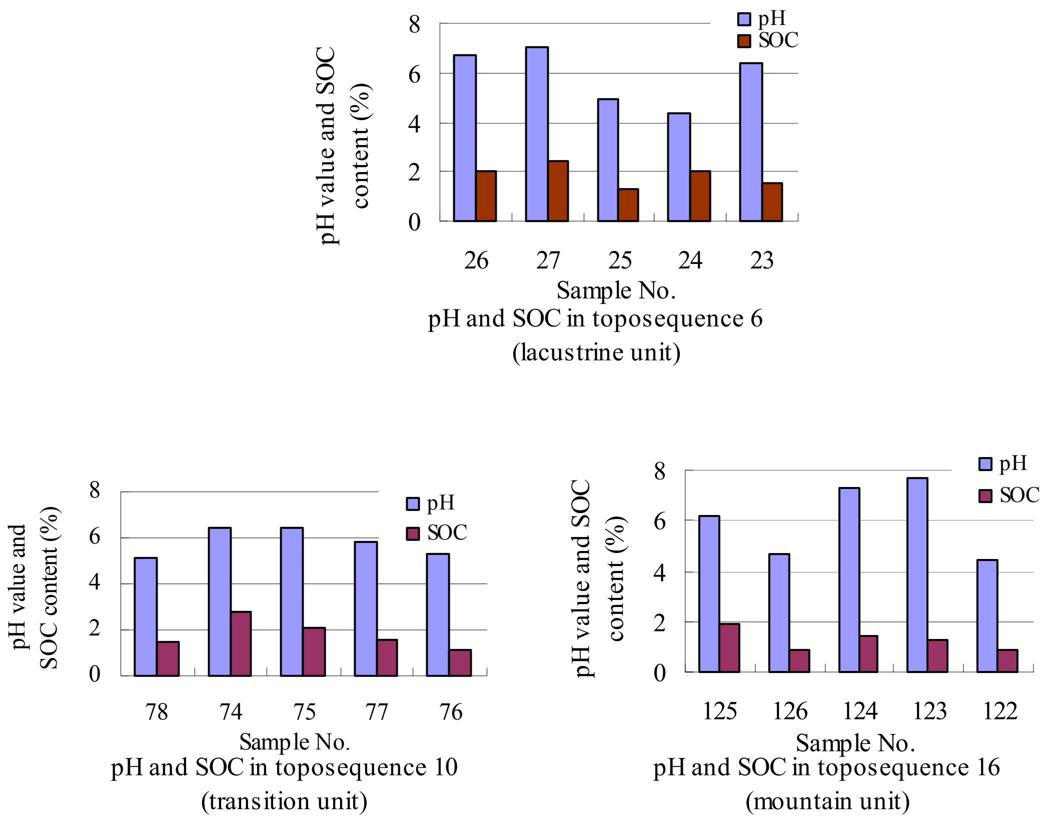


Figure 4.7: pH and SOC contents in three toposequences in the three units.

Physical clay

Mean physical clay (<0.01mm) was 52%, ranging from 20-84% (Annex 4.2). Physical clay of 52% of samples ranged between 40-60%. The mean physical clay is 45, 56, 58% in the lacustrine, transition and mountain units, respectively (Figure 4.8). Comparing the geomorphological units, the mountain unit shows high physical clay contents.

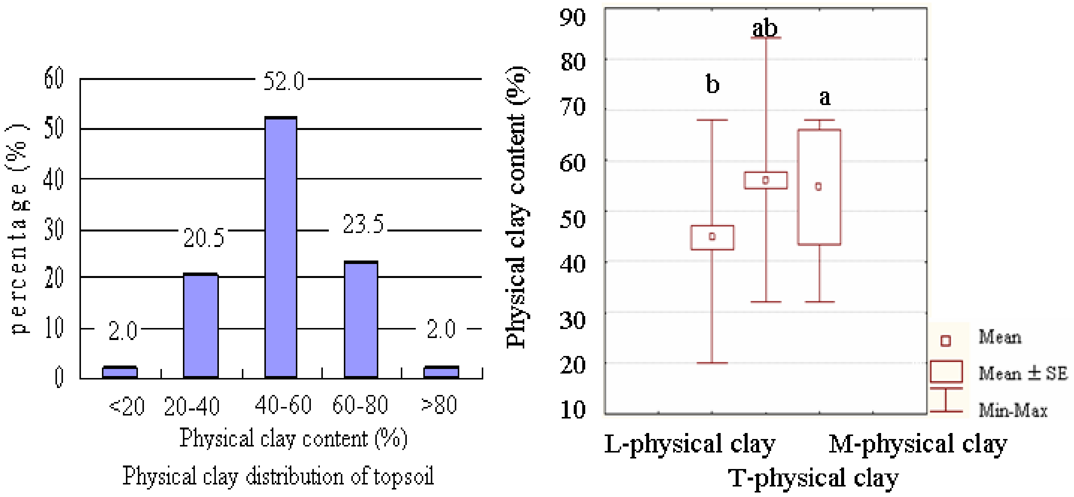


Figure 4.8: Physical clay contents of topsoil samples in the research area and the three units.

SOC and C/N

SOC contents ranged from 0.5-3.7% with a mean 1.5% in topsoil (Figure 4.2, Annex 4.2). SOC contents of 59.1% of samples are between 1-2, and 2.3% >3.0 (Figure 4.9). In the lacustrine unit, mean SOC content was 1.8% with a range between 0.5-3.2%, which is higher than in the transition unit (mean 1.4%), and in the mountain unit (mean 1.3%) (Figure 4.7). SOC contents of samples in toposequences 10 and 16 increase from the top to the foot of the hill, except for No. 125 (Figure 4.7).

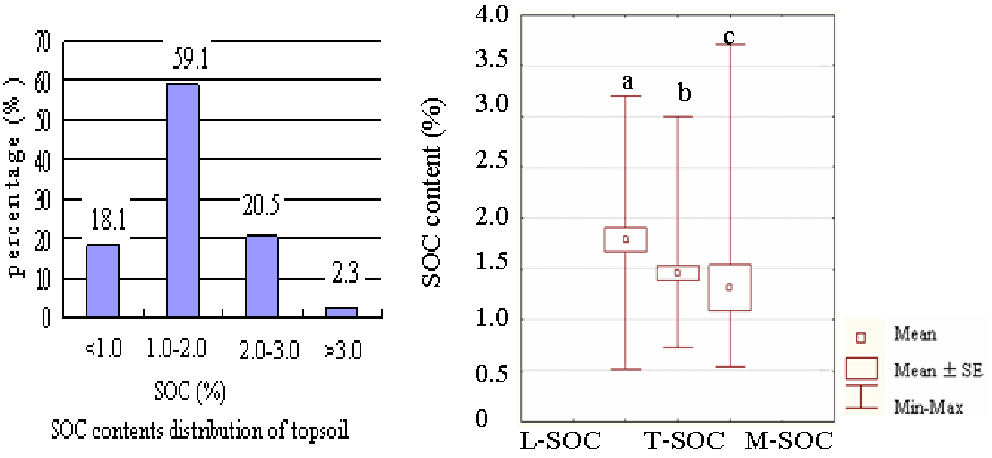


Figure 4.9: SOC contents of topsoil samples in the research area and the three units.

The mean total nitrogen content was 1.6 g/kg in the lacustrine unit, which is higher than in the transition and the mountain units, with consistency to SOC content. The mean C/N ratio was ~10 in the lacustrine and the transition units, while it was 13 in the mountain unit, which suggests a difference in organic matter quality and evolution (Figure 4.2, Annex 4.2).

Cation exchange capacity (CEC)

Soils have a mean CEC of 24.1 cmol/kg, ranging from 8.6-88.5 cmol/kg (Figure 4.2, Annex 4.2). CEC of 54.7% of samples ranged between 10-25 cmol/kg (Figure 4.10). Mean CEC is 29.1, 20.6 and 28.3 cmol/kg in the lacustrine, transition and mountain units, respectively (Figure 4.10). Comparing geomorphological units, the lacustrine unit shows high CEC. The high CEC may be related to higher SOC in the lacustrine unit and higher physical clay content in the mountain unit.

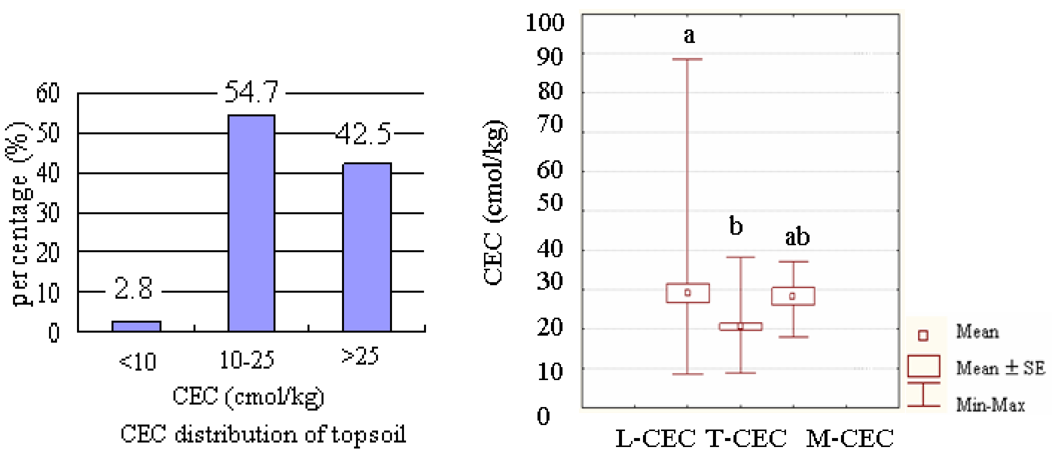


Figure 4.10: CEC of topsoil samples in the research area and the three units.

To summarize, due to different soil parent materials and intensity of agricultural production, the chemical characteristics of soils are variable. In the lacustrine unit, pH, SOC and CEC are higher, while SOC content is the lowest in the mountain unit.

4.3.2. Horizontal distribution of total trace elements

4.3.2.1. Regional approach

Topsoil samples in the lacustrine, transition and mountain units were chosen to assess the regional horizontal distribution of TE. The results summarized by geomorphological units are presented in Annex 4.2, Annex 4.3, Figure 4.2 and Figure 4.11.

Pb: The mean content is 56.7 mg/kg, with range from 27-212.4 mg/kg. In 61.4% of samples, Pb contents are from 40-60 mg/kg, and in two samples located in the lacustrine unit near Dianchi Lake, Pb contents are >200 mg/kg.

Cd: The mean content is 0.47 mg/kg, with range from trace-4.0 mg/kg. In 43.1% of samples, Cd contents are from 0.1-1.0 mg/kg. In 54 out of 130 samples (41.5%), Cd contents are <0.1mg/kg, and 35.4% of samples have a trace of Cd.

Cu: The mean content is 125.7 mg/kg, with range from 20.7-231.7 mg/kg. In 80.7% of samples, Cu contents are from 50-200 mg/kg, and 13 out of 88 (14.8%) with Cu >200 mg/kg.

Zn: The mean content is 114.2 mg/kg, with range from 43.1-238.5 mg/kg. In 44.3% of samples, Zn contents are from 100-150 mg/kg.

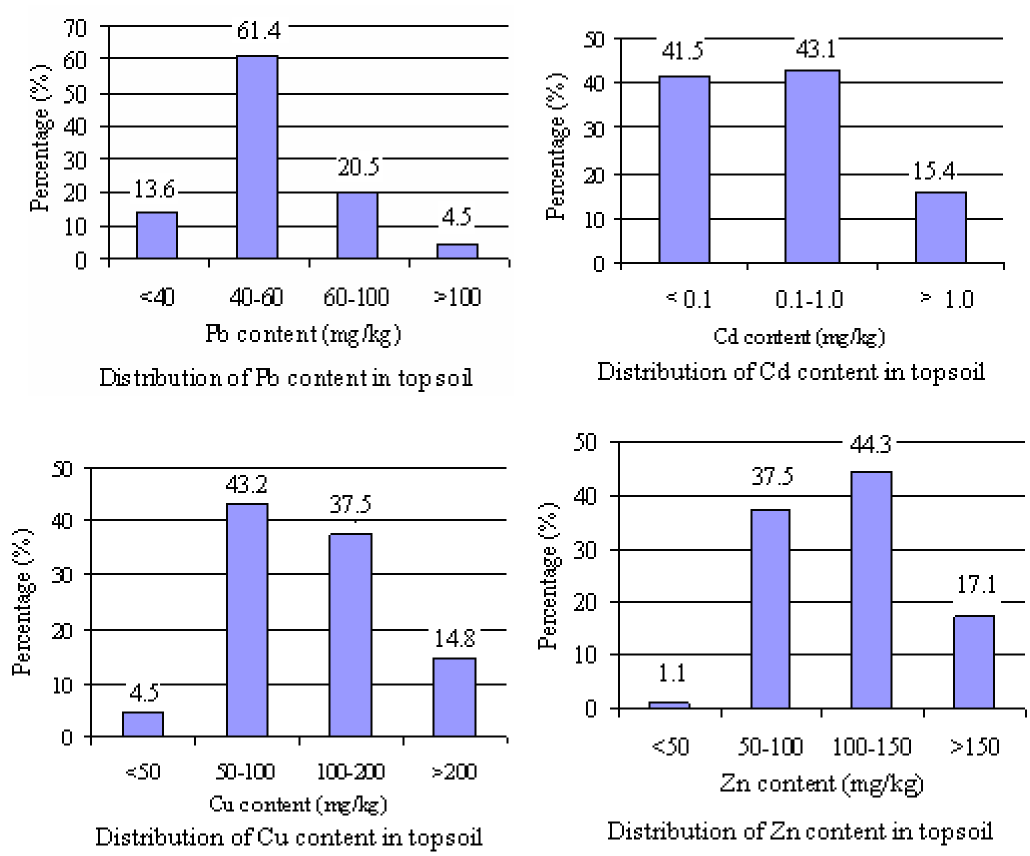


Figure 4.11: Percentages of sample numbers within range TE contents to total sample numbers in topsoil.

4.3.2.2. Relationships between trace element contents and pH, SOC, CEC

Relationships between TE contents and soil properties were analysed and only significant linear relationships considered (Table 4.6, Annex 4.4).

Table 4.6: Regression analysis between TE contents and soil properties

Y	X	Equation	R^2	F	Sig.f	N
Pb	SOC	Y=30.01+12.72 x	0.092	6.200*	0.015	88
	LSOC	Y = 34.18+6.30 x	0.192	6.414*	0.017	31
Cd	SOC	Y=0.11+0.19x	0.049	6.776**	0.011	88
	LSOC	Y = -0.163+0.27 x	0.173	9.186**	0.004	31
	TSOC	Y= -0.11+0.32 x	0.161	13.866**	<0.001	47
	CEC<25	Y= -0.17+3.73E-02 x	0.107	7.417**	0.008	51
	pH, SOC, CEC	$Y = -0.18-5.12\times10^{-2}*pH+0.43*SOC+6.82\times10^{-3}*CEC$	0.190	4.697**	0.005	88
Cu	TCEC	Y = 16.72+6.10 x	0.470	31.987**	<0.001	47

* and ** mean significance with P<0.05 or P<0.01.

pH:

If excluding special sample (Pb: 212.4 mg/kg), negative linear relationships between pH and total Pb content (F=1.821, sig.f=0.182) exist; and negative relationships between pH and total Cu (F=3.158, sig.f=0.081) were also observed, although no significant linear relationship between TE contents and pH is observed. A special sample located near Dianchi Lake with pH 7.5 to be influenced by the effect of irrigation water from Dianchi Lake.

SOC:

Significantly positive relationships between SOC and total Pb, total Cd are observed (Table 4.6). The similar linear relationships are still observed in the lacustrine unit for Pb and Cd, and in the transition unit for Cd.

CEC:

Positive linear relationships are observed between CEC and total Cu content in the transition unit, CEC (<25 cmol/kg) and total Cd content.

4.3.2.3. Total trace element contents versus geomorphology

Figure 4.2 shows the results summarized by geomorphological units (see the end of IV).

Pb:

The mean content in the mountain unit is higher than in the transition and lacustrine units (M>T (L)) (Figure 4.12). In toposequences 10 and 16, Pb contents decreased from hilltop to foot of hill (Figures 4.12, 4.4, 4.5). Pb contents were stable beside the two sides of the hill in toposequence 6 (Figures 4.13, 4.3). An exception occurs with the high Pb content in sample No. 26 close to Dianchi Lake.

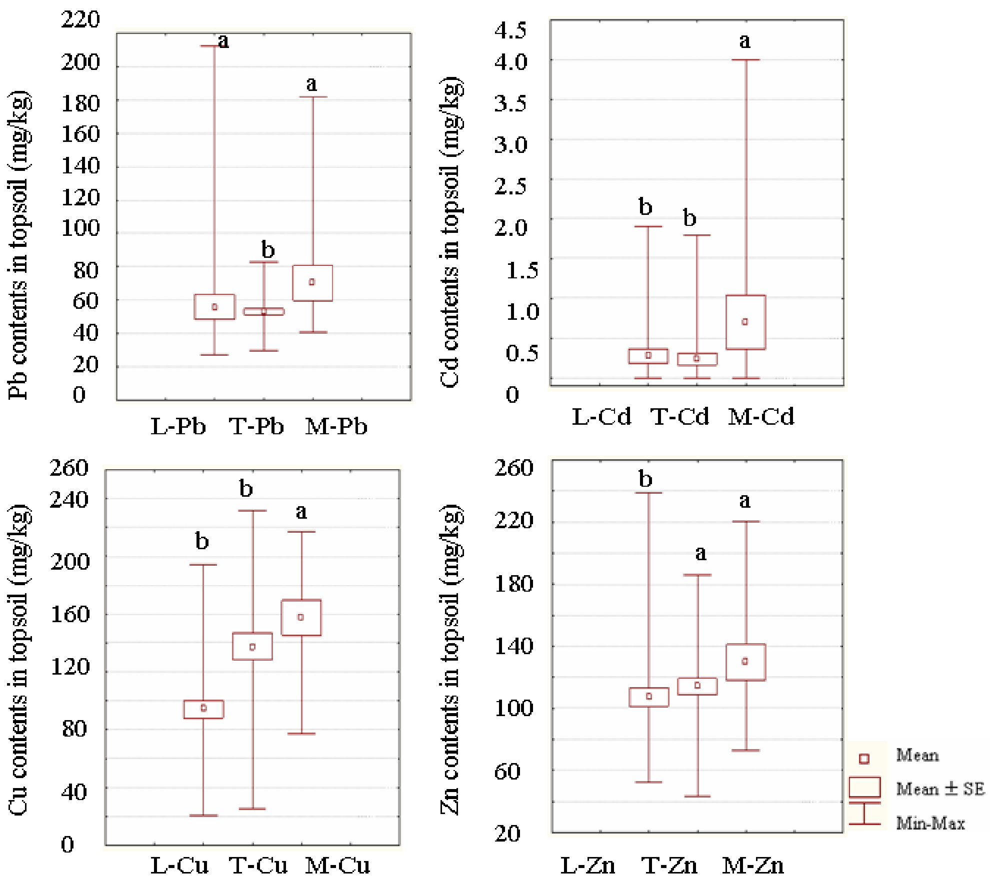


Figure 4.12: Pb, Cd, Cu and Zn contents of topsoil in the three units.

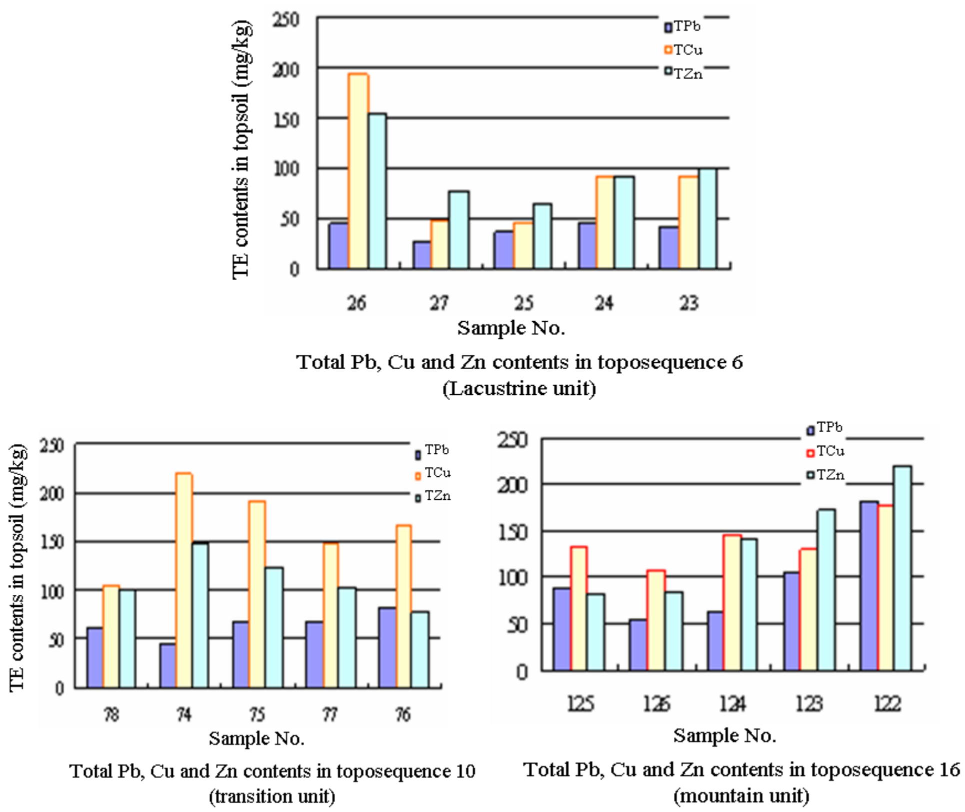


Figure 4.13: Pb, Cu and Zn contents in three toposequences in the three units.

Pb is accumulated in some samples in the research area (Figure 4.14, Annex 4.3). There were relatively high Pb contents from north-east to south-west, which includes Bailongtan village (north-east, mountain unit), Sanchakou village (middle, transition unit) and Yuhua village (south-west, transition unit). There are two small areas with high Pb contents near Kele village (west, lacustrine unit) and Zhongzhuan village (south, transition unit).

Using semivariogram analysis, the spherical model is suitable to Pb distribution (Figure 4.14). The range is 630 m, nugget (C_0) 0.151 and sill (C_0+C) 1.054. The proportion of $C_0/(C_0+C)$ is 14.2%, which is <25%, meaning a strong spatial correlation of Pb is mainly influenced by morphological factors, such as relief and parent materials ($C_0/(C_0+C)<25\%$ means a strong spatial correlation; $25\%<C_0/(C_0+C)<75\%$, a medium spatial correlation; and $C_0/(C_0+C)>75\%$ a weak spatial correlation (Wang X.J., *et al.*, 2005; Goovaerts & Webster, 1994; Tao S., 1995, 1998; Ndiaye & Machin, 1999)).

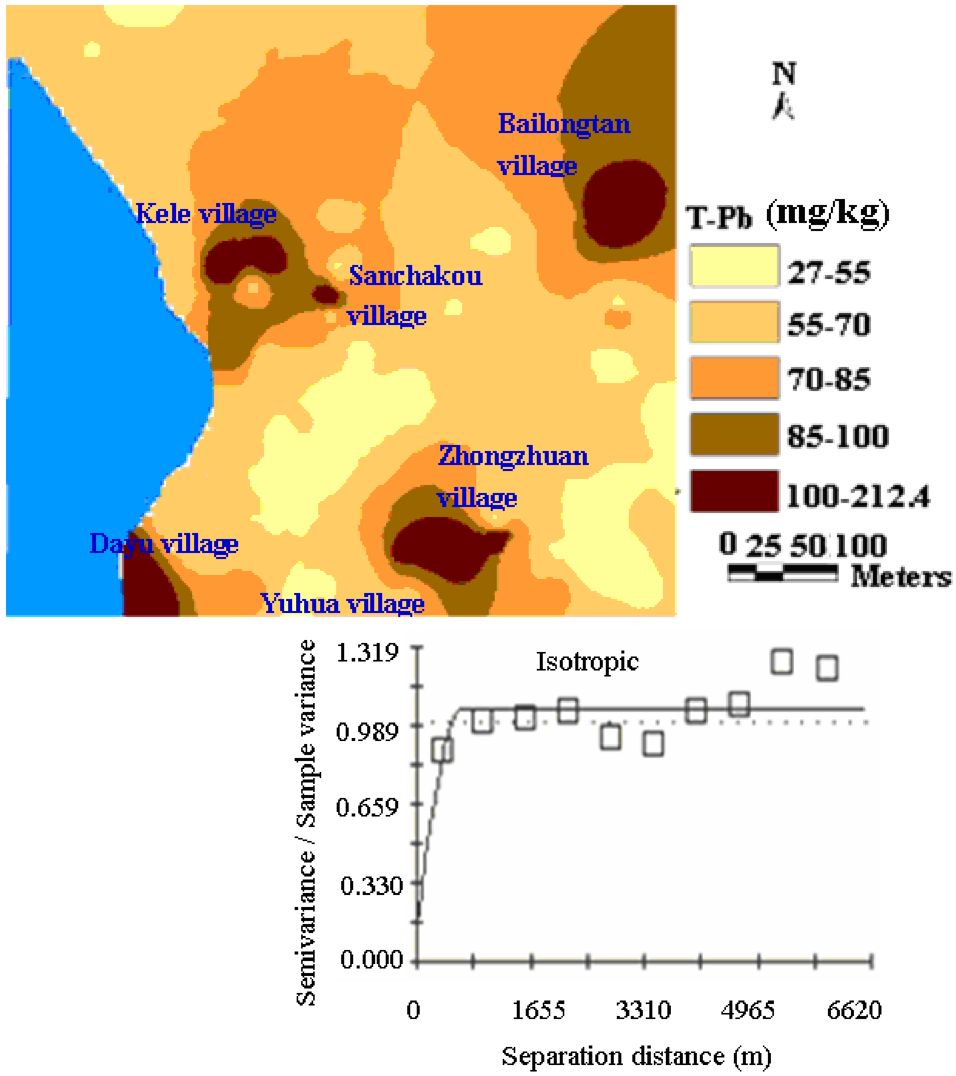


Figure 4.14: Contour map of Pb contents and semivariogram analysis of topsoil in the research area.

Cd:

The mean content in the mountain unit is higher than in the transition and lacustrine units (M>T>L) (Figure 4.12). Considering toposequences, Cd contents in toposequence 16 decreased from 4 mg/kg in the hilltop (No. 122) to 2.3 mg/kg on the hillside (No. 123) and 0.49 mg/kg on the foot (No. 124) of the hill, although Cd contents in some samples in toposequence 10 and toposequence 6 are trace.

About the spatial distribution of Cd in the research area, high Cd contents locate in a small area near Bailongtan village (north-east, the mountain unit) relative to high rock background values. Cd contents decrease from north-east to south-west, which is consistent with elevation gradient (Figure 4.15, Annex 4.3). At the considered study scale, the spatial variability of Cd is strongly influenced by non-pedological factors because there was no spatial continuity to be observed. Contour map was made by inverse distance interpolation.

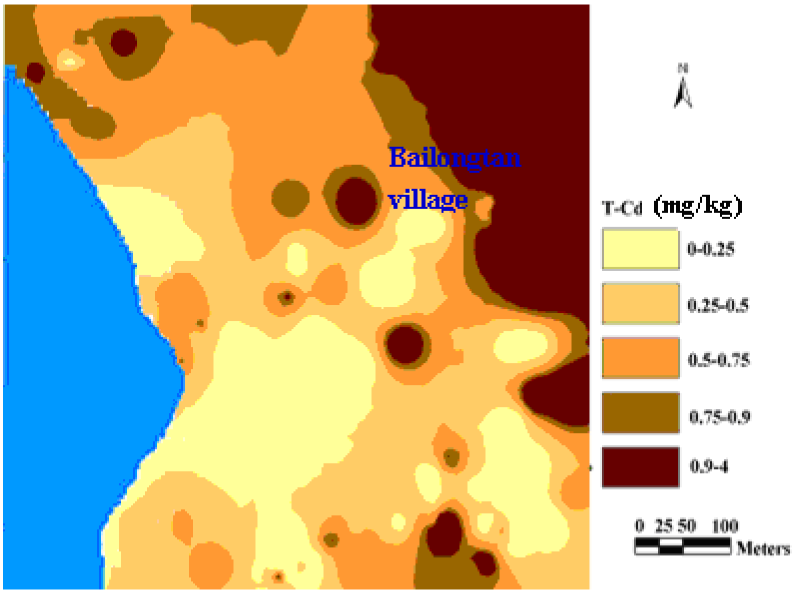


Figure 4.15: Contour map of Cd contents of topsoil in the research area.

Cu and Zn:

The mean of Cu and Zn contents in the mountain unit is higher than in the transition and lacustrine units (M>T>L) (Figure 4.12). Cu and Zn contents are low on the foot of the hill in toposequence 6 and increase with the distance increase from the hill, especially in No. 26 close to Dianchi Lake. Along the slope from hilltop to the foot of the hill, Cu and Zn contents increase in topoquence 10, and decrease in toposequence 16 (Figure 4.12). The spatial distributions of Cu and Zn in the research area show that Cu and Zn have accumulated in two areas. One is near Dianchi Lake in the lacustrine unit; the other from east to south-west in the transition unit (Figures 4.16, 4.17, Annex 4.3). At the considered study scale, the spatial variability of Cu is strongly influenced by non-pedological factors because there was no spatial continuity to be observed. Contour map was made by inverse distance interpolation.

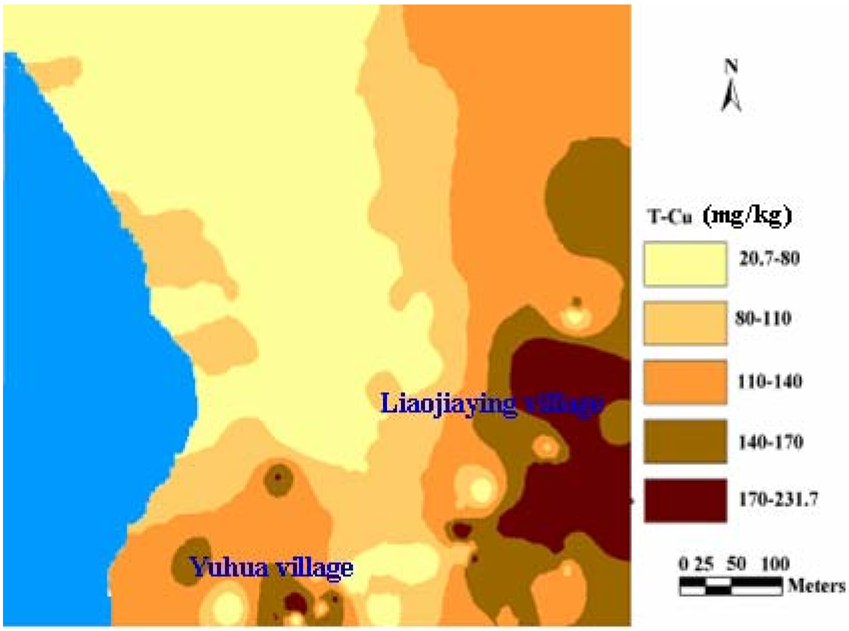


Figure 4.16: Contour map of Cu contents of topsoil in the research area.

Using semivariogram analysis, the exponential model is suitable to Zn distribution (Figure 4.17). The range is 870 m, nugget (C_0) 0.278 and sill (C_0+C) 1.005. The proportion of C_0/(C_0+C) is 27.7%, meaning the medium spatial correlation of Zn is influenced by both morphological factors (relief and soil parent materials) and non-pedological factors (pesticides, fertilizers, irrigation and traffic).

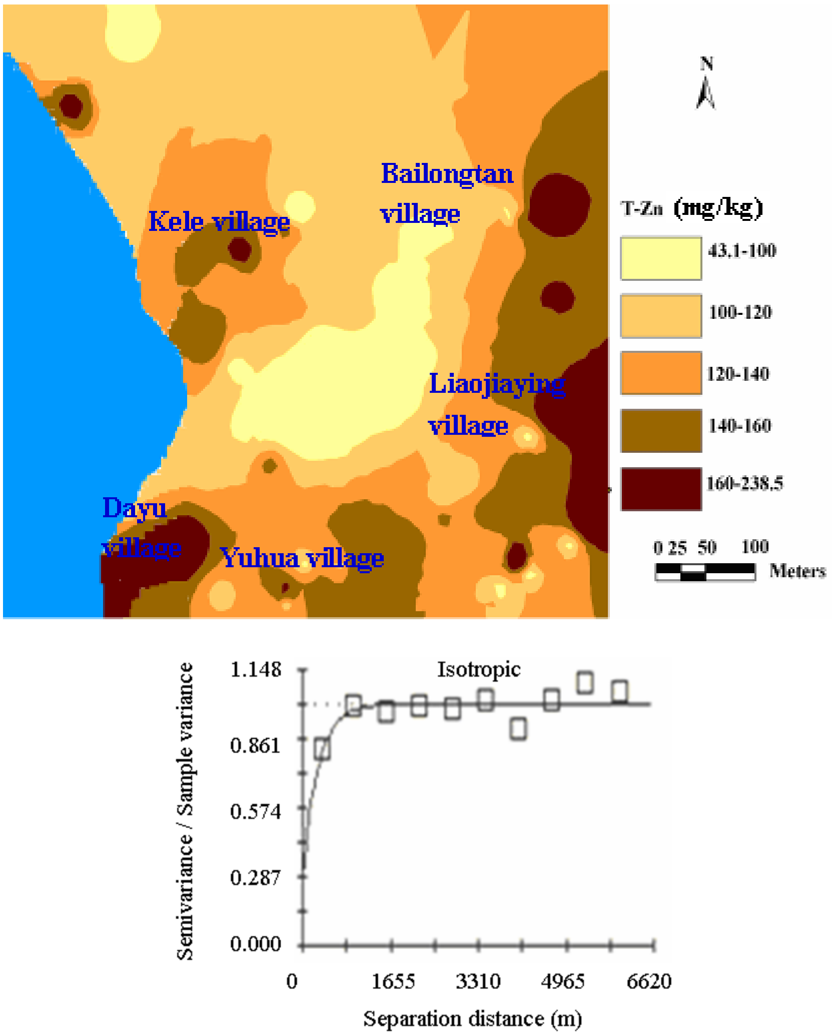


Figure 4.17: Contour map of Zn contents and semivariogram analysis of topsoil in the research area.

