Speciation of Metals in Agricultural Lime and Contaminated Soil

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AAS = atomic absorption spectrometer

AC = alternate current

BCR = basalt of the Columbia river (reference material)

BSEU = Bureau of Standards of the European Union

bw = body weight

CCA = chromate copper arsenate

CCME = Canadian Council of Ministers of the Environment

CEC = cation exchange capacity

CPS = counts per second

CRM = certified reference material

DPTA = Diethylenetriamine penta acetic acid

DC = direct current

dw = dry weight

EAC = EC maximum admissible concentration (MAC)

ECL = effects concentration low

EDTA = Ethylenediaminetetraacetic acid

EMRC = Energy Mines and Resources Canada

EU = European Union

FAAS = flame atomic absorption spectrometer

FRG = Federal Republic of Germany

GSR = geological reference material

G-6-DP = glucose-6-phosphate dehydrogenase

HCL = Hollow-cathode atomic spectral lamps

HF = Hydrofluoric acid

HG-AAS = hydride generation atomic absorption spectroscopy

HSDB = Hazardous Substance Data Bank

HSPE = Ministry of Housing, Spatial Planning and the Environment (Netherland)

ICP = inductively-coupled plasma

ICP-MS = inductively-coupled plasma mass spectrometer

ICRCL = United Kingdom's Interdepartmental Committee on the Redevelopment of Contaminated Land

IUPAC = International Union of Pure and Applied Chemistry

LD_{50} = median lethal dose

MS = mass spectrometer

NAS = National Academy of Sciences

NIST = National Institute of Standards and Technology

NJDEP = New Jersey Department of Environmental Protection

OMEE = Ontario Ministry of the Environment and Energy

PMT = Photomultiplier tube

RF = Radio frequency

RSD = relative standard deviation

SD = standard deviation

SSE = selective sequential extraction

TEC = threshold effects concentration

USGS = United States Geological Survey

WHO = World Health Organization

ww = wet weight

XRF = X-ray fluorescence analysis

Zusammenfassung

Die Verwendung von Metallen zur Entwicklung der heutigen fortschrittlichen technologischen Gesellschaft lässt auf eine lange Geschichte zurück blicken. Im Zuge des letzten Jahrhunderts wurde realisiert, dass die chemischen und radioaktiven Eigenschaften von Metallen eine ernsthafte Bedrohung für die Menschheit darstellen können. In der modernen Geochemie ist es allgemein akzeptiert, dass die spezifischen physikochemische Formen entscheidender sind, als das Verhalten der gesamten Konzentration der Spurenmetalle in der Umwelt. Die Definition der Artbildung kann grob als die Identifizierung und Quantifizierung der verschiedenen Formen oder Phasen für ein Element zugeordnet werden. Die chemische Extraktion ist eine gemeinsame Speziierungstechnik bei der die Fraktionierung des Gesamtmetallgehaltes zur Analyse der Quelle anthropogener Metallkontamination und zur Vorhersage der Bioverfügbarkeit von verschiedenen Metallformen dient. Die Philosophie der partiellen und sequenziellen Extraktionsmethode besteht darin, dass insbesondere das Extraktionsmittel phasenspezifisch unter chemischem Angriff unterschiedlicher Mischungsformen steht. Die Speziation von Metall ist wichtig bei der Bestimmung der Toxizität, Mobilität, Bioverfügbarkeit des Metalls und damit ihr Schicksal in der Umwelt und biologischem System. Die Artenbildungsanalyse kann für das Verständnis der Auswirkung auf die menschliche Gesundheit und bei ökologischen Risiken durch die Quantifizierung von Metallspezies bei einem Untersuchungs-standort angewendet werden und anschließend können Sanierungsstrategien für den Standort umgesetzt werden. Mit Hilfe der Spezifizierung wurden Arsen und Kupfer in landwirtschaftlichem Kalkdünger und Thallium in kontaminierten Böden untersucht und in den folgenden Abschnitten im Einzelnen dargestellt.

Zusammenfassung (As)

Die Kontamination der Umwelt durch Schwermetalle belastet terrestrische Ökosysteme für einen langen Zeitraum. Die Ursache der Kontamination liegt in der Verwitterung des Ausgangsgesteins, in welchem sich die Metalle abscheiden. Der weithin beobachtete Anstieg der Spurenelementkonzentration in landwirtschaftlich geprägten Böden wird durch unterschiedliche anthropogene Quellen beeinflusst, so hat die Kalkdüngung eine potentiell schädigende Wirkung auf den Menschen. Das Absinken des Kalkgehalts auf ein natürliches Niveau hätte für viele Böden ein Absinken des pH-Werts und damit ein Absinken der Fertilität zur Folge. Giftige Metalle und Halbmetalle, z.B. Arsen, können Eisen und Mangan aus ihren Oxiden, welche in kleinen Mengen in Kalkstein vorliegen, ersetzen. Somit werden diese unter verschiedenen Umweltbedingungen aus dem Boden ausgelaugt. Die Adsorption von Arsen im Boden hängt hauptsächlich von dessen physico-chemischen Eintragsverhalten ab. Um die unterschiedlichen Arsenspezies in den verschiedenen metallhaltigen Phasen zu bestimmen, wurde eine sequentielle Extraktion benutzt. In fünf Extraktionsschritten wurden jeweils die Arsen-, Eisen- und Mangangehalte mittels HG-AAS und XRF Techniken bestimmt. Die beobachteten Matrixeffekte der Lösung in der HG-AAS Analyse wurden durch die Zugabe von 1% Cystein als Maskierungsreagenz minimiert. Alle Bodenproben enthielten einen deutlich höheren Arsengehalt als das globale Mittel. Dieses Mittel wird bestimmt für Kalkstein, für Kalksteinpresslinge, die zur pH-Wert Verbesserung in Böden eingesetzt werden, und für MAP/DAP Phosphatdünger. Für die drei unterschiedlichen Matrices konnte festgestellt werden, dass Arsen stark an kristalline Eisenphasen bindet. Die direkte Untersuchung der Proben mit röntgenspektroskopischen Methoden wurde für notwendig erachtet, um eine erneute Verteilung des Arsens zwischen Mangan und restlichen Eisenoxiden, in den ersten drei Extraktionsschritten auszuschließen.

Zusammenfassung (Cu)

Diese Untersuchung beschäftigt sich mit den wichtigsten Gastsystemen und Festphasenspezies von Kupfer in landwirtschaftlichen Kalkproben. Hierbei ist Kupfer einerseits ein essentielles Spurenelement, andererseits jedoch kann es bei übermäßiger Anreicherung in Ökosystemen toxisch wirken. Die in der Landwirtschaft häufig angewendete Kalkung der Felder ist ein möglicher Weg um Kupfer in Böden zu akkumulieren. Die Anreicherung findet dabei an den organischen Bodenbestandteilen statt, da diese gute komplexbildende Eigenschaften besitzen. Eine übermäßige Akkumulation von Kupfer hat auf Pflanzen eine phytotoxische und rhizotoxische Wirkung. Die Kupferspeziation wird als wichtige Informationsquelle für den zukünftigen Umgang mit kupferbelasteten Böden betrachtet. Für die Analyse wurde eine modifizierte Version der sequentiellen Extraktion zur Kupferfraktionierung des BCR angewendet, um die Verteilung des Metalls in die verschiedenen Kupferhaltigen Metallphasen zu untersuchen. Kupfer-, Eisen-, Mangan- und Calciumgehalte in vier Extraktionsfraktionen wurden mittels AAS und XRF Techniken untersucht. Alle untersuchten Kalkproben lagen über dem Normalwert von 2-8 mg/kg, ebenso lagen fünf von sechs Messungen eines Phosphatdüngers über dessen Normalwert (1-13 mg/kg). Die Kupferkonzentration von sechs Teilproben waren 12, 41, 69, 137, 140 und 174 mg/kg, von diesen Teilproben überschritten damit drei das sogenannte „soil health tolerance level“ von 100 mg/kg für Kupfer. Alle beobachteten Konzentrationen führen zu der Vermutung, dass überhöhte Kupfergehalte im Kalk, welcher auf nicht kontaminierten Böden ausgebracht wird, zu Vergiftungserscheinungen in Pflanzen führen können. Die Ergebnisse der sequentiellen Extraktion zeigen, dass Kupfer unter sauren und reduzierenden Bedingungen mobilisiert wird. Das Kupfer des ersten Extraktionsschrittes konnte einer Carbonatmatrix oder oxidischen Dendriden oder einer Mischung aus beidem zugeordnet werden. Es ist sehr wichtig zwischen an Carbonaten oder oxidischen Dendriden gebundenem Kupfer zu unterscheiden, da diese beiden Phasen Kupfer unter verschiedenen Umweltbedingungen (z.B. reduzierenden Bedingungen) wieder freisetzen. Eine direkte Messung mittels röntgenspektroskopischer Methoden wird als nächster Schritt für eine weiterführende Kupferspeziation erachtet.

Zusammenfassung (Tl)

Böden aus der Nähe einer Zementfabrik nahe von Lengerich in Deutschland wurden auf ihre Thallium Belastung hin untersucht. Für zwei Probenahmegebiete (Standort 1 und 2) wurde die mobile und gesamte Thallium Belastung gemessen. Die mobile Fraktion des Ober- und Unterbodens an Standort 1 zeigte eine Thallium Konzentration im Bereich 20-130 und 0-100 µg/kg. Die Gesamtkonzentration am Standort 1 für Ober- und Unterboden war im Bereich von jeweils 0,4-2,4 und 0,3-1,3 mg/kg. Die Konzentration der mobilen Fraktion am Standort 2 war für ober und Unterboden jeweils 20-540 und 10-170 µg/kg. Die Gesamtkonzentration an Thallium am Standort 2 war für Ober- und Unterboden im Bereich von 0,8-3,2 und 0,4-1,4 mg/kg. Es wurde eine Semivarianzanalyse der Ammoniumnitratextrakte und damit der austauschbaren Thallium Gehalte des Oberbodens am Standort 1 durchgeführt. Diese Analyse zeigt eine moderate räumliche Abhängigkeit des austauschbaren Thalliums des Oberbodens. Die Ergebnisse zeigen für beide Probenahmegebiete einen unterschiedlichen Grad der Thallium Kontamination. Ein T-Test für gepaarte Stichproben zeigte für die mobile und gesamte Thallium Konzentration einen statistisch signifikanten Unterschied zwischen Ober und Unterboden für beide Probenahmegebiete. Der anthropogene Eintrag ist eine mögliche Quelle der überhöhten Thallium Konzentration des Oberbodens. Für beide Standorte wurden verschieden mögliche Eintragspfade vorgeschlagen, die die Bodenverschmutzung erklären. Die Grenzwerte für mobiles Thallium, festgelegt durch das Bundesjustizministerium, und für den Gesamtgehalt an Thallium, festgelegt durch die Landesregierung von Nordrhein Westfalen, wird in beiden Standorten in jeweils verschieden großen Bereichen überschritten.

Abstract

There is a long history of human using metals in developing an advanced technological society. It has only been realized until the past century that metal's chemical and radioactive properties can pose serious threat to mankind. In modern day geochemistry it is widely accepted that the specific physiochemical forms rather than the total concentration decides the ultimate trace metal behavior in an environment. The definition of speciation can be broadly classified as the identification and quantification of the different forms or phases for an element. Chemical extraction is a common speciation technique in which fractionating total metal content for analyzing the source of anthropogenic metal contamination and also to predict bioavailability of various metal forms. The philosophy of the partial and sequential extraction method is to assume that particular extractant is phase specific under chemical attack on a mixture of forms. Speciation of metal is important in determining metal's toxicity, mobility, bioavailability and hence their fate in environment and biological systems. Speciation analysis can be applied in understanding the impact on human health and ecological risks by quantifying the metal species at a sampling site and subsequently suitable remediation strategies can be implemented for the location. Speciation of arsenic and copper in agricultural lime and thallium in contaminated soils were investigated and revealed in the following sections.

Abstract (Arsenic)

Heavy metals contamination to the terrestrial environment long exists due to the natural weathering of the parent rocks in which causing metal precipitation in the system. The widely observed increase trace element concentrations in agricultural soil due to various human activities such as liming would lead to potential harmful effects on mankind. Natural reduction in lime status for most soils would increase soil acidity and reduce soil fertility. Toxic metals and metalloids such as arsenic have the abilities to scavenge with Fe and Mn oxides present in low grade limestone and leach out from the soils under severe environmental condition. Adsorption of arsenic into the soil system depends greatly on the physicochemical behaviour in which arsenic enters the soil. Sequential extraction method was used to partition different arsenic species in associated with various metal-bearing phases. As, Fe and Mn contents in five extraction steps were determined by HG-AAS and XRF techniques. Solution matrix effect was observed throughout the HG-AAS analysis and minimized with addition of 1% cysteine as masking agent. All soil sub-samples demonstrated much higher As content than the above global average content of arsenic being found in limestone, pellet limestone for soil pH amendment and MAP/DAP phosphate fertilizers with majority of As showed strong binding with crystalline Fe phases. Direct X-ray spectroscopic analysis was deemed necessary because of possible repartitioning of As between dissolved Mn and residual Fe oxides in the first three extractions steps.

Abstract (Copper)

The main host phases and solid speciation of Cu accumulated in agricultural lime samples were determined. Copper is an essential element for life but can be toxic to ecosystem when it is excessively accumulated. Agricultural liming is one of many ways of accumulating copper in soils and as copper is often accumulated by strongly complexing with soil organic matter. Excessive accumulation of copper would cause Cu phytotoxicity and rhizotoxicity of plants and as a result Cu speciation would be essential on providing necessary information on handling with the Cu contaminated soils in long term future. A modified BCR sequential extraction scheme of Cu fractionation was developed and applied in order to partition metals in different Cu metal-bearing phases. Cu, Fe, Mn and Ca contents in four extraction steps were determined by AAS and XRF techniques. All sub-samples demonstrated above usual 2-8 mg/kg Cu content in limestone for soil amendment and five out of six sub-samples revealed higher than typical phosphate fertilizers Cu level (1-13 mg/kg). The Cu concentrations of six sub-samples were found to be 12, 41, 69, 137, 140 and 174 mg/kg. Three out of the six-subsamples exceeded soil health tolerance level of 100 mg/kg for Cu. All the observed concentrations suggested excessive Cu in lime could be loaded on the uncontaminated soil and cause Cu toxicity to plants. The sequential extraction results showed that Cu was able to be mobilized acidic and reducing conditions. Cu identified in the first step could be associated with the carbonate matrix or the oxide dendrites alone, or the combination of both. It is important to distinguish Cu loaded between carbonate matrix phase and oxide dendrites phase as Cu from these two phases could be mobilized under different environmental condition (e.g. reducing). Direct X-ray spectroscopic speciation analysis was considered to be next stage in depth analysis for the Cu speciation.

Abstract (Thallium)

The surveillance of soils with thallium exposure in the vicinity of a cement plant at Lengerich, Germany was undertaken. The results revealed mobile and total thallium concentration at top and sub-soils at two sampling location (location 1 and 2). Top and sub-soils at sampling location 1 showed exchangeable thallium concentration in a range of 20-130 and 0-100 µg/kg. The total thallium concentration at location 1 for top and sub-soils were in a range of 0.4-2.4 and 0.3-1.3 mg/kg respectively. Top and sub-soils at sampling location 2 showed exchangeable thallium concentration in a range of 20-540 and 10-170 µg/kg. The total thallium concentration at location 2 for top and sub-soils were in a range of 0.8-3.2 and 0.4-1.4 mg/kg respectively. Semivariance analysis of top-soils ammonium nitrate extracts targeting exchangeable thallium at sampling location 1 was applied and suggested exchangeable thallium in top-soils was moderately spatially dependent. The results suggested that soils at both sampling sites showed different degrees of thallium contamination. Paired t-test showed mobile and total thallium concentration between top and sub-soils were considered to be statistically significant difference at both sampling locations. The excessive thallium contents found in the surface soils at the two sampling locations were potentially from anthropogenic emission sources. Several possible pathways of causing soil pollution on the sampling locations were proposed. The top and sub-soils thallium contents at two sampling sites contained different size of areas in where exceeding the safety limit of mobile thallium set by the German Federal Minster of Justice and total thallium established by North-Rhine Westphalia of Federal Republic of Germany.

(1.0) Introduction

(1.1.1) Introduction of arsenic

Arsenic (As) is a ubiquitous element existed in many sources in natural environment ranging from atmosphere, soils, rock to natural waters and organisms. Arsenic has long been drawing special attention from the scientific community due to its risks to human health and ecology. Most of environmental As problems existing in the world are the result of mobilization under natural conditions. The environmental toxicity effects are the consequences of arsenic mobilization under natural processes such as weathering reactions, biological activity and a range of anthropogenic activities.

Human activities also have had further contribution of As to natural environment through several of commercial activities such as mining, fossil fuels combustion, wood preservation (Cr-Cu-As salts) and arsenical pesticides, herbicides (As_2O_3) application. Additional anthropogenic As sources can also be found in the following activities of mankind: High-temperature combustion (oil- and coal burning power plants, waste incineration, cement works); glassware production (discoloring agent); electronics industries (admixture in semiconductor production, arsenide as laser material to convert electrical energy into coherent light); ore production and processing (melting and roasting in non-ferrous smelters, melting in iron works); metal treatment (admixture in bronze production, lead and copper alloys); chemistry (dyes and colours, drying agent for cotton, oil and dissolvent recycling).

In modern days, public pay much attention to arsenic due to the observed harmful effects to people in worldwide. Problems are still pandemic in countries such as Bangladesh and India. Arsenic is not considered an essential element of human metabolism, but is commonly absorbed or ingested and present in the body. Inorganic As compounds can be reabsorbed through human lungs and intestines. Prolong exposure of As can possibly induce skin, bladder, liver, kidneys, lungs and prostate gland cancer, as well as coronal heart diseases. The chronic As exposure is the hyperkeratosis on the palms of the hands and soles of the feet as well as excessive pigmentation of the skin at non-sun-exposed body parts. Malnutrition (Zn-depletion) and high amount of humic substances within As-contaminated water have a positive effect on Blackfoot disease.

There are several pathways for human of undertaking arsenic through for example air (inhalation of volatile arsine AsH_3 in swampy areas), food and drinking water consumption. Drinking water which poses the greatest threat to human health is derived from a variety of sources depending on local availability: surface water (rivers, lakes, reservoirs and ponds), groundwater (aquifers) and rain water. It is understood that approximately 30% of the As intake for human consumption goes via drinking water (Appelo and Postma, 1994). It is worth noticed that the World Health Organization (WHO) guideline value for As in drinking water was provisionally reduced in 1993 from 50 to 10 µg/l due to the increasing awareness of the carcinogenicity of As. The EC maximum admissible concentration (MAC) for As in drinking water has also been reduced to 10 µg/l. Both the WHO guideline value and current national standards are quite frequently exceeded in drinking water resources.

(1.1.2) Arsenic speciation and occurrences in natural environment

Arsenic is a steel-gray, brittle, crystalline metalloid with three allotropic forms (e.g. As_2O_3, As_2O_5 and As_2O_4) and a constituent of more than 245 minerals presented in Group 15 of the periodic table existing in various oxidation states (+5, arsenate), (+3, arsenite), (0, arsenic) and (-3, arsine) in the natural environment. Metalloids have properties of both metals and non-metals with tendencies of forming amphoteric oxides and behaving as semiconductors. Arsenic however, tends to behave like a group V A elements than heavy metals. Elemental arsenic is considered to be non-poisonous. As^{3+} (exists as $H_3AsO_3/H_2AsO_3^-$ in pH range 4-9) exists stably in reducing conditions such as regularly flooded soils and As^{5+} ($H_2AsO_4^-$ or $HAsO_4^{2-}$) presents in a stable form in oxygen-rich environments and well-drained soils and are the main inorganic forms of As in most contaminated soils and sediments. As^{5+} is less soluble, mobile and toxic than As^{3+} due to its stronger association with soil solids. As^{5+} (AsO_4^{3-}) compounds are usually dominating in aerobic soils whereas As^{3+} compounds mainly occur in slightly reduced soils. Organic arsenic species (e.g. monomethylarsonate, dimethylarsenate and arsenobetaine), though toxic, are usually quantitatively insignificant towards the solid phase of forest soils because microorganisms easily degrade these compounds to As^{5+}.

The total amount of As in the earth crust is estimated to be 4.01 x 10^{16} kg (Matschullat, 2000). The crustal abundance of arsenic in natural source is around 1.5-2 mg/kg (National Research Council, 1977). The global average concentration of As in uncontaminated soils is around 5 mg/kg (Dragun and Chiasson, 1991). The following table (1) lists As concentration values obtained in different types of soils.

Table (1) Table shows some observed As concentrations in different soils

Soil type	Average As concentration and/range (mg/kg)	No. of analyses	Reference
Various	7.2 (0.1-55)	327	Boyle and Jonasson (1973)
Peaty and bog soils	13 (2-36)	14	Ure and Berrow (1982)
Acid sulphate soils (Vietnam)	6-41	25	Gustafsson and Tin (1994)
Acid sulphate soils (Canada)	1.5-45	18	Dudas (1984); Dudas et al. (1988)
Soils near sulphide deposits	126 (2-8000)	193	Boyle and Jonasson (1973)

The above As concentrations found in soils are heavily depending on different factors which are local geological conditions, concentration in parent rock materials and a range of industrial activities (e.g. smelting).

Soils can be viewed as an inhomogeneous medium with the humus layer serves as a natural biogeochemical barrier that suppresses the percolation of the element with the seepage water, an as a result strongly accumulates the element. High As concentrations in natural soils are usually associated with sulfide minerals (chalcophilic) and their weathering products. The major As-bearing minerals are mixed sulfides of FeAsS, NiAsS, CoAsS as well as other two-valent metals (e.g. $FeAsS_2$, AsS, NiAs and CoAsS). All these minerals are generally believed to be formed under high temperature especially like arsenopyrite can be derived from hydrothermal solution at 100^oC or more of conditions in the earth's crust. The rules which governing the chemistry and mobility of arsenic in soils are depending on several factors such as soil solution chemistry, pH, redox conditions, soil solid composition, As-bearing phases, adsorption and desorption, biological transformations. The soil constituents related to As mobility are usually oxides of Fe, Al and Mn, clay minerals, and organic matter. Arsenic in soils may distribute among various soil components in different physicochemical forms which are associated with various soil constituents. The prime concern is the chemical associations of As with various soils solid phases instead of its total concentration which affects its mobility, bioavailability and toxicity to the biosphere. The contents of Si, Al, and Fe reflect the intensity of the transformation of primary minerals and the formation of clay ones. Compounds of biophilic elements characterize the fertility and supply of soils with available nutrients. The distribution of pollutants between soil components determines the environmental consequences of soil pollution.

(1.1.3) Arsenic in minerals

Arsenic occurs in most minerals such as elemental As, arsenides, sulphides, oxides, arsenates and arsenite. A list of some of the most common As minerals can be shown in following table (2), (Smedley 2002).

Table (2) Table shows major As minerals in nature

Mineral	Composition	Occurrence
Native arsenic	As	Hydrothermal veins
Niccolite	NiAs	Vein deposits and norites
Realgar	AsS	Vein deposits, often associated with orpiment, clays and limestones, also deposits from hot springs
Orpiment	As_2S_3	Hydrothermal veins, hot springs, volcanic sublimation products
Cobaltite	CoAsS	High-temperature deposits, metamorphic rocks
Arsenopyrite	FeAsS	The most abundant As mineral, dominantly in mineral veins
Tennantite	$(Cu,Fe)_{12}As_4S_{13}$	Hydrothermal veins
Enargite	Cu_3AsS_4	Hydrothermal veins
Arsenolite	As_2O_3	Secondary mineral formed by oxidation of arsenopyrite, native arsenic and other As minerals

Claudetite	As_2O_3	Secondary mineral formed by oxidation or realgar, arsenopyrite and other As minerals
Scorodite	$FeAsO_4 \cdot 2H_2O$	Secondary mineral
Annabergite	$(Ni,Co)_3(AsO_4)_2 \cdot 8H_2O$	Secondary mineral
Hoernesite	$Mg_3(AsO_4)_2 \cdot 8H_2O$	Secondary mineral, smelter wastes
Haematolite	$(Mn,Mg)_4Al(AsO_4)(OH)_8$	
Conichalcite	$CaCu(AsO_4)(OH)$	Secondary mineral
Pharmacoside	$Fe_3(AsO_4)_2(OH)_3 \cdot 5H_2O$	Oxidation product of arsenopyrite and other As minerals

The most abundant As ore mineral is arsenopyrite (FeAsS) with the chemistry of As follows closely with sulphur. Arsenic can also be found in common rock-forming minerals with greatest concentrations of the element in sulphide minerals in which pyrite is the most abundant. Arsenic is usually involved with crystal structure of many sulphide minerals as a substitute for S. High As concentrations can also be found in many oxide minerals and hydrous metal oxides, either as part of the mineral structure or as sorbed species. It is also noticed that arsenic presents in phosphate, silicate and carbonate minerals although their abundances and concentrations are far less compared with oxide minerals.

(1.1.4) Toxicity and mobility of arsenic

Most of the arsenic compounds are toxic such as arsine gas, arsenic trioxide, sodium arsenite and sodium arsenate. Both of the As^{3+} and As^{5+} area capable of inhibiting the energy-linked functions of the mitochondria and also causing inhibition of DNA damage repair. Chronic arsenic poisoning can arise numerous symptoms such as anorexia, hyperkeratosis, cardiovascular diseases and etc. Acute arsenic poisoning may lead to muscle cramps, abdominal pain, renal failure and etc. Human body to certain amount can detoxify the inorganic As^{3+} and As^{5+} compounds by methylation.

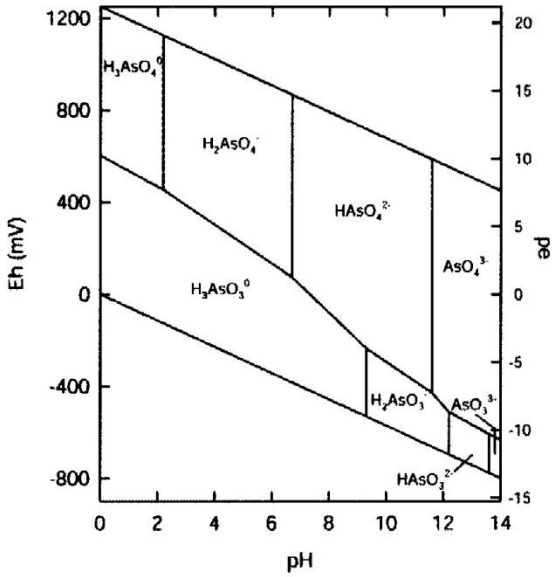


Fig. (1) Eh-pH diagram for aqueous As species in the system As-O_2-H_2O at 25 ^oC and 1 bar total pressure (Section 8.1 Ref. 67)

The above figure (1) shows redox potential (Eh) and pH as key factors in controlling As speciation. For example $H_2AsO_4^-$ is a dominant species at low pH (<6.9) under oxidizing conditions. On the other hand, $HAsO_4^{2-}$ becomes dominant in higher pH. Uncharged arsenite species $H_3AsO_3^0$ predominates in reducing conditions with pH less than 9.2.

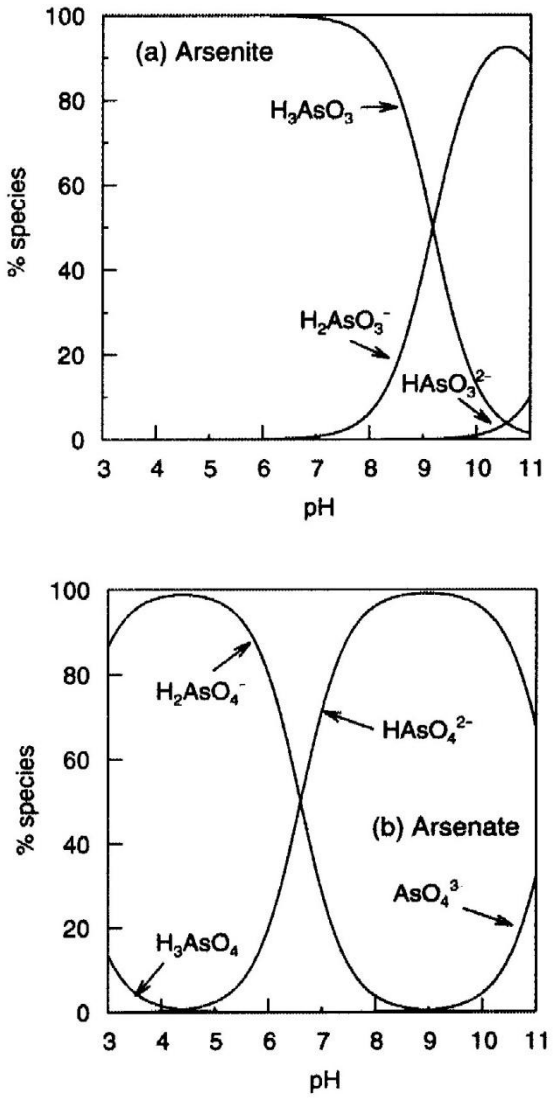


Fig. (2) Arsenite and arsenate speciation as a fuction of pH (ionic strength of about 0.01 M). Redox conditions have been chosen such that the indicated oxidation state dominates the speciation in both cases. (Section 8.1 Ref. 67)

The above figure (2) shows the distribution of As species as a function of pH. It is however important to notice that degree of protonation is an important factor in determining the speciation. Under high concentrations of reduced sulphur can cause significant present of As-sulphide species and on the contrary precipitation of orpiment and realgar favors in reducing acidic conditions.

Species of soil compounds and their contents, the pH value and the redox potential all play an important role for the mobility of arsenic species in soils. Arsenic compounds can adsorb to oxides and hydroxides of Fe (III), Al (III), Mn (III/IV) and clay minerals. High redox potential and acidic condition can keep arsenic out of mobilization. Arsenic can be mobilized when Fe^{3+} and $Mn^{3+/4+}$ are reduced. The adsorption of arsenic by soils depends on the content of amorphous iron oxides and the five most important Fe (III) oxides/hydroxides are Fe(III) hydroxide ($Fe(OH)_3$), goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (γ-FeOOH), and haematite (Fe_2O_3). The fixation of arsenic is highly influenced by the specific surface and crystallinity of the Fe oxides. As^{5+} can form inner-spherical bi-dentate surface complexes and monodentate surface complexes can also be formed when adsorbing to $Fe(OH)_3$. Anionic arsenic compounds can be fixed by hydrated Fe^{3+} oxides in aquatic environment. In addition, arsenic can also co-precipitate with $Fe(OH)_3$. Moreover, sorption of arsenic in soils can be depended on the presence of amorphous hydrated aluminum oxides, Mn oxides present in soils, existence of calcium ions (e.g. change of the surface charge characteristics of the soils) on As^{5+} adsorption. Furthermore, phosphates can suppress As^{3+} and As^{5+} sorption by soils especially when soils contain low amounts of iron oxides (Bissen, 2003).

(1.2.1) Introduction of copper

Copper is a metal existing in different oxidation state (0, +1 and +2) with +2 the most common one. Copper contains the two stable isotopes ^{63}Cu and ^{65}Cu. It is an essential trace element for all the living organisms including humans, plants, animals and micro-organisms. Copper can be found naturally in most soils, fruits and vegetables. Human requires regular intake of copper with the element playing key roles in the production of blood haemoglobin. Copper in plant is used for seed production, disease resistance and regulation of water. In natural environment copper is relatively abundant in the earth crust with most of the copper occurring in unavailable mineral form. The worldwide emission of copper from natural sources were estimated and showed at the follows (table 3) (modified Pacyna 1986).

Table (3) Table shows worldwide emission of copper from natural sources

Sources	Annual emission of copper (kg $x10^6$)
Windblown dust	12
Volcanogenic particles	4
Forest wild fires	0.3
Vegetation	2.5
Sea salt	0.1
Total	18.9

There are numerous human activities which involve usage of copper such as textiles, electrical conductors like copper wire and electromagnets, coins and cooking utensils. Copper can be alloyed with nickel (e.g. cupronickel) and used as corrosive resistant materials in shipbuilding. Copper compounds are active ingredients of pesticides and fungicides (e.g. Bordeaux mixture: $CuSO_4.5H_2O + Ca(OH)_2$). Copper sulphate is the most common source of fertilizers for copper-deficient soils where the soils are used for growth of vegetables. CuO and mixtures of $CuSO_4$ and $Cu(OH)_2$ are also used as copper micronutrients in agriculture. Copper based compounds such as chromate copper arsenate (CCA) were widely used as wood preservatives. Copper according to EMRC (1992) was the fifth most-valued mineral commodity produced in Canada and accounted for 5.8% of the total value of Canadian mineral production.

Copper occurs in a wide range of mineral deposit as primary and secondary minerals. Most copper occurs in the form of sulphide minerals chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), bornite (Cu_5FeS_4) and tetrahedrite ($(CuFe)_{12}Sb_4S_{13}$). During chemical weathering the primary copper sulphide minerals, secondary minerals maybe formed cuprite (Cu_2O), malachite ($Cu_2(CO_3)(OH)_2$), azurite ($Cu_3(CO_3)_2(OH)_2$, brochantite ($Cu_4SO_4(OH)_6$), antlerite ($Cu_3SO_4(OH)_4$. The following table (4) showed the range of copper concentration (ppm) in igneous and sedimentary rocks.

Table (4) Table shows copper concentrations in igneous and sedimentary rocks (modified Cannon et al. 1978)

Rock type	Copper concentration range (ppm)
Basaltic igneous	3-160
Granite igneous	4-30
Shales and Clays	18-120
Black shales	20-200

The association form of copper can be affected by various environmental conditions such as pH, temperature, redox potential, organic matter decomposition, leaching and ion exchange processes and microbial activity. The availability of copper for biological uptake and transport in the environment is controlled by processes at solid-water interfaces and copper speciation in solution. Copper sulphide minerals can be oxidized and the resultant Cu^{2+} ion can be released in complexed hydrated form such as $Cu(H2O)_6^{2+}$. In aqueous phases copper is predominantly in the more stable Cu^{2+} state and when in contacts with water copper can form $[Cu(H_2O)_6]^{2+}$ ion and further complexes with inorganic and organic ligands. The final copper complexes can be absorbed onto clays, sediments and organic particulates. pH, copper concentrations, competing cations and the adsorbent's properties are the factors influencing copper adsorption. Desorption of copper can also occur with the present of Ca^{2+} and Mg^{2+} competing cations. Most of the copper found in natural water is partitioned in sediments. The physiochemical processes determine the transport and distribution of copper and its complexes in soil are adsorption, aqueous-phase solubility, leaching and lateral movement (aeolian and fluvial). Minimal copper can be lost through volatilization and the copper complexes can be broken down to copper ions by physical and biological processes. All these processes control dissolved copper concentrations, copper mobility and bioavailability in the environment. The copper ions in solution can be complexed, precipitated and adsorbed. Copper usually exists in CuO and Cu_2O in high temperature combustion to the atmosphere. Copper in atmosphere can be removed by bulk deposition and wet/dry deposition mechanisms.

(1.2.2) Copper concentrations in unpolluted soils

The amount of copper in soil is depending on the parental rock, distance from natural ore bodies and manmade air emission sources. The copper content in soils is commonly range from 2 to 100 mg/kg (Allaway 1968) with an average value of 30 mg/kg. Various anthropogenic and natural sources such as copper mining, metal smelters, waste incineration, agricultural and industrial application can contribute to the presence of copper in atmosphere and soil. Copper concentrations in soil can vary between soil type, soil amendments, distance from anthropogenic sources, distance from natural ore bodies and composition of bedrock and parent material. According to the ministry of the environment Ontario, Canada the background concentrations of copper in Ontario soils are on average less than 25 mg/kg with exceptional circumstances at 85 mg/kg. The average copper concentration in Canadian soil is estimated to be 20 mg/kg with a range between 2 and 100 mg/kg (British Columbia Ministry of the Environment, Lands and Parks 1992). Reave et al. 2006 reported the total copper contents of 4179 samples from 946 Scottish soil profiles showed the derived mean of copper concentration from all the samples is 10 mg/kg and the normal copper concentration range is between 0.93–110 mg/kg. The copper contents of Tibetan soils were recorded by Xiaoping et al.2002. The collected 205 soil samples from the remote area of Tibet Plateau in 5 soil classes (0–20 cm) were analyzed with the average content of Cu was 19.6 mg/kg (CV=49. 28%). Tibet is one of the few places in this world that are least influenced by human activities and an ideal location of investigating natural background copper concentration and can possibly serve as a reference source for the world. McKeague et al. (1979) reported the highest mean copper concentrations were in Cordilleran region (46 mg/kg) whereas the Canadian Shield contained only a mere 12 mg/kg. The mean copper concentration from all regions in Canada was 22 mg/kg (McKeague and Wolynetz 1980). Mean copper concentrations in rural parkland and old urban parkland surface soils samples (0-5 cm) were found to be 16 and 26 mg/kg respectively by the Ontario Ministry of the Environment and Energy. The city of Trondheim in Norway conducted a soil geochemistry survey in 1994 and 2004 by analyzing 321 surface soil samples (Andersson et al. 2010), the average copper concentrations were found to be 42 mg/kg and 39 mg/kg respectively. In the Peace River, Alberta the surface and subsurface soils mean total copper concentration was found to be 22.1 mg/kg with samples ranging from gleysols, Luvisolic and Solonetzic soils to Podzolic soils (Soon and Abboud, 1990). Lai et al. (2010) conducted a field investigation to evaluate copper

contents in vineyard soils at central Taiwan and the copper concentration was range from 9.1 to 100 mg/kg. Soils samples collected from A and C horizons in southern and western Manitoba were in average of 25 mg/kg (CCME 1997). In southwestern Ontario the soil samples collected from agricultural watersheds, the soils from various horizons (Ap, B and C) showed mean total copper concentrations no more than 27.4 mg/kg (Whitby et al. 1978).

(1.2.3) Copper concentrations in polluted soils

A strong correlation was found between base metal levels in peat and distance from the base metal mining and smelter complex in Flin Flon, Canada (Zoltai 1988). Surface soils in the vicinity of copper smelters were found to be heavily contaminated by atmosphere fallout. Average total copper concentrations were often well above 1000 mg/kg (Hazlett et al. 1983; Hutchinson and Whitby 1974; Kuo et al. 1983). At Coniston, near Sudbury, Ontario, maximum concentrations of copper reached 9700 mg/kg within 0.41 km of the smelter site (Hazlett et al. 1983). The calculated mean for the Cu background level of 25 soil samples in the vicinity of the industrial complex of Port Kembla, NSW, Australia with a copper smelter, steelworks and associated industries was 49 mg/kg at a depth of 0–5 cm with maximum reached 599 mg/kg and 38 mg/kg at the depth of 5-20 cm with maximum reached 1597 mg/kg. Copper concentrations were high closer to the contamination sources and decreased rapidly within the first 5 km, the Cu decrease trend followed an exponential function and the Cu contamination complex was considered to be within 4 km from the complex (Martley et al. 2004). Soils exposed to emissions from the Ventanas copper smelter in central Chile were collected and analyzed. Total copper concentrations in the topsoils were found in a range of 310-640 mg/kg in contrast with 30–60 mg/kg range at depth 30–60 cm (Neaman et al. 2009). Copper in agricultural soils next to over 40 years mining activities at the Jinchang, Gansu province, China showed total Cu content ranged from 131 mg/kg to 828mg/kg with mean total copper concentration 277 mg/kg (Shengli et al. 2009).

Several studies reported copper-enriched roadside soils and dust well over background levels. Mean copper concentrations in Moncton, New Brunswick, roadside soils were 45 mg/kg and ranged from 6 to 162 mg/kg (Cool et al. 1980). Roadside soils and dusts from the UK and New Zealand had higher mean concentrations ranging from 42.5 to 115 mg/kg (Harrison et al. 1981; Thornton et al. 1985; Ward 1990; Ward et al. 1977). Christoforidis et al. (2009) analyzed 96 street dusts and 96 roadside soils samples from three different localities (urban, industrial, peripheral) of the city of Kavala (Greece) and found the mean copper value in street dust was 123.9 mg/kg and roadside soil at 42.7 mg/kg. In general, street and highway dusts contained higher copper concentrations than the corresponding roadside soils.

Total copper was studied in 170 surface layers of soils from seven vineyard regions located in the NWIberian Peninsula (Rías Baixas, Ribeira Sacra, Ribeiro, Monterrei, Valdeorras, O Bierzo and Vinhos Verdes) in Spain. Total Cu content in Ribeiro (248±130 mg/kg) and Ribeira Sacra (259±118 mg/kg) soils were significantly higher than those observed for the rest of the vineyard regions (169±90, 139±122, 115±42, 103±42 and 100±48 mg/kg in Valdeorras, Rías Baixas, O Bierzo, Vinhos Verdes and Monterrei, respectively) (Fernández-Calviño et al. 2009). The increased Copper concentrations were due to long term application of Cu based fungicides. Copper contaminated non-active vineyard soils (168 mg/kg) exceeding EU limit from small wine producers in Marefy area at the Czech Republic was reported. The highest Cu concentrations were found in the superficial soil layers (0–20 cm) and decreased with depth. Copper possessed with non-biodegradable nature, long-term biological half-lives and was immobilized by soil sorption complex. (Komárek et al. 2008). Extremely high concentrations exceeding 3000 mg/kg of Cu have been documented by Mirlean et al. (2007) in Brazilian vineyard soils. Hog manure and sewage sludges are added to soils as a source of essential plant nutrients and organic matter however can also contain high levels of copper. Agricultural amendments can enrich the soils with copper in a range of 50-8000 mg/kg (Ross 1994). High Cu concentrations in soils can potentially contaminate the groundwater and cause serious threat to human community.

(1.2.4) Copper in plant, micro-organisms, animal and the relevant toxicity

The process of metal uptake and accumulation by different plants depend on the concentration and solubility of available metals in soil, and plant species growing on these soils (Barman et al., 2000). Normal concentrations of copper in mature leaf tissue range from 5 to 30 mg/kg (Kabata-Pendias and Pendias 1992) with 20 mg/kg copper concentration at shoots is considered to be at health level. Shengli et al. (2009) demonstrated the sequences of Cu average concentrations in different parts were roots > leaves > shells > grains > stocks for the wheat plants grown in contaminated soils from the oasis, northwest China. Brun et al. (2003) found that increased Cu concentrations affected the phenology, growth and reproduction of some ruderal plant species. In general the copper in plants depend on the soil copper concentration, soil properties (e.g. pH, redox potential), microbial activity of the soil, environmental conditions and the species of the plant (NAS 1977).

The transfer coefficient of copper from soil to plants is relatively low compared to other metals with the order range from 0.1-1 (Kloke et al. 1984). Jeyakumar et al. (2010) showed polplar treated with high copper soil concentrations would result 0.8 bio-concentration factor in maximum. Shengli et al. (2009) showed the average bio-concentration factor of Cu in wheat plants were root > leaves > shell > grain > stock with average range between 0.02-0.25. Plants demand copper in numerous metabolic processes such as oxidation, photosynthesis and protein metabolism. Copper often contributes different roles in CO_2 assimilation and ATP synthesis. Insufficient uptake of copper can lead to wilting, white twisted tips and disturbance of lignifications. This leads to plant growth retardation and leaf chlorosis (Lewis et al. 2001). For various cereals, legumes, and citrus plants, the deficiency limits range from 0.8 to 3.0 mg/kg. Excess of Cu in soil plays a cytotoxic role, induces stress and causes injury to plants (Kabata-Pendias and Pendias 1992).

Copper toxicity affected the growth of Alyssum montanum (Ouzounidou 1994). Copper and Cd in combination have affected adversely the germination, seedling length and number of lateral roots in Solanum melongena (Neelima and Reddy 2002). Snap beans (Phaseous vulgaris) were exposed to $CuSO_4$ in concentration range 0 to 2000 mg/kg in Yolo loam soil (Wallace et al. 1977). Leaf yield at 200 mg/kg Cu concentration was decreased by 26% and at 500 mg/kg the growth of P.vulgaris was stopped completely. Patterson and Olson (1982) tested the effect of copper as $CuSO_4$ on radical elongation in seven tree species grown on a coarse loamy mixed soil. Paper birch (Betula papyrifera) was most sensitive with an 18% decrease in radical elongation when compared to controls at 50 mg/kg. Guo et al. (2010) showed reduced Cu toxicity assessed by barely root elongation with addition of EDTA, NTA. The $CuNTA^-$ and $CuEDTA^{2-}$ complexes were not toxic to barely root elongation. Red pine grown in typical Borohemist soils was much less affected by the addition of high copper concentration due to the higher organic matter content in the typical Borohemist soil when compared to the typical Dystrochrept.

Copper is an essential nutrient for all animals. Copper deficiencies are not unknown and the most common symptons are hypocupremia and inadequate absorption by animals. In western Canada (Brockman 1977; Gooneratne and Christensen 1989) for cattle a liver copper concentration of <6 mg/kg ww (25 mg/kg dry weight) is regarded as a probable indication of copper deficiency (Gooneratne and Christensen 1989). In a survey of 256 Saskatchewan slaughter animals, Gooneratne and Christensen (1989) determined that approximately 48% had liver copper concentrations below 25 mg/kg dry weight.

Interest has been developed in the use of earthworms as an indicator of environmental contamination. Various copper compounds on the reproduction and growth of earthworms had been studied and found out the toxic effects on growth in decreasing order are: nitrate > chloride > acetate = carbonate > sulphate > oxide. Mortality (LC_{50} values), reproduction (cocoon production) and change in body mass are the three most common parameters monitored to evaluate the effects of copper on earthworms (Malecki et al., 1982). Physical properties such as solubility can be a contributing factor to different copper toxicity. Ma (1982) studied the effect of copper chloride on mortality to the earthworm species L. rubellus in a sandy loam soil and found out the LC_{50} in 1000 mg/kg with no observed effect concentrations at 150 mg/kg. Arnold et al. (2009) showed that with an increase of using EDTA as chelating agent could reduce earthworm mortalities in which consistent with the decrease of free Cu^{2+} concentrations. Huang et al. (2009) studied earthworms being exposed to quartz sand percolated with different concentrations of Cu and ciprofloxacin (CIP). The results suggested that with increased application of CIP would decrease free Cu^{2+} ions in solution and mortalities of earthworm. Copper contents in earthworms could increase with CIP resided in heat-stable proteins fraction.

Increased Cu concentrations especially with free Cu^{2+} ions can be to a great extent adversely affecting soil microorganism numbers, diversity and activity (Dumestre et al., 1999). Jeyakumar et al. (2010) showed copper was toxic to soil microorganisms between 12-226 mg/kg Cu addition. Parmelee et al. (1993) conducted a soil microcosm toxicity study for several chemicals on two soil fauna communities (nematodes and microarthropods). Soil from the A-horizon of a mature oak-beech forest was used (CEC = 6.2 meq/100 g, pH = 3.8) as the test medium on which $CuSO_4$ was applied at 0, 100, 200, 400 and 600 mg/kg. The most sensitive organisms were omnivore-predator nematodes and mesostigmata microarthropods, which demonstrated a statistically significant population decline relative to controls at 100 mg/kg. The total nematode and microarthropod population declined when the $CuSO_4$ concentration was greater than 200 mg/kg.

One route of copper exposure in animals is through dietary consumption of soil. Ingested copper can be accumulated in the liver and kidney. High intake level of copper can be de-metabloised with researchers proposed sulphur normally bound within proteins can be released by the microbial flora and be free to combine with dietary copper to from insoluble CuS and then eliminated in the feces. Animal such as sheep are particularly intolerant of excess dietary copper in a result of their inability to maintain copper homeostasis. Chronic exposure to excess dietary copper culminates in acute toxicological symptoms such as haemolysis, jaundice, and/or death. Cattle in contrast are intolerant to low dietary copper levels but tolerate relatively high dietary copper concentrations before exhibiting toxicological symptoms. Swine are relatively tolerant to high dietary copper levels.

Copper is an essential nutrient in humans and animals and is required in many enzymatic reactions. Intake of copper that seems to be adequate and safe is 2.0 mg/d in Canada (HWC 1990) and 1.5-3.0 mg/d in the United States (NAS 1989). The total amount of copper in an adult body is estimated to be 70-80 mg (Leichtmann and Sitrin 1991). Copper can be absorbed in the stomach and small intestine (Leichtmann and Sitrin 1991), in humans, with a dietary intake of 1-3 mg/d, the overall absorption ranges from 25 to 40% of the administered oral dose (Turnlund et al. 1989). Copper can be absorbed from the gastrointestinal tract as ionic copper or bound to amino acids. Absorbed copper can loosely bind to plasma albumin and amino acids in the portal blood circulation and is taken to the liver (Alt et al. 1990; Marceau et al. 1970; Winge and Mehra 1990). In the liver, copper is incorporated into ceruloplasmin and released into the plasma (Alt et al. 1990; Leichtmann and Sitrin 1991). The metabolism of copper consists mainly of its transfer to and from various ligands, most notably sulfhydryl and imidazole groups on amino acids and proteins. In the liver and other tissues, copper is stored bound to metallothionein and amino acids and in association with copper-dependent enzymes (Abdel-Mageed and Oehme 1990a; Winge and Mehra 1990). Copper in liver cells are predominantly in lysosomes and cytosol (Kumaratilake and Howell 1989a). Bile is the major pathway for the excretion of copper (Leichtmann and Sitrin 1991; Winge and Mehra 1990). Under normal circumstances 0.5%-3.0% of daily copper intake is excreted into the urine (Cartwright and Wintrobe 1964). The regulation of the copper balance in the body appears to be controlled by both the absorption and excretion mechanisms.

Hepatotoxicity of copper in animals has been investigated with most prominent toxicity effect is centrilobular necrosis followed by regeneration (ATSDR 1990). Acute LD_{50} values for rats range from 66 to 416 mg/kg bw depending on the chemical form of copper (Janus et al. 1990). Short term toxicity of copper in animals can lead to decreased body weight gain, anorexia, hepatotoxicity, renal toxicity and death (Boyden et al. 1938; Haywood 1980, 1985; Haywood and Comerford 1980; Haywood and Loughran 1985; Haywood et al. 1985; Rana and Kumar 1980; Kumar and Sharma 1987; Epstein et al. 1982). High intake of copper (1500 ppm) for male rats can induce damage to the liver and kidney (Fuentealba et al. 1989 a, b) with the copper being accumulated within the nucleus can directly injure the cell's organelle and lead to the death of the whole kidney and liver cells. Copper can penetrate the placental barrier into the fetus (Adelstein and Vallee 1961; Suzuki et al. 1990). Low levels of copper sulphate in diet can stimulate embryonic development whereas high levels can increase fetal mortality, reduce weight and produce malformations (lecyk 1980).

Ingestion of excess copper to human adults can cause centrolobular necrosis and necrosis of renal tubular cells. Several suicide cases have been reported with intaking copper sulphate (Chuttani et al. 1965). Gastrointestinal, hepatic and renal effects could happen following the consumption of copper-contaminated water with copper sulphate in attempted suicide cases. Acute gastrointestinal effects with various symptoms such as vomiting, diarrhea, nausea, abdominal pain and metallic taste in the mouth were observed when human exposuring Cu^{2+} in a range of 0.07-1421 mg/kg. (Chuttani et al. 1965; Dash 1989; Holleran 1981; Jantsch et al. 1984-1985; Karlson and Noren 1965; Klein et al. 1971; Manzler and Schreiner 1970; Nicholas and Brist 1968; Semple et al. 1960; Walsh et al.1977). World Health Organization estimated the fatal oral human dose of various inorganic copper salts is approximately 200 mg/kg bw with a considerable variability in individual sensitivity.

In West Germany, 21 patients in 15 families were using drinking water from wells with low pH values (5.0-6.2) and highly contaminated with copper after passage through copper pipes (Eife et al. 1989). Eleven patients died between 8 and 13 months of age and six survived with liver cirrhosis. Vineyard sprayer's lung disease was linked with using "Bordeaux mixture" (1%-2.5% solution of basic copper sulphate neutralized by lime) as pesticide. Factory workers who exposed to copper dust or fumes could induce metal fume fever with symptoms such as chills, fever, aching muscles and headache. The regulation of copper balance in the body can be controlled by both the absorption and excretion mechanisms. Human can regulate copper balance by absorption and excretion mechanisms with absorption range in 25-40% orally admitted copper at dietary intake 1-3 mg/d. Acute exposure to copper causes nausea and vomiting in humans at doses 120 µg/kg bw (CCME, 1997). The oral lethal dose for human adults is estimated to be between 50 and 500 mg/kg bw (Janus et al. 1990).

It has been identified that four groups of people may be at a greater risk of copper overexposure/loading: people with Wilson's disease, young children, occupationally exposed workers and individuals with glucose-6-phosphate dehydrogenase (G-6-DP) deficiency. Table (5) shows the general Canadian population being divided into five age classes: infants (birth to 6 months), preschoolers (7 months to 4 years), school-age children (5 to 11 years), adolescents (12 to 19 years), and adults (20 years and older), daily intakes of copper for each age class of the general population were estimated. Copper does not show any significant to be teratogenic or carcinogenic. Chronic exposure in humans resulting in toxic levels is rare. A sufficient intake of copper is desired to maintain good health.

Table (5) Table shows typical copper intake values for the general Canadian population (CCME 1997)

Age class (years)	Body weight (kg)	Air intake (m^3d^{-1})	Water intake† (Ld^{-1})	Soil/dust intake‡ (mgd^{-1})
Infants (birth-6 months)	7	2	Breast fed: 0/0 Formula fed: 0.2/0.75	20
Preschoolers (7 months – 4 years)	13	5	0.2/0.8	80
School-age children (5-11 years)	27	12	0.3/0.9	20
Adolescents (12-19 years)	57	21	0.5/1.3	20
Adults (20+ years)	70	23	0.4/1.5	20

* Reference values for average body weights and air and water intakes were obtained from Human Health Risk Assessment for Priority Substances (HC 1994). The average soil intake estimates were taken from Angus Environmental Limited (1991).

†Water intakes are presented separately as tapwater/tapwater+tapwater-based beverages such as coffee, tea, and reconstituted beverages. Breast-fed infants were assumed not to require additional liquids during the first 6 months. Formula-fed infants are assumed to consume 750 mL of formula made from powdered formula and 750mL tapwater. For the present exposure assessment, the lesser water intake values were chosen because drinking water was already included in water-based food items. Infants exclusively formula-fed with ready-to-serve formula were assumed to consume no tap water. Infants fed a mixed diet were assumed to consume 0.2 L water per day on top of the water already included in foods.

‡Assuming that soil ingestion occurs outdoors for 4 h per day, and that dust ingestion occurs indoors for 20 h per day.

(1.2.5) Existing guidelines of copper in soils and criteria in various media

European Union (EU) recommends warning legislative limit of copper concentration in soil is 50 mg/kg and the critical legislative limit at 140 mg/kg (values above which the application of sewage sludge is not suitable; Council Directive 86/278/EC, 1986). According to the Ministry of the Environment of the Czech Republic (regulation number 13/1994), the limit values of copper concentration in coarse textured agricultural soils (<∼20% clay) is 60 mg/kg and for agricultural soils with high clay contents (>∼20% clay) is 100 mg/kg. In Australian and New Zealand a site is considered to be contaminated if the total copper concentrations in soil exceeding 60 mg/kg with environmental investigation needed (Pietrzaka and McPhail, 2004). In India the proposed safety limit of copper in agricultural soils should be in a range between 135-270 mg/kg (Awashthi 2000).

The Canadian Council of Ministers of the Environment (CCME) interim soil assessment criterion for copper was set at 30 mg/kg for dry soil, adopted from the British Columbia Ministry of the Environment A-level criterion (BC MOE 1989) for soils with >10% clay. The province of Quebec recommends an assessment value of 50 mg/kg dry matter (MENVIQ 1988). The determined CCME interim criteria for the remediation of copper in agricultural, residential/parkland, and commercial/industrial land sites were 150, 100, and 500 mg/kg respectively (CCME 1991). The CCME interim criteria of 150 mg/kg for agricultural land remediation were adopted from the Ontario Ministry of the Environment agriculture/residential/parkland value for coarse soils (CCME 1991). Soil concentrations above this value indicate the need for remedial action. The CCME interim criteria for the remediation of residential/parkland and commercial/industrial land sites were adopted from British Columbia's B-level and C-level criteria (BC MOE 1989).In British Columbia the A, B and C-level soil quality criteria of 30, 100 and 500 mg/kg dry soil based on the Netherlands ABC approach (BC MOE 1989). The recommended levels are in similar with Quebec's A, B and C-level values in which set at 50, 100 and 500 mg/kg dry matter. Exceeding the above values require further investigation and remediation procedure. Under the Ontario Ministry of the Environment and Energy the background copper concentration on rural land is 41 mg/kg compared to 65 mg/kg on old urban land (OMEE 1994a). The authority proposed subsurface soil cleanup with copper concentration exceeding 225 mg/kg.

Various authorities such as United Kingdom's Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL) suggested the safety threshold level of copper should not be above 130 mg/kg. In New Jersey a remediation criterion of 170 mg/kg copper in soil for residential sites is required. (NJDEP 1990). Across Netherlands (HSPE 1994) a soil target value of 36 mg/kg of copper was deemed negligible risks to the environment whereas an intervention value of 190 mg/kg would require urgent cleanup process of the pollution.

According to Canadian Council of Ministers of the Environment (1997) a soil quality guidelines were developed to protect four different types of lands: agricultural, residential/parkland, commercial and industrial (table (6). The threshold effects concentration (TEC), the effects concentration low (ECL), the nutrient and energy cycling check, and the soil quality guidelines for soil contact and soil and food ingestion can be calculated. Further details of calculation can be referred to CCME 1997.

Table (6) Table shows environmental and human health guidelines of copper (CCME 1997)

Guideline	Agricultural (mg/kg)	Residential/parkland (mg/kg)	Commercial (mg/kg)	Industrial (mg/kg)
TEC or ECL				
20^{th} percentile	62	62	Not applicable	Not applicable
25^{th} percentile	63	63	100	100
30^{th} percentile	80	80	100	100
35^{th} percentile	Not applicable	Not applicable	136	136
Nutrient and energy cycling check	430	430	430	430
SQG_{sc}*	63	63	100	100
SQG_{I}	300	Not applicable	Not applicable	Not applicable
SQG_{HH}	1100†	1100	4000	20000
Off-site migration check	Not applicable	Not applicable	Not applicable	16000
CCME interim criteria‡	150	100	500	500

Note: Values in this table are preliminary values only. See CCME 1996b for final recommended values.

*As per the CCME (1996) protocol, the SQG_{sc} for agricultural and residential/parkland land uses corresponds to the 25^{th} percentile for the effects and no effects data distribution when using the weight of evidence method, while the SQG_{sc} for commercial and industrial land uses corresponds to the 25^{th} percentile of the effects data distribution only. The other percentiles are presented for comparison purposes only.

†This guideline applies only to the part of the agricultural land that is used as a residential property.

‡CCME 1991.

(1.2.6) Copper speciation in soils

(1.2.6.1) Properties of Copper in soils

Copper in soil is retained as exchangeable and insoluble complexes. Fixation and availability of copper are influenced by pH, amount of organic matter, clay, micro-organism and calcium carbonate (Peech 1941; and Piper 1942). Soil properties such as the acidity level and organic matter content can affect the amount of copper being taken up. Copper tends to complex strongly with organic matter and is not efficiently extracted by EDTA and DPTA. The most available copper in soils is held in a Cu^{2+} form on surfaces of clay minerals or in association with organic matter. The copper and organic matter association can be due to formation of strong innersphere complexes. Copper existing as an impurity in silicate mineral is largely unavailable. Organic matter and soil pH are the predominant factors influencing copper availability with organic matter can bind copper more tightly than any other micronutrient. Under this condition the organic soils are more likely to be deficient in copper than mineral soils. Adjusting the soil pH by liming can increase the amount of copper held by clay, organic matter, Fe and Mn oxy(hydro) oxides and decrease the copper availability.

Copper is usually strongly adsorbed to soil particles and is comparatively less mobile. Copper in soils tend to be accumulated and being remained in six different conditions listed as follow: (1) Copper in soil solution. (2) Exchangeable copper (Cu being bound electrostatically to charge surfaces). (3) Copper being sorbed and complexed. (4) Copper bound to the soil minerals. (5) Copper associates with humus like organic materials. (6) Copper exists in residual form from the soil parental mineral.

Copper presents in first condition is very mobile while at conditions between two to four the copper can be mobilized under changing soil conditions, pH, cation exchange capacity (CEC) of the soil, organic matter, the amount and type of clay, the existence of oxides of iron, manganese and aluminum and the reduction-oxidation (redox) potential of the soil are all detrimental to the distribution of copper in the above conditions.

Copper is less soluble when pH increases. Adriano (1986) demonstrated positive correlation between adsorbed copper capacity of soil and pH with optimum pH in a range of 6.7-7.8. Copper favors precipitation in alkaline with increasing pH led to hydrolyse or precipitation of Al^{3+} ions. Al is precipitated at above pH 5 however Cu absorption still increases due to sorption on OM. The available exchange sites can therefore be used for copper adsorption.

The cation exchange capacity (CEC) of soil is considered as the maximum number of moles of adsorbed ion charge that can be desorbed from a unit mass of soil under certain environmental conditions such as temperature, pressure and pH. The CEC is further influenced by four key factors listed at following table (7).

Table (7) Table shows key factors affecting cation exchange capacity (CEC)

	Factor
1	the kind of clay mineral present (different clays have different CEC values)
2	the quantity of clay minerals (soils with a finer texture have greater CEC values)
3	the amount of organic matter present (organic matter has a relatively high CEC value)
4	the pH of the soil (CEC increases with increasing soil pH)

Copper has a high affinity to organic matter and can be strongly bounded compared with other trace elements. With this observation, Cu/C ratio (grams per kilogram) is often used in extractions to determine copper availability. For many soils 20 to 50% of copper occurs in organically bound forms (Adriano 1986; Hunter et al. 1987; Loneragan et al. 1981; Slooff et al. 1989). The high adsorption ability of copper with organic matter can be due to high CEC and chelating ability (Adriano 1986; Hunter et al. 1987). Copper ions in this case are mostly bound to carboxyl and phenolic type functional groups of the organic matter. The formation of copper complexes can regulate copper mobility and availability. The amount of clay in soil can also affect the CEC and hence influencing copper adsorption. Copper can be adsorbed by Fe, Al and Mn oxides (Alloway and Jackson 1991). Copper is the most strongly adsorbed divalent transition and trace metals on Fe and Al oxides and oxyhydroxides (Adriano 1986). Studies suggested the binding affinity between soil constituents and copper can be ranked as follow: Mn oxide > organic matter > Fe oxide > clay minerals (Adriano 1986).

Copper minerals in solution is soluble with the order of decreasing solubility: $CuCO_3$ > $Cu_3(OH)_2(CO_3)_2$ (azurite) > $Cu(OH)_2$ > $Cu_2(OH)_2CO_3$ (malachite) > CuO (tenorite) > $CuFe_2O_4$ (cupric ferrite) > soil Cu (Alloway 1990). Divalent Cu^{2+} ion in soil solution can exist in different inorganic and organic complexes. Soil types have finite holding capacities for copper ions, and leaching can occur when the copper levels applied exceed this capacity (Adriano 1986). Mineral soils in the vicinity of the nickel and copper smelters in Coniston, Ontario were acidified to a pH of 2.4 as a result of aerial emission of sulphur-containing compounds over time increasing the mobility of soil copper in the area (Adriano 1986). Acidic rainfall would only result of significant leaching of copper once the pH decreases below 3.0 (HSDB). The transport pathway of copper from soils is lateral movement (Adriano 1986; Williams et al. 1987) such as run-off and erosion result from mechanical cultivation and/or erosion, including aeolian and fluvial transport (McGrath and Lane 1989).

(1.2.6.2) Importance of copper speciation in soils

Speciation in soils refers to both the process and the quantification of the different defined species, forms and phases of a trace element. Copper in soil presents in different chemical forms and demonstrate various physical and chemical behaviors. The speciation of Cu in soil strongly affects its mobility, biological availability and potential toxicity. Copper can be associated with various soil components that differ in their ability to retain or release copper. The distribution of copper among different soil components can influence the mobility and as a result the bioavailability of copper. Factors also affect the forms of bioavailable metal species in soil include pH of soil, redox potential and soil organic matter content. Copper sorbed onto soil minerals and organic matter is the main species in soils. It is important to understand copper sorption mechanisms in soils and how the associated interfacial reactions contribute their roles in the fate of the metals in the environment. All the above factors are inter-correlated and depending on each other.

Copper speciation in soil is not straightforward because soils are heterogeneous with mineralogy and composition. Aging processes determine the extractability, bioavailability and toxicity of copper in soils and it is related to the contact time between the soil and the metallic cation. Copper ions can be retained in soil phases by ion exchange, outer and inner-sphere complexation processes (e.g. adsorption). The characteristics of the particle surface, bond strength and the properties of the solution in contact with the solid samples can significantly influences bioavailability of heavy metals. Concentration level of the potential pollutants alone is not enough to predict the impact of a contamination event in soils. It is also required to estimate the remobilizable fraction from the pollutant sorption-desorption pattern. The fraction demonstrates the amount of pollutant available for environmental processes and hence the potential risk for human populations can be determined. It is therefore vital to identify the exact copper species, how the species associated with mineral surfaces, and the nature of their potential precipitated phases. The assessment of soil metal bioavailability using chemical extractions is a conventional approach used in soil testing (Tessier et al., 1979).

A number of different selective extraction procedures show a great diversity among reagents used for the determination of commonly distinguished metal species which are, in general: (a) easily exchangeable or water soluble, this fraction corresponds to the form of metals that is mostly available for plant uptake. It contains the fractions which are bound by electrostatically at charged surfaces and easily soluble salts of the metal and can be released by extraction with competing with cations in solution. (b) specifically sorbed, this fraction is bound to surfaces in soil by covalent bands as innersphere complex. (c) organically bound, (d) occluded in Fe/Mn oxides and hydroxides, this fraction can be mobilized with increasing reducing or oxidizing conditions of the environment and (e) structurally bound in minerals (residual), this fraction can only be mobilized by weathering.

However, the speciation of metals in soils is not stable, and relatively easy transformation of their forms in soils is observed. Depending upon the variability in physio-chemical characteristics of metals, their affinity to soil components governs their speciation.

Application of sequential extractions can provide detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of trace metals. It can provide a convenient means to determine the metals associated with the principal accumulative phases in soil deposits. The following table (8) provides general descriptions of different sequential extraction fractions.

Table (8) Table shows general characteristics of sequential extraction fractions

Fraction	Summary
Exchangeable	The adsorbed metals on the solid surface are under weak electrostatic interaction. Metals can be released by ion-exchange processes and co-precipitated with carbonates. This fraction can be mobilized by adjusting ionic composition, adsorption-desorption reactions and lowering pH. Metals belong to this fraction is most readily available for the environment.
Acid soluble	Metals in this fraction can be precipitated or co-precipitated with carbonate. Carbonate is an important adsorbent in the absent of organic matter and Fe-Mn oxides. Carbonate fraction is loosely bounded phase and susceptible to pH change (e.g. mild acid).
Reducible	Metals are scavenging by Fe and Mn hydrous oxides as coatings on mineral surfaces by co-precipitation, adsorption, surface complex formation, ion exchange and lattice penetration. Metals on these oxides are unstable under anoxic conditions and can be released by dissolution. In principle, the reducible fraction could be split into three fractions: easily reducible fraction (Mn oxides); moderately reducible fraction (amorphous Fe oxides); and poorly-reducible fraction (crystalline Fe oxides).
Oxidisable	In this fraction the metals can be complexed or bio-accumulated with highly selective divalent ions organic materials in aquatic systems. Metals considered to be pollutants can be re-mobilized by organic matter degradation in oxidizing conditions although high molecular weight humic substances can retain the metals stably. Metals associated with sulfides can also be leached in this step.

(1.2.7) Introduction of thallium

Thallium is heavy metal in Group 13 of the Periodic Table of Elements with oxidation state +1 and +3. Pure thallium is a soft, malleable, bluish-white metal and has long been discovered since 1861 however there is still relatively few literatures concerning about the chemistry, environmental fate and chronic exposure to low levels of this element in soils. Thallium is a widely distributed and naturally occurring element with average concentrations of 0.49 ppm in the continental crust and of 0.013 ppm in the oceanic crust (Delvalls et al., 1999). The common occurrences are ranging from lead, sulfide and zinc ores to association with potassium minerals in clays, soils and granites with mean concentrations of thallium in the earth crust are in a range of 0.1-1.7 mg/kg (John Peter, 2004). The evaluated Tl content of soils largely depend on the geological origin of the parent material across the globe with an average soils concentrations commonly found between 0.1 to 1.0 mg/kg (Kazantzis, 2000) . The range of thallium concentration in non-polluted soil in general between 0.08 to 1.5 mg/kg (Wenqi et al. 1992, Tremel et al. 1997, Von Laar et al. 1994, Lukaszewski et al. 1992).Thallium exhibits both heavy metal and alkali metals chemical behavior with the degree of toxicity along with mercury, lead and cadmium. It exists primarily in a +1 oxidation state ($Tl^{+} \rightarrow Tl^{3+}$, +1.25V oxidation potential), form insoluble halide, sulphate and sulphides compound as well as soluble multihalide complexes. Tl as monovalent thallous cation is highly soluble in natural water and can be readily transported in aqueous environment. The mobility of thallium in soil samples is a crucial factor for the toxic effect of the element. Free metal ion, metal ions complexed, sorbed and exchangeable can be considered as a mobile metal. Exchangeable and sorbed metal is usually extracted with ammonium nitrate or acetate (Rule, 1998).

Thallium is non-essential and extremely toxic to biota at trace levels in environment. Thallium is a noticed mutagen and carcinogen. Thallium exposure can be absorbed through skin. Tl exists at monovalent cation form in mammal's cellular fluids. The Tl toxicity is due to similar ionic radius between Tl+ (1.49Å) and K+ (1.33Å) in which leads to nondiscriminatory uptake in metabolic processes. Symptoms of acute Tl poisoning of human include paralysis, coma and death. Thallium has been used in numerous industrial applications over the past century including human poisonous rodenticide (Tl(I) sulphate), medicine, low temperature thermometers (Tl and Hg), electronic devices (Tl(I) sulphide for semi-conductors), special glasses (Tl and Se) , mercury lamps (Tl(I) halogenids), production of low-melting glasses, high refractory lenses, photoelectric cells, pigments and dyes.

(1.2.7.1) Occurrence and properties of thallium

Most of the heavy industries worldwide only consume small amounts of thallium with 8 tonnes were produced at Germany in 1975 (Zitko, 1975) and an estimated 10-15 tonnes per year in the world (Kemper and Bertram 1991). Davids et al. in 1980 showed estimated thallium emission to air from cement factories at Germany was 25 tonnes per year. Total Tl emissions from brickworks in Germany have been figured out in around 28 tonnes/year and 7.5 tonnes/year emissions from the burning of coal (Brumsack, 1977). Combustion of fossil fuels and flying-dust in Zinc, lead smelters and sulfuric acid plants are the major emitting sources of thallium. Thallium entering along with lead, copper and zinc smelting processes is released into the atmosphere, discharged as solid waste and waste water. The Environmental Agency of West-Germany estimated thallium emissions from ferrous and non-ferrous smelters in the FRG to be ~ 45 tons/years (Davids et al., 1980). Volatile Tl compounds as trace element in large quantities of raw material in fossil fuels, oils and cement during combustion can escape through chimneys without proper filter installations and subsequently fall out on rural and urban area. An estimated of 2000-5000 tonnes Tl can be mobilized per year worldwide through the above processes (Kazantzis, 2000).

Thallium presents in different rocks and minerals. In igneous rocks Tl is enriched in pegmatites by the magmatic differentiation process due to the large size of Tl ion (1.47 Å). Acid and intermediate magmatic rocks consisting of K-feldspar, plagioclase, biotite or muscovite are also characterized with high Tl content. In minerals Tl is commonly associated with K-minerals (e.g. micas and feldspars) and sulphides minerals with thallium as trace element associated mainly with galena, sphalerite and pyrite. During the weathering processes most of Tl compounds can be easily leached in water and transported along with alkaline metals however with great ionic radius the thallium can be immobilized by Mn, Fe oxides and clay minerals in soils especially under reducing conditions. Thallium can also be leach out and enriched in soils from the original bedrock. Thallium can also form stable humic complexes in which the thallium can be maintained in soils. Thallium associated with fly-ash in air usually deposit on the surface layer of soils and less well retained in acid soils. Thallous sulphate was found to be strongly bound in the upper 10 cm of various soil type and strongly resist leaching to lower horizons (Alloway 1990). Yang et al. (2005) showed the order for preferential immobilization of anthropogenic Tl among major soil components could be roughly summarized as: Tl(III) carbonates and hydroxides>Mn oxide–hydroxides>Fe oxide–hydroxides>adsorption sites on the surface of soil with the order can be significantly mediated by the pH conditions in the soils.

(1.2.7.2) Thallium exposure in vicinity of cement factories and safety regulations worldwide

Thallium poses great threat to the populations living in the vicinity of coal-burning power stations and cement works. Extensive sulfide ore mining, treatment and smelting is a major source of anthropogenic dispersion of Tl. Non-volatile Tl can exist in different compound states such as oxide (Tl_2O), hydroxide (TlOH), sulphate (Tl_2SO_4) and sulfide (Tl_2S) from anthropogenic emission. Water soluble thallium compounds (e.g. sulfate and hydroxide) can be dissolved in rain drops and precipitated out from atmosphere. Insoluble water thallium (e.g. oxides) compounds can be transported by atmospheric dispersion and gravitational settling (ATSDR 1992).

The observed harmful potential Tl emission from cement (mixture of limestone and shale or clay) plants was not recognized until 1977 in Lengerich, Germany. The source of Tl was found to be residues of pyrite roasting added as a ferric oxide additive to powdered limestone in order to produce special qualities of cement. The emitted fly-ash thallium is bounded with particle size 0.2-0.8 µm with concentration 2.5 mg/m^3 and by changing the production process can reduce the Tl level to less than 25 $\mu g/m^3$ (Pielow 1979, Prinz et al. 1979 and LIS 1980). Similar investigation of polluted soils around a cement plant at Leimen (SW Germany) had been undertaken and found out to be 3.6 mg/kg of Tl in surface soils 0-10 cm, 0.7 mg/kg at 40-50 cm and 0.1 mg/kg at depth 60-70 cm (Schoer, 1984).

Plants take up thallium and the amount of Tl being taken depends on pH and soil types. Green rape, bush beans and rye grass were found to take up less Tl from weakly acidic soil (pH 6.2) than from more acidic soil (pH 5.6). Studies had also found out that rape plants could take up around 20% of soil Tl from a cement plant soil sample in comparison with only a range between 1.4 to 5.1% Tl in stream sediments in a mining district at Wiesloch in Germany (Scholl et al., 1982). The Tl transfer from soil to plant also depends on root system, kinetics of membrane transport and are species-specific. Uptake of Tl(I) ions can be through all parts of plant by K uptake mechanisms. The distribution of Tl varies in different vegetables, in gardens around Lengerich, leaves of kohlrabi could contain a 350-fold higher concentration than tubes, while in other vegetables the differences in concentrations between leaves and other parts could

vary in a range between 3 to 45 times (Hoffmann et al., 1982). Plant species from Cruciferae family can accumulate Tl up to 450 mg/kg near a cement production site in Germany (McGrath, 1998). Tl in urine and hairs of residents near Lengerich area showed up to ~ 80 µg/l and 600 ppb which was significantly higher than upper normal limit of 1 µg/l (Ewers, 1988). Fruits and vegetables grow nearby the cement plant could lead to high thallium urine level for local inhabitants.

Thallium emissions were observed in West-Germany cement plants due to thallium-bearing roasted pyrite (average 400 ppm) additive to limestone. A cement plant at Lengerich showed emitted flying-dust being enriched with Tl content up to ~ 50,000 ppm with other German plants like Erwitte, Geseke and Paderborn all demonstrated high Tl contents (Ewers, 1988; MAGS, 1980). Soil in an area of 1-2 km radius from the cement plant in Lengerich, Germany showed maximum concentration of 6.9 mg/kg (LIS, 1980). In agricultural soil 4 mg/kg of Tl was found and 6 mg/kg of Tl was reported in house garden soils (Crössmann, 1984). The Tl level in soil samples showed highest Tl concentrations in the upper soil layer and gradually decreased with increasing depth (LIS, 1980). The source of the pyrite roasting residues used by the cement plant in Lengerich, Germany demonstrated high Tl concentration of 160 µg/l (LIS, 1980).

According to FRG General Administration Regulation thallium as a constituent of dust fall-out cannot be exceeding 10 $\mu g/m^2$/day (Ewers, 1988). The potential risk for human of excessive Tl contents in soils is in 1 mg/kg according to North-Rhine Westphalia (FRG). Swiss Ordinance on Soil contaminants suggested the maximum admissible level of thallium in agricultural soil is 1 mg/kg dry weight. In uncontaminated areas, air concentration of thallium is usually less than $1ng/m^3$, in water less than 1µg/l and in water sediments less than 1 mg/kg. The maximum contaminant level in the drinking water is 2 µg/l according to the United States Environmental Protection Agency. For adults the LD_{50} is between 10 to 15 mg/kg (Schoer, 1984; Gosselin et al., 1984). The International Programme on Chemical Safety (IPCS) of the World Health Organisation (1996) suggested in a monograph with the total general population intake of thallium should not be more than 5 µg/day (WHO, 1996).

(2.0) Aim

(2.1) Aim of arsenic project

The aims of this project were: (1) to determine the physicochemical behaviour of arsenic presents in limestone oxide as impurities. (2) to understand the adsorption of heavy metals into the soil system by investigating (i) the form of metal enters the soil (solid particulate in wet or dry deposition or solution), (ii) range of metal species, (iii) charge on the metal entering the soil, (iv) the pH of the receiving environment, (v) the percentage of organic matter in the soil and the redox condition of the receiving environment. (3) to partition metals in different metal-bearing phases in order to gain better understanding of the arsenic's behavior.

(2.2) Aim of copper project

The aims of this project were: (1) to determine the physicochemical behaviour of copper presents in limestone Fe and Mn oxide impurities. (2) to predict copper mobility in soils. (3) to detect the main host phase(s) and soild copper speciation accumulated in agricultural lime samples. (3) to evaluate the risks of soil and ground water contamination when such lime samples are applied to soil pH amendments. (4) to understand long term fate of copper species in environment. (5) to provide information of managing copper contaminated soils in future development.

(2.3) Aim of thallium project

The aim of this project was to determine the mobility of thallium in soil samples in the vicinity of a cement factory at Lengerich, Germany and hence determining the toxic effect of the element. Exchangeable and sorbed thallium metal was extracted by ammonium nitrate solution and the total thallium contents were found by applying aqua regia acid digestion. The two sampling areas have been using for farming and various purposes. The investigation of the soil thallium concentrations could help to identify the effects of mobile thallium on the farm products producing in the areas and the long term health impact to local inhabitants.

(3.0) Method

(3.1) Sequential extraction technique

Chemical extraction is complicated by the fact that no chemical solution uniquely extracts trace elements out of one pool. Sequential extractions, in which a soil samples is reacted with a series of carefully selected chemical solutions of increasing strengths, were developed to increase extraction selectivity of the distinct geochemical fractions.

Chemical speciation analysis in soils and sediments is defined by BCR as: the process of identification and quantification of the different defined species, forms or phases in which an element occurs in the material. Speciation also represents the actual description of the quantity and variety of species. Chemical speciation can be sub-divided in three classes: (1) functionally defined species (e.g. plant available species) where the species are defined by their role or as (2) operationally defined species, characterized by the procedure of isolation and identification (e.g. acid ammonium oxalate extractable fraction) or finally as (3) specific chemical compounds or oxidation states (e.g. AsH_3).

The chemical compounds composition is responsible for the ecological functions of soil. Sequential extraction is a method based on dissolving the chemical substances. It determines groups of compounds (but not individual ones) with identical properties that are dissolved by the same extractants and these compounds have a similar behavior in the environment.

Fractionation is a direct way of obtaining the main compounds content of any element in soils. There are numerous phases which can be pre-defined by this method which are listed in following table (9). The following components permanently interact and characterize the soils in specific manners in natural environment. The following five classification phases demonstrate different fundamental unit of elementary system of chemical compounds in a minimal soil volume (pedon, horizon).

Table (9) Table shows different phases that main element compounds can resident

Number	Possible partition phase
1	Mineral in the structure of primary and clay minerals which is firmly bounded compounds of the soil solid phase (e.g. not easily soluble salts, oxides, hydroxides of Si, Fe, Al and Mn, organic and organomineral substances
2	Mobile compounds of the solid soil phase (e.g. exchangeable, specifically and non-specifically sorbed and chemically bound.
3	compounds of the soil solution
4	compounds of the soil air
5	compounds of soil biota

According to Bureau of Standards of the European Union (BCR) stated in 1987 that fractionation is a quantification of different kinds, forms, or phases of chemical compounds including the studied elements. International Union of Pure and Applied Chemistry (IUPAC) also defines fractionation as a taxonomic separation of substances by their physical (e.g. size, solubility) and chemical (e.g. bonding and reactivity) properties using corresponding physical and chemical methods.

Chemical reagents tailored for extraction purpose are often applied for fractionation of chemical element compounds and these reagent's interactions with definite groups of chemicals are important. The use of an extractant is to dissolve the investigated fraction and keep it soluble. The characteristic reagents can be broadly classified as inorganic, organic, acid and alkaline hydrolysis complex formation, reduction of oxides and hydroxides of Fe and Mn, and displacement of ions from soil exchange complexes by solutions of electrolytes. Reagents can either completely dissolving a certain group of substance or establish an equilibrium solutions in which particular groups of substances are investigated. Microelements in soils do not form independent phases and these elements are constituents of marcoelement compounds. Application of fractionation can dissolve those macro compounds such as C, Fe, and Al compounds and the microelements in the solution can be determined. The biggest obstacle to extractive fractionation of compounds of microelements is non-selective due to interaction between micro- and macro-elements in soils. The assessment and forecast of the ecological status of contaminated soils are impossible without information about the compounds containing pollutants absorbed by the soils. Many fractionation schemes have been developed over the past fifty years and the underlying principles are summarized in following table (10).

Table (10) Table shows association between extractants and different soil solid phases

Extractant	Target phase
Weak salts	Exchangeable ions
Diluted acids	Carbonates
Reducing agents	Fe and Mn oxides
Conc. HNO_3, $HClO_4$ with heating, acidified H_2O_2	Organic compounds

The efficiency of extraction schemes depend on several factors which are (1) sample preparation (e.g. under reducing condition, labile phases can be converted to other phases); (2) concentration of the extractants; (3) sequence of extractants which apply to soil fraction; (4) soil solution ratio; (5) time and temperature of the extraction.

The key of the fractionation is to get further information about the contents of the As and Cu compounds with examples whether they are mobile, weakly mobile and intermediate between two. The As compounds can be stationed in following four different phases which are (1) Substances of the liquid phase of soils; (2) The mobile one of soil solid phase; (3) Mobile forms of the solid phase are easily soluble; (4) Nonspecifically sorbed (exchangeable) and the specifically sorbed compounds are in equilibrium with soil solution. Extraction of these compounds from soils is based on the mechanisms of their bonds with soil components depending on the properties of each microelement (or their groups) and irrespective of the specific features of the macroelements (organic and mineral).

The names of the microelement compounds more firmly bound with soil attest to the composition of the macrocomponents. Compounds of microelements that are held by the main products of soil formation (organic substances and nonsilicate forms of Fe, Al, and Mn) may be called specific soil ones. Elementary soil-forming processes provide the distribution of these products along soil profiles. In technogenic soils, these components are assumed to retain pollutants.

Trace elements occur in soils in certain “pools” or “sinks” of different solubility and mobility in six different soil phases which can be outlined in following table (11).

Table (11) Table shows trace elements in different soil phases

Number	Phases
1	Exchangeable sites as diffuse ions or as outer-sphere complexes
2	Specific adsorption as inner-sphere complexes
3	Associated with insoluble organic matter
4	(co)precipitated as pure as mixed solids
5	Present in the structure of secondary mineral
6	Present in the structure of primary mineral.

It is therefore understandable that arsenic and copper distribution or fractionation in different soil solid phases can be examined by an instrumental surface analytical technique or a selective sequential extraction (SSE) technique.

(3.2) Atomic absorption spectroscopy

The invention of atomic absorption spectroscopy is based on the discovery of the absorption of radiation by atoms since the early part of the nineteenth century. It involves valence electron transitions yielding radiation with wavelengths in the ultraviolet-visible region of the spectrum. Electron orbits in an atom are characterized by the major and azimuthal quantum numbers n and l respectively. An electron undergoes a transition from a higher energy level (E_{nl}) to a lower energy level (E_{n1l1}) with light of frequency is given off (eq.1).

$$v= (E_{nl} – E_{n1l1}) / h = \Delta E/h \qquad \text{(eq.1)}$$

To re-arrange the above equation in terms of wavelength (eq.2),

$$\lambda= c/v = hc/ \Delta E \qquad \text{(eq.2)}$$

The constants h and c in these equations are Planck's constant and the velocity of light respectively. Thus, electronic transitions can be discussed in terms of frequency v, energy E and wavelength λ. All the ΔE, v and λ contain unique values for a given electronic transition and the resultant spectrum demonstrates a series of characteristic sharp lines which represents the particular element.

Absorption can be described with a parallel beam of continuous radiation of intensity I_o passes through a cell containing atomic species of an element. The transmitted radiation I_v will show a frequency of distribution. The atomic species is said to possess an absorption line at frequency v_o, where v_o is the frequency at the center of the line. The absorption coefficient of the atomic vapor k_v is defined by (eq.3).

$$I_v = I_o e^{-kvb} \qquad \text{(eq.3)}$$

The relation between absorption and concentration are further explained by Beer-Lambert law in monochromatic radiation absorption. Lambert's law states that light absorbed in a transparent absorption cell is independent of incident light intensity with an equal fraction of the light is absorbed by each successive layer of absorbing medium. Beer's law suggests the absorption of light is likewise exponentially proportional to the number of absorbing species in the path of the light beam. In following figure(3), it shows with an incident beam of monochromatic radiation Io falls on an absorption cell length b. The transmittance (T) is equal to $T = e^{-kbc}$ and therefore in (eq.4)

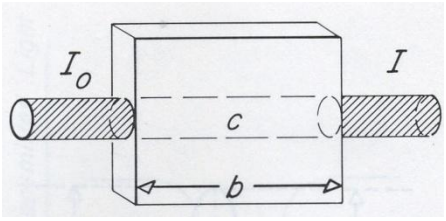


Fig. (3) Atomic absorption cell of length b (Section 8.1 Ref. 78)

$$\log(1/T) = \log(Io/I) = abc \quad \text{and} \quad \log(Io/I) = A \qquad \text{(eq.4)}$$

where A is the absorbance and A = abc. a is a constant for a given system and c is the concentration of the analyte atoms in the flame. The above Beer-Lambert law predicts a linear relationship between absorbance and concentration with a and b stays constant. This relationship only is valid when the concentration of analyte atoms in the atomizer is equivalent to the analyte concentration in the sample solution.

(3.3) Flame atomic absorption spectroscopy (F-AAS)

The fundamental principles underlying the flame atomic absorption spectroscopy (FAAS) is the same as HG-AAS described in above. Analytical liquid sample is aspirated, aerosolized and mixed with combustible gases. The mixture is ignited in a flame and during combustion, atoms of the element of interest in the sample are reduced to free, unexcited ground state atoms, which absorb light at characteristic wavelengths. The amount of light absorbed can be directly related to the amount of the element in the sample.

Hollow-cathode atomic spectral lamps (HCL) are the most common radiation sources for atomic absorption spectroscopy. These lamps can produce resonance radiation of narrow linewidth < 0.01 Å, for most elements that are determinable by atomic absorption. The lamp is evacuated and filled with 2 torr of either argon or neon. A small current is passed between the anode and the cathode resulting in ionization of inert-gas atoms. Atoms of the cathode metal (analyte) are sputtered from the surface due to interactions with these ions. Resonance radiation results when the ground-state atoms are excited and then decay back to the ground state. Although the discharge may appear to the eye to be hot, the cathode temperature is usually only 300-400^{o}C. Excitation results from collisions between analyte atoms and inert-gas ions in the discharge. The cathode is constructed from the metal or an alloy of the element being determined. The spectrum of a good lamp consists mainly of spectral lines of the element of interest.

Atomic absorption is one of the key processes in determining analyte concentration in atomic absorption spectroscopy. The process involves in producing free ground-state atoms of the element of interest and the production of free atoms occurs in atomizers and is called atomization. The laminar flow premix system burner is usually applied in modern day atomic absorption spectroscopy. It contains a nebulizer, a premix chamber and a burner head. The premix chamber is designed to mix fuel, oxidant and sample with an additional purpose of filtering off large droplets as these droplets could enhance light-scattering effects in the flame.

Liquid sample is usually introduced into a burner through the nebulizer by the venture action of the nebulizer oxidant with sample at first being aspirated and passing through the nebulizer the liquid stream is then subsequently broken into a droplet spray. The sample and standard solutions viscosity should stay similar in order to avoid the possibility of physical interference problems and particulate matter is not allowed to be present in samples due to severe damage of nebulizers by clogging. Burner heads for premix burners usually present with a single slot 5-10 cm in length. It allows the radiation beam from the source to traverse a lengthy path of atoms and the magnitude of the absorbance is related to the path length of the radiation beam in the flame.

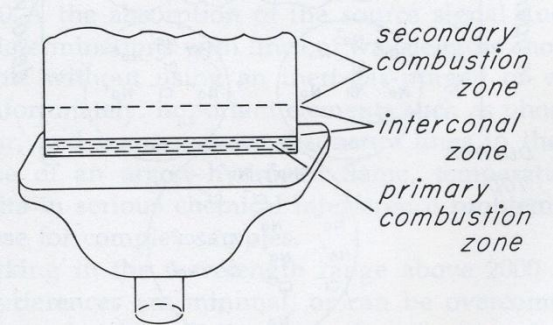


Fig. (4) Zones of a flame burning on a premix burner (Section 8.1 Ref. 78)

Flame is the most ideal atomizer for atomic absorption spectroscopy. Despite extensive research flame is still a rather least well understood component in AAS. However, flames can be broadly defined as primary combustion, interconal, and secondary combustion zones figure(4) with not uniform in composition, length, or cross section. The primary combustion zone is rarely used for absorption work due to reducing and noise conditions and the secondary combustion zone is also not applicable because of the relative low temperature and oxidizing condition. It is therefore only the interconal zone which operates in thermodynamic equilibrium and elongation of the zone can be achieved by shielding a flame.

The atomization process (figure 5) in flames can further be described in follows. Liquid mist produced by the nebulizer and further processed to extract the finest droplets in the premix chamber evaporates on entering the flame. The produced analyte compounds move upward into hotter regions of the flame and agglomerated into small solid particles followed by dissociation into atoms.

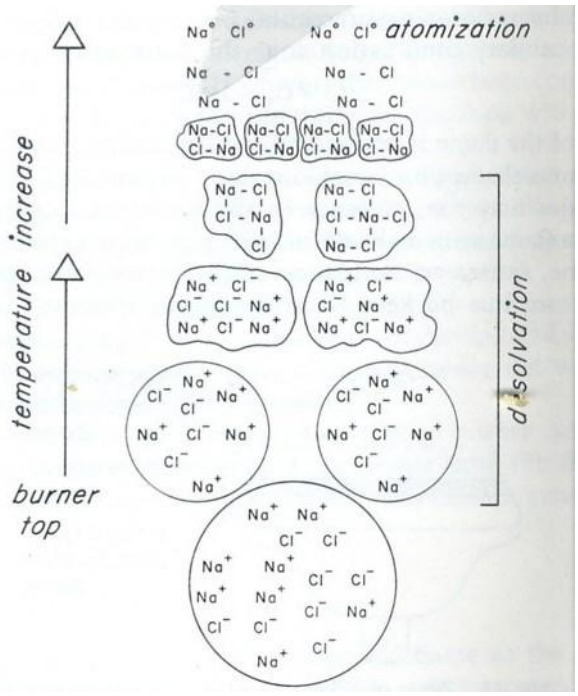


Fig. (5) Atomization processes resulting when liquid mist is introduced into a flame (Section 8.1 Ref. 78)

Air-acetylene flame is most frequently used in atomic absorption. Choice of flame type is governed by the temperature required. High temperature flame is always preferable in order to minimize chemical and nonspecific background interferences. However, hotter flames (e.g. nitrous oxide-acetylene, above 3000 ^{o}C) can cause severe ionization problem with degradation in measurement precision and inferior detection limits. In the region below 200 nm (e.g. arsenic 193.7 nm), flame gas absorption of the source radiation can be a very serious problem and the argon-entrained air-hydrogen flame should be used to produce best flame transparency conditions. Flame temperature can be adjusted by the proportions of oxidant (air, nitrous oxide) and fuel (hydrogen, acetylene). It is widely acceptable that fuel-rich flames are cooler than oxidant rich flames.

(3.4) Hydride generation atomic absorption spectroscopy (HG-AAS)

Metals and metalloids can be analyzed by method like atomic absorption spectroscopy (AAS) but for certain metalloids (e.g. Arsenic) such method is not applicable due to the interferences, poor reproducibility and poor detection limits for the method to several metalloids. Therefore, an improved method so called hydride generation atomic absorption spectroscopy (HGAAS) method has been introduced to rectify the AAS problem with an additional hydride generation module. Many main parts of the HGAAS system are identical to the AAS such as a hollow cathode lamp, air/acetylene flame and optical system. The HGAAS system contains a further complex hydride generation system without using nebulizer and the system is under continuous flow instead of batch flow. The purposes of different parts of the system are briefly summarized in the follows table (12).

Table (12) Table shows components of hydride generation atomic absorption (HGAAS) system

Constituent of the system	Functionalities
Hollow cathode lamp (HCL)	Provide a constant intense analytical beam line for the element of interest
Hydride generation system	-Liquid sample can be taken up at a controlled rate -Mix liquid sample with sodium borohydride and HCl -Create a volatile hydride of the analyte metalloid for the reaction -Gaseous hydride can be transferred into the optical cell
Optical cell and flame	Decomposes the hydride form of the metalloid from the hydride generation module and create atoms of the element of interest (e.g. As^0, Se^0 and Sb^0
Monochromator	-Isolate analytical photon lines passing through the optical cell -Remove scattered light of other wavelength from the optical cell, narrow spectral line impinges on the PMT
Photomultiplier tube (PMT)	Detect the intensity of photons of the analytical line exiting the monochromator

The hollow cathode lamp (HCL) is made up of the element of interest with a low internal pressure of an inert gas. With apply electrical current that the metal can be excited and characteristic spectral lines of particular element can be emitted. The emitted light is directly through the lamp's glass transparent window in UV and visible wavelengths. In the hydride generation system metalloid oxyanions react with sodium borohydride and HCl to produce volatile hydrides (e.g. AsH_3 and SeH_2). Care must be taken to produce the specific metalloid oxidation state before the sample is introduced into the hydride generation system and in addition to ensure the time from reagent mixing and the volatile hydride is separated from the liquid and sent to the optical cell has to be accurate. These can be achieved by using a peristaltic pump and tubing of specific lengths. The liquid mixture flows through a unit length of tube and eventually reaches into a gas/liquid separator where the hydride and some gaseous hydrogen bubble out and being purged into the optical cell via a gas transfer line. The following figure (6) demonstrated the systematic set-up for the hydride generator.

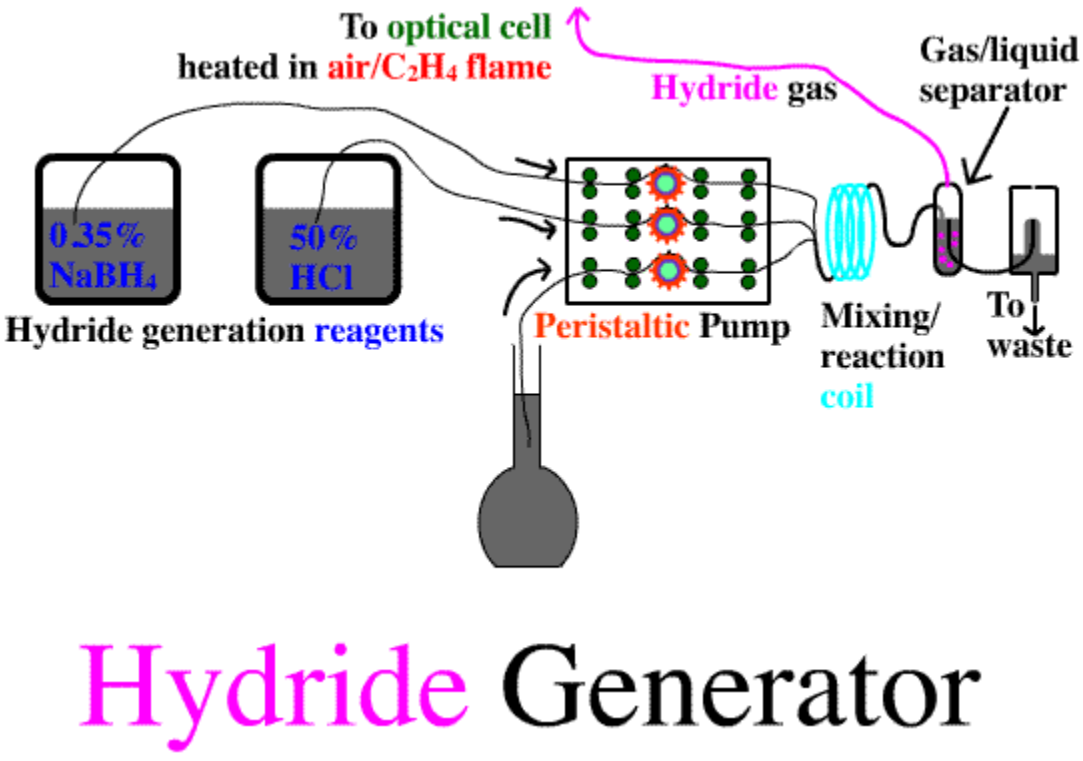


Fig. (6) Figure shows set-up of hydride generator (Section 8.1 Ref. 85)

The optical cell is made of fused silica glass tube in which the hollow cathode lamp beam can pass on the way to the monochromator and PMT. The fused silica glass tube locates on top of the normal AAS air/acetylene flame. The gaseous, metalloidal hydride flows into the optical cell from the hydride generation module pushes by an inert purge gas. In the optical cell it decomposes into the elemental form in which can absorb the hallow cathode light beam. The monochromator can isolate the analytical line emitted from the hollow cathode lamp with a specific wavelength and slit width. The role of the monochromator between HGAAS and AAS are the same in which to allow the light not absorbed by the analyte atoms in the optical cell to reach the PMT. Before an analyte is aspirated, a measured signal is generated by the PMT as light from the HCL passes through the optical cell. When analyte atoms are present in the cell from hydride decomposition and in the mean time the sample is aspirated and some of that light is absorbed by those atoms (with only volatile hydride gets to the optical cell and then only decomposed hydride produces the elemental form). This causes a decrease in PMT signal that is proportional to the amount of analyte. This last is true inside the linear range for that element using that slit and that analytical line. The signal is therefore a decrease in measure light. The following figure (7) revealed the arrangement of the optical cell and the flame in the hydride generation atomic absorption spectroscopy (HGAAS) system.

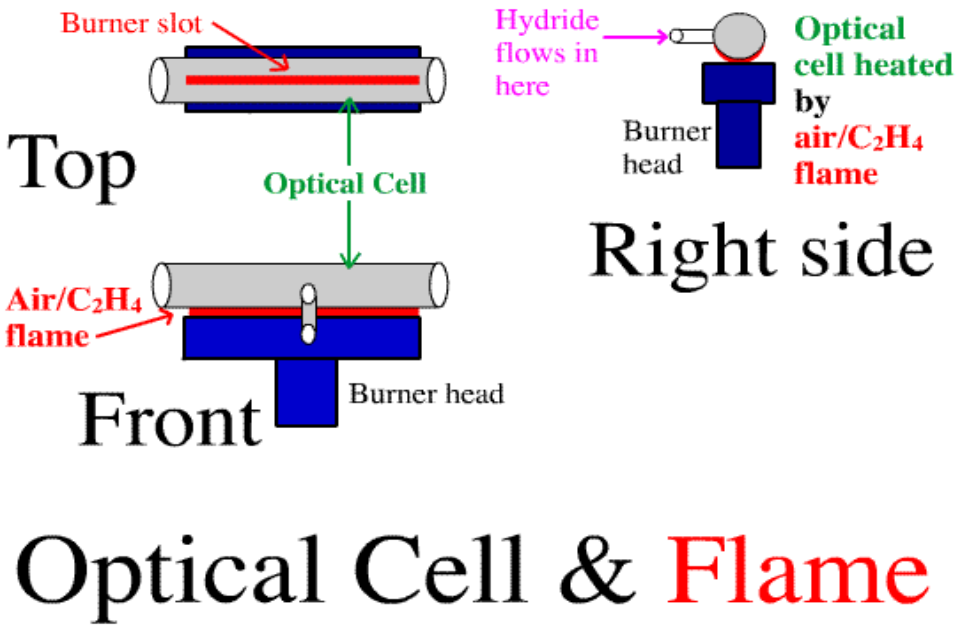


Fig. (7) Figure shows arrangement of optical cell and the flame in HG-AAS (Section 8.1 Ref. 85)

With double beam instrument, a hollow cathode lamp is divided into two paths under a rotating mirror. One pathway passes through the optical cell and another is around the cell. Both beams are recombined in space so they both hit the PMT but separated in time. The beams alternate quickly back and forth along the two paths. One instant the PMT beam is split by the rotating mirror and the sample beam passes through the cell and hits the PMT. In next instance, the HCL beam passes through a hole in the mirror and passes directly to the PMT without passing through the optical cell. The difference between these beams is the amount of light absorbed by atoms in the optical cell. All of the above application is to compensate for drift of the output of the hollow cathode lamp or PMT.

Operation of HG-AAS instrument can further be described in follows. Lighting up AAS flame process involves setting up the optical cell in right position (above the burner) and connecting hydride gas transfer line. Fuel (Appendix C) and oxidant (Appendix C) are turned on and the flame is lit with the instrument's auto ignition system. Few minutes later the flame is stable, acidic blank solution is flowed through the sample inlet tube for 10 minutes and deionized water is aspirated between samples in order to stabilize the system. Fuel/air mixture flow control is crucial due to elemental response is based on successful decomposition of the volatile hydride in the heated optical cell. The flame for decomposing volatile hydride in the heated optical cell should maintain at 800^{o}C throughout the measurement. The instrumental performance can be maximized by ensuring the analyte concentrations in the middle linear response range of the instrument and moreover the fuel/oxidant mix flow should be adjusted until the optimized light absorbance is achieved. Furthermore, the position of burner's head, optical cell and sample uptake rate should be corrected for greatest light absorbance can be obtained. After the measurement, all the inlet tubes (Sodium borohydride, concentrated HCl and sample inlet) should be flowed with deionized water and the fuel supply should be stopped with ignition also to be turned off at the same time. After all the plastic tubing that is stretched around the peristaltic pump head is loosened to length its' lifetime and the purge gas should also be switched off.

(3.5) Nonlinearity in analytical calibration graphs

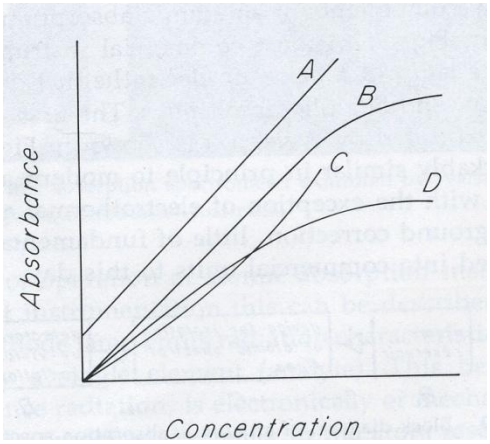


Fig. (8) Calibration graph showing departures from ideality (Section 8.1 Ref. 78)

An element in which can be determined by AAS is generally containing 4 to 5 orders of magnitude concentration working range. At the upper end of the concentration range, it is common to have the graph bend towards the concentration axis (figure 8) (absorbance against concentration). This could be due to the failure of the monochromator and slit system to prevent multiple, close-spaced lines from reaching the detector. Several lines of differing absorption coefficient (e.g. unresolved multiplets or nonaborbing lines) fall on the detector would lead to nonlinear relationship between absorbance and analyte concentration. It is also important to ensure that the emission source linewidth must be narrower than the absorption linewidth due to variation of absorption coefficient at different frequency.

(3.6) X-ray fluorescence analysis

XRF is a noninvasive analytical methods which are now commonly in use. Bulk specimens can be analyzed under this technique with samples prepared as compressed powder pellets or fused glass discs. X-ray then applies to the samples by an x-ray tube in a potential between 10 to 100 kV. Atoms of the sample interact with this primary radiation and leads to ionization of discrete orbital electrons and electronic rearrangement subsequently occurs with electrons de-excites back to the ground state. As a result, the intensity of the characteristic radiation emission can be measured with a wavelength dispersive x-ray spectrometer and different emission lines in wavelength are obtained and compared with a standard sample.

X-ray is a high-frequency electromagnetic radiation of energy intermediate between the far ultraviolet and gamma-ray regions of the spectrum. Moseley (1913, 1914) formulated the wavelength of an x-ray emission (λ) with the atomic number of an element (Z) by a formula.

$$1/\lambda = k(Z-\sigma)^2 \qquad \text{(eq.5)}$$

k = constant for a particular series of lines (K, L, M, etc)

σ = shielding constant

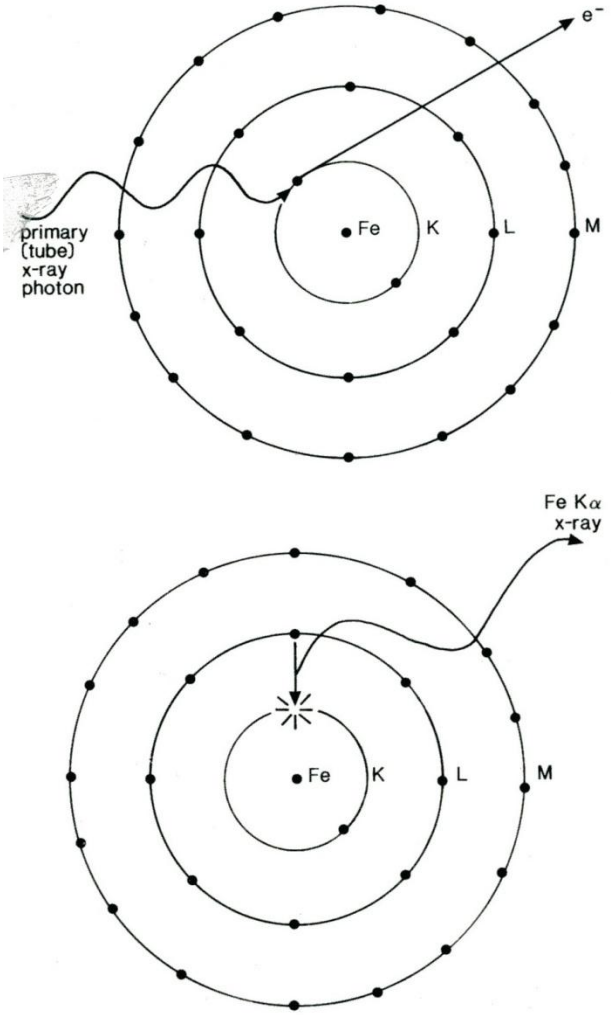


Fig. (9) Example shows schematic representation of the mechanism of x-ray fluorescence of an iron atom leading to the emission of an Fe Kα x-ray (Section 8.1 Ref. 60)

The underlying theory of Moseley is related to transitions of electrons between orbitals of discrete energy in an atom. The following simplified Bohr model (figure 9) can be used as an aid of explaining x-ray spectra.

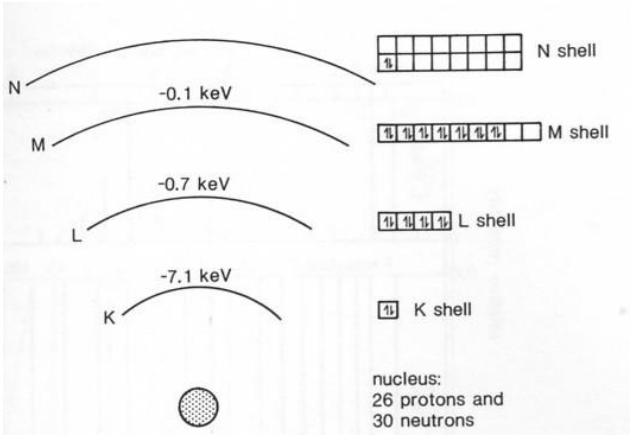


Fig. (10) Diagram of the electron orbital structure of an iron atom. The number of electrons occupying each shell is indicated, together with the corresponding ionization energy (in keV). Interactions between orbital electrons cause individual subshells to split in energy. In these circumstances, it is energetically more favourable for the last two electrons to occupy the N-shell rather than the M-shell, as might otherwise be expected (Section 8.1 Ref. 60)

The energy of an electron orbital is defined as the energy required removing that electron from the influence of the atom and so opposing the electrostatic attraction between negatively charged electron and positively charged nucleus. This energy is measured by the ionization potential of the orbital electron and thus electrons occupying orbital's of the highest ionization represent states that are energetically the most stable. In figure(10), K-shell possess largest ionization potential with L-, M- and N-shells are progressively more weakly bound to the nucleus. A high-energy x-ray photon can interact with an orbital electron and the electrons in any of the occupied shells can be removed from the electron orbitals by ionization. A vacancy left in K-shell (figure (VII)) can leave the atom in a highly unstable state and to restore the stability, an electron from the L- or M- shell falls down the potential energy gradient to refill this vacancy. The surplus energy which must be lost for this transition to take place is emitted as an x-ray having an energy characteristic of the difference between the two orbital levels.

The resultant characteristic x-ray spectra are further complicated by different phenomenon such as selection rules which govern different transitions in quantum theory, the Auger effect and etc. For further details of the XRF principles can be referred to chapter 8 Potts 1987.

(3.7) Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS is a robust trace multi-element analysis technique which encompassed four main components shown at following figure (11).

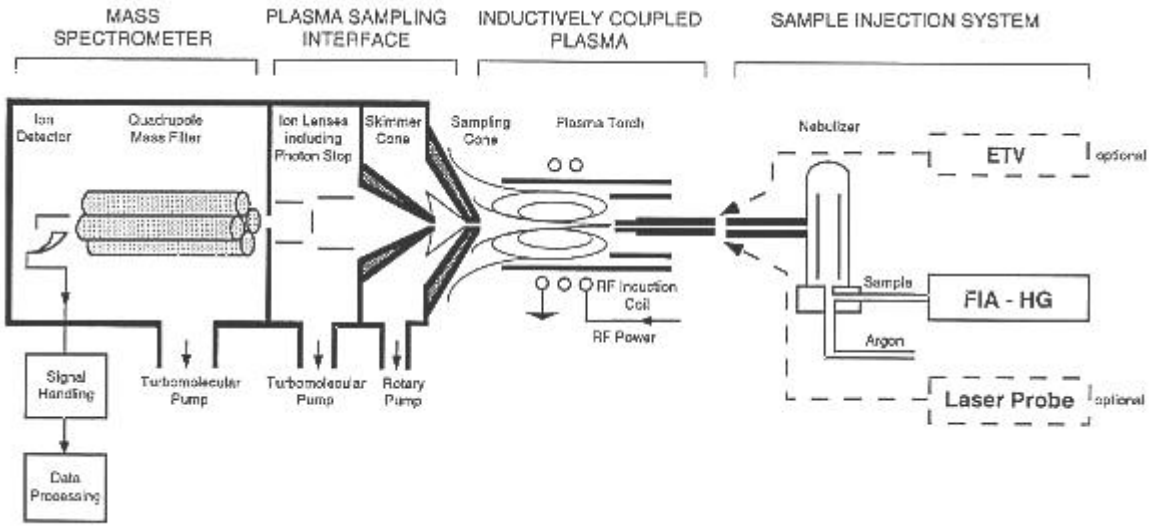


Fig. (11) Figure shows systematic set up of quadrupole ICP-MS (Section 8.3 Ref. 59)

Liquid sample is transferred to the sample injection system in which consists of a spray chamber and nebulizer. The sample is later reached the base of plasma from the sample injector in aerosol form. When the sample passes through different heating zones of the plasma torch the sample becomes dried, vaporized, atomized and ionized. The sample is converted from liquid aerosol to solid particles and finally gaseous form at the analytical zone of the plasma at approximately 6000-7000 K. The gaseous form sample can be eventually transformed to elemental composition of sample. The plasma provides energy to remove electron from the outermost electron orbital and the elemental atom becomes positively charged. The resultant detection of these positively charged ions determine the characteristic ICP-MS ultratrace detection capabilities.

In the sample introduction system when the constant flow of liquid sample being transferred into analytical plasma by the peristaltic pump the aerosol would be generated by the nebulizer and the double-pass spray chamber is used for screening through small droplets to the plasma and being dissociated, atomized and ionized. Pneumatic nebulizer is usually applied in ICP-MS with argon gas flow by mechanic force to generate sample aerosol. Various designs of pneumatic nebulizers can be found such as concentric, micro-concentric, microflow and cross-flow depending on the sample conditions. Double pass and cyclonic spray are the frequent used spray chambers. The commonly used Scott design double-pass spray chamber is able to select the small droplets by directing the aerosol into a central tube. The large droplets emerges from a central tube due to gravity can exit the spray chamber via a drain tube.

Inductively coupled plasmas (ICP) are the most common type of plasma sources. The plasma source can be generated by a plasma torch, a radio frequency (RF) coil and RF power supply. The plasma torch consists of three concentric tubes made by quartz. Argon gas is used to form plasma is passed between the outer and middle tubes. A second auxiliary gas goes through middle tube and the sample injector is used to change the position of the base of the plasma relative to the tube and the injector. The nebulizer gas carries the fine droplet aerosol from the sample introduction system and penetrates through the centre of the plasma.

The formation of plasma discharge can be summarized as follow. A tangential flow of argon gas is directed between the outer and middle tube of a quartz torch. A copper load coil surrounds the top end of the torch and is connected to RF generator. When the RF power is applied to the load coil, an AC current oscillates within the coil at a rate corresponding to the frequency of the generator. Electromagnetic field is created at the top of the torch under RF oscillation. High-voltage spark is applied along with argon gas flowing through the torch. Chain reaction is occurred with a collision inducing ionization of the argon, breaking down the gas into argon atoms, argon ions and electrons. As a result, the inductively coupled plasma (ICP) discharge is formed and sustained by the RF generator. Samples comes out from the injector with high velocity are able to physically penetrate through the centre of the plasma discharge, travelling through the pre-heating zone followed by the radiation zone and the samples become positively charged ion by collisions of energetic argon electrons with the ground state atom. The ions emerge from the plasma is directed to the analytical zone of the mass spectrometer.

The role of the MS interface is to transport the ions efficiently from the plasma to the MS analyzer region. Ions generated from the plasma can pass sampler cone followed by skimmer cone. The ions come out from the skimmer cone are directed through the ion optics and finally arrived into the mass separation device. Secondary discharge as a result of electrostatic coupling of the load coil to the plasma should be minimized. Energy spread of the ions entering the mass spectrometer should be as low as possible to ensure the ions can all be focused efficiently by the ion optics and the mass spectrometer device. Neutral plasma should be maintained to guarantee electrical integrity of the ion beam when passing through the interface region. Cool-plasma to lower the plasma temperature and reduce argon-based polyatomic interferences should also be applied in certain cases.

The ion focusing system is set up for transporting the maximum number of analyte ions from the interface region to the mass separation device and at the same time filtering many of matrix components and non-analyte species. In addition particulates, neutral species and photons are also prevented to get through to the mass analyzer and the detector in order to optimize the signals. Analyte with high concentration of matrix elements can effectively defocusing the ions and altering the transmission characteristics of ion beams as space charge effect. The ion optics is positioned between the skimmer cone and the mass separation device with one or more electrostatically controlled lens components. The role of the ion optic system is to transfer ions from atmospheric plasma via the interface cones to the mass analyzer at high vacuum. The dynamic of ion flow from the plasma through the interface region into the mass spectrometer is crucial with the ion beam composition must be maintained throughout the interface region. Ion beam is positively charged due to rapid drop of lens chamber pressure with result of electrons being diffused out of the ion beam in the first stage charge separation process. In second stage of charge separation the ions are directed into the centre of the ion beam. There are various ion optic designs but in principle the purpose of setting up the ion optic system is to discriminate undesirable matrix- or solvent-based ions and ensure the analyte ions being transmitted to the mass analyzer.

The role of mass analyzer is to separate the ions out from the non-analyte species according to their mass-to-charge ratio (m/z). The most common mass analyzer is the quadrupole mass filter. A quadrupole is composed with four cylindrical stainless steel metallic rods with same length and diameter. With applying direct current (DC) field on one pair of rods and a radio frequency (RF) field on the opposite pair, analyte ions of a selected mass are allowed to pass through the rods to the detector. The analyte ions are subsequently being converted to an electrical pulse by the detector. The ion currents can be converted as electrical pulses and counted by a multi-channel analyzer. Additional factors such as the size of the quadrupole rod, power supply and kinetic energy of the ions are contributing to the resolution ability of a quadrupole.

To summarize in general, the whole ICP-MS measurement process is at first by taking liquid sample followed by generating an aerosol in which is suitable for ionization of plasma. The collecting analyte ions can be transported through the interface and focusing the ions via the ion optics into the mass spectrometer. At the end the ion currents are converted to corresponding electronic signals and analyte concentrations. Reference: (Section 8.3, Ref. (1), (33), (37) and (42)).

(4.0) Materials and methods

(4.1) Site description, sample collection and morphology of arsenic and copper

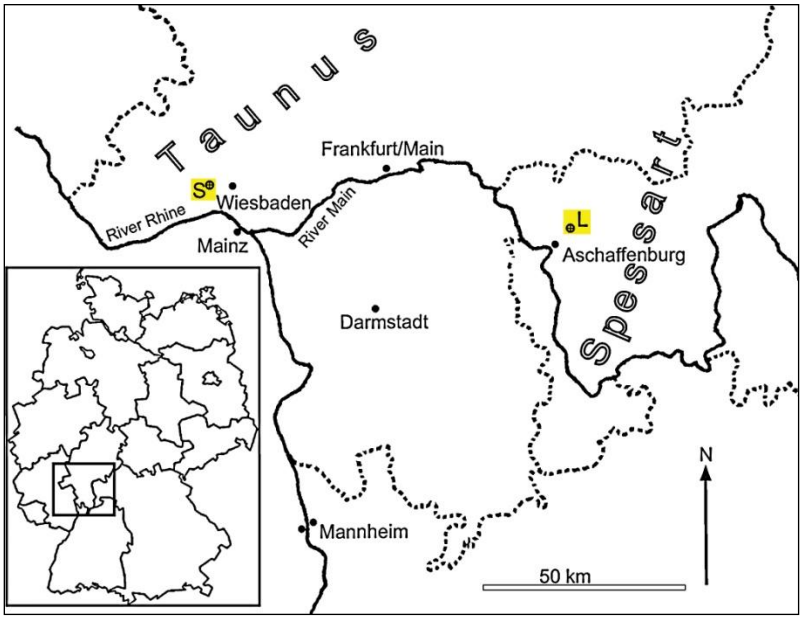


Fig. (12) Location of the collected clayey soil samples

The examined samples originate from the lime works Hufgard in Hösbach-Rottenberg near Aschaffenburg in Germany (figure 12). The lime has been produced by limestone which is used for the production of mineral fertiliser. The main commercial product of the quarry in which is sold for agricultural purposes is called "Carbonatic Magnesium Lime 85". The mineral specifications contain 60% $CaCO_3$, 25% $MgCO_3$, powder of grain size < 3 mm (97%) and < 1 mm (70%). The obtained limestone belongs to part of the hardly bounded "Zechsteindolomit" in German. This consists of the overlying stratum upon the copper shale and the host of high concentrations of the limestone. Two mines are also located nearby in which they both call "Segen Gottes" and "Hilfe Gottes" in German. History showed these two small Cu-Pb-Ag deposits have been heavily extracted in the past. In addition a very rare mineralisation of a Cu-As-Ag-Subtype has also been identified in the deposits. Typical minerals phases found in the deposits are termed Enargit (Cu_3AsS_4), Löllingit ($FeAs_2$) and Tennantit ($Cu_{10}(Fe,Zn)_2As_4S_{13}$) in German. The observed high concentrations of Cu and As in the surrounding dolomite were due to a high mobility of these elements permeating the rock fissure system.

Fig. (13) Pictures of extracted limestone samples.

The extracted limestone was rich in Iron- and Manganese-Oxides (figure 13) and also existed in concentrated forms of dendrites. In addition there are also large concretions of black material (Manganese-Oxide) presented in the rocks and they could be easily removed mechanically. The dendrites mainly show very thin surfaces with shaded colours between dark grey and light brown (figure 13). Concretions of Iron-Oxides were not found in the rocks and rather the deep-brownish colour of large areas of the rocks suggested of a fairly symmetrical distribution of Iron-Oxides. The limestone fertiliser which is sold as a powder form in the current market also contains high concentrations of Iron- and Manganese-Oxides resulting in the dark brown colour.

(4.2) Instrumentation of arsenic

The instrumentation parameters of HG-AAS, FAAS and XRF could be referred to Appendix C.

(4.3) Sequential extraction procedure of arsenic

All inorganic chemicals were of analytical reagent grade or better (Appendix C). All the collected samples were all homogenized, dried and sieved to a powder of grain size < 100 μm by Fritsch planetary ball mill in agate made material to assure no metal contamination prior to any chemical treatment. A 0.4g soil sample was added to a 50 ml polypropylene centrifuge tube (Sep-Cor) in addition with a 40 ml volume of the extractant from the step 1 (from top to bottom in sequential order) shown at the following table (13). Soil was extracted with fresh solution listed for each step. Samples were washed with Milli-Q water between each different extractant for 30 min.

Six subsamples from six different specimen bags of limestone powder provided by the producer, a certified reference material (GBW07108/GSR-6, limestone sample from China) and reagent blank from five different steps shown in table (13) with each of these samples in one duplicate were analyzed. The certified reference material was in a recommended value of As content 4.7 ± 0.4 mg/kg (Standard deviation ± 0.9 mg/kg). The recovery rate of As was above 90% on average with a standard deviation of ± 0.3 mg/kg.

Table (13) Table shows sequential extraction procedure for Arsenic-bearing solid phases

Step	Extractant	Target Phase
1 PO_4	1M NaH_2PO_4, pH 5, 24h, 298K, one water wash	Strongly absorbed As
2 HCl	1M HCl, 1h, 298K, one water wash	Carbonates and amorphous Mn hydroxides
3 Ox	0.2M ammonium oxalate/oxalic acid, pH 3, 2h, 298K, one water wash	Poorly crystalline Fe/Mn hydroxides
4 Ti	0.05M Ti(III)-citrate-EDTA-bicarbonate, pH7, 2h, 298K , one water wash	Crystalline Fe/Mn hydroxides
5 Conc. HCl	Concentrated HCl (32%), 2h, 298K, one water wash	Residual fraction

The applied reagent concentrations and soil-to-extractant ratios are 1:100 (0.4g to 40ml) for each selected step to ensure no exhaustion. All these soil solution suspensions were tumble-shaken in the sealed Sep-Cor tubes for the specified duration, and then centrifuged for 30 minutes at 11000g. The supernatant was decanted using a Teflon-tip syringe with care taken not to remove soil and filtered through 200-nm polycarbonate filters. The next extractant was added to the remaining residue, and the procedure was repeated. All of the decanted extractants were subsequently acidified with 1% concentrated HCl immediately after extractions to preserve Fe and Mn in solution state and stored in refrigerator before analysis. The last extraction step serves as analytical yield control and summation of As concentration from all extraction steps deviated from the concentration derived from treating only with concentrated HCl digestions are less than 10% difference in all samples. The reagent used in step 4 was produced following the pre-existing recommendations for the extraction of crystalline Fe oxides (Ryan and Gschwend, 1991). Great care should be focused on handling hazardous $TiCl_3$ solution with the extraction reagent should be prepared in sealed N_2-filled glove bag. The dissolved As concentration was obtained by using HG-AAS analysis (VGA 76). The detection limit was 0.4 μg/L (total As). All of the samples were diluted by MilliQ water (≈ 18MΩ cm^{-1}resistivity) to appropriate concentration range for HG-AAS and FAAS analysis.

(4.4) Sample preparation for arsenic measurement in HG-AAS

The samples and standards are usually prepared with duplicate acid concentrations (e.g. 10-50%) in which these concentrations are much higher than standard AAS sample preparation. The oxidation state of the analyte metalloid is important in HGAAS measurement. The necessary oxidation state of arsenic to be measured in HGAAS is As^{3+}. Element without this oxidation state (e.g. As^{5+}) behaves erratically and the results obtained from the measurements are non-reproducible. With this problem, all of the arsenic present in the samples and calibration standards must be pre-reduced before analysis. This can be achieved by reducing agent such as potassium iodide (KI). It is also important to notice that optimum concentration of sodium borohydride and hydrochloric acid should be used and the exact optimum condition varies between different elements.

Sample solution is transferred to a volumetric flask with addition of concentrated HCl and of 5% m/v freshly prepared KI solution followed by 5%m/v ascorbic acid solution. The amount of transferred sample and concentrated HCl required was within the detection limit of HG-AAS instrument. The sample solution is left for 60 minutes for complete reduction. The following two equations summarized the reaction processes.

$$As^{5+} + 2e^{-} \rightarrow As^{3+} \qquad \text{(Reduction) (eq.6)}$$

$$As^{3+} \rightarrow AsH_3 \qquad \text{(Hydride transfer) (eq.7)}$$

The dissolved concentration of Fe and Mn was also measured by flame atomic absorption spectrometry (Varian SpectrAAS 300) to validate the accuracy of the As measurement. The detection limits were 0.5 mg/L for Fe and 0.1 for mg/L for Mn. The recommended values of total Fe in Fe_2O_3 content are 2.52 ± 0.03 mg/kg (Standard deviation ± 0.10 mg/kg) for the certified reference material (GSR-6, limestone). The actual Fe content in soil samples were evaluated with multiplication of factor 0.699 (molecular weight of Fe/molecular weight of Fe_2O_3). It is also noted that for the certified reference material (GSR-6, limestone) the recommended values of Mn content are 434 ± 12 mg/kg (Standard deviation ± 41 mg/kg). The experimental error was defined as the standard deviation of the single measurements that were used for averaging.

The concentration of As, Fe and Mn for the above mentioned six identical agricultural lime samples and reference material were analyzed with X-ray fluorescence spectroscopy (XRF, Philips Bj 2002) to ensure the consistency of the extraction scheme. One sample of the certified reference material (GSR-6, limestone) was prepared and analyzed identically throughout the measurement. For calibration of the XRF 35 certified reference materials (described by Govindaraju, 1989) (Appendix B, table 9.1.4.5 and 9.1.4.6) were used covering As in 1.1 – 400 $mgkg^{-1}$ range. All the samples had concentrations above the detection limit of the XRF device of As in 1.1 $mgkg^{-1}$.

All of the above samples were re-analyzed by HG-AAS in the method of standard addition with standard As solution in concentration of 0, 2, 5, 10 and 20 µg/l due to suspect matrix effect in the solution samples. The standard additions technique involves taking the samples, dividing them into separate aliquots, and adding to each increasing quantities of arsenic standard under analysis. These increments are made equal and a minimum of five standard addition mixtures to set up a calibration set. The calibration set consists of one unspiked sample and a set of spiked materials. All of the samples were analyzed and a graph was plotted for analytical absorbance versus the concentration of spike added. These graphs were extrapolated back to the x axis to determine the (negative) concentration of the arsenic presented in the unspiked sample.

Optimum precision of the standard addition increment should be equivalent to the expected concentration of arsenic in the unspiked sample in order to avoid excessive errors in extrapolation from analyzed data. It is also important to ensure the calibration standards posses matrices identical to the samples to be analyzed.

(4.5) Instrumentation of copper

The instrumentation parameters of FAAS and XRF could be referred to Appendix C.

(4.6) Sequential extraction procedure of copper

Samples were taken from six different specimen bags of limestone powder provided by the producer (Section 4.1). All chemicals were of analytical reagent grade or better (Appendix C). All the collected samples were homogenized, dried and sieved to a powder of grain size < 100 µm by Fritsch planetary ball mill in agate made material to assure no metal contamination prior to any chemical treatment. Six subsamples with each of sub-sample from six seperate specimen bags were treated by microwave-assisted total acid (aqua regia) digestion and by a sequential extraction scheme as follows Table (14).

Table (14) Table shows sequential extraction procedure for Copper-bearing solid phases

Step	Extractant	Target Phase
1. Acetic acid	1M acetic acid, pH 2.5, 24h, 298K	Carbonate matrix
2. HAHC	0.5M hydroxylammonium hydrochloride, pH 1.5, 24h, 298K	Mn hydroxides
3. DCB	0.2M Na-dithionite-citrate-bicarbonate, pH 3, 24h, 298K	Fe hydroxides
4. Aqua regia	Concentrated HCl/HNO3, (3:1 ratio) with microwave-assisted	Residual fraction

The pH of the first acetic acid step did not rise beyond a value of 4 (HAc/CaAc buffer) to ensure complete dissolution of the carbonate matrix (Sulkowski and Hirner, 2006). Applied chelating agent to prevent readsorption of copper released at high pH values was not necessary under the above circumstance (Howard and Shu, 1996). Extracting agent targeting organic matter was not required at the absent of this phase in the limestone. The applied extractants in step 2 and 3 showed clear distinction between manganese oxide and iron oxide copper hosts (Tokashiki et al., 2003).

A 1.0g soil sample was added to a 50 ml polypropylene centrifuge tube (Sep-Cor) in addition with a 40 ml volume of the extractant from the step 1 (from top to bottom in sequential order) shown at the above table (14). Soil was extracted with fresh solution listed for each step. Samples were washed with Milli-Q water (<1 $\mu S\ cm^{-1}$) between each different extractant for 30 min. Six subsamples from six different specimen bags of limestone powder provided by the producer, a certified reference material (GBW07108/GSR-6, limestone sample from China) and reagent blank from four different steps shown in table (14) with each of these samples in one duplicate were analyzed.