4.3.2.4. Detailed approach

According to soil properties in the research area, two relatively integrating sub-regions have been selected in order to better assess anthropogenic effects (Figures 4.1 and 3.16).

4.3.2.4.1. Lacustrine unit

A. Total trace element contents

The TE contents in lacustrine unit are presented in Table 4.7 and Annex 4.5.

Pb: Mean content is 10.5 mg/kg, ranging between 4.1-24.2 mg/kg. There are significant differences between Pb contents in L8, L9 and in other lines (Figure 3.15). There are relatively high Pb contents in the northern part of this site, where there is a road. The car exhaust may influence Pb contents in soil near the road. High Pb contents also locate in a small area near Kele village (west, lacustrine unit).

Cd: Cd contents of samples of 5 lines are trace, with high contents in L2. There are significant differences between L2 and other lines, except L8. Cd contents do not vary significantly in this site.

Cu: Mean content is 84.6 mg/kg, ranging between 75.8-98.5 mg/kg. There are significant differences between L7 and other lines, except L9. Cu contents do not vary significantly. Some small areas with relative high Cu contents are located at the north-west part of this site, close to Jiangwei village.

Zn: Mean Zn content is 83.5 mg/kg, ranging 53.6-107.7 mg/kg. There are significant differences between line L1-5 and line L6-9. There is a relative high Zn area at the northern part of this site along a road.

There are significant differences of contents of Pb, Cd, Cu and Zn between lines from south to north, with increase in distance from Chenggong town. However, there is no significant difference between Pb, Cd, Cu and Zn contents between rows from west to east, according to T-tests.

Table 4.7: TE contents (mg/kg) in topsoil in detailed approach samples in the lacustrine unit

Lines	Pb			Cd			Cu			Zn		
	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range
L0-0-9	4.8c	5.8	0 - 8.6	Trace	trace	trace	82.0bc	84.2	49.3 - 95.9	94.3ab	97.0	58.2 - 114.5
L1-0-9	9.2bc	8.9	2.6 - 17. 4	Trace	trace	trace	87.8bc	85.9	73.7 - 104.8	53.6d	48.0	39.3 - 84.5
L2-0-9	6.1bc	5.7	2.9 - 11.5	0.150a	0	0 - 0.790	83.0bc	83.0	71.1 - 96.7	59.9d	51.4	319 - 98.4
L3-0-9	7.5bc	2.7	0 - 52.1	Trace	trace	trace	75.8c	76.8	66.4 - 84.5	55.9d	54.4	23.7 - 95.9
L4-0-9	4.1c	4.2	0 - 13.1	0.047b	0	0 - 0.466	79.2bc	81.3	53.8 - 99.8	67.5cd	64.6	47.2 - 87.9
L5-0-9	6.3bc	7.4	0.6 - 9.4	Trace	trace	trace	77.8bc	81.1	58.5 - 92.7	77.6bc	75.5	43.4 - 111.4
L6-0-9	9.4bc	8.4	5 - 16.3	Trace	trace	trace	85.2bc	96.0	1.3 - 114.4	107.7a	102.3	82 - 149.4
L7-0-9	11.9b	8.4	0 - 26.1	0.006b	0	0 - 0.056	98.5a	98.9	58.1 - 126.6	106.9a	102.9	74.6 - 139.5
L8-0-9	21.6a	22.1	14 - 28	0.063ab	0.049	0 - 0.205	80.9c	84.5	9.1 - 120.4	104.1a	103.7	93.8 - 117.5
L9-0-9	24.2a	24.5	19.9 - 29.3	0.026b	0	0 - 0.153	95.9ab	98.0	80.4 - 110.9	106.8a	107.9	75.4 - 120.6

* Mean content with different letter means significant difference ($P<0.05$), according to T-tests, n=10.

B. Trace element contents in five greenhouses close together

Pb: Mean content in 5 greenhouses is 5.0 mg/kg, ranging between 2.4-13.3 mg/kg, with the highest, 13.3 mg/kg, in greenhouse No. 1. There are significant differences of Pb contents between greenhouse No. 1 and the other greenhouses (Table 4.8).

Cd: Content is trace in greenhouses.

Cu: Mean content in 5 greenhouses is 90.8 mg/kg, ranging between 83.7-101.5 mg/kg, with the highest, 101.5 mg/kg, in greenhouse No. 1. There are significant differences of Cu contents between greenhouses No. 1, 3 and 4.

Zn: Mean content in 5 greenhouses is 91.1 mg/kg, ranging between 83.0-95.0 mg/kg, with the highest in greenhouse No. 1. No significant difference of total Zn contents between greenhouses is observed.

To summarize, although 5 greenhouses are near each other, contents of Pb, Cu and Zn in greenhouse No. 1 are the highest, while TE contents in the other four greenhouses are similar.

Table 4.8: TE contents (mg/kg) in five greenhouses in the lacustrine unit

Greenhouse	Contents	Pb	Cu	Zn
1	Mean	13.3a	101.5a	95.0a
	Median	11.3	106.9	99.4
	Range	0 - 25.9	87.7 - 109.0	74.6 - 106.8
2	Mean	3.4b	89.8ab	94.7a
	Median	3.1	90.5	98.8
	Range	1.8 - 5.6	76.9 - 99.7	83.6 - 104.8
3	Mean	3.7b	87.2b	83.0a
	Median	4.5	94.1	86.5
	Range	0 - 6.9	72.1 - 101.9	63.5 - 99.4
4	Mean	2.5b	83.7b	91.1a
	Median	2.8	86.5	89.2
	Range	0 - 4.3	72.2 - 89.7	82.1 - 103.3
5	Mean	2.4b	91.7ab	91.5a
	Median	2.3	94.2	88.3
	Range	0.6 - 3.9	80.6 - 98.8	78.3 - 105.0

* Mean content with different letter means significant difference ($P<0.05$), according to T-tests, n=5.

4.3.2.4.2. Transition unit

A.Total trace element contents

TE contents in the transition unit are summarized in Table 4.9 and Annex 4.5.

Pb: Mean content is 17.5 mg/kg, with range from 10.5-35.9 mg/kg. The mean Pb content in T0 (26.1 mg/kg), close to the mountain (Figure 3.16), is higher than in other rows, which could be linked to the rock background value. No significant difference is observed between rows and lines. Pb contents decrease from south to north, which is consistent with elevation gradient.

Cd: Mean content is 0.298 mg/kg, with range from trace to 2.264 mg/kg. The mean Cd content in T1 (0.692 mg/kg), close to the mountain, is higher than in other rows. Mean of Cd content in T6 is the lowest. No significant difference is observed between lines (Table 4.9). Samples with high Cd contents (T0 and T1) are located at southeast part near the mountain with high rock background value. Cd contents decrease from south-east to north-west, which is consistent with elevation gradient.

Cu: Mean content is 137.4 mg/kg, with range from 53.9-223.0 mg/kg. The mean Cu content in T3 (172.6 mg/kg) is higher than in other rows, which could be linked to a road close to T3.

Zn: Mean content is 117.7 mg/kg, with range from 48.1-192.1 mg/kg. The mean Zn content in T1 (138.5 mg/kg) and T3 (146.7 mg/kg) is significantly higher than in other rows, which could be linked to rock background value (T1) and a road close to T3 (Table 4.9).

No significant difference in contents of Cu and Zn is observed between lines. Accumulation of Cu and Zn are from west to east located in the middle of the area selected for this detailed approach and relative to a road across this area.

Table 4.9: TE contents (mg/kg) in topsoil of detailed approach samples in the transition unit

Lines	Pb			Cd			Cu			Zn		
	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range
T0-0-6	20.1a	28.1	18.8 - 29.3	0.392a b	0.347	0.266 - 0.565	128.99b	133.49	49.25 - 95.85	123.38ab	120.99	58.18 - 114.45
T1-0-6	17.7b	16.6	14.4 – 21	0.692a	0.407	0.259 - 2.264	148.8ab	152.7	97 - 156.9	138.5a	137.5	92.4 - 192.1
T2-0-6	16.3bc	15.6	14.6 - 19	0.275bc	0.251	0.214 - 0.392	148.8ab	144.5	101.6 - 182.7	128.6ab	121.8	110.1 - 166.3
T3-0-6	18.7b	17.9	16.6 – 23	0.274bc	0.221	0.154 - 0.565	172.8a	170.3	131.6 - 202.5	146.7a	152.1	125.4 - 169.6
T4-0-6	13.7c	153	10.5 - 15.5	0.167bc	0.184	0.094 - 0.244	137.3b	136.1	89.5 - 165.3	107.6b	108.7	66.2 - 133.6
T5-0-6	13.4c	13.5	12.2 - 14.1	0.236bc	0.139	Tr. - 0.856	137.7b	125.5	110.4 - 155.1	105.9b	104.5	60.0 - 1589
T6-0-6	16.8bc	16.5	11.5 - 27.5	0.049c	0.064	Tr. - 0.131	89.6b	86.8	53.9 - 133.1	72.9c	73.4	48.1 - 95.7

* Mean content with different letter means significant difference ($P<0.05$), according to T-tests, n=7.

B. Trace element contents in five greenhouses close together

Pb: Mean content in 5 greenhouses is 15.70 mg/kg, ranging from 14.29-21.79 mg/kg, with the highest in greenhouse No. 5. There are significant differences of Pb contents between No. 5, 1 and 3 (Table 4.10).

Cd: Cd content is trace in 5 greenhouses.

Cu: Mean content in 5 greenhouses is 177.21 mg/kg, ranging from 144.52-203.87 mg/kg, with the highest in greenhouse No. 2. There is significant difference of Cu contents between No. 1 and No. 2.

Zn: Mean content in five greenhouses is 141.09 mg/kg, ranging from 110.33-155.94 mg/kg, with the highest in greenhouse No. 5. There are significant differences of Zn contents between No. 1 and the other greenhouses.

To sum up, contents of Pb and Zn in greenhouse No. 5 are the highest, and Cu in No. 2. While in No. 1, contents of Pb, Cu and Zn are the lowest. It is suggested that TE could still be brought about from agricultural practices.

Table 4.10: TE contents (mg/kg) in five greenhouses in the transition unit

Greenhouse	Contents	Pb	Cu	Zn
1	Mean	14.3b	144.5c	110.3b
	Median	15.374	158.8	121.6
	Range	9.1 - 17.5	87.2 - 188.1	67.6 - 140.4
2	Mean	177ab	203.9a	154.9a
	Median	16.7	206.6	157.9
	Range	16.4 - 21.6	185.7 - 222.9	142.2 - 167.0
3	Mean	16.6b	168.4bc	140.1a
	Median	17.6	176.4	145.9
	Range	10.9 - 20.2	132.9 - 193.0	112.6 - 152.4
4	Mean	18.2ab	173.3abc	144.2a
	Median	18.9	174.8	147.9
	Range	13.9 - 20.2	125.9 - 208.2	112.5 - 166.2
5	Mean	21.8a	195.9ab	155.9a
	Median	19.6	195.7	150.1
	Range	19.0 - 30.6	185.0 - 217.3	130.8 - 195.4

* Mean content with different letter means significant difference ($P<0.05$), according to T-tests, n=5.

4.3.3. Vertical distribution of total trace elements

4.3.3.1. Trace element contents in subsoil

TE contents in subsoil are shown in Figure 4.2, Figure 4.18 and Annex 4.6.

Pb: Mean content is 58.2 mg/kg, ranging from 33.4-116.8 mg/kg. In 65.6% samples, Pb contents are between 40-60 mg/kg. In 2 out of 32 samples (6.2%), which are located in the mountain unit, Pb contents are >100 mg/kg.

Cd: Mean content is 0.89 mg/kg, ranging from trace to 2.30 mg/kg. In 59.4% samples, Cd contents are between 0.1-1.0 mg/kg and Cd contents of 34.4% samples are >1.0 mg/kg, distributed in the three units.

Cu: Mean content is 129.2 mg/kg, ranging from 26.8-218.2 mg/kg. In 43.7% samples, Cu contents are between 100-200 mg/kg, in 31.3% samples Cu contents are between 50-100 mg/kg. In 6 out of 32 samples (18.8%), located in the transition unit, Cu contents are >200 mg/kg.

Zn: Mean content is 97.0 mg/kg, range from 15.7-176.3 mg/kg. In 53.1% samples, Zn contents are between 50-100 mg/kg, in 28.1% samples Zn contents are between 100-150 mg/kg. In 3 out of 32 samples (9.4%), Zn contents are >150 mg/kg.

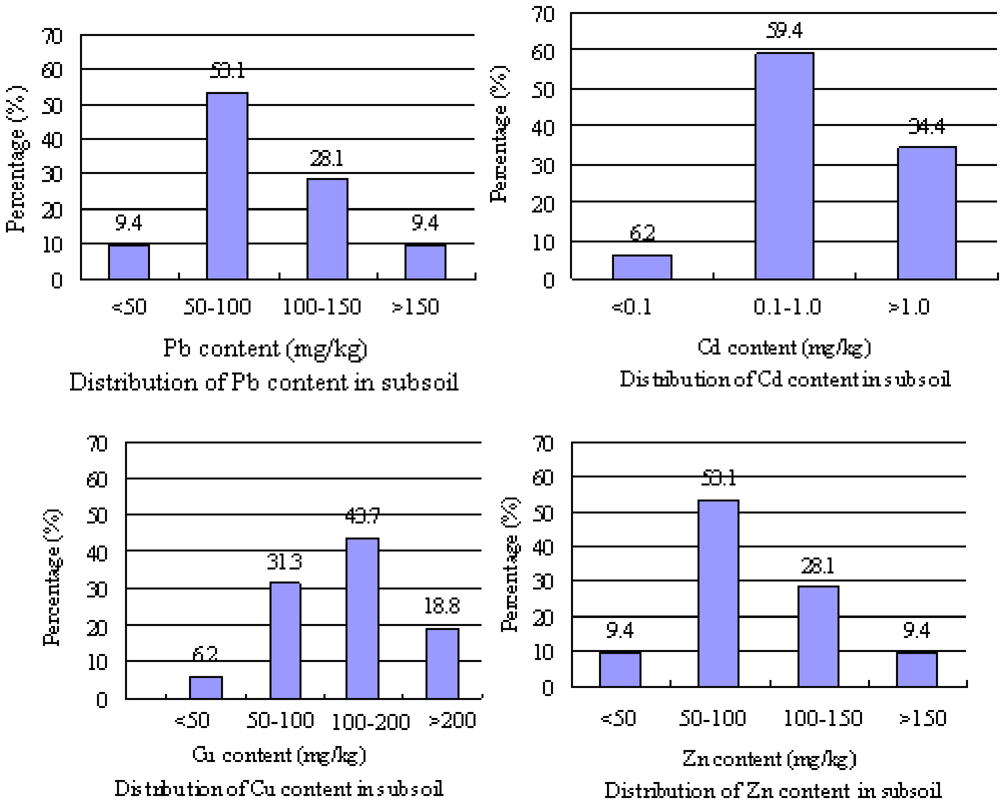


Figure 4.18: Percentages of sample numbers within range TE contents to total sample numbers in subsoil

<u>4.3.3.2. Relationships between total trace element contents in subsoil and soil morphological properties</u>

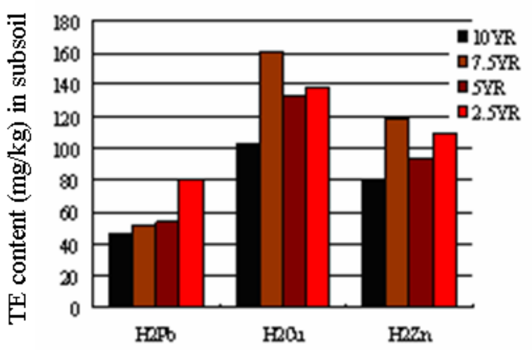
Colour:

According to field observations, colour of subsoil is brown or reddish brown, including 10YR, 7.5YR, 5YR and 2.5YR based on Munsell Codes. In 28.1% of samples, colour is 10YR with mean Pb: 46.8, Cd: 0.7, Cu: 102.5 and Zn: 79.9 mg/kg, Colour of 12.5% of samples is 7.5 YR with mean Pb: 51.6, Cd: 0.88, Cu: 160.3 and Zn: 118.6 mg/kg. Colour of 12.5% of samples is 5 YR, with mean Pb: 54.3, Cd: 0.72, Cu: 132.8 and Zn 93.4: mg/kg. In 25% of samples, colour is 2.5 YR, with mean Pb: 79.9, Cd: 1.36, Cu: 138.2 and Zn: 110.3 mg/kg.

The relationships between TE contents and colour show 10 YR samples with lowest TE contents, 2.5 YR samples with highest contents of Pb and Cd, and 7.5 YR samples with highest contents of

Cu and Zn. Except for 7.5 YR samples, TE contents increase with colour from brown to reddish brown (Figure 4.19).

TE contents in subsoil samples with colour (7.5YR + 10YR) (Pb: 48.3, Cd: 0.76, Cu: 120.3 and Zn: 91.8 mg/kg) are lower than with colour (5YR + 2.5YR) (Pb: 65.0, Cd: 0.99, Cu: 135.09 and Zn: 100.5 mg/kg).



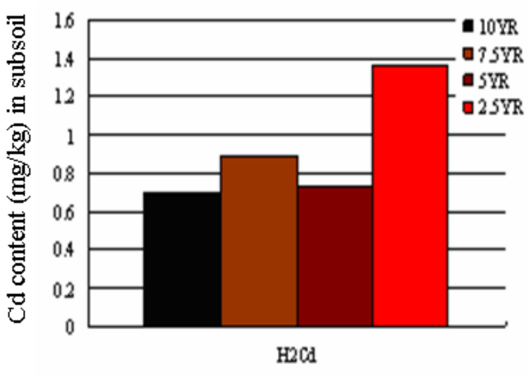


Figure 4.19: TE contents in subsoil (H2) with different colour.

Relief:

In the lacustrine unit, the mean TE contents in subsoil are Pb: 4l.55, Cd: 0.72, Cu: 82.4 and Zn: 69.4 mg/kg. Three (No. 22, 29, 46) out of 8 samples close to Dianchi Lake, in which mean TE contents (Pb: 45.7, Cd: 0.81, Cu: 83.2 and Zn: 79.1 mg/kg) are higher in samples far from the Lake (Pb: 43.2, Cd: 0.57, Cu: 80.2 and Zn: 65.2 mg/kg).

The mean of TE contents in the transition unit are Pb: 53.4, Cd: 0.74, Cu: 160.8 and Zn: 94.8 mg/kg. Mean TE contents in samples originating from two hilltops are lower than in samples originating from the intermediate foot slope, except for Pb (50.3 mg/kg on hilltop, 57.1 mg/kg on foot slope) (Figure 4.20).

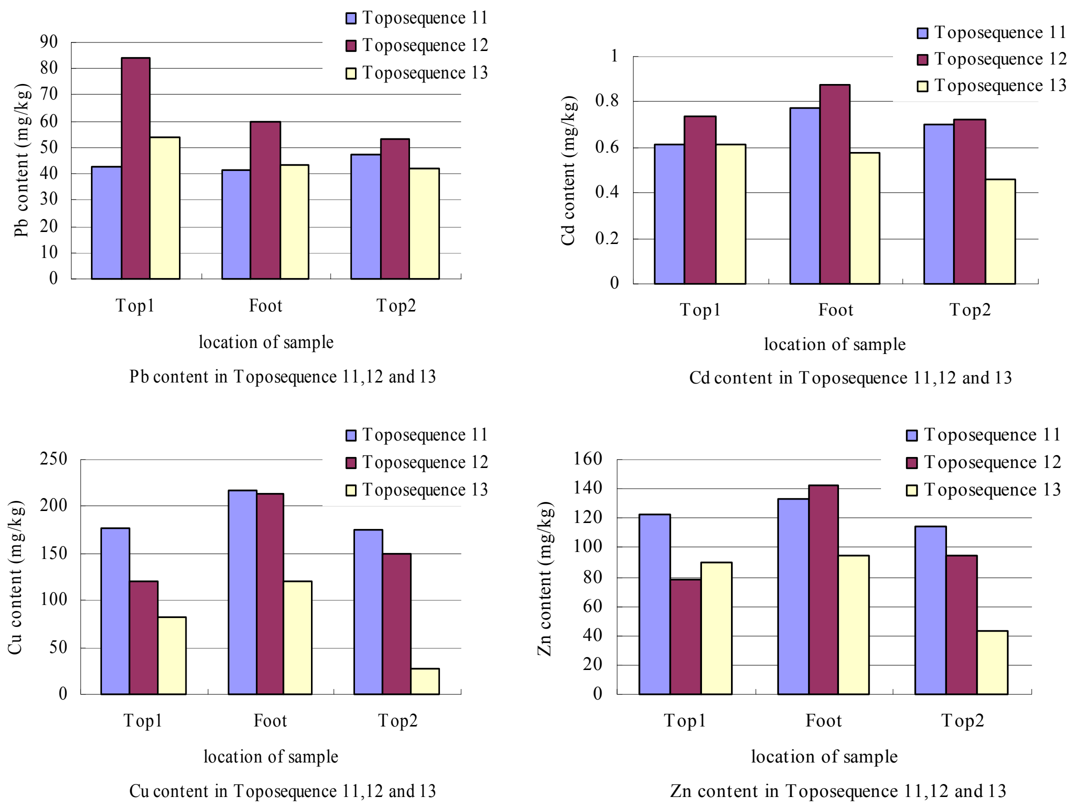


Figure 4.20: TE contents in subsoil in toposequences 11, 12 and 13.

The mean of TE contents in the mountain unit are Pb: 108.20, Cd: 2.2, Cu: 114.8 and Zn: 155.00 mg/kg. TE contents in the mountain unit are higher than in the lacustrine and transition units (M>T>L), except for Cu (T>M>L) (Figure 4.21).

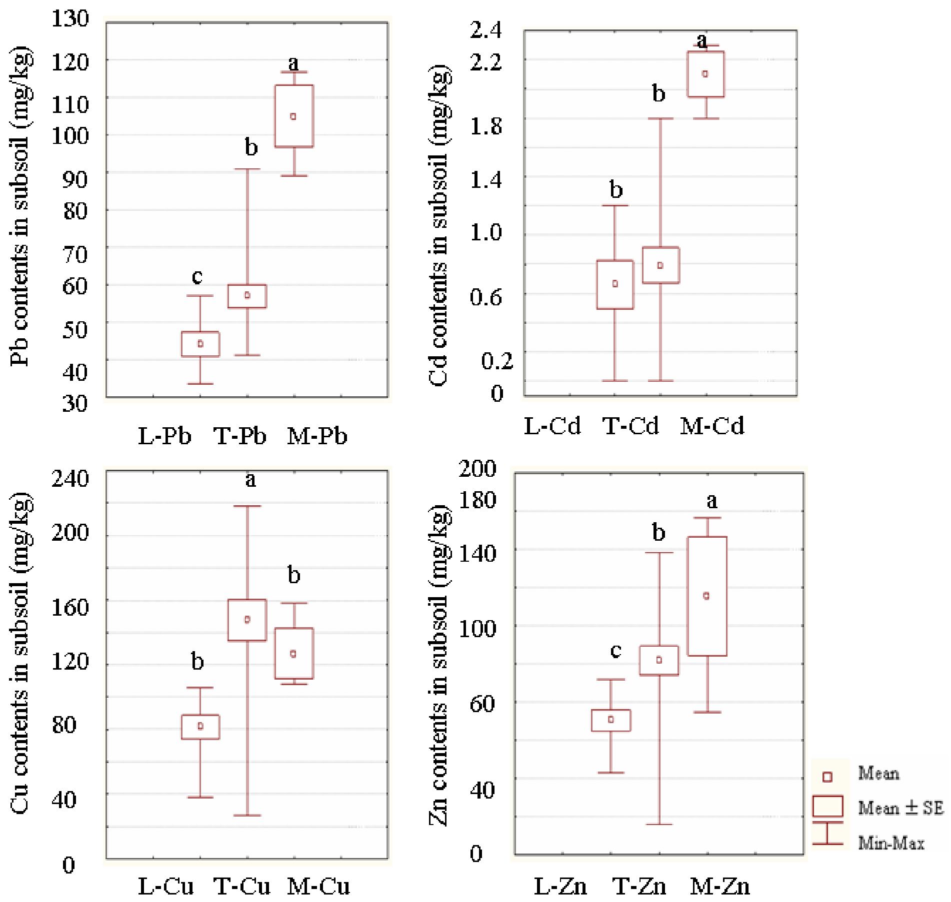


Figure 4.21: TE contents in subsoil in the three units.

Parent materials and stoniness:

Stoniness is <15% in subsoil. Pb and Cd contents (Pb: 45.8 and Cd: 0.45 mg/kg) are lower with no stoniness than with stoniness (Pb: 59.5 and Cd: 0.94 mg/kg). For Cu and Zn, it is just the opposite. Cu (174.9 mg/kg) and Zn (118.6 mg/kg) contents are higher with no stoniness than with stoniness (Cu: 124.3 and Zn: 94.8 mg/kg).

Sandstone and limestone are the main types of stones in the subsoil. Mean TE contents in samples with sandstone are lower than in samples with limestone, except for Cu. The other special "stoniness" is shell, in which mean TE contents of subsoil are lower than with sandstone and limestone, except for Zn (Figure 4.22).

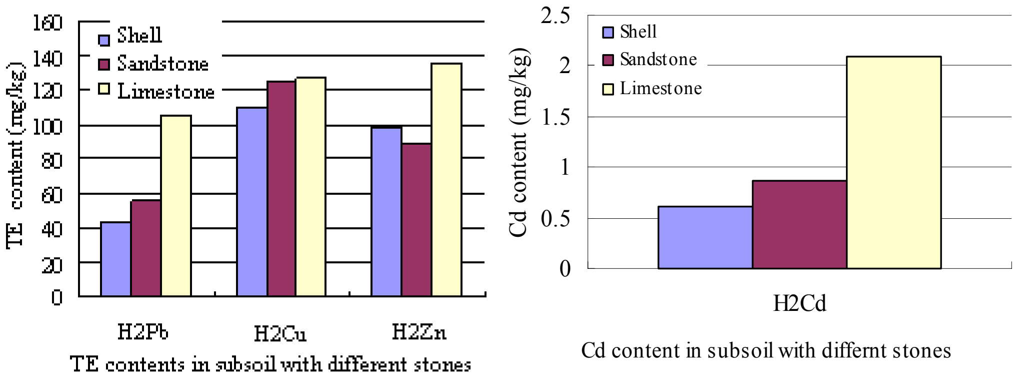


Figure 4.22: TE contents in subsoil with different stones.

Texture:

In 20 out of 32 samples (62.5%), texture is clay in subsoil. Mean TE contents with clay texture are Pb: 59.7, Cd: 0.85, Cu: 129.2 and Zn: 93.2 mg/kg, which are higher than in samples with sandy texture (Pb: 42.6 mg/kg, Cd: 0.55 mg/kg, Cu: 82.1 mg/kg, Zn: 71 mg/kg), and in samples with sandy loam texture (Pb: 37.6, Cd: 0.68, Cu: 85.8 and Zn: 91.7 mg/kg).

Mottles:

According to mottles in subsoil, samples are classified into two groups, one group with many black, red or yellow mottles due to organic matter and redox reactions, and the other group with few mottles. Mean TE contents with many mottles are for Pb: 52.6, Cd: 0.70, Cu: 142.1 and Zn: 97.4 mg/kg, which is lower than for Cu (161.5 mg/kg) and Zn (108.8 mg/kg) in samples with few mottles, higher than for Cd (0.57 mg/kg) and similar for Pb (52.8 mg/kg).

4.3.3.3. Relationships between total trace element contents in topsoil and subsoil

The mean Pb and Zn contents in topsoil are higher than in subsoil. But the mean contents of Cd and Cu are almost the similar in topsoil and subsoil (Figure 4.23).

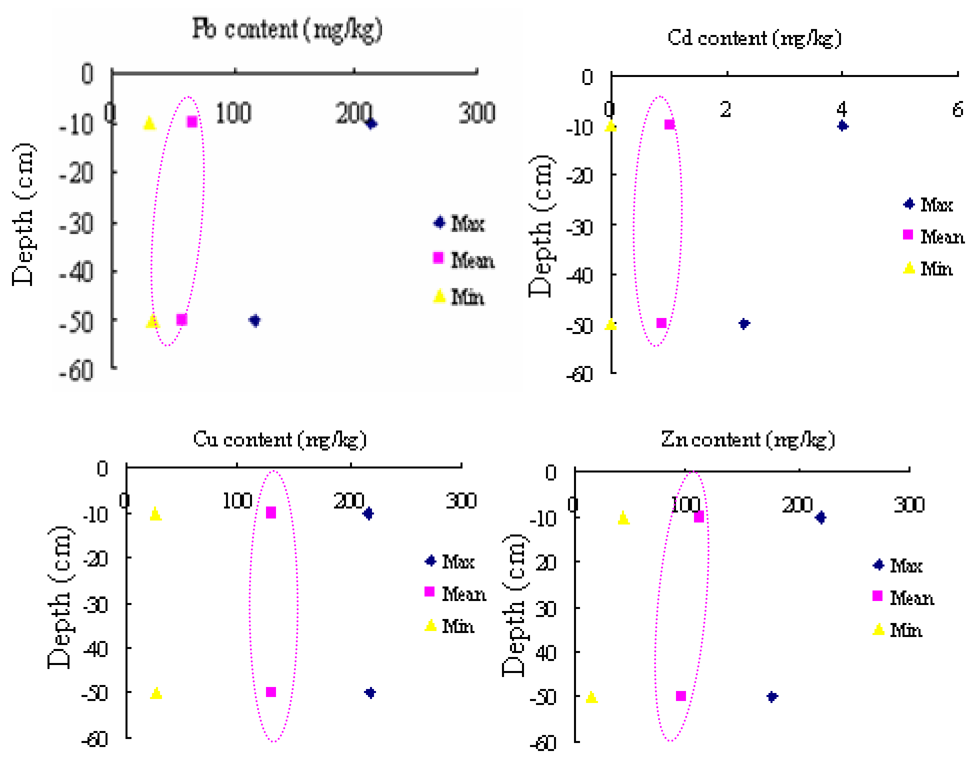


Figure 4.23: Total TE contents in topsoil and subsoil.

The ratio of mean TE contents in top/subsoil (RTS) is shown in Annex 4.6. Mean RTS of Pb and Zn are 1.47 (0.74-11.51) and 1.38 (0.76-8.13), respectively. RTS of Pb, Zn in 84.4% of samples are >1.0. The highest RTS of Pb are located in the transition (11.51) and lacustrine units (3.73). The highest RTS of Zn is located in the mountain unit (8.13). The mean RTS of Cd and Cu are 1.30 (0.70-8.43) and 1.03 (0.73-1.65), respectively. Some 75.9 % of samples are with Cd RTS ≤1.0, while 78.3% of samples are with Cu RTS ≤1.0 (Figure 4.24).

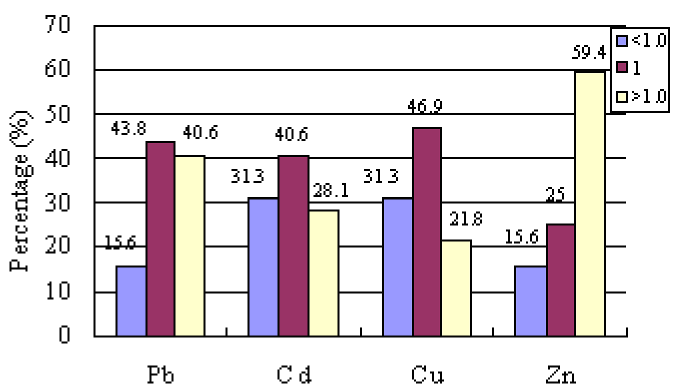


Figure 4.24: Percentage of sample numbers within range RTS to total top/sub pair numbers.

In the lacustrine unit: Mean TE contents in topsoil are higher than in subsoil (Figure 4.25). The mean RTS is >1, with Pb: 1.48, Cd: 1.18, Cu: 1.11 and Zn: 1.45. Some 87.5% of samples with RTS>1.0 for Pb and Zn are observed. It is suggested that TE accumulate in topsoil.