The applied reagent concentrations and soil-to-extractant ratios were 1:40 (1.0 g to 40 mL) in the first three steps and 1:20 in the last step. An orbital shaker was used for all steps instead of an end-over-end shaker in order to prevent material blow-out due to CO_2 overpressure in the first step. The pH was monitored in the second extraction step in order to ensure that no transfer of any CaAc/HAc buffer solution from the first step increased the pH of the second one. After centrifugation for 30 minutes at 1100 g, the supernatant was decanted into a syringe and filtered through 0.2 μm polycarbonate filters. All extractants were acidified with 1% concentrated HCl immediately after separation and stored in the refrigerator before analysis. The concentrations of dissolved Cu, Mn, and Fe were determined using flame atomic absorption spectrometry (Varian SpectrAAS 300). The sum of all four extraction steps for Cu was at 100% ± 15% (SD of triplicate subsamples out of the 6 specimen bags) in comparison to the amount of Cu determined by the total acid digested sub-samples, the X-ray fluorescence spectroscopy (XRF) analysis and the certified reference material GBW07108/GSR-6 used for analytical quality assessment and control (a commercial limestone CRM from China with an enhanced Cu content of 23 ± 3 mg/kg). The detailed description of Fe and Mn concentration measurements by FAAS could be referred to section 4.4.

(4.7) Site description and extraction procedure of thallium

Site description

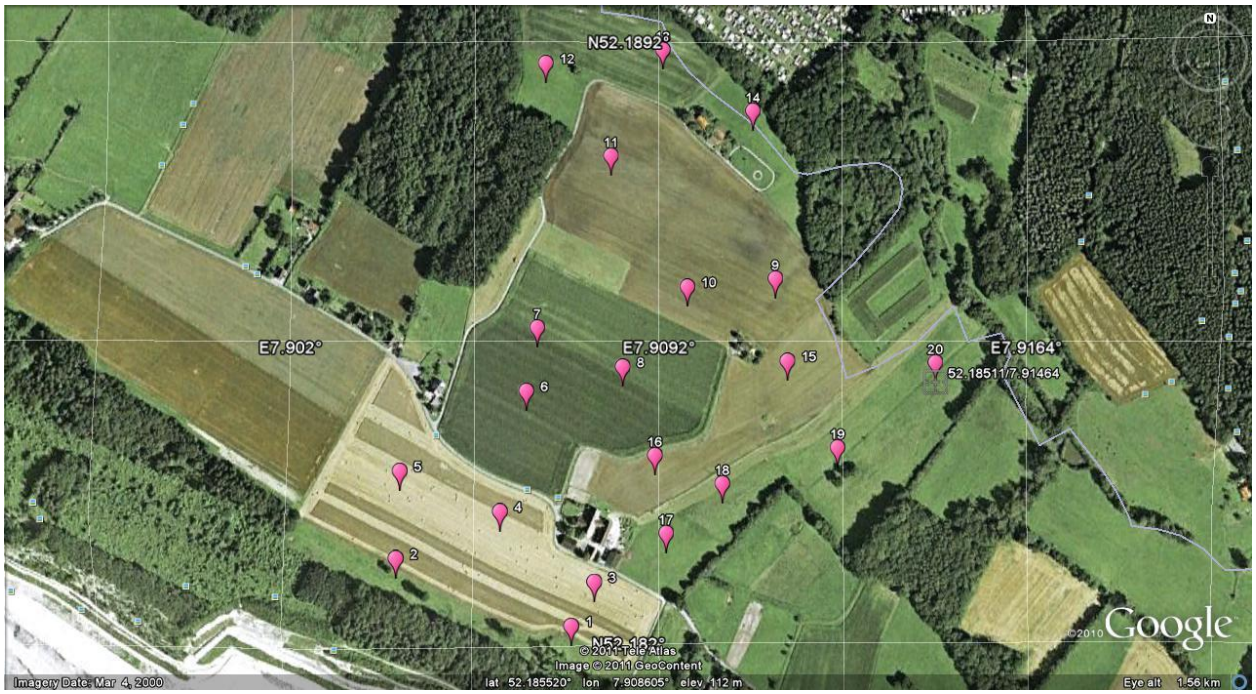


Fig. (14) Location of the collected soil samples and the sampling points (No. 1-20)

The above figure 14 showed the collected soil sampling points in pink spots at sample location 1. Table (15) demonstrated the location of each sampling point and the depth of samples collected at each sampling point. The purpose of land use at each sampling points could be referred to Table (19). The sampling location 1 was at the northeast of local cement factory.

The sampling area covered 45 hectares. Each sampling point represented homogeneously of the local sampling area. The sampling area is broadly divided as land for agricultural purpose and Greenland. The soil sampling core was collected by using stainless steel split-tube sampler (produced by Eijkelkamp company) with no metal contamination sampler was ensured before the sampling process. The size of 5 cm inner diameter of the sampler drill could ensure the top and sub-soils undisturbed during the soil profile removal process. The soil sampling core was immediately transferred to PVC-tubes (produced by Eijkelkamp company) and sample storage fridge before the thallium extraction procedure.

The topsoils sampling points which were identified for agricultural purpose had been subjected extensively to plowing process. On the contrary, the subsoils remained rather intact and closely resemblance with thallium concentration of the parental rocks. The soil core from the agricultural land was characterized with deep dense, dark brown, loamy-sandy till-silty soils. The soil core from the Greenland was characterized with sandy soils.

Table (15) Table shows sampling location of the collected soils at location 1

Sample number location (GPS-coordinate in decimal degrees ^{o}N/^{o}E	Sample depth (cm)	Sample number location (GPS-coordinate in decimal degrees ^{o}N/^{o}E	Sample depth (cm)
1 52,18200/7,90750	0-10 10-30 30-40	11 52,18760/7,90826	0-30 30-40
2 52,18281/7,90414	0-10 10-30 30-40	12 52,18871/7,90698	0-10 10-30 30-40
3 52,18250/7,90794	0-30 30-40	13 52,18888/7,90928	0-10 10-30 30-40
4 52,18334/7,90611	0-30 30-40	14 52,18814/7,91105	0-10 10-30 30-40
5 52,18382/7,90416	0-30 30-40	15 52,18513/7,91172	0-30 30-40
6 52,18477/7,90661	0-30 30-40	16 52,18400/7,90912	0-30 30-40
7 52,18553/7,90682	0-30 30-40	17 52,18307/7,90934	0-10 10-30 30-40
8 52,18506/7,90849	0-30 30-40	18 52,18366/7,91044	0-10 10-30 30-40
9 52,18612/7,91149	0-30 30-40	19 52,18409/7,91270	0-10 10-30 30-40
10 52,18602/7,90976	0-30 30-40	20 52,18511/7,91464	0-30 30-40

Fig. (15) Location of the collected soil samples and the sampling points (No. 1-13)

The above figure 15 showed the collected soil sampling points in light blue spots at sample location 2. Table (16) demonstrated the location of each sampling point and the depth of samples collected at each sampling point. The purpose of land use at each sampling points could be referred to Table (20). The sampling location 2 was also located at the northeast of cement factory.

The sampling area covered 55 hectares. Each sampling point represented homogeneously of the local sampling area. The sub-sampling points were mainly located in forest with the others being in Greenland and cottage. The soil sampling core was collected by the same method described in above location 1. The soils collected from the sample location 2 were characterized as sandy soils. The sampling points were not involved with agricultural purposes since 1970 and could well be served as Tl concentration reference points to sample location 1.

Table (16) Table shows sampling location of the collected soils at location 2

Sampling number (GPS-coordinate in decimal minutes $^{o}N/^{o}E$	Sample depth (cm)	Sampling number (GPS-coordinate in decimal minutes $^{o}N/^{o}E$	Sample depth (cm)
1 11.171/53.766	0-10 10-30 30-40	8 11.266/54.305	0-10 10-30 30-40
2 11.143/53.817	0-10 10-30 30-40	9 11.359/54.264 (Core-drill)	0-10 10-20 20-50 50-70 70-90 90-100
3 11.120/53.884	0-10 10-30 30-40	10 11.419/54.154	0-10 10-30 30-40
4 11.091/53.929 (Core-drill)	0-10 10-20 20-50 50-70 70-90 90-100	11 11.483/54.027 (Core-drill)	0-10 10-20 20-50 50-70 70-90 90-100
5 11.052/54.036	0-10 10-30 30-40	12 11.443/53.937	0-10 10-30 30-40
6 11.001/54.120	0-10 10-30 30-40	13 11.203/54.081	0-10 10-30 30-40
7 11.205/54.345	0-10 10-30 30-40		

Extraction procedure of thallium

Soil samples were collected from different sampling points described in the above section 4.7. All chemicals were of ultrapure reagent grade (Appendix C). Ultrapure water was used for dilution purpose and the water content was checked following German DIN ISO 11465 prior the experiment. The sample preparation was conducted based on German DIN ISO 11464:1994.

All of the collected soil samples were homogenized, dried at 40 ^{o}C in drying oven and sieved to a powder of grain size < 2 mm by Fritsch planetary ball mill in agate made material to ensure no metal contamination prior to any chemical treatment. Each soil subsamples listed in above section 4.7 was extracted by ammonium nitrate solution and microwave-assisted total acid (aqua regia) digestion separately. 1M NH_4NO_3 and aqua regia total acid digestion were used as soil extracts to find out the available and leachable portions of thallium based on operationally defined procedures. NH_4NO_3 is unbuffered mild extractants which target the exchangeable fraction of the element. The aqua regia total acid digestion aimed to extract total thallium content presented in the sub-samples. The final Tl concentrations were defined in the extractants. The extraction procedure was followed by German DIN 19730:1997-06 and summarized as follows.

All glassware was acid washed to ensure that no metal ions were present on the glass surface. The glassware was first washed in detergent and well rinsed in tap water. The detergent-cleaned glassware was rinsed with MilliQ water (~ 18 MΩ cm^{-1} resistivity) and then heated in 5M HNO_3 (Analar) for 4 hours and left for 24 hours before it was rinsed with MilliQ water and heated in a water bath (MilliQ) for a further 4 hours. The clean glassware was again rinsed with MilliQ water and dried in a drying cabinet, before being sealed with clingfilm for storage prior to the usage. The procedure was repeated for polypropylene centrifuge tubes, 50ml polytetrafluoroethylene (PTFE) syringe and PTFE extractant storage bottles.

A 10.0 ± 0.1 g soil sample was added to a 50 ml polypropylene centrifuge tube (Sep-Cor) after homogenized by the cone and quarter technique and followed by a 25 ml volume of fresh 1 M NH_4NO_3 solution. The soil solution was transferred to an end-over-end shaker and shaken for 2 hours in 20 revolutions per minute at room temperature (20 ± 2 ^oC). The soil solution suspension was subsequently centrifugated for 30 minutes at 1100 g and the supernatant was decanted into 50 ml PTFE syringe and filtered through 0.45 μm membrane filters (DIN 19730:1997-06, Section 5.7) with the first 5ml of extractant being discarded and transferred to PTFE storage bottle. All extractants were acidified with 1% concentrated nitric acid (e.g. 0.4 ml nitric acid to 40 ml extractant) immediately after separation and stored in the refrigerator before analysis.

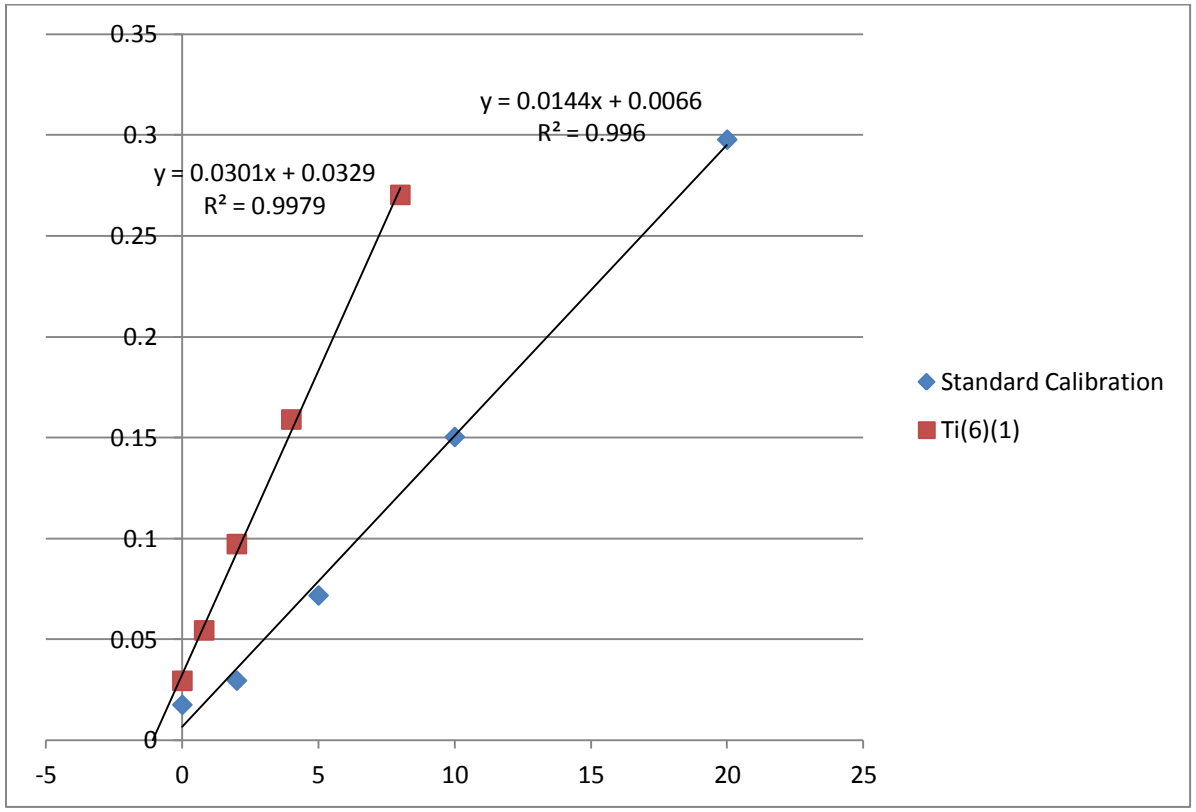
All of the subsamples listed in section 4.7, two certified reference material (GSD-08 and GSS-4) and reagent blank with each of these samples in two duplicate were analyzed immediately after extraction. The applied reagent concentrations and soil-to-extractant ratios were 1:25 (20.0 g to 50 mL) in ammonium nitration extraction and 1:20 in the aqua regia acid digestion. The concentrations of dissolved Tl were determined using optimized inductively coupled plasma mass spectrometry (ICP-MS) (HP 4500 Model) (spike with internal standard) with ten repetitive measurements of Tl counts per second for each sub-sample. An average Tl counts per second against corresponding Tl concentration relationship was deduced after external Tl standard calibration and sub-samples measurements. The amount of Tl in 1 M NH_4NO_3 extractant solution and total acid digested sub-samples were compared with the certified reference materials GSD-08 and GSS-4 used for analytical quality assessment and control. The recovery rate of Tl for GSD-08 (0.70 ± 0.09 mg/kg) and GSS-4 (0.88 ± 0.15 mg/kg) were shown at 90 and 94% respectively. No solution matrix effect was observed throughout all the ICP-MS measurements.

The geostatistical analyses were performed using the VESPER program (v.1.6). All isoline plots were produced using Surfer 8.0 and GIS software ArcMap (version 9.2). Pair T-test was performed by GraphPad QuickCalcs software. The instrumentation parameters of ICP-MS, could be referred to Appendix C.

(5.0) Results and discussion

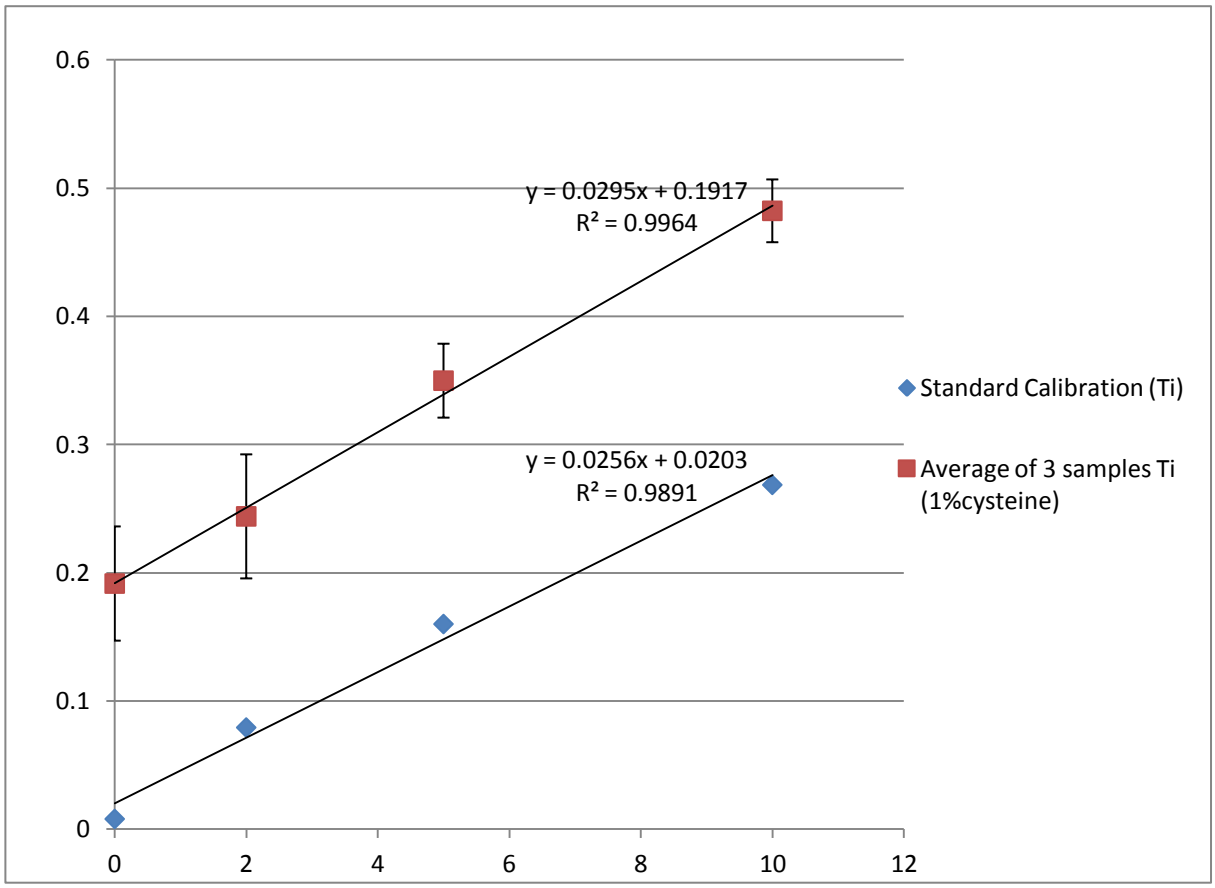
(5.1) Matrix effect of arsenic

Initial HG-AAS measurements showed that the total As concentration (∑5 steps) was not comparable with XRF results (total element content). A suspect matrix effect was discovered on samples in all steps all sub-samples (Appendix B, 9.2.1) under the HG-AAS measurements and the samples were subsequently re-measured by method of standard addition (addition of known amount of As standard) to each sample. The results (figure 16) demonstrated that around "a factor of two" concentration difference were observed in all samples and all steps when samples were measured by standard addition method in comparison with samples being measured without standard addition..



Arsenic absorbance obtained in HG-AAS against Arsenic concentration in samples

Fig. (16) Graph plot shows actual arsenic sample concentration measured by the method of standard addition



Arsenic absorbance in HG-AAS (absorbances obtained in average of 3 sub-samples) against Arsenic concentration in samples

Fig. (17) Graph plot shows actual arsenic sample concentration measured by the method of standard addition with addition of 1% cysteine in the sample

The plausible mechanism of this observed interference could be due to the interferent is precipitated as the metal (e.g. copper) and the mechanism probably involves capture and decomposition of the gaseous hydride at the freshly precipitated metal (Welz et al., 1984). The interference could be caused by a chemical reaction rather than physical adsorption and then followed by chemical reaction. All of the above matrix effect observed in the HG-AAS measurement in all steps and all samples could be minimized successfully with addition of 1% cysteine as masking agent in all steps all sub-samples (Appendix B, 9.2.2-9.2.3) to complex the trace amounts of metal. The above figure (17) demonstrated that such effect was reduced and the recorded arsenic absorbances were found to be ascending in right proportion compared with the standard calibration line.

(5.2) The sequential extraction of arsenic

The following table (17) and figure (18) show the amount of arsenic, copper and manganese being partitioned in the five different sequential extraction steps. Further details of each sub-sample content and percentage distribution of As, Cu and Mn can be referred to Appendix (A, 9.1.1-9.1.5).

Table (17) Table shows average contents of As, Fe and Mn in the sequential extraction scheme

As	Average As content of 6 sub-samples(mg/kg)	Fe	Average Fe content of 6 sub-samples(g/kg)	Mn	Average Mn content of 6 sub-samples(g/kg)
PO_4	11.3±2.7	PO_4	0.1±0.1	PO_4	0.2±0.1
1M HCl	2.3±1.2	1M HCl	2.1±1.3	1M HCl	2.5±1.3
Ox	10.3±5.5	Ox	1.5±1.0	Ox	2.0±1.4
Ti	46.2±21.8	Ti	4.0±2.2	Ti	0.6±0.3
Conc.HCl	1.9±1.2	Conc.HCl	0.8±0.4	Conc.HCl	0.6±0.4
Sum of As in 5 sequential extraction steps (average of 6 sub-samples)	72.0±27.8	Sum of Fe in 5 sequential extraction steps (average of 6 sub-samples)	8.5±2.2	Sum of Mn in 5 sequential extraction steps (average of 6 sub-samples)	5.9±1.8
As content under XRF analysis (average of 6 sub-samples)	72.2±19.5	Fe content under XRF analysis (average of 6 sub-samples)	11.3±2.6	Mn content under XRF analysis (average of 6 sub-samples)	7.4±2.2

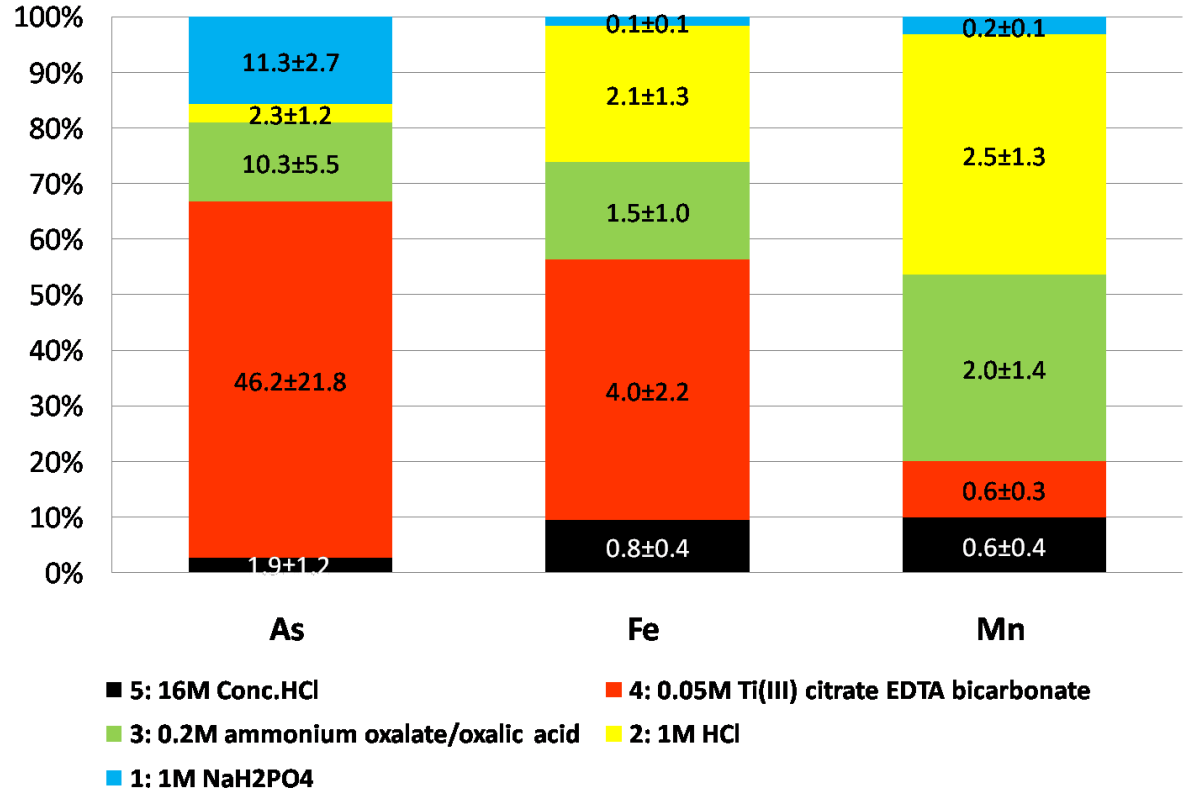


Fig. (18) Figure shows distribution of As, Fe and Mn (% range) in the sequential extraction scheme

The observed As content under sequential extraction and XRF were found to be highly consistent (table 17). The global average content of arsenic being found in limestone is around 2.6 mg/kg according to Baur and Onishi (1969) and the As present in pellet limestone for soil pH amendment were found to be between 2-4 mg/kg (McBride and Spiers, 2001; Price and Pichler, 2006). It was also noticed that As in MAP/DAP phosphate fertilizers were in a typical range of 10-16 mg/kg (Charter et al., 1995; Raven and Loeppert, 1997). All of the measured sub-samples demonstrated much higher As content than the above mentioned usual limit.

The measured Fe and Mn concentration in FAAS were 25% and 20% lower compared with direct XRF measurement of all lime samples included the reference material (table 17). The reason could be due to Fe/Mn bearing minerals (e.g. silicates) are not soluble in HCl (Step 2 and 5) and such missing Fe and Mn could still be left in the residue.

The geochemical similarity between P and As has leaded to an assumption that both P and As should be associated with similar constituents in the soils. The theories underlying this phosphate extraction step is due to similar electronic configuration and ability to form triprotic acids with similar dissociation constants followed by competitive exchange between phosphate and arsenate in soils. The nature of PO_4^{3-} contains smaller size and higher charge density than arsenate would cause arsenate to be preferably desorbed in competition with phosphate (Wenzel et al., 2001; Keon et al., 2001) and these were revealed in the result's figure (18) that a significant 17 ± 4% of As was mobilized by the first phosphate step.

Both of the mobilized Fe and Mn (both <4%) were minimal and could be neglected in the first extraction step. It was also noticed that only less than 3% of arsenic was mobilized in second step even though 25% and 42% total Fe and Mn were dissolved in this HCl-soluble step. The valences of these elements (e.g. Fe^{2+} or Fe^{3+}, and Mn^{2+} or Mn^{4+}) were not known and it was therefore not possible to clearly determine the extraction yield was from a carbonate or as an amorphous oxide species.

The third oxalate moderately acid-reducing extraction extracted 18%, 33% and 14% of Fe, Mn and As respectively. The fourth strongly-reducing Ti step dissolved 46% (4.0 ± 2.2 g/kg) of the Fe content and 64% of the total As were also be dissolved, with a molar ratio As/Fe = $1.1 \cdot 10^{-2}$. With the observed results, it demonstrated that the Fe fraction is dominated with crystalline oxides like goethite. On the contrary, only less than 1g/kg of Mn was mobilized in step 4.

The last 5th step extracted further 9% of the Fe content and negligible fractions of As and Mn (<2%). None of the As had been remained after 5 steps of extraction and however there was still 25% of both Fe and Mn being contained in the non-dissolved residual portion compared between the AAS and XRF analyses.

The above description stated how all the three elements distributed across five different steps. The major discovery in above was a comparatively strong binding between As and crystalline Fe phases. It was worth noticing that a significant one third of As managed to be mobilized under exchangeable to mildly acid-reducing conditions (sum of steps 1-3: 35 ± 6%, or 24.0 ± 6.1 mg/kg). This occurrence was because of readsorption of released metals is a common process in sequential extraction with potential sorbents are not exhausted and pH conditions are above the adsorption edge of the respective metal (Wenzel et al., 2001; Van Herreweghe et al., 2003). It was undesired for arsenate oxoanions to be adsorbed even under moderately acidic conditions and these observed results present uncertainty about whether the As load on the residual Fe oxide is the original or there is a considerable repartitioning of As between dissolved Mn and residual Fe oxides in the first three extractions steps and hence the predominance of As binding to crystalline Fe oxides over Mn oxides could not be assured in above circumstances. Therefore, direct X-ray spectroscopic analysis was considered to be essential for further analysis.

(5.3) The sequential extraction of copper

The following table (18) and figure (19) show the amount of copper, iron and manganese being partitioned in the four different sequential extraction steps. Further details of each sub-sample content and percentage distribution of Cu, Fe and Mn can be referred to Appendix A (9.1.6-9.1.10).

Table (18) Table shows average contents of Cu, Fe and Mn in the sequential extraction scheme

Cu	Average Cu content of 6 sub-samples(mg/kg)	Fe	Average Fe content of 6 sub-samples(g/kg)	Mn	Average Mn content of 6 sub-samples(g/kg)	Ca	Average Ca content of 6 sub-samples(g/kg)
Acetic acid	33.5±24.4	Acetic acid	2.8±2.0	Acetic acid	3.8±2.0	Acetic acid	232.8±7.4
HAHC	17.2±20.7	HAHC	1.0±0.8	HAHC	2.0±1.7	HAHC	23.2±6.9
DCB	20.0±20.0	DCB	1.7±0.8	DCB	0.2±0.1	DCB	4.6±4.0
Aqua regia	26.3±17.1	Aqua regia	3.3±2.1	Aqua regia	0.1±0.04	Aqua regia	0.6±0.6
Sum of Cu in 4 sequential extraction steps (average of 6 sub-samples)	98.7± 69.8	Sum of Fe in 4 sequential extraction steps (average of 6 sub-samples)	8.5±2.2	Sum of Mn in 4 sequential extraction steps (average of 6 sub-samples)	5.9±1.8		
Cu content under XRF analysis (average of 6 sub-samples)	95.5±64.0	Fe content under XRF analysis (average of 6 sub-samples)	11.3±2.6	Mn content under XRF analysis (average of 6 sub-samples)	7.4±2.2		

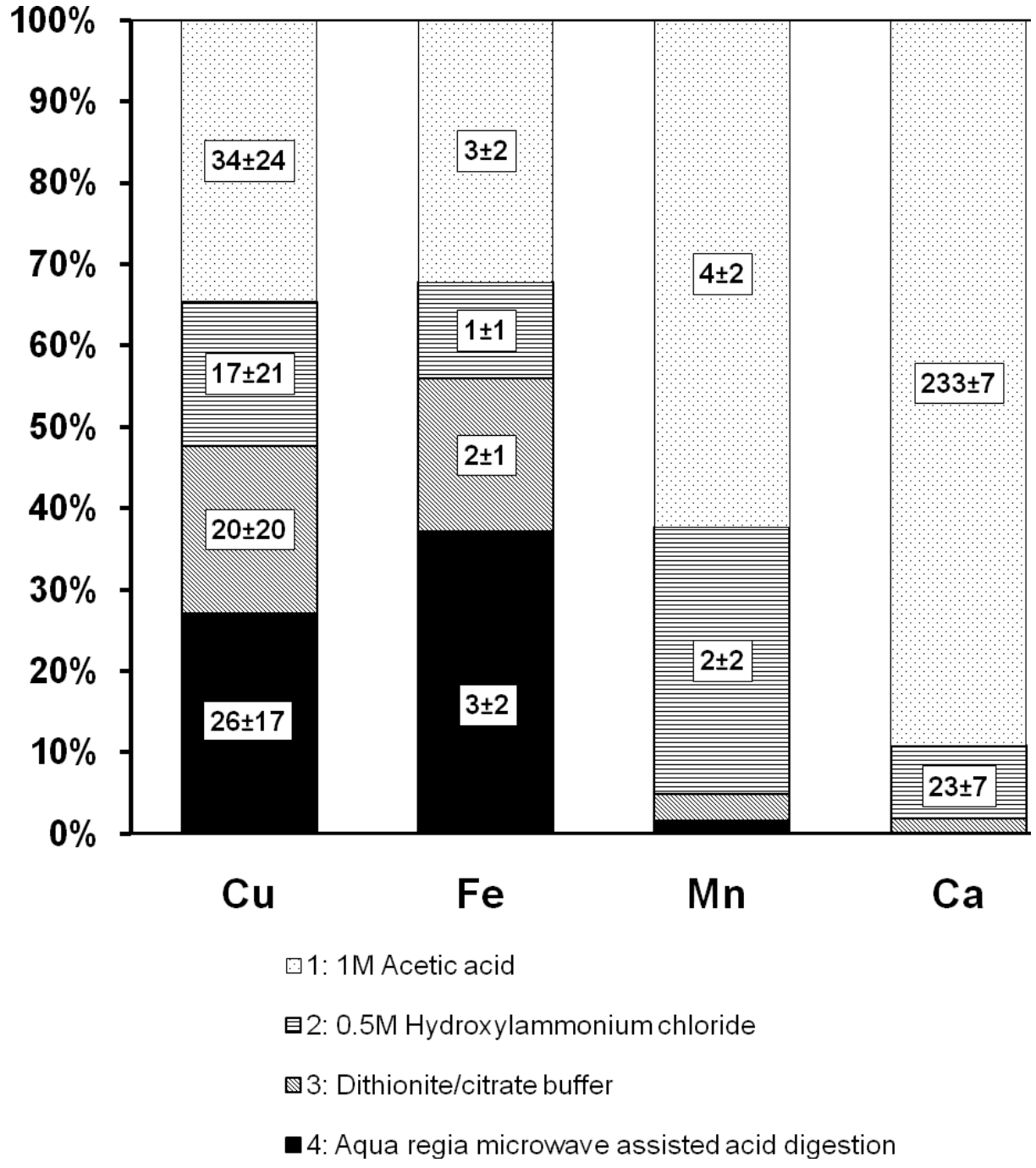


Fig. (19) Bar chart shows average percentage recoveries for the six lime sub-subsamples under the sequential extraction scheme of Cu and the matrix elements of Fe, Mn and Ca.

Total acid (HCl) digestion of the six different lime charges yielded bulk Fe, Mn and Cu concentrations of 8.5 ± 2.2 g/kg, 5.9 ± 1.8 g /kg, and 98.7 ± 69.8 mg/ kg, respectively (average of six subsamples). Each of the six individual sub-sample indicated Cu concentrations of 12, 41, 69, 137, 140 and 174 mg/kg. The vast standard deviation of Cu content is due to inhomogeneous lime composition but not analytical variance. All of the above sub-samples Cu concentrations showed higher copper concentrations than Cu content of 2-8 mg/kg limestone commonly used for soil pH amendment (McBride and Spiers, 2001). The copper concentrations of three sub-samples demonstrated Cu contents exceeding the recommended limit of 100 mg/kg soil health tolerance level (Korthals et al., 1996). XRF analysis showed all the lime sub-samples contained 25% higher total Fe concentrations (11.3% ± 2.6%) and Mn concentrations (7.4 ± 2.2%), the extra Fe and Mn could be contained in HCl-insoluble Fe and Mn-bearing silicate minerals although no significant amount of Cu being presented in these residual phases according to XRF results (95 ± 64 mg/kg).

The average percentage recoveries for the six lime sub-subsamples under the sequential extraction scheme of Cu and the matrix elements of Fe, Mn and Ca were shown in Figure (19) and each of six sub-samples recoveries could be referred to Appendix A (9.1.10.1) (p.212-214). The total amount of Cu extracted by the sequential procedure (Σsteps 1-4) was in good accordance with both the results of a separate single microwave-assisted aqua regia digestion and the direct XRF analyses. Copper was partitioned almost evenly among four steps. Around one third of Cu was mobilized by the first acetic acid step which is generally considered to target at exchangeable and carbonate-bound metal. The Cu associated with carbonate-bound metal was confirmed by the approximate 90% recovery for the carbonate matrix element of Ca (Figure 19). The result showed carbonate minerals could be important for Cu fixation. An association of contaminant Cu with dolomite fragments in soil in form of malachite precipitates has already been reported (e.g. by McBride and Bouldin 1984). The above figure (19) showed that over 30% of the total Fe and 60% of Mn were dissolved along with the first step. The dissolved Fe and Mn contents could be due to Fe/Mn-bearing carbonates and also from poor stability of nanocrystalline oxide under the acidic condition of 1.0 M acetic acid in first step (pH ~ 2.5; Whalley and Grant, 1994).

An average of 18 ± 12% of Cu was mobilized by the second moderately reducing HAHC step. This step targets both Mn oxyhydroxides and amorphous Fe oxyhydroxides in which Fe was released more than Mn. However this second step in comparison only dissolved a minor proportion (12%) of total Fe but a significant proportion (34%) of total Mn. The calculated Cu/Mn ratios are the same for both of the first and second extraction step but not the case for the Cu/Fe ratios. The third step dissolved further 21 ± 10% on average of Cu in which associated with non-silicate, strongly reducible Fe oxides, with the Mn proportion contributed no significant role. The last step dissolved an additional 27 ± 8% on average of Cu, with one third of Fe and nearly nothing of Mn being left in this residual portion. This residue consists of silicates and other resistant minerals which usually play no significant role in environmental assessments. All of the copper was recovered as the result of total Cu in ∑1-4 steps matched with the direct XRF analysis.

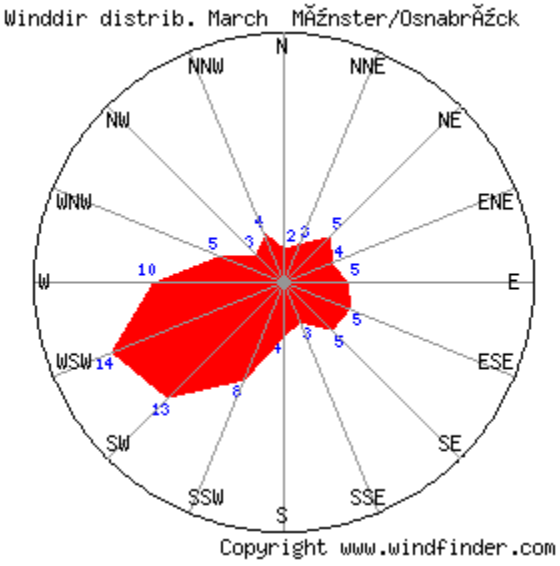
The sequential extraction results suggest the copper can be mobilized under both acidic and reducing conditions. The results however do not reveal the exact phase Cu being associated with as the first acetic acid step can dissolve both Cu in the carbonate matrix and also the poorly crystalline oxides. Cu can possibly be hosted by the carbonate matrix or the oxide dendrite, or by the both phases. In addition it is important to distinguish Cu loaded between Mn and Fe hydroxide dendrites phases as Cu associated with the Mn hydroxide dendrites can be mobilized under reducing (e.g., submerged) soil conditions but not the Cu in the Fe hydroxide dendrites. Direct X-ray spectroscopic speciation analysis should be introduced to resolve these uncertainties.

An attempted sequential extraction with modified 1st step with 1M sodium acetate and acetic acid buffer was applied (Appendix A, 9.1.10.2) (p.215) and successfully recovered all of the Cu in the six lime sub-samples (Appendix A, 9.1.10.2) (p.215) however it was unfortunate that the first step in which targeting exchangeable and carbonate-bound Cu metal did not reveal high percentage recovery of carbonate matrix element of Ca. The low percentage recovery of carbonate matrix element of Ca indicated the recovered Cu metal in step 1 did not successfully partition all the Cu metal which is associated with exchangeable and carbonate-bound Cu metal phase.

(5.4) Thallium concentration profiles of top and sub soils at sampling location 1

Month of year	Jan 01	Feb 02	Mar 03	Apr 04	May 05	Jun 06	Jul 07	Aug 08	Sep 09	Oct 10	Nov 11	Dec 12	SUM 1-12
Dominant Wind dir.													
Wind probability > = 4 Beaufort (%)	24	25	30	21	18	19	22	14	14	17	18	19	**20**
Average Wind speed (Knots)	8	8	9	8	8	8	8	7	7	7	7	7	**7**
Average air temp. (°C)	3	4	7	13	16	19	21	20	17	12	8	3	11

Select month (Help) Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec Year



Wind direction Distribution March(%)

Fig. (20) Figure shows wind and weather statistic of Münster/Osnabrück. Statistics based on observations taken between 7/2001 - 12/2010 daily from 7am to 7pm local time. (Section 8.3 Ref. 53)

The above figure (20) demonstrated the last 10 years statistical observation for the wind direction from 2001 to 2010 at Münster/Osnabrück region. The finding suggested the dominant wind direction throughout the years were mainly towards northeast. The sampling location 1 and 2 are positioned at the northeast of cement factory in Lengerich. All of the sampling points from location 1 and 2 were located less than 3km away from the centre of the radius of the cement factory.

Table (19): Table shows soil thallium (Tl) concentrations extracted by ammounium nitrate and aqua regia total acid digestion at location 1

Sample number location (GPS-coordinate in decimal degrees ^{o}N/^{o}E	Property of the area (Type of crops or vegetables being grown)	Sample depth (cm)	Tl content extracted by ammonium nitrate (µg/kg)(ppb)	Tl content extracted by aqua regia total acid digestion (mg/kg)(ppm)
1 52,18200/7,90750	Greenland	0-10 10-30 30-40	116.91 ± 6.27 80.64 ± 10.54 43.42 ± 10.21	1.71 ± 0.32 1.08 ± 0.45 0.87 ± 0.31
2 52,18281/7,90414	Greenland	0-10 10-30 30-40	131.96 ± 5.33 32.22 ± 4.83 7.56 ± 1.79	2.41 ± 0.33 0.94 ± 0.19 0.28 ± 0.18
3 52,18250/7,90794	Mustard	0-30 30-40	95.27 ± 9.05 57.63 ± 8.12	0.99 ± 0.11 0.62 ± 0.16
4 52,18334/7,90611	Mustard	0-30 30-40	91.59 ± 10.65 62.81 ± 7.38	1.16 ± 0.33 0.94 ± 0.21
5 52,18382/7,90416	Mustard	0-30 30-40	66.85 ± 9.00 23.86 ± 3.88	1.06 ± 0.16 0.70 ± 0.16
6 52,18477/7,90661	Harvested	0-30 30-40	116.84 ± 10.04 99.56 ± 15.89	0.94 ± 0.12 0.92 ± 0.15
7 52,18553/7,90682	Harvested	0-30 30-40	52.66 ± 7.20 64.04 ± 2.01	0.89 ± 0.11 0.90 ± 0.11
8 52,18506/7,90849	Harvested	0-30 30-40	69.30 ± 8.51 72.82 ± 10.90	0.75 ± 0.14 0.73 ± 0.22
9 52,18612/7,91149	Corn	0-30 30-40	67.63 ± 1.78 52.46 ± 15.00	0.80 ± 0.28 0.49 ± 0.15
10 52,18602/7,90976	Corn	0-30 30-40	22.91 ± 8.95 12.04 ± 3.41	0.84 ± 0.28 0.80 ± 0.18

11 52,18760/7,90826	Corn	0-30 30-40	37.98 ± 1.51 40.80 ± 2.92	0.71 ± 0.19 0.67 ± 0.17
12 52,18871/7,90698	Greenland	0-10 10-30 30-40	39.47 ± 1.90 27.03 ± 0.25 8.81 ± 1.84	1.77 ± 0.31 0.84 ± 0.10 0.37 ± 0.06
13 52,18888/7,90928	Greenland	0-10 10-30 30-40	50.68 ± 2.09 49.55 ± 4.35 48.34 ± 1.19	0.60 ± 0.30 0.55 ± 0.15 0.47 ± 0.11
14 52,18814/7,91105	Greenland	0-10 10-30 30-40	71.37 ± 6.50 57.65 ± 4.65 53.98 ± 4.53	0.46 ± 0.08 0.44 ± 0.17 0.30 ± 0.05
15 52,18513/7,91172	Mustard	0-30 30-40	79.97 ± 6.53 44.55 ± 1.58	0.63 ± 0.18 0.67 ± 0.17
16 52,18400/7,90912	Mustard	0-30 30-40	43.20 ± 4.42 22.04 ± 2.04	0.84 ± 0.26 0.32 ± 0.08
17 52,18307/7,90934	Greenland	0-10 10-30 30-40	29.03 ± 8.61 37.09 ± 3.65 15.76 ± 1.23	1.16 ± 0.30 0.69 ± 0.07 0.31 ± 0.04
18 52,18366/7,91044	Greenland	0-10 10-30 30-40	44.23 ± 2.32 34.22 ± 2.22 31.66 ± 2.45	1.32 ± 0.22 1.34 ± 0.35 0.40 ± 0.07
19 52,18409/7,91270	Greenland	0-10 10-30 30-40	52.08 ± 9.46 47.26 ± 3.53 14.55 ± 1.04	1.14 ± 0.15 0.64 ± 0.05 0.03 ± 0.04
20 52,18511/7,91464	Corn	0-30 30-40	24.68 ± 0.15 22.05 ± 9.42	0.73 ± 0.26 0.31 ± 0.05

The above table (19) showed the exchangeable thallium (extracted by ammonium nitrate) and total thallium concentrations in different sampling points and depths. The exchangeable thallium concentration of top and sub-soils could be compared.

A simple paired T-test of exchangeable and total thallium concentrations between top and sub-soils were carried out separately. The assumption for the observed data were from same subject (Location 1 in this case) and drawn from a population with a normal distribution. The test statistic was t with n-1 degrees of freedom. If the p-value associated with t was low (< 0.05), there was evident to reject the null hypothesis. As a result there was an evident that there was a difference in means across the paired observations.

The exchangeable thallium t-test value was 3.4998 with degree of freedom equal to 61 and p = 0.0009. The p-value associated with t was low (< 0.05). The small p-value indicated rejection of the null hypothesis. The paired exchangeable thallium concentration between top and sub-soils was considered to be statistically significant difference. The t-test was also applied for total thallium extracted by aqua regia acid digestion. T-test value was 3.5134 with degree of freedom equal to 59 and p = 0.0009. The paired total thallium concentration between top and sub-soils was also considered to be statistically significant difference.

The results suggested that the exchangeable thallium concentration was highest in surface soils and gradually decreasing with increasing sample depth at sampling point 1, 2, 12 and 19 (all were from Greenland) (Fig. 9.1.14.1, Appendix A) (p.219). The high thallium concentration observed on the surface soils was possibly due to anthropogenic emission and not from the natural parental minerals. It has been suggested that the atmospheric Tl pollution can contribute to soil contamination in the vicinity of Tl emission sources. (Brockhaus et al. 1981). Tl soil contamination is mainly caused by dust fall-out from emissions of cement plants (ATSDR, 1992). In the above figure (20) suggested that the majority of the wind direction in the region was recorded towards north-east direction. Therefore a strong indication was shown due to the sampling site 1 is located at the north-east of the local cement factory. Samples 13, 14 and 18 from Greenland also demonstrated decreased exchangeable thallium concentrations with increasing sample depth (except sample 17) (Fig. 9.1.14.1, Appendix A) (p.219). These four sampling points showed less drastic decrease of the thallium concentrations with increase sampling depth. Overall all of the above Greenland samples showed highest exchangeable thallium concentrations on the surface soils with decrease Tl concentrations by increasing sample depths.

Aqua Regia acid digestion as a weaker acid extractant in which aimed at dissolving pseudo-total thallium content in the soil samples were carried out. A hydrofluoric acid digestion method could be employed to figure out the so called "real total content". (Utermann et al. 1999; 2000) suggested a comprehensive analytical investigations to compare the above two elemental fractions. A set of regression functions was derived for transforming element contents between the above two fractions with a given statistical certainty. The Federal Institute for Geosciences and Natural Resources (BGR) and Geological Survey of North Rhine-Westphalia (GD NRW) (http://www.bgr.de/app/FISBoBGR_Stoffhaushalt/index.htm) provides practical transformation for certain elements except for Tl under these circumstances. HF is extremely toxic and corrosive to mankind by absorption through skin contact with 2% of skin exposure of body area can be fatal. HF can penetrate through skin and decalcify bones as the HF molecules can react with calcium and magnesium ions and lead to heart and organ failure. Splashing into eyes can cause irreversible damage to the cornea (Government of Western Australia, Section 8.3, Ref. 19). With the huge safety concerns, it would be preferable to replace HF with less hazardous mineral acid as the above measurements required large amount of sample handling for the two sampling locations (~500 times sample extractions being carried out). Although the applied aqua regia acid digestion was not able to digest the "real total" however the present "pseudo" total thallium content could still serve a good reference in analyzing total metal content. Numerous research in the past suggested the data employed from two above methods are closely resemblance let alone not complete identical.

The thallium contents in aqua regia acid digestion also demonstrated highest thallium concentration in the surface soils and with significant decreasing Tl concentrations of increasing sample depth at all Greenland sampling points (except sample 13 and 14) (Fig. 9.1.14.2, Appendix A) (p.220). Exchangeable and total thallium concentration in agricultural sampling points was shown in graph plot and suggested rather mixed results with increasing sample depth (Fig. 9.1.14.3, Appendix A) (Fig. 9.1.14.4, Appendix A) (p.221-222). This could be due to extensive plowing process from the local farmers and as a result mixing the top and sub-soils thoroughly. Hence, no obvious trends could be revealed with increasing sample depth.

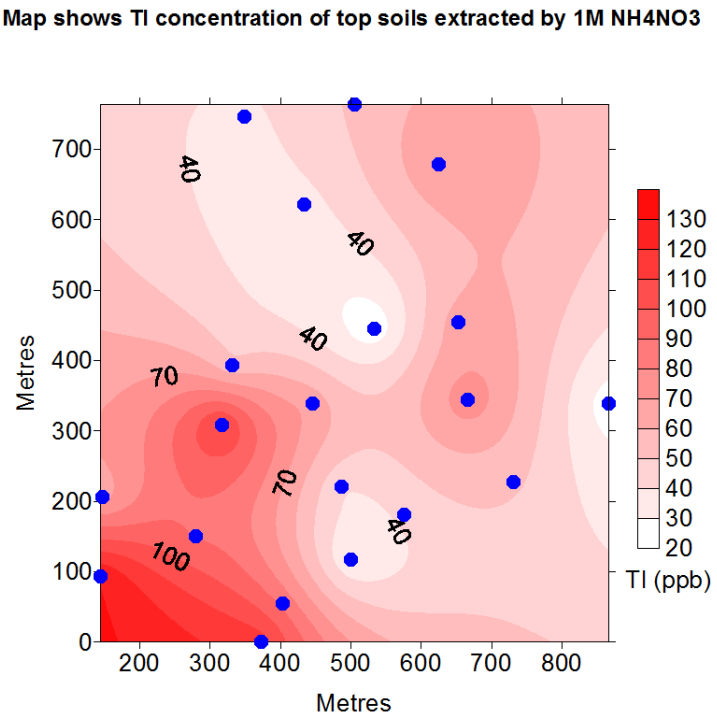


Fig. (21) Isoline plot for thallium top-soils extracted by ammonium nitrate after kriging estimation at location 1 (Blue dot represents corresponding sampling point)

The above isoline plot showed concentration profile of exchangeable thallium concentration of top soil. The concentration map suggested the hot spot in which the exchangeable thallium concentration exceeding the suggested safety limit by soil conservation regulation under Federal Minster of Justice (BodenSchutzVerordnung, Bundesministerium der Justiz) were located at the bottom left corner of the entire sampling site. The suggested safety value was below 100 µg/kg for thallium extracted by ammonium nitrate. According to figure (21) areas under sampling point 1 and 2 should require remediation control. The agricultural area was however not revealing exchangeable thallium concentration exceeding the threshold value.

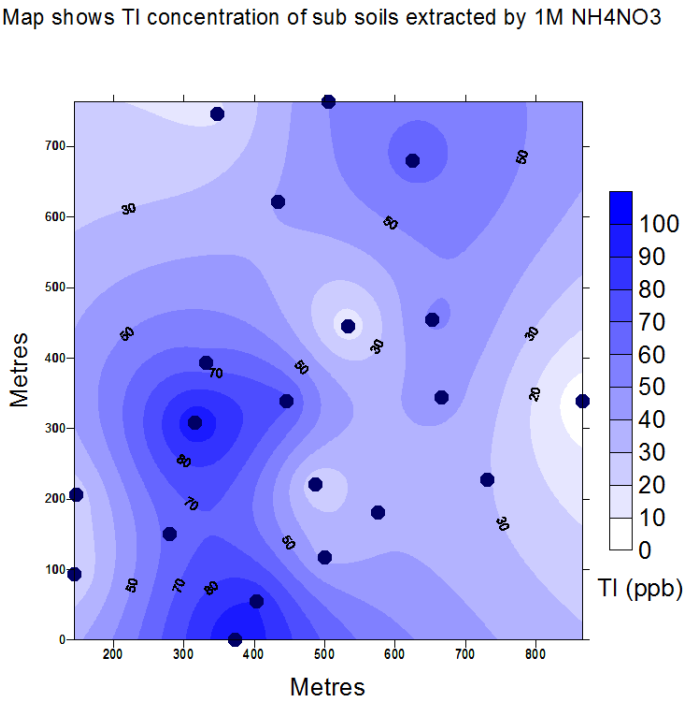


Fig. (22) Isoline plot for thallium sub-soils extracted by ammonium nitrate after kriging estimation at location 1(Blue dot represents corresponding sampling point)

Figure (22) showed the sub-soils exchangeable thallium concentration profile at sampling location 1. The map suggested the exchangeable thallium concentration did not exceed the safety limit of the soil conversation regulation at all the sampling points. The sampling points with relatively higher exchangeable thallium concentrations were again mainly located at the bottom left corner of the sampling site.

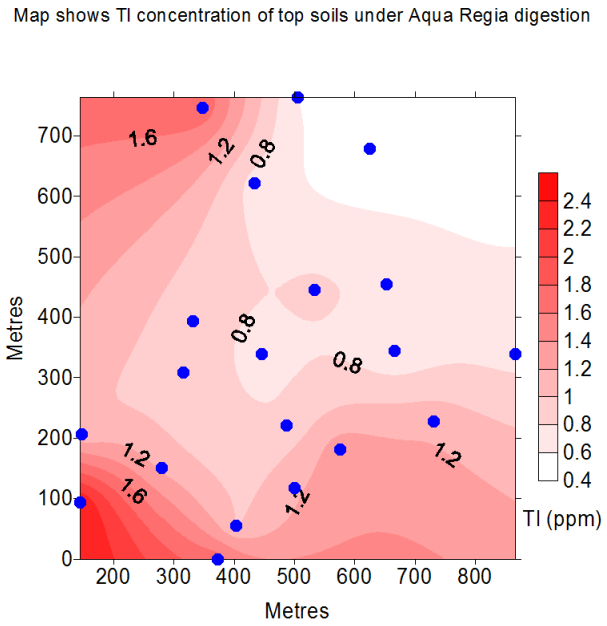


Fig. (23) Isoline plot for thallium top-soils extracted by aqua regia acid digestion after kriging estimation at location 1(Blue dot represents corresponding sampling point)

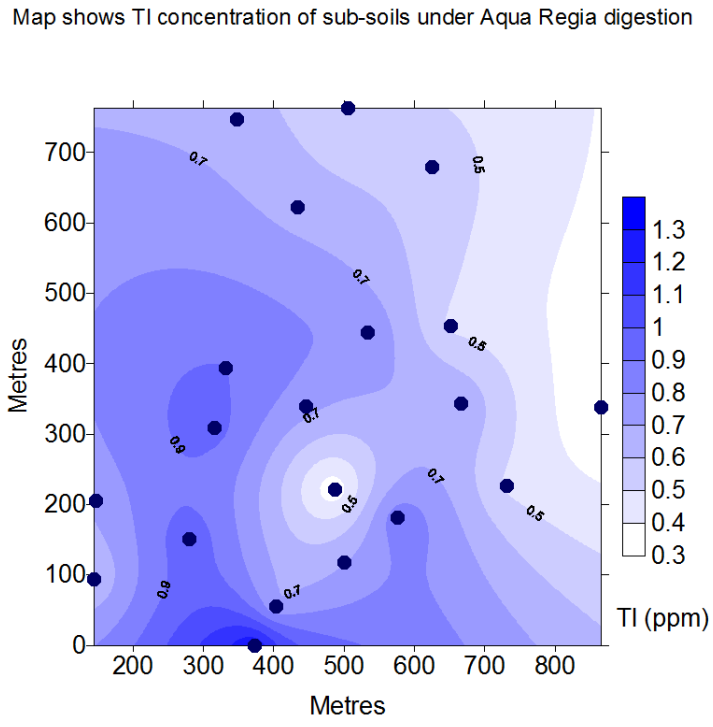
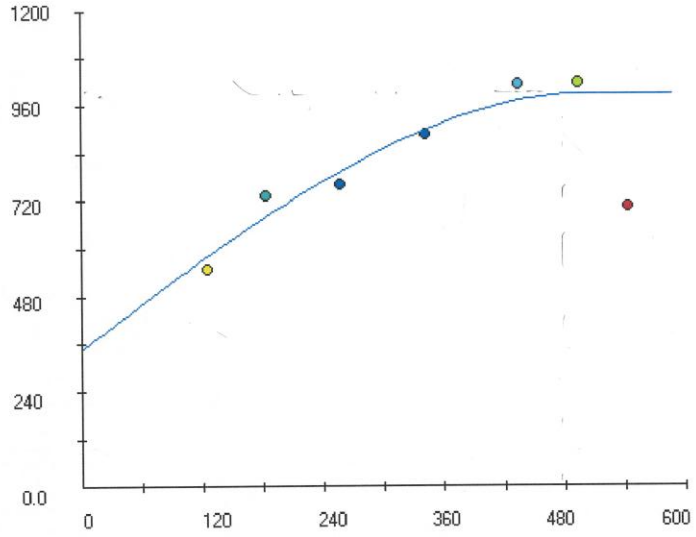


Fig. (24) Isoline plot for thallium sub-soils extracted by aqua regia acid digestion after kriging estimation at location 1(Blue dot represents corresponding sampling point)

Figure (23) and (24) showed the total thallium concentration of top and sub-soils at the sampling location 1. The results suggested that highest total thallium concentrations were identified at the top-soils with the concentration range between 0.4-2.4 ppm in comparison with 0.3-1.3 ppm concentration range in the sub-soils. Several Tl hot spots in which exceeding the 1 mg/kg value were also found in the figure (24). The following table (9.1.13.1, Appendix A) (p.218) summarized the average Tl content (mg/kg) in different minerals. Soils in which formed by weathering of rocks and by knowing the thallium concentrations in rock-forming minerals could be able to estimate the fate of Tl in soils. Table (9.1.13.2, Appendix A) (p.218) shows thallium concentrations in the upper soil layers at various countries. The results in figure (23) and (24) suggested that the total thallium concentration was higher than common soils Tl concentration in which below 1 mg/kg (Kazantzis, 2000) and exceeded the potential risk for human of excessive Tl contents in soils being set up by the North-Rhine Westphalia (FRG) (1 mg/kg). The sub-sampling points contained relatively high Tl concentrations were cluster around the bottom left corner of the sampling site. The total thallium concentrations of top and sub-soils were revealed. Sub-sampling points in above figure (23) and (24) which demonstrated above 1 mg/kg thallium content should require careful monitoring by the corresponding authority.



y-axis = Semivariogram, x-axis = distance lag (m)

Fig. (25) Empirical semivariogram (dots) and the fitted model (line) of LnP (spherical model: C_o = 347.1; C_o + C_1 = 347.1+643.2; a = 507.8 m) (no. of lags = 5; lag tolerance: % of lags = 60%; define maximum distance = 600m)

Semivariance analysis of top-soils ammonium nitrate extracts targeting exchangeable thallium at sampling location 1 (Fig. 21) was carried out. A semivariogram was calculated in order to describe the spatial variation of soil. No evidence of anisotropy in the variogram of LnP data was found. The top soils exchangeable thallium concentrations varied similarly in all directions of the study area and the semivariance depended only on the distance between samples.

The experimental variogram was fitted with a spherical model shown at figure (25). The fitted spherical semivariogram function contained a range of 507.8 m, a sill of 990.3, and nugget of 347.1. The nugget effect was calculated as follows.

Nugget effect = (347.1/990.3) x 100%

= 35.0%

The nugget effect accounted for 35.0% of the total sill. A rough guideline suggested the variable is considered to have a strong spatial dependence if the nugget-to-sill ratio is < 25%, a moderate spatial dependence if the ratio is between 25% and 75%, and a weak spatial dependence if the ratio is > 75% (Cambardella et al., 1994). The above findings suggested exchangeable thallium in top-soils was moderately spatially dependent. Variables which are strongly spatially dependent may be controlled by intrinsic variations whereas weak spatial dependence may indicate that variability is controlled more by extrinsic variations. The definition of the range of the semivariogram is the maximum distance between correlated measurements and this factor is effective in terms of selecting a sampling design to map soil properties (Utset et al., 1998).

(5.5) Thallium concentration profiles of top and sub soils at sampling location 2

Table (20): Table shows soil thallium (Tl) concentrations extracted by ammounium nitrate and aqua regia total acid digestion at location 2

Sampling number (GPS-coordinate in decimal minutes ^{o}N/^{o}E	Property of the area (Type of crops or vegetables being grown)	Sample depth (cm)	Tl content extracted by ammonium nitrate (µg/kg)(ppb)	Tl content extracted by aqua regia total acid digestion (mg/kg)(ppm)
1 11.171/53.766	Cottage	0-10 10-30 30-40	84.40 ± 0.60 118.72 ± 1.04 104.13 ± 0.65	1.05 ± 0.018 1.04 ± 0.001 1.06 ± 0.002
2 11.143/53.817	Forest	0-10 10-30 30-40	554.50 ± 2.22 86.43 ± 0.62 19.62 ± 0.11	3.17 ± 0.012 0.72 ± 0.009 0.23 ± 0.002
3 11.120/53.884	Forest	0-10 10-30 30-40	190.83 ± 1.25 70.82 ± 0.33 17.98 ± 0.24	2.87 ± 0.014 1.14 ± 0.007 0.41 ± 0.002
4 11.091/53.929 (Core-drill)	Forest	0-10 10-20 20-50 50-70 70-90 90-100	150.23 ± 1.19 243.09 ± 0.80 73.91 ± 0.23 11.40 ± 0.03 1.56 ± 0.02 0.14 ± 0.02	1.64 ± 0.004 2.27 ± 0.018 0.63 ± 0.004 0.21 ± 0.002 0.15 ± 0.001 0.24 ± 0.002
5 11.052/54.036	Forest	0-10 10-30 30-40	244.89 ± 0.43 268.89 ± 1.14 69.82 ± 0.56	2.52 ± 0.010 2.37 ± 0.014 0.54 ± 0.004

6 11.001/54.120	Forest	0-10 10-30 30-40	227.61 ± 1.04 159.86 ± 0.27 16.77 ± 0.05	2.60 ± 0.009 1.24 ± 0.004 0.29 ± 0.001
7 11.205/54.345	Forest	0-10 10-30 30-40	107.21 ± 0.88 64.01 ± 0.28 26.94 ± 0.31	1.24 ± 0.005 0.62 ± 0.002 0.24 ± 0.002
8 11.266/54.305	Forest	0-10 10-30 30-40	205.71 ± 1.19 120.24 ± 0.91 18.26 ± 0.19	1.46 ± 0.025 0.68 ± 0.006 0.23 ± 0.002
9 11.359/54.264 (Core-drill)	Forest	0-10 10-20 20-50 50-70 70-90 90-100	147.65 ± 0.40 93.76 ± 0.95 42.40 ± 0.25 17.10 ± 0.15 36.53 ± 0.38 Not available	1.59 ± 0.015 0.92 ± 0.006 0.45 ± 0.010 0.19 ± 0.002 0.29 ± 0.004 Not available
10 11.419/54.154	Forest	0-10 10-30 30-40	48.99 ± 0.25 21.27 ± 0.05 4.20 ± 0.05	1.47 ± 0.001 1.13 ± 0.015 0.32 ± 0.003
11 11.483/54.027 (Core-drill)	Greenland	0-10 10-20 20-50 50-70 70-90 90-100	94.55 ± 0.17 76.91 ± 0.29 7.92 ± 0.04 6.33 ± 0.07 3.52 ± 0.03 Not available	1.26 ± 0.004 0.81 ± 0.008 0.37 ± 0.001 0.33 ± 0.002 0.31 ± 0.001 Not available
12 11.443/53.937	Greenland	0-10 10-30 30-40	37.75 ± 0.23 63.27 ± 0.23 5.62 ± 0.02	0.84 ± 0.005 0.94 ± 0.005 0.24 ± 0.002
13 11.203/54.081	Cottage	0-10 10-30 30-40	125.66 ± 0.48 116.30 ± 0.85 31.49 ± 0.10	1.18 ± 0.002 0.88 ± 0.009 0.37 ± 0.003

The above table (20) showed the exchangeable thallium (extracted by ammonium nitrated) and total thallium concentrations in different sampling points and depths.

Figure 9.1.14.5 and 9.1.14.6 in Appendix A (p. 223-224) showed the general trends of exchangeable thallium and total thallium concentrations at each sub-samples with increasing sample depth. Both of the figures demonstrated similar overall trends. All of the sub-samples revealed highest thallium concentrations (except sub-samples 4, 5 and 15) on the top-soils with decreasing Tl concentrations at increasing sample depth. 9 out of 13 sub-samples measured with exchangeable thallium concentrations were bigger than 100 µg/kg safety limit for mobile thallium. Sub-sample 2 was identified with highest mobile thallium concentration of thallium in the surface soil with 554.50 ± 2.22 µg/kg in which was approximately over 5-folds higher than the safety limit set by the German Federal. The trend showed mobile thallium concentration returned to below safety limit with the sample depth greater than 30 cm. Similar trend was also found in total thallium with 12 out of 13 sub-samples contained less than 1 mg/kg total thallium with sample depth above 30 cm. 4 sub-samples on the surface soils showed total thallium content above 2.5 mg/kg in the trend. The above table (20) indicated the high thallium concentrations could be also due to anthropogenic emission in similar with the results obtained at location 1 albeit with much higher mobile thallium concentration being observed in top-soils.