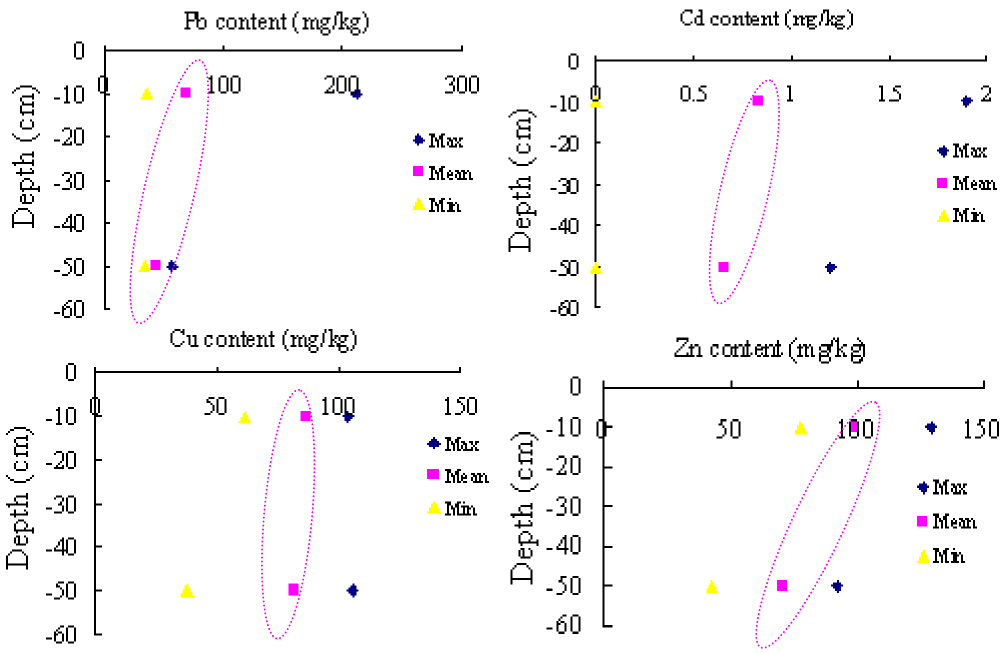


Figure 4.25: Total TE contents in topsoil and subsoil in the lacustrine unit.

In the transition unit: Mean Pb and Zn contents in topsoil are higher than in subsoil (Figure 4.26). The RTS is Pb: 1.51, Cd: 0.98, Cu: 0.97 and Zn: 1.39. One sample with the highest RTS of Pb (11.51) is located on the foot slope (Toposequence 10), and Cd (8.44) and Zn (8.13) located on toposequence 15. It is suggested that in the transition unit there is a Pb and Zn accumulation in topsoil.

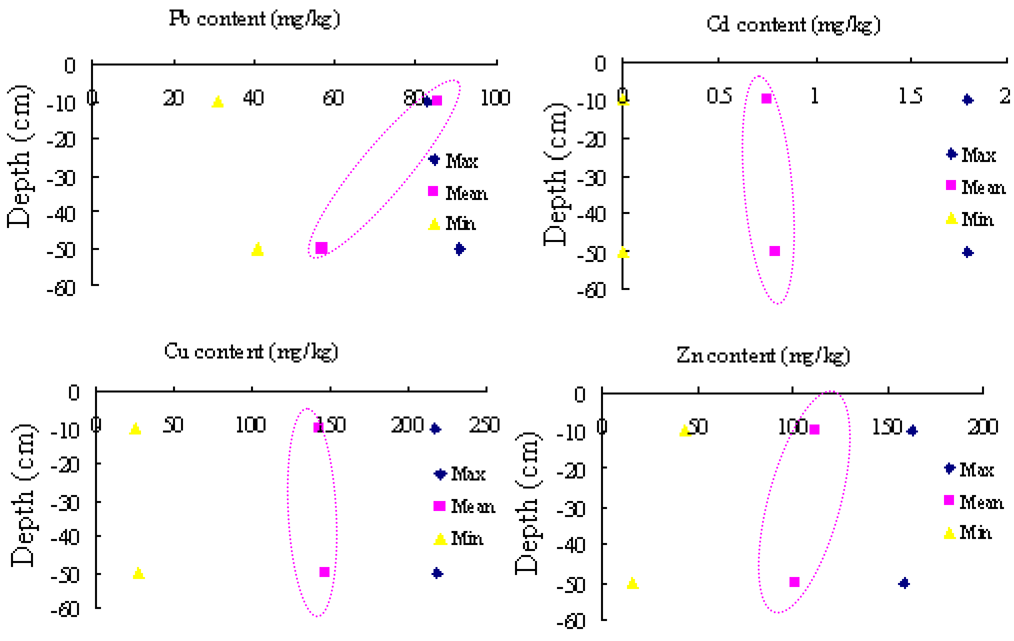


Figure 4.26 Total TE contents in topsoil and subsoil in the transition unit.

In the mountain unit: The mean TE contents in topsoil are higher than that in subsoil (Figure 4.27). The mean RTS is Pb: 1.16, Cd: 1.24, Cu: 1.20 and Zn: 1.16.

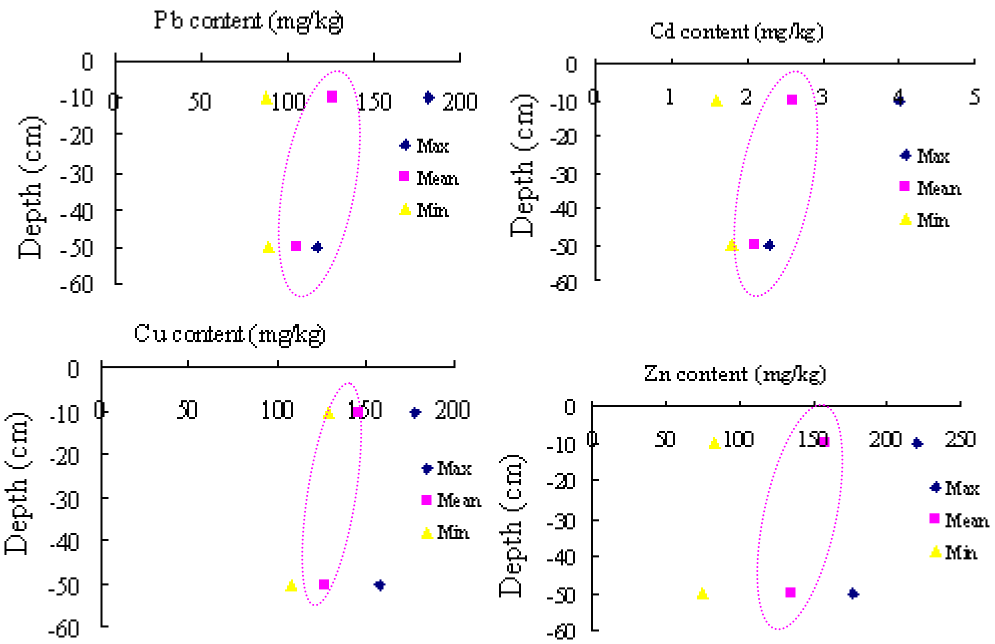


Figure 4.27: Total TE contents in topsoil and subsoil in the mountain unit.

To summarize, TE accumulation in topsoil is more often observed. There are strongly significant positive relationships between Cd, Cu and Zn contents in topsoil and subsoil (Table 4.11, Annex

4.6). Significant relationships between Pb content in topsoil and subsoil are observed when special sample with Pb 212.4 mg/kg is excluded.

Table 4.11: Relationships between TE contents in topsoil and subsoil

TE	Equation	R^2	F	Sig of f	N
Pb*	Y=17.09+0.67x	0.745	81.83	<0.001	31
Cd	Y=0.04+1.10x	0.816	137.06	<0.001	32
Cu	Y=12.17+0.91x	0.895	262.95	<0.001	32
Zn	Y=37.63+0.78x	0.605	45.86	<0.001	32

* Special sample with Pb 212.4 mg/kg in topsoil is excluded.

4.4. DISCUSSION

4.4.1. Soil identification in the three units

According to field observations and soil characteristics, parent material types can be distinguished in the three units:

➢ In the lacustrine unit, lake sediments are clearly identified in the lakeside and subsoil. They consist of silt and fine sand. Dark colour is due to frequent waterlogging keeping high SOC content in reducing conditions. From the end of the Tertiary to the beginning of the Quaternary, the land in the eastern lakeside rose up and Dianchi Lake level fell, resulting in the soil gradually de-swamping.

Colluvium and lacustrine-alluvial mixed deposits characterize the topsoil. Texture is sandy clay, loam or loamy clay (physical clay: 44.76%) according to observation and enriched with clay due to soil erosion or human activities taking soils from the transition unit to improve soil texture. Soil colour is brown, mean pH: 6.8, SOC: 1.8% and CEC: 29.12 cmol/kg.

➢ In the transition unit, colluvium and lacustrine-alluvial mixed deposits are also observed. Samples present loamy clay and clay textures according to observation (mean physical clay 56%) more often. Colour in certain places is a little redder, due to increased Fe and Mn contents and rubefaction. High pH and SOC are noticed on foot slopes. Mean pH in topsoil is 5.8, SOC content is 1.4%, and mean CEC is 20.61 cmol/kg.

- In the mountain unit, soils result from the weathering of limestone, marlstone and diluvium deposits. Soils present clay texture (physical clay: 58%). The reaction is acid (pH: 6.3) and due to decarbonation (Poncin, 2004). According to saturation ratio decreasing in subsoil, and Al^{3+} increased in subsoil (Poncin, 2004), low pH is related to the strong leaching of base ions and accumulation of Al^{3+}. The pH of samples is low on the foot slope. Colour is reddish brown more often in all horizons due to iron-manganese concretion particles and high Fe contents (Poncin, 2004). SOC content in topsoil is 1.3% and mean CEC is 28.30 cmol/kg.

4.4.2. Horizontal distribution of trace elements and anthropogenic effects

Trace element contents in regional horizontal approach

TE contents in topsoil are respectively Pb: 49.5, Cd: 1.148, Cu: 104.4 and Zn: 106.9 mg/kg. TE contents are influenced by soil characteristics. TE contents in soils appear linked to pH and cation retention. Negative relationships between pH and Pb (Cu) contents are observed. Positive relationships between SOC and Pb (Cd) contents, CEC and Cu contents are observed. The variation of Pb could be explained by SOC from one soil to another, Cd by SOC and CEC, and Cu by CEC. Meanwhile, pH and CEC present a significant relationship according to PCA (Figure 4.28). In fact, a positive relationship between pH and CEC exists with regression analysis (CEC=5.83+4.87pH, R^2=0.288, F=23.41 sig.f<0.001, n=88).

Correlation matrix (Pearson (n)):

Variables	pH	SOC	CEC
pH	**1**	0.217	0.545
SOC	0.217	**1**	0.000
CEC	0.545	0.000	**1**

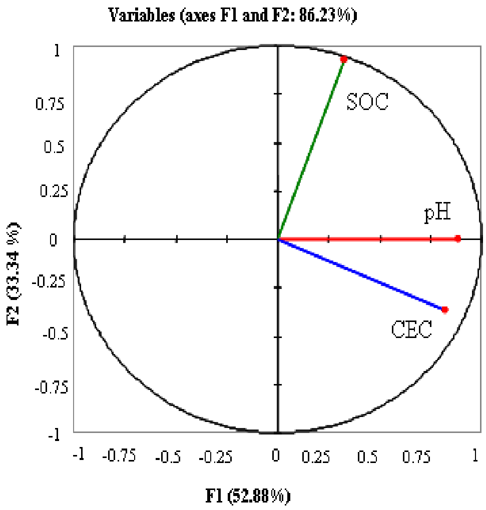


Figure 4.28: PCA of pH, SOC and CEC of topsoil.

<u>Trace elements versus geomorphology</u>

The mean TE contents in the mountain unit are higher than in the transition and the lacustrine units (M>T(L) for Pb, M>T>L for Cd, Cu Zn. From north-east to south-west, TE contents are from high to low, which is consistent with elevation gradient. Relief and soil types play key roles in the TE regional distribution. The high TE mean contents in the mountain unit can be linked to the high rock background values. The parent material is another key factor controlling the distribution of TE to some extent, especially in the limestone area.

On the other hand, total TE contents in topsoil are also affected by human activities. The spherical model is suitable to Pb and the exponential model suitable for Zn with semivariogram analysis, besides strong spatial variability of Cu and Cd. The proportion of $C_0/(C_0+C)$ of Pb is 14.2%, which means the variability of Pb is mainly influenced by morphological factors (relief and soil parent materials). The proportion of $C_0/(C_0+C)$ of Zn is 27.7%, which means the variability of Zn is mainly influenced by non-pedological factors (pesticides, fertilizers, irrigation and road traffic) mixed with morphological factors (relief and soil parent materials).

Variability of detailed approach to trace element contents

Significant differences of TE contents between lines are observed from south to north with the distance changing from Chenggong town in the lacustrine unit in 1 km^2 grid. Near the city, TE contents are mainly relative to water irrigation, sludge applications and atmospheric deposits.

Relative high Pb and Zn contents are observed at the northern part of lacustrine unit, along the road from Gucheng to Jiangwei villages. Meanwhile, accumulations of Cu and Zn in the centre of the transition unit are relative to a road across this site. It is suggested there are sources of TE from the road, such as Bordeaux mixture, pesticides with Cu and Zn piled aside the road, organic fertilizers with high Cu and Zn contents piled beside the road origin from animal food additives, and car exhaust from vehicles.

From south to north in the transition unit, Pb and Cd contents are from high to low, which is consistent with elevation gradient and linked to the high rock background values near the mountain. However, there is no significant difference of Pb, Cd, Cu and Zn contents between rows (from west to east), which could be relative to the similar agricultural practices and organic matter application methods in those detailed approach sites.

Variability of trace elements in 5 greenhouses close together

Although five greenhouses are close to each other, significant differences of Pb, Cu and Zn contents exist, whilst Cd contents are trace. TE could be continually brought about from agricultural practices, especially organic fertilizer applications.

4.4.3. Trace element vertical distribution and estimation of natural and contaminated values

Trace element contents in subsoil

TE contents in subsoil have relationships with soil properties, such as colour, relief, stoniness, parent materials, texture and mottles. TE contents in subsoil samples with colour ≤5YR are higher than in samples with colour >5YR. Except for 7.5 YR, TE contents increase with colour from brown to reddish brown. Reddish brown soils have abundant Fe_2O_3 to fix TE, and low pH in reddish brown soil should be linked to high TE contents.

Considering the relief, changes in TE contents in subsoil are linked to sites of samples, parent materials, textures and stoniness. For example, TE contents in samples close to Dianchi Lake are higher than in samples far from the Lake in the lacustrine unit. Mean TE contents in samples located on the hilltop are lower than in samples located on the foot of the hill in the transition unit, except for Pb, which should be relative to human activities and soil erosion from hilltop to foot slope.

Sandstone and limestone are the main types of stones in subsoil, besides shell. TE contents show limestone>sandstone>shell, especially high Pb and Cd contents in subsoil with stoniness <15%, and high Cu and Zn contents in subsoil with no stoniness. The same as Cu and Zn in subsoil with few mottles are higher than in group with many mottles. Therefore, Cu and Zn have different behaviour than Pb and Cd in subsoil, linked to stoniness and mottles. Pb and Cd should be maintained more strongly with weathering products. Mean TE contents in subsoil with clay texture are higher than in subsoil with sandy texture and sandy loam texture, which should be relative to TE fixed to clay.

Relationships between trace element contents in topsoil and subsoil

Accumulation of TE exists in topsoil, especially Pb and Zn. Mean Pb and Zn contents in topsoil are higher than in subsoil. Mean RTS of Pb and Zn is 1.47 and 1.38, respectively. Some 84.4% of samples are RTS $\geq$1.0 (Pb, Zn). Accumulation of TE in topsoil exists in cultivated soil widely, and linked to climate, anthropogenic activities and organic matter applications to topsoil.

Cd and Cu are mobile in dissolved forms, and transfer easily from topsoil to subsoil. Mean contents of Cd and Cu are almost the similar in topsoil and subsoil. Some 75.9% (Cd) and 78.3% (Cu) of samples are with RST $\leq$1.0. On the one hand, Cd and Cu are easy to transfer under the influence of precipitation and anthropogenic activities. Especially, Cu and Cd will be more readily transferable in soil with high moisture and ground water in the lacustrine unit. On the other hand, because TE has strong affinity with organic matter, and TE could move along the profile accompanying organic matter is distribution along the profile. Anthropogenic activities are still continuing to introduce TE to topsoil.

4.5. CONCLUSIONS

Soil types and soil identification:

Soil texture varies from loam in the lacustrine unit to clay in the transition unit, then to heavy clay in the mountain unit (based on the FAO texture system). Soil colour is brown, and darker near the Lake and redder in the mountain unit. Mean pH is 6.2, indicating soils are slightly acid in the research area. Mean SOC is 1.5%, physical clay (<0.01 mm): 51.88% and CEC: 24.09 cmol/kg. Comparing the geomorphological units, mean pH, SOC and CEC in the lacustrine unit appear to be slightly higher than in the other two units, which is linked to different soil parent materials and more intense agricultural practices. In the three units, texture of samples in subsoil is mainly clay, besides sandy clay near the Lake. Colour in subsoil is darker brown in the lacustrine unit, and reddish brown in the transition and mountain units.

Horizontal distribution of trace elements and anthropogenic effects:

Contents of regional trace elements: The mean Pb, Cd, Cu and Zn contents in topsoil are 56.7, 0.47, 125.7 and 114.2 mg/kg, respectively. The pH, SOC and CEC are the principal components influencing soil TE contents. Variation in Pb could be affected by SOC, Cd by SOC and CEC, while Cu by CEC.

Geomorphology of regional trace element contents: From north-east to south-west, contents of Pb, Cd and Zn are from high to low, which is consistent with elevation gradient. The mean contents of Pb, Cd, Cu and Zn in the mountain unit are higher than in the transition and lacustrine units (M>T(L) for Pb, M>T>L for Cd, Cu and Zn.

Variability of detailed approaches to trace element contents: Significant differences of TE contents are observed from south to north with distance from Chenggong town in the lacustrine unit and from the mountain in the transition unit. But, there is no significant difference between TE contents from west to east with distance from Dianchi Lake in the lacustrine unit and between two villages in the transition unit. However, accumulation of TE is usually along roads. Meanwhile, even though greenhouses are close to each other, there are still significant differences of Pb, Cu and Zn contents, except Cd contents are trace.

Vertical distribution of trace element contents: The mean TE contents in subsoil are Pb: 58.2, Cd: 0.89, Cu: 129.1 and Zn: 97.0 mg/kg.

Relationships between trace element contents in subsoil and soil morphological properties: Except for 7.5 YR, TE contents increase with colour from brown to reddish brown. TE contents in subsoil in the mountain unit are higher than in the lacustrine and transition units (M>T>L), except for Cu (T>M>L). Mean TE contents in subsoil samples with limestone are higher than samples with sandstone and shell. Mean TE contents in subsoil samples with clay texture are higher than in samples with sandy texture and sandy loam texture. Cu and Zn contents in subsoil with few mottles are higher than with many mottles, while Pb is close to each other, and Cd is lower.

Relationships between trace element contents in topsoil and subsoil: Although strong significant relationships between TE contents in topsoil and subsoil are observed, mean Pb and Zn contents in topsoil are higher than in subsoil, most of RTS of Pb and Zn ≥1.0. Mean contents of Cd and Cu are similar in topsoil and subsoil, most of RTS of Cd and Cu ≤1.0.

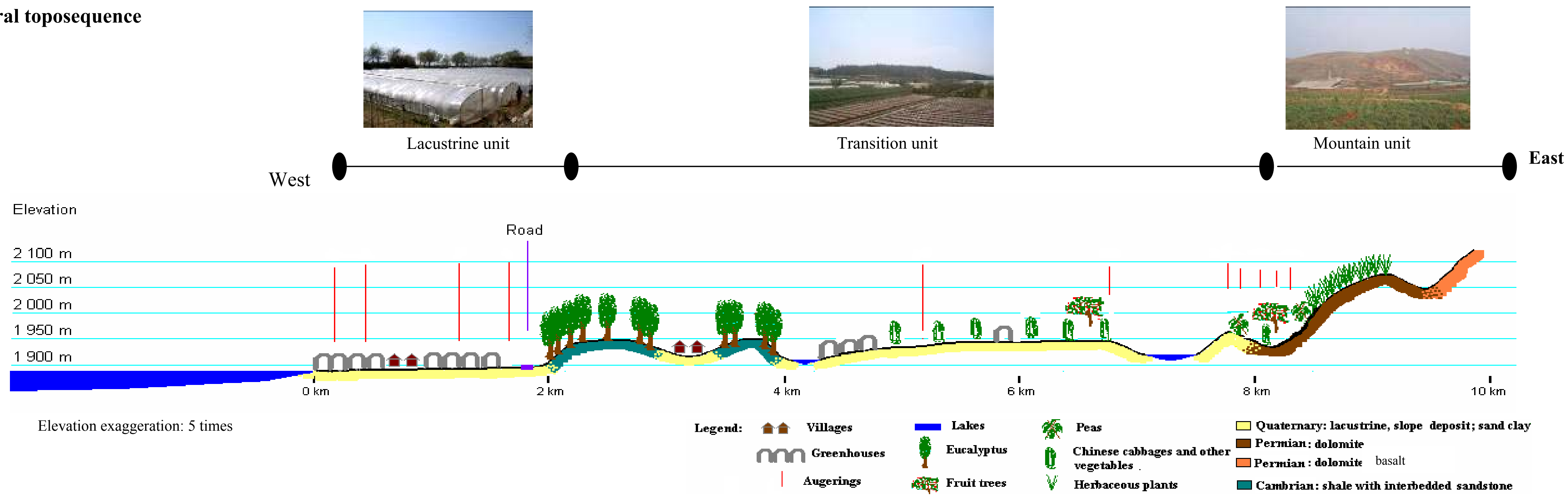
To summary, the factors influencing TE content in the research area are influenced by morphological factors (relief and soil parent materials) and non-pedological factors (pesticides, fertilizers, irrigation and road traffic) (Table 4.12).

Table 4.12: Summary for factors influencing TE contents in the research area

Factors	Pb	Cd	Cu	Zn
Morphological factors	M>T(L) (topsoil and subsoil contents)	M>T>L (topsoil and subsoil contents)	M>T>L (topsoil contents); T>M>L (subsoil contents)	M>T>L (topsoil and subsoil contents)
	High on hilltop in M*	High on hilltop in M	High on hilltop in M	High on hilltop in M
	Accumulation in M (regional approach)	Accumulation in M (regional approach)	Accumulation on eastern (regional approach)	Accumulation on eastern (regional approach)
		Accumulation near M (detailed approach)		
	2.5YR>10YR (subsoil)	2.5YR>10YR (subsoil)	2.5YR>10YR (subsoil)	2.5YR>10YR (subsoil)
	Stoniness>no stoniness (subsoil)	Stoniness>no stoniness (subsoil)		
	Limestone>sandstone>shell (subsoil)	Limestone>sandstone> shell (subsoil)	Limestone (sandstone)>shell (subsoil)	Limestone>sandstone>shell (subsoil)
	Clay>sandy (loam) (subsoil)	Clay>sandy (loam) (subsoil)	Clay>sandy (loam) (subsoil)	Clay>sandy (loam) (subsoil)
		Many mottles>few mottles (subsoil)		
	$C_0/(C+C_0) = 14.2\%$			$C_0/(C+C_0) = 27.7\%$
		RTS<1	RTS<1	
Non-pedological factors	Positive relationship with SOC	Positive relationship with SOC		
	Accumulation near villages and roads (regional and detailed approaches)		Accumulation near villages and roads (regional and detailed approaches)	Accumulation near villages and roads (regional and detailed approaches)
	Greenhouse differences		Greenhouse differences	Greenhouse differences
				$C_0/(C+C_0) = 27.7\%$
	RTS>1			RTS>1

* L: lacustrine unit; T: transition unit; M: mountain unit.

Figure 4.2:
General toposequence



Parameters			Lacustrine unit	Transition unit	Mountain unit
Elevation (m)			1,881 – 1,897	1,883 – 1,976	1,940 – 1,995
Slopes (%)			0 – 1	0 – 15	0 – 30
Outcrop			Purple shale + sandstone	Purple shale + sandstone	Sandstone + limestone + dolomite
Parent rock (geological map)			Lacustrine and slope deposit: sand clay	Lacustrine and slope deposit: sand clay (+ shale with interbedded sandstone (hills))	diluvium deposit: sand clay + dolomite + basalt
Surface soil colour			10 YR; 7.5 YR,; 5 YR	5 YR; 7.5 YR;10 Y R; 2.5 YR	5 YR ; 2.5YR
Land cover			Vegetables (cabbages, celery, lettuce, radish,…) → greenhouses	Vegetables (with and without greenhouses) + eucalyptus (hills) + fruit trees	Vegetables (without greenhouses) + fruit trees
Geopedology	Clay (%)	Topsoil // subsoil	23 – 45 // 18 – 35	42 – 58 // 36 – 76	68.7 – 81.0 // 67.6 – 77.9
Synthesis	pH $_{H2O}$	Topsoil // subsoil	4.1 – 7.8 // 7.3 – 8.2	4.4 – 7.1 // 6.4 – 7.0	4.4 – 7.8 // 4.5 – 7.9
	CEC (cmol/kg)	Topsoil // subsoil	8.6 – 88.5 // 15.3 – 20.6	8.9 – 38.1 // 14.6 – 24.8	17.9 – 37.1 // 25.5 – 30.5
Agropedology	SOC (%)	Topsoil // subsoil	0.5 – 3.2 // 0.1 – 2.5	0.7 – 3.0 // 0.1 – 1.6	0.5 – 3.7 // 0.2 – 1.5
	C/N	Topsoil // subsoil	6 – 25 // 7 – 12	3 – 16 // 8 – 17	6 – 27 // 15 - 23
Environmental	Cd (mg/kg)	Topsoil // subsoil	0 – 1.9 // 0 – 1.2	0 – 1.8 // 0 – 1.8	1.6 – 4.0 // 1.8 – 2.3
	Cu (mg/kg)	Topsoil // subsoil	61.2 – 103.6 // 37.8 – 105.8	25 – 217.5 // 26.8 – 218.2	129.3 – 177.6 // 107.8 – 158.3
	Pb (mg/kg)	Topsoil // subsoil	35.2 – 212.4 // 33.4 – 57.0	30.9 – 82.8 // 41.1– 91.0	87.6 – 181.6 // 89.2 – 116.8
	Zn (mg/kg)	Topsoil // subsoil	77.1 – 129.5 // 42.7 – 91.7	43.1 – 162.8 // 15.7 – 158.2	82 – 220.3 // 74.6 – 176.3
Limiting factors			Redox reaction	-	Relief/pH
Reference toposequences			1 →6	7 →15	16 → 17

V: SOIL ASSESSMENT AND TRANSFER FROM SOILS TO VEGETABLES

5.1. INTRODUCTION

Trace elements (TE) in soil originate from natural sources and anthropogenic activities (Nan Z.R., *et al.*, 2002; Michalska & Asp, 2001). Especially in periurban intensive vegetable garden soils, TE contents in soil increase with agricultural practises (Yusuf, *et al.*, 2003; Jansson & Oborn, 2000). In order to guarantee human health, it is necessary to assess soil quality and vegetable security. Soil assessment and vegetable assessment have been described in Section 2.5.

Contaminated soil and plant assessments have been undertaken in several periurban vegetable production areas around some major Chinese cities, such as Beijing, Shanghai and Naijing (Wang Y.G. & Zhang S.R., 2001; Zhang Q.L., *et al.*, 2005). Chenggong County, located near Kunming City, is an important vegetable production area in Yunnan Province. By field investigation, this part of the research aims to: 1) assess soil and vegetable TE contents, according to Chinese legal thresholds, and 2) evaluate the potential transfers of TE from soils to vegetables.

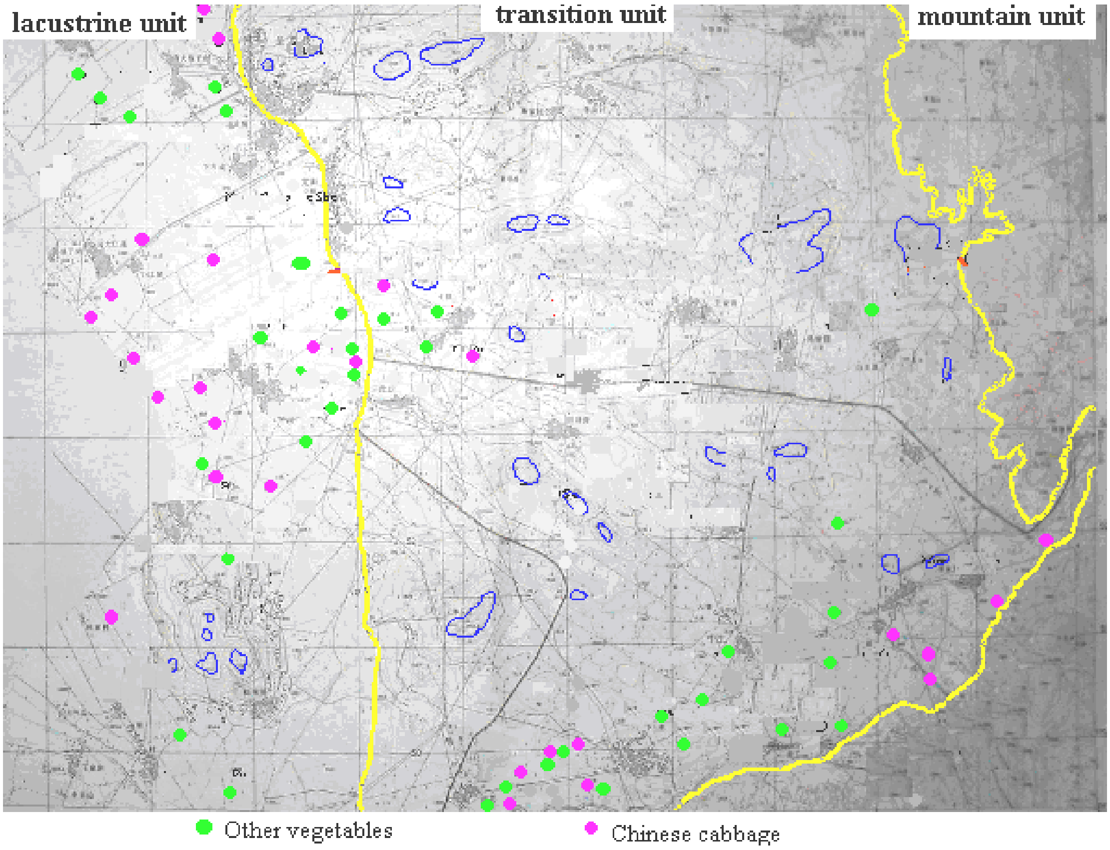
5.2. MATERIALS AND METHODS

In order to assess the degree of soil contamination by TE, total TE contents of topsoil samples were measured, as described in Section 4.3.2. Signal index of contamination (Pi) and integrative index of contamination (P) of TE, described in Section 2.5.3, have been used according to soil quality standard values in China (GB15618-1996 and HJ332-2006). Vegetables growing in various conditions of soil contamination are compared in terms of TE contents.

Vegetable sampling

TE contents were measured in seven vegetable species (63 samples), including cauliflower, celery, lettuce, tomato, radish, Chinese cabbage and peas (6 fields for each and 27 fields for Chinese cabbage samples) (Figure 5.1, Annex 5.2). Chinese cabbage, cauliflower and celery are very important in terms of the most often consumed vegetables. Chinese cabbage is retained because of its strong accumulation of TE (Wang Y.G. & Zhang S.R., 2001; Chen H.M., *et al.*, 2006), especially Cd, and its enormous consumption by the Chinese. Lettuce, tomato and radish are interesting because they are representative of plants differently consumed, stem, fruit and roots, respectively. Pea is chosen as representative of legumes.

At the same place, plant sample and the topsoil sample were collected. In order to obtain samples representative of each plot, plant sample and the topsoil sample were composed of three elementary samplings in 1 m × 1 m plots. Analyses were thus performed on composite samples composed of different plants from the same plot, and the corresponding soils. As far as possible, samples were taken at sufficient distance from the limits of the plot, in the medium of the cultivated rows, in order to avoid border effects. Samples were collected during harvest time.



*Vegetable samples **in the lacustrine unit***: NO.1-15, 30, 33-39, 42-44; 26 samples

Vegetable samples in the transition unit: NO. 47-73, 91-99, 112; 37 samples.

Figure 5.1: Location of vegetable samples in the research area.

Preparation of vegetable samples

Vegetable samples were separated in the two parts, i.e. eaten part and non-consumed part (Table 5.1). Each part was washed three times with tap water, in order to remove soil particles at the surface, so that only the fraction incorporated in plant tissues was taken into account when analysing TE contents. The composite sample was cut into small pieces, dried at 105 °C for 1 h, and at 65-70°C for 2 days, until it could be ground to powder with a glass pestle in a porcelain mortar.

Table 5.1: Presentation of eaten parts and non-consumed parts of the vegetables

Vegetables	Eaten parts	Non-consumed parts
Cauliflower	The flower	The leaves and lignin-rich skin of the floral peduncle
Celery	The tender parts of the stem	The leaves and the fibrous parts of the stem
Chinese cabbage	The tender leaves	The exterior leaves
Lettuce	The stem	The leaves
Pea	The seeds and the pods	The leaves
Radish	The root	The leaves
Tomato	The fruit	The leaves and the stem

Determination methods

Trace element contents in vegetable: Dry ash method (GB/T 5009.12, 13, 14, 15-1996)

10 g of plant powder in a 100 ml quartz-beaker, put in muffle furnace, increase the temperature to 200°C, for 1 hour, then to 560°C for 12 hours. l0 ml $HClO_4 : HNO_3$ (1:1) are added when ash is cooled down. Ashes are dried, cooled and add 5 ml 1 N HCl to dissolve the deposition. After cooling, samples are filtered through filter paper and diluted to 50 ml with deionized water. Then they are analysed by graphite furnace atomic absorption spectrometry.

Statistical analysis

The general description data are analysed with descriptive statistics and expressed as means using Excel 2003 and STATISTICA 6.0. The regression analysis is carried out for linear models of TE contents and other factors by SPSS and XLSTAT at $P < 0.05$ or $P < 0.01$ levels. Only significant relationships are considered.

5.3. RESULTS

5.3.1. Soil assessment

General approach of the research area

Two sets of data are used for soil assessment. One set of data (SA) is from topsoil samples of the regional approach, the other set of data (SB) is selected for corresponding plants. First, 88 topsoil samples are used for general soil assessment of Pb, Cu and Zn and 130 topsoil samples for Cd (SA). Mean TE contents in topsoil are 2-7 times of mean TE contents in world soils (Figure 5.2, Table 3.3). Especially, the ratio of mean Cd and Cu contents in topsoil to that in world soils are 7.5 and 5.6, respectively, which show that the most serious problematical elements could be Cd and Cu. Compared to mean TE contents in Kunming soils (Table 3.3), the ratio is still >1, especially Cd and Cu (>2) (Figure 5.2).

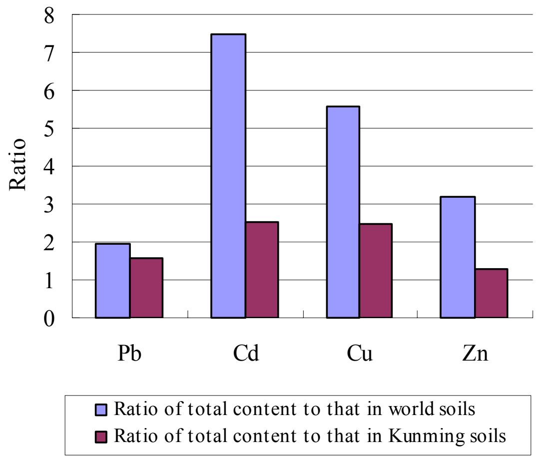


Figure 5.2: Ratio of mean total TE contents in topsoil to that in world and Kunming soils.

Pi and P of topsoil TE are also considered for soil TE contamination assessment according to Chinese standard values (GB15618-1996). The results are shown in Table 5.2 and Annex 5.1.

Pb: Comparing to soil quality standard values of Pb (Table 2.7), Pb contents in the research area are lower than standard in level II, which indicates a low contaminated level. Mean Pi (1.09) and median Pi (1.07) of Pb are <2, ranging from 0.77-1.83, confirm this low contamination level.

Cd: Cd contents present great variability. Mean Pi of Cd is 1.03, which corresponds to a low contaminated level, even if there are some samples with medium or high contaminated levels.

Cu: Cu contents are close to standard value of class III. Mean Pi (2.24) and median Pi (2.01) of Cu are >2, corresponding to medium contaminated level. Considering the distribution of Cu, high Pi for some samples are found in the research area.

Zn: Pi of Zn is similar to Pi of Pb. Mean (1.07) and median (1.05) Pi for Zn are <2. Soil contamination by Zn does not appear very serious.

The integrative index of contamination (P) of TE is 5.94 (Table 5.2), which indicates high contaminated level. The main contaminating elements are Cd and Cu. High P of TE in soil is due to high Cd and Cu contents.

Table 5.2: Soil TE contamination assessment in the research area

Unit	Statistic	Signal index of contamination (Pi)				N
		Pb	Cd	Cu	Zn	
All	Median	1.05	0	2.01	1.05	88
	Mean	1.09	1.03	2.24	1.07	
	Min	0.77	0	0.59	0.43	
	Max	1.83	8.29	4.03	1.92	
Lacustrine unit	Median	1.05	0.20	1.86	1.04	31
	Mean	1.09	0.98	1.87	1.03	
	Min	0.77	0	0.59	0.53	
	Max	1.83	5.29	2.80	1.92	
Transition unit	Median	1.08	0	2.15	1.01	47
	Mean	1.08	0.82	2.42	1.07	
	Min	0.84	0	0.71	0.43	
	Max	1.22	5.12	4.03	1.57	
Mountain unit	Median	1.09	0	2.21	1.18	10
	Mean	1.16	1.83	2.52	1.18	
	Min	1.03	0	1.65	0.73	
	Max	1.68	8.29	3.81	1.80	
Integrative index of contamination (P)		5.94				88

Non contamination; Low contaminated level; Medium contaminated level; High contaminated level;

Then, taking into account 63 vegetable samples, SB is used to assess soil contamination. Mean Pi of TE is for Pb: 1.19 (1-1.76), Cd: 1.88 (0-4.55), Cu: 1.91 (0.56-4.03) and Zn: 1.33 (0.52-2.04)

(Annex 5.1). As far as SA, Pi of Pb, Cd, Cu and Zn is <2, and corresponds also to low contaminated level by these elements, according to soil quality standard values (GB15618-1996). The value of P=3.41, indicates a high contaminated level due to some samples with high Cd and Cu contents. Meanwhile, based on Farmland Environmental Quality Evaluation Standards for Edible Agricultural Production for vegetable production (HJ 332-2006), some 60.3% of samples exceed the standard value of soil for vegetable growth for Pb (50 mg/kg), 58.7% for Cd (0.3 mg/kg), 73.0% for Cu (50 mg/kg) and 9.5% for Zn (200 mg/kg).

Differences between the three units

Considering the different units, ratios of Cd and Cu to that in world soils are higher in the mountain unit than in the transition unit and lacustrine unit (M>T>L), and ratios of Pb and Zn to that in world soils in the three units are similar (Figure 5.3). Mean Cd contents are 11.7 times of world soils and 3.9 times of Kunming soils in the mountain unit and 7.2 times and 2.4 times in the lacustrine unit. Ratio of total Zn contents to Kunming soils is ~1.3 times in the three units, just close to the background value in Kunming Prefecture.

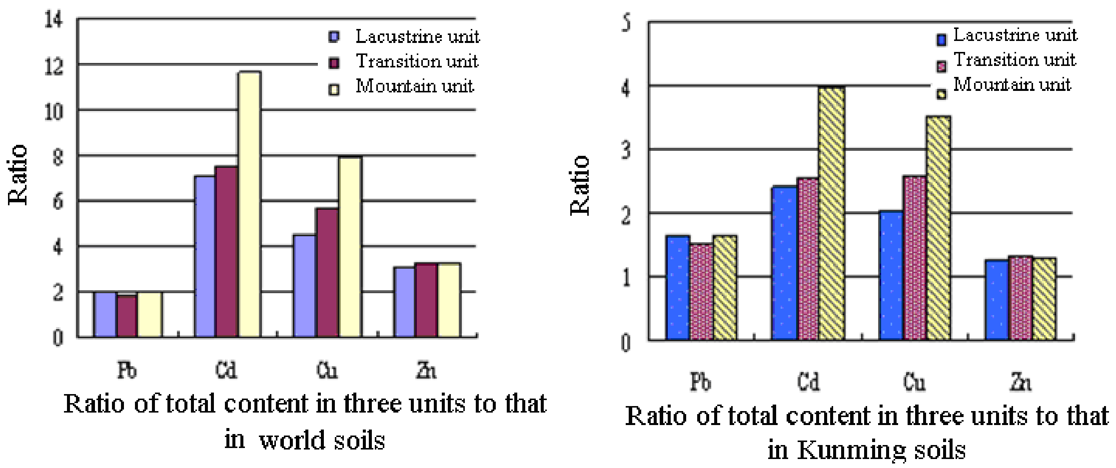


Figure 5.3: Ratio of mean total TE content in topsoil in the three units to that in world and Kunming soils.

Pi gradients for Cd and Cu follow the order: mountain unit>transition unit>lacustrine unit (M>T>L). Pi of Pb and Zn is between 1-2, and is similar in the three units (Figure 5.4).

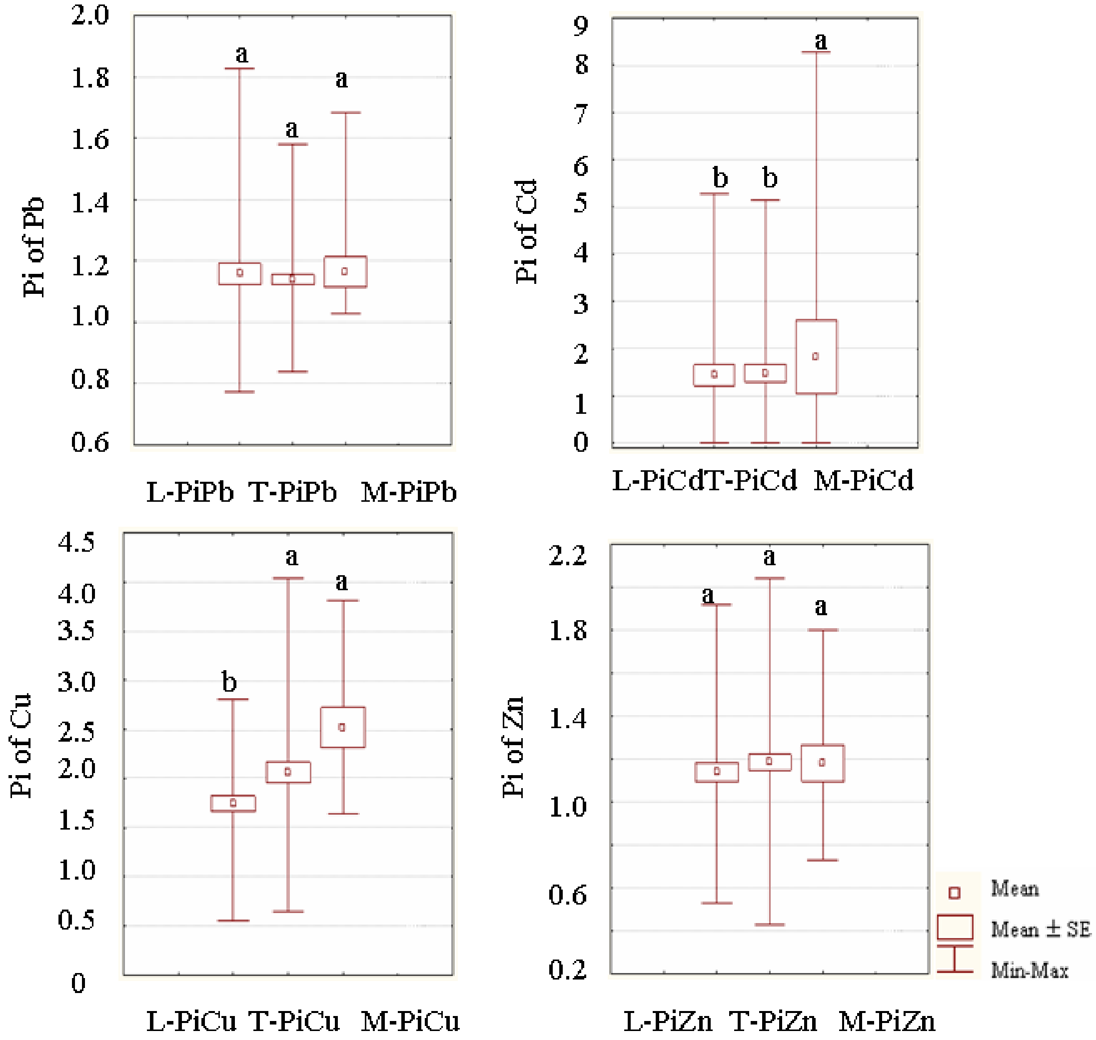


Figure 5.4: Pi of Pb, Cd, Cu and Zn in the three units.

5.3.2. Trace element contents in plant and plant assessment

A: Eaten part

Vegetables: 63 samples, including 27 Chinese cabbage samples, are taken to assess plant TE contents. TE contents refer to fresh materials (FM) in order to compare to Chinese standard values for vegetables.

Pb: Pb contents range between 0.08-4.12 mg/kg FM (Table 5.3). Some 95.2% of samples both in the lacustrine and transition units exceed the standard value for Pb (0.2 mg/kg FM, GB14935-1994) in vegetables. There are some differences between the vegetables: the highest Pb contents are in cauliflower (2.64 mg/kg FM), and the lowest in tomato (0.27 mg/kg FM) (Figure 5.5).

Table 5.3: TE contents in the eaten part of vegetables (mg/kg FM) (n=6)

Vegetables	Statistic	Pb	Cd	Cu	Zn
Celery	Mean	0.45	0.02	5.88	10.60
	Range	0.28 - 0.73	0.01 - 0.05	3.48 - 6.88	6.48 - 15
Chinese cabbage*	Mean	0.33	0.03	0.97	3.45
	Range	0.22 - 0.96	Trace - 0.13	0.23 - 5.19	1.74 - 14.16
Lettuce	Mean	0.37	0.04	5.42	5.03
	Range	0.09 - 0.58	Trace - 0.16	1.53 - 9.26	1.37 - 13.35
Radish	Mean	0.79	0.03	8.58	9.53
	Range	0.08 - 1.25	Trace - 0.06	3.20 - 18.60	5.20 - 13.70
Pea	Mean	1.05	0.01	17.35	19.30
	Range	0.10 - 2.26	Trace - 0.05	5.92 - 27	7.84 - 32.32
Tomato	Mean	0.27	0.01	0.65	2.69
	Range	0.20 - 0.37	Trace - 0.01	0.60 - 0.77	0.73 - 5.78
Cauliflower	Mean	2.64	0.01	16.62	8.41
	Range	1.26 - 4.12	Trace - 0.04	9.37 - 23.36	2.04 - 16.48
China standard values for vegetables		≤0.2	≤0.05	≤10	≤20

* n=27 for Chinese cabbage.

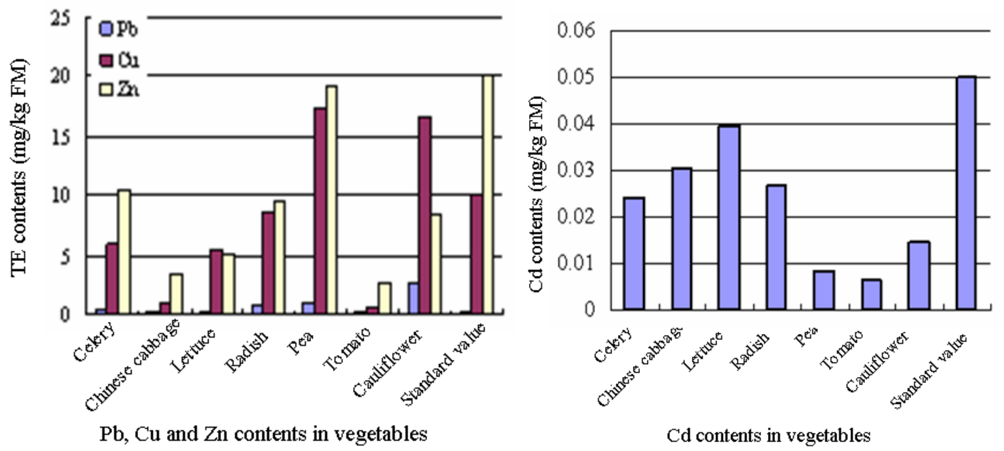


Figure 5.5: TE mean contents in the eaten part of vegetables.

Cd: Cd contents range between trace and 0.16 mg/kg FM. Some 9.5% of samples exceed the standard value for Cd（0.05mg/kg FM, GB15201-1994) in vegetables, these samples are located in the lacustrine unit. The highest Cd contents are in lettuce and Chinese cabbage, and the lowest in tomato (0.01 mg/kg FM) (Figure 5.5).

Cu: Cu contents range between 0.60-27.00 mg/kg FM. Some 19.1% of samples exceed the standard value for Cu (10 mg/kg FM, GB15199-1994) in vegetables; these samples are located in the transition unit. The highest Cu contents are in pea (17.35 mg/kg FM), and the lowest in tomato (0.65 mg/kg FM) (Figure 5.5).

Zn: Zn contents range between 0.73-32.32 mg/kg FM. Some 3.2% of samples in the lacustrine unit exceed the standard value for Zn (20 mg/kg FM, GB13106-1991) in vegetables. The highest Zn contents are in pea (19.30 mg/kg FM), and lowest in tomato (2.69 mg/kg FM) (Figure 5.5).

For eaten parts, the highest TE contents are found in:

- Cauliflower for Pb.
- Lettuce and Chinese cabbage for Cd.
- Pea for Cu and Zn.

While, the lowest TE contents are found in tomato.

Chinese cabbage: Mean TE contents are 0.33 mg/kg FM (0.22-0.96 mg/kg FM) for Pb, 0.03 mg/kg FM (trace-0.13 mg/kg FM) for Cd, 0.97 mg/kg FM (0.23-5.19 mg/kg FM) for Cu and 3.45 mg/kg FM (1.74-14.16 mg/kg FM) for Zn (Annex 5.2).

Pb contents of 100% of cabbages located in the lacustrine and transition units are higher than the standard value (0.2 mg/kg FM). Some 11.1% of cabbages (3 samples from the lacustrine unit) present Cd contamination. Cu and Zn contents in cabbages are lower than standard values of Cu and Zn. TE contents for the eaten part of Chinese cabbage in the lacustrine unit are higher than in the transition unit (L>T) (Figure 5.6).

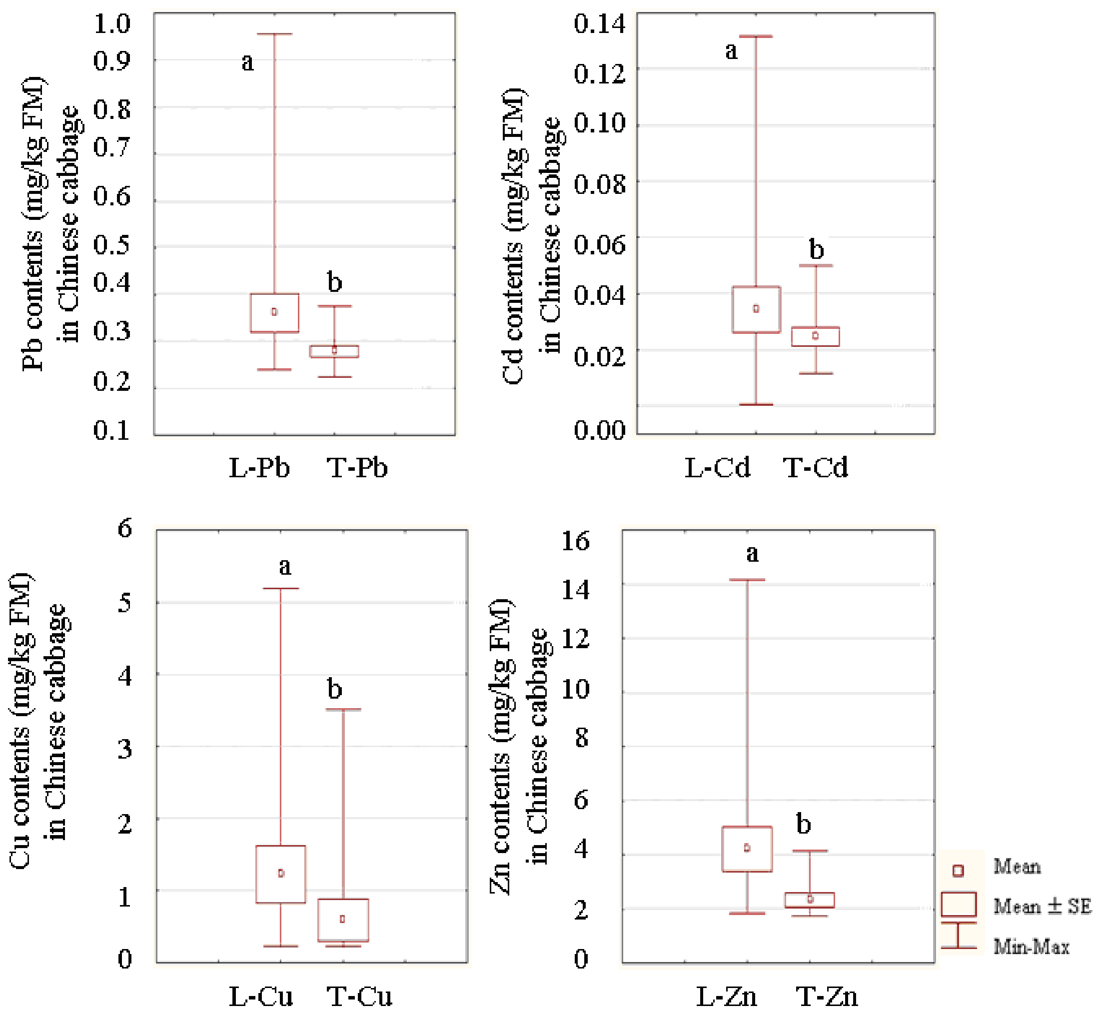


Figure 5.6: TE contents (mg/kg FM) in the eaten part of Chinese cabbage in the lacustrine and transition units

B: Non-consumed part

TE contents range between 0.02-5.28 mg/kg FM for Pb, trace-0.93 mg/kg FM for Cd, 1.44-38.46 mg/kg FM for Cu and 1.17-29.23 mg/kg FM for Zn (Table 5.4). Some 91.7% of samples for Pb and 83.3% for Cd exceed the standard values for vegetables, 22.2% for Cu and 19.4% for Zn. The contamination by Pb and Cd are very serious in the non-consumed part of vegetables (Table 5.4, Annex 5.3).

Table 5.4: TE contents in the non-consumed part of vegetables (mg/kg FM) (n=6)

Vegetables	Statistic	Pb	Cd	Cu	Zn
Celery	Mean	0.49	0.35	7.18	19.50
	Range	0.02 - 0.69	0.01 - 0.68	6.54 - 7.92	6.46 - 23.74
Chinese cabbage	Mean	0.44	0.15	3.76	4.72
	Range	0.29 - 1.00	0.11 - 0.30	1.44 - 6.99	1.78 - 12.07
Lettuce	Mean	1.06	0.06	10.29	7.51
	Range	0.18 - 2.20	Trace - 0.19	3.22 - 14.46	1.17 - 11.05
Radish	Mean	1.20	0.58	10.37	11.70
	Range	0.04 - 2.06	0.42 - 0.70	4.80 - 20.49	4.81 - 17.73
Pea	Mean	1.89	0.13	26.12	18.16
	Range	0.78 - 2.83	0.03 - 0.33	9.42 - 38.46	8.10 - 29.34
Tomato	Mean	4.05	0.49	4.35	11.41
	Range	2.68 - 5.28	0.12 - 0.93	2.46 - 5.20	10.29 - 12.82
Cauliflower	Mean	2.07	0.12	17.00	9.44
	Range	0.99 - 2.91	0.01 - 0.33	8.51 - 33.83	5.63 - 11.19

5.3.3. Relationships between soil and plant total trace element contents

When the whole of Chinese cabbage samples are analysed, there is no significant correlation between total Pb and Cu contents in soil and in the eaten part of Chinese cabbage. Cd and Zn contents in Chinese cabbage increase with Cd and Zn contents in soil, and significant positive linear relationships are observed (Cd: Y=0.42+0.88x, F=5.64, R^2=0.184, sig.f=0.026, n=21; Zn: Y=-66.01+0.94x, F=16.13, R^2=0.392, sig.f<0.001, n=21) (Figure 5.7). Even if significant, these correlations are weak. Available TE and TE sequential extraction fraction (SEF) in soil should better assess TE transfer from soil to plants.

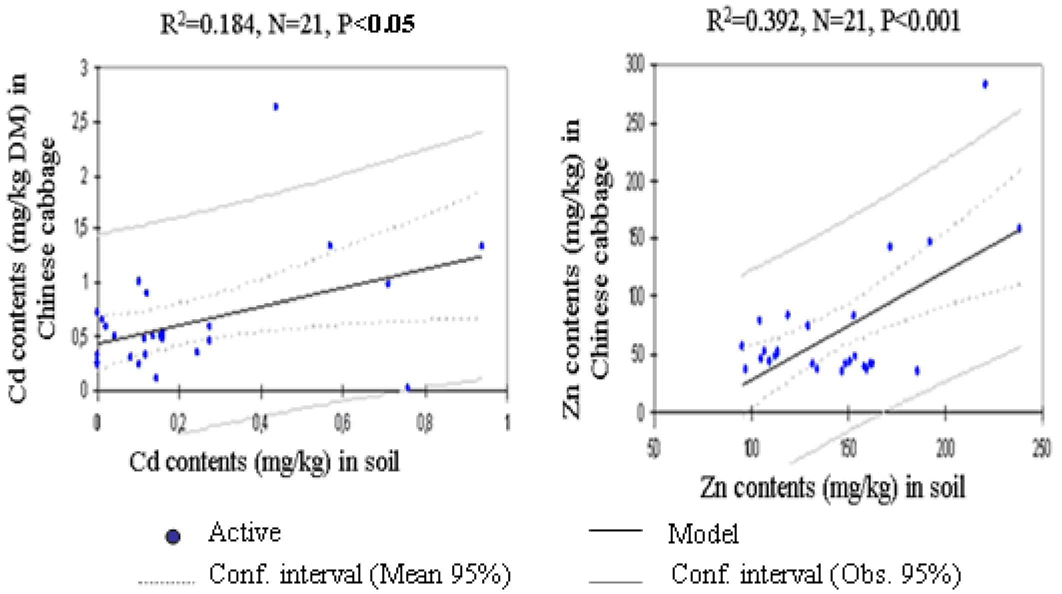


Figure 5.7: Relationships between contents of Cd and Zn in soil and in Chinese cabbage.

5.3.4. Soil available trace elements and trace element sequential extraction fractions

Some 21 topsoil samples of Chinese cabbage fields are chosen within the lacustrine and transition units to analyse available TE and TE contents of sequential extraction fractions (SEF: A, B and C) (Annex 5.2). A-fraction is acetic-acid extractable TE, which includes soluble, exchangeable and carbonate bound TE. B-fraction is hydroxylamine hydrochloride extractable TE, which includes Fe-Mn oxide bound and a part of organic bound TE. C-fraction is hydrogen peroxide and ammonium acetate extractable TE, which is partly organic bound TE.

A. Available contents of trace elements

The mean available TE contents are 7.4 for Pb, 0.19 for Cd, 16.9 for Cu, and 12.2 mg/kg for Zn (Table 5.5).

Table 5.5: Available TE contents (mg/kg) in soils for Chinese cabbage growing

Unit	Statistic	Pb	Cd	Cu	Zn	N
Lacustrine unit	Mean	9.3	0.21	14.3	15.3	11
	Range	6.2 - 16	0.11 - 0.56	8.1 - 20	6.5 - 43	
Transition unit	Mean	5.3	0.16	19.7	8.8	10
	Range	4.1 - 6.6	0.10 - 0.23	18 - 23	6.8 - 14	
All	Mean	7.4	0.19	16.9	12.2	21
	Range	4.1 - 16	0.10 - 0.56	8.1 - 23	6.5 - 43	

The mean available contents of Pb, Cd and Zn in the lacustrine unit are higher than in the transition unit (L>T). We observe high available Pb and Zn contents in certain places of the lacustrine unit including the highest Pb content (16 mg/kg). Distribution areas of high available Cd and Cu are found in both units. Nevertheless, the mean available Cu contents in the lacustrine unit are lower than in the transition unit (T>L) (Annex 5.2, Figure 5.8). Therefore, the available Pb, Cd and Zn contents are higher in the lacustrine unit than in the transition unit (L>T), and inversely for Cu (T>L).

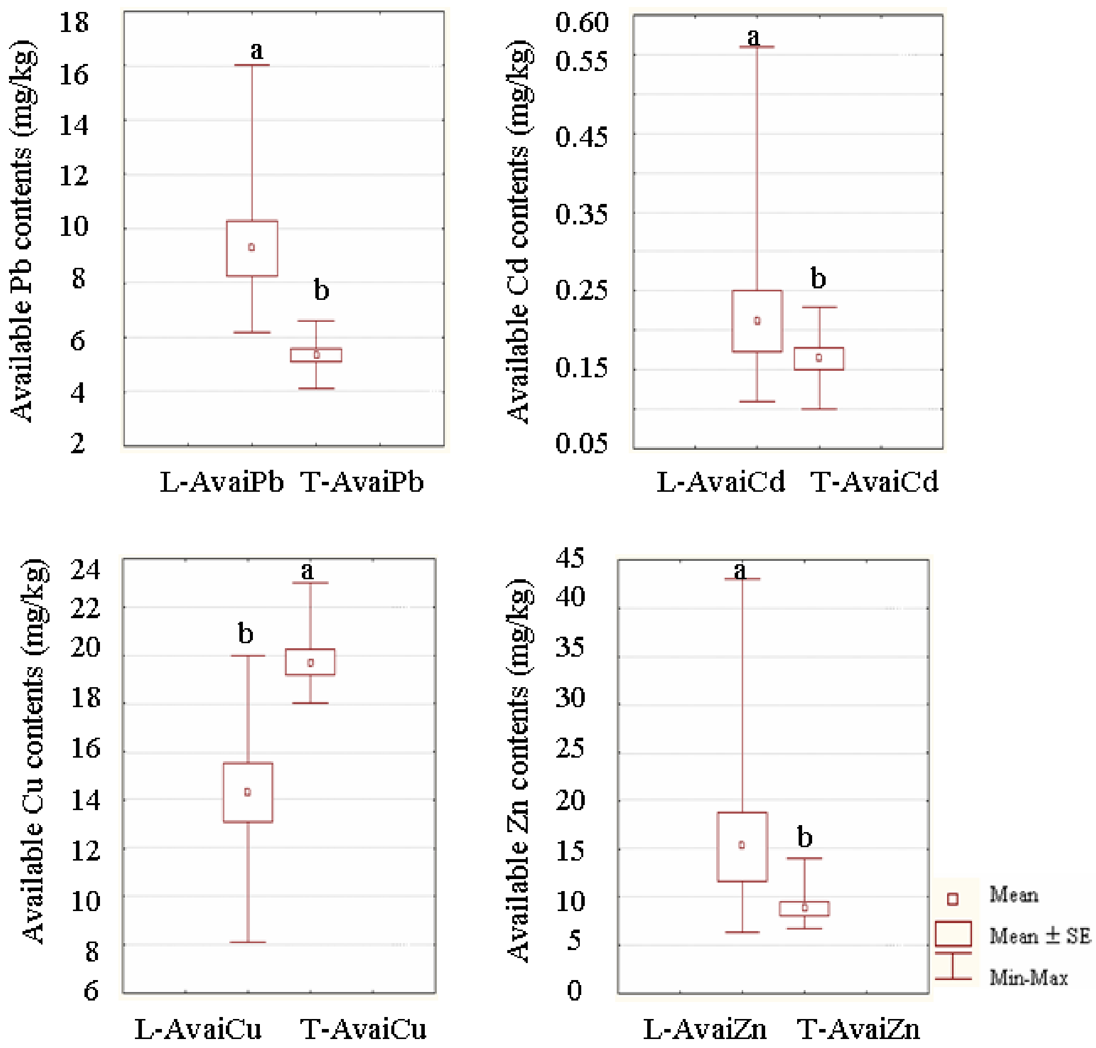


Figure 5.8: Available TE contents in topsoil in the lacustrine and transition units.

B. Trace element contents of sequential extraction fractions

Pb: The mean contents are 1.38 mg/kg for A, 6.53 mg/kg for B and 5.80 mg/kg for C fractions (Table 5.6, Annex 5.2), with the B-fraction higher than the C- and A-fractions (B>C>A) (Figure 5.9).

Table 5.6: SEF TE contents (mg/kg) in soil for Chinese cabbage growing

Unit	Statistic	Pb			Cd			Cu			Zn			N
		A	B	C	A	B	C	A	B	C	A	B	C	
L*	Mean	1.4	6.3	5.3	0.08	0.16	0.05	1.2	2.2	13.9	2.1	17.1	15.8	11
	Range	0.7 - 2.6	3.5 - 12.1	1.6 - 8.9	0.07 - 0.09	0.11 - 0.22	0.02 - 0.1	1.0 - 1.5	0.8 - 4.4	6.2 - 26.4	0.4 - 12	8.5 - 44	9.9 - 38.9	
T	Mean	1.4	6.8	6.3	0.05	0.11	0.04	1.3	7.2	23.4	1.6	15.8	24.4	10
	Range	0.7 - 2.9	4.2 - 10	4.6 - 11.3	0 - 0.07	0.08 - 0.16	0.01 - 0.08	1.0 - 1.5	5.5 - 9.5	0.4 -3 0.6	1.0 - 2.8	13.3 - 20	18.9 - 32	
All	Mean	1.34	6.5	5.8	0.06	0.13	0.05	1.3	4.6	18.4	1.9	16.5	19.9	21
	Range	0.7 - 2.9	3.5 - 12.1	1.6 - 11.3	0 - 0.09	0.08 - 0.22	0 - 0.10	1.0 - 1.5	0.8 - 9.5	0.4 - 30.6	0.4 - 12	8.5 - 44	9.9 - 38.9	

*L: lacustrine unit; T: transition unit.