The exchangeable thallium t-test value was 3.2036 with degree of freedom equal to 38 and $p = 0.0027$. The p-value associated with t was low (< 0.05). The small p-value indicated rejection of the null hypothesis. The paired exchangeable thallium concentration between top and sub-soils was considered to be statistically significant difference. The t-test was also applied for total thallium extracted by aqua regia acid digestion. T-test value was 4.9004 with degree of freedom equal to 38 and $p = 0.0001$. The paired total thallium concentration between top and sub-soils was also considered to be statistically significant difference.

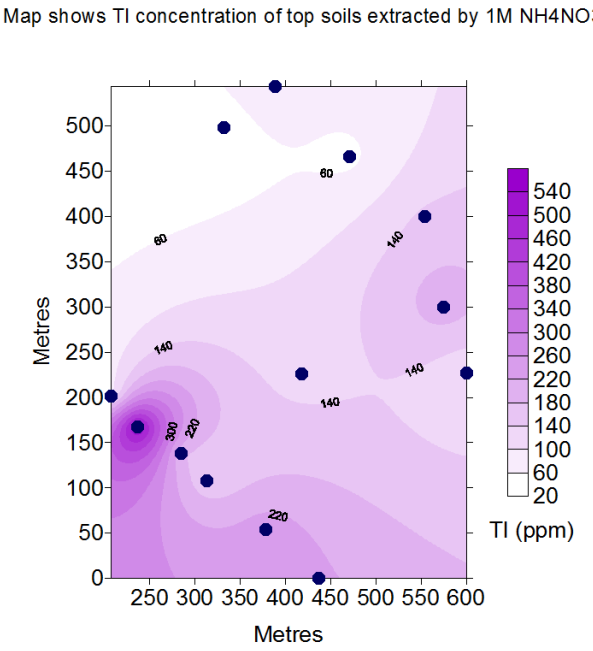


Fig. (26) Isoline plot for thallium top-soils extracted by ammonium nitrate after kriging estimation at location 2 (Blue dot represents corresponding sampling point)

The above figure (26) showed the mobile thallium concentration map at the sampling location 2. The highest thallium concentration was located at bottom left corner forest region (sub-sample 2) and the hot spot area was also identified at the same region in the isoline plot. The maximum mobile thallium concentration was found to be ≈ 540 µg/kg in comparison with ≈ 130 µg/kg at location 1 for mobile thallium. In the isoline plot above 50% of the total area showed mobile thallium concentration exceeding the safety limit. Larger area in location 2 showed mobile thallium concentration exceeding the safety limit than location 1 (Figure 21 and 26). The kriging estimation in above suggested the area next to sampling points 1-6 if in which being used for agricultural purpose could be potentially not suitable for consumption.

The concentration map suggested the hot spot in which the exchangeable thallium concentration exceeding the suggested safety limit by soil conservation regulation under Federal Minster of Justice (BodenSchutzVerordnung, Bundesministerium der Justiz) were located at sub-sampling point 2. The suggested safety value was below 100 µg/kg for thallium extracted by ammonium nitrate. Most of the area in above figure 26 demonstrated mobile thallium concentration much higher than the safety value. Remediation control should be implemented under the above circumstances.

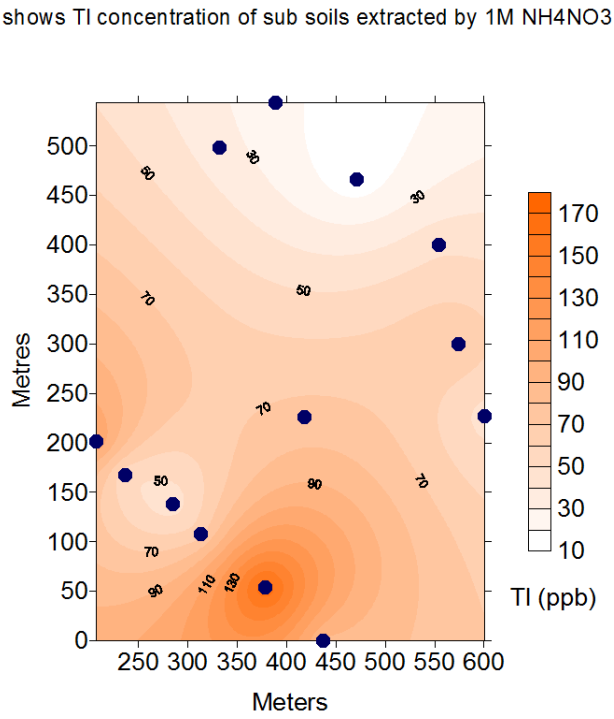


Fig. (27) Isoline plot for thallium sub-soils extracted by ammonium nitrate after kriging estimation at location 2 (Blue dot represents corresponding sampling point)

The above figure (27) showed exchangeable thallium concentration in the sub-soils at location 2. The maximum mobile thallium concentration was found to be ≈ 170 µg/kg in comparison with ≈ 100 µg/kg at location 1. The sub-soils demonstrated mobile thallium in the majority of the area was below the safety limit and the hot spot was found at sub-sample 5. Only an approximately 50 m from the centre of radius surrounding the sub-sample 5 showed mobile thallium content above the safety limit. Overall the mobile thallium content in the sub-soils showed significantly less than the top-soils.

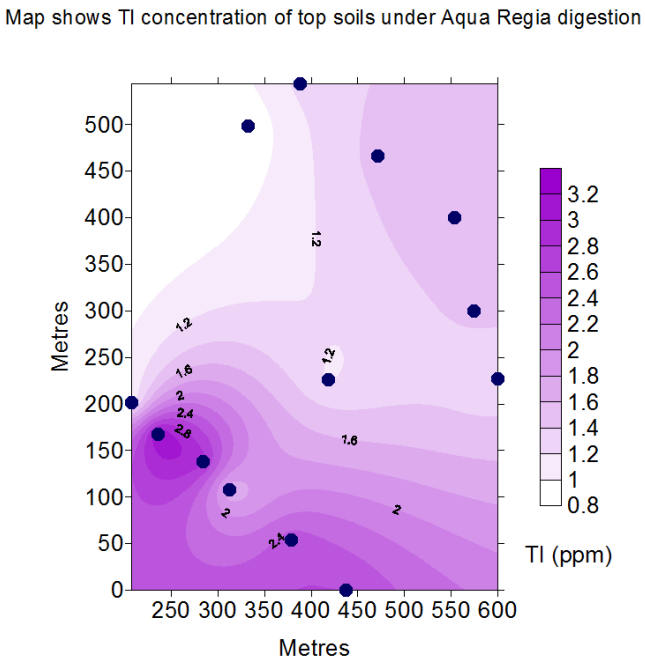


Fig. (28) Isoline plot for thallium top-soils extracted by aqua regia acid digestion after kriging estimation at location 2 (Blue dot represents corresponding sampling point)

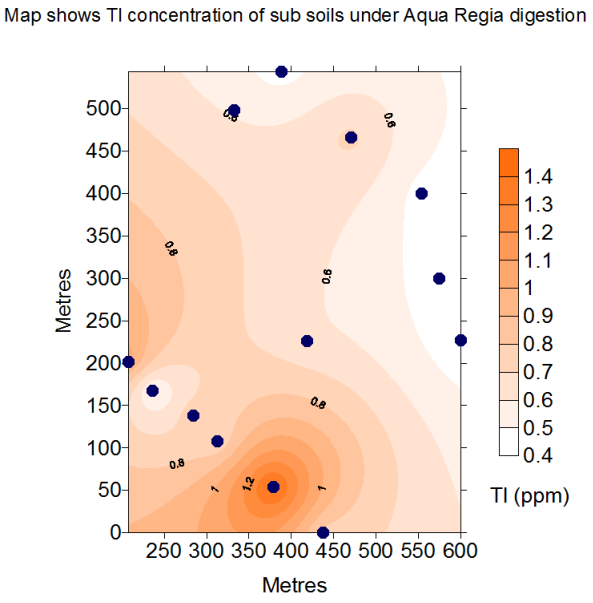


Fig. (29) Isoline plot for thallium sub-soils extracted by aqua regia acid digestion after kriging estimation at location 2 (Blue dot represents corresponding sampling point)

Figure (28) and (29) showed the total thallium concentration of top and sub-soils at the sampling location 2. The results suggested that highest total thallium concentrations were identified at the top-soils with the concentration range between 0.8-3.2 ppm in comparison with 0.4-1.4 ppm concentration range in the sub-soils. The sub-soils total Tl content (figure 29) was in similar range with sampling location 1(figure 24).

The maximum total thallium content in the top-soil was 33% higher in this case compared with location 1(figure 23). The majority of the area showed total thallium concentration was in above 1 mg/kg limit (FRG) and the area which above this threshold value was larger than in sample location 1. The result was over 3-folds of the common occurrence of soil Tl concentration. A Tl hot spots (sub-sample 5) in which exceeding the 1 mg/kg value was found in the figure 29. Tl content exceeding the safety limit was mainly located at sub-samples 1-6 and the surrounding area. Sub-sampling points in above figure 28 and 29 which demonstrated above 1 mg/kg thallium content should require careful monitoring by the corresponding authority.

By comparing the above results from top and sub-soils at sampling location 2, the found excessive Tl contents on the surface soils indicated that the excessive Tl was from the external source but not from the parental origin. This could be revealed by both locations 1 and 2 sub-soils total thallium were in similar concentration (figure 24 and 29) however the top-soils suggested rather various maximum total Tl concentrations (figure 23 and 28).

In between of the isoline plot of figure 21, 22, 26 and 27, all of these concentration maps demonstrated that the top soils at location 2 was more Tl contaminated than at the location 1. Previous studies in the past suggested the source of Tl from cement factory was found to be residues of pyrite roasting added as a ferric oxide additive to powdered limestone and fly-dust with majority occurring at water soluble Tl(I) chloride compound. The major source of thallium in air was found to be emission of fly-ash (LIS, 1980). Installation of filter was efficient in reducing cement dust (99%) but not the Tl-containing particles (50%) (Pielow 1979, Prinz et al. 1979 and Weisweiler et al. 1985). Alternation of production method could reduce the thallium emission by more than 99% (< 25µg/m^3) (Pielow 1979, Prinz et al. 1979 and LIS 1980). However, the above results suggested the current soil thallium concentration at location 1 and 2 still showed different degrees of thallium contamination. Thallium itself is a non-volatile heavy metal. In anthropogenic sources thallium exists as an oxide (Tl_2O), hydroxide (TlOH), sulphate (Tl_2SO_4) and sulfide (Tl_2S).

In the cement production calcination process heating a mixture of limestone and shale or clay up to 1000 ^oC is usually required. Thallium compounds are volatile at high temperatures and are not efficiently retained by most emission control facilities. Thallium sulphate and hydroxide could be precipitated out from the atmosphere and the thallium oxides could be removed by atmosphere dispersion and gravitational settling (EPA, 1988). These were possible speculative anthropogenic sources and mechanisms causing soil thallium contamination at the above two sampling locations (location 1 and 2).

Overall, the mobile and total thallium contents in the top and sub-soils at the vicinity of cement factory in Lengerich, Germany were demonstrated.

(6.0) Conclusions

(6.1) Arsenic

The physicochemical behaviour of arsenic presents in limestone oxide as impurities had been thoroughly investigated. The observed results suggested that arsenic could be partitioned in different metal-bearing phases by the applied sequential extraction scheme and hence arsenic in different forms in the soil system could be identified.

The arsenic contents in five different extraction steps were successfully measured with hydride generation atomic absorption spectroscopy (HG-AAS) under standard addition method to the sub-samples. The accuracy of the measurement was confirmed with the matching As content of the reference material and in addition the total As content of the summation of the 5 extraction steps measured by HG-AAS was in resemblance with the X-ray fluorescence analysis (XRF) of the total arsenic (bulk) in each sub-samples.

All of the measured sub-samples demonstrated much higher As content than the above global average content of arsenic being found in limestone, pellet limestone for soil pH amendment and MAP/DAP phosphate fertilizers. The matrix effect observed in the HG-AAS measurement could be minimized with addition of 1% cysteine as masking agent and the inference mechanism could involve capture and decomposition of the gaseous hydride at the freshly precipitated metal. A significant amount of As was being mobilized by small and high charge density phosphate and one third of the total As managed to be mobilized under exchangeable to mildly acid-reducing conditions. Although the majority of As showed strong binding with crystalline Fe phases, however, uncertainty arouse due to possible repartitioning of As between dissolved Mn and residual Fe oxides in the first three extractions steps. Direct X-ray spectroscopic analysis was important for future analysis.

(6.2) Copper

The physicochemical behaviour of copper presents in limestone oxide as impurities had been thoroughly investigated. The observed results suggested that copper could be partitioned in different metal-bearing phases by the applied sequential extraction scheme and hence copper in different forms in the soil system could be identified.

The copper contents in four different extraction steps were successfully measured with atomic absorption spectroscopy (AAS) to the sub-samples. The accuracy of the measurement was confirmed with the matching Cu content of the reference material and in addition the total Cu content of the summation of the 4 extraction steps measured by AAS was in resemblance with the X-ray fluorescence analysis (XRF) of the total copper (bulk) in each sub-samples.

All of the measured sub-samples demonstrated much higher Cu content than Cu content of 2-8 mg/kg limestone commonly used for soil pH amendment (McBride and Spiers, 2001). The recovered copper was partitioned almost evenly among the four extraction steps. The results suggested that copper was mobilized under both acidic and reducing conditions but not possible to identify Cu associated with different specific metal-bearing solid phases (e.g. carbonate matrix or the oxide dendrite). Direct X-ray spectroscopic speciation analysis is required to resolve these uncertainties.

(6.3) Thallium

The investigation of soils with thallium exposure in the vicinity of a cement plant at Lengerich, Germany was successfully carried out. The results showed mobile and total thallium concentration at top and sub-soils at two sampling location (location 1 and 2) with both sampling sites contained different level of thallium pollution. Statistical analysis suggested that there were significantly statistic differences of the thallium concentrations between top and sub-soils in the two locations. The variance was potentially due to anthropogenic emission sources.

Semivariance analysis of top-soils ammonium nitrate extracts targeting exchangeable thallium at sampling location 1 had also been performed and the outcome suggested that exchangeable thallium in top-soils was classified as moderately spatially dependent.

Suspect pathways of leading to the soil contamination on the sampling locations were predicted from the possible water soluble thallium compounds being precipitated out from the atmosphere. Thallium containing fly-ash could be volatized and escaped through chimneys and under atmosphere dispersion and gravitational settling with eventually polluting proximity of the soils.

The top and sub-soils thallium concentrations at two sampling sites were demonstrated with different area sizes in where exceeding the safety limit of mobile thallium set by the German Federal Minster of Justice and total thallium established by North-Rhine Westphalia of Federal Republic of Germany (FRG). Remediation control by the corresponding authority was recommended.

All of the chemical extraction methods applied in the above sections successfully identified various arsenic and copper species in agricultural lime and anthropogenic thallium contamination in soils.

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This section has been deleted in conformity with the rules stipulated by the internet publisher (ArchiMeD). I am grateful to all the people for their help, comments, discussions and support. Their names are listed in the print-version of this thesis.

(8.0) References

(8.1) Arsenic

1) Appelo, C.A.J., D. Postma (1994) Geochemistry, groundwater and pollution. A.A. Balkema Publishers, The Netherlands, 536 pp.
2) Aggett, J., Aspell, A. C., 1976. The Determination of Arsenic(III) and Total Arsenic by Atomic-absorption Spectroscopy. Analyst Vol. 101, 341-347.
3) Aggett, J., Hayashi, Y., 1987. Obervations on the Interference by Copper(II), Cobalt(II) and Nickel(II) on the Determination of Arsenic by Arsenic Generation Atomic Absorption Spectrometry. Analyst Vol.112, 277-282.
4) Agterdenbos, D. B. J., Worrell, E., Kolmer, J. B., 1988. The mechanism of transition metal interference in hydride generation atomic absorption spectrometry. Spectrachimica Acta Vol.43B Nos9 11,1349-1354.
5) Antosiewicz, D. M., Escude-Duran, C., Wierzbowska, E., Sklodowska, A., 2008. Indigenous Plant Species with the Potential for the Phytoremediation of Arsenic and Metals Contaminated Soil. Water Air Soil Pollution 210, 193-197.
6) Batley, Graeme E., 1989. Trace Element Speciation: Analytical Methods and Problems.CRC Press, Inc.
7) Bauer, Markus, Blodau, Christian, 2006. Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. Science of the Total Environment 354, 179-190.
8) Bauer, Markus, Fulda, Beate, Blodau, Christian, 2008. Groundwater derived arsenic in high carbonate wetland soils: Sources, sinks, and mobility. Science of the Total Environment 401, 109-120.
9) Baur, W.H., and B.H. Onishi. 1969. Arsenic. p. A1-A33. In K.H. Wedepohl (ed.) Handbook of Geochemistry. Springer-Verlag, Berlin.

10) Berg, M., Trang, P. T. K., Stengel, C., Buschmann, J., Viet, P. H., Van Dan, N., Giger, W., Stüben, D., 2008. Hydrological and sedimentary controls leading to arsenic contamination of groundwater in the Hanoi area, Vietnam: The impact of iron-arsenic ratios, peat, river bank deposits, and excessive groundwater abstraction. Chemical Geology 249, 91-112.

11) Bissen, Monique, Frimmel, Fritz H., 2003. Arsenic- a Review. Part I: Occurrence, Toxicity, Speciation, Mobility. Acta hydrochim. Hydrobiol. 31, 9-18

12) Boyle, R.W., Jonasson, I.R., 1973. The geochemistry of As and its use as an indicator element in geochemical prospecting. J. Geochem. Explor. 2, 251-296.

13) Brown, Richard J. C., Roberts, Matthew R., Milton, Martin J. T., 2007. Systematic error arising from 'Sequential' Standard Addition Calibrations: Quantification and correction. Analytica Chimica Acta 587, 158-163.

14) Cai, Y., Cabrera, J. C., Georgiadis, M., Jayachandran, K., 2002. Assessment of arsenic mobility in the soils of some golf courses in South Florida. The Science of the Total Environment 291, 123-134.

15) Charter, R.A., M.A. Tabatabai, and J.W. Schafer. 1995. Arsenic, molybdenum, selenium, and tungsten contents of fertilizers and phosphate rocks. Commun. Soil Sci. Plant Anal. 26:3051-3062.

16) Chaillou, Gwenaelle, Schafer, Jorg, Anschutz, Pierre, Lavaux, Gilbert, Blanc, Gerard, 2003. The behavior of arsenic in muddy sediments of The Bay of Biscay (France). Geochimica et Cosmochimica Acta Vol.67 No.16, 2993-3003.

17) Chen, Hengwu, Brindle, I. D., Le, X. C., 1992. Prereduction of arsenic(V) to arsenic(III), enhancement of the signal, and reduction of interferences by L-cysteine in the determination of arsenic by hydride generation. Anal. Chem. 64, 667-672.

18) Creed, Patricia A., Gallawa, Christina M., Young, Andrea R., Schwegel, Carol A., Lytle, Darren, Sorg, Thomas J., Creed, John T., 2006. Investigation of sequential and enzymatic extraction of arsenic from drinking water distribution solids using ICP-MS. J. Environ. Monit., 8, 968-972.

19) Dixit, Suvasis, Hering, Janet G., 2003. Comparison of Arsenic(V) and Arsenic(III) Sorption onto Iron Oxide Minerals: Implications for Arsenic Mobility. Environ. Sci. Technol. 37, 4182-4189.

20) Dousova, B., Martaus, A., Filippi, M., Kolousek, D., 2008. Stability of Arsenic Species in Soils Contaminated Naturally and in an Anthropogenic Manner. Water Air Soil Pollution 187, 233-241.

21) Dragun, J., and Chiasson, A. (1991). In *Elements in North American Soils,* pp. 26–31. Hazardous Materials Control Resources Institute, Greenbelt, MD.

22) Dudas, M.J., 1984. Enriched levels of arsenic in post-active acid sulfate soils in Alberta. Soil Sci. Soc. Am. J. 48, 1451-1452.

23) Dudas, M.J., Warren, C.J., Spiers, G.A., 1988. Chemistry of arsenic in acid sulfate soils of northern Alberta. Comm. Soil Sci. Plant Anal. 19, 887-895.

24) Eiche, E., Neumann, T., Berg, M., Weinman, B., Van Geen, A., Norra, S., Berner, Z., Trang, P., T., K., Viet, P. H., Stüben, D., 2008. Geochemical processes underlying a sharp contrast in groundwater arsenic concentrations in a village on the Red River delta, Vietnam. Applied Geochemistry 23, 3143-3154.

25) Fedotov, P. S., Fitz, W. J., Wennrich, R., Morgenstern, P., Wenzel, W. W., 2005. Fractionation of arsenic in soil and sludge samples: continuous-flow extraction using rotating coiled columns versus batch sequential extraction. Analytica Chimica Acta 538, 93-98.

26) Francesconi, K. A., Kuehnelt, D., 2004. Determination of arsenic species: A critical review of methods and applications, 2003. Analyst 129, 373-395.

27) Frau, Franco, Biddau, Riccardo, Fanfani, Luca, 2008. Effect of major anions on arsenate desorption from ferrihydrite-bearing natural samples. Applied Geochemistry 23, 1451-1466.

28) Goh, Kok-Hui, Lim, Teik-Thye, 2005. Arsenic fractionation in a fine soil fraction and influence of various anions on its mobility in the subsurface environment. Applied Geochemistry 20, 229-239.

29) Goldschmidt, V. M., 1937. The Principles of Distribution of Chemcial Elements, etc. The Seventh Hugo Müller Lecture, delivered before the Chemical Society on March 17th, 1937.

30) Guo, Huaming, Yang, Suzhen, Tang, Xiaohui, Li, Yuan, Shen, Zhaoli, 2008. Groundwater geochemistry and its implications for arsenic mobilization in shallow aquifers of the Hetao Basin, Inner Mongolia. Science of the Total Environment 393, 131-144.

31) Gustafsson, J. P., Jacks, G., 1995. Arsenic geochemistry in forested soil profiles as revealed by solid-phase studies. Applied Geochemistry 10, 307-315.

32) Haque, S., Ji, Junfeng, Johannesson, Karen H., 2008. Evaluating mobilization and transport of arsenic in sediments and groundwaters of Aquia aquifer, Maryland, USA. Journal of Contaminant Hydrology 99, 68-81.

33) Hall, G. E. M., MacLaurin, A. I., Pelchat, J. C., Gauthier, G., 1997. Comparison of the techniques of atomic absorption spectrometry and inductively coupled plasma mass spectrometry in the determination of Bi, Se and Te by hydride generation. Chemical Geology 137, 79-89.

34) Heron, Gorm, Christensen, Thomas H., Tjell, Jens Chr., 1994. Oxidation Capacity of Aquifer Sediments. Environ. Sci. Technol. 28, 153-158.

35) Hiemstra, T., Van Riemsdijk, W. H., 2006. On the relationship between charge distribution, surface hydration, and the structure of the interface of metal hydroxides. Journal of Colloid and Interface Science 301, 1-18.

36) Jay, J. A., Blute, N. K., Lin, K., Senn, D., Hemond, H. F., Durant, J. L., 2005. Controls on Arsenic Speciation and Solid-Phase Partitioning in the Sediments of a Two-Basin Lake. Environ. Sci. Technol. 39, 9174-9181.

37) Jessen, Soren, Larsen, Flemming, Koch, Christian Bender, Arvin, Erik, 2005. Sorption and Desorption of Arsenic to Ferrihydrite in a Sand Filter. Environ. Sci. Technol. 39, 8045-8051.

38) Keon, N. E., Swartz, C. H., Brabander, D. J., Harvey, C., Hemond, H., F., 2001. Validation of an Arsenic Sequential Extraction Method for Evaluating Mobility in Sediments. Environ. Sci. Technol. 35, 2778-2784.

39) Kirkbright, G. F., Taddia, M., 1978. Application of masking agents in minmizing interferences from some metal ions in the determination of arsenic by atomic absorption spectrometry with the hydride generation technique. Analytica Chimica Acta 100, 145-150.

40) Kinniburgh, D. G., Kosmus, W., 2002. Arsenic contamination in groundwater: some analytical considerations. Talanta 58, 165-180.

41) Lumsdon, D. G., Meeussen, J.C.L., Paterson, E., Garden, L.M., Anderson, P., 2001. Use of solid phase characterization and chemical modeling for assessing the behavior of arsenic in contaminated soils. Applied Geochemistry 16, 571-581.

42) Luh, Ming-Dean, Baker, R. A., Henley, Don E., 1973. Arsenic analysis and toxicity-A Review. The Science of the Total Environment 2, 1-12.

43) Maity, S., Chakravarty, S., Thakur, P., Gupta, K. K., Bhattacharjee, S., Roy, B. C., 2004. Evaluation and standardisation of a simple HG-AAS method for rapid speciation of As(III) and As(V) in some contaminated groundwater samples of West Bengal, India. Chemosphere 54, 1199-1206.

44) Manning, Bruce A., Fendorf, Scott E., Goldberg, Sabine, 1998. Surface Structures and Stability of Arsenic(III) on Geothite: Spectroscopic Evidence for Inner-Sphere Complexes. Environ. Sci. Technol. 32, 2383-2388.

45) Matschullat, Jörg, 2000. Arsenic in the geosphere- a review. The Science of the Total Environment 249, 297-312.

46) McBride, M.B., and G. Spiers. 2001. Trace element content of selected fertilizers and dairy manures as determined by ICP-MS. Comm. Soil Sci. Plant Anal. 32:139-156.

47) Metral, J., Charlet, L., Bureau, S., Basu, S., Chakarborty, S., Ahmed, K. M., Rahman, M.W., Cheng, Zhongqi, Van Geen, A., 2008. Comparison of dissolved and particulate arsenic distributions in shallow aquifers of Chakdaha, India, and Araihazar, Bangladesh. Geochemical Transactions 9:1.

48) Motuzova, G. V., Aptikaev, R. S., Karpova, E. A., 2006. Fractionation of Soil Arsenic Compounds. Eurasian Soil Science Vol.39 No.4, 387-396.

49) Moulder, D. S., Williamson, P., 1986. Estuarine and Coastal Pollution: Detection, Research and Control. Waster Science and Technology Vol. 18 Numbers. 4/5.

50) Nath, B., Berner, Z., Chatterjee, D., Mallik, S. B., Stüben, D., 2008. Mobility of arsenic in West Bengal aquifers conducting low and high groundwater arsenic. Part II: Comparative geochemical profile and leaching study. Applied Geochemistry 23, 996-1011.

51) National Research Council. 1977. Arsenic. National Academy of Sciences. Washington, DC.

52) Navas, Ana, Machin, Javier, 2002. Spatial distribution of heavy metals and arsenic in soils of Aragon (northeast Spain): controlling factors and environmental implications. Applied Geochemistry 17, 961-973.

53) Näykki, T., Perämäki, P., Kujala, J., Mikkonen, A., 2001. Optimization of a flow injection hydride generation atomic absorption spectrometric method for the determination of arsenic, antimony and selenium in iron chloride/sulphate-based water treatment chemical. Analytica Chimica Acta 439, 229-238.

54) Ngoc, K. C., Nguyen, N. V., Dinh, B. N., Thanh, S. L., Tanaka, S., Kang, Y., Sakurai, K., Iwasaki, K., 2009. Arsenic and Heavy Metal Concentrations in Agricultural Soils Around Tin and Tungsten Mines in the Dai Tu district, N. Vietnam. Water Air Soil Pollution 197, 75-89.

55) Novoa-Munoz, J. C., Queijeiro, J. M. G., Blance-Ward, D., Alvarez-Olleros, C., Garcia-Rodeja, E., Martinez-Cortizas, A., 2007. Arsenic fractionation in agricultural acid soils from NW Spain using a sequential extraction procedure. Science of the Total Environment 378, 18-22.

56) Pantsar-Kallio, M., Manninen, P. K. G., 1997. Speciation of mobile arsenic in soil samples as a function of pH. The Science of the Total Environment 204, 193-200.

57) Peacock, C. J., Singh, S. C., 1981. Inexpensive, Simple Hydride Generation System with Minimum Interferences for the Atomic-absorption Spectrophotometry of Arsenic. Analyst Vol.106, 931-938.

58) Pitten, F. –A., Muller, G., Konig, P., Schmidt, D., Thurow, K., Kramer, A., 1999. Risk assessment of a former military base contamined with organoarsenic-based warfare agents: uptake of arsenic by terrestrial plants. The Science of the Total Environment 226, 237-245.

59) Postma, D., Larsen, F., Hue, N. T. M., Duc, M. T., Viet, P. H., Nhan, P. Q., Jessen, S., 2007. Arsenic in groundwater of the Red River floodplain Vietnam: Controlling geochemical processes and reactive transport modeling. Geochimica et Cosmochimica Acta 71, 5054-5071.

60) Potts, P. J., 1987. A Handbook of Silicate Rock Analysis, first edition, Blackie & Son Ltd.

61) Price, R.E., and T. Pichler. 2006. Abundance and mineralogical association of arsenic in the Suwannee limestone (Florida): Implications for arsenic release during water-rock interaction. Chem. Geol. 228:44-56.

62) Radloff, K. A., Manning, A. R., Mailloux, B., Zheng, Y., Rahman, M. M., Hug, M. R., Ahmed, K. M., Van Geen, A., 2008. Considerations for conducting incubations to study the mechanisms of As release in reducing groundwater aquifers. Applied Geochemistry 23, 3224-3235.

63) Raven, K.P., and R.H. Loeppert. 1997. Trace element composition of fertilizers and soil amendments. J. Environ. Qual. 26:551-557.

64) Reimann, C., Matschullat, J., Birke, M., Salminen, R., 2009. Arsenic distribution in the environment: the effects of scale. Applied Geochemistry, doi:10.1016/j.apgeochem.2009.03.013

65) Root, R. A., Dixit, S., Campbell, K. M., Jew, A. D., Hering, J. G., O'Day, P. A., 2007. Arsenic sequestration by sorption processes in high-iron sediments. Geochimica et Cosmochimica Acta 71, 5782-5803.

66) Ryan, Joseph N., Gschwend, Philip M., 1991. Extaction of iron oxides from sediments using reductive dissolution by titanium(III). Clays and Clay Minerals Vol.39, No.5, 509-518.

67) Smedley, P. L., Kinniburgh, D.G., 2002. A review of the source, behavior and distribution of arsenic in natural waters. Applied Geochemistry 17, 517-568.

68) Smith, A. E., 1975. Interferences in the Determination of Elements that Form Volatile Hydrides with Sodium Borohydride Using Atomic-absorption Spectrophotometry and the Argon-Hydrogen Flame. Analyst Vol. 100, 300-306.

69) Swartz, Christopher H., Ulery, April L., Gschwend, Philip M., 1997. An AEM-TEM study of nanometer-scale mineral associtations in an aquifer sand: Implications for colloid mobilization. Geochimica et Cosmochimica Acta Vol.61, No.4, 707-718.

70) Swartz, C. H., Blute, N. K., Badruzzman, B., Ali, A., Brabander, D., Jay, J., Besancon, J., Islam, S., Hemond, H. F., Harvey, C. F., 2004. Mobility of arsenic in a Bangladesh aquifer: Inferences from geochemical profiles, leaching data, and mineralogical characterization. Geochimica et Cosmochimica Acta Vol. 68 No.22, 4539-4557.

71) Tareq, S. M., Safiullah, S., Anawar, H. M., Rahman, M. M., Ishizuka, T., 2003. Arsenic pollution in groundwater: a self-organizing complex geochemical process in the deltaic sedimentary environment, Bangladesh. The Science of the Total Environment 313, 213-226.

72) Tlustos, Pavel, Szakova, Jirina, Starkova, Alena, Pavlikova, Daniela, 2005. A comparison of sequential extraction procedures for fractionation of arsenic, cadium, lead, and zinc in soil. Central European Journal of Chemistry 3(4), 830-851.

73) Ure, A. M., Davidson, C. M., 2002.Chemical Speciation in the Environment, second edition, Blackwell Science.

74) Ure, A., Berrow, M., 1982. Chapter 3. The elemental constituents of soils. In: Bowen, H.J.M. (Ed.), Environmental Chemistry. Royal Society of Chemistry, London, pp.94-203.

75) Van Geen, A., Radloff, K., Aziz, Z., Cheng, Z., Huq, M. R., Ahmed, K. M., Weinman, B., Goodbred, S., Jung, H. B., Zheng, Y., Berg, M., Trang, P.T.K., Charlet, L., Metral, J., Tisserand, D., Guillot, S., Chakraborty, S., Gajurel, A. P., Upreti, B.N., 2008. Comparison of arsenic concentrations in simultaneously-collected groundwater and aquifer particles from Bangladesh, India, Vietnam, and Nepal. Applied Geochemistry 23, 3244-3251.

76) Van Geen, A., Zheng, Y., Cheng, Z., Aziz, Z., Horneman, A., Dhar, R. K., Mailloux, B., Stute, M., Weinman, B., Goodbred, S., Seddique, A.A., Hoque, M.A., Ahmed, K.M., 2006. A transect of groundwater and sediment properties in Araihazar, Bangladesh: Further evidence of decoupling between AS and Fe mobilization. Chemical Geology 228, 85-96.

77) Van Herreweghe, S., Swennen, R., Vandecasteele, C., Cappuyns, V., 2003. Solid phase speciation of arsenic by sequential extraction in standard reference materials and industrially contaminated soil samples. Environmental Pollution 122, 323-342.

78) Van Loon, Jon C., 1980. Analytical Atomic Absorption Spectroscopy Selected Methods, Academic Press.

79) Wallmann, K., Kersten, M., Gruber, J., Förstner, U., 1993. Artifacts in the determination of trace metal binding forms in anoxic sediments by sequential extraction. Intern. J. Environ. Anal. Chem. Vol.51, 187-200.

80) Wang, Suiling, Mulligan, Catherine N., 2006. Occurrence of arsenic contamination in Canada: sources, behavior and distribution. Science of the Total Environment 366, 701-721.

81) Welz, B., Melcher, M., 1984. Mechanisms of Transition Metal Interferences in Hydride Generation Atomic-absorption Spectrometry: Part 1. Influence of Cobalt, Copper, Iron and Nickel on Selenium Determination. Analyst Vol.109, 569-572.

82) Wenzel, W. W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., Adriano, D. C., 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. Analytica Chimica Acta 436, 309-323.

83) Yang, Li, Donahoe, R. J., 2007. The form, distribution and mobility of arsenic in soils contaminated by arsenic trioxide, at sites in southeast USA. Applied Geochemistry 22, 320-341.

84) Zheng, Y., Van Geen, A., Stute, M., Dhar, R., Mo, Z., Cheng, Z., Horneman, A., Gavrieli, I., Simpson, H. J., Versteeg, R., Steckler, M., Grazioli-Venier, A., Goodbred, S., Shahnewaz, M., Shamsudduha, M., Hoque, M. A., Ahmed, K. M., 2005. Geochemical and hydrogeological contrasts between shallow and deeper aquifers in two villages of Araihazar, Bangladesh: Implications for deeper aquifers as drinking water sources. Geochimica et Cosmochimica Acta Vol.69 No.22, 5203-5218.

85) Chasteen T. G. Department of Chemistry, Sam Houston State University, Huntsville, Texas 77341. U.S.A. (http://www.shsu.edu/~chm_tgc/primers/HGAAS.html).

(8.2) Copper

1) Abdel-Mageed, A.B., and F.W. Oehme. 1990a. Areview on biochemical roles, toxicity and interactions of zinc, copper and iron: IV. Interactions. Vet. Hum.Toxicol. 32(5): 456-458.
2) Adelstein, S. J., and B. L. Vallee. 1961. Copper metabolism in man. N. Engl. J. Med. 265:892-897. (Cited in Agarwal et al. 1989.)
3) Adriano, D. C. 1986. Trace elements in the terrestrial environment. New York: Springer Verlag New York Inc.
4) Agrawal, H. P. and Singh, B. P. 1974 Adsorption and release of applied copper by soils. Proc. Indian Nat. Sci. Acad. Part A 40, 292-296.
5) Allaway WH (1968) Agronomic control over the environmental cycling of trace elements. Adv Agron 20:235–274.
6) Alloway, B.J. 1990. Soil processes and the behavior of metals. In Heavy metals in soils, ed. B. J. Alloway. Glasgow: Blackie and Son Ltd.
7) Alloway, B. J., and A. P. Jackson. 1991. The behavior of heavy metals in sewage sludge-amended soils. Sci. Total Environ. 100:151-176.
8) Alt, E. R., I. Sternlieb, and S. Goldfischer. 1990. The cytopathology of metal overload. Int. Rev. Exp. Pathol. 31:165-188.
9) Andersson M., Ottesen R.T., Langedal M., 2010. Geochemistry of urban surface soils- Monitoring in Trondheim, Norway. Geoderma 156, 112-118.
10) ATSDR (Agency for Toxic Substances and Disease Registry). 1990. Toxicological profile for copper. Prepared by Syracuse Research Corporation for ATSDR, U.S. Public Health Service. TP-90-08.
11) Awashthi SK (2000) Prevention of Food Adulteration Act no 37 of 1954. Central and State Rules as Amended for 1999. Ashoka Law House, New Delhi.
12) Barman, S.C., Sahu, R.K., Bhargava, S.K., Chaterjee, C., 2000. Distribution of heavy metals in wheat, mustard, and weed grown in field irrigated with industrial effluents. Bulletin of Environmental Contamination and Toxicology 64, 489–496.

13) BC MOE (British Columbia Ministry of the Environment) 1898. Criteria for managing contaminated sites in British Coumbia-Draft. Prepared by the Waste Management Program, Ministry of Environment, Victoria, British Columbia.

14) Berggren D., 1992. Speciation of copper in solutions from podzols and cambisols of s.Sweden. Water, Air, and Soil Pollution 62, 111-123.

15) Boyden, R., V. R. Potter, and C. A. Elvehjem. 1938. Effect of copper on ethionine carcinogenesis. J. Nutr. 15:397-402. (Cited in ATSDR 1990.)

16) Brockman, R. P. 1977. Concentration of copper in livers of Saskatchewan cattle at slaughter. Can. Vet. J. 18:168-169.

17) Brun, L.A., Le Corff, J., Maillet, J., 2003. Effects of elevated soil copper on phenology, growth and reproduction of five ruderal plant species. Environ. Pollut. 122, 361–368

18) Cannon HL, Connally GG, Epstein JB, Parker JG, Thornton I, Wixson G (1978) Rocks: geological sources of most trace elements. In: report to the workshop at south scas plantation Captiva Island, FL, US. Geochem Environ 3:17–31.

19) Cartwright, G. E., and M. M. Wintrobe. 1964. Copper metabolism in normal subjects. Am. J. Clin. Nutr. 14:224-232. (Cited in ATSDR 1990.)

20) CCME (Canadian Council of Ministers of the Environment). 1991. Canadian interim environmental quality criteria for contaminated sites. Prepared for the CCME National Contaminated Sites Task Group. CCME EPC-CS34. Manitoba.

21) CCME (Canadian Council of Ministers of the Environment). 1997. Canadian Soil Quality Guidelines for Copper: Environmental and Human Health. Winnipeg, Manitoba. ISBN 0-662-25520-8. En 108-4/11-1997E.

22) Christoforidis A., Stamatis N., 2009. Heavy metal contamination in street dust and roadside soil along the major national road in Kavala´s region, Greece. Geoderma 151, 257-263.

23) Chuttani, H. K., P. S. Gupta, S. Gulati, et al. 1965. Acute copper sulphate poisoning. Am. J. Med. 39:849-854. (Cited in ATSDR 1990.)

24) Claff S.R., Burtonm E. D., Sullivan L. A., Bush R. T., 2010. Effect of sample pretreatment on the fractionation of Fe, Cr, Ni, Cu, Mn, and Zn in acid sulphate soil materials. Geoderma 159, 156-164.

25) Cool, M., F. Marcoux, A. Paulin, and M. C. Mehra. 1980. Metallic contaminants in street soils of Moncton, New Brunswick, Canada. Bull. Environ. Contam. Toxicol. 25:409-415.

26) Dash, S. C. 1989. Copper sulphate poisoning and acute renal failure [editorial]. Int. J. Artif. Organs. 12(10):610.

27) Dumestre A, Sauve S, McBride M, Baveye P, Berthelin J. 1999. Copper speciation and microbial activity in long-term contaminated soils. Archives of Environmental Contamination and Toxicology Volume: 36 Issue: 2 Pages: 124-131.

28) Eife, R., J. Mueller-Hoecker, M. Weiss, P. Schramel, H. Dieter, D. Feist, and K. Reiter. 1989. Familial infantile liver cirrhosis and hemolytic anemia due to chronic copper intoxication via tapwater from copper pipes. Annual Meeting of the European Society for Pediatric Research, Krakow, Poland, June 11-14, 1989. Pediatr. Res. 26(5):525.

29) EMRC (Energy Mines and Resources Canada). 1992. Copper. In Canadian minerals yearbook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. Draft.

30) Epstein, O., R. Spisni, S. Parbhoo, et al. 1982. The effect of oral copper loading and portasystemic shunting on the distribution of copper in the liver, brain, kidney, and cornea of the rat. Am. J. Clin. Nutr. 35:551-555. (Cited in ATSDR 1990.)

31) Fernández-Calviño D., Nóvoa-Muñoz J. C., Díaz-Raviña M., Arias-Estévez M., 2009. Copper accumulation and fractionation in vineyard soils from temperate humid zone (NW Iberian Peninsula). Geoderma 153, 119-129.

32) Filgueiras A. V., Lavilla I. and Bendicho C., 2002. Chemical sequential extraction for metal partitioning in environmental solid samples. J. Environ. Monit., 4, 823-857.

33) Fuentealba, I.C., S. Haywood, and J. Foster. 1989a. Cellular mechanisms of toxicity and tolerance in the copper-loaded rat. III. Ultrastructural changes and copper localization in the kidney. Br. J. Exp. Pathol. 70(5):543-556.

34) Fuentealba, I.C., S. Haywood, and J. Foster. 1989b. Cellular mechanisms of toxicity and tolerance in the copper-loaded rat. II. Pathogenesis of copper toxicity in the liver. Exp. Mol. Pathol. 50(1):26-37.

35) Gooneratne, S. R., and D. A. Christensen. 1989. A survey of maternal copper status and fetal tissue copper concentrations in Saskatchewan bovine. Can. J. Anim. Sci. 69:141-150.

36) Guo, Xueyan, Ma, Yibing, Wang, Xuedong, Chen, Shibao. 2010. Re-evaluating the effects of organic ligands on copper toxicity to barley root elongation in culture solution. Chemical Speciation and Bioavailablity Volume: 22 Issue: 1 Pages: 51-59.

37) Harrison, R. M., D. P. H. Laxen, and S. J. Wilson. 1981. Chemical associations of lead, cadmium, copper, and zinc in street dusts and roadside soils. Environ. Sci. Technol. 15(11):1378-1383.

38) Haywood, S. 1980. The effect of excess dietary copper on the liver and kidney of the male rat. J. Comp. Pathol. 90:217-232. (Cited in ATSDR 1990.)

39) Haywood, S. 1985. Copper toxicosis and tolerance in the rat. J. Pathol. 145:148-158. (Cited in ATSDR 1990.)

40) Haywood, S., and B. Comerford. 1980. The effect of excess dietary copper on the plasma enzyme activity and on the copper content of the blood of the male rat. J. Comp. Pathol. 90:233-238. (Cited in ATSDR 1990.)

41) Haywood, S., and M. Loughran. 1985. Copper toxicosis and tolerance in the rat. II. Tolerance- A liver protective adaption. Liver 5:267-275. (Cited in ATSDR 1990.)

42) Hazlett, P. W., G. K. Rutherford, and G.W. vanLoon. 1983. Metal contaminants in surface soils and vegetation as a result of nickel/copper smelting at Coniston, Ontario, Canada. Reclam. & Reveg. Res. 2:123-137.

43) Hazlett, P. W., G. K. Rutherford, and G.W. vanLoon. 1984. Characteristics of soil profiles affected by smelting of nickel and copper at Coniston, Ontario, Canada. Geoderma 32:272-285.

44) Holleran, R. S. 1981. Copper sulphate overdose. J. emerg. Nurs. 7:136-137 (Cited in ATSDR 1990.)

45) HSDB (Hazardous Substance Data Bank). 1993. Copper. Micromedex Inc. Vol.17.

46) HSPE (Ministry of Housing, Spatial Planning and the Environment) 1994. Environmental quality objectives in the Netherlands: A review of environmental quality objectives and their policy framework in the Netherlands. Risk Assessment

and Environmental Quality Division Directorate for Chemicals, External Safety and Radiation Protection, Bilthoven, The Netherlands.

47) Huang, Rixiang, Wen, Bei, Pei, Zhiguo, Shan, Xiao-Quan, Zhang, Shuzhen, Williams, Paul N. 2009. Accumulation, Subcellular Distribution and Toxicity of Copper in Earthworm (Eisenia fetida) in the Presence of Ciprofloxacin. Environmental Science & Technology. Volume:43 Issue:10 Pages: 3688-3693

48) Hunter, B.A., M.S. Johnson, and D. J. Thompson. 1987. Ecotoxicology of copper and cadmium in a contaminated grassland ecosystem: I. Soil and vegetation contamination. J. Appl. Ecol. 24:573-586.

49) Hutchinson, T. C. and L. M. Whitby. 1974. Heavy-metal pollution in the Sudbury mining and smelting region of Canada. I. Soils and vegetation contamination by nickel, copper, and other metals. Environ. Conserv. 1(2): 123-132.

50) HWC (Health and Welfare Canada). 1990. Nutrition recommendations- The report of the Scientific Review Committee-1990. Cat. No.:H49-42/1990E. Supply and Services Canada, Ottawa.

51) Jantsch, W., K. Kulig, and B. H. Rumack. 1984-1985. Massive copper sulfate ingestion resulting in hepatotoxicity. J. Toxicol. Clin. Toxicol. 22:585-588. (Cited in ATSDR 1990.)

52) Janus, J, A., J. H. Canton, C.A. M. van Gestel, and E. Heijna-Merkus. 1989. Integrated criteria document, copper: Effects. Re-publication of Report No. 758474003. Appendix to Report No. 758474009. June 1989, Bilthoven, The Netherlands.

53) Jeyakumar, P., Loganathan, P., Sivakumaran, S., Anderson, C. W. N., McLaren, R. G. 2010. Bioavailability of copper and zinc to poplar and microorganisms in a biosolids-amended soil. Australian Journal of Soil Research Volume: 48 Issue: 5 Pages: 459-469.

54) Junhui Li, Ying Lu, Hojae Shim, Xianglian Deng, Jin Lian, Zhenglei Jia and Jianhua Li, 2010. Use of the BCR sequential extraction procedure for the study of metal availability to plants. . J. Environ. Monit., 12, 466-471.

55) Kabata-Pendias A., 2004. Soil-plant transfer of trace elements-an environmental issue. Geoderma 122, 143-149.

56) Kabata-Pendias, A. and H. Pendias. 1992. Trace elements in soils and plants. 2nd ed. Boca Raton, Florida: CRC Press Inc.

57) Karlson, B., and L. Noren. 1965. Ipecacuanha and copper sulphate as emetics in intoxications in children. Acta Paediatr. Scand. 54:331-335. (Cited in ATSDR 1990.)

58) Klein, W. J., Jr., E. N. Metz, and A. R. Price. 1972. Acute copper intoxication. A hazard of hemodialysis. Arch. Intern. Med. 129:578. (Cited in Beutler 1990.)

59) Kloke, A., D. R. Sauerbeck, and H. Vetter. 1984. The contamination of plants and soils with heavy metals and the transport of metals in terrestrial food chains. In Changing metal cycles and human health, ed. J. O. Nriagu, pp113-141. New York: Springer-Verlag.

60) Komárekn M. , Száková J., Rohošková M., Javorská H., Chrastný V., Balík J., 2008. Copper contamination of vineyard soils from small wine producers: A case study from the Czech Republic. Geoderma 147, 16-22.

61) Korthals, G.W., A.D. Alexiev, T.M. Lexmond, J.E. Kammenga, and J.E. Bongers. 1996. Longterm effects of copper and pH on the nematode community in an agroexosystem. Environ. Toxicol. Chem. 15:979-985.

62) Kumar, A., and C. B. Sharma. 1987. Hematological indices in copper-poisoned rats. Toxicol. Lett. 38:275-278. (Cited in ATSDR 1990.)

63) Kumaratilake, J. S., and J. M. Howell. 1989a. Intracellular distribution of copper in the liver of copper loaded sheep- A subcellular fractionation study. J. Comp. Pathol. 101(2):161-76.

64) Kuo, S., P. E. Heilman, and A. S. Baker. 1983. Distribution of copper, zinc, cadmium, iron, and manganese in soils near a copper smelter. Soil Sci. 135(2):101-109.

65) Lai H. Y., Juang K. W., Chen B. C., 2010. Copper concentrations in grapevines and vineyard soils in central Taiwan. Soil Science and Plant Nutrition 56, 4, 601-606.

66) Lecyk, M. 1980. Toxicity of copper sulphate in mice embryonic development. Zool. Pol. 28:101-106. (Cited in Agarwal 1989 and ATSDR 1990.)

67) Leichtmann, G. A., and M.D. Sitrin. 1991. Update on trace elements. Compr. Ther. 17(1):42-48.

68) Lewis S, Donkin ME, Depledge MH (2001) Hsp 70 expression in Enteromorpha intestinalis (Chlorophyta) exposed to environmental stressors. Aqua Toxicol 51:277–291.

69) Lombi E., Stevens D. P., McLaughlin M. J., 2010. Effect of water treatment residuals on soil phosphorus, copper and aluminium availability and toxicity. Environmental Pollution 158, 2110-2116.

70) Loneragan, J.F., A.D. Robson and R. D. Graham. 1981. Copper in soils and plants. Toronto: Academic Press.

71) Ma, W. 1982. The influence of soil properties and worm related factors on the concentration of heavy metals in earthworms. Pedobiologia 24:109-119.

72) Malecki, M. R., E. F. Neuhauser, and R. C. Loehr. 1982. The effects of metals on the growth and reproduction of Eisenia foetida (Oligochaeta, Lumbricidae). Pedobiologia 24:129-137.

73) Manzler, A. D., and A. W. Schreiner. 1970. Copper-induced acute hemolytic anemia. A new complication of hemodialysis. Ann. Intern. Med. 73:409. (Cited in Beutler 1990.)

74) Marceau, N., N. Aspin, and A. Sass-Kortsak. 1970. Absorption of copper 64 from gastrointestinal tract of the rat. Am. J. Physiol. 218:377-383. (Cited in ATSDR 1990.)

75) Martı´nez-Alcala´I., Walker D. J., Bernal M. P., 2010. Chemical and biological properties in the rhizosphere of Lupinus albus alter soil heavy metal fractionation. Ecotoxicology and Envrionmental Safety 73, 596-602.

76) Martley E., Gulson B. L., Pfeifer H. –R., 2004. Metal concentrations in soils around the copper smelter and surrounding industrial complex of Port Kembla, NSW, Australia. Science of the Total Environment 325, 113-127.

77) McBride, M.B., and D. Bouldin. 1984. Long term reactions of copper(II) in a contaminated calcareous soil. Soil Sci. Soc. Am. J. 48:56-59.

78) McBride, M.B., and G. Spiers. 2001. Trace element content of selected fertilizers and dairy manures as determined by ICP-MS. Comm. Soil Sci. Plant Anal. 32:139-156.

79) McGrath, S. P., and P. W. Lane. 1989. An explanation for the apparent losses of metals in a long-term field experiment with sewage sludge. Environ. Pollut. 60:235-256.

80) McKeague, J. A. and M. S. Wolynetz. 1980. Background levels of Minor elements in Canadian soils. Geoderma 24:299-307.

81) McKeague, J. A., J. D. Desjardins, and M. S. Wolynetz 1979. Minor elements in Canadian soils. Agriculture Canada. LRRI Publication #21.

82) MENVIQ (ministere de l' Environnement du Quebec). 1988. Contaminated Sites Rehabilitation Policy. Prepared by the Direction des Substances Dangereuses. MENVIQ, Ste.Foy, Quebec.

83) Nagajyoti P.C., Lee K.D., Sreekanth T. V. M., 2010. Heavy metals, occurrence and toxicity for plants: a review. Environ. Chem. Lett. 8, 199-216. DOI 10.1007/s10311-010-0297-8.

84) NAS (National Academy of Sciences). 1977. Copper. Committee on Medical and Biologic Effects of Environmental Pollutants, Division of Medical Sciences Assembly of Life Sciences, National Research Council, National Academy of Sciences, Washington, D. C.

85) NAS (National Academy of Sciences). 1989. Recommended daily allowances. 10^{th} ed. Food and Nutrition Board, National Academy of Sciences, Washington, D.C.

86) Neaman A., Reyes L., Trolard F., Bourrié G., Sauvé S., 2009. Copper mobility in contaminated soils of the Puchuncaví valley, central Chile. Geoderma 150, 359-366.

87) Neelima P, Reddy KJ (2002) Interaction of copper and cadmium with seedlings growth and biochemical responses in Solanum melongena. Envi Pollu Technol 1:285–290.

88) Nicholas, P.O., and M. B. Brist. 1968. Food poisoning due to copper in the morning tea. Lancet. 2:84-87. (Cited in ATSDR 1990.)

89) NJDEP (New Jersey Department of Environmental Protection). 1990. Basis for NJDEP Interim soil action levels. Prepared by the Division of Hazardous Site Mitigation, Bureau of Environmental Evaluation and Risk Assessment.

90) OMEE (Ontario Ministry of the Environment and Energy). 1994a. Ontario typical range of chemical parameters in soil, vegetation, moss bags and snow. Version 1.0a., April 1994. PIBS 2792. Phytotoxicology Section, Standards Development Branch, Toronto.

91) Ouzounidou G (1994) Change in chlorophyll fluorescence as a result of copper treatment: dose response relations in Silene and Thlaspi. Photosynthetica. 29:455–462

92) Pacyna JM (1986) Atmospheric trace elements from natural and anthropogenic sources. In: Nriagu JO, Davidson CI (eds) Toxic metals in the atmosphere, Chap 2. Wiley, New York.

93) Parmelee, R. W., R. S. Wentsel, C. T. Phillips, M. Simini, and R. T. Checkai. 1993. Soil microcosm for testing the effects of chemical pollutants on soil fauna communities and trophic structure. Environ. Toxicol. Chem. 12:1477-1486.

94) Patterson, W. A., III, and J. J. Olson. 1982. Effects of heavy metals on radical growth of selected woody species germinated on filter paper, mineral and organic soil substrates. Can. J. For. Res. 13:233-238.

95) Peech, M. 1941. Availability of ions in light sandy soil as affected by soil reaction. Soil Sci., 51, 473.

96) Pietrzak U, McPhail DC. 2004. Copper accumulation, distribution and fractionation in vineyard soils of Victoria, Australia. Geoderma Volume: 122 Issue: 2-4 Pages: 151-166.

97) Piper, C. S. 1942. Investigation on copper deficiency in plants. J. Agric. Sci., 3, 143.

98) Rana, S.V.S., and A. Kumar. 1980. Biological, hematological and histological observations in copper-poisoned rats. Ind. Health. 18:9-17. (Cited in ATSDR 1990.)

99) Reaves G. A., Berrow M. L., 1984. Total copper contents of Scottish soils. Journal of Soil Science 35, 4, 583-592.

100) Rixiang H., Bei W., Zhiguo P., Xiao-Quan S., Shuzhen Z., Williams P. N., 2009. Accumulation, subcellular distribution and toxicity of copper in earthworm (Eisenia fetida) in the presence of ciprofloxacin. Environ. Sci. Technol. 43, 3688-3693.

101) Ross SM (1994) Toxic metals in soil–plant systems. Wiley, Chichester, p 469

102) Sayen S., Guillon E., 2010. X-ray absorption spectroscopy study of Cu^{2+} geochemical partitioning in a vineyard soil. Journal of Colloid and Interface Science 344,611-615.

103) Semple, A.B., W. H. Parry, and D. E. Phillips. 1960. Acute copper poisoning: An outbreak traced to contaminated water from a corroded geyser. Lancet. 2:700 701 (Cited in ATSDR 1990.)

104) Shengli Wang, Zhongren Nan, Xiaowen Liu, Yuan Li, Song Qin, Haixia Ding, 2009. Accumulation and bioavailability of copper and nickel in wheat plants grown in contaminated soils from the oasis, northwest China. Geoderma 152, 290-295.

105) Slooff, W., R. F. M. J. Clevan, J. A. Janus, and J. P. M. Ros. 1989. Integrated criteria document- Copper. Report No. 758474009. National Institute of Public Health and Environmental Protection, Bilthoven, The Netherlands.

106) Soon, Y. K., and S. Abboud. 1990. Trace elements in agricultural soils of northwestern Alberta. Can. J. Soil Sci. 70:277-288.

107) Suzuki, K. T., H. Tamagawa, K. Takakashi, and N.Shimojo. 1990. Pregnancy-induced mobilization of copper and zinc bound to renal metallothionein in cadmium-loaded rats. Toxicology 60(3):199-210.

108) Tessier A., P. G. C. Campbell and M. Bisson, Anal. Chem., 1979, 51, 844.

109) Thornton, I., E. Culbard, S. Moorcroft, J. Watt, M. Wheatly, M. Thompson, and J. F. A. Thomas. 1985. Metals in urban dusts and soils. Environ. Technol. Lett. 6:137-144.

110) Turnlund, J. R., W. R. Keyes, H. L. Anderson, and L. L. Acord. 1989. Copper absorption and retention in young men at three levels of dietary copper by use of the stable isotope 65Cu. Am. J. Clin. Nutr. 49(5):870-878.

111) Wallace, A., E. M. Romney, C. V. Alexander, and J. Kinnear. 1977. Phytotoxicity and some interactions of the essential trace metals iron, manganese, molybdenum, zinc, copper, and boron. Commun. Soil Sci. Plant Anal. 8(9):741-750.

112) Walsh, F. M., F. J. Crosson, J.Bayley, et al. 1977. Acute copper intoxication. Am. J. Dis. Child. 131:149-151. (Cited in ATSDR 1990.)

113) Ward, N. I. 1990. Multielement contamination of British motorway environment. Sci. Total Environm. 93:393-401.

114) Ward, N. I., R. R. Brooks, and E. Roberts. 1977. Heavy-metal pollution from automotive emissions and its effect on roadside soils and pasture species in New Zealand. Environ. Sci. Technol. 11(9):917-921.

115) Whalley, C., and A. Grant. 1994. Assessment of the phase selectivity of the European Community Bureau of Reference (BCR) sequential extraction procedure for metals in sediment. Anal. Chim. Acta 542 291:287-295.

116) Whitby, L. M., J. Gaynor, and A. J. Maclean 1978. Metals in soils of some agricultural watersheds in Ontario. Can. J. Soil Sci. 58:325-330.

117) Williams, D. E., J. Vlamis, A.H. Pukite, and J. E. Corey. 1987. Metal movement in sludge-amended soils: A nine-year study. Soil Sci. 143(2):124-131.

118) Winge, D. R., and R. K. Mehra. 1990. Host defenses against copper toxicity. Int. Rev. Exp. Pathol. 31:47-83.

119) Xiangdong Li, Thornton I., 2001. Chemical partitioning of trace and major elements in soils contaminated by mining and smelting activities. Applied Geochemistry 16, 1693-1706.

120) Xiaoping Z., Xiuyi Y., Xueming Y., 2002. Copper content and its distribution in soils of Tibet. Journal of Geographical Sciences 12, 3, 343-347. DOI: 10.1007/BF02837555.

121) Zhao F. J., McGrath S.P., Merrington G., 2007. Estimates of ambient background concentrations of trace metals in soils for risk assessment. Environmental Pollution 148, 221-229.

122) Zoltai, S.C. 1988. Distribution of base metals in peat near a smelter at Flin Flon, Manitoba. Water Air Soil Pollut. 37:217-228.

(8.3) Thallium

1) Adams F., Gijbels R., and Van Grieken R., Inorganic Mass Spectrometry (John Wiley and Sons, New York, 1988.).
2) Al-Najar H., Schulz R., Römheld V., 2001. Plant availability of thallium in the rhizosphere of hyperaccumulator plants: a key factor for assessment of phytoextraction. Plant and Soil 249: 97-105.
3) Alloway, B.J. (ed.). 1990. Heavy metals in soils. John Wiley and Sons, Inc., New York.
4) Andronikov, S. V., Davidson, D. A., Spiers, R. B. (2000): Variability in contamination by heavy metals: sampling implications. Water, Air Soil Pollut. 120, 29-45.
5) Agency for Toxic Substances and Desease Registry (ATSDR) (1992). - Toxicological profile for thallium. - Atlanta, Georgia, Agency for Toxic Substances and Disease Registry, pp 1-90 (ATSDR/TP-91/26).
6) Brockhaus A., Dolgner R., Ewers U., Kramer U., Soddemann H., Wiegand H. (1981). – Intake and health effects of thallium among a population living in the vicinity of a cement plant emitting thallium containing dust. – International Archives Occupational and Environmental Health 48, pp.375-389.
7) Brumsack H. -J. (1977).- Potential metal pollution in grass and soil samples around brickworks. –Environ Geol, 2, pp. 33-41.
8) Bunzl K., Trautmannsheimer M., Schramel P., Reifenhäuser W., 2001. Availability of arsenic, copper, lead, thallium, and zinc to various vegetables grown in slag-contaminated soils. J. Environ. Qual. 30:934-939.
9) Cambardella, C. A., Moorman, A. T., Novak, J. M., Parkin, T. B., Karlen, D. L., Turco, R. F., Konopka, A. E. (1994): Field-scale variability of soil properties in central lowa soils. Soil Sci. Soc. Am. J. 58, 1501-1511.
10) Canadian soil quality guidelines for the protection of environmental and human health thallium 1999. Canadian Environmental Quality Guidelines, Canadian Council of Ministers of the Environment.
11) Crössmann G. (1984). - Thallium - a new environmental contamination - Angew. Bot., 58, pp. 3-10 (in German).

12) Davids P., G. Güthner, M. Lange, W. Lohrer and F. Vahrenholt, Stand und Perspektiven der Luftreinhaltetechnik. Staub- Reinhalt Luft, 40 (1980) 392-402.

13) Delvalls TA, Saenz V, Arias AM, Blasco J. Thallium in the marine environment: first ecotoxicological assessments in the Guadalquivir estuary and its potential adverse effect on the Don˜ana European natural reserve after the Aznalcollar mining spill. Cienc Mar 1999;25(2):161–75.

14) EPA (1988).-Health and environmental effects document for thallium and compounds. Cincinnati, OH: U.S.- Environmental Protection Agency, Office of Solid Waste and Emergency Response. ECAO-CIN-G031.

15) Ewers U., 1988. Environmental exposure to thallium. The Science of the Total Environment 71:285-292.

16) Frattini P., 2005. Thallium properties and behavior- A literature study. Geological Survey of Finland.

17) Fu W., Tunney H., Zhang C., 2010. Spatial variation of soil test phosphorus in a long-term grazed experimental grassland field. J. Plant Nutr. Soil Sci. 173:323-331. DOI:10.1002/jpln.200800275

18) Gosselin, RE; Smith, RP; Hodge, HC. (1984) Clinical toxicology of commercial products. 5th edition. Batimore, MD: Williams and Wilkins; pp.III-379-III-383. (As cited in CalEPA, 1999).

19) Government of Western Australia, Department of Commerce, WorkSafe Divison, Westcentre, Level 5, 1260 Hay Street, West Perth, Western Australia 6005. www.worksafe.wa.gov.au

20) Heim M., Wappelhorst O., Markert B., 2002. Thallium in terrestrial environments-occurrence and effects. Ecotoxicology 11:369-377.

21) Hoffmann G., Schweiger P., & School W. (1982). - Uptake of thallium by agriculturally and horticulturally useful plants. – Landwirtsch. Forsch., 35, pp. 45-54 (in German).

22) Ivanov, V. V. (1996)- Ecological geochemistry of elements. – manual in 6 volumes. Nedra Moscow. (in Russian).

23) Jacobson A. R., McBride M.B., Baveye P., Steenhuis T. S., 2005. Environmental factors determining the trace-level sorption of silver and thallium to soils. Science of the Total Environment 345: 191-205.

24) John Peter A.L., Viraraghavan T., 2004. Thallium: a review of public health and environmental concerns. doi:10.1016/j.envint.2004.09.003

25) Kabata-Pendias A. & Pendias H. (2001).-Trace Elements in Soils and Plants.-CRC Press, 3rd edition, Boca Ration.

26) Kazantzis G., 2000. Thallium in the environment and health effects. Environmental Geochemistry and Health 22: 275-280.

27) Kemper F. H. , H. P. Bertram, Thallium In: Metalle in der Umwelt (Merian E, Ed.) (1984) 571-584. Verlag Chemie, Weinheim.

28) Li W., Kubota M., Higashi T., Fujimura T., 2004. Evaluation of a sequential extraction procedure for the fractionation of thallium in soils and determination of the content by flame atomic absorption spectrometry. Soil Sci. Plant Nutr., 50 (3), 339-347.

29) Lis J., Pasieczna A., Karbowska B., Zembrzuski W., Lukaszewski Z., 2003. Thallium in Soils and Stream Sediments of a Zn-Pb Mining and Smelting Area. Environ. Sci. Technol. 37:4569-4572.

30) LIS (Land Institute for Protection against Emissions) (1980). - Environmental burden by thallium. Investigations in the neighbourhood of the Dyckerhoff cement plant in Lengerich and other thallium-emitting plants in the country NW. - Bonn, Bonn University Press (in German).

31) Lukaszewski Z., Zembrzuski W., Talanta, 1992, 39, 221.

32) MAGS (Ministerium für Arbeit, Gesundheit und Soziales des Landes NW). Umweltbelastung durch Thallium, Düsseldorf, 1980.

33) Montasser, Inductively Coupled Plasma Mass Spectrometry (Wiley-VCH, Berlin,1998).

34) McGrath S. P. (1998). – Phytoextraction for soil remediation. – Plants that Hyperaccumulate Heavy Metals. – Brooks, R. R., Ed., CAB Intern., 261.

35) Pielow E. (1979). –Pollution by thallium in the environment of a cement plant.-Umwelt, 5, pp.394-396 (in German).

36) Prinz B., Krause G.H.M., & Stratmann H. (1979).-Damages by thallium in the neighbourhood of the dyckerhoff cement plant in Lengerich, Westfalen. – Staub-Reinhalt Luft, 39, pp.457-462 (in German).

37) Poperechna N., Heumann K. G., (2005) Simultaneous multi-species determination of trimethyllead, monomethylmercury and three butyltin compounds by species-specific

isotope dilution GC–ICP–MS in biological samples. Anal Bioanal. Chem 383:153-159, DOI 10.1007/s00216-005-0036-3

38) Rule J. H., in Adsorption and its Applications in Industry and Environmental Protection. Studies in Surface Science and Catalysis, Elsevier Science B. V. Vol. 120 (Ed: A. Darbrow-ski), Elsevier, New York 1998.

39) Schaefer K., Einax J. W., Simeonov V., Tsakovski S., 2010. Geostatistical and multivariate statistical analysis of heavily and manifoldly contaminated soil samples. Anal Bioanal Chem 396:2675-2683.

40) Schoer J. (1984). - In: Hutzinger O. ed.: The Handbook of Environmental Chemistry, Vol. 3 (C9. – Spinger-Verlag, Berlin, pp. 143-214.

41) Scholl W. & Metzger F. (1982). - Determinations of the thallium burden of useful plants on contaminated soils in the region of Lengerich. - Landwirtsch Forsch, 35, pp. 216-223 (in German).

42) Thomas R., 2008. Practical Guide to ICP-MS: A Tutorial for Beginners, Second Edition, Scientific Writing Solutions, Gaithersburg, Maryland, USA. CRC Press.

43) Tremel A., Masson P., Sterckman T., Baize D. & Mench M. 1997.-Thallium in French agrosystems. Thallium contents in arable soils.-Environmental pollution, Vol. 95, no.3, pp. 293-302.

44) Utermann, J., Düwel, O., Gäbler, H.-E. & R. Hindel (1999): Substrate- and element specific relation of real total vs. aqua regia soluble contents of heavy metals in soils.- 5th International Conference on the Biochemistry of Trace Elements. 11.- 15.07.1999 Vienna.

45) Utermann, J., Düwel, O., Gäbler, H.-E. & R. Hindel (2000): Beziehung zwischen Totalgehalten und königswasserextrahierbaren Gehalten von Schwermetallen in Böden. In Rosenkranz, D., Einsele, G., Harreß, H.-M. & G. Bachmann [Hrsg.] Bodenschutz: ergänzbares Handbuch der Maßnahmen u. Empfehlungen für Schutz, Pflege u. Sanierung von Böden. 31. Lfg.

46) Utset, A., Ruiz, M. E., Herrera, J., Leon, D. P. (1998): A geostatistical method for soil salinity sample site spacing. Geoderma 86, 143-151.

47) U.S. Environmental Protection Agency, Washington DC. Toxicological review of thallium and compounds, 2009. CAS No. 7440-28-0. In support of summary information on the integrated risk information system (IRIS). EPA/635/R-08/001F, www.epa.gov/iris

48) Von Laar C., Reinke R., Simon J., Fresenius J. Anal. Chem. 1994, 349, 692.

49) Weisweiler W., Blome K., & Kaeding L. (1985).- Quantitative determination. Thallium and lead cycles in rotary kilns for cement production. –Staub-Reinhalt Luft, 45 pp. 461-466 (in German).

50) Wenqi Q., Yalei C., Jieshan C., Intern. J. Environ. Studies 1992, 40,311.

51) WHO: 1996, *Thallium. Environmental Health Criteria 182*, World Health Organisation, Geneva, 274 pp.

52) Wilcke W., Müller S., Kanchanakool N., Zech W., 1998. Urban soil contamination in Bangkok: heavy metal and aluminium partitioning in topsoils. Geoderma 86:211-228.

53) http://www.windfinder.com

54) Xiao T., Boyle D., Guha J., Rouleau A., Hong Y., Zheng B., 2003. Groundwater-related thallium transfer processes and their impacts on the ecosystem: southwest Guizhou Province, China. Applied Geochemistry 18:675-691.

55) Xiao T., Guha J., Boyle D., Liu C. Q., Chen J. (2003).- Environmental concerns related to high thallium levels in soils and thallium uptake by plants in southwest Guizhou, China.-The Science of Total Environment 318, pp.223-244.

56) Xiao T., Guha J., Liu C. Q., Zheng B., Wilson G., Ning Z., He L., 2007. Potential health risk in areas of high natural concentrations of thallium and importance of urine screening. Applied Geochemistry 22:919-929.

57) Yang C., Chen Y., Peng P., Li C., Chang X., Xie C., 2005. Distribution of natural and anthropogenic thallium in the soils in an industrial pyrite slag disposing area. Science of the Total Environment 341: 159-172.

58) Zitko V. (1975). - Chemistry, applications, toxicity, and pollution potential of thallium. - Department of the Environment, Fisheries and Marine Service, Research and Development Directorate (Technical Report No. 518).

59) Schilling J. G. and Kingsley R. Graduate School of Oceanography, University of Rhode Island, South Ferry Rd. Narragansett, R.I. 02882. U.S.A. (http://www.gso.uri.edu/icpms/how_does.htm).

(9.0) Appendix

(9.1) Appendix A

(9.1.1) Arsenic (As)

Table (9.1.1.1) Table shows mass of sub-samples applied in sequential extraction schemes for As measurments

Name of soil sub-samples	Mass of soil sub-samples in sequential extraction scheme 1 (SE1) (g)	Mass of soil sub-samples in sequential extraction scheme 2 (SE2) (g)
Huf1	0.4019	0.4019
Huf2	0.4017	0.40277
Huf4	0.40201	0.40279
Huf5	0.4005	0.40018
Huf6	0.40154	0.40516
Huf7	0.40138	0.40079
Huf Rock (reference material)	0.40372	0.40251

Table (9.1.1.2) Table shows soil sub-samples pH before and after acidification

pH	Sample No.	1	2	4	5	6	7	Rock (GSR-6)	Ref (extractant solution blank)
PO4	Before SE 1	4.340	4.424	4.502	4.494	4.296	4.392	4.922	4.036
	After SE 1	1.409	1.497	1.335	1.262	1.176	1.245	1.306	1.328
	Before SE2	4.298	4.439	4.502	4.475	4.314	4.412	4.916	4.054
	After SE2	1.201	1.387	1.318	1.406	1.393	1.412	1.424	1.349
1M HCl	SE 1	0.865	0.685	0.785	0.787	0.725	0.759	0.805	0.559
	SE2	0.900	0.719	0.804	0.794	0.730	0.753	0.798	0.576
Ox	Before SE 1	2.930	2.984	2.960	2.989	2.972	2.944	2.827	2.789
	After SE 1	1.225	1.422	1.488	1.616	1.308	1.375	1.357	1.438
	Before SE2	2.905	2.988	2.945	2.995	2.991	2.945	2.829	2.764
	After SE2	1.343	1.225	1.196	1.392	1.413	1.382	1.117	1.322
Ti	Before SE 1	6.952	6.918	6.982	6.946	6.994	6.949	7.103	7.116
	After SE 1	1.006	1.767	1.117	1.356	1.108	1.175	1.236	1.399
	Before SE2	6.943	6.924	6.956	6.931	6.967	6.922	7.059	7.126
	After	1.063	1.294	1.311	1.386	1.212	1.111	1.150	1.356

	SE2								
Conc.HCl	SE 1	-1.659	-1.593	-1.539	-1.307	-1.383	-1.621	-1.408	-1.473
	SE2	-1.356	-1.605	-1.346	-1.385	-1.358	-1.634	-1.302	-1.465

Before = sample's pH before acidification

After = sample's pH after acidification

SE1 = soil sub-samples in sequential extraction scheme 1

SE 2= soil sub-samples in sequential extraction scheme 2

Table (9.1.1.3) Table shows calibration absorabances of arsenic (As) HG-AAS measurements against different As standard solutions

	PO4 (1)	PO4 (2)	1M HCl (1)	Ox (1)	Ox (2)	Ox (3)	Ti (1)	Ti (2)	Ti(3)	Ti(4)	Conc. HCl (1)
Concentration of standard As solution (µgl-1)	abs	abs	abs	abs	abs	abs	abs	abs	abs	abs	abs
0	0.0147	0.0018	0.0048	0.0185	0.0131	0.0106	0.0068	0.0071	0.0036	0.0175	0.0184
2	0.0493	0.0561	0.0452	0.0442	0.0462	0.045	0.0419	0.0369	0.0336	0.0295	0.0362
5	0.1119	0.1214	0.1111	0.1105	0.1191	0.1098	0.0977	0.1019	0.1063	0.0717	0.0997
10	0.227	0.2254	0.2154	0.2386	0.231	0.2138	0.2098	0.1805	0.2245	0.1503	0.1722
20	0.4009	0.3888	0.3951	0.4128	0.3971	0.391	0.3651	0.2942	0.3251	0.2977	0.3663

Abs = absorbance

(1),(2),(3) and (4) = number of standard calibration

Table (9.1.1.4) Table shows concentrations and absorbances of arsenic (As) in soil samples (Step 1)

Step and Sample No.			µg/l		Average concentration after triplicate measurement (µg/l)				Abs		Average absorbance after triplicate measurement (abs)
PO4 (0.5-25ml)											
Huf 1(1)	2	3.14	3.06		3.1		0.0539	0.082	0.0799		0.08095
Huf 2(1)	1.3	1.73	1.7		1.715		0.0358	0.0469	0.0462		0.04655
Huf 4(1)	1.17	1.58	1.58		1.58		0.0324	0.043	0.0431		0.04305
Huf 5(1)	2.08	3.47	3.63		3.55		0.0559	0.0898	0.0935		0.09165
Huf 6(1)	1.82	2.65	2.62		2.635		0.0481	0.0701	0.0694		0.06975
Huf 7(1)	1.92	2.84	2.79		2.815		0.0519	0.0748	0.0735		0.07415
Huf Rock(1)	0.27	0.37	0.46		0.415		0.0076	0.0106	0.013		0.0118
PO4 (0.5-25ml)											
(0µg/l)1(1)	1.79	3.05	3.13		3.09		0.0485	0.0799	0.0817		0.0808
(2µg/l)1(1)	2.98	4.6	4.56		4.58		0.0781	0.1157	0.1149		0.1153
(5µg/l)1(1)	4.3	7.17	7.27		7.22		0.109	0.1705	0.1725		0.1715
(10µg/l)1(1)	6.65	10.93	10.48		10.705		0.1598	0.2417	0.2338		0.23775
(20µg/l)1(1)	11.41	18.62	18.32		18.47		0.2504	0.3676	0.363		0.3653
PO4 (0.5-25ml)											
(0µg/l)2(1)	1.22	1.95	1.88		1.915		0.0335	0.0525	0.0509		0.0517
(2µg/l)2(1)	2.55	3.13	3.41		3.27		0.0677	0.0818	0.0884		0.0851
(5µg/l)2(1)	3.37	5.44	5.72		5.58		0.0875	0.1342	0.1404		0.1373
(10µg/l)2(1)	6.09	9.36	9.83		9.595		0.1482	0.2131	0.2219		0.2175
(20µg/l)2(1)	10.75	16.95	17.11		17.03		0.2387	0.342	0.3444		0.3432
PO4 (0.5-25ml)											
(0µg/l)4(1)	1.91	2.19	2.11		2.15		0.0515	0.0586	0.0565		0.05755
(2µg/l)4(1)	2.31	3.28	3.43		3.355		0.06	0.0853	0.0889		0.0871
(5µg/l)4(1)	3.34	5.64	5.45		5.545		0.0868	0.1387	0.1345		0.1366
(10µg/l)4(1)	6.02	9.75	10.09		9.92		0.1468	0.2204	0.2266		0.2235
(20µg/l)4(1)	10.83	17.87	17.9		17.885		0.2158	0.3561	0.3566		0.35635

PO4 (0.5-25ml)											
(0µg/l)5(1)	2.66	3.7	3.83		3.765		0.0704	0.0953	0.0983		0.0968
(2µg/l)5(1)	3.27	5.16	5.23		5.195		0.0851	0.1281	0.1297		0.1289
(5µg/l)5(1)	4.69	7.36	7.81		7.585		0.1179	0.1743	0.1833		0.1788
(10µg/l)5(1)	7.61	11.63	11.46		11.545		0.1792	0.2542	0.2512		0.2527
(20µg/l)5(1)	12.23	19.13	19.45		19.29		0.2399	0.3753	0.3801		0.3777
PO4 (0.5-25ml)											
(0µg/l)6(1)	1.95	3.02	3.01		3.015		0.0527	0.0791	0.0788		0.07895
(2µg/l)6(1)	3.03	4.56	4.57		4.565		0.0794	0.1149	0.1151		0.115
(5µg/l)6(1)	6.09	6.58	6.94		6.76		0.1151	0.1584	0.1659		0.16215
(10µg/l)6(1)	6.51	10.85	10.96		10.905		0.157	0.2404	0.2423		0.24135
(20µg/l)6(1)	12.42	18.68	18.15		18.415		0.2679	0.3685	0.3605		0.3645
PO4 (0.5-25ml)											
(0µg/l)7(1)	2.05	3.14	3.07		3.105		0.055	0.082	0.0803		0.08115
(2µg/l)7(1)	2.64	4.72	4.39		4.555		0.0698	0.1186	0.1111		0.11485
(5µg/l)7(1)	4.09	6.64	6.83		6.735		0.1042	0.1596	0.1635		0.16155
(10µg/l)7(1)	6.84	10.75	11.03		10.89		0.135	0.2386	0.2436		0.2411
(20µg/l)7(1)	11.55	18.61	18.59		18.6		0.2528	0.3675	0.3672		0.36735
PO4 (0.5-25ml)											
(0µg/l)Rock(1)	0.49	0.61	0.65		0.63		0.0138	0.017	0.0182		0.0176
(2µg/l)Rock(1)	0.91	0.99	1.06		1.025		0.0252	0.0273	0.0293		0.0283
(5µg/l)Rock(1)	2.67	4.24	4.21		4.225		0.0705	0.1076	0.1069		0.10725
(10µg/l)Rock(1)	5.13	8.21	8.51		8.36		0.1276	0.191	0.1969		0.19395
(20µg/l)Rock(1)	9.63	15.8	16.06		15.93		0.2181	0.3238	0.3279		0.32585

Table (9.1.1.5) Table shows concentrations and absorbances of arsenic (As) in soil samples (Step 2)

Step and Sample No.			µg/l		Average concentration after triplicate measurement (µg/l)				Abs		Average absorbance after triplicate measurement (abs)
1M HCl (1-25ml)											
Huf 1(1)	0.54	0.88	0.9		0.89		0.0122	0.02	0.0202		0.0201
Huf 2(1)	0.84	1.25	1.36		1.305		0.0189	0.0282	0.0306		0.0294
Huf 4(1)	1.2	1.81	1.7		1.755		0.027	0.0408	0.0382		0.0395
Huf 5(1)	0.52	0.8	0.82		0.81		0.0117	0.018	0.0186		0.0183
Huf 6(1)	0.01	0.23	0.26		0.245		0.0003	0.0052	0.0059		0.00555
Huf 7(1)	0.44	0.96	0.91		0.935		0.0101	0.0216	0.0206		0.0211
Huf Rock(1)	-0.82	-0.99	-0.95		-0.97		-0.0187	-0.0223	-0.0216		-0.02195
1M HCl (1-25ml)											
(0µg/l)1(1)	0.23	0.67	0.73		0.7		0.0053	0.0152	0.0165		0.01585
(2µg/l)1(1)	1.36	2.23	2.12		2.175		0.0307	0.0502	0.0478		0.049
(5µg/l)1(1)	2.91	4.16	4.25		4.205		0.0653	0.0929	0.0949		0.0939
(10µg/l)1(1)	4.65	7.52	7.88		7.7		0.1036	0.1648	0.1723		0.16855
(20µg/l)1(1)	8.64	13.89	14.26		14.075		0.1806	0.2904	0.2972		0.2938
1M HCl (1-25ml)											
(0µg/l)2(1)	0.63	1.14	1.16		1.15		0.0142	0.0258	0.0261		0.02595
(2µg/l)2(1)	1.56	2.61	2.6		2.605		0.0351	0.0585	0.0583		0.0584
(5µg/l)2(1)	3.11	4.59	4.68		4.635		0.0696	0.1022	0.1041		0.10315
(10µg/l)2(1)	6.59	8.25	8.31		8.28		0.1452	0.1801	0.1813		0.1807
(20µg/l)2(1)	9.08	14.26	14.65		14.455		0.1971	0.2972	0.3043		0.30075
1M HCl (1-25ml)											
(0µg/l)4(1)	1.84	2.08	2.03		2.055		0.0415	0.0468	0.0456		0.0462
(2µg/l)4(1)	2.3	3.4	3.5		3.45		0.0518	0.0762	0.0783		0.07725
(5µg/l)4(1)	3.7	6.47	6.4		6.435		0.0827	0.1428	0.1412		0.142
(10µg/l)4(1)	5.44	8.91	9.13		9.02		0.1206	0.1936	0.198		0.1958

(20µg/l)4(1)	9.17	14.79	15.26		15.025		0.1988	0.3068	0.3153		0.31105
1M HCl (1-25ml)											
(0µg/l)5(1)	0.34	0.94	0.82		0.88		0.0076	0.0212	0.0186		0.0199
(2µg/l)5(1)	1.5	2.49	2.44		2.465		0.0339	0.056	0.0549		0.05545
(5µg/l)5(1)	3.1	4.24	4.39		4.315		0.0695	0.0946	0.0979		0.09625
(10µg/l)5(1)	4.78	7.92	7.65		7.785		0.1064	0.1732	0.1625		0.16785
(20µg/l)5(1)	8.3	13.41	13.98		13.695		0.1811	0.2815	0.2921		0.2868
1M HCl (1-25ml)											
(0µg/l)6(1)	0.05	0.37	0.27		0.32		0.0011	0.0083	0.0062		0.00725
(2µg/l)6(1)	1.16	1.73	1.78		1.755		0.0262	0.0391	0.0401		0.0396
(5µg/l)6(1)	2.76	4.05	4.01		4.03		0.062	0.0904	0.0896		0.09
(10µg/l)6(1)	4.52	7.57	7.48		7.525		0.1008	0.166	0.1639		0.16495
(20µg/l)6(1)	8.6	13.89	13.27		13.58		0.1873	0.2904	0.2882		0.2893
1M HCl (1-25ml)											
(0µg/l)7(1)	0.68	1.21	1.21		1.21		0.0154	0.0273	0.0273		0.0273
(2µg/l)7(1)	1.46	2.37	2.49		2.43		0.0328	0.0533	0.086		0.06965
(5µg/l)7(1)	3.15	4.55	4.41		4.48		0.0706	0.1013	0.0984		0.09985
(10µg/l)7(1)	4.92	7.92	8.28		8.1		0.1093	0.1732	0.1806		0.1769
(20µg/l)7(1)	8.92	14.27	14.91		14.59		0.1937	0.2973	0.3089		0.3031
1M HCl (1-25ml)											
(0µg/l)Rock(1)	-0.62	-0.65	-0.66		-0.655		-0.0141	-0.0146	-0.0149		-0.01475
(2µg/l)Rock(1)	0.23	0.63	0.62		0.625		0.0051	0.0143	0.014		0.01415
(5µg/l)Rock(1)	1.82	2.73	2.82		2.775		0.0409	0.0612	0.0632		0.0622
(10µg/l)Rock(1)	3.75	6.51	6.76		6.635		0.0838	0.1435	0.1488		0.14615
(20µg/l)Rock(1)	7.84	12.91	12.83		12.87		0.1716	0.2722	0.2706		0.2714

Table (9.1.1.6) Table shows concentrations and absorbances of arsenic (As) in soil samples (Step 3)

Step and Sample No.			µg/l		Average concentration after triplicate measurement (µg/l)				Abs		Average absorbance after triplicate measurement (abs)
Ox (0.5-25ml)											
Huf 1(1)	1.41	2.14	2.06		2.1		0.0317	0.0479	0.0461		0.047
Huf 2(1)	2.7	4.26	4.12		4.19		0.0603	0.0944	0.0914		0.0929
Huf 4(1)	1.58	2.09	2.11		2.1		0.0354	0.0468	0.0471		0.04695
Huf 5(1)	3.01	4.75	4.74		4.745		0.0671	0.1048	0.1047		0.10475
Huf 6(1)	1.33	1.58	1.64		1.61		0.0298	0.0353	0.0367		0.036
Huf 7(1)	1.49	2.14	2.13		2.135		0.0333	0.0479	0.0477		0.0478
Huf Rock(1)	-0.07	-0.17	-0.2		-0.185		-0.0016	-0.0037	-0.0046		-0.00415
Ox (0.5-25ml)											
(0µg/l)1(1)	1.21	1.96	1.95		1.955		0.0272	0.0439	0.0437		0.0438
(2µg/l)1(1)	2.22	3.42	3.53		3.475		0.0496	0.076	0.0784		0.0772
(5µg/l)1(1)	3.69	5.66	5.62		5.64		0.0819	0.1243	0.1235		0.1239
(10µg/l)1(1)	6.01	9.07	9.37		9.22		0.1318	0.1949	0.2009		0.1979
(20µg/l)1(1)	10.31	15.76	16.04		15.9		0.2197	0.3208	0.3256		0.3232
Ox (0.5-25ml)											
(0µg/l)2(1)	2.48	4.14	4.25		4.195		0.0553	0.0917	0.094		0.09285
(2µg/l)2(1)	3.63	5.8	5.72		5.76		0.0807	0.1274	0.1256		0.1265
(5µg/l)2(1)	4.95	7.88	7.53		7.705		0.1092	0.1709	0.1636		0.16725
(10µg/l)2(1)	7.43	11.39	11.31		11.35		0.1616	0.2405	0.239		0.23975
(20µg/l)2(1)	11.36	18.05	17.62		17.835		0.24	0.3596	0.3525		0.35605
Ox (0.5-25ml)											
(0µg/l)4(1)	0.72	2.23	2.3		2.265		0.0161	0.0498	0.0513		0.05055
(2µg/l)4(1)	2.54	3.76	3.87		3.815		0.0566	0.0835	0.086		0.08475
(5µg/l)4(1)	3.74	5.94	5.89		5.915		0.083	0.1304	0.1293		0.12985
(10µg/l)4(1)	6.54	9.62	9.96		9.79		0.143	0.2061	0.2127		0.2094
(20µg/l)4(1)	10.38	16.37	16.74		16.555		0.221	0.3314	0.3377		0.33455

Ox (0.5-25ml)											
(0µg/l)5(1)	4.1	5.25	5.37		5.31		0.0903	0.1156	0.1182		0.1169
(2µg/l)5(1)	4.4	6.6	6.44		6.52		0.0973	0.1442	0.1409		0.14255
(5µg/l)5(1)	7.04	8.67	8.8		8.735		0.1535	0.1869	0.1895		0.1882
(10µg/l)5(1)	8.28	12.28	12.32		12.3		0.179	0.2576	0.2584		0.258
(20µg/l)5(1)	12.35	18.65	18.78		18.715		0.259	0.3695	0.372		0.37075
Ox (0.5-25ml)											
(0µg/l)6(1)	1.33	2	1.86		1.93		0.0299	0.0447	0.0416		0.04315
(2µg/l)6(1)	2.23	3.34	3.38		3.36		0.0499	0.0743	0.0752		0.07475
(5µg/l)6(1)	4.59	5.64	5.57		5.605		0.1014	0.1239	0.1225		0.1232
(10µg/l)6(1)	5.95	8.9	9.4		9.15		0.1306	0.1916	0.2017		0.19665
(20µg/l)6(1)	11.11	15.8	15.72		15.76		0.2351	0.3214	0.3201		0.32075
Ox (0.5-25ml)											
(0µg/l)7(1)	1.73	2.4	2.54		2.47		0.0389	0.0537	0.0568		0.05525
(2µg/l)7(1)	2.61	4.02	3.92		3.97		0.0582	0.0891	0.087		0.08805
(5µg/l)7(1)	3.95	6.02	5.71		5.865		0.0876	0.1321	0.1254		0.12875
(10µg/l)7(1)	6.25	9.96	9.81		9.885		0.1369	0.2127	0.2097		0.2112
(20µg/l)7(1)	11.56	16.01	16.03		16.02		0.2439	0.3251	0.3358		0.33045
Ox (0.5-25ml)											
(0µg/l)Rock(1)	0.14	0.07	-0.01		0.03		0.0032	0.0015	-0.0012		0.00015
(2µg/l)Rock(1)	1.08	1.41	1.53		1.47		0.0243	0.0317	0.0343		0.033
(5µg/l)Rock(1)	2.5	3.84	3.85		3.845		0.0559	0.0852	0.0555		0.07035
(10µg/l)Rock(1)	4.97	7.86	7.81		7.835		0.1096	0.1704	0.1694		0.1699
(20µg/l)Rock(1)	9.65	14.61	14.7		14.655		0.2066	0.3004	0.3021		0.30125

Table (9.1.1.7) Table shows concentrations and absorbances of arsenic (As) in soil samples (Step 4)

Step and Sample No.			µg/l		Average concentration after triplicate measurement (µg/l)				Abs		Average absorbance after triplicate measurement (abs)
Ti(0.5-25ml)											
Huf 1(1)	5.17	9.71	9.3		9.505		0.1069	0.1967	0.1888		0.19275
Huf 2(1)	7.3	11.9	12.39		12.145		0.1456	0.2372	0.246		0.2416
Ti Huf(4)(1)	0.74	0.98	1		0.99		0.0108	0.0143	0.0147		0.0145
Ti Huf(5)(1)	2.2	3.52	3.76		3.64		0.0323	0.0517	0.0553		0.0535
Ti Huf(6)(1)	1.05	1.46	1.52		1.49		0.0153	0.0215	0.0223		0.0219
Ti Huf(7)(1)	0.76	1.34	1.4		1.37		0.0112	0.0196	0.0206		0.0201
Huf Rock(1)	1.06	0.43	0.29		0.36		0.022	0.0088	0.006		0.0074
Ti(0.5-25ml)											
(0µg/l)1(1)	5.51	9.76	10.13		9.945		0.1137	0.1976	0.2046		0.2011
(2µg/l)1(1)	7.02	11.68	11.53		11.605		0.1442	0.2332	0.2306		0.2319
(5µg/l)1(1)	8.87	14.02	13.89		13.955		0.1805	0.2746	0.2723		0.27345
(10µg/l)1(1)	10.96	17.36	17.56		17.46		0.22	0.329	0.3321		0.33055
Ti(0.5-25ml)											
(0µg/l)2(1)	7.12	13.69	13.9		13.795		0.1462	0.2689	0.2725		0.2707
(2µg/l)2(1)	9.18	15.13	15.53		15.33		0.1866	0.2932	0.2999		0.29655
(5µg/l)2(1)	11.05	17.01	17.27		17.14		0.2217	0.3236	0.3276		0.3256
(10µg/l)2(1)	13.36	21.45	21.51		21.48		0.2632	0.3882	0.389		0.3886
Ti(0.25-100ml)											
(0µg/l)4(1)	0.31	0.99	1.04		1.015			0.0146	0.0153		0.01495
(2µg/l)4(1)	1.75	2.57	2.79		2.68			0.0378	0.041		0.0394
(5µg/l)4(1)	3.9	5.5	5.7		5.6		0.0573	0.081	0.084		0.0825
(10µg/l)4(1)	6.39	9.75	9.77		9.76		0.0941	0.1441	0.1443		0.1442
(20µg/l)4(1)	12.22	16.95	17.58		17.265		0.1811	0.2522	0.2618		0.257
Ti(0.25-100ml)											

(0µg/l)5(1)	3.34	4.04	3.86		3.95		0.049	0.0594	0.0568		0.0581
(2µg/l)5(1)	4.15	6.17	5.72		5.945		0.061	0.0909	0.0842		0.08755
(5µg/l)5(1)	4.72	7.69	8.23		7.96		0.0695	0.1134	0.1213		0.11735
(10µg/l)5(1)	8.02	12.28	12.07		12.175		0.1184	0.1819	0.1788		0.18035
(20µg/l)5(1)	14.09	18.88	19.72		19.3			0.2816	0.2943		0.28795
Ti(0.25-100ml)											
(0µg/l)6(1)	2.43	2.06	1.94		2		0.0357	0.0303	0.0285		0.0294
(2µg/l)6(1)	2.49	3.67	3.24		3.455		0.0366	0.0539	0.0549		0.0544
(5µg/l)6(1)	4.31	6.6	6.59		6.595		0.0635	0.0972	0.0972		0.0972
(10µg/l)6(1)	7.36	10.8	10.68		10.74		0.1086	0.1598	0.1581		0.15895
(20µg/l)6(1)	13.42	18.32	17.96		18.14		0.1991	0.273	0.2676		0.2703
Ti(0.25-100ml)											
(0µg/l)7(1)	2.2	2.17	2.06		2.115		0.0322	0.0319	0.0302		0.03105
(2µg/l)7(1)	2.76	3.9	3.9		3.9		0.0406	0.0574	0.0574		0.0574
(5µg/l)7(1)	4.45	6.52	6.42		6.47		0.0655	0.0961	0.0946		0.09535
(10µg/l)7(1)	7.6	10.75	10.83		10.79		0.1121	0.1591	0.1603		0.1597
(20µg/l)7(1)	14.99	18.08	18.35		18.215		0.2227	0.2694	0.2735		0.27145
Ti(0.5-25ml)											
(0µg/l)Rock(1)	0.57	0.78	0.67		0.725		0.0117	0.0161	0.0139		0.015
(2µg/l)Rock(1)	1.58	2.26	2.29		2.275		0.0327	0.0467	0.0474		0.04705
(5µg/l)Rock(1)	3.03	4.47	4.46		4.465		0.0628	0.0925	0.0923		0.0924
(10µg/l)Rock(1)	5.29	8.72	8.83		8.775		0.1092	0.1775	0.1797		0.1786
(20µg/l)Rock(1)	9.48	14.82	15.46		15.14		0.1921	0.2881	0.2987		0.2934

Table (9.1.1.8) Table shows concentrations and absorbances of arsenic (As) in soil samples (Step 5)

Step and Sample No.			µg/l		Average concentration after triplicate measurement (µg/l)				Abs		Average absorbance after triplicate measurement (abs)
Conc.HCl(2-25ml)											
Huf 1(1)	0.95	0.76	0.59		0.675		0.0174	0.014	0.0109		0.01245
Huf 2(1)	1.58	2.12	2.28		2.2		0.0291	0.0389	0.0419		0.0404
Huf 4(1)	2.69	2.5	2.61		2.555		0.0494	0.046	0.048		0.047
Huf 5(1)	2.33	3.26	3.11		3.185		0.0429	0.0599	0.0571		0.0585
Huf 6(1)	0.87	0.62	0.56		0.59		0.016	0.0114	0.0102		0.0108
Huf 7(1)	2.57	4.05	3.96		4.005		0.0473	0.0745	0.0728		0.07365
Huf Rock(1)	0.67	0.16	0.1		0.13		0.0123	0.0029	0.0027		0.0028
Conc.HCl(2-25ml)											
(0µg/l)1(1)	0.3	0.38	0.35		0.365		0.0054	0.0069	0.0064		0.00665
(2µg/l)1(1)	1.38	2.12	2.11		2.115		0.0253	0.039	0.0387		0.03885
(5µg/l)1(1)	2.73	4.37	4.79		4.58		0.0503	0.0803	0.088		0.08415
(10µg/l)1(1)	5.14	8.61	8.57		8.59		0.0946	0.1581	0.1574		0.15775
(20µg/l)1(1)	9.92	15.39	15.85		15.62		0.182	0.2813	0.2897		0.2855
Conc.HCl(2-25ml)											
(0µg/l)2(1)	2.34	2.67	2.4		2.535		0.0431	0.0491	0.0441		0.0466
(2µg/l)2(1)	2.57	3.83	4.14		3.985		0.0473	0.0704	0.0761		0.07325
(5µg/l)2(1)	4.22	6.58	6.51		6.545		0.0776	0.121	0.1196		0.1203
(10µg/l)2(1)	6.1	9.74	10.22		9.98		0.1122	0.1788	0.1875		0.18315
(20µg/l)2(1)	10.36	16.94	17.3		17.12		0.1901	0.3091	0.3155		0.3123
Conc.HCl(2-25ml)											
(0µg/l)4(1)	1.64	2.39	2.43		2.41		0.0302	0.0439	0.0446		0.04425
(2µg/l)4(1)	2.65	3.83	3.98		3.905		0.0487	0.0705	0.0733		0.0719
(5µg/l)4(1)	3.87	6.3	6.48		6.39		0.0711	0.1159	0.119		0.11745
(10µg/l)4(1)	6.5	10.16	10.12		10.14		0.1195	0.1864	0.1857		0.18605

(20µg/l)4(1)	10.08	16.66	17.22		16.94		0.1849	0.3041	0.3141		0.3091
Conc.HCl(2-25ml)											
(0µg/l)5(1)	2.56	2.92	2.56		2.74		0.0471	0.0536	0.0471		0.05035
(2µg/l)5(1)	3.44	4.91	5		4.955		0.0633	0.0902	0.092		0.0911
(5µg/l)5(1)	4.5	7.36	7.14		7.25		0.0828	0.1352	0.1312		0.1332
(10µg/l)5(1)	6.25	10.38	10.81		10.595		0.1149	0.1904	0.1982		0.1943
(20µg/l)5(1)	10.53	17.41	17.41		17.41		0.1931	0.3175	0.3175		0.3175
Conc.HCl(2-25ml)											
(0µg/l)6(1)	1.9	1.42	1.29		1.355		0.035	0.0261	0.0257		0.0259
(2µg/l)6(1)	4.03	3.37	3.45		3.41		0.074	0.062	0.0635		0.06275
(5µg/l)6(1)	4	6.03	5.68		5.855		0.0736	0.1109	0.1045		0.1077
(10µg/l)6(1)	7.24	10.2	9.45		9.825		0.1331	0.1872	0.1735		0.18035
(20µg/l)6(1)	12.09	18.39	17.39		17.89		0.2215	0.3351	0.3172		0.32615
Conc.HCl(2-25ml)											
(0µg/l)7(1)	4.17	5.43	5.24		5.335		0.0767	0.0998	0.0964		0.0981
(2µg/l)7(1)	5.55	7.81	7.52		7.665		0.102	0.1435	0.1382		0.14085
(5µg/l)7(1)	6.2	8.63	9.01		8.82		0.1139	0.1584	0.1654		0.1619
(10µg/l)7(1)	8.44	13.06	12.67		12.865		0.1549	0.2392	0.2321		0.23565
(20µg/l)7(1)	14.17	20.1	19.41		19.755		0.2592	0.3654	0.3552		0.3603
Conc.HCl(2-25ml)											
(0µg/l)Rock(1)	4.78	1.5	1.26		1.38		0.0879	0.0276	0.0232		0.0254
(2µg/l)Rock(1)	2.63	2.76	2.72		2.74		0.0484	0.0508	0.05		0.0504
(5µg/l)Rock(1)	3.9	5.2	4.99		5.095		0.0717	0.0956	0.0918		0.0937
(10µg/l)Rock(1)	6.4	9.31	9.34		9.325		0.1175	0.1709	0.1714		0.17115
(20µg/l)Rock(1)	12.02	18.44	16.92		17.68		0.2203	0.336	0.3088		0.3224

Table (9.1.1.9) Table shows re-calculated As concentrations after standard addition extrapolation

	μg/l	Dilution factor				
Step and Sample No.		x12.5	x25	x50	x400	As Content (mg/kg)
PO4						
Huf1	2.56			128		12.7
Huf2	1.62			81		8.1
Huf4	1.61			80.5		8.0
Huf5	2.95			147.5		14.7
Huf6	2.46			123		12.3
Huf7	2.45			122.5		12.2
Huf Rock	0.416			20.8		2.1
1MHCl						
Huf1	0.63		15.75			1.6
Huf2	0.94		23.5			2.3
Huf4	1.78		44.5			4.4
Huf5	0.83		20.75			2.1
Huf6	0.4		10			1.0
Huf7	1.032		25.8			2.6
Huf Rock	0		0			0.0
Ox						
Huf1	1.45			72.5		7.2
Huf2	3.05			152.5		15.2
Huf4	1.61			80.5		8.0
Huf5	3.79			189.5		18.9
Huf6	1.42			71		7.1
Huf7	1.03			51.5		5.1

Huf Rock	0			0		0.0
Ti						
Huf1	6.37			318.5		31.7
Huf2	9.31			465.5		46.4
Huf4	0.59				236	23.5
Huf5	2.17				868	86.7
Huf6	1.09				436	43.4
Huf7	1.14				456	45.4
Huf Rock	0.62			31		3.1
Conc.HCl						
Huf1	0.34	4.25				0.4
Huf2	1.48	18.5				1.8
Huf4	1.44	18				1.8
Huf5	1.88	23.5				2.3
Huf6	0.83	10.375				1.0
Huf7	3.25	40.625				4.0
Huf Rock	0.58	7.25				0.7

Table (9.1.1.10) Table shows total arsenic after summation of 5 sequential extraction steps in different sub-samples

Sub-sample No.	∑5 steps of total As (mg/kg)
Huf1	53.6
Huf2	73.8
Huf4	45.7
Huf5	124.8
Huf6	64.8
Huf7	69.4
Huf Rock	5.9

Table (9.1.1.11) Table shows distribution of arsenic in different extraction steps

											Total As (mg/kg)
	PO4(24hrs)(mg/kg)	PO4(24hrs)%	1M HCl (mg/kg)	1M HCl %	Ox (mg/kg)	Ox %	Ti (mg/kg)	Ti %	Conc. HCl(mg/kg)	Conc.HCl%	
Huf1	12.7	23.7	1.6	2.9	7.2	13.5	31.7	59.1	0.4	0.8	53.6
Huf2	8.1	10.9	2.3	3.2	15.2	20.6	46.4	62.8	1.8	2.5	73.8
Huf4	8.0	17.5	4.4	9.7	8.0	17.5	23.5	51.4	1.8	3.9	45.7
Huf5	14.7	11.8	2.1	1.7	18.9	15.2	86.7	69.5	2.3	1.9	124.8
Huf6	12.3	18.9	1.0	1.5	7.1	10.9	43.4	67.0	1.0	1.6	64.8
Huf7	12.2	17.6	2.6	3.7	5.1	7.4	45.4	65.5	4.0	5.8	69.4
Rock	2.1	35.2	0.0	0.0	0.0	0.0	3.1	52.5	0.7	12.3	5.9
average	11.3	16.8	2.3	3.8	10.3	14.2	46.2	62.5	1.9	2.8	72.0
SD	2.7	4.8	1.2	3.0	5.5	4.7	21.8	6.5	1.2	1.8	27.8
										RSD	38.7

Table (9.1.1.12) Table shows mass of sub-samples applied with concentrated HCl digestion in As measurements

Name of soil sub-samples	Mass of soil sub-samples in sequential extraction scheme 1 (SE1) (g)	Mass of soil sub-samples in sequential extraction scheme 2 (SE2) (g)
Huf1	0.40445	0.40159
Huf2	0.40293	0.40159
Huf4	0.40286	0.40315
Huf5	0.40032	0.40227
Huf6	0.40317	0.40095
Huf7	0.40288	0.40175
Huf Rock (reference material)	0.40027	0.4029

Table (9.1.1.13) Table shows concentration of As with sub-samples treated with concentrated HCl digestion

		1st measurement (µg/l)	2nd measurement (µg/l)	3rd measurement (µg/l)	4th measurement (µg/l)		Average concentration of 4 measurement (µg/l)
Conc.HCl (1) x25,50ml	1	7.92	9.53	9.77	9.86		9.72
1st sample	2	11.96	14.51	15.49	14.4		14.80
	4	12.96	16.83	16.67	16.79		16.76
	5	11.9	13.2	14.45	14.09		13.81
	6	9.81	11.53	11.56	10.99		11.29
	7	10.59	12.45	12.64	12.55		12.57
	Rock	7.31	7.36	7.39	7.24		7.33
	ref(x25ml)	7.66	7.19	7.48	7.27		7.40
Conc.HCl (2) x25,50ml	1	15.33	18.57	18.64	18.52		18.58
2nd sample	2	12.28	18.13	17.95	17.74		17.94
	4	10.63	13.36	13.21	13.97		13.51
	5	14.68	18.93	19.12	19.07		18.93
	6	12.52	14.31	13.98	13.84		14.06
	7	13.37	16.03	16.61	15.62		16.08
	Rock	9.86	9.27	9.17	9.27		9.39
	ref(x25ml)	7.66	7.19	7.48	7.27		7.40

Table (9.1.1.14) Table shows absorbance of As with sub-samples treated with concentrated HCl digestion

		H_20 washes 1^{st} (µg/l)	H_20 washes 2^{nd} (µg/l)	H_20 washes 3^{rd} (µg/l)	H_20 washes 4^{th} (µg/l)		average H2O background concentration (µg/l)		Average As concentration after deduction of H_2O and reference background (µg/l)
Conc.HCl (1) x25,50ml	1	0.31	0.48	0.8	1.09		0.67		7.92
1st sample	2	3.28	2.31	2.38			2.66		11.01
	4	4.67	3.37	3.44	3.37		3.71		11.92
	5	4.3	3.03	3.17	3.23		3.43		9.25
	6	5.29	3.88	4.05	4.02		4.31		5.84
	7	5.52	4.6	4.66			4.93		6.51
	Rock	7.12	5.59	5.66			6.12		0.07
	ref(x25ml)	6.99	5.96	5.98	6.13		6.27		0.00
Conc.HCl (2) x25,50ml	1	7.27	6.62	6.78	6.68		6.84		10.60
2nd sample	2	4.21	3.98	4.07	4.37		4.16		12.65
	4	2.65	2.05	2.13			2.28		10.10
	5	6.59	5.3	5.37	5.44		5.68		12.12
	6	6.98	5.96	5.97	6.17		6.27		6.66
	7	7.69	6.74	6.59	6.77		6.95		7.99
	Rock	7.77	7.41	7.63	7.34		7.54		0.72

Table (9.1.1.15) Table shows absorbance of As with sub-samples treated with concentrated HCl digestion

		Average As concentration after deduction of H_2O and reference background (µg/l)	0.25x 25ml dilution (µg/l)	0.25x 50ml dilution (µg/l)	As content in (mg/kg)
Conc.HCl (1) x25,50ml	1	7.92	791.50		78.28
1st sample	2	11.01	1100.83		109.28
	4	11.92	1191.58		118.31
	5	9.25		1849.00	184.75
	6	5.84		1168.00	115.88
	7	6.51		1301.67	129.24
	Rock	0.07	6.67		0.67
	ref(x25ml)	0.00	0.00		
Conc.HCl (2) x25,50ml	1	10.60	1060.42		105.62
2nd sample	2	12.65	1264.75		125.97
	4	10.10	1010.17		100.23
	5	12.12		2424.50	241.08
	6	6.66		1331.50	132.83
	7	7.99		1598.50	159.15
	Rock	0.72	72.00		7.15

Table (9.1.1.16) Table shows total As contents in soil-subsamples treated with concentrated HCl

Sub-samples no.	SE1	SE2	Average of SE1 and SE2	SD
1	78.28	105.62	91.95	19.33
2	109.28	125.97	117.63	11.80
4	118.31	100.23	109.27	12.79
5	184.75	241.08	212.92	39.83
6	115.88	132.83	124.36	11.99
7	129.24	159.15	144.19	21.15
rock	6.35	5.63	5.99	0.51
		Average	114.89	
		SD	62.50	
		RSD	54.40	

SD = standard deviation

SE = sequential extraction scheme number

(9.1.2) Iron (Fe) in arsenic measurement

Table (9.1.2.1) Table shows mass of sub-samples applied in sequential extraction schemes for Fe measurments

Name of soil sub-samples	Mass of soil sub-samples in sequential extraction scheme 1 (SE1) (g)	Mass of soil sub-samples in sequential extraction scheme 2 (SE2) (g)
Huf1	0.40374	0.40196
Huf2	0.4023	0.40445
Huf4	0.40493	0.40324
Huf5	0.40162	0.40261
Huf6	0.40535	0.40446
Huf7	0.40222	0.40084
Huf Rock (reference material)	0.40617	0.40305

Table (9.1.2.2) Table shows concentrations of iron (Fe) in soil samples

Fe data		1st measure mg/l	2nd measure mg/l	3rd measure mg/l		average Fe reading (mg/l)		average H20value (mg/l)		"Fe" reading minus H2O minus ref mg/l
PO4 (1)	1	2.995	3.013	2.973		2.994		0		2.336
1st sample	2	3.753	3.818	3.737		3.769		0		3.112
24hrs	4	4.763	4.749	4.641		4.718		0		4.060
no dilution	5	2.469	2.468	2.461		2.466		0		1.808
	6	3.301	3.285	3.25		3.279		0		2.621
	7	3.344	3.333	3.481		3.386		0		2.728
	Rock	2.1	2.114	2.077		2.097		0		1.439
	ref(x10ml)	0.676	0.692	0.678		0.682		0.02425		0.000
PO4 (2)	1	2.676	2.615	2.599		2.630		0.045		1.927
2nd sample	2	3.438	3.42	3.387		3.415		0.0635		2.694
24hrs	4	4.161	4.136	4.057		4.118		0.0805		3.380
no dilution	5	2.24	2.183	2.218		2.214		0.0775		1.478
	6	2.712	2.677	2.572		2.654		0.09		1.906
	7	2.798	2.886	2.825		2.836		0.12		2.059
	Rock	1.759	1.763	1.713		1.745		0.1875		0.900
	ref(x10ml)									
1M HCl (1)	1	10.495	10.287	10.34		10.374		0.227		10.121
1st sample	2	45.957	45.581	45.225		45.588		0.225		45.336
no dilution	4	43.918	43.829	43.799		43.849		0.2635		43.559
	5	9.976	9.793	9.613		9.794		0.2755		9.492
	6	17.069	17.114	17.314		17.166		0.289		16.850

	7	16.318	16.302	15.701		16.178		0.302		15.850
	Rock (1ml-10ml)	10.116	10.119	10.033		10.089		0.632		9.431
	ref(x10ml)	0.365	0.339	0.356		0.353		0.327		0.000
1M HCl (2)	1	10.248	10.285	10.324		10.286		0.327		9.932
2nd sample	2	44.586	45.126	45.19		44.967		0.374		44.567
no dilution	4	41.142	41.607	41.825		41.525		0.3975		41.101
	5	9.39	9.548	9.434		9.457		0.393		9.038
	6	16.973	16.797	16.866		16.879		0.399		16.453
	7	16.093	16.114	15.885		16.031		0.409		15.595
	Rock (1ml-10ml)	9.82	9.872	9.995		9.896		0.635		9.234
	ref(x10ml)									
Ox (1)	1	3.141	3.094	3.128		3.121		0.456		2.665
1st sample	2	1.992	1.982	1.936		1.970		0.459		1.511
no dilution	4	4.71	4.692	4.785		4.729		0.512		4.217
	5	24.661	24.783	24.098		24.514		0.584		23.930
	6	3.288	3.298	3.301		3.296		0.648		2.648
	7	3.265	3.137	3.054		3.152		0.646		2.506
	Rock	8.37	8.796	8.46		8.542		0.68		7.862
	ref(x10ml)	0.761	0.766	0.7		0.742		0.758		-0.016
Ox (2)	1	3.027	2.949	2.902		2.932		0.738		2.194
2nd sample	2	1.978	2.011	1.861		1.950		0.715		1.235
no dilution	4	3.58	3.45	3.396		3.475		0.73		2.745
	5	17.972	15.012	14.739		15.437		0.7095		14.728

	6	2.318	2.252	2.149		2.240		0.727		1.513
	7	2.325	2.343	2.284		2.317		0.741		1.576
	Rock	4.095	4.067	3.693		3.808		0.677		3.131
	ref(x10ml)									
Ti (1)5-10ml	1	5.8	5.918	5.823		5.847		0.783		5.064
1st sample	2	5.757	5.878	5.862		5.832		0.757		5.075
	4	5.439	5.389	5.319		5.382		0.764		4.618
	5	10.714	10.068	9.959		10.158		0.783		9.375
	6	6.139	6.057	6.015		6.070		0.666		5.404
	7	6.45	6.473	6.548		6.490		0.641		5.849
	Rock	3.065	2.997	3.003		3.022		0.559		2.463
	ref(x10ml)	11.38	11.406	11.289		11.358		0		11.358
Ti (2)5-10ml	1	4.17	4.234	4.152		4.185		0.586		3.599
2nd sample	2	4.978	4.907	4.931		4.939		0.566		4.373
	4	4.45	4.452	4.251		4.384		0.561		3.823
	5	4.833	4.78	4.88		4.831		0.571		4.260
	6	4.533	4.609	4.531		4.558		0.638		3.920
	7	3.93	3.903	3.954		3.929		0.637		3.292
	Rock	2.665	2.524	2.599		2.596		0.62		1.976
	ref(x10ml)									
5th Conc.HCl (1)	1	6.901	6.719	6.686		6.769		0		6.756
1st sample	2	1.611	1.611	1.559		1.594		0		1.581
no dilution	4	7.41	7.457	7.286		7.384		0		7.372

	5	15.645	15.527	15.12		15.431		0.0345		15.384
	6	26.199	26.056	26.345		26.200		0.064		26.123
	7	7.479	7.583	7.628		7.563		0.0935		7.457
	Rock	19.772	19.971	19.856		19.866		0.1225		19.731
	ref(x10ml)	0.149	0.135	0.165		0.150		0.137		0.000
5th Conc.HCl (2)	1	13.287	13.245	13.283		13.272		0.1535		13.106
2nd sample	2	1.915	1.946	1.882		1.914		0.174		1.728
no dilution	4	8.451	8.294	8.228		8.324		0.21		8.102
	5	44.312	43.712	44.151		44.058		0.239		43.807
	6	30.499	30.752	30.241		30.497		0.2825		30.202
	7	19.814	20.226	20.595		20.212		0.2875		19.912
	Rock	19.924	20.26	19.92		20.035		0.307		19.715
	ref(x10ml)									

() shows sequential scheme number.

Table (9.1.2.3) Table shows concentrations of iron (Fe) in soil samples

Fe data			"Fe" reading minus H2O minus ref mg/l-1	x0 dilution mg/l	x 2 dilution mg/l	x 5 dilution mg/l	x 10 dilution mg/l	Fe content in mg/kg
PO4 (1)	1		2.336	2.336				231.4
1st sample	2		3.112	3.112				309.4
24hrs	4		4.060	4.060				401.0
no dilution	5		1.808	1.808				180.1
	6		2.621	2.621				258.6
	7		2.728	2.728				271.3
	Rock		1.439	1.439				141.7
	ref(x10ml)		0.000	0.000				
PO4 (2)	1		1.927	1.927				191.8
2nd sample	2		2.694	2.694				266.4
24hrs	4		3.380	3.380				335.3
no dilution	5		1.478	1.478				146.9
	6		1.906	1.906				188.5
	7		2.059	2.059				205.4
	Rock		0.900	0.900				89.3
	ref(x10ml)							
1M HCl (1)	1		10.121	10.121				1002.7
1st sample	2		45.336	45.336				4507.7
no dilution	4		43.559	43.559				4302.9
	5		9.492	9.492				945.4

	6		16.850	16.850				1662.8
	7		15.850	15.850				1576.2
	Rock (1ml-10ml)		9.431				94.310	9287.7
	ref(x10ml)		0.000	0.000				
1M HCl (2)	1		9.932	9.932				988.4
2nd sample	2		44.567	44.567				4407.7
no dilution	4		41.101	41.101				4077.1
	5		9.038	9.038				897.9
	6		16.453	16.453				1627.2
	7		15.595	15.595				1556.3
	Rock (1ml-10ml)		9.234				92.340	9164.1
	ref(x10ml)							
Ox (1)	1		2.665	2.665				264.0
1st sample	2		1.511	1.511				150.2
no dilution	4		4.217	4.217				416.6
	5		23.930	23.930				2383.3
	6		2.648	2.648				261.3
	7		2.506	2.506				249.2
	Rock		7.862	7.862				774.3
	ref(x10ml)		-0.016	-0.016				
Ox (2)	1		2.194	2.194				218.3
2nd sample	2		1.235	1.235				122.1
no dilution	4		2.745	2.745				272.3

	5		14.728	14.728				1463.2
	6		1.513	1.513				149.6
	7		1.576	1.576				157.3
	Rock		3.131	3.131				310.8
	ref(x10ml)							
Ti (1)5-10ml	1		5.064		10.128			1003.4
1st sample	2		5.075		10.151			1009.3
	4		4.618		9.237			912.4
	5		9.375		18.751			1867.5
	6		5.404		10.809			1066.6
	7		5.849		11.699			1163.4
	Rock		2.463		4.925			485.1
	ref(x10ml)		11.358		22.717			
Ti (2)5-10ml	1		3.599		7.199			716.4
2nd sample	2		4.373		8.745			864.9
	4		3.823		7.647			758.5
	5		4.260		8.520			846.5
	6		3.920		7.839			775.3
	7		3.292		6.584			657.0
	Rock		1.976		3.952			392.2
	ref(x10ml)							
5th Conc.HCl (1)	1		6.756	6.756				669.3
1st sample	2		1.581	1.581				157.2
no	4		7.372	7.372				728.2

dilution								
	5		15.384	15.384				1532.1
	6		26.123	26.123				2577.9
	7		7.457	7.457				741.6
	Rock		19.731	19.731				1943.1
	ref(x10ml)		0.000	0.000				
5th Conc.HCl (2)	1		13.106	13.106				1304.2
2nd sample	2		1.728	1.728				170.9
no dilution	4		8.102	8.102				803.7
	5		43.807	43.807				4352.3
	6		30.202	30.202				2986.9
	7		19.912	19.912				1987.0
	Rock		19.715	19.715				1956.6
	ref(x10ml)							

Table (9.1.2.4) Table shows soil sub-samples Fe contents treated by concentrated HCl

Fe data		1st measure mg/l	2nd measure mg/l	3rd measure mg/l		average Fe reading (mg/l)		average H20value (mg/l)		"Fe" reading minus H2O minus ref mg/l-1
1st Conc.HCl (1)	1	11.451	11.089	11.254		11.265		0.327		10.887
1st sample	2	19.471	18.908	19.032		19.137		0.3605		18.726
2ml-10ml	4	19.642	19.974	20.022		19.879		0.39		19.439
	5	25.839	26.17	26.088		26.032		0.4075		25.575
	6	18.368	18.257	18.797		18.474		0.416		18.008
	7	14.793	15.193	15.331		15.106		0.4345		14.621
	Rock	19.61	20.068	19.669		19.782		0.449		19.283
	ref(x10ml)	0.502	0.538	0.518		0.519		0.469		0.000
1st Conc.HCl (2)	1	11.114	11.216	10.909		11.080		0.486		10.543
2nd sample	2	19.009	19.153	19.204		19.122		0.515		18.557
2ml-10ml	4	19.983	20.491	20.162		20.212		0.53		19.632
	5	25.988	26.51	26.042		26.180		0.5475		25.582
	6	18.582	19.256	19.093		18.977		0.5785		18.348
	7	15.391	15.489	15.603		15.494		0.5835		14.861
	Rock	21.211	21.076	21.114		21.134		0.597		20.486
	ref(x10ml)									

Table (9.1.2.5) Table shows soil sub-samples Fe contents treated by concentrated HCl

Fe data			"Fe" reading minus H2O minus ref mg/l-1	x0 dilution mg/l	x 2 dilution mg/l	x 5 dilution mg/l	x 10 dilution mg/l	Fe content in mg/kg
1st Conc.HCl (1)	1		10.887			54.437		5393.2
1st sample	2		18.726			93.631		9309.6
2ml-10ml	4		19.439			97.195		9601.2
	5		25.575			127.873		12735.7
	6		18.008			90.038		8885.0
	7		14.621			73.104		7270.1
	Rock		19.283			96.415		9495.0
	ref(x10ml)		0.000			0.000		
1st Conc.HCl (2)	1		10.543			52.717		5246.0
2nd sample	2		18.557			92.783		9176.2
2ml-10ml	4		19.632			98.158		9737.0
	5		25.582			127.911		12708.2
	6		18.348			91.741		9072.9
	7		14.861			74.303		7414.7
	Rock		20.486			102.432		10165.7
	ref(x10ml)							

Table (9.1.2.6) Table shows Fe contents in the sequential extraction steps

Sequential extraction steps	Sub-samples no.	SE1	SE2	Average of SE1 and SE2
PO4	1	231.43	191.79	211.61
	2	309.38	266.41	287.90
	4	401.05	335.26	368.15
	5	180.10	146.88	163.49
	6	258.63	188.49	223.56
	7	271.32	205.43	238.37
	rock	141.74	89.29	115.52
1M HCl	1	1002.69	988.39	995.54
	2	4507.71	4407.66	4457.69
	4	4302.85	4077.06	4189.95
	5	945.39	897.94	921.66
	6	1662.79	1627.19	1644.99
	7	1576.22	1556.27	1566.24
	rock	9287.74	9164.12	9225.93
Ox	1	264.03	218.31	241.17
	2	150.24	122.14	136.19
	4	416.57	272.33	344.45
	5	2383.35	1463.20	1923.28
	6	261.27	149.60	205.44
	7	249.22	157.30	203.26
	rock	774.26	310.75	542.50
Ti	1	1003.42	716.36	859.89
	2	1009.26	864.91	937.09
	4	912.42	758.52	835.47
	5	1867.49	846.48	1356.98
	6	1066.60	775.29	920.94
	7	1163.41	657.02	910.22
	rock	485.05	392.21	438.63
Conc.HCl	1	669.34	1304.16	986.75
	2	157.20	170.87	164.03
	4	728.19	803.66	765.92

	5	1532.14	4352.27	2942.21
	6	2577.85	2986.91	2782.38
	7	741.60	1986.98	1364.29
	rock	1943.14	1956.58	1949.86

'SE' = sequential extraction schme

Table (9.1.2.7) Table shows sum of 5 extraction steps of total Fe contents in soil-subsamples

Sequential extraction steps	Sub-samples no.	SE1 (∑5steps)	SE2 (∑5steps)	Average of SE1 and SE2 (∑5steps)	SD
∑5steps	1	3170.91	3419.00	3294.95	175.4
	2	6133.79	5831.99	5982.89	213.4
	4	6761.08	6246.83	6503.95	363.6
	5	6908.46	7706.77	7307.62	34.1
	6	5827.15	5727.48	5777.32	70.5
	7	4001.77	4562.99	4282.38	396.8
	rock	12631.93	11912.96	12272.44	508.4
			Average	6488.79	
			SD	2885.37	
			RSD	44.46	

SD = standard deviation

Table (9.1.2.8) Table shows total Fe contents in soil-subsamples treated by acid digestion

Sequential extraction steps	Sub-samples no.	SE1	SE2	Average of SE1 and SE2	SD
Concentrated HCl	1	5393.2	5246.0	5319.6	104.1
	2	9309.6	9176.2	9242.9	94.3
	4	9601.2	9737.0	9669.1	96.0
	5	12735.7	12708.2	12721.9	19.5
	6	8885.0	9072.9	8979.0	132.9
	7	7270.1	7414.7	7342.4	102.3
	rock	9495.0	10165.7	9830.3	474.2
			Average	9015.02	
			SD	2285.49	
			RSD	25.35	

SE = sequential extraction scheme number

Table (9.1.2.9) Table shows distribution of iron in different extraction steps

											Total Fe (mg/kg)
	PO4(24hrs)(mg/kg)	PO4(24hrs)%	1M HCl (mg/kg)	1M HCl %	Ox (mg/kg)	Ox %	Ti (mg/kg)	Ti %	Conc. HCl(mg/kg)	Conc.HCl%	
Huf1	211.61	6.42	995.54	30.21	241.17	7.32	859.89	26.10	986.75	29.95	3294.95
Huf2	287.90	4.81	4457.69	74.51	136.19	2.28	937.09	15.66	164.03	2.74	5982.89
Huf4	368.15	5.66	4189.95	64.42	344.45	5.30	835.47	12.85	765.92	11.78	6503.95
Huf5	163.49	2.24	921.66	12.61	1923.28	26.32	1356.98	18.57	2942.21	40.26	7307.62
Huf6	223.56	3.87	1644.99	28.47	205.44	3.56	920.94	15.94	2782.38	48.16	5777.32
Huf7	238.37	5.57	1566.24	36.57	203.26	4.75	910.22	21.25	1364.29	31.86	4282.38
Rock	28.88	1.15	0.00	0.00	542.50	21.52	0.00	0.00	1949.86	77.34	2521.25
average	217.42	4.24	1968.01	35.26	513.75	10.15	831.51	15.77	1565.06	34.58	5095.77
SD	105.40	1.94	1698.77	26.52	635.68	9.63	406.96	8.18	1041.05	24.52	1763.49
										RSD	34.61

(9.1.3) Manganese (Mn) in arsenic measurement

Table (9.1.3.1) Table shows mass of sub-samples applied in sequential extraction schemes for Mn measurements

Name of soil sub-samples	Mass of soil sub-samples in sequential extraction scheme 1 (SE1) (g)	Mass of soil sub-samples in sequential extraction scheme 2 (SE2) (g)
Huf1	0.40374	0.40196
Huf2	0.4023	0.40445
Huf4	0.40493	0.40324
Huf5	0.40162	0.40261
Huf6	0.40535	0.40446
Huf7	0.40222	0.40084
Huf Rock (reference material)	0.40617	0.40305

Table (9.1.3.2) Table shows concentrations of manganese (Mn) in soil samples

Mn data		1st measure mg/l	2nd measure mg/l	3rd measure mg/l		average Mn reading (mg/l)		average H20value (mg/l)		"Mn" reading minus H2O minus ref mg/l
PO4 (1)	1	3.879	3.906	3.902		3.896		0.000		3.742
1st sample	2	3.835	3.645			3.740		0.000		3.586
24hrs	4	2.583	2.946	3.293		4.056		0.000		3.902
no dilution	5	2.188	2.16	2.074		2.141		0.000		1.987
	6	2.638	2.403	2.271		2.437		0.000		2.283
	7	2.564	2.312	2.189		2.355		0.000		2.201
	Rock	1.013	1.157	1.589		1.253		0.000		1.099
	ref(x10ml)	0.158	0.15			0.154		0.000		0.000
PO4 (2)	1	2.963	3.241	3.212		3.139		0.000		2.985
2nd sample	2	3.81	2.793	3.275		3.249		0.421		2.674
24hrs	4	4.358	5.34	4.924		5.435		0.000		5.281
no dilution	5	2.959	2.759	2.816		2.845		0.199		2.492
	6	2.993	3.003	3.113		3.036		0.108		2.774
	7	3.813	3.75	3.939		3.834		0.299		3.382
	Rock	2.493	2.604	2.387		2.495		0.625		1.716
	ref(x10ml)									
1M HCl (1)	1	17.885	17.394	17.579		17.619		0.504		17.043
1st sample	2	6.531	6.556	6.572		6.553		0.000		6.480
no dilution	4	6.73	6.805	6.691		6.742		0.000		6.669
	5	20.445	20.086	20.513		20.348		0.809		19.466
	6	31.426	31.338	30.923		31.229		0.823		30.334

	7	28.16	27.691	28.169		28.007		0.917		27.017
	Rock (1ml-10ml)	2.425	2.347	2.317		2.363		1.079		1.212
	ref(x10ml)	1.162	1.15	1.104		1.139		1.066		0.000
1M HCl (2)	1	17.341	16.808	17.544		17.231		1.486		15.673
2nd sample	2	6.71	6.71	6.595		6.672		0.000		6.599
no dilution	4	6.71	6.498	6.78		6.663		0.000		6.590
	5	20.184	19.882	19.516		19.861		1.791		17.997
	6	30.716	31.053	31.508		31.092		1.820		29.200
	7	27.993	28.057	28.543		28.198		1.913		26.212
	Rock (1ml-10ml)	3.472	3.563	3.36		3.465		2.066		1.327
	ref(x10ml)									
Ox (1)	1	7.15	7.095	7.114		7.120		2.216		4.678
1st sample	2	1.253	1.363	1.297		1.304		0.212		0.866
no dilution	4	2.491	2.7	2.889		2.693		0.380		2.088
	5	20.025				20.025		0.000		19.799
	6	16.7	17.354	16.896		16.983		0.549		16.208
	7	12.612	12.519	12.641		12.591		0.673		11.692
	Rock	0.839	0.764			0.802		1.060		0.000
	ref(x10ml)	0.932	1.059	1.21		1.067		0.841		0.000
Ox (2)	1	6.476	6.643	6.498		6.539		1.126		5.188
2nd sample	2	2.63	2.792	2.886		2.769		1.699		0.844
no dilution	4	3.983	3.895	3.787		3.888		2.507		1.155
	5	34.283	34.874	35.768		34.975		2.558		32.192

	6	15.231	15.524	15.02		15.258		2.731		12.302
	7	11.136	11.151	10.847		11.045		2.313		8.506
	Rock	1.997	2.02	2.156		2.058		2.105		0.000
	ref(x10ml)									
Ti (1)5-10ml	1	0.394	0.486	0.313		0.398		0.000		0.000
1st sample	2	0.663	0.682	0.761		0.702		0.049		0.176
	4	1.249	1.429	1.279		1.319		0.000		0.842
	5	1.863	1.723	1.914		1.833		0.000		1.357
	6	1.53	1.437	1.377		1.448		0.000		0.971
	7	0.933	0.906	1.024		0.954		0.000		0.478
	Rock	0.351	0.136	0.332		0.273		0.000		0.000
	ref(x10ml)	0.474	0.413	0.552		0.480		0.003		0.000
Ti (2)5-10ml	1	0.526	0.364	0.641		0.461		0.000		0.000
2nd sample	2	0.573	1.155	0.799		0.818		0.000		0.341
	4	1.297	1.251	1.208		1.252		0.000		0.775
	5	1.32	1.154	1.278		1.251		0.000		0.774
	6	0.848	0.588	0.746		0.746		0.000		0.270
	7	0.716	0.686	0.853		0.752		0.000		0.275
	Rock	0.442	0.453	0.545		0.480		0.127		0.000
	ref(x10ml)									
5th Conc.HCl (1)	1	0.202	0.161	0.246		0.203		0.000		0.170
1st sample	2	0.448	0.346	0.264		0.353		0.000		0.319
no dilution	4	0.932	0.695	0.758		0.795		0.289		0.472

	5	0.914	0.909	0.894		0.906		0.373		0.500
	6	4.27	4.25	4.236		4.252		0.232		3.987
	7	0.582	0.714	0.264		0.582		0.518		0.030
	Rock	0.413	0.428	0.542		0.461		0.397		0.031
	ref(x10ml)	0.457	0.352	0.469		0.426		0.393		0.000
5th Conc.HCl (2)	1	0.608	0.606	0.461		0.558		0.399		0.126
2nd sample	2	0.488	0.519	0.564		0.524		0.370		0.120
no dilution	4	0.925	0.846	0.974		0.915		0.198		0.684
	5	2.507	2.599	2.372		2.493		0.267		2.193
	6	0.902	0.96	1.37		1.077		0.465		0.579
	7	0.888	0.989	0.91		0.929		0.441		0.455
	Rock	0.588	0.839	0.581		0.636		0.459		0.143
	ref(x10ml)									

() shows sequential scheme number.