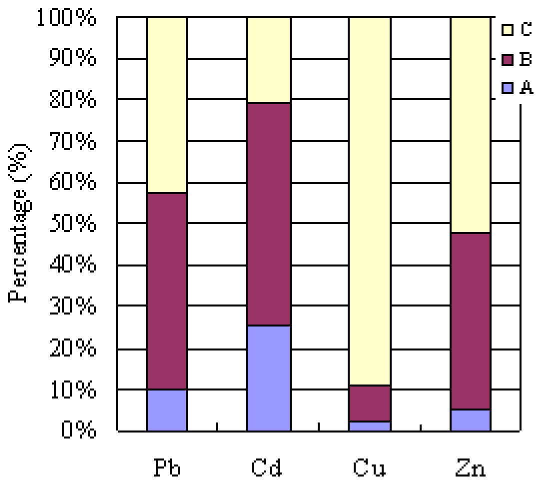


Figure 5.9: Percentage of TE contents of A, B, C fractions in soils.

The mean A-Pb contents in the lacustrine unit are close to that in the transition unit. The mean B-Pb contents in the lacustrine and transition units do not show significant differences. High C-Pb contents are found in both units (Figure 5.10). Thus, there is no significant difference between Pb fractions in both units.

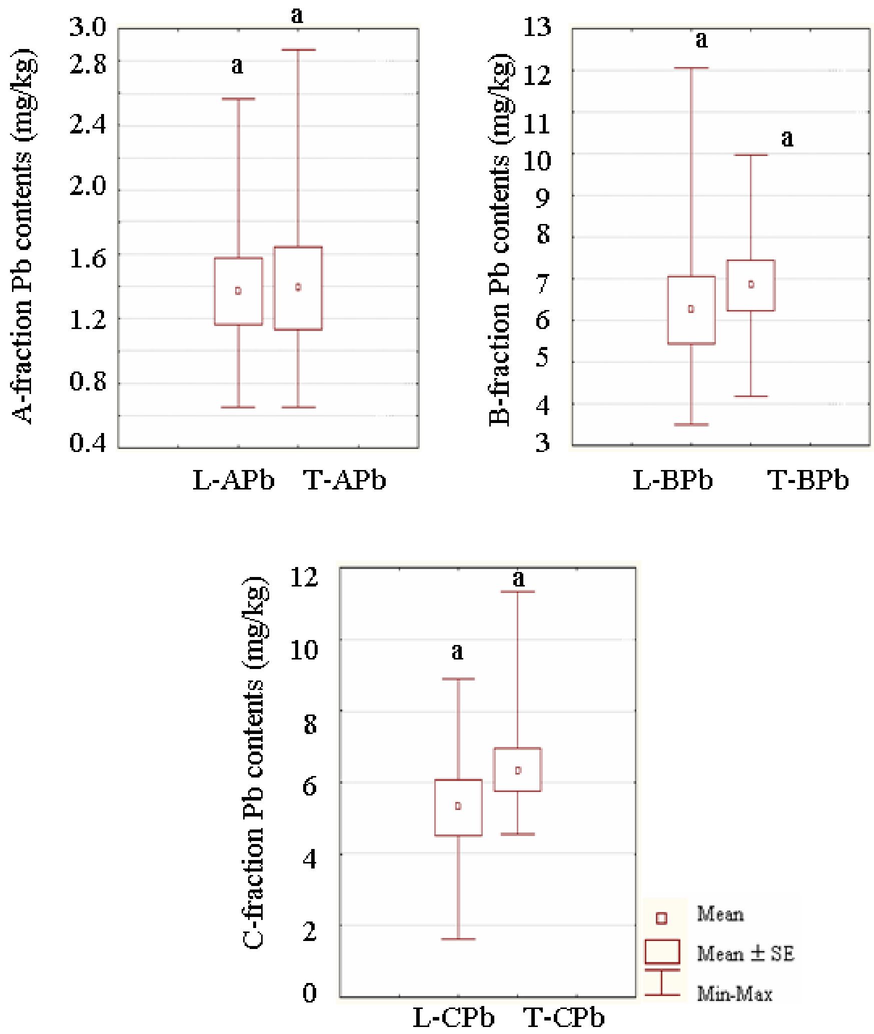


Figure 5.10: SEF contents of Pb in topsoil in the two units.

Cd: The mean contents are 0.06 mg/kg for A, 0.13 mg/kg for B and 0.045 mg/kg for C-fractions (Table 5.6, Annex 5.2). The highest content fraction is B-fraction, followed by A and C-fractions (B>A>C), which is suggested differences in bioavailability (Figure 5.9). Mean A and B-fraction contents in the lacustrine unit are higher than in the transition unit. High Cd contents of C-fraction are found in both units (Figure 5.11).

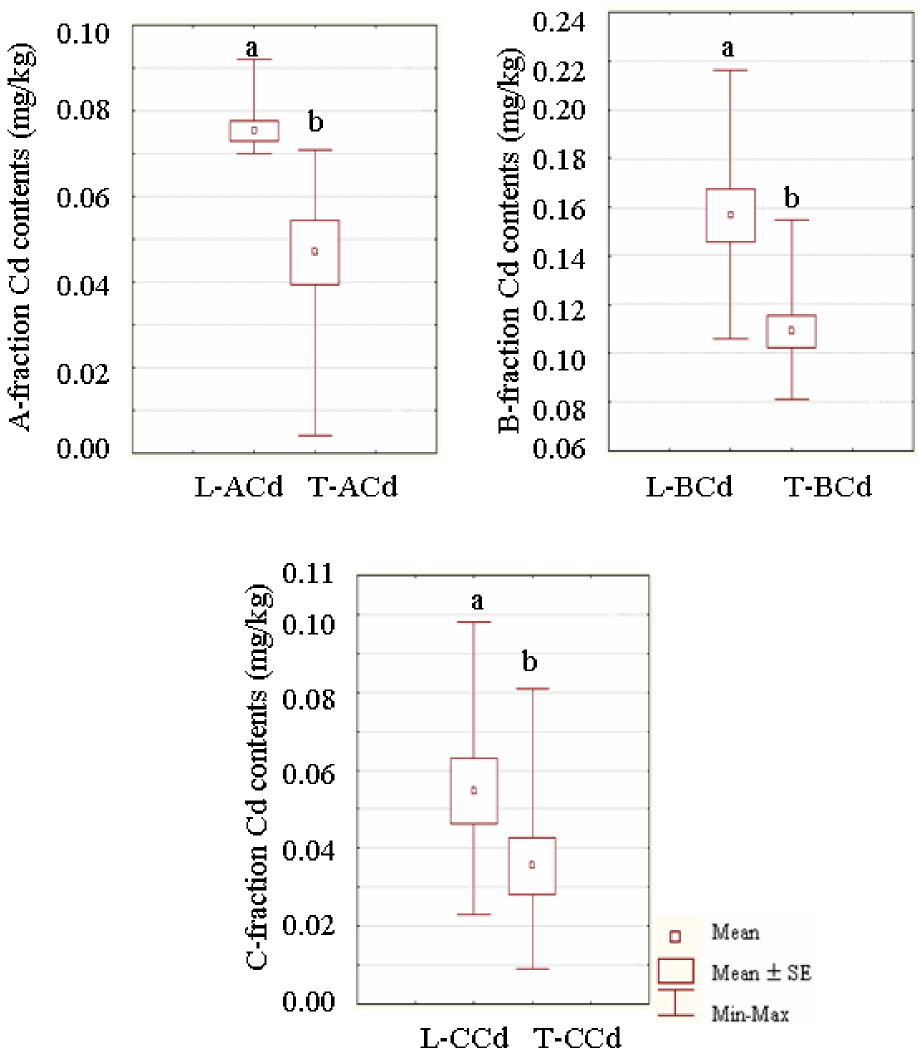


Figure 5.11: SEF contents of Cd in topsoil in the two units.

Cu: The mean contents are 1.25 mg/kg for A, 4.57 mg/kg for B and 18.4 mg/kg for C-fractions (Table 5.6). The highest Cu content part is C-fraction, followed by the B and A-fractions (C>B>A) (Figure 5.9). The SEF Cu contents in the transition unit are higher than in the lacustrine unit (Figure 5.12). High Cu contents of A and B-fractions are near Dianchi Lake, and high Cu contents in C fractions are found in both units.

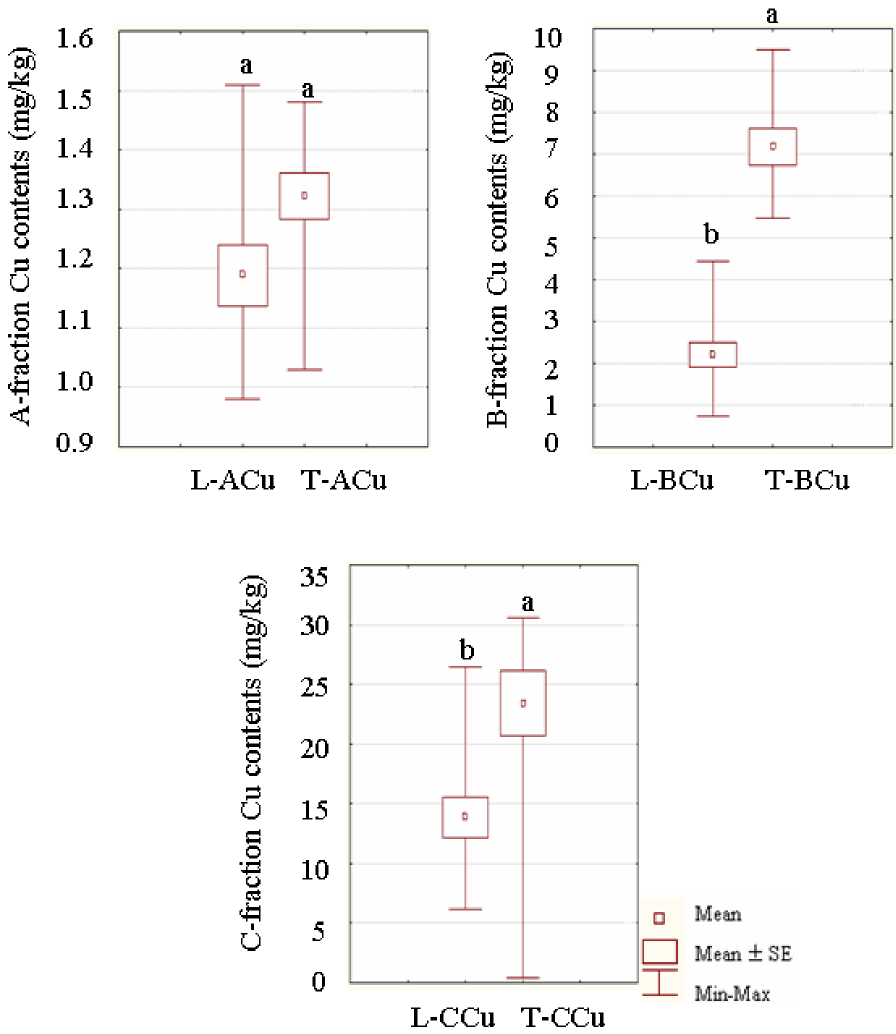


Figure 5.12: SEF contents of Cu in topsoil in the two units.

Zn: The mean Zn contents are 1.85 mg/kg for A, 16.49 mg/kg for B and 19.89 mg/kg for C-fractions (Table 5.6, Table 5.6). The highest Zn content part is C-fraction, followed by the B and A-fractions (C>B>A) (Figure 5.9). The mean A and B-fraction contents in the lacustrine unit are higher than in the transition unit. Mean C-fraction contents in the transition unit are higher than in the lacustrine unit, and high Zn contents of C-fraction are found in both units (Figure 5.13).

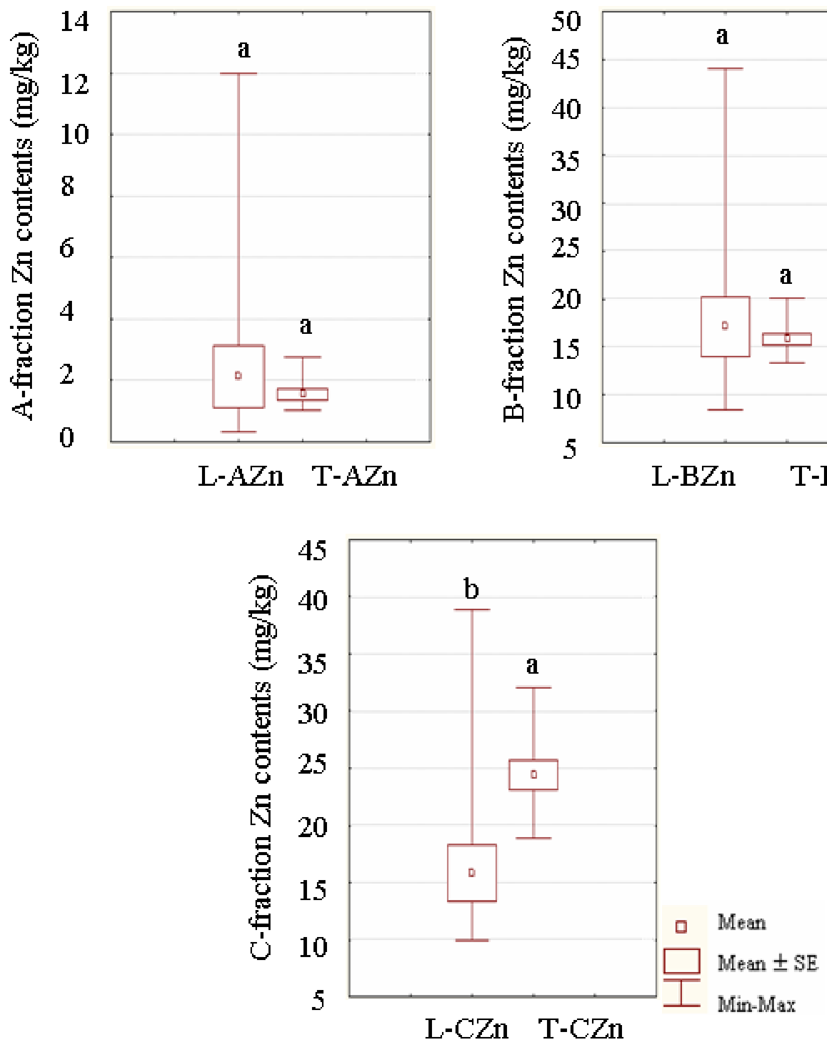


Figure 5.13: SEF contents of Zn in topsoil in the two units.

Therefore, the A-fraction TE contents are higher in the lacustrine unit than in the transition unit (L>T), except for Cu (T>L). High contents of A-fraction are found more often in the lacustrine unit. As for the available TE contents, anthropogenic activities are still continuing as a source of TE in topsoil. High B-fraction contents are observed in the transition unit and the high contents of C-fraction are found in both units.

5.3.5. Relationships between available trace elements and trace element sequential extraction fractions in soil and trace element contents in the eaten part of Chinese cabbage

When relationships between available TE and SEF TE contents in soil and TE contents in Chinese cabbage are analysed, significant linear relationships are found.

Pb: Globally, a significant negative relationship between Pb in Chinese cabbage and B-fraction Pb contents in soil is observed. A similar relationship is observed in the lacustrine unit. But there is no significant relationship between Pb contents in Chinese cabbage and SEF Pb contents in soil in the transition unit (Table 5.7, Figure 5.14). It is suggested that the Fe-Mn oxide concretions in soil could trap Pb and reduce plant absorption.

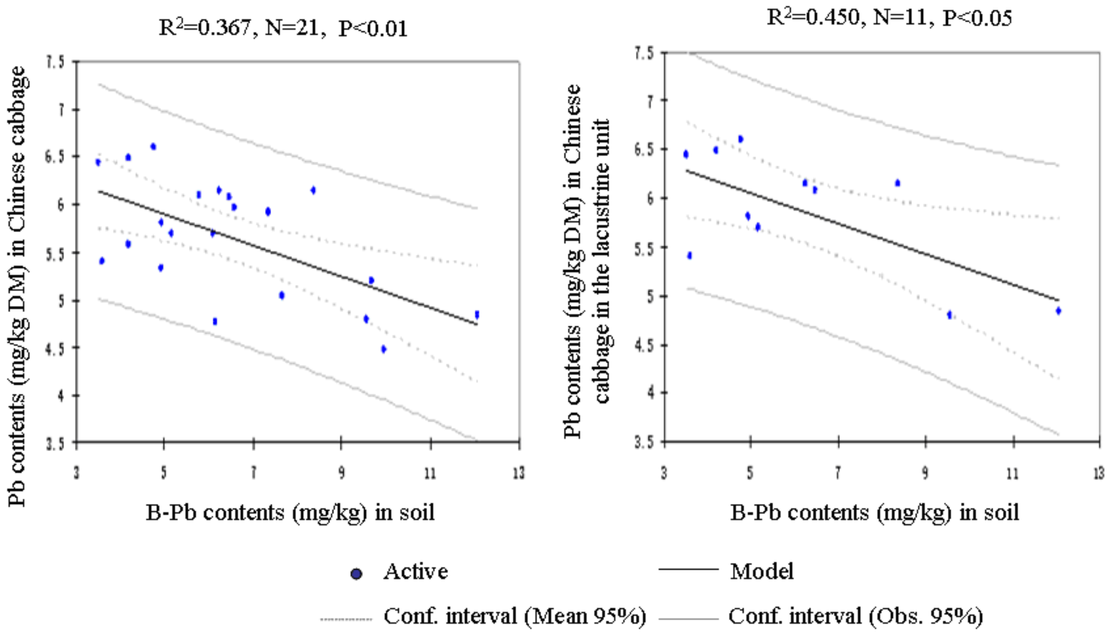


Figure 5.14: Relationships between Pb contents in Chinese cabbage and B-fraction Pb contents in soil.

Cd: There is a significant positive relationship between Cd contents in Chinese cabbage and available Cd contents in soil. In the lacustrine unit, the correlation between available Cd and vegetable Cd is also very strongly significant (Table 5.7, Figure 5.15, Annex 5.4). But, when the sample with the highest available Cd is not considered, the relationship is not significant. No significant relationship between Cd contents in Chinese cabbage and SEF Cd fractions in soil is observed.

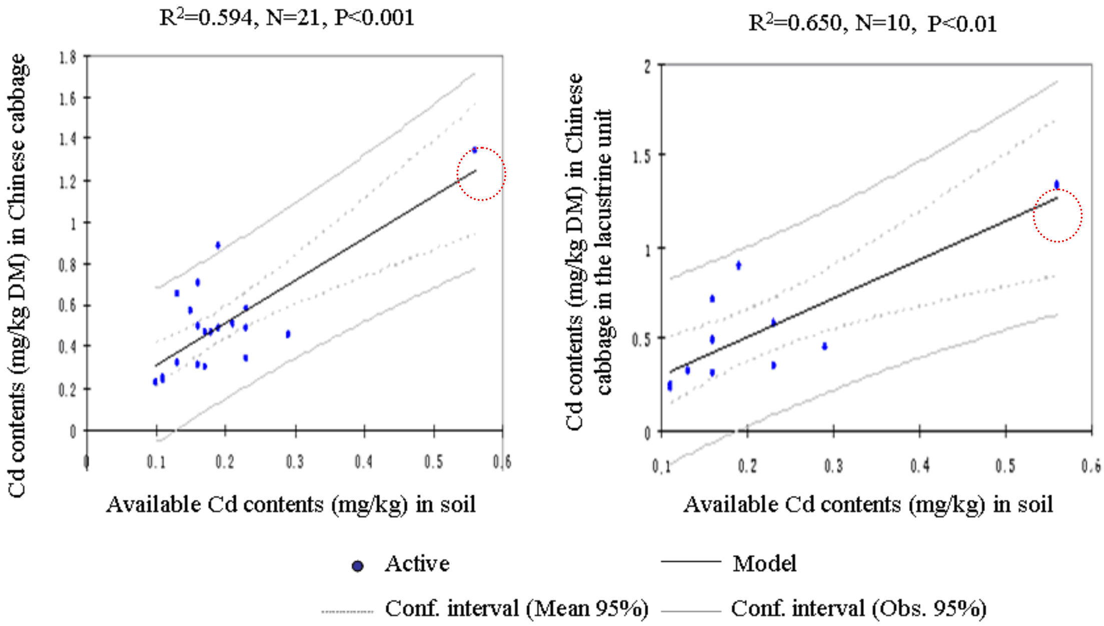


Figure 5.15: Relationships between Cd contents in Chinese cabbage and available Cd contents in soil.

Cu: Globally, no significant relationship between Cu content in Chinese cabbage and SEF Cu in soil is observed. There is a significant positive relationship between B-fraction contents in soils and Cu contents in Chinese cabbage in the lacustrine unit. A significant positive relationship between C-fraction and Cu in Chinese cabbage is also observed in the lacustrine unit, when a sample with high Cu content (7.7 mg/kg) is excluded (Table 5.7, Figure 5.16, Annex 5.4). No significant relationship in the transition unit is observed. It is suggested that B and C-fraction in soil could be absorbed by Chinese cabbage and thus become bioavailable.

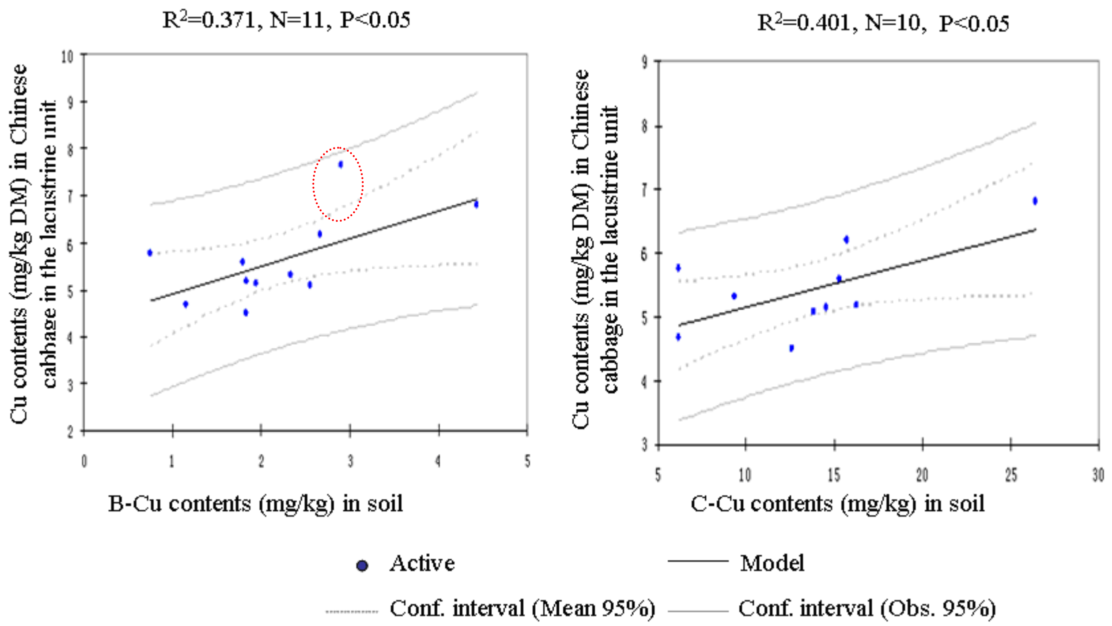


Figure 5.16: Relationships between Cu contents in Chinese cabbage and SEF Cu contents in the lacustrine unit.

Zn: Significant positive relationships between Zn content in Chinese cabbage and available Zn contents, A-fraction and B-fraction contents in soil are observed, but no significant relationship is observed when the highest Zn content (4.2 mg/kg) is excluded in Chinese cabbage. Similar relationships are observed in the lacustrine unit, besides a positive relationship between Zn contents in Chinese cabbage and C-fraction (Table 5.7, Figure 5.17, Figure 5.18, Annex 5.4). No significant relationship is observed in the transition unit. It is also suggested that B and C-fractions in soil could be absorbed by Chinese cabbage and thus become bioavailable.

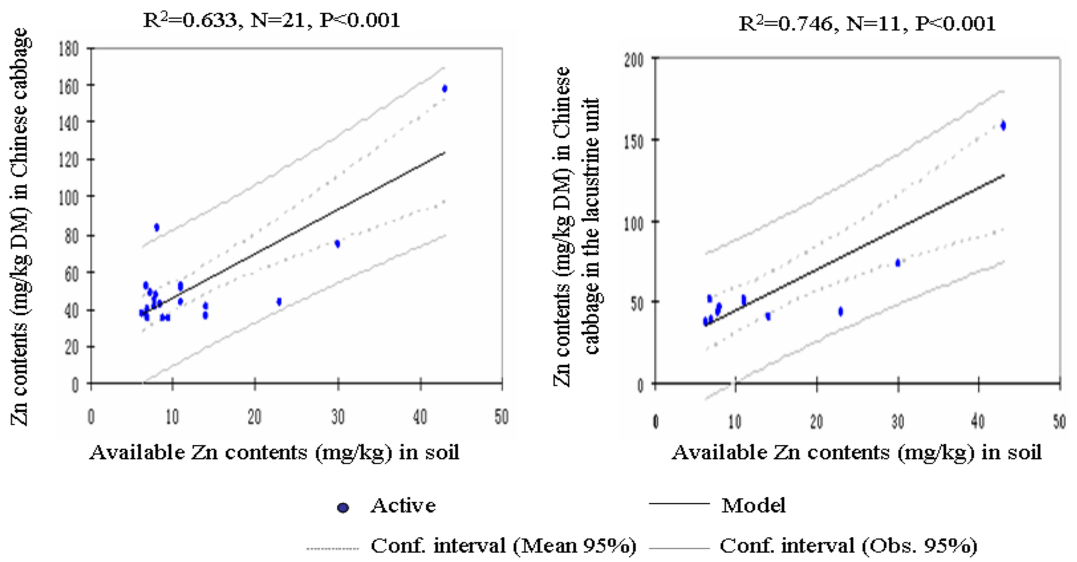


Figure 5.17: Relationships between Zn contents in Chinese cabbage and available Zn contents in soil.

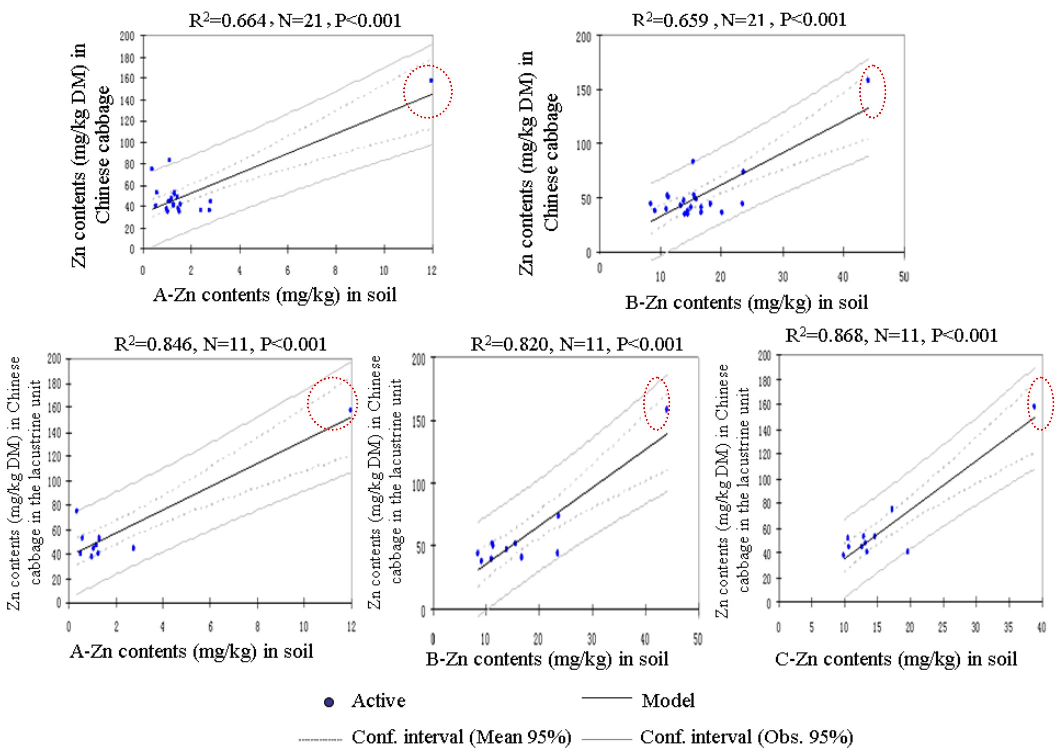


Figure 5.18: Relationships between Zn contents in Chinese cabbage and SEF Zn contents in soil.

Table 5.7: Relationships between TE fractions contents in soil and TE contents in Chinese cabbage

TE (Y)	Unit	Fraction in soil (X)	Equation	F	R^2	Sig.f	N
Pb	All*	B fraction	Y=6.70-0.16X	11.027	0.367	0.004	21
	Lacustrine	B fraction	Y=6.83-0.16X	7.372	0.450	0.024	11
Cd	All	Available	Y=0.11+2.04X	27.744	0.594	<0.001	21
	Lacustrine	Available	Y=0.093+2.10X	16.726	0.650	0.003	10
Cu	Lacustrine	B fraction	Y=4.32+0.59X	5.302	0.371	0.047	11
		C fraction	Y=4.39+0.075X	5.326	0.401	0.049	10
Zn	All	Available	Y=22.23+2.37X	32.819	0.633	<0.001	21
		A fraction	Y=34.08+9.24X	37.477	0.664	<0.001	21
		B fraction	Y=2.21+2.79X	36.673	0.659	<0.001	21
	Lacustrine	Available	Y=19.84+2.50X	26.399	0.746	<0.001	11
		A fraction	Y=37.87+9.52X	49.418	0.846	<0.001	11
		B fraction	Y=6.18+3.03	41.139	0.820	<0.001	11
		C fraction	Y=-3.88+3.92X	59.230	0.868	<0.001	11

* All Chinese cabbage samples in the lacustrine and transition units.

These results show that available and B-fraction TE contents in soil present the most satisfactory relationships with plant contents. However, relationships between available TE and total TE are weak for Pb and Zn, if high results are excluded (Figure 5.19, Annex 5.4).

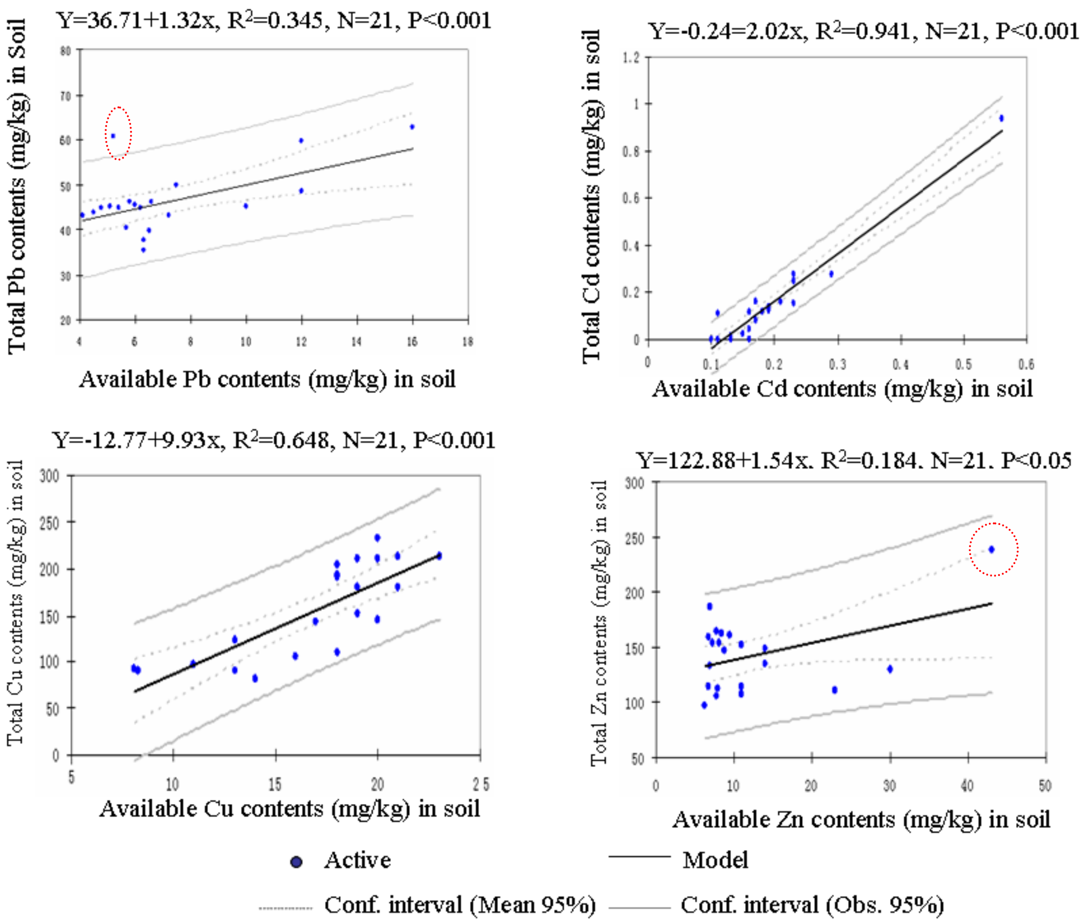


Figure 5.19: Relationships between total and available TE contents in soil.