Table (9.1.3.3) Table shows concentrations of iron (Mn) in soil samples

Mn data			"Mn" reading minus H2O minus ref mg/l	x0 dilution mg/l	x 2 dilution mg/l	x 5 dilution mg/l	x 10 dilution mg/l	Mn content in mg/kg
PO4 (1)	1		3.742	3.742				370.7
1st sample	2		3.586	3.586				356.5
24hrs	4		3.902	3.902				385.4
no dilution	5		1.987	1.987				197.9
	6		2.283	2.283				225.3
	7		2.201	2.201				218.9
	Rock		1.099	1.099				108.2
	ref(x10ml)		0.000	0.000				
PO4 (2)	1		2.985	2.985				297.0
2nd sample	2		2.674	2.674				264.4
24hrs	4		5.281	5.281				523.8
no dilution	5		2.492	2.492				247.6
	6		2.774	2.774				274.4
	7		3.382	3.382				337.4
	Rock		1.716	1.716				170.3
	ref(x10ml)							
1M HCl (1)	1		17.043	17.043				1688.5
1st sample	2		6.480				64.803	6443.3
no dilution	4		6.669				66.693	6588.1
	5		19.466	19.466				1938.8
	6		30.334	30.334				2993.3

	7		27.017	27.017				2686.8
	Rock (1ml-10ml)		1.212	1.212				119.3
	ref(x10ml)		0.000	0.000				
1M HCl (2)	1		15.673	15.673				1559.6
2nd sample	2		6.599				65.990	6526.4
no dilution	4		6.590				65.900	6537.0
	5		17.997	17.997				1788.0
	6		29.200	29.200				2887.8
	7		26.212	26.212				2615.7
	Rock (1ml-10ml)		1.327	1.327				131.7
	ref(x10ml)							
Ox (1)	1		4.678	4.678				463.5
1st sample	2		0.866	0.866				86.1
no dilution	4		2.088	2.088				206.2
	5		19.799	19.799				1971.9
	6		16.208	16.208				1599.4
	7		11.692	11.692				1162.7
	Rock		0.000	0.000				0.0
	ref(x10ml)		0.000	0.000				
Ox (2)	1		5.188	5.188				516.2
2nd sample	2		0.844	0.844				83.5
no dilution	4		1.155	1.155				114.6
	5		32.192	32.192				3198.3

	6		12.302	12.302				1216.6
	7		8.506	8.506				848.8
	Rock		0.000	0.000				0.0
	ref(x10ml)							
Ti (1)5-10ml	1		0.000		0.000			0.0
1st sample	2		0.176		0.353			35.1
	4		0.842		1.685			166.4
	5		1.357		2.713			270.2
	6		0.971		1.943			191.7
	7		0.478		0.955			95.0
	Rock		0.000		0.000			0.0
	ref(x10ml)		0.000		0.000			
Ti (2)5-10ml	1		0.000		0.000			0.0
2nd sample	2		0.341		0.682			67.5
	4		0.775		1.551			153.8
	5		0.774		1.548			153.8
	6		0.270		0.539			53.3
	7		0.275		0.550			54.9
	Rock		0.000		0.000			0.0
	ref(x10ml)							
5th Conc.HCl (1)	1		0.170	0.170				16.8
1st sample	2		0.319	0.319				31.7
no dilution	4		0.472	0.472				46.6

	5		0.500	0.500				49.7
	6		3.987	3.987				393.4
	7		0.030	0.030				3.0
	Rock		0.031	0.031				3.0
	ref(x10ml)		0.000	0.000				
5th Conc.HCl (2)	1		0.126	0.126				12.5
2nd sample	2		0.120	0.120				11.9
no dilution	4		0.684	0.684				67.8
	5		2.193	2.193				217.8
	6		0.579	0.579				57.3
	7		0.455	0.455				45.4
	Rock		0.143	0.143				14.2
	ref(x10ml)							

Table (9.1.3.4) Table shows soil sub-samples Mn contents treated by concentrated HCl

Mn data		1st measure mg/l	2nd measure mg/l	3rd measure mg/l		average Mn reading (mg/l)		average H20value (mg/l)		"Mn" reading minus H2O minus ref mg/l
1st Conc.HCl (1)	1	8.53	8.42	8.573		8.508		0.503		8.005
1st sample	2	19.564	19.702	20.244		19.837		0.596		19.241
2ml-10ml	4	21.053	20.627	21.33		21.003		0.557		20.446
	5	19.773	20.059	19.95		19.927		0.612		19.316
	6	16.507	16.555	16.63		16.564		0.574		15.990
	7	14.623	14.257	14.666		14.515		0.662		13.853
	Rock	1.673	1.635	1.574		1.627		0.648		0.980
	ref(x10ml)	0.478	0.71	0.646		0.611		0.628		0.000
1st Conc.HCl (2)	1	6.075	5.879	5.876		5.943		0.000		5.943
2nd sample	2	15.34	15.222	15.187		15.250		0.000		15.250
2ml-10ml	4	16.127	16.109	16.163		16.133		0.000		16.133
	5	14.963	14.885	15.108		14.985		0.000		14.985
	6	12.631	12.926	12.63		12.729		0.000		12.729
	7	10.553	10.557	10.54		10.550		0.000		10.550
	Rock	0.231	0.154	0.093		0.165		0.000		0.165
	ref(x10ml)									

Table (9.1.3.5) Table shows soil sub-samples Mn contents treated by concentrated HCl

Mn data			"Mn" reading minus H2O minus ref mg/l-1	x0 dilution mg/l	x 2 dilution mg/l	x 5 dilution mg/l	x 10 dilution mg/l	Mn content in mg/kg
1st Conc.HCl (1)	1		8.005			40.026		3965.5
1st sample	2		19.241			96.206		9565.6
2ml-10ml	4		20.446			102.232		10098.7
	5		19.316			96.579		9619.0
	6		15.990			79.950		7889.5
	7		13.853			69.267		6888.4
	Rock		0.980			4.899		482.5
	ref(x10ml)		0.000			0.000		
1st Conc.HCl (2)	1		5.943			29.717		2957.2
2nd sample	2		15.250			76.248		7540.9
2ml-10ml	4		16.133			80.665		8001.7
	5		14.985			74.927		7444.1
	6		12.729			63.645		6294.3
	7		10.550			52.750		5263.9
	Rock		0.165			0.823		81.7
	ref(x10ml)							

Table (9.1.3.6) Table shows Mn contents in the sequential extraction steps

Sequential extraction steps	Sub-samples no.	SE1	SE2	Average of SE1 and SE2
PO4	1	370.70	297.01	333.86
	2	356.55	264.43	310.49
	4	385.40	523.82	454.61
	5	197.87	247.55	222.71
	6	225.32	274.37	249.85
	7	218.89	337.44	278.16
	rock	108.23	170.32	139.27
1M HCl	1	1688.48	1559.64	1624.06
	2	6443.28	6526.39	6484.84
	4	6588.13	6537.05	6562.59
	5	1938.78	1788.03	1863.41
	6	2993.35	2887.82	2940.58
	7	2686.79	2615.71	2651.25
	rock	119.34	131.68	125.51
Ox	1	463.48	516.22	489.85
	2	86.14	83.50	84.82
	4	206.24	114.61	160.42
	5	1971.91	3198.28	2585.10
	6	1599.44	1216.62	1408.03
	7	1162.71	848.78	1005.75
	rock	0.00	0.00	0.00
Ti	1	0.00	0.00	0.00
	2	35.07	67.48	51.27
	4	166.42	153.82	160.12
	5	270.24	153.80	212.02
	6	191.70	53.32	122.51
	7	95.01	54.88	74.95
	rock	0.00	0.00	0.00
Conc.HCl	1	16.79	12.49	14.64
	2	31.73	11.88	21.81
	4	46.64	67.80	57.22

	5	49.75	217.85	133.80
	6	393.42	57.29	225.36
	7	2.99	45.40	24.20
	rock	3.00	14.22	8.61

'SE' = sequential extraction schme

Table (9.1.3.7) Table shows sum of 5 extraction steps of total Mn contents in soil-subsamples

Sequential extraction steps	Sub-samples no.	SE1 (∑5steps)	SE2 (∑5steps)	Average of SE1 and SE2 (∑5steps)	SD
∑5steps	1	2539.46	2385.36	2462.41	108.96
	2	6952.77	6953.69	6953.23	0.65
	4	7392.83	7397.10	7394.96	3.01
	5	4428.55	5605.51	5017.03	832.24
	6	5403.23	4489.43	4946.33	646.16
	7	4166.39	3902.22	4034.30	186.79
	rock	230.58	316.21	273.40	60.55
			Average	4440.24	
			SD	2485.74	
			RSD	55.98	

SD = standard deviation

Table (9.1.3.8) Table shows total Mn contents in soil-subsamples treated by acid digestion

Sequential extraction steps	Sub-samples no.	SE1	SE2	Average of SE1 and SE2	SD
Concentrated HCl	1	3965.5	2957.2	3461.3	713.0
	2	9565.6	7540.9	8553.3	1431.6
	4	10098.7	8001.7	9050.2	1482.8
	5	9619.0	7444.1	8531.5	1537.9
	6	7889.5	6294.3	7091.9	1127.9
	7	6888.4	5263.9	6076.2	1148.7
	rock	482.5	81.7	282.1	283.4
			Average	6149.50	
			SD	3225.23	
			RSD	52.45	

SE = sequential extraction scheme number

Table (9.1.3.9) Table shows distribution of manganese in different extraction steps

											Total Mn (mg/kg)
	PO4(24hrs)(mg/kg)	PO4(24hrs)%	1M HCl (mg/kg)	1M HCl %	Ox (mg/kg)	Ox %	Ti (mg/kg)	Ti %	Conc. HCl(mg/kg)	Conc.HCl%	
Huf1	333.86	13.56	1624.06	65.95	489.85	19.89	0.00	0.00	14.64	0.59	2462.41
Huf2	310.49	4.47	6484.84	93.26	84.82	1.22	51.27	0.74	21.81	0.31	6953.23
Huf4	454.61	6.15	6562.59	88.74	160.42	2.17	160.12	2.17	57.22	0.77	7394.96
Huf5	222.71	4.44	1863.41	37.14	2585.10	51.53	212.02	4.23	133.80	2.67	5017.03
Huf6	249.85	5.05	2940.58	59.45	1408.03	28.47	122.51	2.48	225.36	4.56	4946.33
Huf7	278.16	6.89	2651.25	65.72	1005.75	24.93	74.95	1.86	24.20	0.60	4034.30
Rock	34.82	80.17	0.00	0.00	0.00	0.00	0.00	0.00	8.61	19.83	43.43
average	269.21	17.25	3160.96	58.61	819.14	18.31	88.69	1.64	69.38	4.19	4407.38
SD	127.68	27.93	2482.10	31.91	935.66	18.89	80.39	1.52	81.26	7.06	2550.66
										RSD	57.87

(9.1.4) X-ray fluorescence analysis (XRF)

Powder pellets

Table (9.1.4.1) Table shows mass of samples used for glass pellets preparation of XRF analysis

Sub-samples no.	(g)	(g)
Huf1	5.2030	0.3928
Huf2	5.2043	0.3948
Huf4	5.2043	0.3943
Huf5	5.2048	0.3970
Huf6	5.2018	0.3993
Huf7	5.2034	0.3974
Huf Rock	5.2026	0.3999

Loss of ignition

Table (9.1.4.2) Table shows mass of samples in loss on ignition (LOI)

Sub-samples no.	Mass of crucible (g)	Mass of crucible with sample(g)	Mass of sample (g)	Mass of crucible with sample after loss on ignition(g)	Mass of sample after loss on ignition(g)	Sample after loss on ignition (%)
Huf1	10.7313	11.2923	0.5610	11.0324	0.2599	46.33
Huf2	10.2424	10.8203	0.5779	10.5556	0.2647	45.80
Huf4	10.7904	11.3648	0.5744	11.1024	0.2624	45.68
Huf5	10.4493	11.0342	0.5849	10.7698	0.2644	45.20
Huf6	11.8449	12.3827	0.5378	12.1431	0.2396	44.55
Huf7	9.7806	10.3972	0.6166	10.1226	0.2746	44.53
Huf Rock	13.3948	14.0256	0.6308	13.8089	0.2167	34.35

Table (9.1.4.3) Table shows XRF analysis of soil sub-samples of different elements

Sample	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	P_2O_5 (%)	LOI (%)	Sum (%)
Huf1	0.85	0.15	1.04	0.47	20.59	30.51	-0.05	0.04	0.02	0.01	46.33	99.97
Huf2	0.35	0.09	1.68	1.17	18.79	31.79	-0.06	0.02	0.01	0.01	45.80	99.64
Huf4	0.55	0.09	1.67	1.21	19.11	31.42	-0.06	0.02	0.01	0.02	45.68	99.70
Huf5	0.92	0.14	2.18	1.13	19.37	30.25	-0.06	0.03	0.01	0.01	45.20	99.24
Huf6	2.72	1.03	1.69	0.94	19.49	29.15	-0.04	0.24	0.05	0.04	44.55	99.87
Huf7	2.98	1.08	1.42	0.84	19.35	29.38	-0.03	0.26	0.05	0.02	44.53	99.86
Rock (GSR-6)	15.69	5.11	2.54	0.06	5.21	36.20	-0.03	0.78	0.33	0.05	34.35	100.37

Table (9.1.4.4) Table shows XRF analysis of soil sub-samples of different elements

	V (ppm)	Cr (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	Rb (ppm)	Sr (ppm)	Y (ppm)	Zr (ppm)	Nb (ppm)	Ba (ppm)	Pb (ppm)	As (ppm)
Huf1	6	7	7	2	12	33	1	5	51	4	19	1	2010	0	43
Huf2	8	4	30	4	69	21	1	4	24	5	18	1	773	0	68
Huf4	10	11	16	2	174	27	1	5	34	4	18	1	990	0	66
Huf5	2	5	27	4	41	27	2	5	52	5	18	3	3783	0	103
Huf6	13	21	16	7	140	38	2	14	40	7	25	2	1466	3	74
Huf7	20	17	11	6	137	41	2	16	43	6	27	2	1303	0	79
Rock (GSR-6)	63	51	16	16	21	49	8	33	852	9	62	6	186	10	4

Table (9.1.4.5) Table shows internal standard program applied in XRF measurement (Part 1)

Nachweisgrenzen und Fehlerbetrachtung der Spurenelementeichung							
für As, Cd, Sn, Sb und Pb							
für das RFA-Spektrometer MagiXPRO, Fa. Philips, Bj 2002							
Anode Rh, Anregungsleistung 3,6 kW							
Präparation: unverdünnte Pulverpresslinge						Stand März 2004	
Element	mittl. Konz.	RMS	LLD	Messzeit	max.Konz.	RMSrel	
				Peak	der Eichung		
	(ppm)	(ppm)	(ppm)	(sec)	(ppm)	(%)	
As	210	3.3	1.1	20	400	1.6	
Cd	30	1	1.4	120	100	3.3	
Sn	41	3.2	2.7	20	100	7.8	
Sb	50	2.4	3	20	200	4.8	
Pb	600	10.4	1.5	30	6000	1.7	

$$RMS = \frac{1}{n-1} \times \sqrt{\sum_{i=1}^{N} \left(X_i - \overline{X}\right)^2}$$

(root mean square)

$$LLD = \frac{n\sqrt{2}}{s} \times \sqrt{\frac{r_b}{t_b}}$$

(lower limit of detection)

Table (9.1.4.6) Table shows internal standard program applied in XRF measurement (Part 2)

Fehlerbetrachtung der Hauptelementeichung MzGeo14						
für das RFA-Spektrometer MagiXPRO, Fa. Philips, Bj 2002						
Anode Rh, Anregungsleistung 3,2 kW						
Präparation: Schmelztabletten, 14-fache Verdünnung						Stand Apr. 2007
Oxid	mittl.Konz.	RMS	Messzeit	Kalibrations	RMSrel	
			Peak	bereich		
	(Gew%)	(Gew%)	(sec)	(Gew%)	(%)	
SiO2	65	0.28	26	0,1 - 100	0.4	
TiO2	1.6	0.016	18	0,02 - 4,0	1.0	
Al2O3	16	0.11	48	0,1 - 40	0.7	
Fe2O3	10	0.08	20	0,2 - 20	0.8	
MnO	0.17	0.003	30	0,02 - 0,25	1.8	
MgO	25	0.08	48	0,04 - 50	0.3	
CaO	35	0.16	18	0,1 - 62	0.5	
Na2O	4.5	0.06	48	0,02 - 10	1.3	
K2O	5	0.04	18	0,01 - 14	0.8	
P2O5	0.75	0.008	24	0,01 - 33	1.1	
Cr2O3	0.25	0.005	24	0,002 - 3,5	2.0	
NiO	0.2	0.0015	24	0,002 - 0,35	0.8	
SO3	*0.5*	*0.02*	*48*	*0,02 - 5*	*4.0*	

$$RMS = \frac{1}{n-1} \times \sqrt{\sum_{i=1}^{N} \left(X_i - \overline{X}\right)^2}$$ (root mean square)

Verwendete Standards:						
JG-1a	JB-1	NIM-P	CCH-1	TB	BCR-32	
JG-2	JB-3	NIM-D	DWA-1	GSR-4	BX-N	
GSP-1	JA-2	DZE-2	BCS782	GSD-08	FER-2	
RGM-1	JGb-1	SARM-39	KH-2	GSS-3	JF-1	
STM-1	W-2	JP-1	GSR-6		AL-I	
GA	BHVO-1	SDU-1	JLs-1		SiO2 JMC	
GH	BCR-2	DTS-1	X0207		FK-N	

G-2	BE-N	UB-N	X0201		97a	
AC-E	DR-N	PCC-1	3506		98a	
MA-N	AN-G		909			
GSR-1	AGV-1					
QLO-1						
JR-1						
GM						
GS-N						
T-1						
Konzentrationen aus:		K.Govindaraju, Special Issue of Geostandards Newsletters, July 1989				

(9.1.5) Standard addition of samples with masking agent (1% Cysteine)

Table (9.1.5.1) Table shows calibration absorbance of arsenic (As) HG-AAS measurements against different As standard solutions with addition of 1% cysteine masking agent in each sample

	PO4	1MHCl	Ox	Ti	Conc HCl
Standard Calibration(µg/l)					
0	0.014	0.0035	0.0067	0.008	0.0031
2	0.0643	0.0638	0.0711	0.0793	0.0541
5	0.1661	0.1603	0.1505	0.16	0.1198
10	0.2354	0.2869	0.2125	0.2685	0.2194

Table (9.1.5.2) Table shows measured As absorbances in HG-AAS measurements by standard addition with 1% cysteine masking agent in each samples (Step 1)

	Absorbance			Average absorbance			
PO4 (0.5-25ml)							
(0µg/l)5(1)	0.119	0.120	0.122	0.120			
(2µg/l)5(1)	0.213	0.213	0.212	0.213			
(5µg/l)5(1)	0.330	0.335	0.330	0.332			
(10µg/l)5(1)	0.499	0.493	0.499	0.497			
(20µg/l)5(1)	0.680	0.705	0.698	0.693			
PO4 (0.5-25ml)						average absorbance of sample 5,6 and 7	Standard deviation(SD)
(0µg/l)6(1)	0.117	0.109	0.109	0.112	(0µg/l)	0.123	0.014
(2µg/l)6(1)	0.198	0.196	0.199	0.198	(2µg/l)	0.201	0.010
(5µg/l)6(1)	0.304	0.312	0.332	0.316	(5µg/l)	0.321	0.009
(10µg/l)6(1)	0.478	0.488	0.487	0.484	(10µg/l)	0.482	0.016
(20µg/l)6(1)	0.672	0.683	0.671	0.680	(20µg/l)	0.675	0.020
PO4 (0.5-25ml)							
(0µg/l)7(1)	0.140	0.140	0.136	0.138			
(2µg/l)7(1)	0.191	0.194	0.194	0.193			
(5µg/l)7(1)	0.321	0.318	0.309	0.316			
(10µg/l)7(1)	0.462	0.465	0.467	0.465			
(20µg/l)7(1)	0.657	0.656	0.654	0.653			

Table (9.1.5.3) Table shows measured As absorbances in HG-AAS measurements by standard addition with 1% cysteine masking agent in each samples (Step 2)

	Absorbance			Average absorbance			
1M HCl (1-25ml)							
(0μg/l)5(1)	0.052	0.051	0.051	0.051			
(2μg/l)5(1)	0.145	0.141	0.147	0.144			
(5μg/l)5(1)	0.260	0.256	0.259	0.258			
(10μg/l)5(1)	0.430	0.404	0.415	0.416			
(20μg/l)5(1)	0.626	0.630	0.621	0.627			
1M HCl (1-25ml)						average absorbance of sample 5,6 and 7	Standard deviation(SD)
(0μg/l)6(1)	0.044	0.036	0.035	0.038	(0μg/l)	0.072	0.048
(2μg/l)6(1)	0.130	0.129	0.129	0.130	(2μg/l)	0.137	0.007
(5μg/l)6(1)	0.250	0.252	0.249	0.250	(5μg/l)	0.265	0.018
(10μg/l)6(1)	0.391	0.395	0.393	0.393	(10μg/l)	0.406	0.012
(20μg/l)6(1)	0.702	0.716	0.735	0.708	(20μg/l)	0.652	0.048
1M HCl (1-25ml)							
(0μg/l)7(1)	0.125	0.126	0.130	0.127			
(2μg/l)7(1)	0.141	0.137	0.136	0.138			
(5μg/l)7(1)	0.282	0.290	0.285	0.286			
(10μg/l)7(1)	0.409	0.410	0.412	0.410			
(20μg/l)7(1)	0.617	0.623	0.628	0.621			

Table (9.1.5.4) Table shows measured As absorbances in HG-AAS measurements by standard addition with 1% cysteine masking agent in each samples (Step 3)

	Absorbance			Average absorbance			
Ox (0.5-25ml)							
(0µg/l)5(1)	0.146	0.153	0.144	0.148			
(2µg/l)5(1)	0.229	0.235	0.234	0.232			
(5µg/l)5(1)	0.331	0.325	0.332	0.329			
(10µg/l)5(1)	0.469	0.461	0.475	0.469			
(20µg/l)5(1)	0.666	0.648	0.602	0.646			
Ox (0.5-25ml)						average absorbance of sample 5,6 and 7	Standard deviation(SD)
(0µg/l)6(1)	0.073	0.066	0.067	0.068	(0µg/l)	0.095	0.046
(2µg/l)6(1)	0.180	0.181	0.172	0.177	(2µg/l)	0.196	0.032
(5µg/l)6(1)	0.299	0.289	0.293	0.294	(5µg/l)	0.306	0.020
(10µg/l)6(1)	0.420	0.424	0.425	0.423	(10µg/l)	0.438	0.027
(20µg/l)6(1)	0.622	0.630	0.637	0.631	(20µg/l)	0.636	0.009
Ox (0.5-25ml)							
(0µg/l)7(1)	0.073	0.066	0.067	0.068			
(2µg/l)7(1)	0.180	0.181	0.172	0.177			
(5µg/l)7(1)	0.299	0.289	0.293	0.294			
(10µg/l)7(1)	0.420	0.424	0.425	0.423			
(20µg/l)7(1)	0.622	0.630	0.637	0.631			

Table (9.1.5.5) Table shows measured As absorbances in HG-AAS measurements by standard addition with 1% cysteine masking agent in each samples (Step 4)

	Absorbance			Average absorbance			
Ti(0.25-100ml)							
(0μg/l)5(1)	0.215	0.215	0.217	0.216			
(2μg/l)5(1)	0.292	0.307	0.299	0.299			
(5μg/l)5(1)	0.389	0.386	0.377	0.382			
(10μg/l)5(1)	0.514	0.504	0.513	0.508			
(20μg/l)5(1)	0.682	0.675	0.683	0.680			
Ti(0.25-100ml)						average absorbance of sample 5,6 and 7	Standard deviation(SD)
(0μg/l)6(1)	0.142	0.142	0.137	0.140	(0μg/l)	0.192	0.045
(2μg/l)6(1)	0.208	0.214	0.210	0.211	(2μg/l)	0.244	0.048
(5μg/l)6(1)	0.321	0.330	0.328	0.326	(5μg/l)	0.350	0.029
(10μg/l)6(1)	0.460	0.466	0.459	0.460	(10μg/l)	0.482	0.024
(20μg/l)6(1)	0.654	0.655	0.663	0.661	(20μg/l)	0.670	0.010
Ti(0.25-100ml)							
(0μg/l)7(1)	0.216	0.213	0.218	0.219			
(2μg/l)7(1)	0.225	0.219	0.230	0.222			
(5μg/l)7(1)	0.341	0.336	0.346	0.341			
(10μg/l)7(1)	0.478	0.475	0.478	0.479			
(20μg/l)7(1)	0.662	0.681	0.673	0.670			

Table (9.1.5.6) Table shows measured As absorbances in HG-AAS measurements by standard addition with 1% cysteine masking agent in each samples (Step 5)

	Absorbance			Average absorbance			
Conc.HCl(2-25ml)							
(0µg/l)5(1)	0.050	0.048	0.050	0.050			
(2µg/l)5(1)	0.130	0.130	0.128	0.129			
(5µg/l)5(1)	0.242	0.250	0.242	0.244			
(10µg/l)5(1)	0.403	0.394	0.398	0.398			
(20µg/l)5(1)	0.592	0.582	0.587	0.587			
Conc.HCl(2-25ml)						average absorbance of sample 5,6 and 7	Standard deviation(SD)
(0µg/l)6(1)		-0.015	-0.018	-0.017	(0µg/l)	0.031	0.041
(2µg/l)6(1)	0.080	0.077	0.077	0.078	(2µg/l)	0.115	0.032
(5µg/l)6(1)	0.195	0.202	0.199	0.199	(5µg/l)	0.229	0.026
(10µg/l)6(1)	0.346	0.347	0.344	0.346	(10µg/l)	0.375	0.026
(20µg/l)6(1)	0.556	0.544	0.551	0.550	(20µg/l)	0.573	0.020
Conc.HCl(2-25ml)							
(0µg/l)7(1)	0.063	0.058	0.057	0.059			
(2µg/l)7(1)	0.137	0.137	0.137	0.137			
(5µg/l)7(1)	0.241	0.243	0.245	0.243			
(10µg/l)7(1)	0.378	0.385	0.379	0.380			
(20µg/l)7(1)	0.575	0.583	0.585	0.581			

(9.1.6) Copper

Table (9.1.6.1) Table shows mass of sub-samples applied in sequential extraction schemes for Cu measurments

Name of soil sub-samples	Mass of soil sub-samples in sequential extraction scheme 1 (SE1) (g)	Mass of soil sub-samples in sequential extraction scheme 2 (SE2) (g)
Huf1	1.0083	1.006
Huf2	1.0132	1.0078
Huf4	1.001	1.0124
Huf5	1.0066	1.0152
Huf6	1.005	1.0015
Huf7	1.0049	1.0229
BCR631 (reference material)	1.0289	1.0405
Huf 2 (stock 3)	1.00524	
Huf 6 (stock 3)	1.00413	
Huf 7 (stock 3)	1.00277	

Table (9.1.6.2) Table shows concentrations and absorbances of Copper (Cu) in soil samples (Step 1)

BCR Cu		1st measure mg/l -1	2nd	3rd	average	background	final concentration	x2 dilution	x4 dilution	1st abs	2nd abs	3rd abs	actual litre in solution	BCR Cu in mg
acetic acid (1st step)	1	0.195	0.187		0.191	0.002	0.1865			0.0254	0.0244		0.0425	0.007926
Huf	2	0.675	0.668		0.6715	0.002	0.667			0.0862	0.0853		0.045	0.030015
1	4	0.762	0.765	0.743	0.756667	0.002		1.508833		0.0916	0.0919	0.0892	0.045	0.067898
	5	0.195	0.195		0.195	0.002	0.1905			0.0254	0.0254		0.0425	0.008096
	6	0.923	0.937		0.93	0.002	0.9255			0.1146	0.1161		0.045	0.041648
	7	0.234	0.239		0.2365	0.002			0.9415	0.0306	0.0312		0.0425	0.040014
	BCR631	0.539	0.526	0.524	0.529667	0.002		1.054833		0.0641	0.0626	0.0624	0.0475	0.050105
	ref	0.002	0.003		0.0025	0.002	-0.002			0.0003	0.0004		0.04	-0.00008
2	1	0.191	0.193		0.192	0.002	0.1875			0.0249	0.0252		0.0425	0.007969
	2	0.679	0.686		0.6825	0.002	0.678			0.0866	0.0874		0.045	0.03051
	4	0.922	0.919	0.913	0.918	0.002		1.8315		0.1144	0.1141	0.1135	0.0425	0.077839
	5	0.18	0.181		0.1805	0.002	0.176			0.0235	0.0236		0.0425	0.00748
	6	0.873	0.901		0.887	0.002	0.8825			0.1091	0.1122		0.0475	0.041919
	7	0.247	0.248		0.2475	0.002			0.9855	0.0323	0.0324		0.0425	0.041884
	BCR631	0.595	0.58	0.596	0.590333	0.002		1.176167		0.0765		0.0766	0.045	0.052928
3	2	0.66	0.665		0.6625	0.002	0.658			0.0843	0.0849		0.045	0.02961
	6	0.906	0.904		0.905	0.002	0.9005			0.1127	0.1125			0.040523
	7	1.011	1.008		1.0095	0.002	1.005			0.124	0.1237			0.045225

Table (9.1.6.3) Table shows concentrations and absorbances of Copper (Cu) in soil samples (Step 2)

BCR Cu		1st measure mg/l -1	2nd	3rd	average	background	final concentration	x2 dilution	x4 dilution	1st abs	2nd abs	3rd abs	actual litre in solution	BCR Cu in mg
hydroxylammonium chloride (2nd step)	1	0.084	0.083		0.0835	0.002	0.075			0.0109	0.0108		0.04	0.003
Huf	2	0.048	0.046		0.047	0.002	0.0385			0.0063	0.0059		0.04	0.00154
1	4	0.266	0.267		0.2665	0.002	0.258			0.0347	0.0348		0.04	0.01032
	5	0.129	0.132		0.1305	0.002	0.122			0.0168	0.0172		0.04	0.00488
	6	0.608	0.592	0.597	0.599	0.002		1.1895		0.078	0.076	0.0767	0.04	0.04758
	7	0.96	0.913	0.923	0.932	0.002	0.9235			0.0736	0.0705	0.0712	0.04	0.03694
	BCR631	0.811	0.788	0.767	0.788667	0.002	0.780167			0.1021	0.0994	0.097	0.04	0.031207
	ref	0.006	0.007		0.0065	0.002	-0.002			0.0007	0.001		0.04	-0.00008
2	1	0.074	0.072		0.073	0.002	0.0645			0.0096	0.0093		0.04	0.00258
	2	0.041	0.039		0.04	0.002	0.0315			0.0053	0.0051		0.04	0.00126
	4	0.154	0.154		0.154	0.002	0.1455			0.0201	0.0201		0.04	0.00582
	5	0.085	0.082		0.0835	0.002	0.075			0.0111	0.0106		0.04	0.003
	6	0.592	0.606	0.617	0.605	0.002		1.2015		0.0761	0.0777	0.0791	0.04	0.04806
	7	0.506	0.515	0.507	0.509333	0.002		1.010167		0.0654	0.0666	0.0683	0.04	0.040407
	BCR631	0.617	0.613		0.615	0.002	0.6065			0.0791	0.0786		0.04	0.02426
3	2	0.05	0.051		0.0505	0.002	0.042			0.0065	0.0066		0.04	0.00168
	6	0.639	0.641	0.626	0.635333	0.002		1.262167		0.0818	0.0803	0.08	0.04	0.050487
	7	0.5	0.495	0.476	0.490333	0.002		0.972167		0.0646	0.0641	0.0617	0.04	0.038887

Table (9.1.6.4) Table shows concentrations and absorbances of Copper (Cu) in soil samples (Step 3)

BCR Cu		1st measure mg/l -1	2nd	3rd	average	background	final concentration	x2 dilution	x4 dilution	1st abs	2nd abs	3rd abs	actual litre in solution	BCR Cu in mg
Dithionite/citrate buffer (3rd step)	1	0.054	0.053		0.0535	0.002	0.026			0.007	0.0069		0.04	0.00104
Huf	2	0.339	0.34		0.3395	0.002	0.312			0.0441	0.0443		0.04	0.01248
1	4	0.816	0.82	0.783	0.806333	0.002		1.585167		0.1027	0.1031	0.0989	0.04	0.063407
	5	0.234	0.232		0.233	0.002	0.2055			0.0305	0.0303		0.04	0.00822
	6	0.375	0.392		0.3835	0.002	0.356			0.0488			0.04	0.01424
	7	0.474	0.484		0.479	0.002	0.4515			0.0614	0.0626		0.04	0.01806
	BCR631	0.789	0.817		0.803	0.002	0.7755			0.0995	0.1027		0.04	0.03102
	ref	0.025	0.026		0.0255	0.002	-0.002			0.0033	0.0034		0.04	-8E-05
2	1	0.057	0.059		0.058	0.002	0.0305			0.0074	0.0077		0.04	0.00122
	2	0.353	0.377		0.365	0.002	0.3375			0.046	0.049		0.04	0.0135
	4	0.692	0.707	0.681	0.693333	0.002		1.359167					0.04	0.054367
	5	0.287	0.286		0.2865	0.002	0.259			0.0374	0.0373		0.04	0.01036
	6	0.424	0.441		0.4325	0.002	0.405			0.0551	0.0572		0.04	0.0162
	7	0.565	0.568		0.5665	0.002	0.539			0.0728	0.0731		0.04	0.02156
	BCR631	0.805	0.803		0.804	0.002	0.7765			0.1013	0.1011		0.04	0.03106
3	2	0.479	0.491		0.485	0.002	0.4575			0.062	0.0635		0.04	0.0183
	6	0.471	0.476		0.4735	0.002	0.446			0.061	0.0616		0.04	0.01784
	7	0.584	0.574		0.579	0.002	0.5515			0.0751	0.0738		0.04	0.02206

Table (9.1.6.5) Table shows concentrations and absorbances of Copper (Cu) in soil samples (Step 4)

BCR Cu		1st measure mg/l -1	2nd	3rd	average	background	final concentration	x2 dilution	x4 dilution	1st abs	2nd abs	3rd abs	actual litre in solution	BCR Cu in mg
Aqua riga (1:3 nitric acid/conc.HCl) (4th step)	1	0.077	0.079		0.078	0.002	0.065			0.0101	0.0103		0.053	0.003445
Huf	2	0.353	0.35		0.3515	0.002	0.3385			0.046	0.0455		0.05	0.016925
1	4	0.571	0.568	0.574	0.571	0.002	0.558			0.0735	0.0732		0.05	0.0279
	5	0.324	0.316		0.32	0.002	0.307			0.0422	0.0412		0.05	0.01535
	6	0.511	0.523	0.537	0.523667	0.002		1.034333		0.0661	0.0676		0.05	0.051717
	7	0.435	0.445	0.442	0.440667	0.002		0.868333		0.0565	0.0577	0.0574	0.05	0.043417
	BCR631	0.456	0.446	0.442	0.448	0.002			1.779	0.0591	0.0587		0.05	0.08895
	ref	0.011	0.011		0.011	0.002	-0.002			0.0014	0.0014		0.05	-0.0001
2	1	0.103	0.107		0.105	0.002	0.092			0.0135	0.0139		0.05	0.0046
	2	0.355	0.357		0.356	0.002	0.343			0.0463	0.0465		0.05	0.01715
	4	1.059	1.036	1.031	1.042	0.002	1.029			0.129	0.1266		0.05	0.05145
	5	0.334	0.34		0.337	0.002	0.324			0.0436	0.0443		0.05	0.0162
	6	0.461	0.46	0.471	0.464	0.002		0.915		0.0597	0.0596	0.061	0.05	0.04575
	7	0.426	0.413	0.41	0.416333	0.002		0.819667		0.0553	0.0537	0.0532	0.05	0.040983
	BCR631	0.444	0.454	0.44	0.446	0.002			1.771	0.0575	0.0588		0.05	0.08855
	ref	0.014	0.015		0.0145	0.002	0.0015			0.0018	0.0019			
3	2	0.216	0.221		0.2185	0.002	0.2055			0.0281	0.0288		0.05	0.010275
	6	0.449	0.432	0.432	0.437667	0.002		0.862333		0.0582	0.056	0.0561	0.05	0.043117

(9.1.7) Iron (Fe) in copper measurement

Table (9.1.7.1) Table shows concentrations and absorbances of Iron (Fe) in soil samples (Step 1)

BCR Fe			1st measure mg/l -1	2nd	3rd	average	background	final concentration	x0 dilution	x10 dilution	final in mg/l	actual litre in solution	BCR Fe in mg
acetic acid (1st step)		1	33.294	34.421	33.076	33.597	0	33.58667	33.58667		33.58667	0.0425	1.427433
Huf	x10	2	13.208	12.966	12.972	13.04867	0.051	12.98733		129.8733333	129.8733	0.045	5.8443
1	x10	4	11.269	11.162	10.971	11.134	0.053	11.07067		110.7066667	110.7067	0.045	4.9818
	x10	5	2.288	2.17	2.201	2.219667	0.054	2.155333		21.55333333	21.55333	0.0425	0.916017
	x10	6	4.896	4.686	4.737	4.773	0.06	4.702667		47.02666667	47.02667	0.045	2.1162
	x10	7	5.36	5.425	5.211	5.332	0.009	5.312667		53.12666667	53.12667	0.0425	2.257883
	x10	BCR631	0.566	0.58	0.533	0.559667	0.037	0.512333		5.123333333	5.123333	0.0475	0.243358
		ref	0.007	0.023	0.001	0.010333	0	0				0.04	0
2		1	32.137	32.331	32.74	32.40267	0	32.39233	32.39233		32.39233	0.0425	1.376674
	x10	2	13.35	13.279	13.505	13.378	0.06	13.30767		133.0766667	133.0767	0.045	5.98845
	x10	4	12.971	13.097	12.597	12.88833	0.031	12.847		128.47	128.47	0.0425	5.459975
	x10	5	2.019	1.954	2.008	1.993667	0.038	1.945333		19.45333333	19.45333	0.0425	0.826767
	x10	6	4.341	4.376	4.263	4.326667	0.031	4.285333		42.85333333	42.85333	0.0475	2.035533
	x10	7	5.088	5.01	4.934	5.010667	0.018	4.982333		49.82333333	49.82333	0.0425	2.117492
	x10	BCR631	0.593	0.591		0.592	0.013	0.568667		5.686666667	5.686667	0.045	0.2559
3	x10	2	10.714	10.782	10.95	10.81533	0.014	10.791		107.91	107.91	0.045	4.85595
	x10	6	4.106	4.12	4.009	4.078333	0.017	4.051		40.51	40.51	0.045	1.82295
	x10	7	4.237	4.298	4.312	4.282333	0	4.272		42.72	42.72	0.045	1.9224

Table (9.1.7.2) Table shows concentrations and absorbances of Iron (Fe) in soil samples (Step 2)

BCR Fe			1st measure mg/l -1	2nd	3rd	average	background	final concentration	x0 dilution	x10 dilution	final in mg/l	actual litre in solution	BCR Fe in mg
hydroxylammonium chloride (2nd step)		1	13.682	13.596	13.369	13.549	0	13.54533	13.54533		13.54533	0.04	0.541813
Huf		2	21.238	22.007	21.65	21.63167	0	21.628	21.628		21.628	0.04	0.86512
1		4	24.871	24.555	24.132	24.51933	0	24.51567	24.51567		24.51567	0.04	0.980627
		5	75.994	74.872	74.428	75.098	0	75.09433	75.09433		75.09433	0.04	3.003773
		6	18.113	17.351	17.527	17.66367	0	17.66	17.66		17.66	0.04	0.7064
		7	14.957	14.597	14.781	14.77833	0	14.77467	14.77467		14.77467	0.04	0.590987
	x10	BCR631	10.847	10.894	10.253	10.66467	0	10.661		106.61	106.61	0.04	4.2644
		ref	0	0.027	-0.016	0.003667	0	0	0			0.04	0
2		1	12.747	13.079	12.841	12.889	0	12.88533	12.88533		12.88533	0.04	0.515413
		2	19.01	18.442	19.173	18.875	0	18.87133	18.87133		18.87133	0.04	0.754853
		4	19.018	18.879	18.497	18.798	0	18.79433	18.79433		18.79433	0.04	0.751773
		5	59.234	60.191	61.501	60.30867	0	60.305	60.305		60.305	0.04	2.4122
		6	14.73	15.685	14.576	14.997	0	14.99333	14.99333		14.99333	0.04	0.599733
		7	15.161	14.942	14.756	14.953	0	14.94933	14.94933		14.94933	0.04	0.597973
	x10	BCR631	13.143	12.391	12.57	12.70133	0	12.69767		126.9766667	126.9767	0.04	5.079067
3		2	27.551	28.854	28.979	28.46133	0	28.45767	28.45767		28.45767	0.04	1.138307
		6	19.541	19.07	18.515	19.042	0	19.03833	19.03833		19.03833	0.04	0.761533
		7	17.079	17.296	17.271	17.21533	0	17.21167	17.21167		17.21167	0.04	0.688467

Table (9.1.7.3) Table shows concentrations and absorbances of Iron (Fe) in soil samples (Step 3)

BCR Fe			1st measure mg/l -1	2nd	3rd	average	background	final concentration	x0 dilution	x10 dilution	final in mg/l	actual litre in solution	BCR Fe in mg
Dithionite/citrate buffer (3rd step)		1	20.219	20.287	20.303	20.26967	0	20.164	20.164		20.164	0.04	0.80656
Huf		2	35.92	37.489	37.535	36.98133	0	36.87567	36.87567		36.87567	0.04	1.475027
1		4	54.861	55.215		55.038	0	54.93233	54.93233		54.93233	0.04	2.197293
		5	74.145	74.475	74.326	74.31533	0	74.20967	74.20967		74.20967	0.04	2.968387
		6	26.903	27.552	27.78	27.41167	0	27.306	27.306		27.306	0.04	1.09224
		7	29.485	29.405	29.677	29.52233	0	29.41667	29.41667		29.41667	0.04	1.176667
		BCR631	66.741	66.937	65.713	66.46367	0	66.358	66.358		66.358	0.04	2.65432
		ref	0.106	0.096	0.115	0.105667	0	0	0			0.04	0
2		1	22.862	22.829	22.301	22.664	0	22.55833	22.55833		22.55833	0.04	0.902333
		2	37.006	38.988	37.641	37.87833	0	37.77267	37.77267		37.77267	0.04	1.510907
		4	44.171	43.573	43.779	43.841	0	43.73533	43.73533		43.73533	0.04	1.749413
		5	86.036	85.81	87.067	86.30433	0	86.19867	86.19867		86.19867	0.04	3.447947
		6	30.709	30.484	30.002	30.39833	0	30.29267	30.29267		30.29267	0.04	1.211707
		7	34.014	35.11	35.617	34.91367	0	34.808	34.808		34.808	0.04	1.39232
		BCR631	67.09	64.604	64.141	65.27833	0	65.17267	65.17267		65.17267	0.04	2.606907
3		2	44.372	45.099	43.595	44.35533	0	44.24967	44.24967		44.24967	0.04	1.769987
		6	30.482	31.347	29.814	30.54767	0	30.442	30.442		30.442	0.04	1.21768
		7	30.822	29.845	29.157	29.94133	0	29.83567	29.83567		29.83567	0.04	1.193427

Table (9.1.7.4) Table shows concentrations and absorbances of Iron (Fe) in soil samples (Step 4)

BCR Fe			1st measure mg/l - 1	2nd	3rd	average	background	final concentration	x0 dilution	x10 dilution	final in mg/l	actual litre in solution	BCR Fe in mg
Aqua riga (1:3 nitric acid/conc.HCl) (4th step)		1	25.891	26.967	25.49	26.116	0	26.06333	26.06333		26.06333	0.053	1.381357
Huf		2	30.015	30.001	29.11	29.70867	0	29.656	29.656		29.656	0.05	1.4828
1		4	27.957	27.61	27.252	27.60633	0	27.55367	27.55367		27.55367	0.05	1.377683
	x10	5	11.879	11.172	11.683	11.578	0.053	11.47233		114.7233333	114.7233	0.05	5.736167
	x10	6	15.267	14.334	15.645	15.082	0.071	14.95833		149.5833333	149.5833	0.05	7.479167
		7	75.331	73.962	72.523	73.93867	0	73.886	73.886		73.886	0.05	3.6943
	x10	BCR631	67.036	67.54	65.907	66.82767	0.05	66.725		667.25	667.25	0.05	33.3625
		ref	0.064	0.054	0.04	0.052667	0	0				0.05	0
2		1	43.539	42.169	42.626	42.778	0.033	42.69233	42.69233		42.69233	0.05	2.134617
		2	29.08	29.452	28.517	29.01633	0.054	28.90967	28.90967		28.90967	0.05	1.445483
		4	34.766	35.149	33.555	34.49	0.054	34.38333	34.38333		34.38333	0.05	1.719167
	x10	5	8.715	8.898	9.115	8.909333	0.055	8.801667		88.01666667	88.01667	0.05	4.400833
	x10	6	11.946	11.829	11.954	11.90967	0.062	11.795		117.95	117.95	0.05	5.8975
		7	82.542	84.065	84.188	83.59833	0.068	83.47767	83.47767		83.47767	0.05	4.173883
	x10	BCR631	67.127	65.11	63.679	65.30533	0.064	65.18867		651.8866667	651.8867	0.05	32.59433
		ref	0.13	0.13	0.118	0.126	0.07	0.003333					
3		2	20.916	20.26	20.617	20.59767	0.057	20.488	20.488		20.488	0.05	1.0244
	x10	6	11.359	11.614	11.447	11.47333	0.051	11.36967		113.6966667	113.6967	0.05	5.684833

(9.1.8) Manganese (Mn) in copper measurement

Table (9.1.8.1) Table shows concentrations and absorbances of Manganese (Mn) in soil samples (Step 1)

BCR Mn			1st measure mg/l -1	2nd	3rd	average	background	final concentration	x0 dilution	x10 dilution	final in mg/l	actual litre in solution	BCR Mn in mg
acetic acid (1st step)		1	48.338	48.198		48.268	0	48.261	48.261		48.261	0.0425	2.051093
Huf	x10	2	14.584	14.337	15.498	14.80633	0	14.79933		147.9933333	147.9933	0.045	6.6597
1	x10	4	13.789	13.331	13.376	13.49867	0	13.49167		134.9166667	134.9167	0.045	6.07125
	x10	5	4.963	4.965	4.854	4.927333	0	4.920333		49.20333333	49.20333	0.0425	2.091142
	x10	6	7.45	7.255	7.11	7.271667	0	7.264667		72.64666667	72.64667	0.045	3.2691
	x10	7	7.397	7.395	7.474	7.422	0	7.415		74.15	74.15	0.0425	3.151375
	x10	BCR631	0.766	0.76	0.752	0.759333	0	0.752333		7.523333333	7.523333	0.0475	0.357358
		ref	0.012	0.002		0.007	0	0				0.04	0
2		1	48.857	47.572		48.2145	0	48.2075	48.2075		48.2075	0.0425	2.048819
	x10	2	14.887	15.017	15.028	14.97733	0	14.97033		149.7033333	149.7033	0.045	6.73665
	x10	4	16.276	16.483	16.16	16.30633	0	16.29933		162.9933333	162.9933	0.0425	6.927217
	x10	5	4.384	4.508	4.639	4.510333	0	4.503333		45.03333333	45.03333	0.0425	1.913917
	x10	6	6.869	6.752	6.82	6.813667	0	6.806667		68.06666667	68.06667	0.0475	3.233167
	x10	7	7.451	7.206	7.166	7.274333	0	7.267333		72.67333333	72.67333	0.0425	3.088617
	x10	BCR631	0.821	0.827	0.793	0.813667	0	0.806667		8.066666667	8.066667	0.045	0.363
3	x10	2	12.514	12.514	12.801	12.60967	0	12.60267		126.0266667	126.0267	0.045	5.6712
	x10	6	6.192	6.28	6.155	6.209	0	6.202		62.02	62.02	0.045	2.7909
	x10	7	6.212	6.162	6.125	6.166333	0	6.159333		61.59333333	61.59333	0.045	2.7717

Table (9.1.8.2) Table shows concentrations and absorbances of Manganese (Mn) in soil samples (Step 2)

BCR Mn			1st measure mg/l -1	2nd	3rd	average	background	final concentration	x0 dilution	x10 dilution	final in mg/l	actual litre in solution	BCR Mn in mg
hydroxylammonium chloride (2nd step)		1	20.809	19.939		20.374	0.007	20.352	20.352		20.352	0.04	0.81408
Huf		2	18.091	17.881		17.986	0.008	17.963	17.963		17.963	0.04	0.71852
1		4	28.246	27.766		28.006	0.007	27.984	27.984		27.984	0.04	1.11936
	x10	5	12.595	13.312	12.919	12.942	0.004	12.923		129.23	129.23	0.04	5.1692
		6	64.75	64.569		64.6595	0.01	64.6345	64.6345		64.6345	0.04	2.58538
		7	48.72	48.249		48.4845	0.009	48.4605	48.4605		48.4605	0.04	1.93842
		BCR631	2.051	2.09		2.0705	0.012	2.0435	2.0435		2.0435	0.04	0.08174
		ref	0.015			0.015	0	0	0			0.04	0
2		1	18.892	19.302		19.097	0.011	19.071	19.071		19.071	0.04	0.76284
		2	16.157	16.124		16.1405	0.015	16.1105	16.1105		16.1105	0.04	0.64442
		4	19.652	19.326		19.489	0	19.474	19.474		19.474	0.04	0.77896
	x10	5	12.76	12.962	12.758	12.82667	0	12.81167		128.1166667	128.1167	0.04	5.124667
		6	61.844	60.593		61.2185	0.016	61.1875	61.1875		61.1875	0.04	2.4475
		7	49.872	49.836		49.854	0.011	49.828	49.828		49.828	0.04	1.99312
		BCR631	2.559	2.578		2.5685	0.015	2.5385	2.5385		2.5385	0.04	0.10154
3		2	26.781	26.75		26.7655	0.033	26.7175	26.7175		26.7175	0.04	1.0687
	x10	6	7.088	7.269	7.173	7.176667	0	7.161667		71.61666667	71.61667	0.04	2.864667
		7	54.357	56.121		55.239	0	55.224	55.224		55.224	0.04	2.20896

Table (9.1.8.3) Table shows concentrations and absorbances of Manganese (Mn) in soil samples (Step 3)

BCR Mn			1st measure mg/l -1	2nd	3rd	average	background	final concentration	x0 dilution	x10 dilution	final in mg/l	actual litre in solution	BCR Mn in mg
Dithionite/citrate buffer (3rd step)		1	0.316	0.305		0.3105	0.016	0.258	0.258		0.258	0.04	0.01032
Huf		2	4.765	4.832		4.7985	0.012	4.75	4.75		4.75	0.04	0.19
1		4	10.197	10.107		10.152	0.02	10.0955	10.0955		10.0955	0.04	0.40382
		5	5.796	5.987		5.8915	0.021	5.834	5.834		5.834	0.04	0.23336
		6	2.071	2.017		2.044	0.016	1.9915	1.9915		1.9915	0.04	0.07966
		7	1.958	2.008		1.983	0.019	1.9275	1.9275		1.9275	0.04	0.0771
		BCR631	0.805	0.811		0.808	0.009	0.7625	0.7625		0.7625	0.04	0.0305
		ref	0.037	0.036		0.0365	0	0	0			0.04	0
2		1	0.33	0.333		0.3315	0.019	0.276	0.276		0.276	0.04	0.01104
		2	4.012	3.98		3.996	0.026	3.9335	3.9335		3.9335	0.04	0.15734
		4	6.506	6.159		6.3325	0.023	6.273	6.273		6.273	0.04	0.25092
		5	8.273	8.259		8.266	0.026	8.2035	8.2035		8.2035	0.04	0.32814
		6	2.87	2.843		2.8565	0.013	2.807	2.807		2.807	0.04	0.11228
		7	2.946	2.85		2.898	0.018	2.8435	2.8435		2.8435	0.04	0.11374
		BCR631	0.874	0.852		0.863	0.02	0.8065	0.8065		0.8065	0.04	0.03226
3		2	7.29	7.372		7.331	0.028	7.2665	7.2665		7.2665	0.04	0.29066
		6	3.491	3.434		3.4625	0.031	3.395	3.395		3.395	0.04	0.1358
		7	2.694	2.465	2.54	2.566333	0	2.529833	2.529833		2.529833	0.04	0.101193

Table (9.1.8.4) Table shows concentrations and absorbances of Manganese (Mn) in soil samples (Step 4)

BCR Mn			1st measure mg/l -1	2nd	3rd	average	background	final concentration	x0 dilution	x10 dilution	final in mg/l	actual litre in solution	BCR Mn in mg
Aqua riga (1:3 nitric acid/conc.HCl) (4th step)		1	0.198	0.201	0.202	0.200333	0.021	0.149833	0.149833		0.149833	0.053	0.007941
Huf		2	1.721	1.762		1.7415	0.02	1.692	1.692		1.692	0.05	0.0846
1		4	2.382	2.401		2.3915	0.027	2.335	2.335		2.335	0.05	0.11675
		5	1.818	1.842		1.83	0.021	1.7795	1.7795		1.7795	0.05	0.088975
		6	1.573	1.514		1.5435	0.026	1.488	1.488		1.488	0.05	0.0744
		7	1.1	1.167		1.1335	0.026	1.078	1.078		1.078	0.05	0.0539
		BCR631	7.236	7.163		7.1995	0.023	7.147	7.147		7.147	0.05	0.35735
		ref	0.031	0.028		0.0295	0	0				0.05	0
2		1	0.236	0.237		0.2365	0.02	0.187	0.187		0.187	0.05	0.00935
		2	1.166	1.158		1.162	0.024	1.1085	1.1085		1.1085	0.05	0.055425
		4	1.592	1.59		1.591	0.019	1.5425	1.5425		1.5425	0.05	0.077125
		5	2.397	2.427		2.412	0.017	2.3655	2.3655		2.3655	0.05	0.118275
		6	1.733	1.715		1.724	0	1.6945	1.6945		1.6945	0.05	0.084725
		7	1.077	1.072		1.0745	0.025	1.02	1.02		1.02	0.05	0.051
		BCR631	7.504	7.607		7.5555	0.025	7.501	7.501		7.501	0.05	0.37505
		ref	0.022	0.024		0.023	0.023	-0.0295					
3		2	3.957	3.81		3.8835	0.028	3.826	3.826		3.826	0.05	0.1913
		6	2.003	1.973		1.988	0.028	1.9305	1.9305		1.9305	0.05	0.096525

(9.1.9) Calcium (Ca) in copper measurement

Table (9.1.9.1) Table shows concentrations and absorbances of Calcium (Ca) in soil samples (Step 1)

BCR Ca		1st measure mg/l -1	2nd	3rd	average	background	average-background	x 10 dilution	x25 dilution	final in mg/l	actual litre in solution	BCR Ca in mg
acetic acid (1st step)	1	218.791	218.573	219.187	218.8503	-0.439	219.2893		5482.233333	5486.253	0.0425	233.1658
Huf	2	215.678	214.434		215.056	-0.582	215.638		5390.95	5394.97	0.045	242.7737
1	4	216.474	216.734		216.604	-0.609	217.213		5430.325	5434.345	0.045	244.5455
	5	215.414	216.489	214.695	215.5327	-0.609	216.1417		5403.541667	5407.562	0.0425	229.8214
	6	202.415	202.151	204.295	202.9537	-0.277	203.2307		5080.766667	5084.787	0.045	228.8154
	7	213.833	212.704	213.515	213.3507	-0.166	213.5167		5337.916667	5341.937	0.0425	227.0323
	BCR631	29.175	28.71	28.775	28.88667	-0.201	29.08767		727.1916667	731.2117	0.0475	34.73255
	ref	-0.115	-0.537	-0.554	-0.402	0		-4.02			0.04	0

Table (9.1.9.2) Table shows concentrations and absorbances of Calcium (Ca) in soil samples (Step 2)

BCR Ca		1st measure mg/l -1	2nd	3rd	average	background	average-background	x 10 dilution	x25 dilution	final in mg/l	actual litre in solution	BCR Ca in mg
hydroxylammonium chloride (2nd step)	1	12.504	12.608	12.754	12.622	0.007	12.615		315.375	308.5083	0.04	12.34033
Huf	2	24.15	24.193		24.1715	0.008	24.1635		604.0875	597.2208	0.04	23.88883
1	4	31.953	31.541		31.747	0.007	31.74		793.5	786.6333	0.04	31.46533
	5	19.113	19.719	18.94	19.25733	0.004	19.25333		481.3333333	474.4667	0.04	18.97867
	6	29.527	28.431	28.841	28.933	0.01	28.923		723.075	716.2083	0.04	28.64833
	7	25.142	25.011	24.689	24.94733	0.009	24.93833		623.4583333	616.5917	0.04	24.66367
	BCR631	2.024	2.279	2.3	2.201	0.012	2.189		54.725	47.85833	0.04	1.914333
	ref	0.823	0.568	0.735	0.708667	0.022	0.686667	6.866667			0.04	0

Table (9.1.9.3) Table shows concentrations and absorbances of Calcium (Ca) in soil samples (Step 3)

BCR Ca		1st measure mg/l -1	2nd	3rd	average	background	average-background	x 10 dilution	x25 dilution	final in mg/l	actual litre in solution	BCR Ca in mg
Dithionite/citrate buffer (3rd step)	1	0.648	0.073	0.436	0.385667	-0.209	0.594667		14.86666667	13.73667	0.04	0.549467
Huf	2	7.617	7.33		7.4735	0.365	7.1085		177.7125	176.5825	0.04	7.0633
1	4	12.39	12.471		12.4305	0.76	11.6705		291.7625	290.6325	0.04	11.6253
	5	3.299	2.902	2.79	2.997	0.345	2.652		66.3	65.17	0.04	2.6068
	6	3.367	3.337	3.503	3.402333	0.513	2.889333		72.23333333	71.10333	0.04	2.844133
	7	3.604	3.817	3.62	3.680333	0.79	2.890333		72.25833333	71.12833	0.04	2.845133
	BCR631	1.029	1.494	1.256	1.259667	0.529	0.730667		18.26666667	17.13667	0.04	0.685467
	ref	0.988	0.679	0.757	0.808	0.695	0.113	1.13			0.04	0

Table (9.1.9.4) Table shows concentrations and absorbances of Calcium (Ca) in soil samples (Step 4)

BCR Ca		1st measure mg/l -1	2nd	3rd	average	background	average-background	x 10 dilution	x25 dilution	final in mg/l	actual litre in solution	BCR Ca in mg
Aqua riga (1:3 nitric acid/conc.HCl) (4th step)	1	0.684	1.102	0.486	0.757333	0.039	0.718333		7.183333333	6.623333	0.053	0.351037
Huf	2	2.771	3.159		2.965	0.161	2.804		28.04	27.48	0.05	1.374
1	4	3.164	3.176		3.17	0.429	2.741		27.41	26.85	0.05	1.3425
	5	1.214	1.266		1.24	0.965	0.275		2.75	2.19	0.05	0.1095
	6	1.132	1.315		1.2235	0.039	1.1845		11.845	11.285	0.05	0.56425
	7	1.642	1.737		1.6895	1.513	0.1765		1.765	1.205	0.05	0.06025
	BCR631	8.472	8.901		8.6865	1.213	7.4735		74.735	74.175	0.05	3.70875
	ref	2.282	2.122		2.202	2.146	0.056		0.56		0.05	0

Table (9.1.9.5) Table shows concentrations of Calcium (Ca) in each of sub-samples in four extraction steps

	Sub-sample number	Ca concentration of sub-sample (g/kg)
acetic acid (1st)	1	231.25
1	2	239.61
	4	244.30
	5	228.31
	6	227.68
	7	225.93
	BCR631	33.76
hydroxylammonium chloride (2nd step)	1	12.24
1	2	23.58
	4	31.43
	5	18.85
	6	28.51
	7	24.54
	BCR631	1.86
Dithionite/citrate buffer (3rd step)	1	0.54
1	2	6.97
	4	11.61
	5	2.59
	6	2.83
	7	2.83
	BCR631	0.67
Aqua riga (1:3 nitric acid/conc.HCl) (4th step)	1	0.35
	2	1.36
	4	1.34
	5	0.11
	6	0.56
	7	0.06
	BCR631	3.60

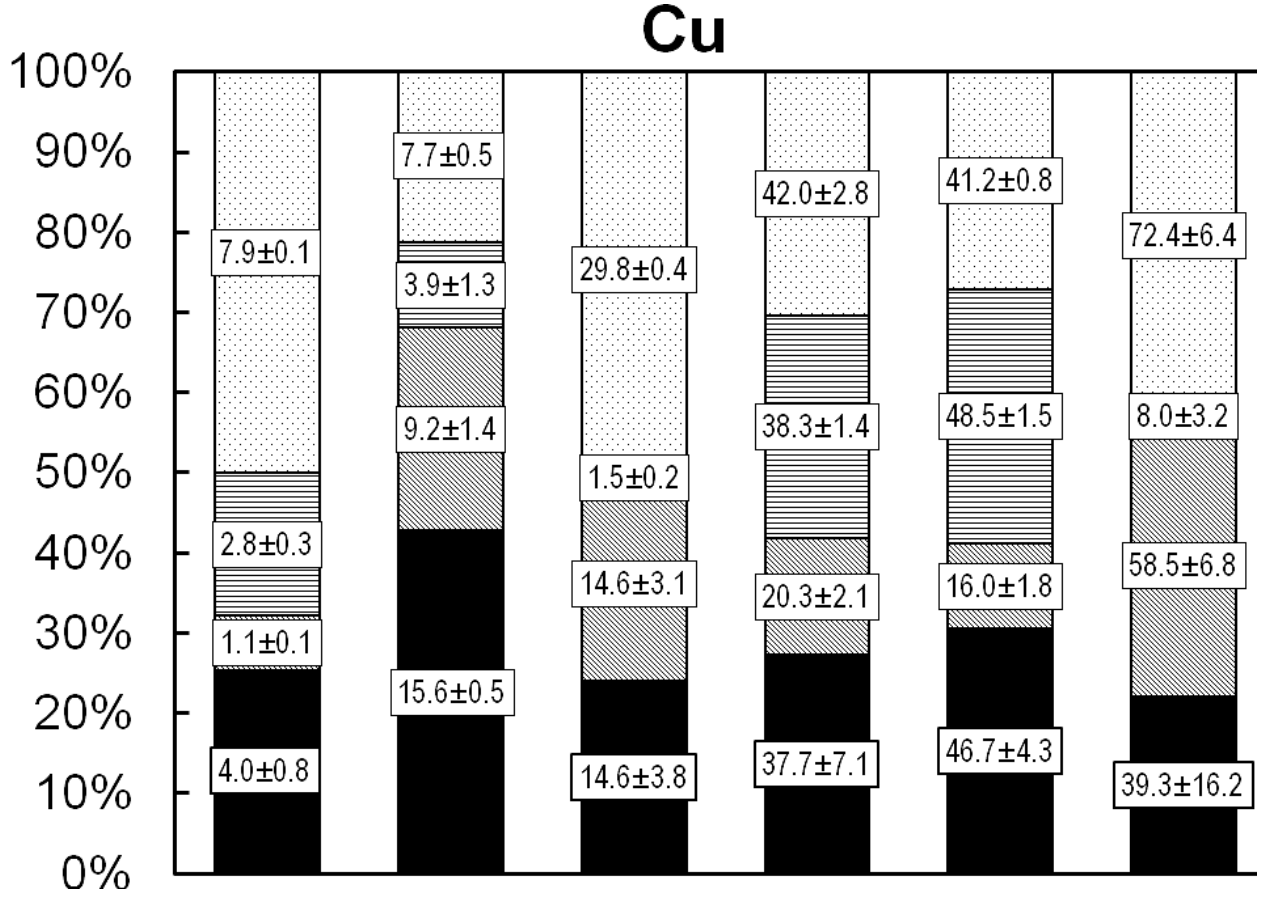
Table (9.1.9.6) Table shows 6 sub-samples average concentrations of Calcium (Ca) in 4 extraction steps

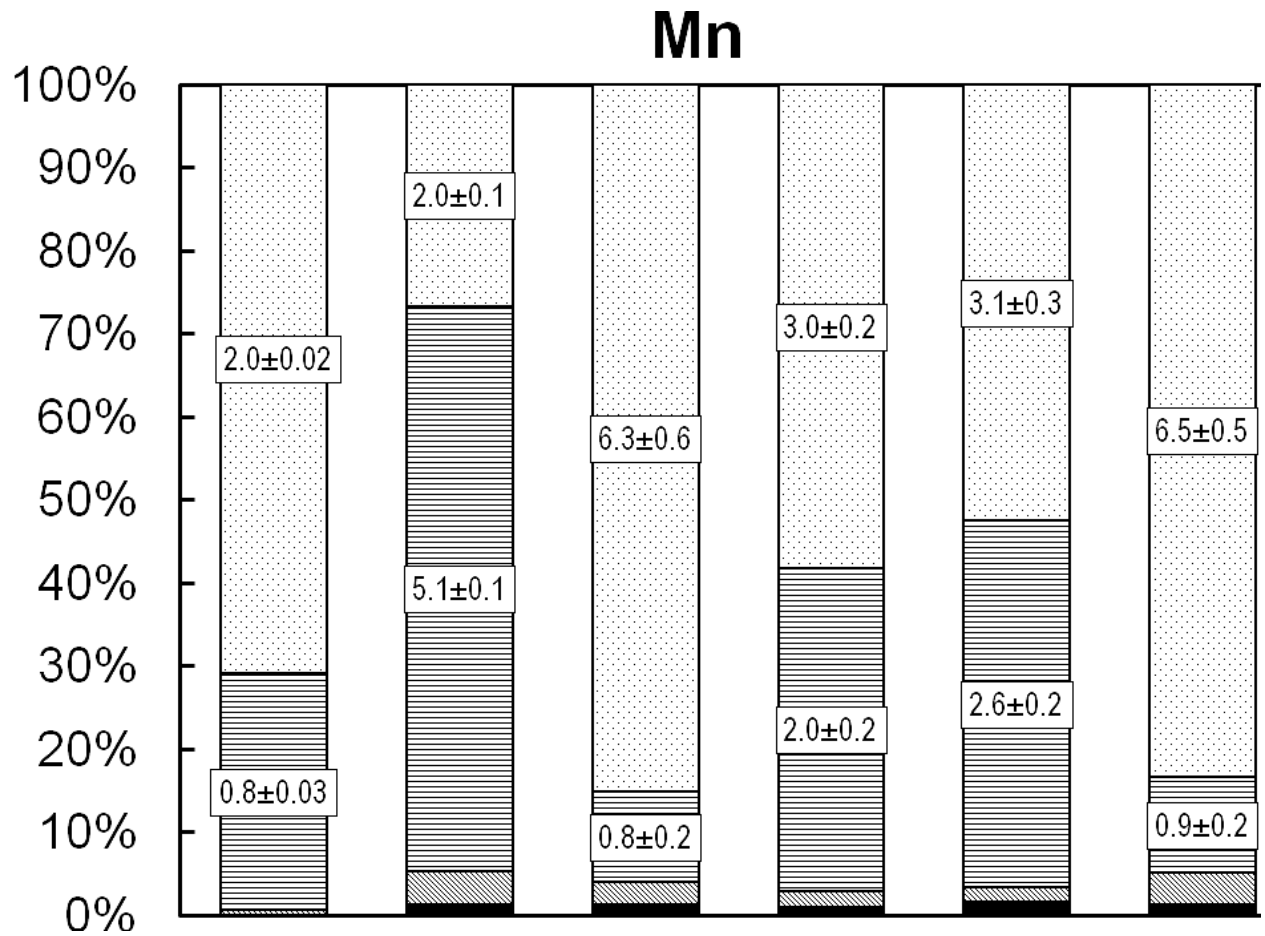
		Average concentration of 6 sub-samples (g/kg)
acetic acid (1st)	1st	232.8
hydroxylammonium chloride (2nd step)	2nd	23.2
Dithionite/citrate buffer (3rd step)	3rd	4.6
Aqua riga (1:3 nitric acid/conc.HCl) (4th step)	4th	0.6
	Sum	261.2

Table (9.1.9.7) Table shows 6 sub-samples total concentrations of Calcium (Ca) in summation of 4 extraction steps

Sub-sample number	Total concentration of Ca in ∑1-4 steps (g/kg)
1	244.38
2	271.52
4	288.69
5	249.87
6	259.57
7	253.36
BCR631	39.89

(9.1.10) Copper sequential extraction bar chart of six sub-samples




Mn
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
2.0±0.02
0.8±0.03
2.0±0.1
5.1±0.1
6.3±0.6
0.8±0.2
3.0±0.2
2.0±0.2
3.1±0.3
2.6±0.2
6.5±0.5
0.9±0.2

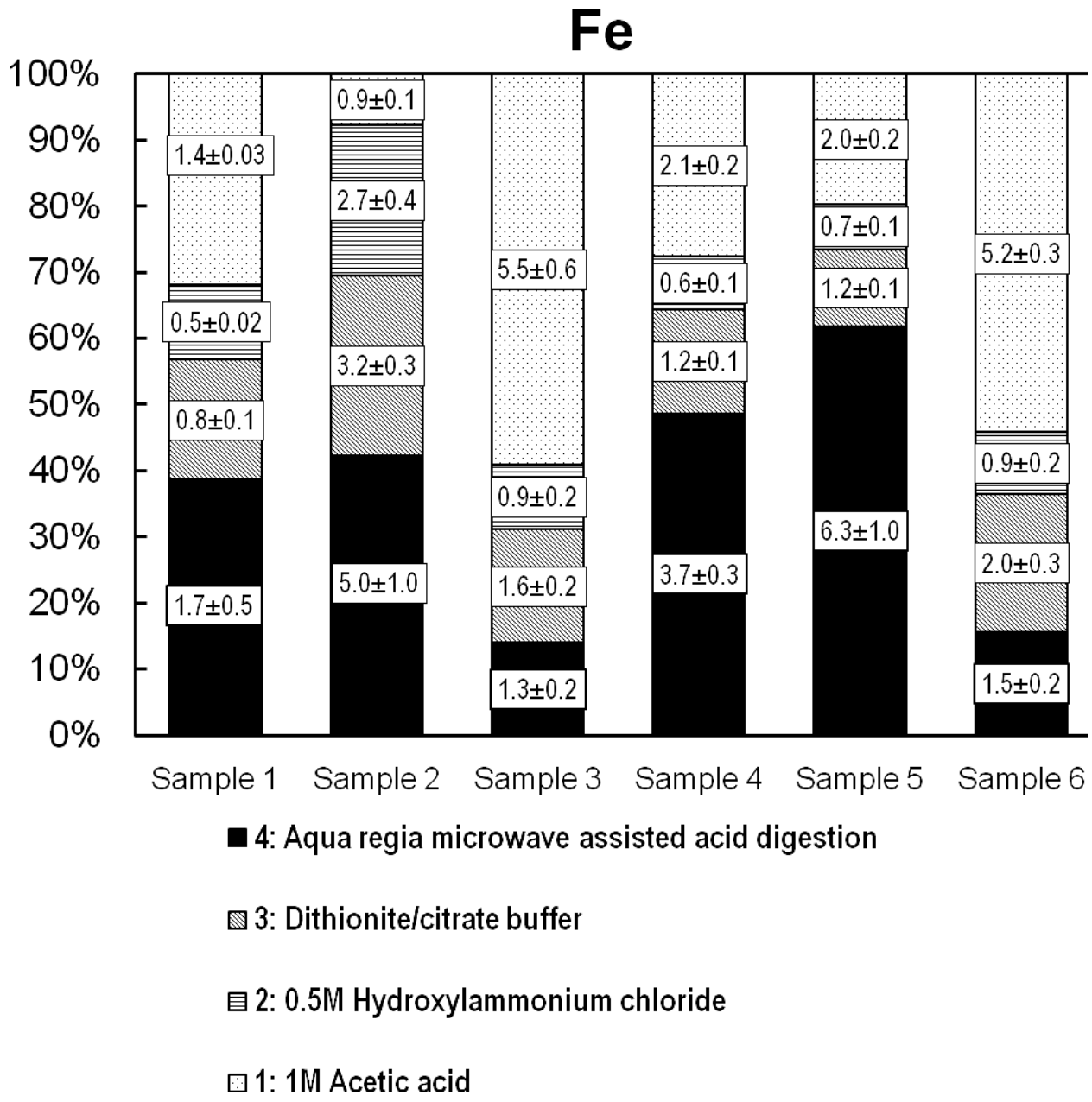


Fig (9.1.10.1) Bar chart of sequential extraction of copper (mg/kg) manganese (g/kg) and iron (g/kg) distribution in six sub-samples among 4 steps. Cu, Mn and Fe concentrations are displayed within the related bar stacks.

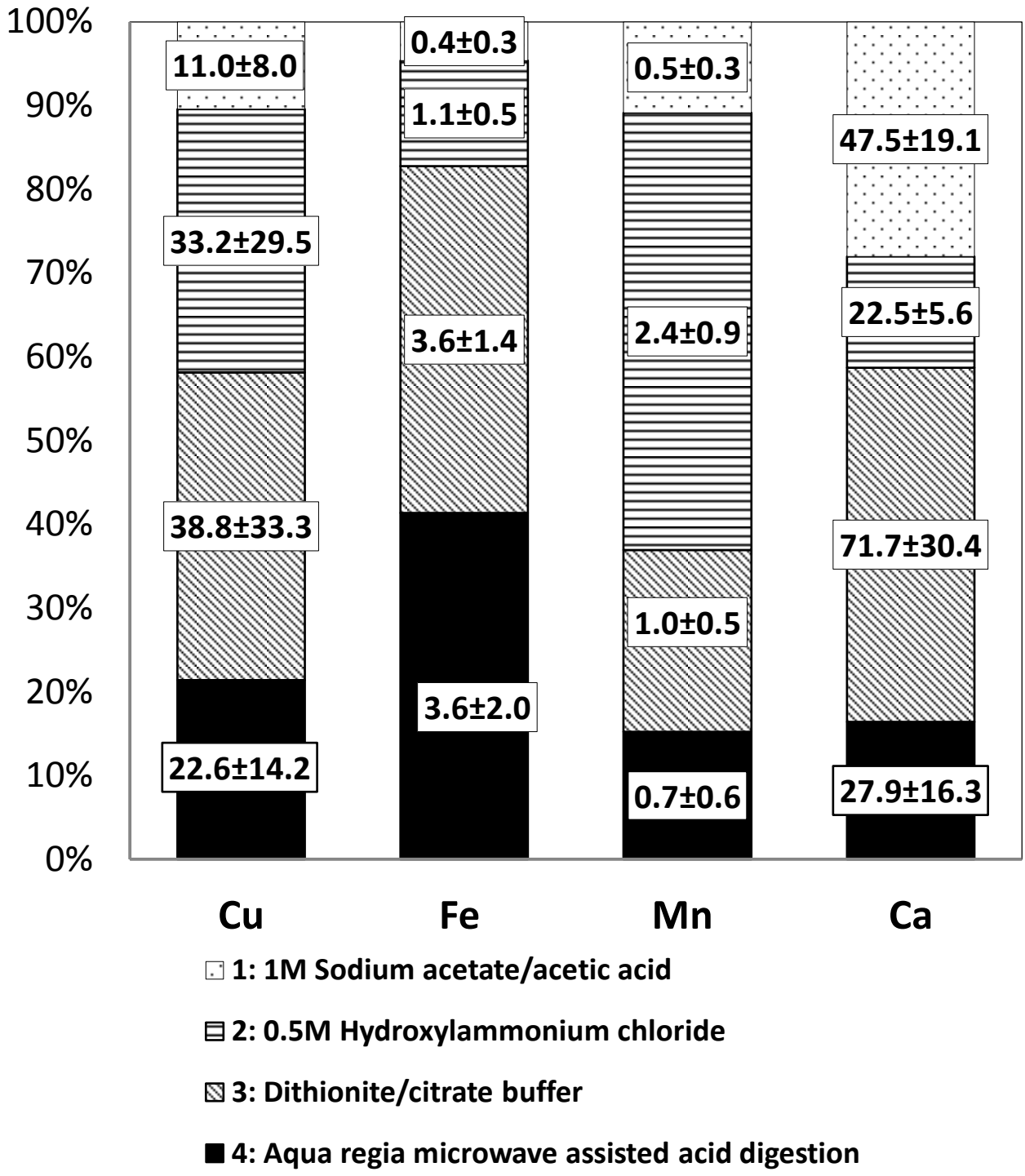


Fig (9.1.10.2) Bar chart shows average percentage recoveries for the six lime sub-subsamples under the sequential extraction scheme of Cu and the matrix elements of Fe, Mn and Ca.

(9.1.11) Copper with sodium acetate/acetic acid in first extraction step

The obtained copper, iron, manganese and calcium absorbances against corresponding concentrations data of six individual sub-samples in figure 9.1.10.2 could be referred to the attached CD in the thesis. The following table 9.1.11.1 shows the file name for each measured elements.

Table (9.1.11.1) Table shows measured element absorbance data files in attached CD

Element	Attached excel file (.xls)
Copper	BCRscheme(Naacetate)Cu
Iron	BCRscheme(Naacetate)Fe
Manganese	BCRscheme(Naacetate)Mn
Calcium	BCRscheme(Naacetate)Ca(2)

(9.1.12) Thallium sub-sample concentrations measured by ICP-MS

The obtained ^{203}Tl, ^{205}Tl and ^{103}Rh counts per second (CPS) against corresponding concentrations data of different soil samples could be referred to the attached CD in the thesis. The following table 9.1.12.1 shows the corresponding file names for the thallium measurements.

Table (9.1.12.1) Table shows measured element CPS data files in attached CD

Element	Attached excel file (.xls)
Ammonium nitrate extraction (site 1)	AmmoniumNitrateTl(site1)
Aqua Regia acid digestion (site 1)	AquaRegiaTl(site1)
Ammonium nitrate extraction and aqua regia acid digestion (site 2)	Tl(site2)

(9.1.13) Thallium concentrations in minerals and soils

Table (9.1.13.1) Table shows Tl concentrations range (ppm) in silicates and sulphides minerals (Ivanov, 1996)

Mineral	Concentration	Mineral	Concentration
Biotite	3.3-389	Chalcopyrite	0 – 33
K-feldspars	0.5-610	Pyrite	≤ 8500
Muscovite	1.5-145	Sphalerite	≤ 1057
Amphibole	0-2.6	Pyrrhotite	≤ 20
Plagioclase	≤ 10	Galenite	≤ 700
Pyroxene	0.044 – 0.50		
Chloride	0.23 – 27		
Garnet	0.009 – 0.019		

Table (9.1.13.2) Table shows Tl concentrations (ppm) in upper soil layers at various countries [1)]Tremel et al. 1997, [2)]Kabata-Pendias et al. (2001),[3)] Xiao et al. (2004).

Country	n	Median value	Mean value
Thüringen (FRG)[1)]	51	0.460	
Upper Austria[1)]	460		0.300
Switzerland[1)]	369	0.050	
Great Britain[3)]		0.03-0.99	
France[1)]	244	0.292	1.513
Canada[2)]		0.25-0.71	
China[3)]	853	0.580	
World[1),3)]		0.200	

(9.1.14) Thallium sub-sampling points concentrations across the sample depth

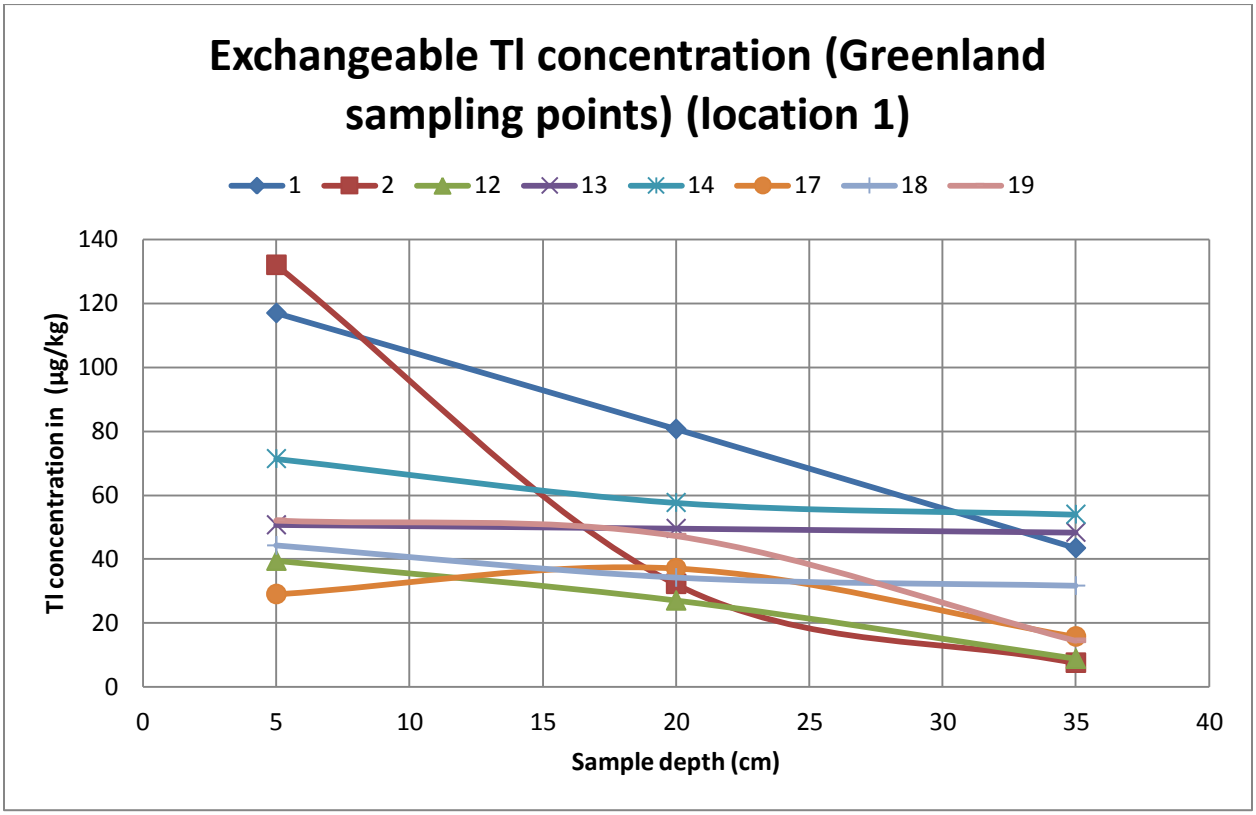


Fig (9.1.14.1) Graph plot shows trend of Greenland sub-samples thallium concentrations extracted by ammonium nitrate solution with increasing sample depth at location 1.

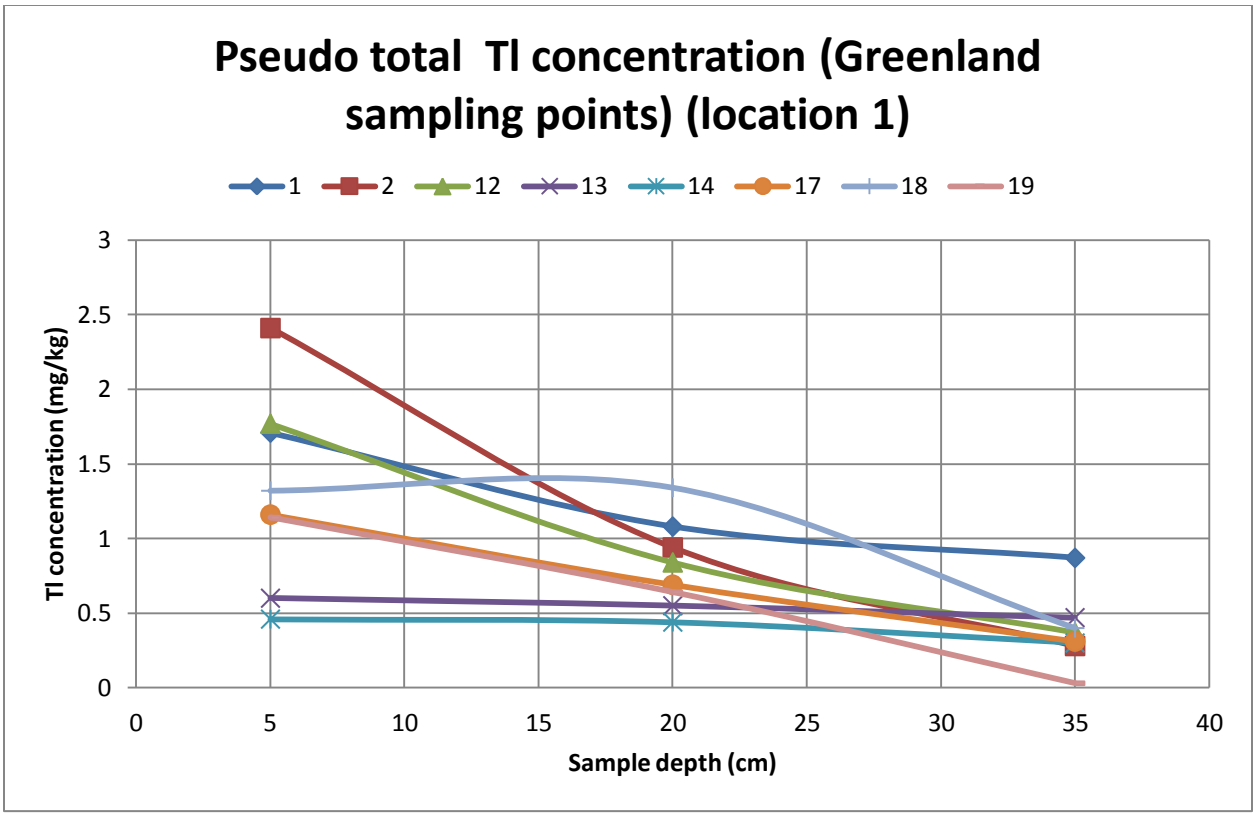


Fig (9.1.14.2) Graph plot shows trend of Greenland sub-samples thallium concentrations extracted by aqua regia acid digestion with increasing sample depth at location 1.

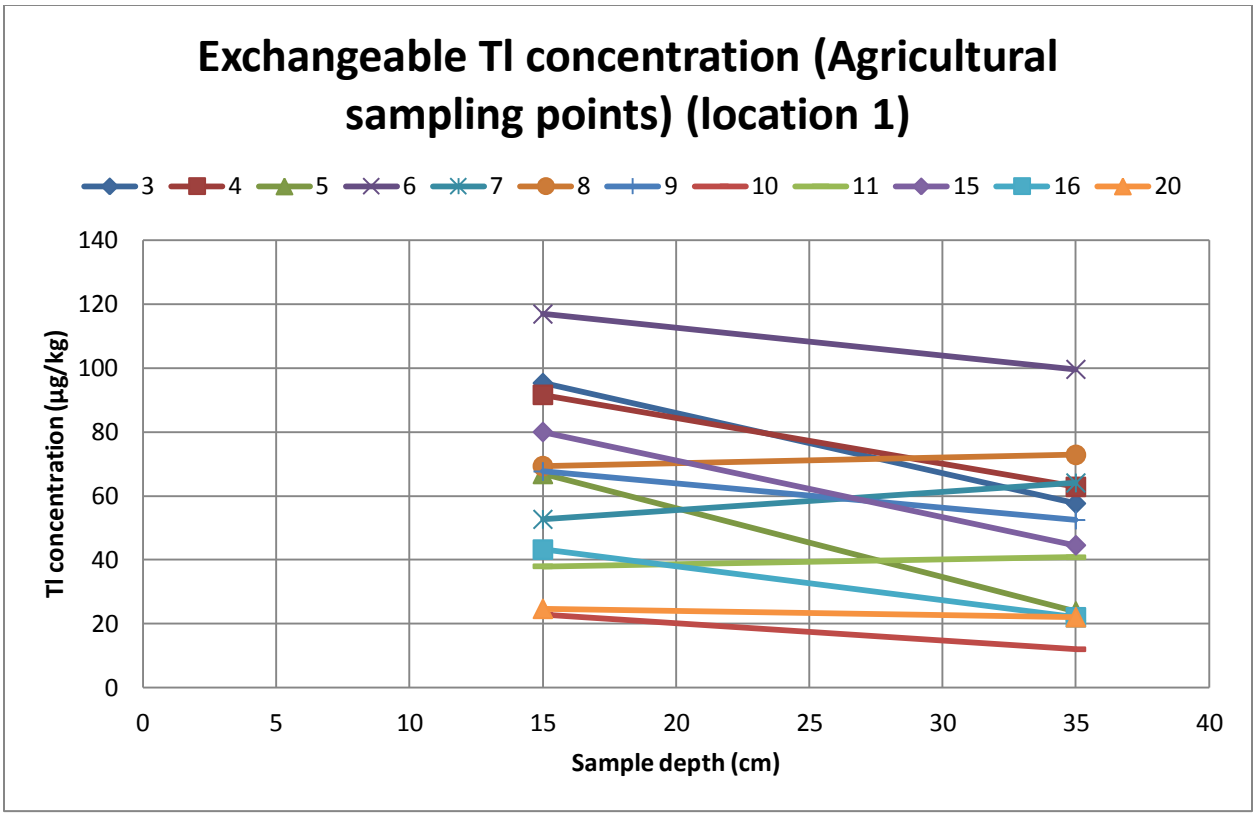


Fig (9.1.14.3) Graph plot shows trend of agricultural sub-samples thallium concentrations extracted by ammonium nitrate solution with increasing sample depth at location 1.

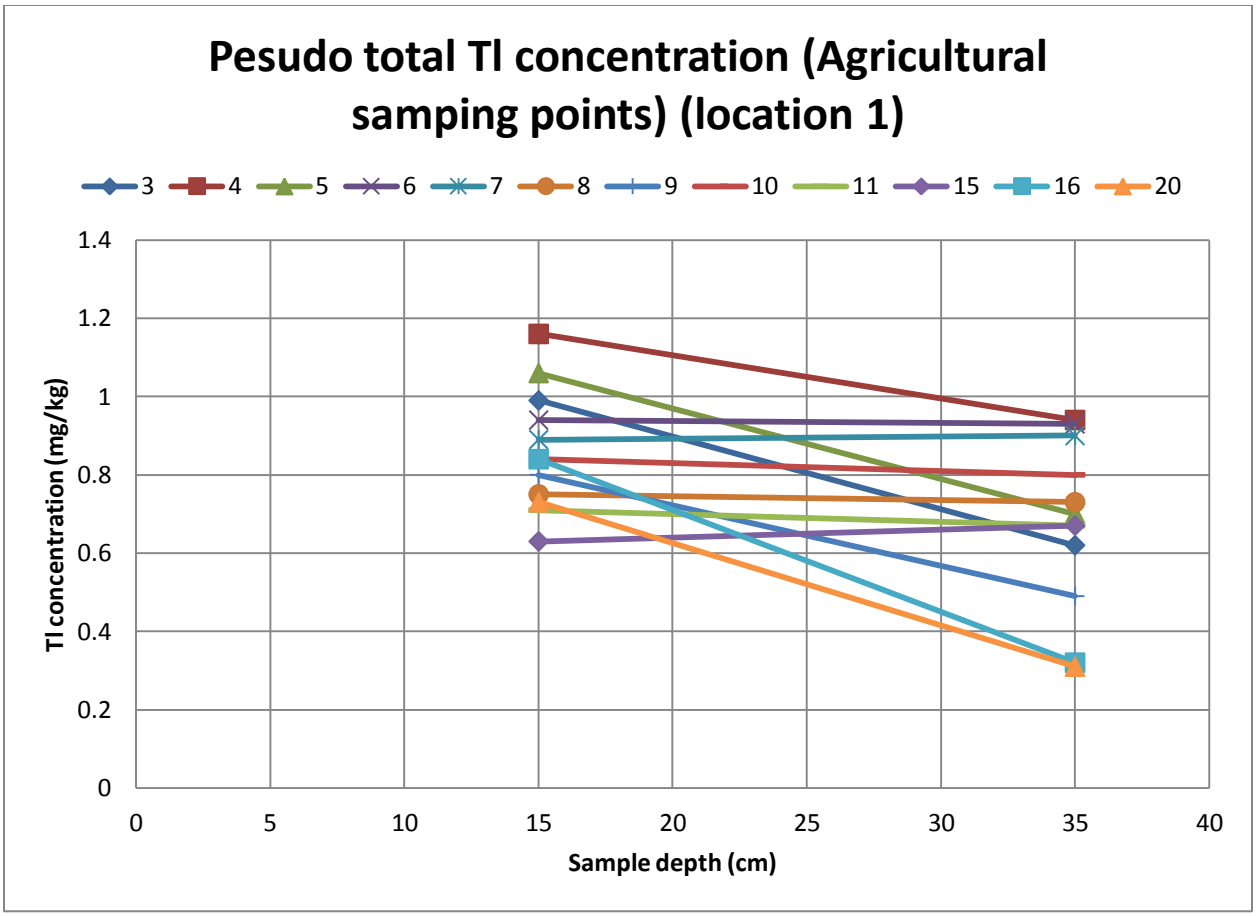


Fig (9.1.14.4) Graph plot shows trend of agricultural sub-samples thallium concentrations extracted by aqua regia acid digestion with increasing sample depth at location 1.

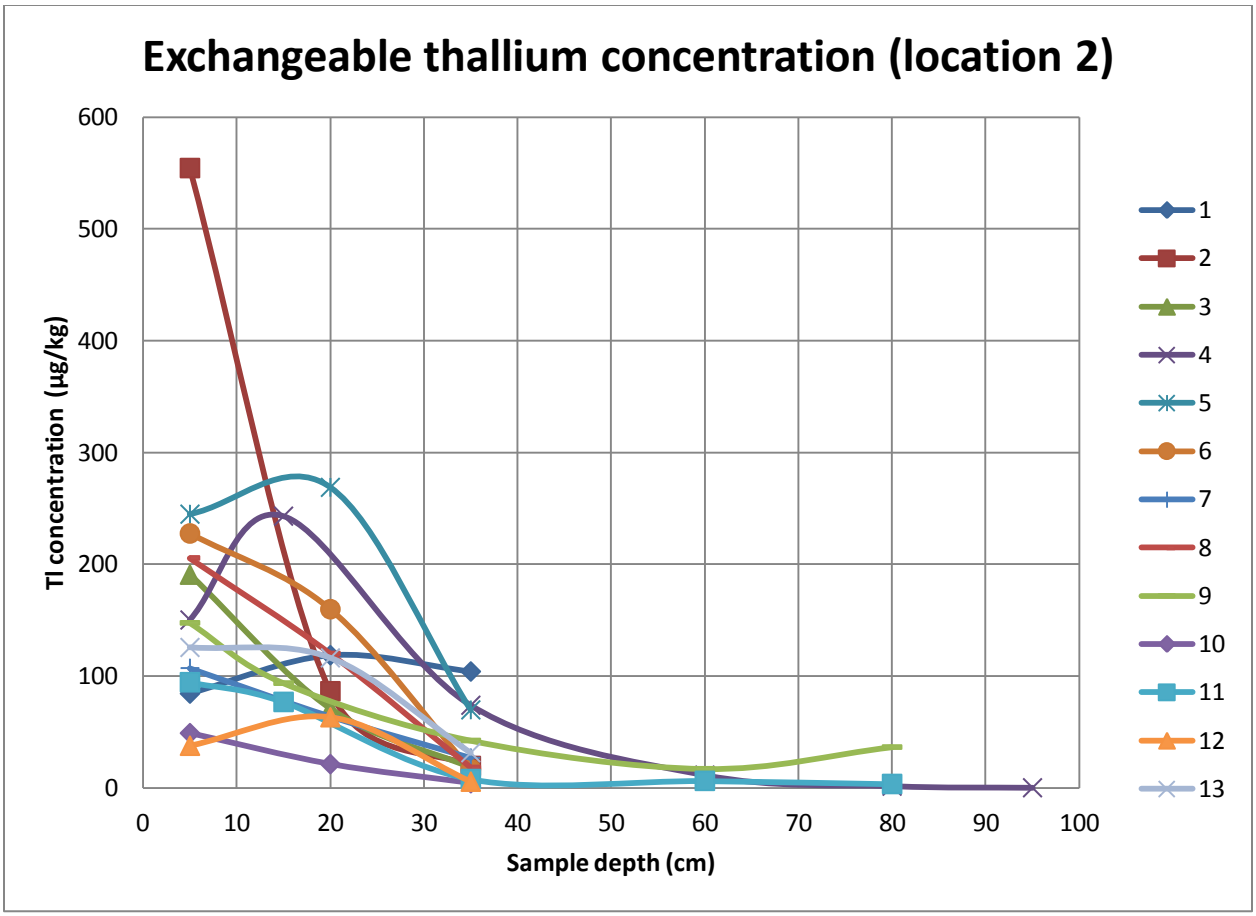


Fig (9.1.14.5) Graph plot shows trend of sub-samples thallium concentrations extracted by ammonium nitrate solution with increasing sample depth at location 2.

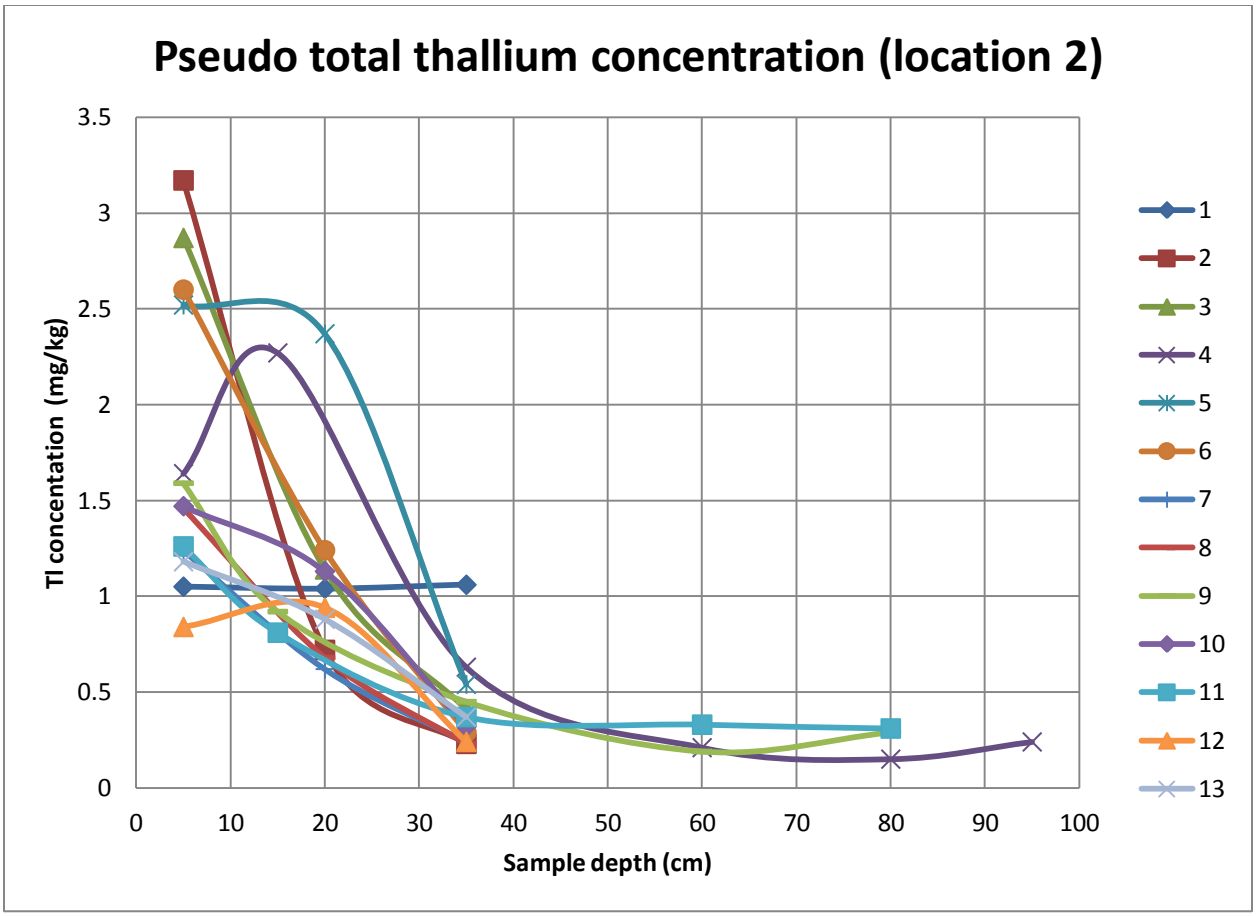


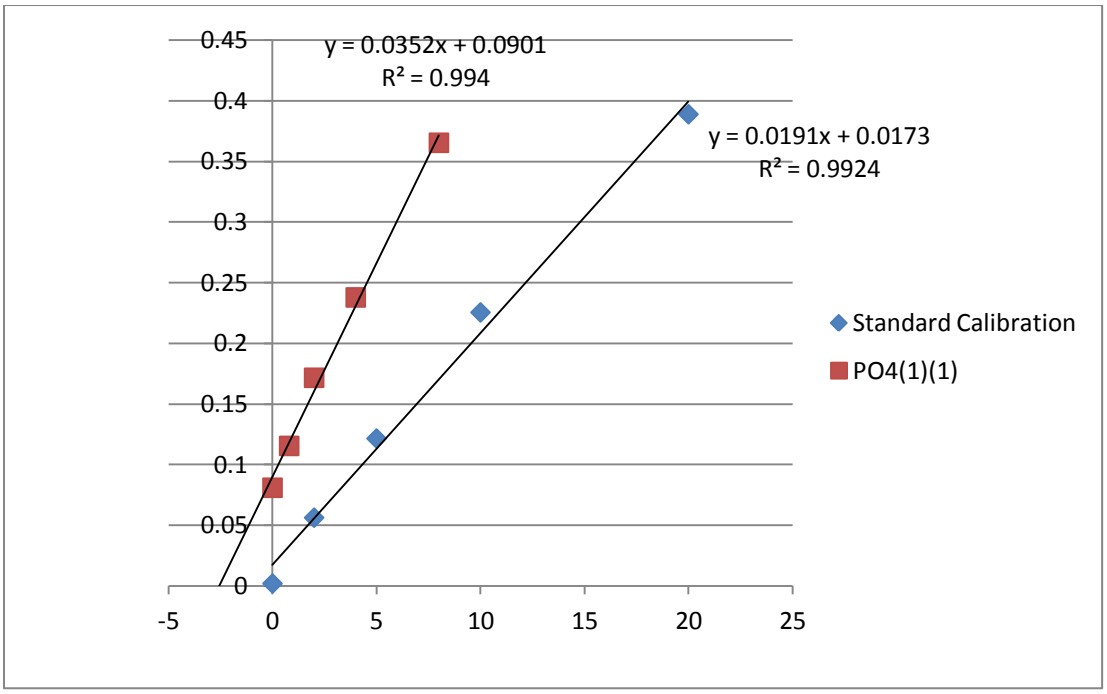
Fig (9.1.14.6) Graph plot shows trend of sub-samples thallium concentrations extracted by aqua regia acid digestion with increasing sample depth at location 2.

(9.2) Appendix B

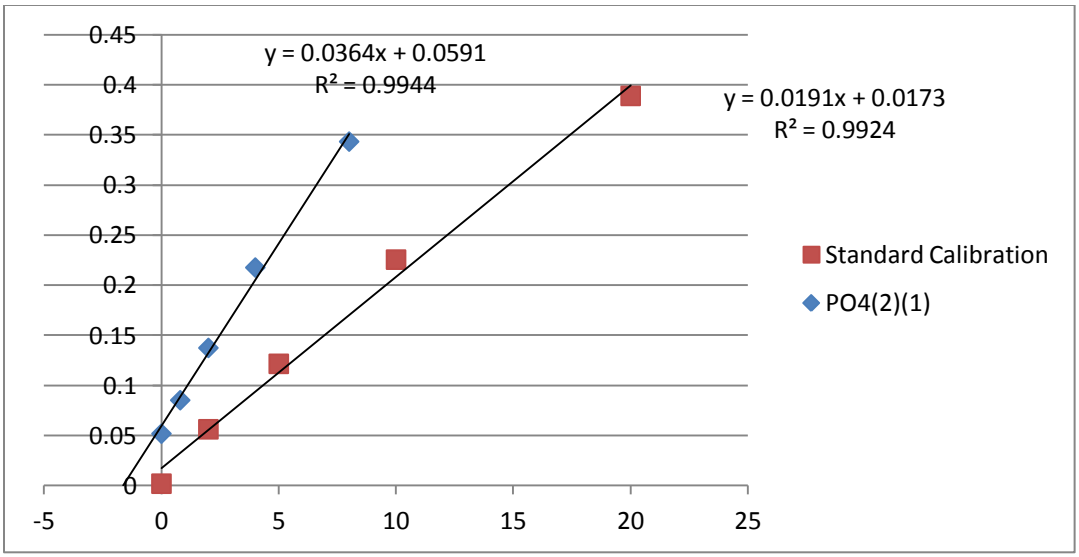
(9.2.1) As (Standard addition graph plot)

PO4 step

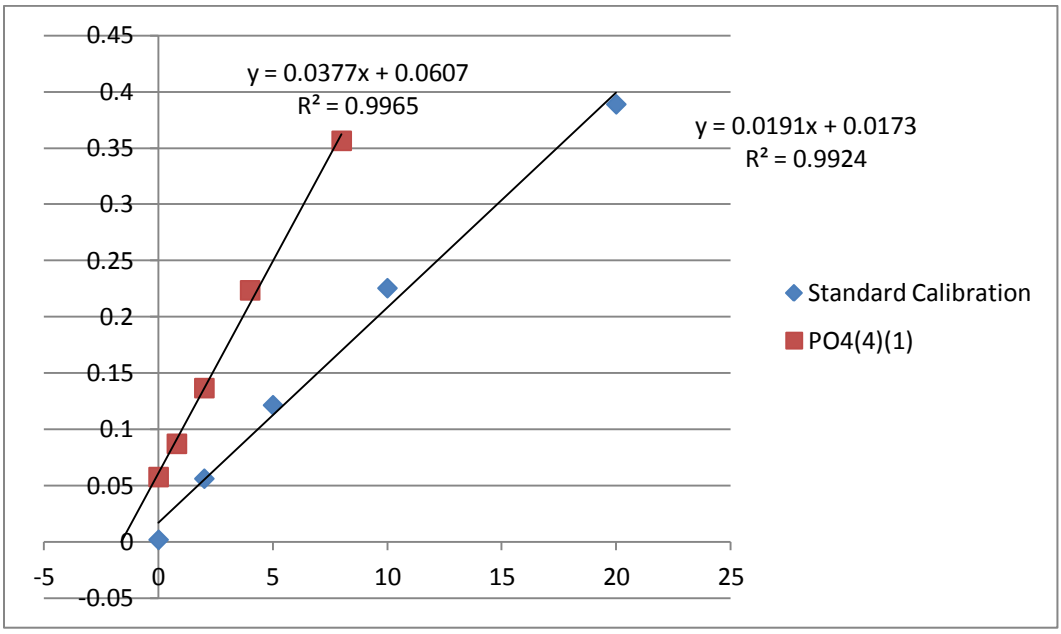
Graph plot A



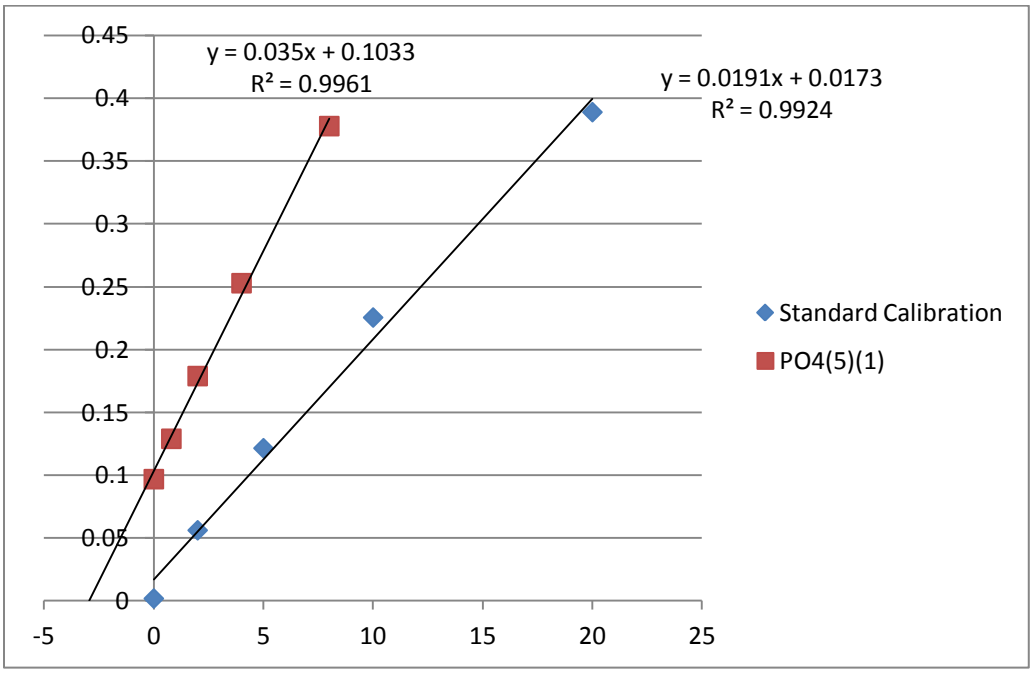
Graph plot B



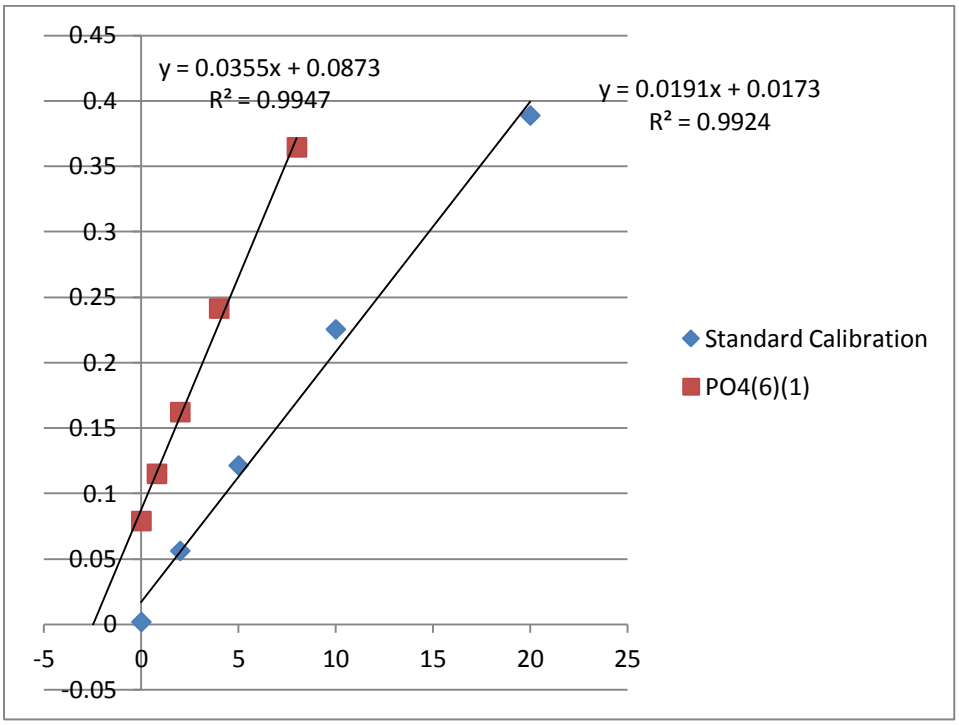
Graph plot C



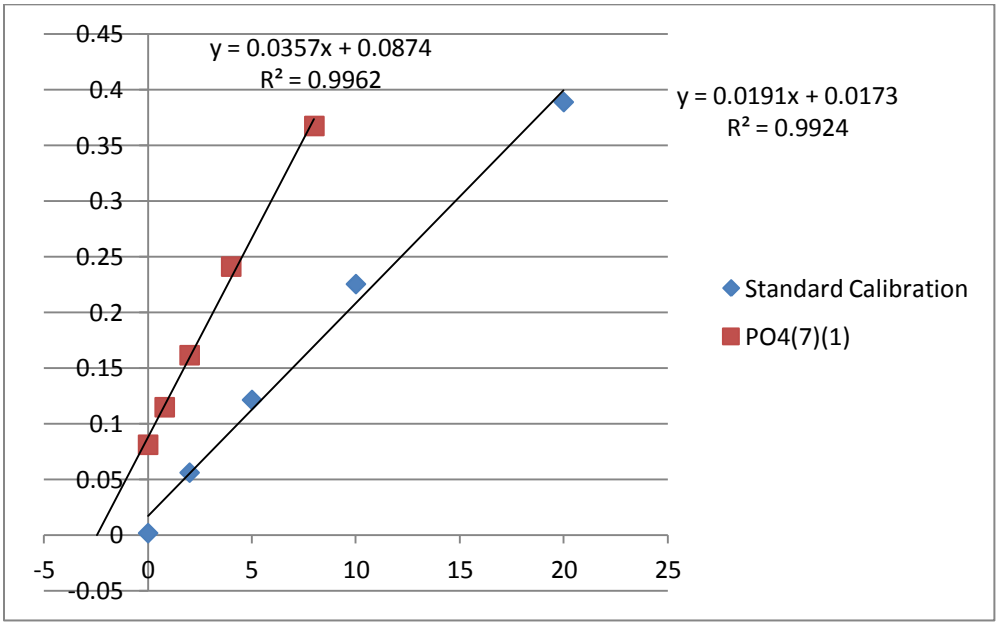
Graph plot D



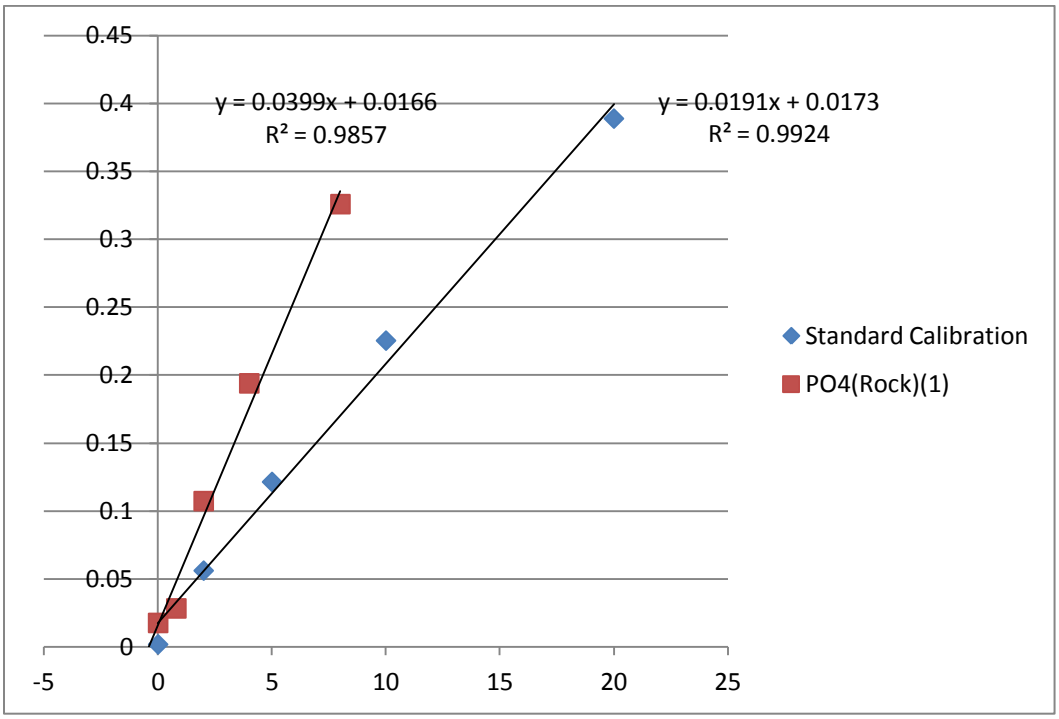
Graph plot E



Graph plot F

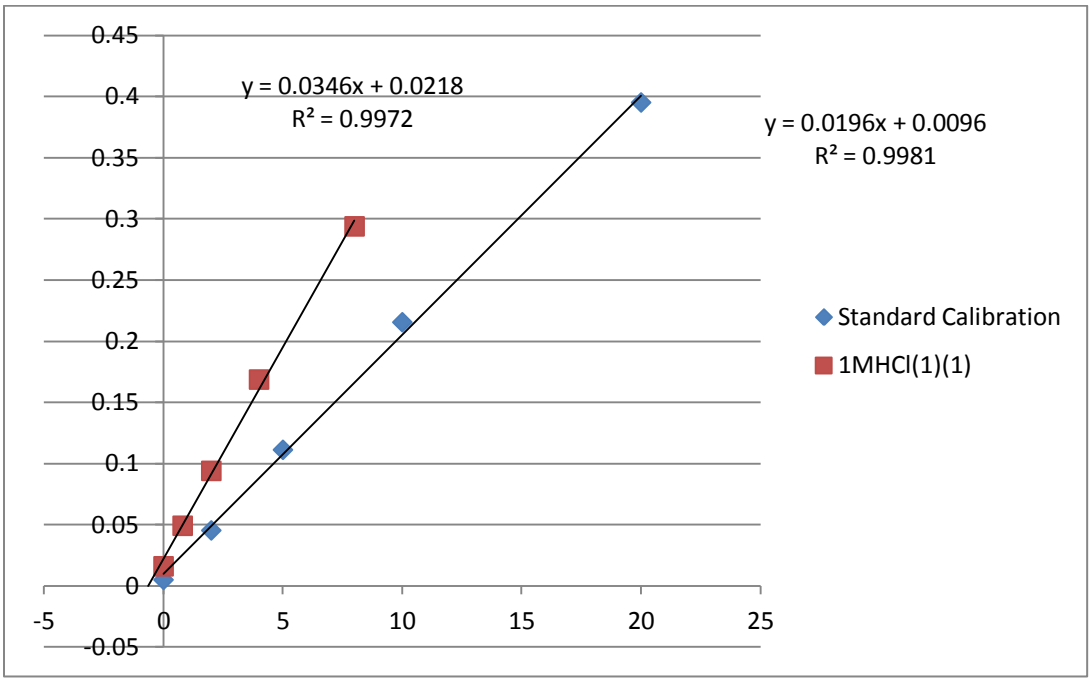


Graph plot G

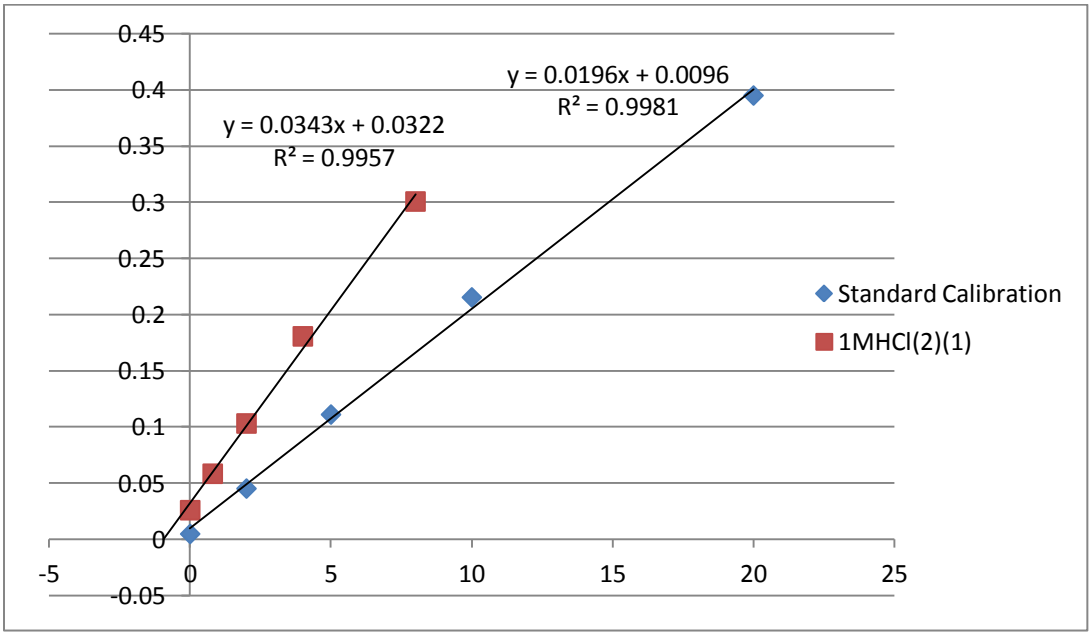

0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
-5
0
5
10
15
20
25
y = 0.0399x + 0.0166
R² = 0.9857
y = 0.0191x + 0.0173
R² = 0.9924
Standard Calibration
PO4(Rock)(1)