Plants only can absorb the bioavailable fractions of TE in soils. The correlation analyses show that different fractions of TE have different contributions to TE contents in Chinese cabbage. These observations underline the fact that it is very important to take into account total, available and SEF contents of TE in soil to understand the accumulation of TE in vegetables.

The available and SEF contents of TE in soils could influence TE contents in vegetables, especially in Chinese cabbage. Pb contents in Chinese cabbage decrease with B-fraction Pb contents in soil. Cd and Zn contents in Chinese cabbage increase with available contents of Cd and Zn in soil. The B and C-fractions seem to increase the absorption of Cu and Zn by vegetables. Bioavailability of TE of course could be influenced by soil characteristics, such as pH, organic matter content and soil texture.

5.4. DISCUSSION

5.4.1. Relationship between soil assessment and plant assessment

Trace element contents in vegetables and plant assessment

There are some differences of TE contents among vegetables. The highest TE content in cauliflower is Pb, Cd in lettuce and Chinese cabbage, Cu and Zn in pea. But the lowest Pb, Cd, Cu and Zn contents are in tomato. Different species of vegetables show different TE accumulation ability. In this investigation, leaf vegetables easily absorb Cd, and legumes accumulate Cu and Zn. The order of accumulation ability depends on species and varieties. Moreover, Pb, Cd, Cu and Zn contents in Chinese cabbage samples seem to be different from one land unit to another. Samples with Pb, Cd and Zn contents in Chinese cabbage exceed of standard value are in the lacustrine unit, which is consistent with high soil available Pb, Cd and Zn contents in the lacustrine unit. Moreover, samples with Cu contents exceeding standard values are located in the transition unit, which is consistent with high soil available Cu contents in this unit.

In order to understand the effect of agricultural practises on TE accumulation in the research area of Chenggong County, questionnaires were distributed to farmers (21 families) who planted Chinese cabbage in the 21 plots in the research area in 2006. The results show that the cultivated area for a family is limited (0.03-0.45 ha), most (52.4%) of families cultivated area between 0.05-0.08 ha. Rotations include 3-4 cultures each year, mainly: Chinese cabbage-celery-cabbage-spinach, Chinese cabbage-cabbage-celery-flowers, Chinese cabbage-celery-Chinese cabbage-celery. The yields of Chinese cabbage range between 30,000-112,500 kg/ha, most (76.2%) of them are >45,000 kg/ha. The irrigation water is from Dianchi Lake in the lacustrine unit and from wells in the transition unit. More attention should be paid to the quality of irrigation water.

Due to this intensive system, pesticides and fertilizers are important. Pesticides are sprayed 2-3 times per culture. Application rate of compound fertilizers (mainly 15-15-15) are 750-1,125 kg/ha. The main single inorganic fertilizers are urea and super-phosphate. Organic fertilizers are mainly cow manure and pig manure, at a rate ranging between 11,250-82,500 kg/ha, most (57.1%) of them being 33,750-60,000 kg/ha (Table 5.8). From questionnaire answers, it seems that the numbers of pesticide application and fertilizer rate per culture in the lacustrine unit are higher than in the transition unit. Anthropogenic activities should be relative to high TE contents, especially in the lacustrine unit.

Table 5.8: Agricultural practice information for planting Chinese cabbage in Chenggong County

Unit	No.	Crop rotation system (times/year)	Yield (kg/ha)		Irrigation water	Pesticides (times/growing season)	Fertilizers (kg/ha)		
							Inorganic		Organic
			Chinese cabbage	Intercropping vegetable			Compound	Single	
L*	30	4	63,750	48,750	Dianchi Lake	4 - 5	750	525 (urea)	22,500
	33	4	46,500	39,000	Dianchi Lake	1	750	300 (urea)	11,250
	34	3 - 4	63,000	68,000	Well	2 - 3	750	1,200 (super-phosphate)	37,500 (cow manure)
	35	3 - 4	63,000	69,000	Dianchi Lake	2 - 3	750	1,200 (super-phosphate)	15,000 (cow manure)
	36	4	63,000	49,500	Dianchi Lake	2 - 3	1125	No	15,000 (cow manure)
	37	4 - 5	112,500	33,750	Dianchi Lake	1	1125	2,250 (super-phosphate)	18,750 (cow manure)
	38	4	63,750	48,750	Dianchi Lake	3 - 4	750	No	15,000
	39	4	63,000	49,500	Dianchi Lake	1	750	No	11,250
	42	3 - 4	75,000	75,000	Well	2 - 3	525	375 (urea)	33,750
	43	4	56,250	60,000	Dianchi Lake	1	1850	No	82,500
	44	4	37,500	30,000	Dianchi Lake	1		375 (urea)	56,250
T	91	4	37,500	30,000	Well	1	no	975 (ammonium carbonate)	22,500
	92	4	42,750	63,000	Well	1	375	975 (potassium nitrate)/ 150 (urea)	37,500
	93	4	56,250	41,250	Well	2	525	525 (super-phosphate) /975 (urea)	41,250 (cow manure)
	94	4	45,000	37,500	Well	2	375	No	26,250
	95	4	30,000	26,250	Well	2	600	No	33,750
	96	4	37,500	32,250	Well	1	no	750 (urea)/ 750 (potassium sulphate)	65,625
	97	3	75,000	56,250	Well	1	750	525 (urea)	57,000
	98	3 - 4	75,000	750,000	Well	1	750	No	52,500
	99	3	56,250	37,500	Well	2	750	No	48,750 (cow manure)
	112	3	45,000	30,000	well	1	no	225 (urea)	56,250 (cow manure)

*L: lacustrine unit; T: transition unit.

For the non-consumed part of vegetables, Pb, Cd, Cu and Zn contents are higher than in eaten parts. In 91.7% of non-consumed part, Pb contents exceed standard value for vegetables, and 83.3% for Cd, 22.2% for Cu and 19.4% for Zn. The contamination by Cd and Pb are very serious in the non-consumed part. In Chenggong County, the non-consumed part is used to make fertilizers or just piled beside the plots or even are used for animal feeding, which should result in TE using recycled back to the soil. More attention should be paid to the reuse of the non-consumed part of vegetables.

<u>Relationship between soil assessment and plant assessment</u>

Pb: Pb contamination in all vegetable samples and Chinese cabbage samples is the most serious. However, proportion of samples which are at Pb suitable (S) level for soil is not consistent with Pb suitable level in vegetables (Table 5.9, Figure 5.20). So maybe the Pb in vegetables is not just absorbed from the soil. Pb in vegetables may be come partly from the air, because the road network and traffic are really important in this area.

Table 5.9: Percentage of samples with TE contents exceeding standard values

Percentage (%)	Pb	Cd	Cu	Zn
Soil for vegetables growing	60.3 (38/63)*	58.7 (37/63)	73.0 (46/63)	9.5 (6/63)
Vegetables	95.2 (60/63)	9.3 (8/63)	19.1 (12/63)	3.2 (2/63)
Soil for Chinese cabbage growing	11.1 (3/21)	4.8 (1/21)	100 (21/21)	4.8 (1/21)
Chinese cabbage	100 (21/21)	11.1 (3/21)	0 (0/21)	0 (0/21)

*(Sample numbers exceeding standard value/total sample numbers).

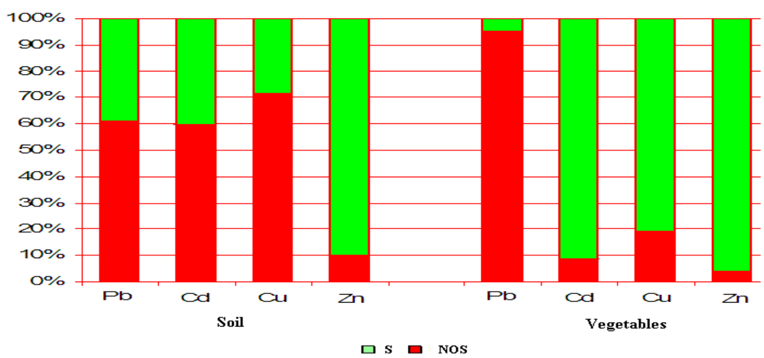


Figure 5.20: Assessment of soils and the eaten part of vegetables in the research area, according to Chinese standard values (Proportions of samples which are at suitable (S) and not suitable (NOS) levels for food production (soil) and consumption (plants)).

Cd: A positive relationship is observed between Cd contents in Chinese cabbage and in soil. However, some 58.7% of samples exceed the standard value (0.3 mg/kg, pH<7.5) of soil for vegetable production, which is inconsistent with 9.3% of vegetables not suitable with Cd (Figure 5.20). That is suggested that soil Cd present a high potential risk of transfer to vegetables, which is consistent with high available Cd and A-fraction contents in soil.

Cu: Soil Cu contamination is medium and 19.1% of vegetable samples are higher than the standard value for Cu. Some 100% of soils with Chinese cabbage samples exceed the standard value for Cu in soil for vegetable production, but no sample of Chinese cabbage is higher than standard values for Cu. That means that soil Cu would be the potential source to transfer from soils to vegetables, though no significant relationship between total Cu contents in soil and Cd contents in vegetables exists. The proportion of soil samples which are at unsuitable level with Cu (NOS) is high (Table 5.9, Figure 5.20). The whole of soils corresponding to vegetable production presents contamination in Cu with a high risk of transfer towards vegetables.

Zn: Positive relationships are observed between Zn contents in vegetables, in Chinese cabbage and in soils. Assessments of Zn in soil and in vegetables both indicate low contaminated level, meaning that the assessment of Zn in soil and in vegetables is consistent in the research area.

Assessment methods based on Chinese national thresholds

The integrative index of contamination (P) of TE is >3, due to high Cd and Cu contents, which indicate high TE contaminated level. P value is very high, because special samples with high Pi of Cd and Cu led to Pi_{max} being extremely high in the formulation. Pi_{max} is >3 here, in which the formulation Pi = 3 + (Ci-Xh)/Xh should be used instead of formulation Pi = 3 + (Ci-Xh)/(Xh-Xm) (Section 2.5.3). It is suggested that the calculated formulation of signal index and integrative index of contamination should be improved to avoid the effect of extreme samples.

Water content of vegetable also will affect TE contents in fresh materials and vegetable assessment. For example, the lowest TE contents in tomato link to high water content in tomato fruit. Therefore, it should be better to express TE threshold values in dry materials. The percentage of Pb, Cd and Cu at unsuitable level for soils and vegetables are not consistent. The reason may be relative to standard values for soils and vegetables. Pb standard values in soil for vegetable growth (50 mg/kg) may be too high for soil of Chinese cabbage production; or too low for Chinese cabbage (0.2 mg/kg FM). On the contrary, Cd (0.3 mg/kg) and Cu (50 mg/kg) standard values in soil for vegetable growth may be too low for soil of Chinese cabbage production or too high (Cd 0.05 mg/kg FM; Cu 10 mg/kg FM) for Chinese cabbage. Therefore, modification of standard values is necessary for Chinese cabbage.

5.4.2. Bioavailability of trace elements from soils to vegetables

Available trace elements and trace element contents of sequential extraction fractions in soils

TE contents in sequential extraction fractions show:

- B-fraction contents are higher than C and A-fractions (B>C>A) for Pb and Cd.
- C-fraction contents are higher than B and A-fractions (C>B>A) for Cu and Zn.

C-Pb contents excluding the highest (11.3 mg/kg) have positive linear relationship with SOC (Annex 5.5). It is suggested that organic fertilizers should enhance C-Pb contents. There is no significant relationship between C-Cd, -Cu and -Zn contents and SOC. That could be due to the high SOC and application rate of organic fertilizers in the research area.

For geomorphological units, available TE and SEF TE contents show:

- Available TE and A-fraction TE contents are higher in the lacustrine unit than in the transition unit (L>T), except for A-Cu (T>L).
- C and B-fraction TE contents are higher in the transition unit than in the lacustrine unit (T>L).

<u>Relationships between available trace elements and trace element contents of sequential extraction fractions in soil and trace element contents in vegetables</u>

Pb: A significant negative relationship is observed between Pb in Chinese cabbage and B-Pb in soil. Fe-Mn oxides could trap Pb in soil and influence Pb bioavailability. C-Pb seems to play the same role to trap Pb in soil according to PCA (Annex 5.6).

Cd: A significant relationship is observed between Cd contents in Chinese cabbage and available Cd contents in soil. It is suggested that Cd is easily transferred and Cd contents in Chinese cabbage is influenced by available Cd. Available Cd is well correlated with SEF Cd, according to PCA (Annex 5.6).

Cu: According to the national standards for soil quality, the whole of soil for Chinese cabbage growing presents contamination in Cu with a considerable risk of transfer towards the plants. Available Cu, B and C-Cu contents are in the same group according to PCA (Annex 5.6).

Significantly positive relationships are observed between Cu contents in Chinese cabbage and B and C-Cu in soils in the lacustrine unit. That should be related to the soluble organic matter increasing the mobility and biological activity of TE, for example fulvic acid. B and C-Cu in soil should be taken into account as a potential source of Cu.

Zn: Significant positive linear relationships are observed between Zn contents in Chinese cabbage and available and SEF Zn contents in soil. Available Zn, and B-Zn are in the same group according to PCA (Annex 5.6). It is suggested that TE contents in Chinese cabbage are easily influenced by Zn contents in soil, and could be influenced by human activities.

The total, available and SEF TE contents in soils could influence TE contents in vegetables, especially in Chinese cabbage, as follows:

- Pb contents in Chinese cabbage decrease as B-Pb increases.
- Cd contents in Chinese cabbage increase with soil available Cd increase.
- B and C-Cu seem to increase Cu absorption by vegetables, especially in the lacustrine unit.
- Zn contents in Chinese cabbage increase with increasing total, available and SEF Zn contents in soils.

Moreover, Pb, Cd, Cu and Zn contents in Chinese cabbages seem to be different from one land unit to another. The cabbages in the lacustrine unit absorb more TE than those located in the transition unit, due to higher available and A-fraction TE contents. In order to assess soil suitability, available and SEF TE contents better indicate the TE potential risk for vegetables. Different soil TE fractions could be suggested (√) for soil assessment indicators, according to their relationships with TE contents in Chinese cabbage (Table 5.10).

Table 5.10: Suggested indicators for soil assessment for Chinese cabbage production

Indicator	Pb	Cd	Cu	Zn
Available		√		√
A-fraction				√
B-fraction	√		√	√
C-fraction			√	

Although significant relationships between available and SEF TE contents in soil and TE contents in Chinese cabbage exist, estimating TE standard values cannot be suggested using our data. On the one hand, TE contents in Chinese cabbage exceed standard value for Pb and all are below standard values for Cu and Zn. On the other hand, the objectives of this research are not to establish standard values. Thus, it is necessary to make continuous research and obtain new data sets to establish standard values and to assess their relations with soil characteristics.

5.5. CONCLUSIONS

Soil assessment: Total TE mean contents in topsoil are 2-7 times of TE contents in world soils and higher than in Kunming soils.

The Pi of Pb, Zn and Cd are <2, indicating low contaminated level, and it is similar in the three units. Pi of Cu >2 indicates medium contaminated level for all soil samples and <2 indicates low contaminated level in soil corresponding to vegetable samples. Some samples with high Pi of Cd and Cu are observed, and found in the three units. Pi gradient of Cd and Cu is mountain unit>transition unit>lacustrine unit (M>T>L). Meanwhile, the integrative index of contamination (P) of TE is >3, indicating high contaminated levels due to high Pi of Cd and Cu.

Trace element contents in vegetables and plant assessment: In 95.2% of vegetable samples, Pb contents in the eaten part exceed the standard value for vegetables. In 9.5, 19.1 and 3.2%, respectively, of vegetable samples, Cd, Cu and Zn contents of eaten part exceed standard values. Pb contamination in vegetables and Chinese cabbage is the most serious. The highest contents are observed for Pb in cauliflower, Cd in lettuce and Chinese cabbage and Cu and Zn in pea. But the lowest contents of Pb, Cd, Cu and Zn all are in tomato. Mean TE contents in Chinese cabbage are 0.33 mg/kg FM for Pb, 0.02 mg/kg FM for Cd, 0.97 mg/kg FM for Cu and 3.45 mg/kg FM for Zn.

Pb, Cd, Cu and Zn contents in the non-consumed part of vegetables are more than in eaten part. For the non-consumed part of vegetables, 91.7% for Pb, 83.3% for Cd, 22.2% for Cu and 19.4% for Zn exceed the standard values for vegetables. The contamination of Cd and Pb are very serious in the non-consumed part of vegetables.

Trace element transfer from soils to vegetables:

- The available TE contents are 7.4 for Pb, 0.19 for Cd, 16.9 for Cu and 12.2 mg/kg for Zn.
- A-fraction TE contents are 1.38 for Pb, 0.06 for Cd, 1.25 for Cu and 1.85 mg/kg for Zn.
- B-fraction TE contents are 6.53 for Pb, 0.13 for Cd, 4.57 for Cu and 16.49 mg/kg for Zn.
- C-fraction TE contents are 5.80 for Pb, 0.045 for Cd, 18.4 for Cu and 19.89 mg/kg for Zn.

For SEF TE contents, B-fraction TE contents are higher than C and A-fraction TE contents (B>C>A) for Pb and Cd, and C-fraction TE contents are higher than B and A-fraction TE contents (C>B>A) for Cu and Zn. Available and A-fraction TE contents in the lacustrine unit are higher than in the transition unit (L>T). Pb contents in Chinese cabbage decrease with B-Pb increase. Cd contents in Chinese cabbage increase with available Cd increase. Increased B and C-Cu seem to increase Cu absorption by vegetables, especially in the lacustrine unit. Zn contents in Chinese cabbage increase with total, available and SEF contents of Zn in soil.

VI: EXPERIMENTS TO LIMIT TRACE ELEMENT TRANSFER FROM SOILS TO PLANTS

6.1. INTRODUCTION

With the rapid development of the economy and human activities, soil TE contamination is becoming more serious in periurban areas. Strategies to control the mobility of soil TE *in situ* should be applied considering the precious soil resources (Dermatas & Meng XG, 1996; Alpaslan & Yukselen, 2002). Agronomic practices for controlling mobility of TE have been described in Section 2.6.

In order to decrease TE contents in vegetables produced on soils contaminated by TE in the intensive periurban area in Chenggong County, field experiments were conducted in lacustrine, transition and mountain units. Pot experiments were conducted in YAU with the same soil as field experiments. Aims are to evaluate:

1) Effects of lime and pig manure on TE mobility.

2) Growth of Chinese cabbage amended with lime and pig manure.

Possible ways will be investigated to decrease TE in Chinese cabbage to safe contents.

6.2. MATERIALS AND METHODS

6.2.1. Chinese cabbage and land requirements

Chinese cabbage (*Brassica campestris subspecies pekinensis* (Lour) Olssom, Brassicaceae), presents four variants: Chinese cabbage spreading leaves (A) (*var. dissoluta)*, Chinese cabbage semi-wrapping leaves (B) (*var. infarota* Li), Chinese cabbage with white leaves inside (C) (*var .laxa* Tsen et Lee) and Chinese cabbage wrapping leaves (D) (*var. cephalata* Tsen et Lee) (Liu Y.S., 1998) (Figure 6.1).

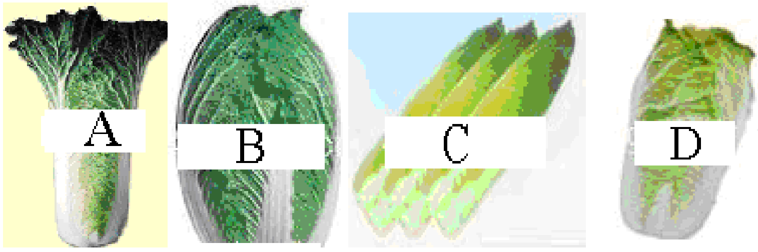


Figure 6.1: Variants of Chinese cabbage.

Vegetables are important in China, and they form a major income for many farmers. The vegetable area represented 12% of crop area in China in 2003 (Figure 6.2). Chinese cabbage is called the "national vegetable" and is one of the favourite vegetables in China. Some 4% of Chinese cabbage total area was planted in Yunnan Province in 2003, whilst the main plant areas were in southern and central China.

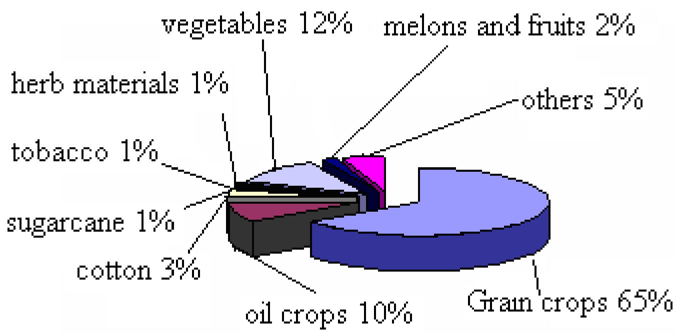


Figure 6.2: Percentage of area of main crops in China in 2003

(Source: Zhao Q.G., *et al.*, 2006).

Chinese cabbage has two growth stages: vegetative and reproductive. The growing period is 70-90 days (sometimes 100 days). The factors influencing organoleptic qualities of Chinese cabbage include texture and nutrient contents. Usually, the water content in Chinese cabbage is 93-95.7%. Some 19-23.2% of dry materials are crude protein, 2.1-3.1% being total sugar, and 1.8-2.8% being reducing sugar. Vitamin C contents are 15.2-25.4 mg/100g (Liu Y.S., 1998).

Growth of Chinese cabbage requires specific conditions of soil and climate. Chinese cabbage is planted in an area with temperature between 7-25 ^{o}C, lasting 70-80 days. The most suitable soils for Chinese cabbage are loam or light loam with sand/clay ratio of 2:3, and with pH ranging between 6.5-7.0, and the ideal content of physical sand (>0.01 mm) ranges between 76-78% and physical clay (<0.01 mm) ranges between 22-24%. The root system of Chinese cabbage is shallow and grows fast, so it is important to keep the soil loose and fertile. Total N, P_2O_5 and K_2O quantities required for the production of 1000 kg FM Chinese cabbage are 1.8-2.6 kg, 0.8-1.2 kg and 3.2-3.7 kg, respectively. Ideal ratio of N: P_2O_5: K_2O is 1:0.5:2. It is usually planted in Autumn. The suitable period to sow is from the middle of August to October, and to harvest in November to December in Kunming Prefecture. The width of inter-rows is 50-65 cm and spacing inter-plants is 35-50 cm. Ideal density of Chinese cabbage is 30,000-37,500 per ha (Liu Y.S., 1998).

More attention should be paid to the chemical contents of Chinese cabbage, due to its high ability to accumulate harmful substances. The quality of Chinese cabbage depends on environmental quality, soil characteristics and cultivars. TE contents in Chinese cabbage are becoming an increasingly serious barrier for improving quality and export. Chinese cabbage is one of the highest TE accumulative vegetables, while intraspecific differences in TE accumulation exist. Dai H.L., *et al.* (2007) reported the Zn accumulation of four Chinese cabbage cultivars. Accumulation and transfer of Zn in Fengkang 78 and Fengyuan Gaokang 2 cultivars are higher than in the other two, i.e. Fengkang 80 and Fengkang 90. The accumulation of TE in Chinese cabbage is influenced by soil types, organic matter content and pH. In general, it is important to improve Chinese cabbage quality and decrease TE contents in Chinese cabbage for vegetable production, export, economic income and human health.

6.2.2. Lime and its application

Lime is one of several alkaline amendments to increase soil pH of acid soil and to decrease TE mobility and leaching ability. The mechanism for pH influencing availability of TE has been described in Section 2.6. Lime includes limestone ($CaCO_3$), quick lime (CaO) and hydrated lime ($Ca(OH)_2$). Quick lime is widely used in agricultural practices in China. Quick lime changes easily to small powder (hydrated lime) with water, which should be well mixed with soil in the field. Application rates of lime in acid red soils are recommended by the Nanjing Institute of Soil Science, Chinese Academy of Sciences (Table 6.1).

Table 6.1: Application rate of lime in acid soil (kg/ha)

(Source: Nanjing Institute of Soil Science, Chinese Academy of Sciences)

pH	Clay soil	Loam soil	Sandy soil
4.5 - 5.0	2,250	1,500	750 - 1,125
5.0 - 6.0	1,125 - 1,875	750 - 1,125	375 - 750
6.0	750	375 - 750	375

6.2.3. Organic matter and its application

TE could be bound with Organic matter which decrease their bioavailability in soil. The mechanism for organic matter influencing availability of TE has been described in Section 2.6. Organic fertilizers can be used to improve soil. They mainly include farmyard manure, poultry manure, sewage sludge, domestic refuse and straw (Suran, *et al.*, 1998; Guo G.L., *et al.*, 2006). Pig, cow and poultry manures, which could be easily brought from the market (Plate 6.1), are the most popular organic fertilizers in Chenggong County.

Plate 6.1: Market for manure in Chenggong County.

6.2.4. Pot experiments

Experimental Design:

Four pot experiments were conducted in the laboratory. The first pot experiment (FPOT) only used lime application. In this experiment, the soil taken from the lacustrine unit of Chenggong County has been chosen with low pH, in order to give oriented information for other experiments, even if conducted with less acid soils.

Lime is used to increase soil pH. Soil moisture was kept at field capacity in FPOT for 3 months after lime application. Then Chinese cabbage (Qingdao 83-1) was planted in soil for another 3 months. Meanwhile, soil pH was analysed each week, and contents of the acetic-acid extractable Pb, Cd, Zn (A-fraction) in soils were analysed at the end of 1^{st}, 3^{rd} and 6^{th} month. Biomass of Chinese cabbage and contents of Pb, Cd and Zn in Chinese cabbage were analysed when Chinese cabbages were harvested at the end of the 6^{th} month. Each pot is filled with 5 kg air-dried soil (<2 mm) mixed well with lime powders (<2 mm). FPOT included seven treatments, and was performed in quadruplicate for each treatment.

The latter pot experiments were used for lime and pig manure application in order to increase pH and fix the soil TE. Soils were from lacustrine (LPOT), transition (TPOT) and mountain (MPOT) units (Plate 6.2). Lime and pig manure powders (<2 mm), which were gently broken up and passed through a 2.0 mm sieve after being air-dried, were mixed with air-dried soil (<2 mm) and soil moisture was kept at field capacity for 1 week. Chinese cabbage was planted in soils for 3 months when Chinese cabbages were harvested in the field in order to have the same growing time between pot experiments and field experiments. Then contents of Pb, Cd, Cu and Zn in the eaten part of Chinese cabbage and the acetic-acid extractable TE (A-fraction) in soils were determined.

Plate 6.2: Pot experiments and Chinese cabbage seed bag.

Soil characteristics:

Characteristics of soil of FPOT, LPOT, TPOT and MPOT are shown in Table 6.2.

Table 6.2: Characteristics of soil used in experiments

Experiments	pH	OM (%)	Total N (%)	CEC (cmol/kg)	Available P (mg/kg)	Available K (mg/kg)	Total Pb (mg/kg)	Total Cd (mg/kg)	Total Cu (mg/kg)	Total Zn (mg/kg)
FPOT	4.9	6.7	0.38	27.4	201.1	503.1	40.4	0.98	112	187.3
MPOT/MFD	4.8	2.1	0.12	26.8	65.3	135.6	30.5	0.91	119.3	94.1
TPOT/TFD	6.8	2.3	0.24	31.1	104.9	668.9	16.9	0.37	108.3	129.6
LPOT/LFD	6.2	2.2	0.11	35.2	98.4	290.2	17.7	0.29	61.6	68.9

Amount of lime and pig manure:

Considering that the application rate of lime in acid red soils recommended by the Nanjing Institute of Soil Science is 2,250 kg/ha in clay soil with pH 4.5-5.0, treatments of FPOT were established to frame and check this value (L4), as shown in Table 6.3.

Table 6.3: Treatments of lime in FPOT

Amount	Treatments						
	CK	L1	L2	L3	L4	L5	L6
Lime (g/kg DM soil)	0	0.2	0.4	0.6	1.0	1.5	2.5
Lime* (kg/ha)	0	450	900	1,350	2,250	3,375	5,625

* Weight of soil is estimated with 2,250 t/ha.

According to the results obtained with the different samples with lime application in FPOT, different lime treatments were chosen according to different initial pH. Meanwhile, due to no significant differences of pH between L1, L2 and L3 observed in FPOT, treatments in MPOT were modified to T1 (0.5 mg/kg), T2 (1.0 mg/kg), T3 (1.5 mg/kg) and T4 (3.0 mg/kg) with pH 4.8, which is relative to (L2 - L3), L4, L5 and (L6) in FPOT.

Pig manure amounts were chosen according to field questionnaires (Section 5.4.2). The main organic fertilizers are pig manure and cow manure. Application rates range between 11,250-82,500 kg/ha in Chenggong County. The treatments of pig manure were based on the popular amount 33,750 kg/ha in this research. The treatments of MPOT were shown in Table 6.4, which were CK (control), T1, T2, T3, T4; T1P1, T2P1, T3P1, T4P1; T1P2, T2P2, T3P2, T4P2.

Lime treatments in LPOT and TPOT with pH 6.2 and pH 6.8 were T2 (1.0 mg/kg) and T4 (3.0 mg/kg). The treatments were CK (control), T2, T4; P1 ; P2 ; T2P1, T4P1; T2P2, T4P2 (Table 6.4). Each pot is filled with 5 kg air-dried soil (<2 mm) mixed well with lime and pig manure powders (<2 mm). Each treatment was conducted in triplicate. Contents of TE in lime and pig manure are shown in Table 6.5. Lime and pig manure were brought in different local markets in the three same units, and so could then be of different quality, especially Cu and Zn contents.

Table 6.4: Treatments of lime and pig manure in pot and field experiments

Treatments	Control (CK)	Lime				Pig manure	
		T1	T2	T3	T4	P1	P2
Amount (g/kg)	0	0.5	1.0	1.5	3.0	7.5	15
Amount* (kg/ha)	0	1,125	2,250	3,375	6,750	16,875	33,750

* Weight of soil is estimated with 2,250 t/ha.

Table 6.5: TE contents in lime and pig manure (mg/kg)

Materials	Pot experiments	Pb	Cd	Cu	Zn
Lime	FPOT	1.4	0.02	0.7	4.8
	MPOT	14.1	trace	0.6	31.0
	TPOT	2.0	0.21	0.8	5.4
	LPOT	2.3	0.08	1.6	5.6
Pig manure	MPOT	11.6	0.17	101.2	77.4
	TPOT	21.3	0.69	375.9	336.7
	LPOT	7.6	0.25	86.9	214.8

Measures and analysis:

Analysis methods of pH, total and A-fraction TE contents in soil are described in Section 3.4. Analysis methods of TE contents in vegetables are shown in Section 5.3. In order to overcome the effect of water content, TE contents in this chapter are expressed with dry materials. Biomass of Chinese cabbage in FPOT is expressed in fresh materials per each pot at harvest.

The general description data are analysed with descriptive statistics and expressed in means (using Excel 2003). The statistical differences are analysed with T-tests by Excel at $P < 0.05$ or $P < 0.01$. The regression analysis is carried out for linear models using SPSS at $P < 0.05$ or $P < 0.01$.

6.2.5. Field experiments

Experimental design:

Lime and organic manure were applied in field in lacustrine, transition and mountain units (Plate 6.3).

Plate 6.3: Application of lime and pig manure in the field.

As in pot experiments, lime and pig manure were used, respectively, to increase pH and organic matter in the lacustrine (LFD), transition (TFD) and mountain (MFD) units. Soil was cultivated with soil moisture kept at field capacity for 1 week. Then seeds of Chinese cabbage (Qingdao 83-1) were planted and Chinese cabbage grown for ~3 months (Plate 6.4).

According to the greenhouse size and plot size, the area of each sub-plot is 10 m^2 in the lacustrine unit, 16 m^2 in the transition unit and 20 m^2 in the mountain unit. There were triplicate sub-plots randomly arranged in the plot. The width of inter-rows was 45 cm and spacing inter-plants was 35 cm.

Plate 6.4: Field experiments.

Soil characteristic:

Soil characteristics and TE contents were the same as pot experiments (Table 6.2).

Amount of lime and pig manure:

Treatments were the same as for pot experiments (Table 6.4). TE contents in lime and pig manure were also the same as for pot experiments (Table 6.5).

Measures and analysis:

The biomass of Chinese cabbage and contents of Pb, Cd, Cu and Zn in the eaten part of Chinese cabbage were analysed at harvest stage. Biomass is expressed in fresh materials per each plot, and TE contents in this chapter are expressed in dry materials at harvest.

6.3. RESULTS

6.3.1. Effects of lime application

6.3.1.1. Effects of lime application on soil pH

After lime application in FPOT, soil pH fluctuated during the first 5 weeks and became more stable after the 10^{th} week (Table 6.6, Figure 6.3). Biological activities and organic matter evolution were influenced during the first 5 weeks after lime application.

Table 6.6: pH ± SD with lime application after 1, 5, 10 and 15 weeks (n=4)

Time	Control (CK)	L1	L2	L3	L4	L5	L6
1 week	5.0 ± 0. 1	5.3 ± 0. 1	5.4 ± 0.1	6.0 ± 0. 1	6.0 ± 0. 1	6.3 ± 0. 4	6.9 ± 0. 1
5 weeks	5.7 ± 0.2	5.8 ± 0.2	5.7 ± 0.1	6.0 ± 0.2	6.3 ± 0.1	6.3 ± 0.1	6.6 ± 0.1
10 weeks	5.3 ± 0. 2	5.7 ± 0. 6	5.4 ± 0. 1	5.5 ± 0. 1	5.7 ± 0. 2	5.8 ± 0. 1	6.2 ± 0. 2
15 weeks	5.3 ± 0. 1	5.8 ± 0. 2	5.8 ± 0. 1	5.8 ± 0. 1	6.1 ± 0. 2	6.3 ± 0. 2	6.5 ± 0. 1

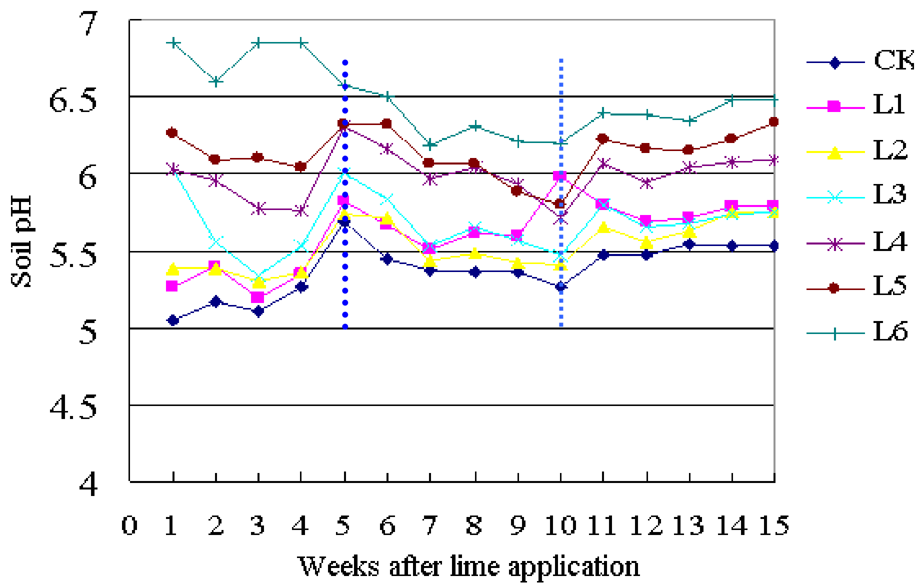


Figure 6.3: Soil pH with lime application.

Significant positive linear relationships between pH at week 1 (R^2=0.950, n=7, P<0.001), week 5 (R^2=0.896, n=7, P<0.001), week 10 (R^2=0.736, n=7, P<0.001), and week 15 (R^2=0.896, n=7, P<0.001) and application rate of lime were observed (Figure 6.4). It is suggested that lime effectively increased soil pH in Chenggong County, and decreased the potential transfer of soil TE from soil to vegetables.

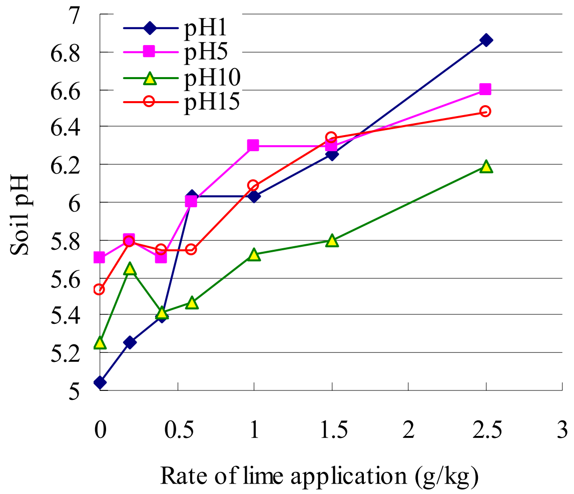


Figure 6.4: Relationships between rate of lime and pH

after 1 (pH1), 5 (pH5), 10 (pH10) and 15 (pH15) weeks.

At week 15, significant differences among control (CK) and treatments were observed, except for L1 (Figure 6.5). No significant differences existed between L1, L2 and L3.

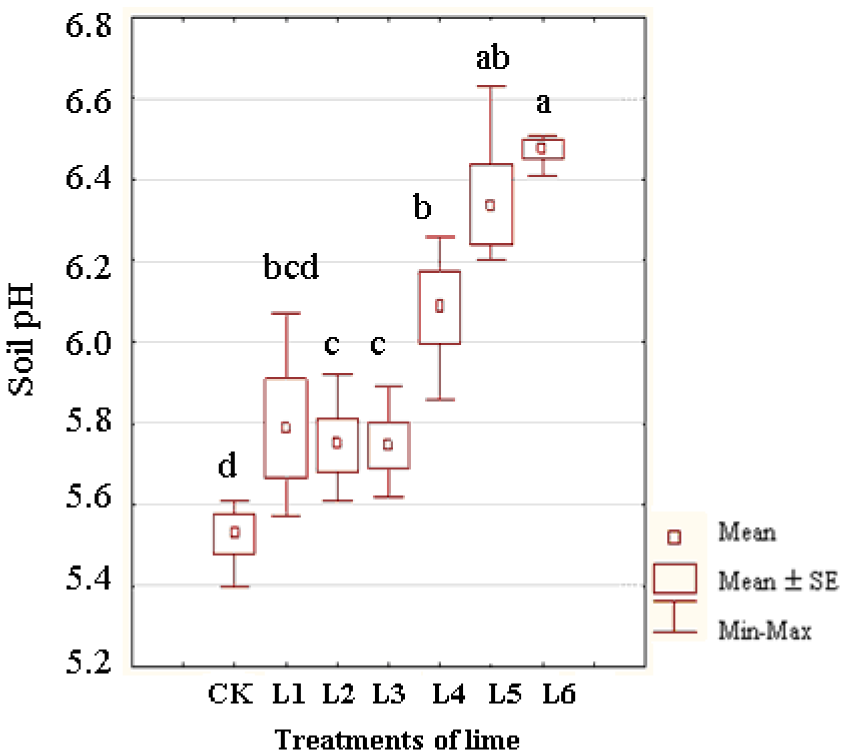


Figure 6.5: Soil pH with different rate of lime application at week 15.

6.3.1.2. Effects of lime application on acetic-acid extractable trace elements in soil

Acetic-acid extractable (A-fraction) TE includes soluble, exchangeable and carbonate bound fractions.

Pb: A-fraction contents decreased with increase in application rate of lime after 1 month (5 weeks) (Y=3.48-0.51X, R^2=0.723, $P<0.05$, n=7) (Figure 6.6). A-fraction Pb contents were trace after 3 (15 weeks) and 6 months.

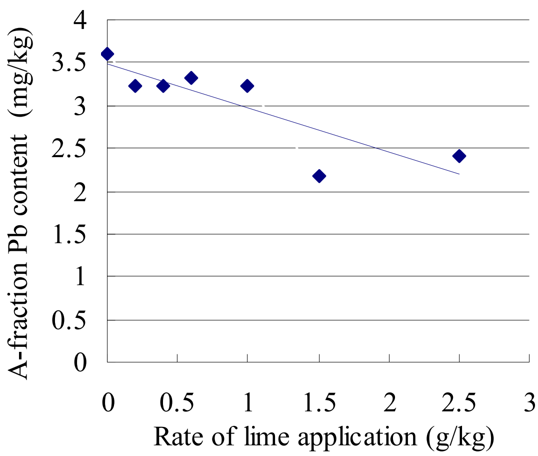


Figure 6.6: A-fraction Pb contents after 1 month.

Cd and Zn: A-fraction contents decreased with increase in application rate of lime after 3 and 6 months (Figure 6.7). However, no significant difference between A-fraction contents in 3 and 6 months was observed. There were significant negative relationships between A-fraction of Cd, Zn and application rate of lime after 6 months (Cd: Y=0.97-0.28X, R^2=0.768, $P<0.05$, n=7; Zn: Y=10.8-2.83X, R^2=0.793, $P<0.05$, n=7). It is suggested that A-fraction contents of Cd and Zn are strongly influenced by lime and soil pH (Annex 6.1).

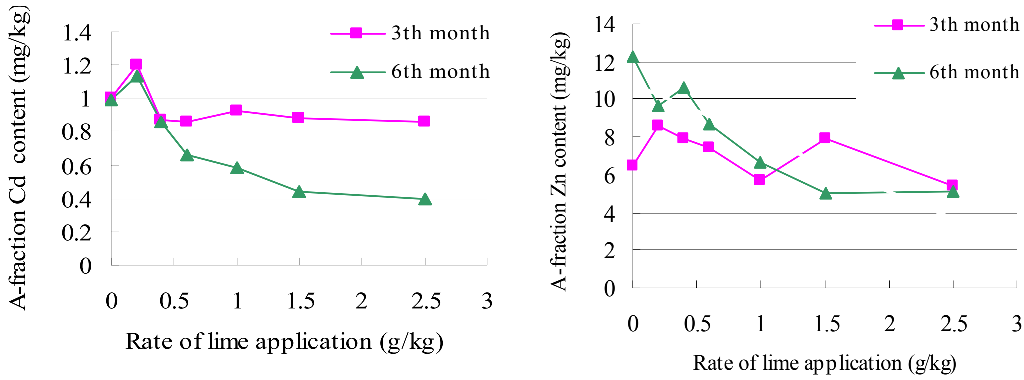


Figure 6.7: A-fraction contents of Cd and Zn after 3 and 6 months.

Comparing with the A-fraction of Cd and Zn in the control (CK) after 3 and 6 months, ratio of A-fraction contents of Cd and Zn in treatments relative to those in CK (RRCT) decreased significantly with application rate of lime after 6 months (Cd: Y=0.96-0.27X, F=10.16, R^2=0.717, P<0.05, n=6; Cu: Y=0.83-0.20X, F=12.88, R^2=0.763, P<0.05, n=6) (Figure 6.8).

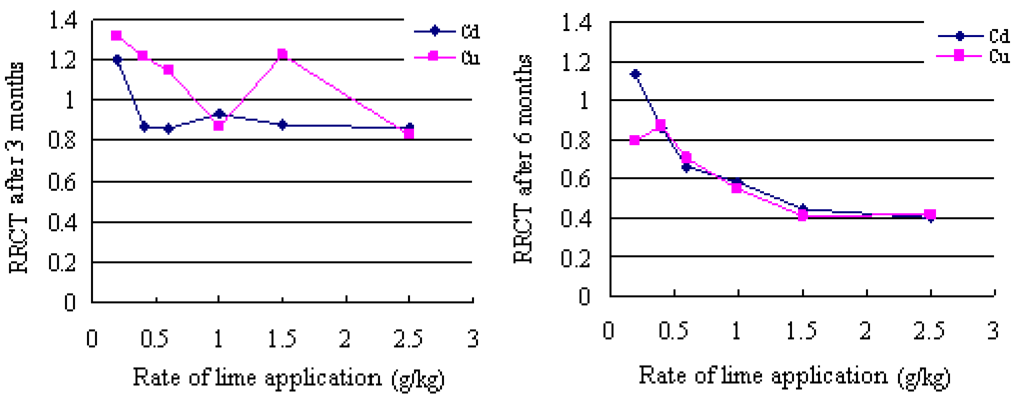


Figure 6.8: RRCT of Cd and Zn after 3 and 6 months.

Cu: At the FPOT, Cu was not considered. With the development of soil investigations in this research (Section 4.3), attention was paid latter to Cu.

6.3.2. Effects of lime and pig manure application on trace element transfer from soil to the eaten part of Chinese cabbage

Three pot experiments (LPOT, TPOT, MPOT) were used to understand TE transfer from soil to Chinese cabbage under lime and pig manure application. TE contents in the eaten part of Chinese cabbage and A-fraction TE contents in soil were analysed after 3 months when Chinese cabbages were harvested in the field, in order to have the same growing time between pot experiments and field experiments.

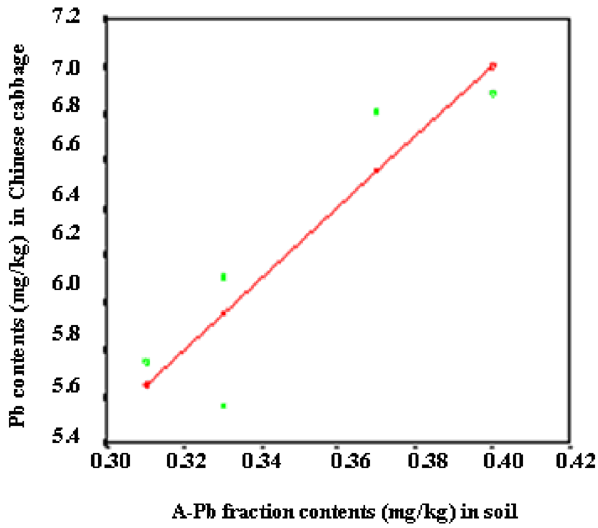
TE contents in the eaten part of Chinese cabbage were shown in Annex 6.1. Contents range from 0.6-7.4 mg/kg DM for Pb in Chinese cabbage in three pot experiments, from 0.07-2.28 mg/kg DM for Cd, from 2.9-18.4 mg/kg DM for Cu and from 22.3-78.1 mg/kg DM for Zn. Contents of A-fraction TE in soils were shown in Annex 6.2 and Table 6.7. Contents of A-fraction Pb and Cd, which were trace in TPOT and LPOT, were from 0.3-0.4 mg/kg and from 0.03-0.05 mg/kg in MPOT. Contents of A-fraction Cu and Zn were from 0.2-15.1 mg/kg and from 0.6-49.3 mg/kg in three pot experiments, respectively.

Table 6.7: A-fraction TE content ranges (mg/kg) in soils in LPOT, TPOT and MPOT

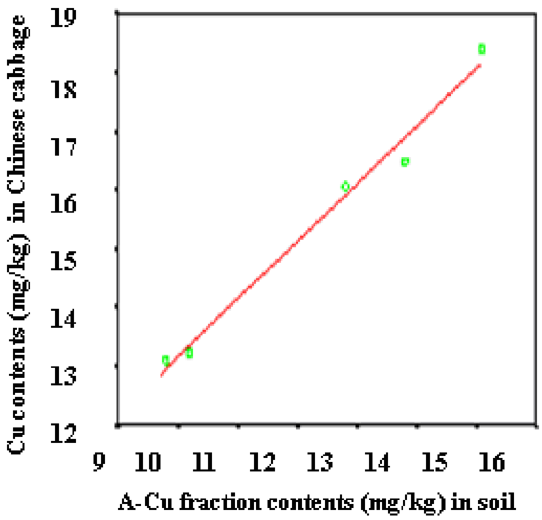
Pot experiments	Pb	Cd	Cu	Zn
LPOT	Trace	Trace	0.2 - 2.5	13.5 - 49.3
TPOT	Trace	Trace	0.9 - 4.9	2.8 - 6.1
MPOT	0.3 - 0.4	0.03 - 0.05	1.6 - 15.1	0.6 - 1.2

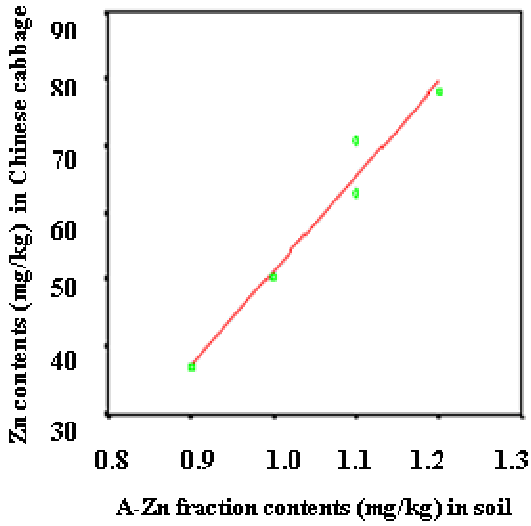
A: Relationships between acetic-acid extractable trace elements in soil and trace elements in Chinese cabbage

Lime: Positive relationships between acetic-acid extractable (A-fraction) TE contents in soil and TE contents in Chinese cabbage were observed, except for Cd (F=8.68, R^2=0.743, sig.f=0.060, n=5), when lime is applied in MPOT (Figure 6.9).



(Y=0.97+15.10x, F= 13.67, R^2=0.820, sig.f= 0.034, n=5)





(Y=3.29+0.98x, F=210.27, R^2=0.986, sig.f<0.001, n=5) (Y=-89.62+141.06x, F=80.02, R^2=0.964, sig.f=0.003,n=5)

Figure 6.9: Relationships between A-fraction TE contents in soil and TE contents in Chinese cabbage in MPOT.

Pig manure: Contents of A-Cu and A-Zn fractions with treatment of high pig manure (P2) in TPOT and LPOT were lower than with low pig manure (P1) (Annex 6.2). That made Cu and Zn contents in Chinese cabbage with treatment P2 lower than with treatment P1.

Lime + pig manure: Relationships between A-fraction TE contents in soil and TE contents in Chinese cabbage were complex when lime and pig manure were applied together. Contents of A-fraction Zn in soil and Zn in Chinese cabbage both decreased with increased rate of lime application in treatments of lime + pig manure. However, this relationship was not observed for Cu.

B: Enrichment coefficient related to trace element availability (AEC)

AEC is the ratio of TE contents in the eaten part of Chinese cabbage to A-fraction TE contents in soil, which can help understanding the transfer of TE from soil to plant. The value of this ratio increases with transfer increases from soil to plant.

Lime: AEC of Pb ranged from 16.8-18.5 with no significant differences among control (CK) and lime treatments in MPOT. AEC of Cd decreases with increase in rate of lime application in MPOT (Figure 6.10). A-fraction Pb and Cd were trace in soils of TPOT and LPOT, Thus, it is impossible to compare AEC of Pb and Cd in TPOT and LPOT. AEC of Cu ranged from 1.2-1.3 in MPOT, TPOT and LPOT with no significant difference between control (CK) and lime treatments.

AEC of Zn decreased with increased rate of lime application (Figure 6.10). Comparing with 3 pot experiments, AEC of Zn in MPOT was higher than in TPOT and LPOT with treatments of T2 (1 g/kg) and T4 (3 g/kg) (Figure 6.10).

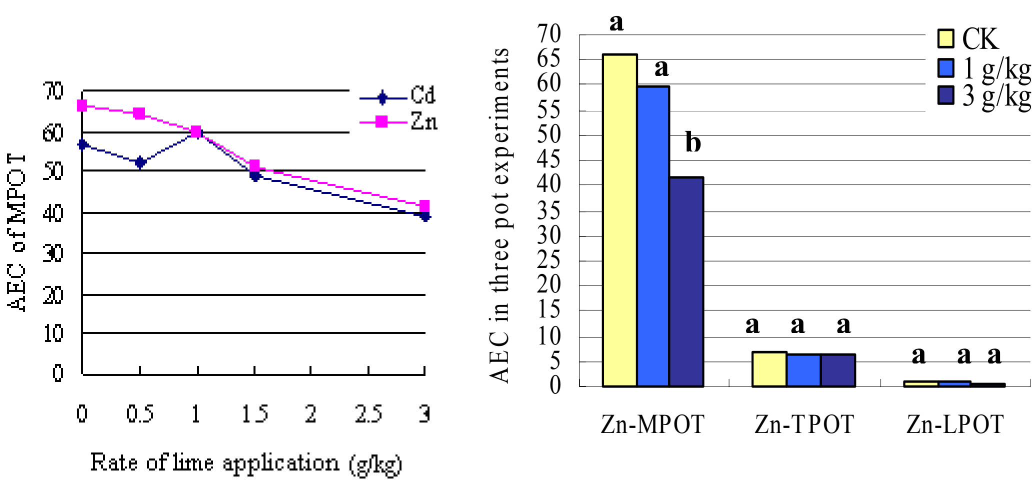


Figure 6.10: AEC in pot experiments with lime application.

Pig manure: AEC of Cu (2.96-6.99) and Zn (6.8-10.1) were higher in TPOT than in LPOT (Cu: 1.7-2.98, Zn: 0.87-2.01). AEC of Cu and Zn with pig manure application is higher than in the control (CK) (Figure 6.11).

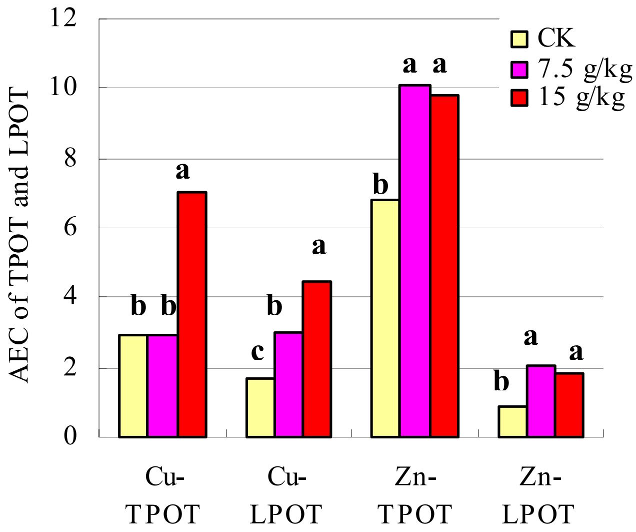


Figure 6.11: AEC in pot experiments with pig manure application.

Lime + pig manure: AEC of Pb in MPOT ranged from 17.1-19.6 with no significant difference among treatments of lime + pig manure (Figure 6.12). AEC of Cd ranged from 17.6-59.7. AEC of Cd with lime application was higher than with lime + pig manure. No significant differences between AEC of Cu, which is between 1.2-2.7, were observed with treatments of lime + pig manure. AEC of Zn, which with lime + pig manure application was higher than in the treatment of lime, except for T1, is between 53-81.3.

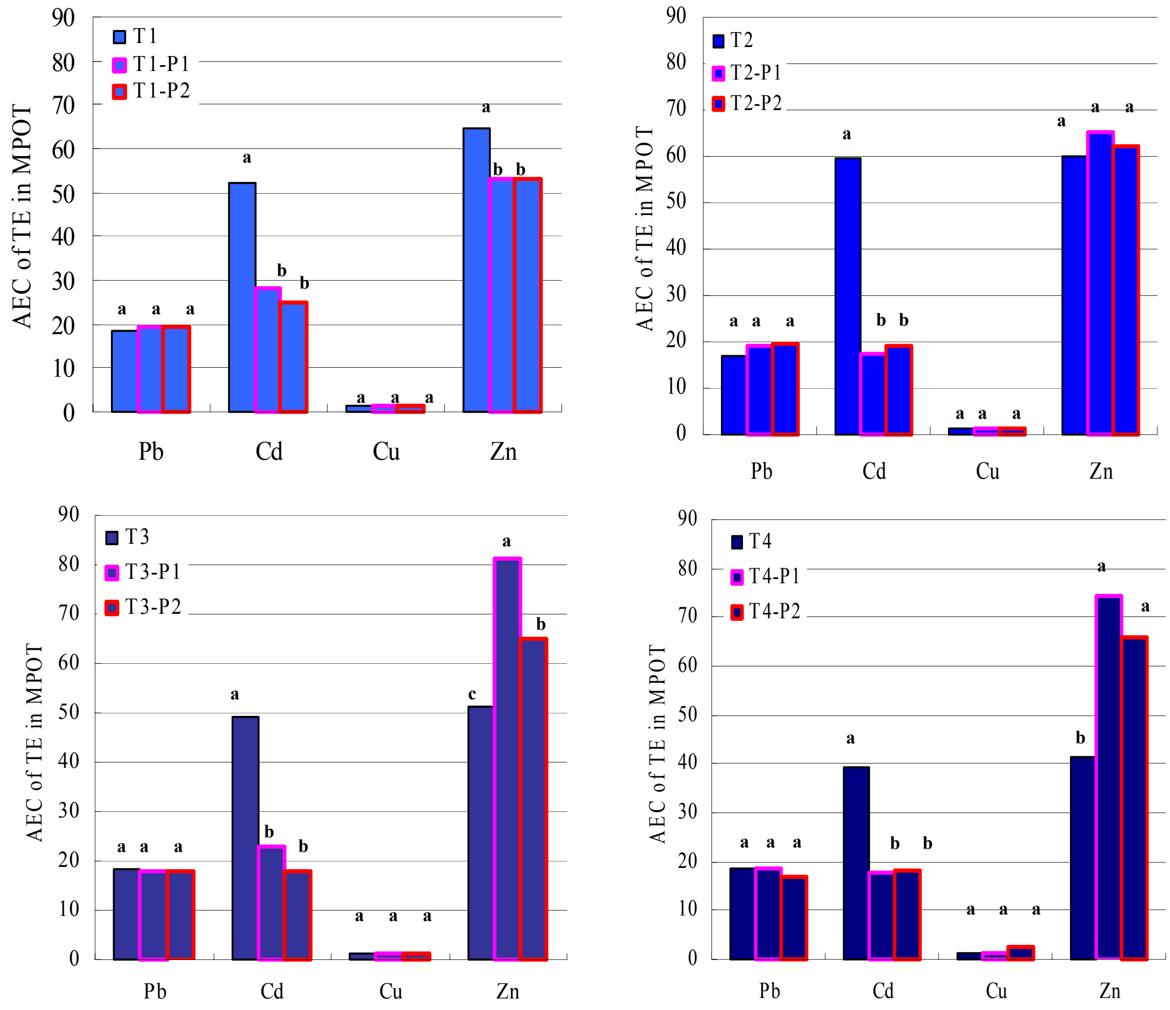
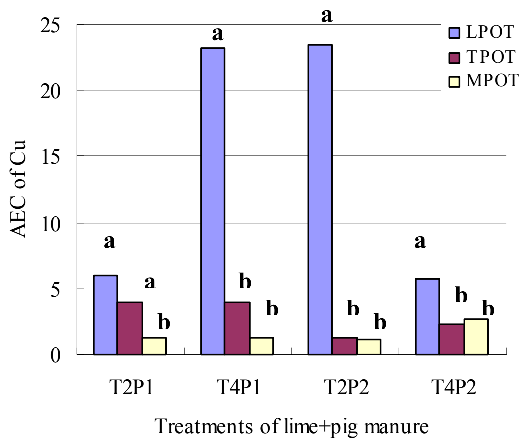


Figure 6.12: AEC in MPOT with application of lime + pig manure.

Comparing the three units, AEC of Cu was higher in the lacustrine unit than in the transition and mountain units (L>T>M). AEC of Zn was the opposite, higher in the mountain unit than in the transition and lacustrine units (L<T<M) (Figure 6.13).



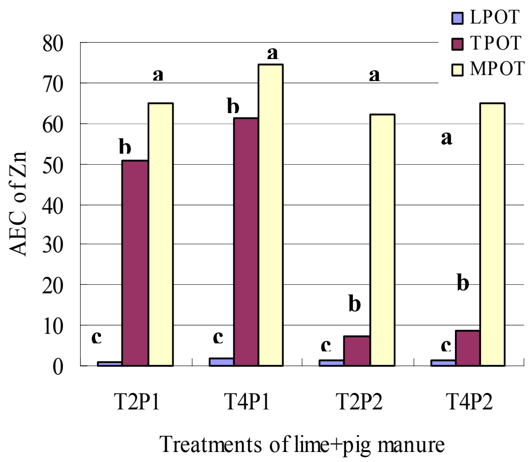


Figure 6.13: AEC of Cu and Zn in pot experiments with application of lime + pig manure.

In summary, the relative importance of transfer from soil to plant is shown in Table 6.8, with an adjacent (+), (-), and (=) and (NS) for no significant results.

Table 6.8: Conclusion on transfer from soil to plant in LPOT, TPOT and MPOT

TE	Lime			Pig manure			Lime + pig manure		
	LPOT	TPOT	MPOT	LPOT	TPOT	MPOT	LPOT	TPOT	MPOT
Pb	NS	NS	=	NS	NS	NS	NS	NS	=
Cd	NS	NS	-	NS	NS	NS	NS	NS	-
Cu	=	=	=	+	+	NS	=	=	=
Zn	-	-	-	+	+	NS	+	+	+

6.3.3. Effects of lime and pig manure application on quality and biomass of Chinese cabbage

FPOT and three field experiments (MFD, TFD, LFD) were undertaken for this research on the effects of lime and pig manure application on TE contents in the eaten part and biomass of Chinese cabbage cultivated in field conditions.

A: Trace element contents in the eaten part of Chinese cabbage

FPOT: Contents of Pb, Cd and Zn in the eaten part of Chinese cabbage were determined when harvested in FPOT. Contents of Pb, Cd and Zn decreased with application rate of lime (Table 6.9). A significant linear negative relationship between Pb contents and application rate of lime was observed (Y=12.21-2.19x, F=6.73, R^2=0.574, P<0.05, n=7) (Figure 6.14).

Table 6.9: Contents of Pb, Cd and Zn (mg/kg DM) and biomass ± SD (g FM/pot) in Chinese cabbage with lime application in FPOT (n=4)

Treatments	CK	L1	L2	L3	L4	L5	L6
Pb	12.5 ± 1.6	14.8 ± 2.0	9.8 ± 2.0	9.3 ± 2.5	9.8 ± 1.4	8.0 ± 0.7	7.8 ± 0.1
Cd	3.2 ± 1.7	1.6 ± 0.5	1.6 ± 0.4	2.9 ± 1.2	1.5 ± 1.4	1.3 ± 1.1	1.0 ± 1.8
Zn	69.8 ± 4.9	56.6 ± 2.7	40.1 ± 1.9	51.4 ± 10.8	54.3 ± 8.4	50.0 ± 4.1	43.8 ± 2.1
Biomass	22.0 ± 2.0	55.7 ± 3.1	68.3 ± 2.4	63.7 ± 3.4	71.6 ± 3.5	70.5 ± 8.8	82.4 ± 4.5

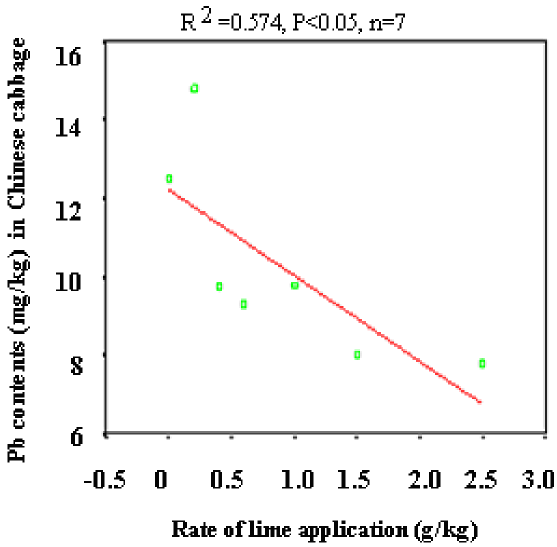


Figure 6.14: Relationship between Pb contents in Chinese cabbage and rate of lime application in FPOT.

Field experiments:

Lime: TE contents decreased with increased rate of lime application. Pb contents were higher than standard values for Chinese cabbage, except for treatment T3 and T4 in the mountain unit (MFD). In LFD and TFD, Pb contents in Chinese cabbage were lower than standard values, except for P2 and T4P1 in TFD. Cd, Cu and Zn contents were lower than control (CK) and standard values of

Chinese cabbage with lime treatments in TFD and LFD (Figure 6.15, Table 6.10). It is suggested that treatments T3 (3,375 kg/ha) and T4 (6,750 kg/ha) could be used to improve TE contents in Chinese cabbage to meet the standard values.

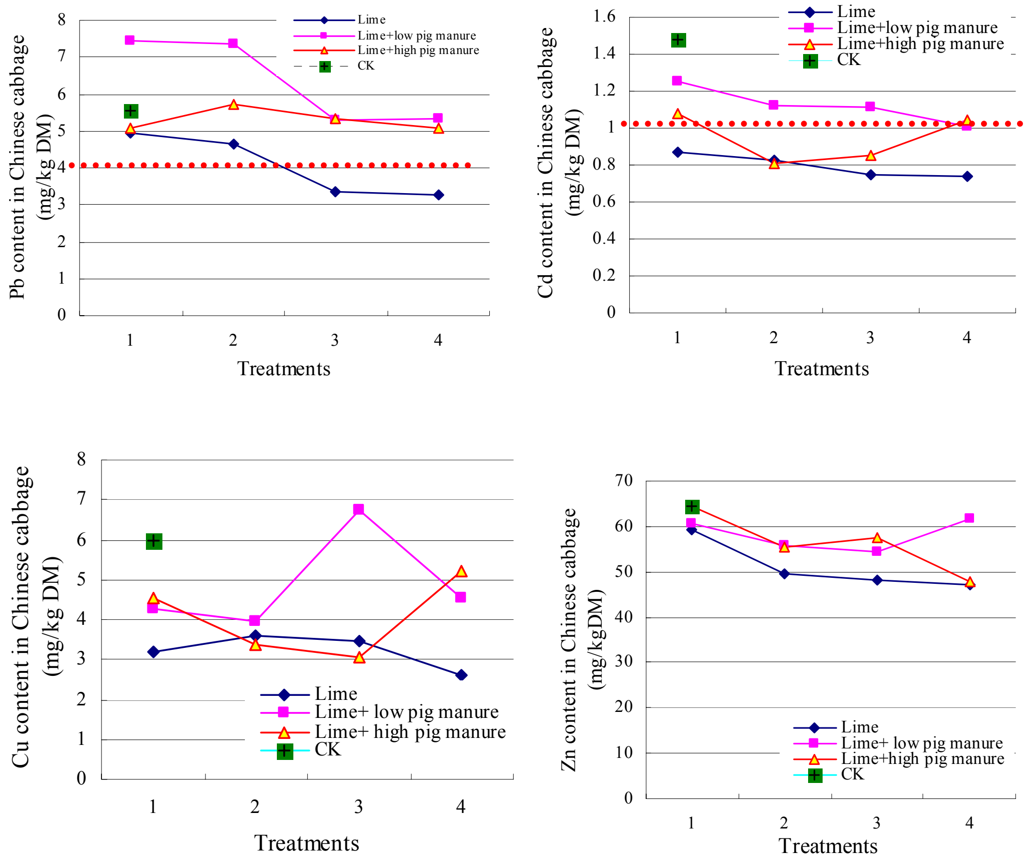


Figure 6.15: TE contents in Chinese cabbage with lime application in MFD

(....Standard value estimated with water content of 95% in Chinese cabbage).

Pig manure: TE contents with treatments of pig manure were lower than in CK, except for Pb in TFD and Cd and Zn in LFD (Figure 6.15, Table 6.10). TE contents with low pig manure were lower than with high pig manure, except for Pb in TFD and Cd and Zn contents in LFD (Figure 6.16). However, no significant difference in TE contents between low pig manure and high pig manure application was observed.

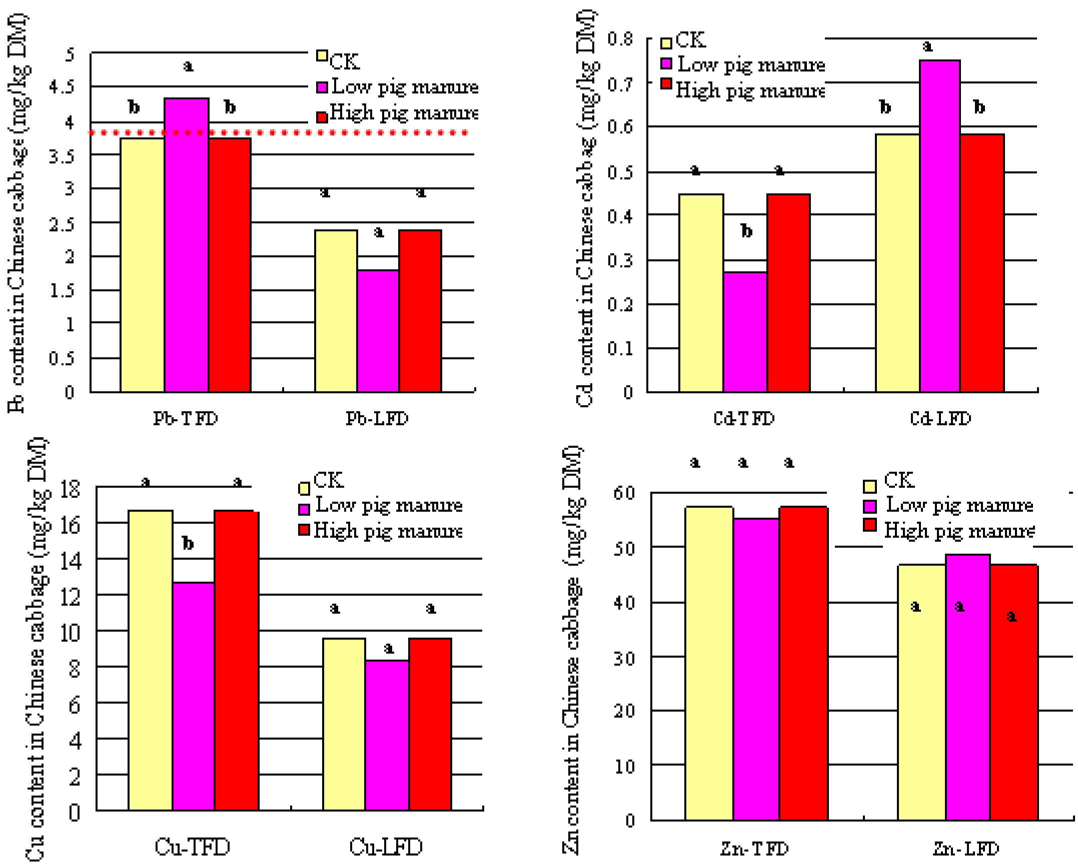


Figure 6.16: TE contents in Chinese cabbage with pig manure application in TFD and LFD.

(.... Standard value estimated with water content of 95% in Chinese cabbage)

Lime + pig manure: TE contents decreased with rate of lime application of treatments of lime + pig manure. On the one hand, TE contents with lime + pig manure were higher than with lime application in three field experiments (Figure 6.15, Table 6.10). On the other hand, Pb and Cd contents with high pig manure were lower than with low pig manure, whilst Zn contents were similar in MFD. No significant difference in TE contents between low pig manure and high pig manure was observed in TFD and LFD. It is suggested that lime alone should be better than lime + pig manure together, and low pig manure application alone (16,875 kg/ha) should be enough to decrease TE contents in Chinese cabbage at effective low cost compared with high pig manure. Therefore, it is possible to decrease TE contents in Chinese cabbage with lime application, but pig manure application could result in Pb and Cd contents in Chinese cabbage exceeding standard values in the mountain unit. This poses the problem of the quality of pig manure used. This pig manure could be slightly acid and contain TE, especially Cu and Zn from animal feed.

Table 6.10: TE contents (mg/kg DM) ± SD in the eaten part of Chinese cabbage in three field experiments (n=3)

Experiments	Treatments		Pb	Cd	Cu	Zn
MFD	Control (CK)		5.5 ± 1.0	1.48 ± 0.09	6.0 ± 1.6	64.3 ± 6.5
	Lime	T1	4.9 ± 0.8	0.87 ± 0.06	3.2 ± 1.5	59.3 ± 6.3
		T2	4.6 ± 1.1	0.83 ± 0.10	3.6 ± 2.1	49.7 ± 5.8
		T3	3.4 ± 0.6	0.75 ± 0.02	3.5 ± 1.3	48.0 ± 9.1
		T4	3.3 ± 0.1	0.74 ± 0.03	2.6 ± 1.9	47.3 ± 7.6
	Lime + low pig manure (P1)	T1P1	7.5 ± 0.6	1.25 ± 0.09	4.3 ± 2.1	60.8 ± 8.2
		T2P1	7.4 ± 0.3	1.12 ± 0.08	4.0 ± 0.9	55.7 ± 6.5
		T3P1	5.3 ± 0.8	1.11 ± 0.04	6.7 ± 0.8	54.5 ± 4.3
		T4P1	5.3 ± 0.6	1.01 ± 0.06	4.6 ± 0.6	61.6 ± 3.2
	Lime + high pig manure (P2)	T1P2	5.1 ± 0.4	1.08 ± 0.05	4.5 ± 1.3	64.5 ± 9.8
		T2P2	5.7 ± 1.0	0.81 ± 0.08	3.4 ± 1.2	55.6 ± 8.7
		T3P2	5.3 ± 1.1	0.85 ± 0.09	3.1 ± 0.6	57.5 ± 5.6
		T4P2	5.1 ± 0.6	1.04 ± 0.10	5.2 ± 2.0	47.8 ± 4.6
TFD	Control (CK)		3.7 ± 0.6	0.45 ± 0.03	16.8 ± 3.1	57.1 ± 5.2
	Lime	T2	2.7 ± 0.4	0.41 ± 0.06	13.4 ± 3.6	58.8 ± 6.3
		T4	2.1 ± 0.4	0.34 ± 0.04	12.9 ± 2.5	38.4 ± 4.3
	Pig manure	P1	3.3 ± 0.3	0.27 ± 0.05	13.4 ± 4.2	49.5 ± 5.9
		P2	4.3 ± 0.9	0.27 ± 0.10	12.7 ± 6.2	55.0 ± 9.1
	Lime + low pig manure (P1)	T2P1	3.1 ± 0.7	0.37 ± 0.11	13.5 ± 2.3	57.7 ± 8.1
		T4P1	4.2 ± 0.9	0.23 ± 0.03	11.6 ± 2.1	55.6 ± 6.5
	Lime + high pig manure (P2)	T2P2	3.9 ± 0.2	0.49 ± 0.09	12.6 ± 2.6	45.6 ± 5.7
		T4P2	2.8 ± 0.6	0.23 ± 0.05	11.2 ± 2.0	55.0 ± 5.9
LFD	Control (CK)		2.4 ± 0.3	0.58 ± 0.06	9.5 ± 1.6	46.6 ± 7.8
	Lime	T2	2.1 ± 0.5	0.55 ± 0.03	10.2 ± 2.9	44.5 ± 5.3
		T4	1.7 ± 0.4	0.54 ± 0.10	9.1 ± 2.1	45.9 ± 6.1
	Pig manure	P1	1.9 ± 0.3	0.61 ± 0.05	9.6 ± 0.6	49.3 ± 8.0
		P2	1.8 ± 0.2	0.75 ± 0.04	8.4 ± 0.9	48.5 ± 5.7
	Lime + low pig manure (P1)	T2P1	1.6 ± 0.5	0.77 ± 0.08	10.6 ± 1.2	48.9 ± 5.3
		T4P1	1.3 ± 0.6	0.59 ± 0.06	9.5 ± 1.6	45.7 ± 6.4
	Lime + high pig manure (P2)	T2P2	2.2 ± 0.4	0.74 ± 0.11	10.3 ± 2.1	49.1 ± 7.0
		T4P2	1.7 ± 0.2	0.45 ± 0.06	10.0 ± 1.8	44.9 ± 5.4

* Chinese standard values estimated: Pb: 4, Cd: 1, Cu: 200 and Zn: 400 mg/kg DM estimated with water content = 95% in Chinese cabbage.

B: Biomass

FPOT: Biomass of Chinese cabbage increased with rate of lime application in FPOT ($Y=-12.3X^2+47.16X+37.95$, $R^2=0.717$, $P<0.05$, $n=7$), which means that lime application would be used to improve Chinese cabbage growth (Table 6.9, Figure 6.17). Hence, 0.4 g/kg (900 kg/ha) lime should be sufficient for obtaining suitable biomass, according to this curve (Figure 6.17).

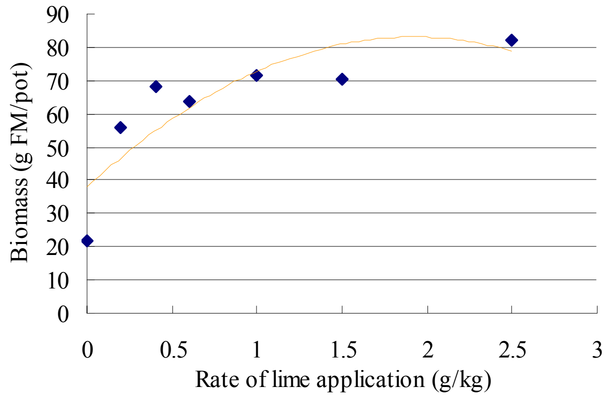


Figure 6.17: Effect of lime application on biomass of Chinese cabbage in FPOT.

Field experiments: Biomass also increased with lime and pig manure application in the field (Figure 6.18, Table 6.11). In LFD and TFD, biomass of all treatments was higher than in CK.

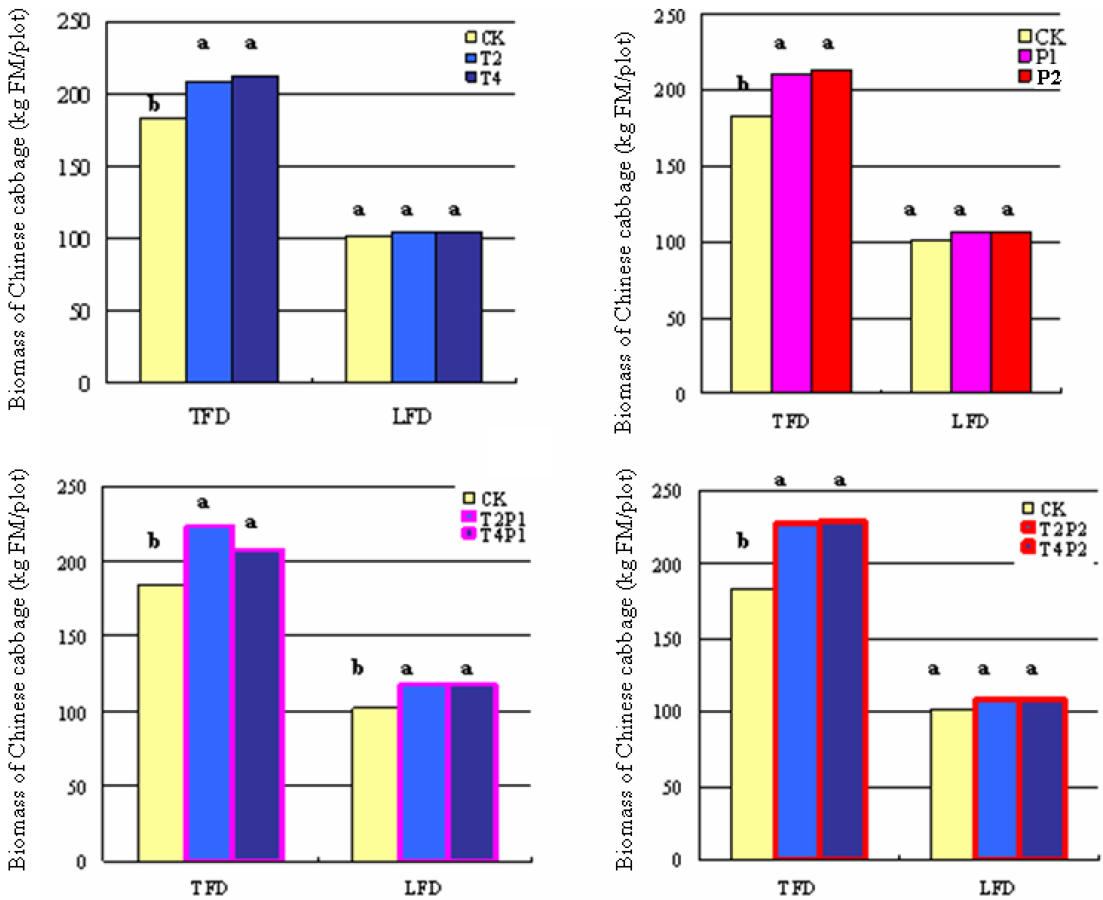


Figure 6.18: Biomass of Chinese cabbages in TFD and LFD.

Considering biomass and TE contents, TE accumulation in Chinese cabbage (TE content × biomass) with treatments was lower than in control (CK) in LFD and TFD, except for Pb and Cd in TFD (Table 6.11). Pb accumulation in TFD with treatments of pig manure and lime +pig manure was higher than or close to CK. Cd accumulation in T2P2 was higher than CK.

Table 6.11: Biomass (kg FM/plot) ± SD and TE accumulated amounts (mg DM/plot) in Chinese cabbage in TFD and LFD (n=3)

Experiment	Treatments		Biomass	Accumulated amounts			
				Pb	Cd	Cu	Zn
TFD	Control (CK)		183.3 ± 12.3	34.3	4.1	153.7	523.7
	Lime	T2	208.8 ± 12.6	27.7	4.3	139.7	613.9
		T4	211.7 ± 13.6	21.7	3.6	136.1	406.0
	Pig manure	P1	211.7 ± 20.1	34.4	2.9	142.2	523.5
		P2	213.9 ± 20.2	46.4	2.9	135.6	588.5
	Lime + low pig manure (P1)	T2P1	223.3 ± 22.4	35.1	4.1	151.1	644.6
		T4P1	208.3 ± 23.1	43.9	2.4	120.7	578.7
	Lime + high pig manure (P2)	T2P2	228.9 ± 23.5	44.2	5.6	143.7	521.8
		T4P2	230.1 ± 20.1	31.9	2.6	133.7	633.3
LFD	Control (CK)		101.7 ± 11.2	12.2	2.9	48.3	236.9
	Lime	T2	103.2 ± 12.0	11.0	2.8	52.4	229.6
		T4	103.6 ± 13.2	8.5	2.8	47.2	238.1
	Pig manure	P1	106.7 ± 13.6	10.2	3.3	51.3	263.1
		P2	106.3 ± 12.5	9.6	4.0	44.5	257.6
	Lime + low pig manure (P1)	T2P1	117.3 ± 13.2	9.1	4.5	62.0	286.7
		T4P1	117.3 ± 15.0	7.8	3.5	55.4	268.0
	Lime + high pig manure (P2)	T2P2	107.8 ± 12.2	11.6	4.0	55.3	264.4
		T4P2	109.8 ± 12.0	9.2	2.5	54.9	246.6

6.4. DISCUSSION

6.4.1. Soil pH and acetic-acid extractable trace element contents in response to lime application

Significant positive linear relationships between application rate of lime and pH after weeks 1, 10 and 15 were observed. It is confirmed that lime application could increase soil pH in Chenggong

County. This is consistent with the observation that liming has been used traditionally as a soil amendment to increase alkalinity and reduce TE mobility.

During the first 5 weeks, pH fluctuated. For example, pH of L1 increased and pH of L6 decreased. Many biological processes should occur during this period under lime application. Lime application improves organic matter decomposition, increases biological activities, resulting in pH variations (Dermatas & Meng X.G., 2003; Tang L.N. & Xiong D.Z., 2003). This may be also a question of dissolution rate of lime. After 5 weeks, a new balance of soil processes was reached and pH became stable. It is suggested that effects of lime on pH and TE mobility do not happen immediately, but need at least 5 weeks. But the experiment is not long enough to show the duration of the effect on pH.

Lime application increases soil pH, resulting in decreasing contents of A-fraction Pb, Cd and Zn. Significant negative relationships between contents of A-fraction Cd and Zn and rate of lime application were observed after 6 months. It is suggested that contents of A-fraction Cd and Zn are influenced by lime and pH. RRCT decreased with rate of lime application after 6 months. Contents of A-fraction TE in soil with lime application can be kept at low levels compared with control (CK), resulting in the low potential availability of TE transfer from soil to plant. Because no significant difference in contents of A-fraction Cd and Zn between 3 and 6 months was observed in FPOT, contents of A-fraction Cd and Zn were influenced by pH and kept stable under plant growth, although root exudates from plant may cause variations in soil pH.

6.4.2. Changes in transfer of trace elements from soil to Chinese cabbage with lime and pig manure application

Significant positive relationships between A-fraction TE in soil and TE contents in Chinese cabbage were observed. It is suggested that Chinese cabbage more easily absorbs A-fraction TE and accumulates TE. This fraction mainly includes water soluble and exchangeable TE.

No significant difference in AEC of Pb and Cu between CK and lime treatments in MPOT was observed. It is suggested that AEC of Pb and Cu is stable and could not be changed by lime. Due to no significant differences in AEC of Pb and Cu between lime and pig manure application, AEC of Pb and Cu should not be influenced by pig manure. Zimdahl & Foster (1976) believed that organic matter addition did not offer much promise as a method to reduce Pb availability to plants. However, this research shows addition of lime and organic matter could decrease Pb and Cu availability in soil, but do not change AEC of Pb and Cu in Chinese cabbage.

AEC of Cd and Zn decreased with increased rate of lime application in MPOT. AEC of Zn in MPOT was higher than in TPOT and LPOT, which should be relative to original low pH in the mountain unit. That means that AEC of Cd and Zn was high in low pH, and decreased with increased pH. AEC of Cu and Zn increased with increased pig manure. AEC of Cd and Zn varied with lime and pig manure application. AEC of Cd and Zn with lime application was higher than with lime + pig manure. AEC of Cd and Zn decreased with lime and pig manure application together, resulting in decreased TE accumulation.

6.4.3. Trace element contents and biomass of Chinese cabbage

A. Trace element contents in Chinese cabbage

In FPOT and field experiments, TE contents in Chinese cabbage decreased with rate of lime application. A significant negative linear relationship between Pb contents and rate of lime application was observed. Pb contents in Chinese cabbage with T3 and T4 in the mountain unit were lower than Chinese standard values. Cd, Cu and Zn contents were lower than control (CK) and standard values of Chinese cabbage with lime treatments. It is suggested that treatments of lime at 3,375 and 6,750 kg/ha could be used to decrease TE contents in Chinese cabbage to meet standard value and improve its quality. Activity of microbes and availability of phosphate are improved with lime application (Meng C.F., *et al.*, 2004). Meanwhile, pathogenic bacteria, pest eggs and weeds will be killed, and clubroot could be prevented from Chinese cabbage due to alkalinity. Lime application is regarded as a useful practice for controlling TE transfer from soil to plant (Chen N.C. & Chen H.M., 1996; Xia H.P., 1997). Ideal pH 6.5-7.0 should be a target for this area. This will improve both Chinese cabbage growth and quality related more specially to TE contents.

With pig manure application, contents of Pb and Cd in Chinese cabbage with high pig manure were lower than with low pig manure; Zn contents were similar in MFD. No significant difference in TE contents between with low pig manure and high pig manure was observed in TFD and LFD. The mechanism for OM influencing availability of TE lies in humus in organic mater bound with TE to form stable chelates (metal-HA complex), especially humin. Because of dilution of organic fertilizer, TE contents in Chinese cabbage decreased in soil. Meanwhile, some elements in organic fertilizer have antagonism with TE.

With lime + low pig manure, TE contents in Chinese cabbage decreased with rate of lime application in the three units. But differences in TE contents between low lime + low pig manure (T2P1) and high lime + low pig manure (T4P1) are not significant in LFD and TFD, possibly due to the “higher” original pH. TE contents in Chinese cabbage decreased with rate of lime application in all three units with lime + high pig manure. Zn contents in TFD were high, which could be relative to high Zn contents in pig manure, whilst contents of Pb, Cd and Cu in LFD were higher than the control (CK). High pig manure should result in TE content increase. Massive amounts of organic matter would be required to achieve small increases in soil organic content and exert an effect on TE accumulation by plants. Further research is necessary to determine the effect of organic material applications on TE availability. Despite differences in opinion, organic matter with low TE contents does have a protective value and fixed TE. Hence, it is possible to increase pH in soil and decrease TE contents in Chinese cabbage with lime and pig manure application without TE.

B. Biomass of Chinese cabbage

Biomass of Chinese cabbage increased with rate of lime and pig manure application. Application of lime and pig manure would improve Chinese cabbage growth. Organic fertilizers may improve soil structure, and decrease TE mobility, and then improve plant growth. Crops grow well when soil pH is between 6.5-7.0 and nutrients are more available. The yield of crops increases with soil pH increase in the optimal pH range. However, although TE accumulation of each plot decreased more often with biomass increase, Pb accumulation in TFD with the pig manure and lime + pig manure treatments were great or close to control level (CK), and Cd accumulation of treatment T2P2 was higher than the control (CK). That should be relevant to the quality of lime and pig manure. Especially, Pb and Cd contents in pig manure in TFD were 2.81 times and 2.76 times of that in LFD, respectively. Cd contents in lime in TFD were 2.63 times of LFD. Quality of lime and organic fertilizers should be taken into account when they were used for amendment additives *in situ* to soil contaminated by TE. More attention should be paid to Pb, Cd , Cu and Zn contents in pig manure.

6.5. CONCLUSIONS

With increases in lime and pH, contents of acetic-acid extractable TE in soil and TE contents in Chinese cabbage decrease. AEC of Pb and Cu is stable and could not be changed, and the AEC of Cd and Zn decrease with lime application. AEC of Cd and Zn was high in low pH, and decreased with increased pH. Treatments of lime at 3,375 kg/ha could be used to improve the quality of Chinese cabbage. With pig manure application, Pb and Cd contents with high pig manure were lower than with low pig manure. Zn contents were similar in MFD. AEC of Pb and Cu was stable and could not be changed, and of Cd and Zn decreased with pig manure application.

With lime + low pig manure application together, AEC of Pb and Cu could not be influenced, and the AEC of Cd and Zn decreased. TE contents in Chinese cabbage decreased and biomass of Chinese cabbage increased. More attention should be paid to TE accumulation in Chinese cabbage. Lime and pig manure would be more effective with low pH in the mountain unit. Optimal rate of lime (T3: 3,375 kg/ha) and pig manure (P1: 16,875 kg/ha) should be considered by farmers as effective at low cost and with beneficial effects on soil structure. In general, TE contents in the eaten part of Chinese cabbage and biomass may be changed with lime and pig manure application, including decreasing TE contents and improving the quality of Chinese cabbage (+), increase and affect the quality of Chinese cabbage (-). Moreover, some results were not significant (NS) (Table 6.12).

Table 6.12: Conclusions on the effects of lime and pig manure on the quality and biomass of Chinese cabbage

Parameter	Lime			Pig manure			Lime + pig manure		
	LFD*	TFD	MFD	LFD	TFD	MFD	LFD	TFD	MFD
Pb	+++	+++	+++	+	+	NS	++	+	+
Cd	+++	+++	+++	-	+	NS	+	++	+
Cu	+	+++	+++	+	+	NS	+	++	+
Zn	+	++	+++	-	+	NS	+	+	+
Biomass	+	++	NS	++	++	NS	+++	+++	NS

*LFD: field experiment in the lacustrine unit; TFD: field experiment in the transition unit; MFD: field experiment in the mountain unit.

VII: GENERAL CONCLUSIONS

Field investigations were conducted in 2002-2006 in Chenggong County, in order to understand natural TE contents and anthropogenic contamination in soil, to assess TE contamination in soils and vegetables, as well as the transfer of TE from soils to vegetables in Chenggong County. Geomorphopedological investigations lead to the research area being divided into three units: lacustrine unit, transition unit and mountain unit.

Geomorphological soil characteristics: Topsoil texture of samples tended to sandy and loam near Dianchi Lake, and clay close to the mountain. Soil colour is brown and dark near the lake, while red in the mountain unit. Mean pH, physical clay (<0.01 mm), SOC content and CEC are 6.2, ~51.9%, 1.5% and 24.1 cmol/kg, respectively. In the three units, subsoil texture is mainly clay. Sandy clay texture is also found near the lake. Subsoil colour is dark brown in the lacustrine unit, while reddish brown in the transition and mountain units.

TE total contents: As a whole, mean TE contents in topsoil are 56.7 for Pb, 0.47 for Cd, 125.7 for Cu and 114.2 mg/kg for Zn. TE contents decrease from north-east to south-west, which is consistent with the elevation gradient. Thus, the mean contents of Pb, Cd, Cu and Zn in the mountain unit are higher than in the transition and lacustrine units: M>T(L) for Pb, M>T>L for Cd, Cu and Zn.

The detailed approach has shown that there are significant differences of TE contents from south to north with distance from Chenggong town in the lacustrine unit and with distance to the mountain in the transition unit. However, there is no significant difference between TE contents from west to east with distance from Dianchi Lake in the lacustrine and between the two selected villages in the transition unit. TE accumulation is usually observed along the road in the two selected sites. Although the greenhouses are close to each other, significant differences of Pb, Cu and Zn contents in soil still exist, except for Cd (for which content it is only trace).

As a whole, mean TE contents in subsoil are Pb: 58.2, Cd: 0.89, Cu: 129.1 and Zn: 97.0 mg/kg. TE contents in subsoil with red colour and clay texture are higher than with brown colour and sandy texture (sandy loam). Mean TE contents in subsoil are higher with limestone than with sandstone and shell. Contents of Cu and Zn in subsoil with few mottles are higher than with more mottles, but it is the opposite for Cd. Most of the ratio of TE contents in top/subsoil (RTS) for Pb and Zn are ≥1.0, and most of RTS for Cd and Cu are ≤1.0, which indicates relative accumulation of Pb and Zn in topsoil and Cu and Cd in subsoil.

Soil assessment based on total contents: Mean total TE contents in the topsoil are 2-7 times of TE contents observed in world soils and even Kunming Prefecture soils. The signal index of contamination (Pi) of TE are <2, indicating to low contaminated levels, except for Cu which presents a medium contaminated level. Pi of Cd and Cu in the mountain unit are higher than in the lacustrine and transition units (M>L>T). The integrative index of contamination (P) of TE is >3, indicating a globally high contaminated level.

Vegetable quality: For 95.2% of the vegetable samples, mean Pb contents in eaten parts exceed the Chinese standard value. This situation is observed with only 9.5% of the samples for Cd, 19.1% for Cu and 3.2% for Zn. The highest contents are observed for Pb in cauliflower, Cd in lettuce and Chinese cabbage, Cu and Zn in pea. But tomato has the lowest contents of Pb, Cd, Cu and Zn. Mean TE contents in Chinese cabbage are 0.33 for Pb, 0.02 for Cd, 0.97 for Cu and 3.45 mg/kg FM for Zn.

Soil-plant relationship: Two different ways to estimate the bioavailability of soil TE for Chinese cabbage have been tested: available and sequential extraction fraction (SEF) TE contents.

- The mean available TE contents are 7.4 for Pb, 0.19 for Cd, 16.9 for Cu and 12.2 mg/kg for Zn.
- A-fraction TE contents are 1.38 for Pb, 0.06 for Cd, 1.25 for Cu and 1.85 mg/kg for Zn.
- B-fraction TE contents are 6.53 for Pb, 0.13 for Cd, 4.57 for Cu and 16.49 mg/kg for Zn.
- C-fraction TE contents are 5.80 for Pb, 0.045 for Cd, 18.4 for Cu and 19.89 mg/kg for Zn.

SEF TE contents show that B-fraction TE contents are higher than C-fraction and A-fraction (B>C>A) for Pb and Cd, and C-fraction TE contents are higher than B-fraction and A-fraction (C>B>A) for Cu and Zn.

Available and A-fraction TE contents in the lacustrine unit are higher than in the transition unit (L>T). Pb contents in Chinese cabbage decrease with B-fraction Pb increase. Cd contents in Chinese cabbage increase with increase in available Cd. Increasing in B and C-fractions Cu seems to increase Cu absorption by vegetables, especially in the lacustrine unit. Zn contents in Chinese cabbage increase with increase in total, available and SEF contents of Zn. In order to assess soil suitability, available TE and SEF TE contents better indicate the potential risk for vegetables. Different soil TE fractions are suggested for soil assessment indicators.

Experiment approach: Pot and field experiments have been conducted to propose modified additives in order to decrease the TE contents in Chinese cabbage and improve its quality. Lime and pig manure have been applied to modify soil pH and more generally to reduce the mobility of TE *in situ*. The results show that pH fluctuates during the first 5 weeks and then remains stable. With increasing lime rate and pH, contents of acetic-acid extractable fraction (A-fraction) TE in soil decrease. Enrichment coefficients relative to TE availability (AEC) of Pb and Cu are stable and are not changed by lime or pig manure. AEC of Cd and Zn, which are high in low pH, decrease with increasing pH and application rate of lime and pig manure.

TE contents in Chinese cabbage decrease with rate of lime and pig manure application. Lime and pig manure would be more effective on low pH soil in the mountain unit. Biomass of Chinese cabbage increases with rate of lime and pig manure application. Quality of lime and organic fertilizers should be taken into account when they are used for trapping TE in soil contaminated by TE.

Limitations of the research: This research, which began with the programme PRA 01-02, lasted four years. Many shortcomings should be overcome in the future. Soil and vegetables samples were taken during two years. Pot and field experiments were also conducted during different years.

The first pot experiment was conducted in Autumn 2003, field experiments in the mountain unit being conducted in Spring 2004 and others in Autumn 2006. That makes some difficulty in comparing results. Especially, it was the rainy season when Chinese cabbage grew in the field in the mountain unit, and it suffered from disease just before harvest, making it difficult to evaluate biomass. Meanwhile, lime and pig manure were bought in the markets just before application. It is difficult to know immediately their TE contents, which makes the results more complicated.

For the field experiments, the suitable plots were difficult to choose. On the one hand, the farmers should agree to apply lime and pig manure as treatments. On the other hand, in order to obtain more significant results, it is should be better to work with soil with low pH and high TE contents. The area of plots was not the same in the three units, which were limited by greenhouses and boundaries.

Suggestions for future research: Many research projects should be conducted in the future:

- Indicators of available TE and SEF TE in soil are recommended, which need more field investigations to obtain the threshold values according to soil pH and soil types.
- Application rate of lime is recommended in the mountain unit, which also should be thoroughly verified in the field.
- It is necessary to decide vegetables standard values in dry materials, due to the different water content in vegetables. More attention should be paid to TE accumulation in vegetables and food chain links to human health.
- More attention should be paid to the quality of pig manure and other organic fertilizers applied in Chenggong County. On the one hand, quality of animal food additives should be strict with acidity and TE contents meet relative standards, especially Cu and Zn contents which are used in animal food. On the other hand, supervision and management from government should consider TE contents in markets of organic fertilizers. It should be considered which kind of organic fertilizer could be used and what to do with the pig manure.
- The non-consumed part of vegetables should be treated carefully due to high TE contents, if not, TE will continue to be recycled within soils. It is important to find possible methods to treat the non-consumed part of vegetables. Furthermore, increasing quantities of sludge will

be applied into agricultural soil. Attention should be paid to their quality and how to use them.

- Because TE in soil and vegetables is still introduced from atmospheric deposits, Dianchi Lake, fertilizers and pesticides, detailed research about the sources of TE should be undertaken.
- With the development of Kunming City, persistent monitoring of soil quality and vegetable quality should be maintained, as a key to guarantee human health.
- It would be useful to co-operate with different counties, including research strategy, analytical methods and TE standard values.

In general, results have been obtained to evaluate TE contents in soil, assess soil quality and vegetable quality, and improve Chinese cabbage quality, even though some shortcomings exist. More research should be taken into sources of soil TE, quality of organic fertilizers, suitable utilization of the non-consumed part of vegetables, recommended standard values for soil and vegetables, and amendment methods for soil contaminated by TE in the future.

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