1MHCl step

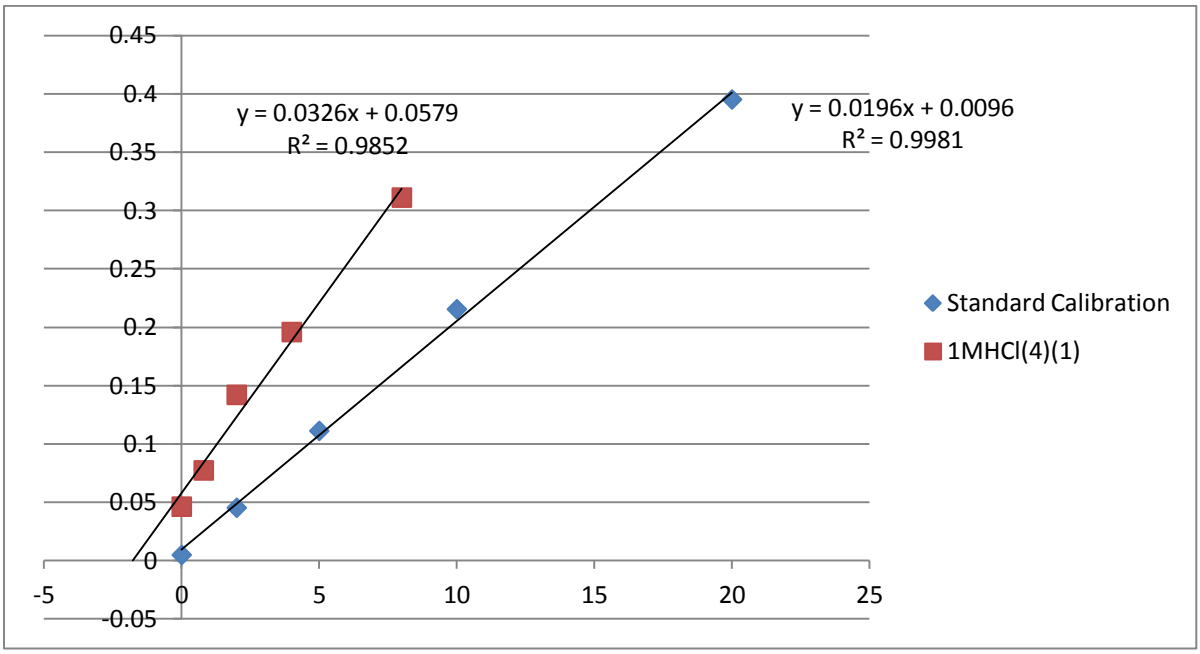
Graph plot H



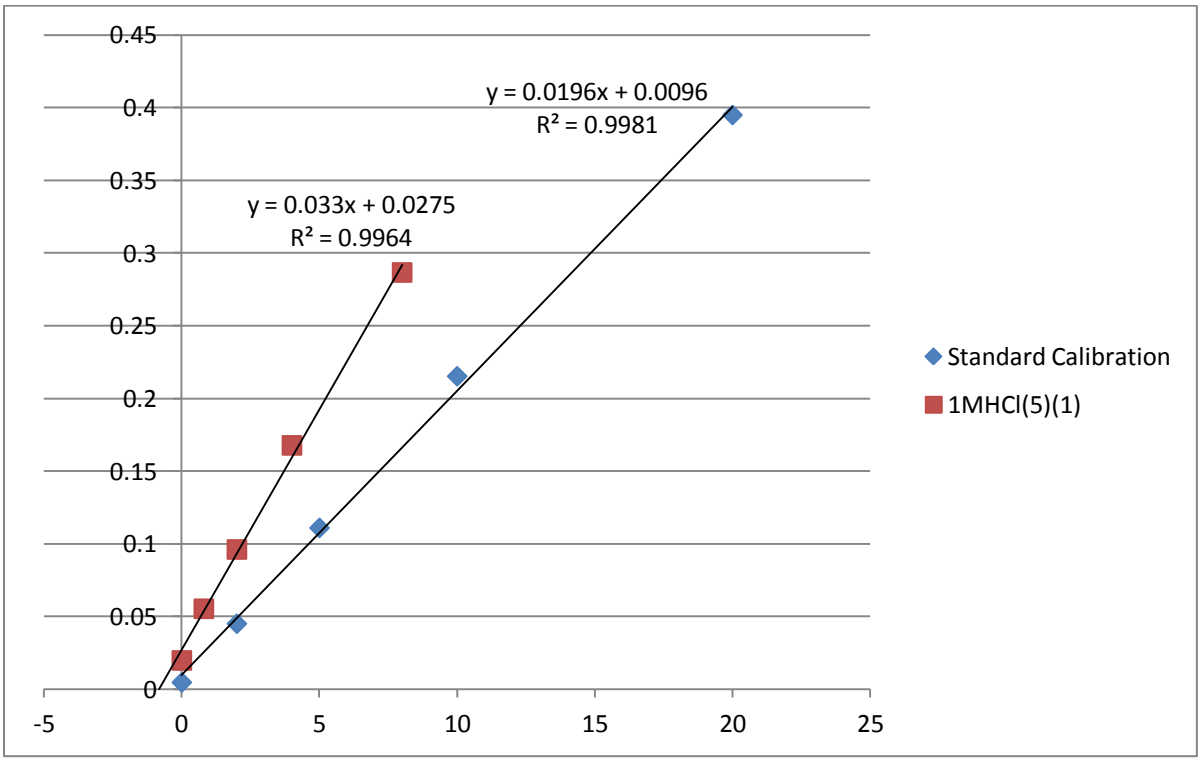
Graph plot I



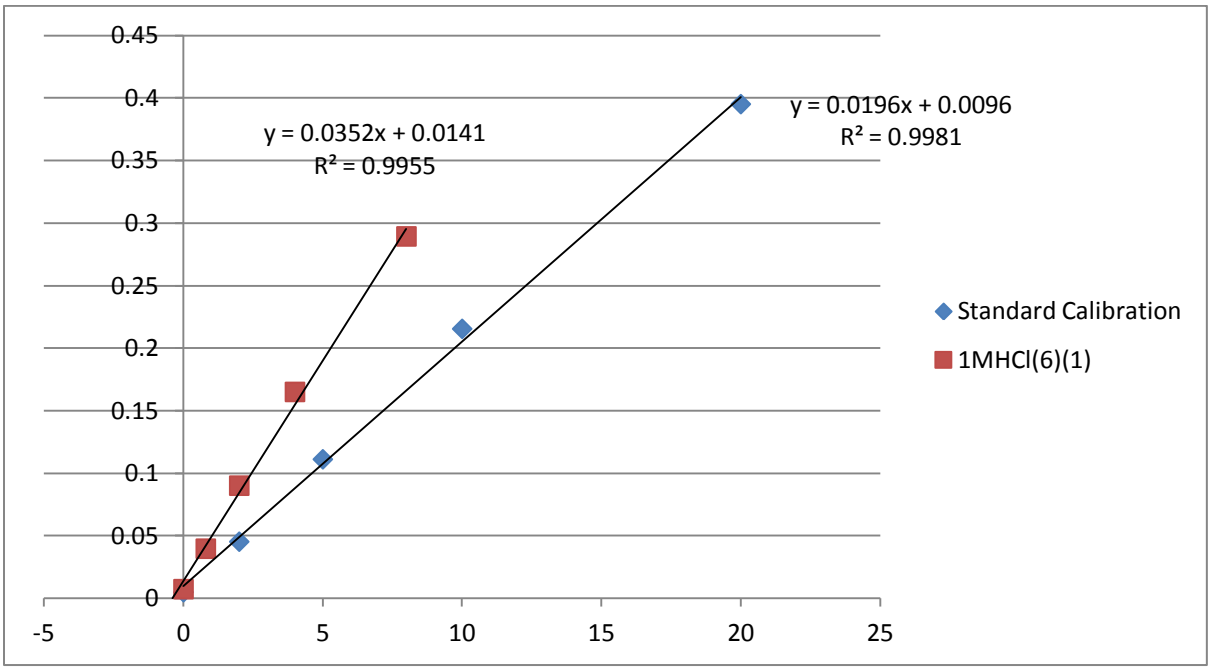
Graph plot J



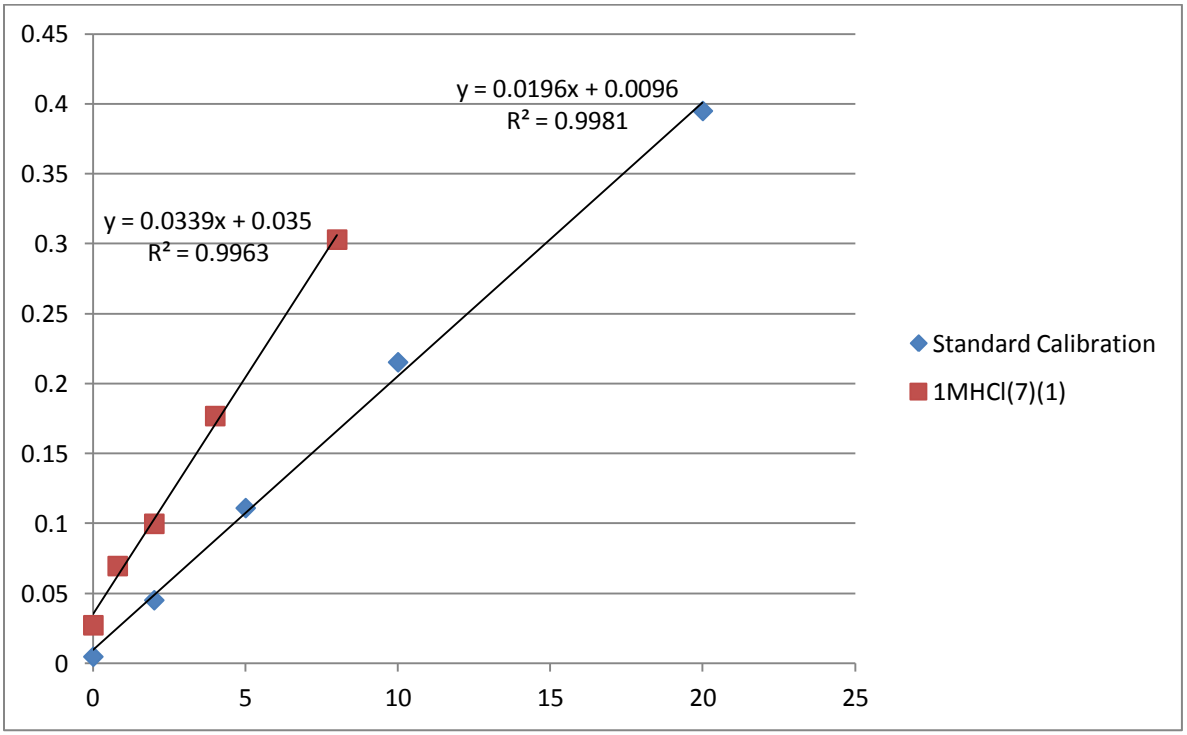
Graph plot K



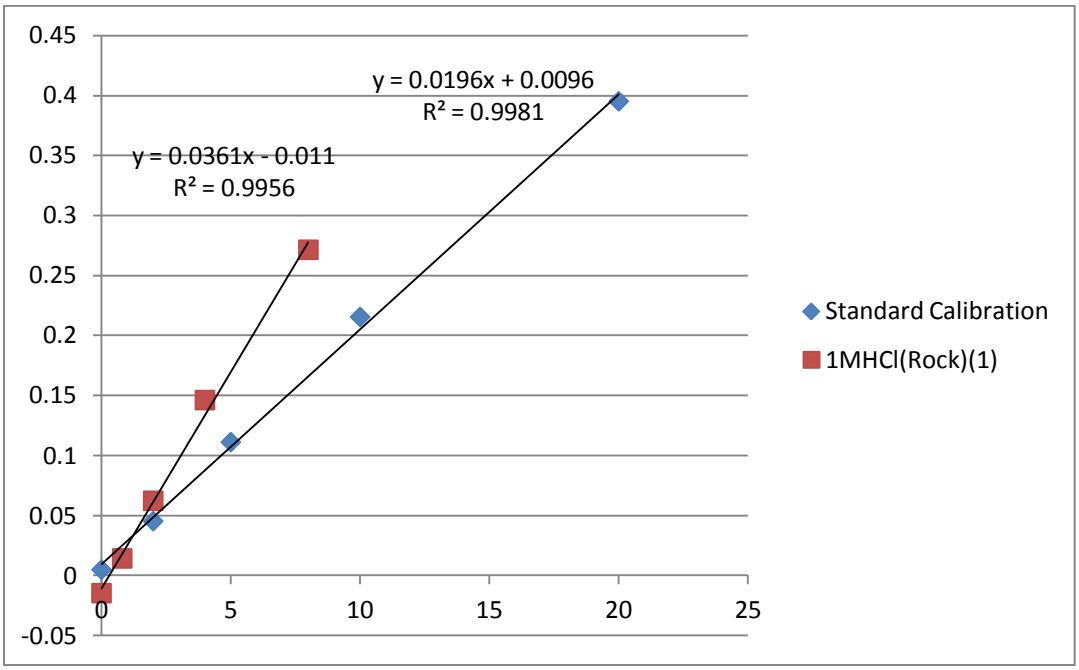
Graph plot L



Graph plot M

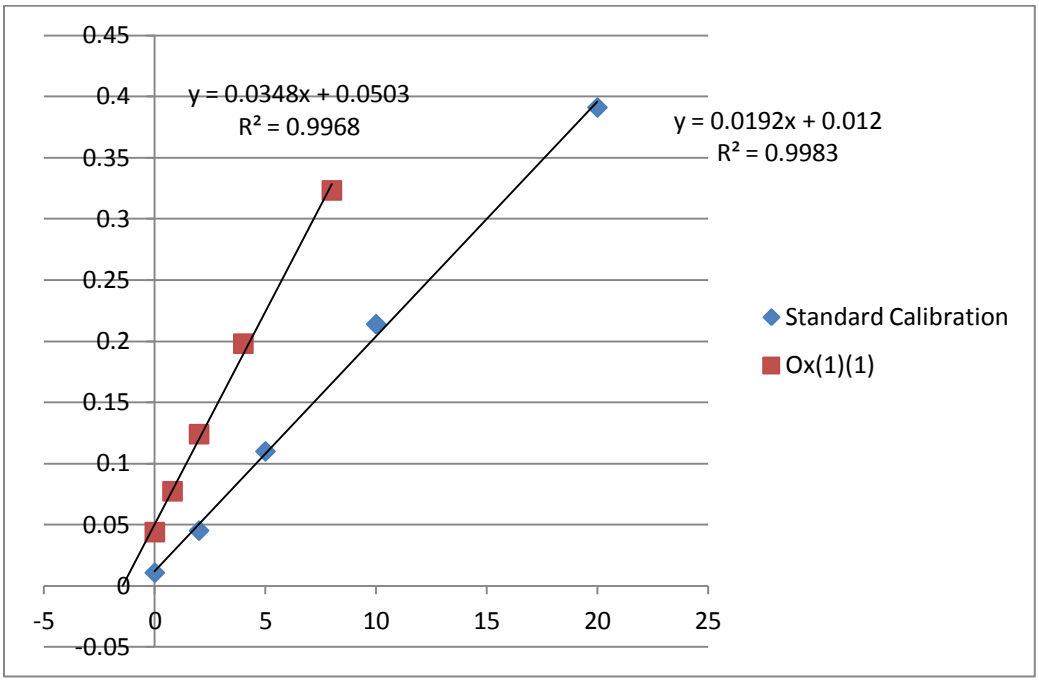


Graph plot N

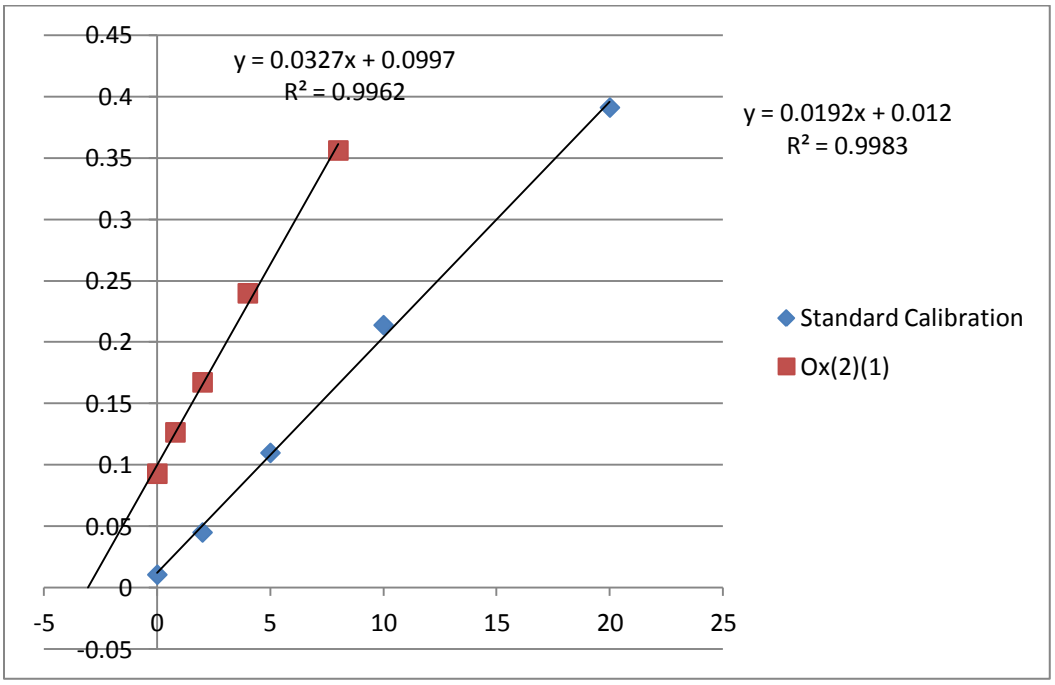

0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
0
5
10
15
20
25
y = 0.0196x + 0.0096
R² = 0.9981
y = 0.0361x - 0.011
R² = 0.9956
Standard Calibration
1MHCl(Rock)(1)

Ox step

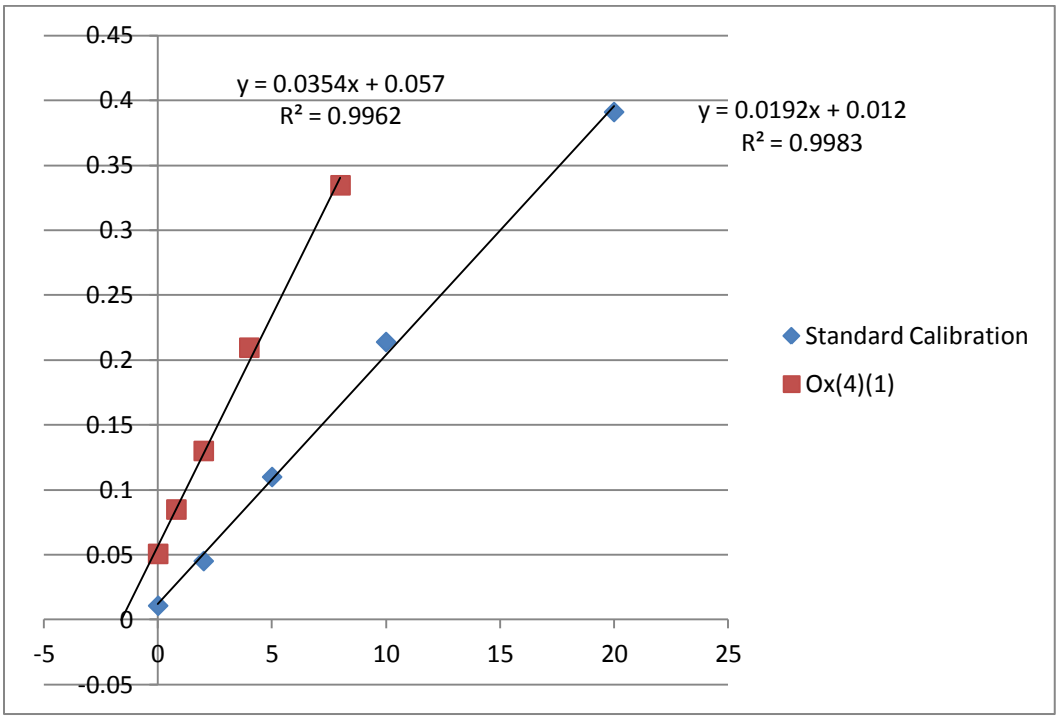
Graph plot O



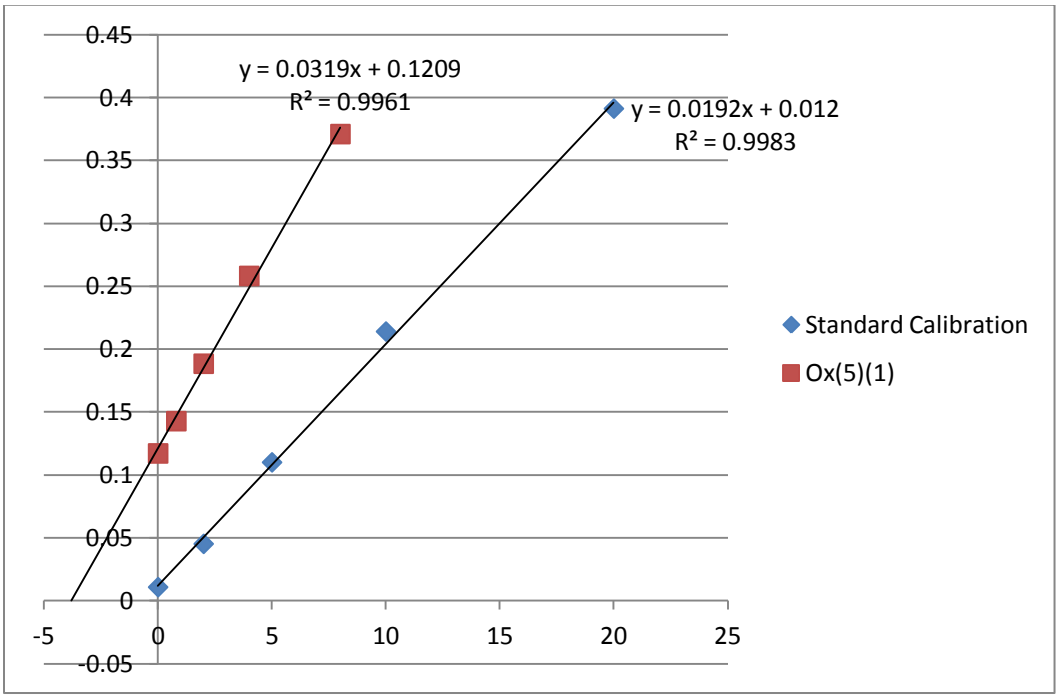
Graph plot P



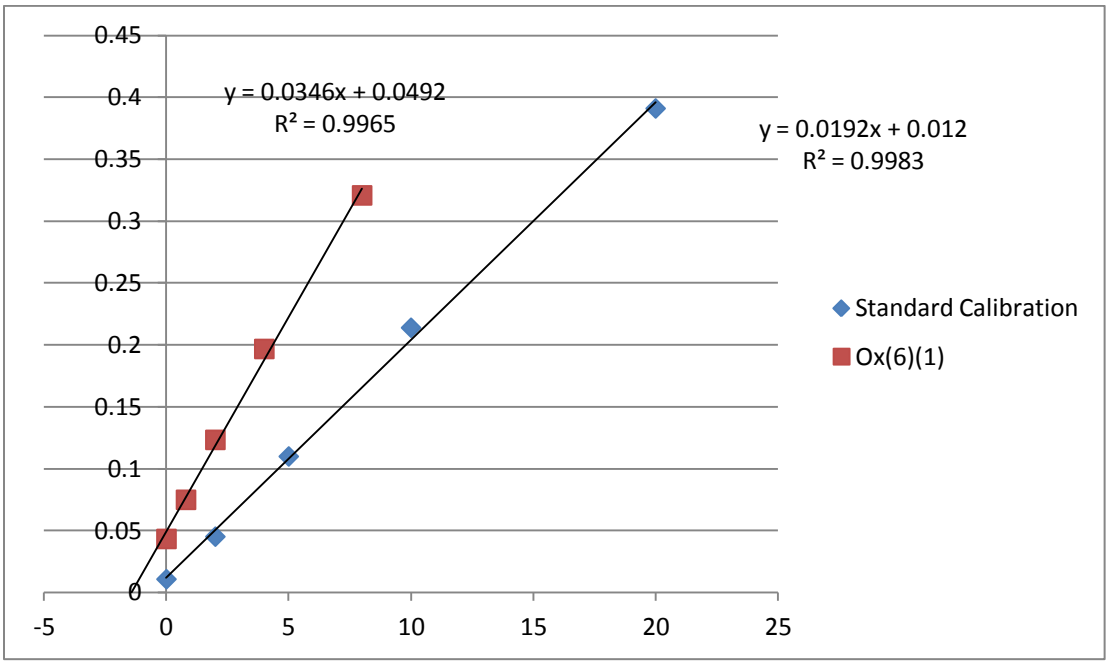
Graph plot Q



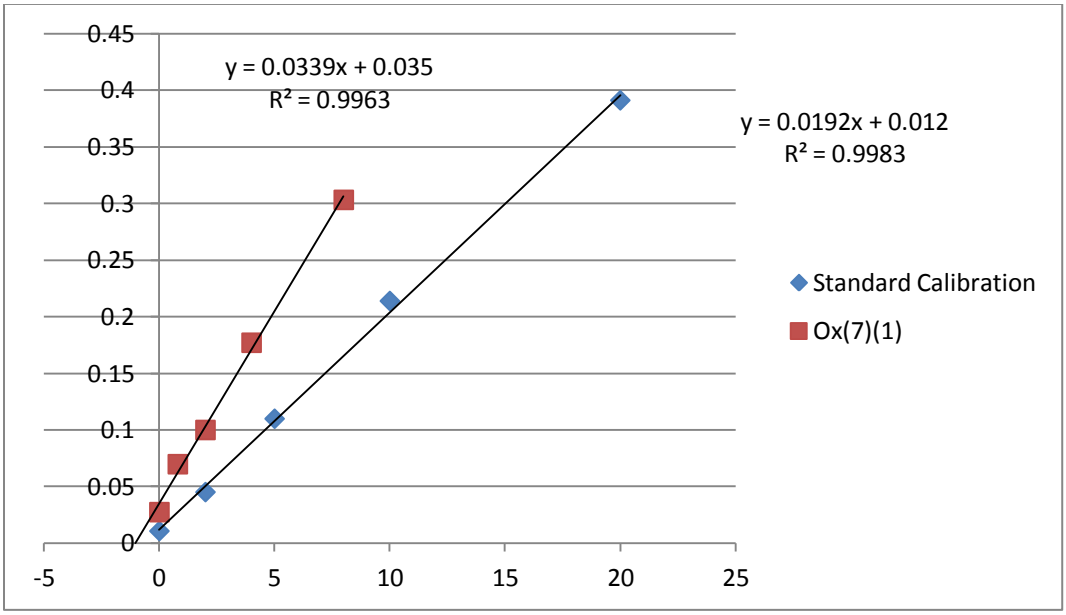
Graph plot R



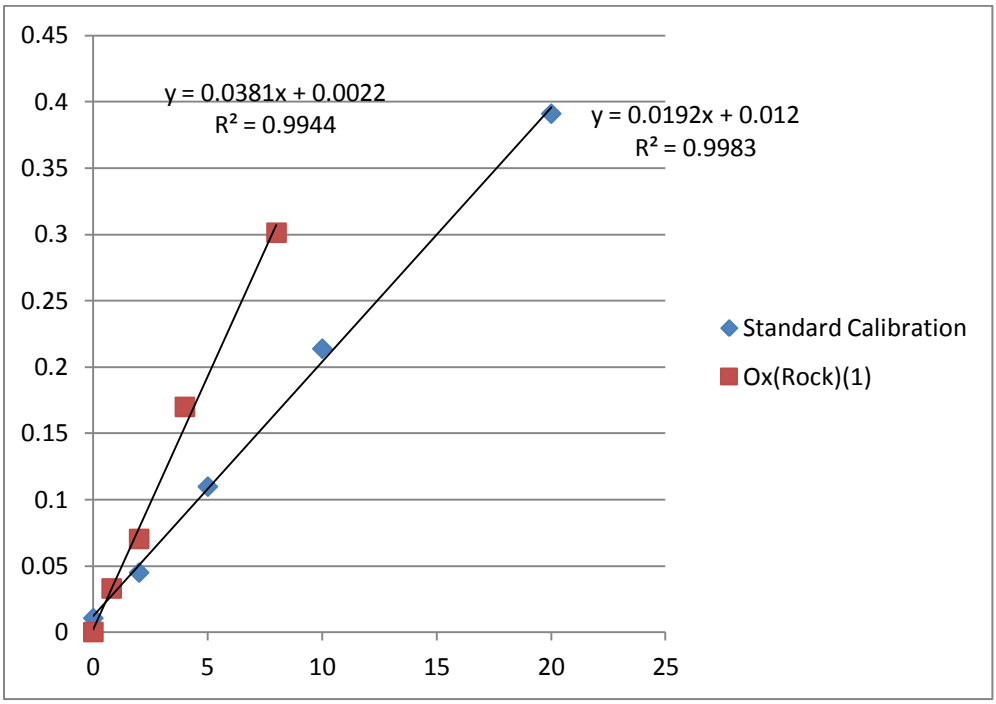
Graph plot S



Graph plot T

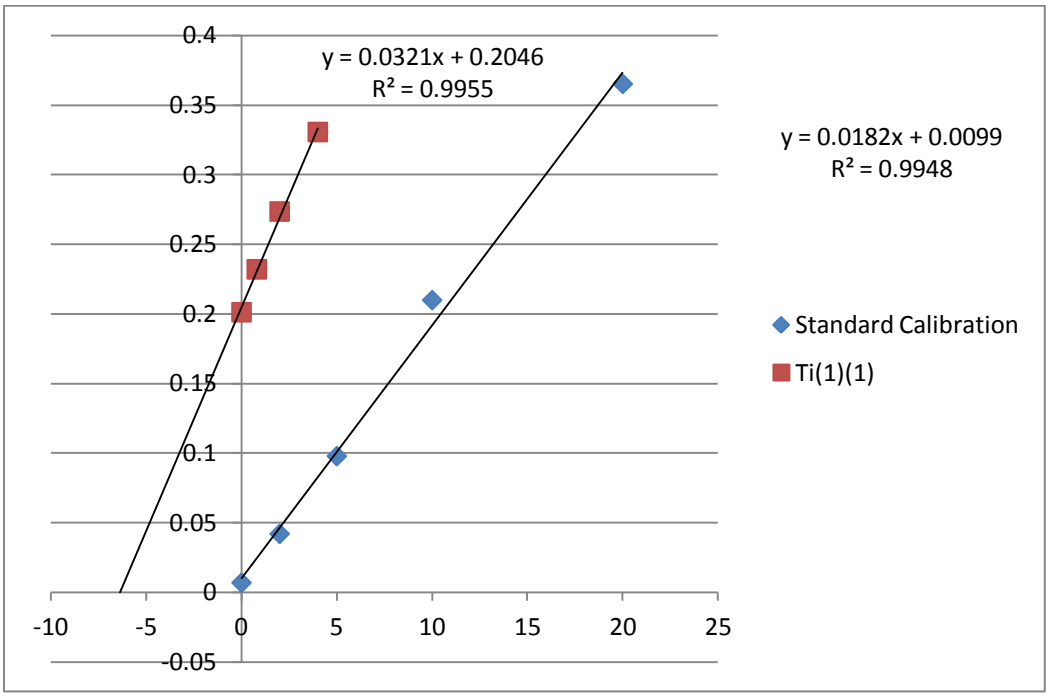


Graph plot U

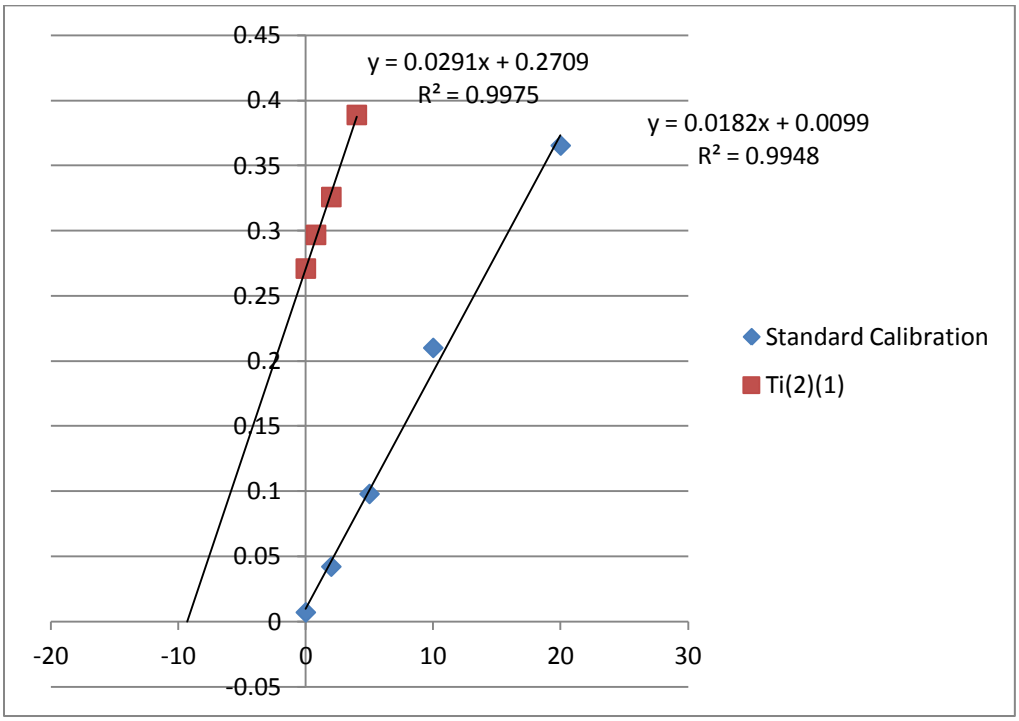

0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
5
10
15
20
25
y = 0.0381x + 0.0022
R² = 0.9944
y = 0.0192x + 0.012
R² = 0.9983
Standard Calibration
Ox(Rock)(1)

Ti step

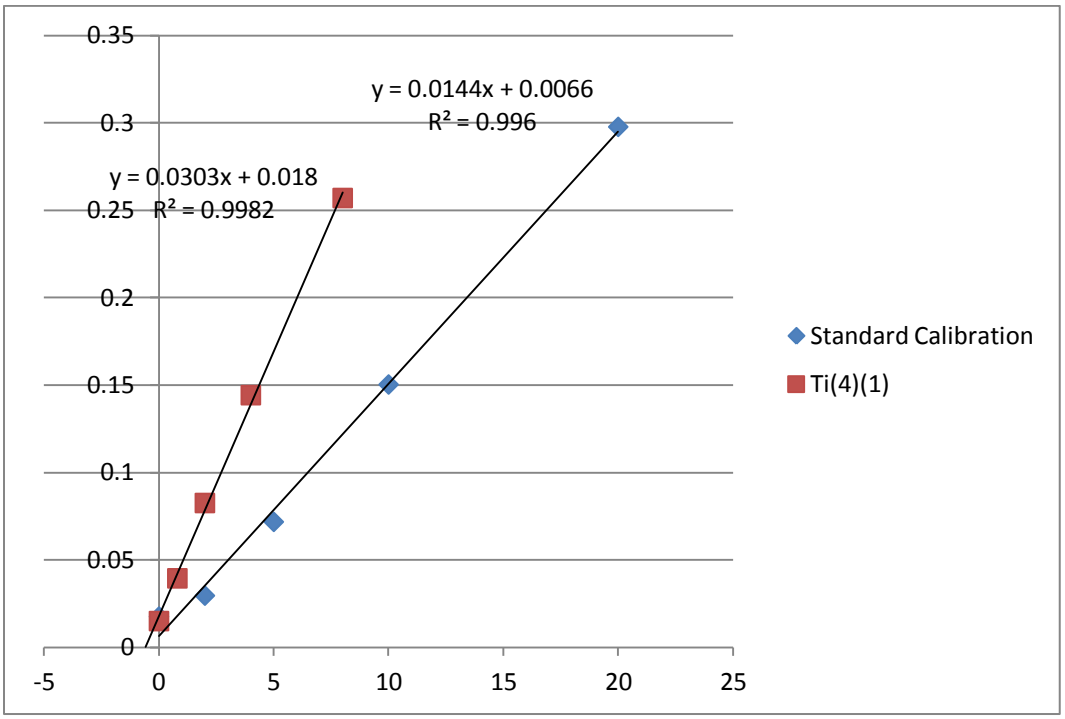
Graph plot V



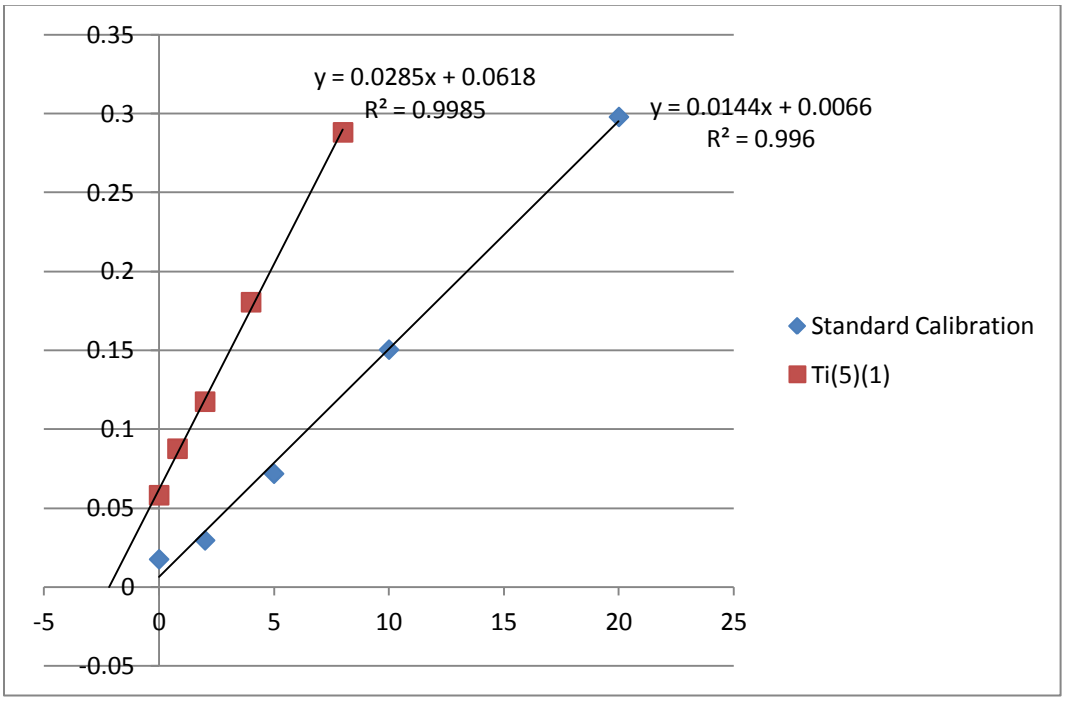
Graph plot W



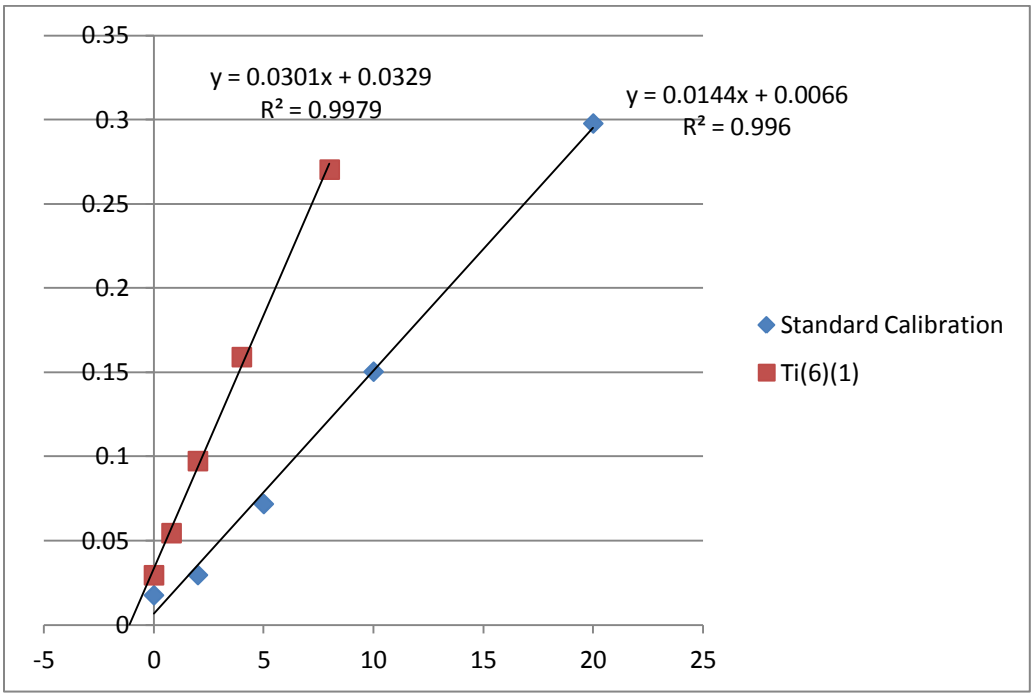
Graph plot X



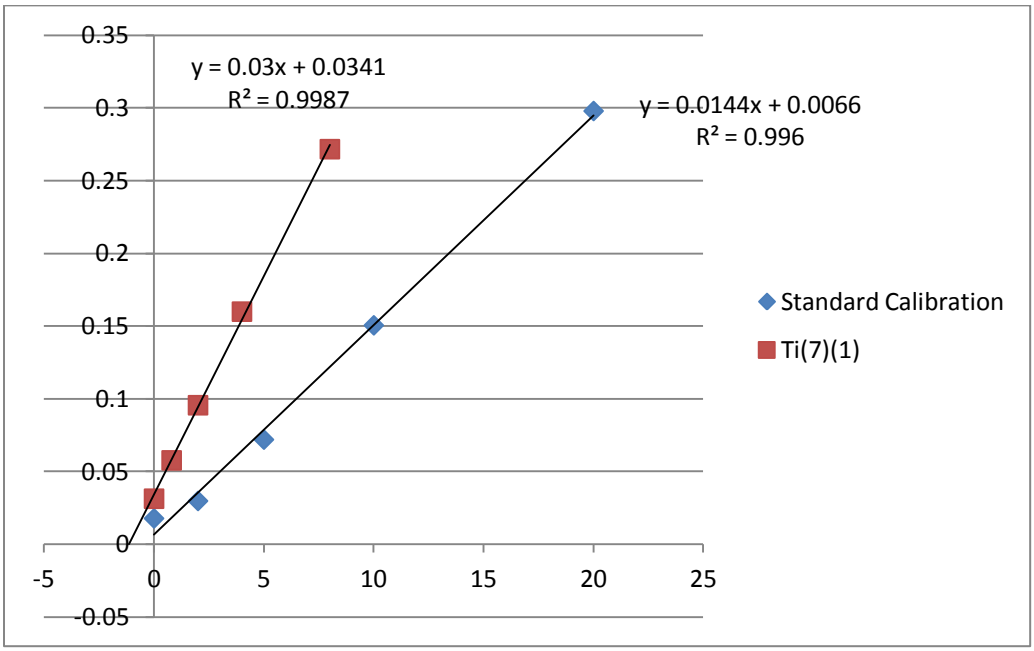
Graph plot Y



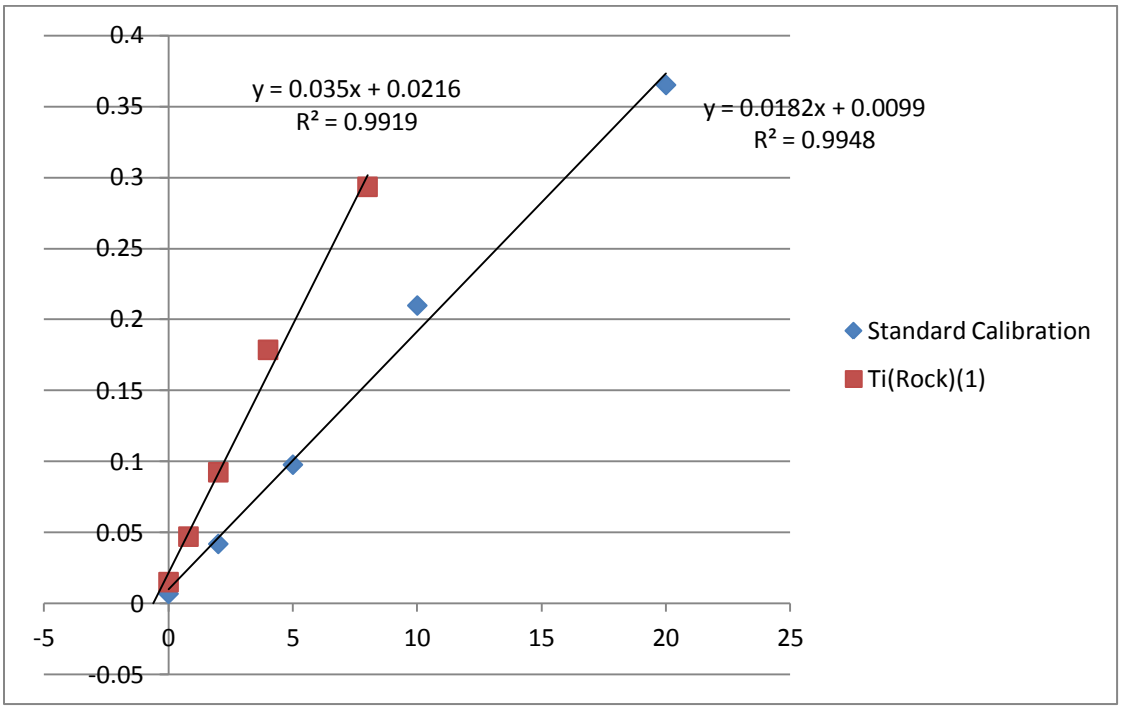
Graph plot Z



Graph plot AA

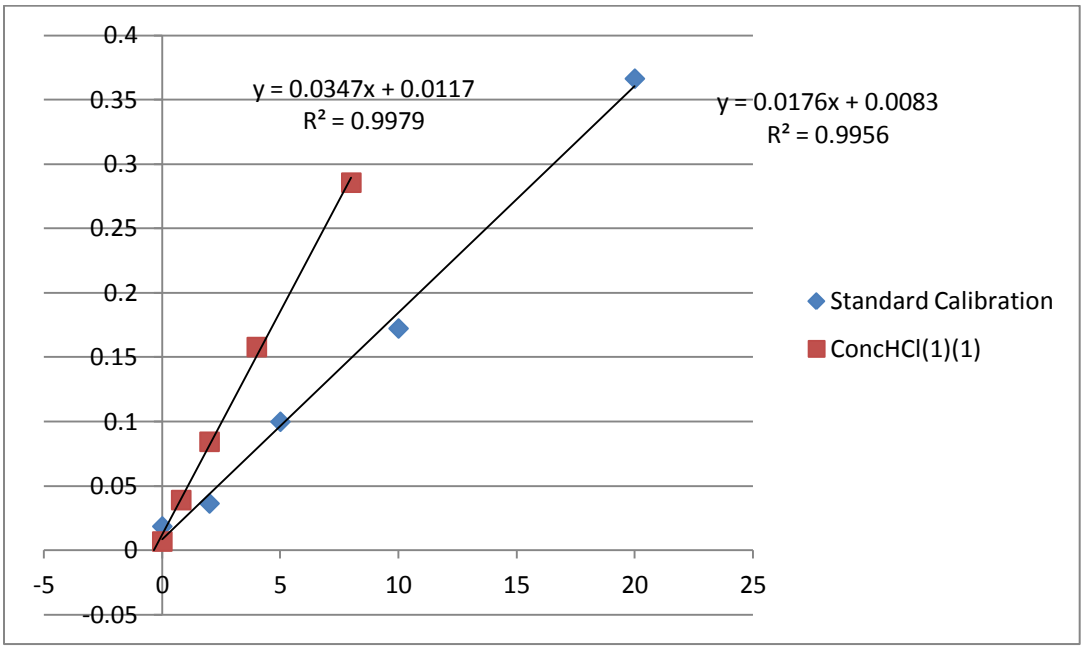


Graph plot AB

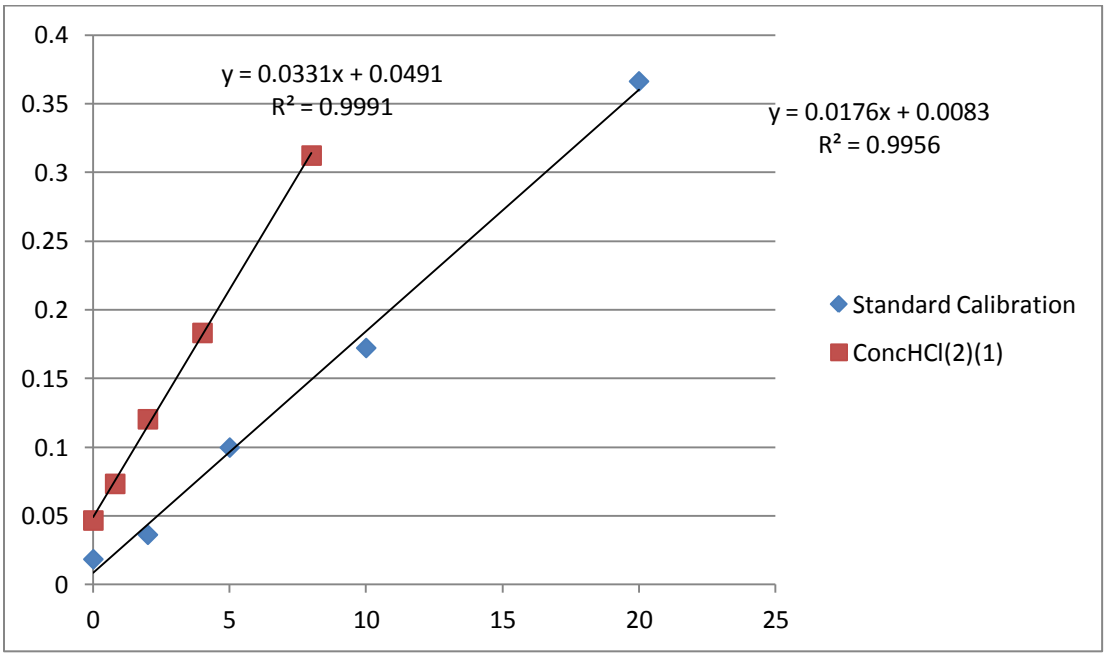


Conc.HCl step

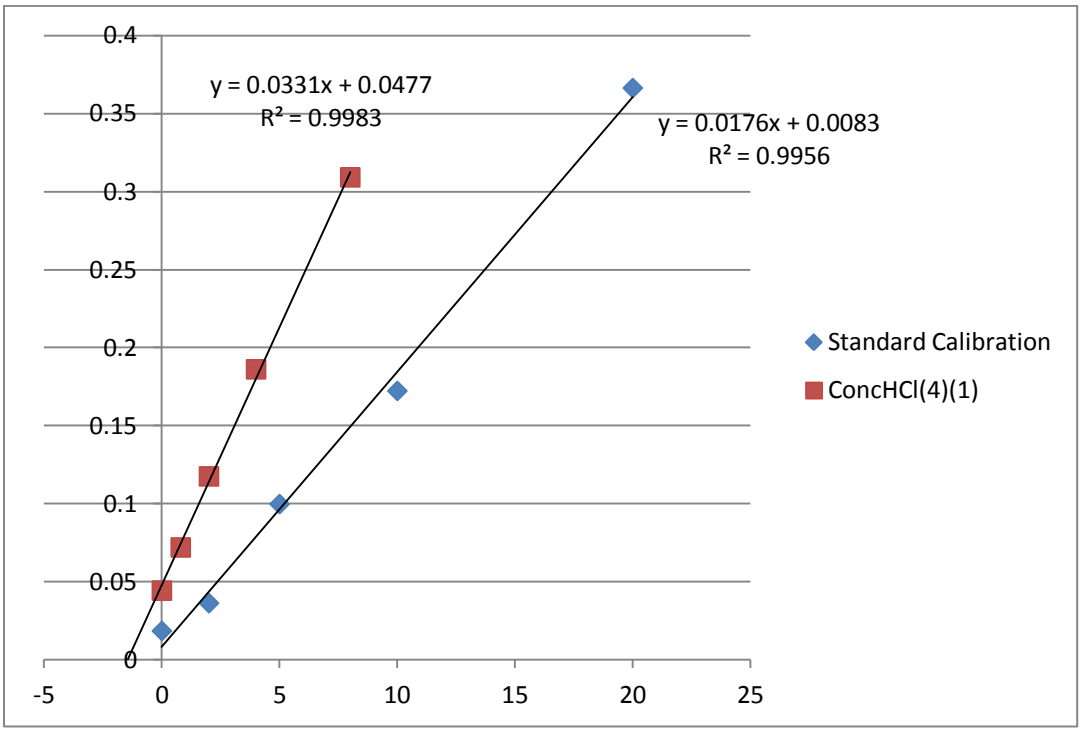
Graph plot AC



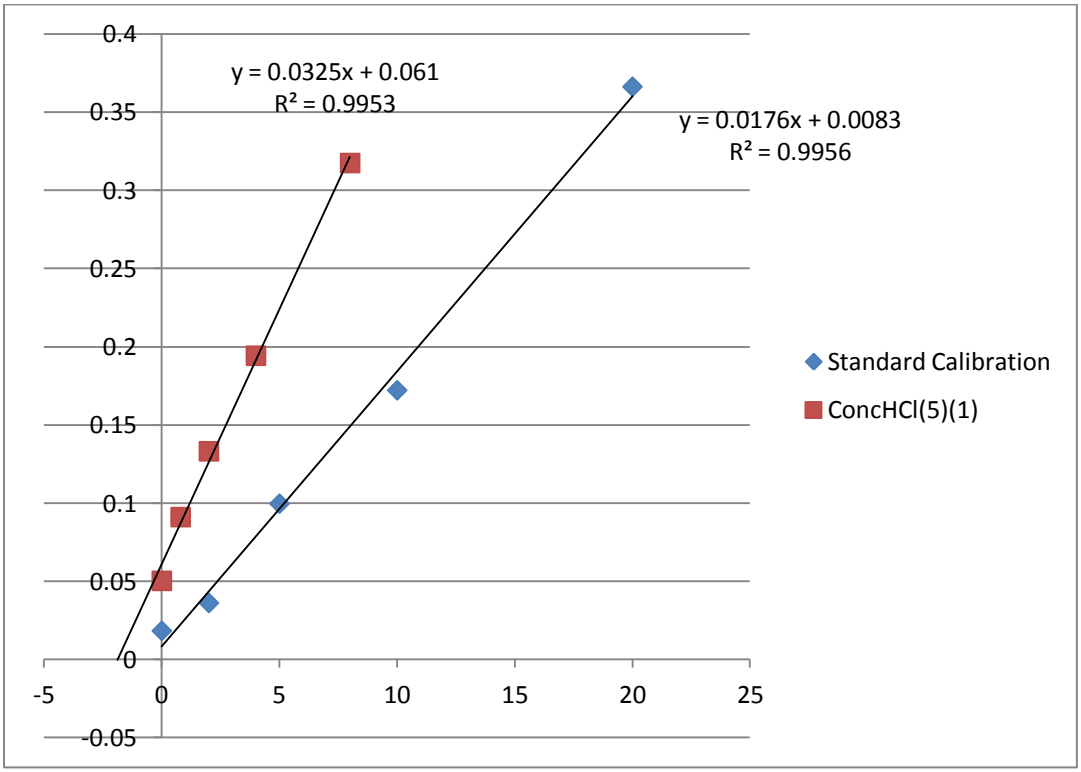
Graph plot AD



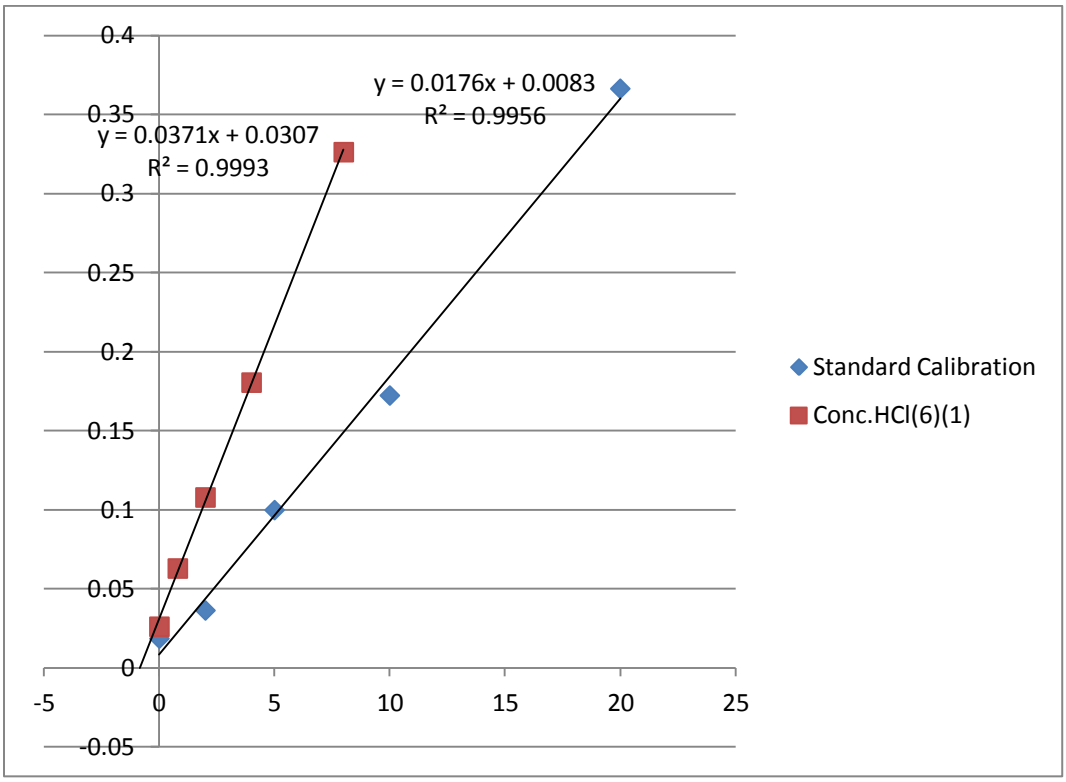
Graph plot AE



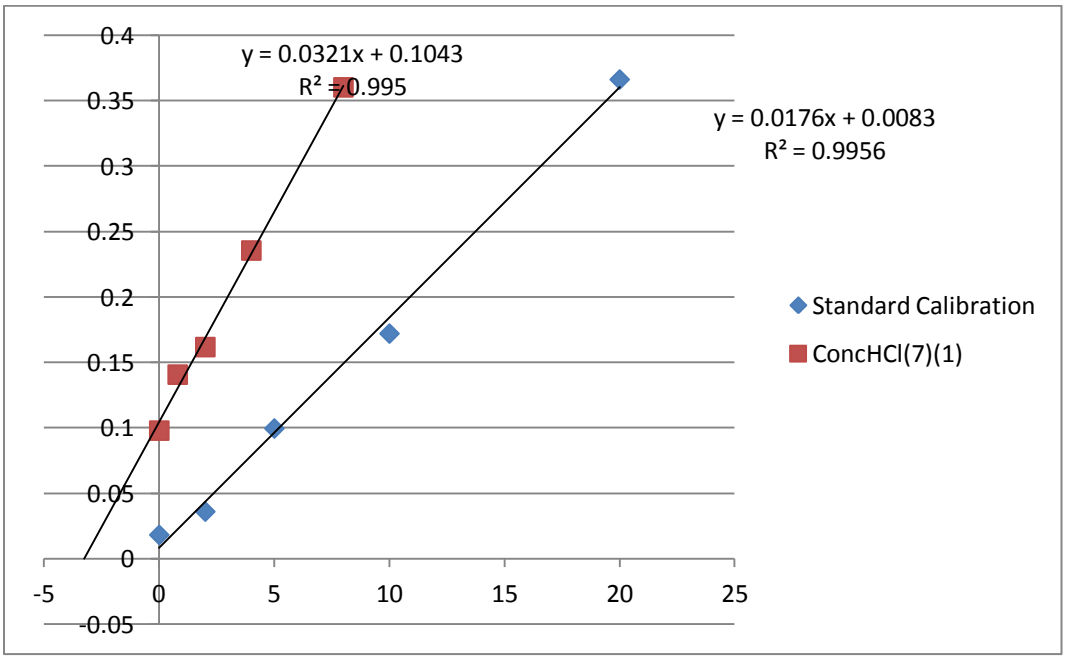
Graph plot AF



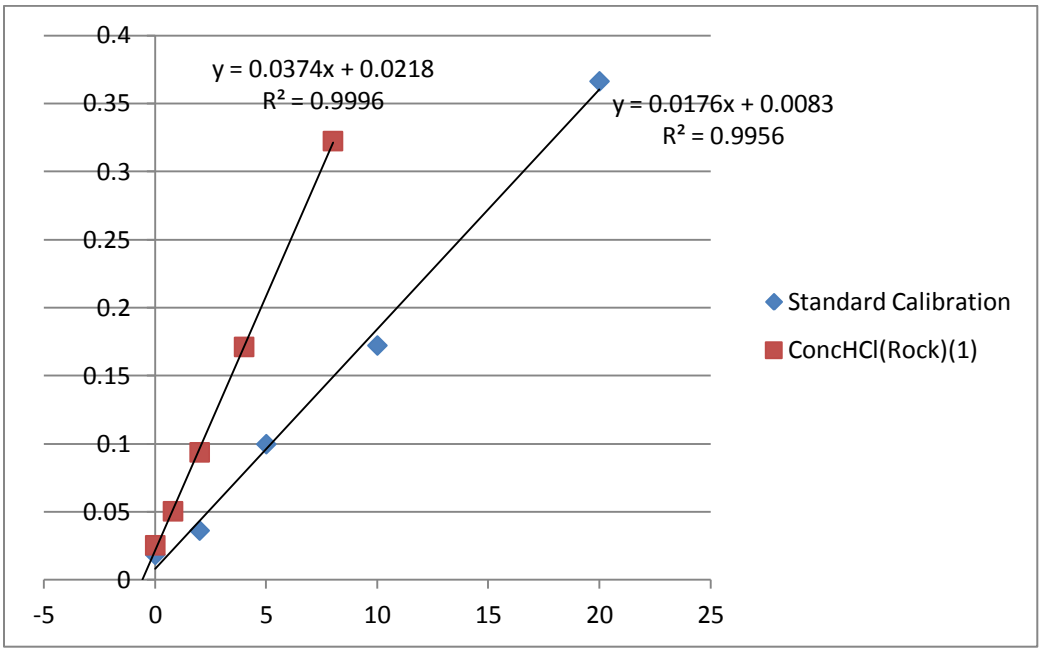
Graph plot AG



Graph plot AH



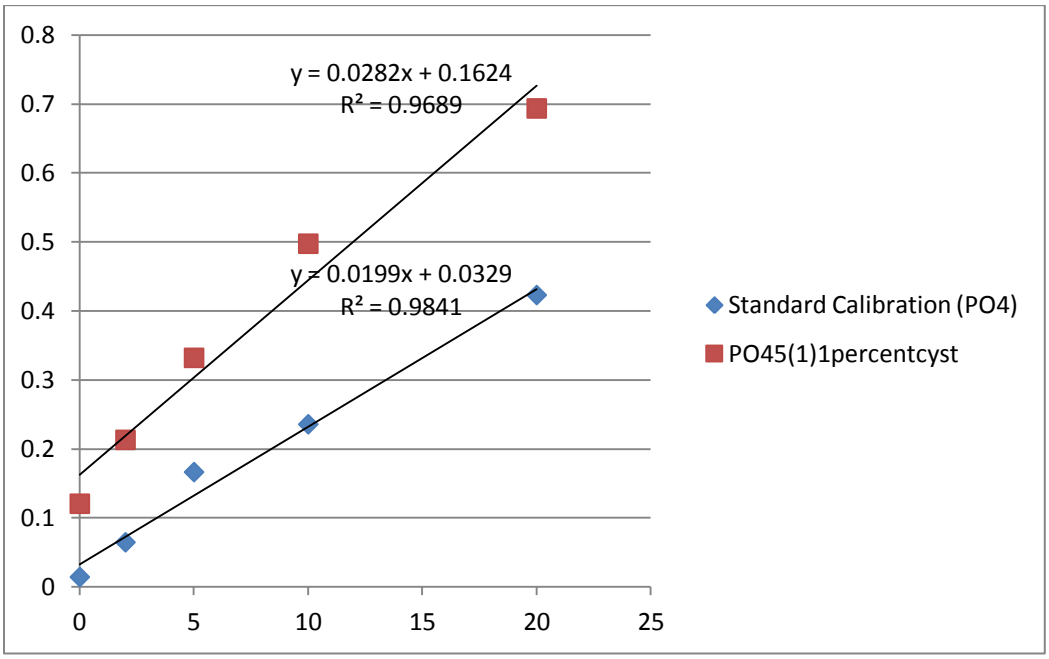
Graph plot AI



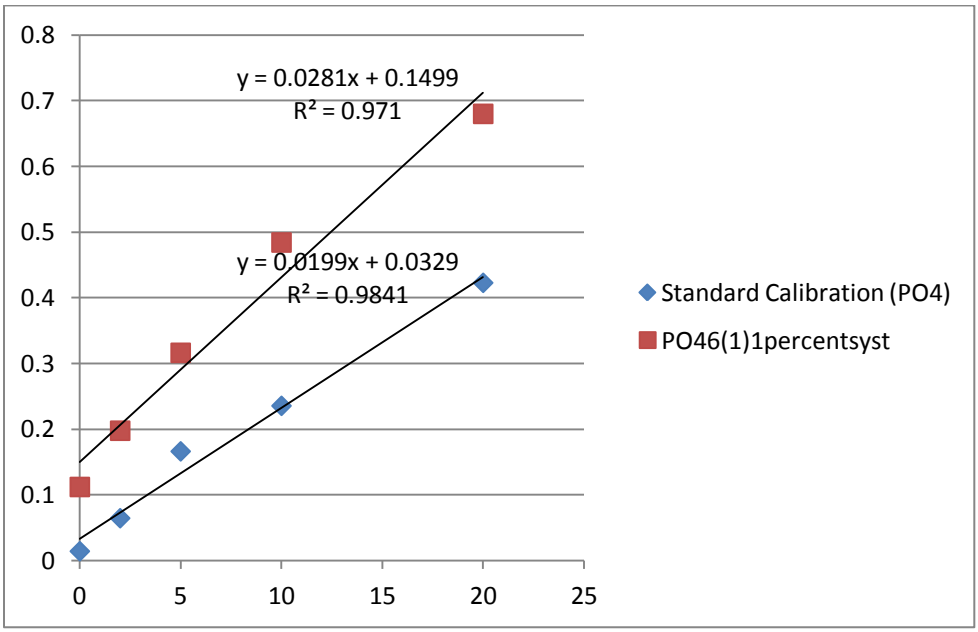
(9.2.2) As (Standard addition graph plot with 1% cysteine added to each sample)

PO4 step

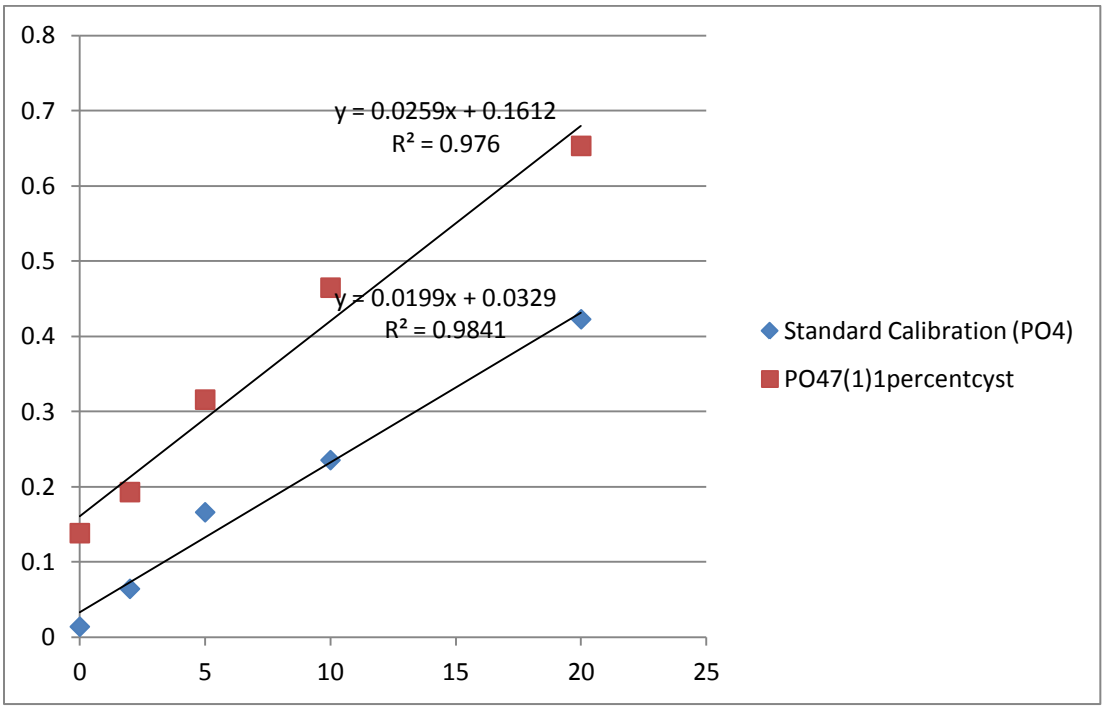
Graph plot AJ



Graph plot AK

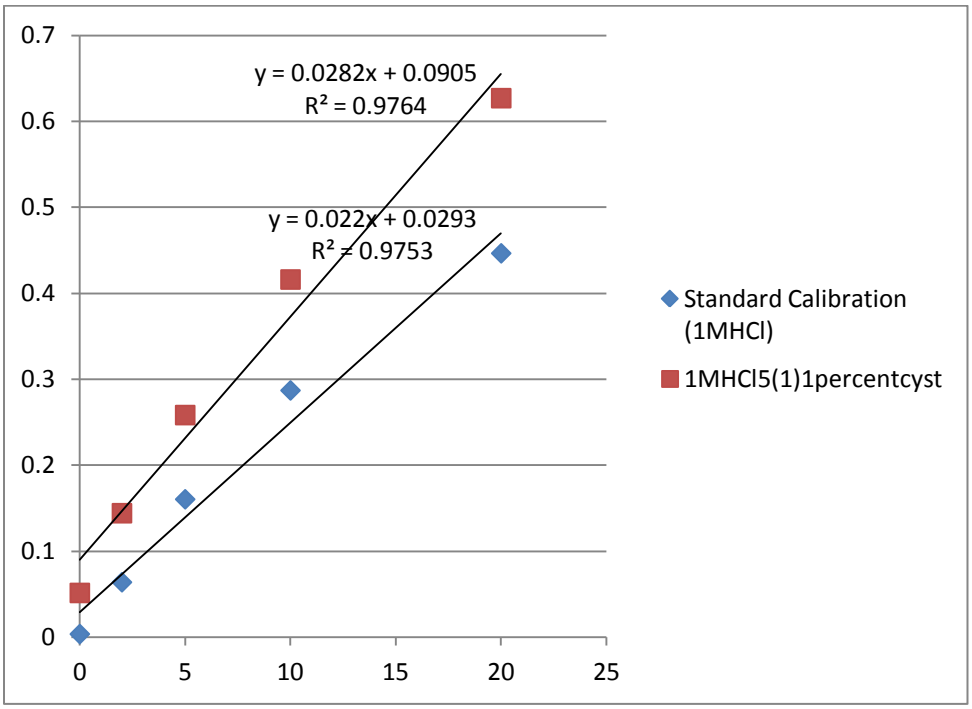


Graph plot AL

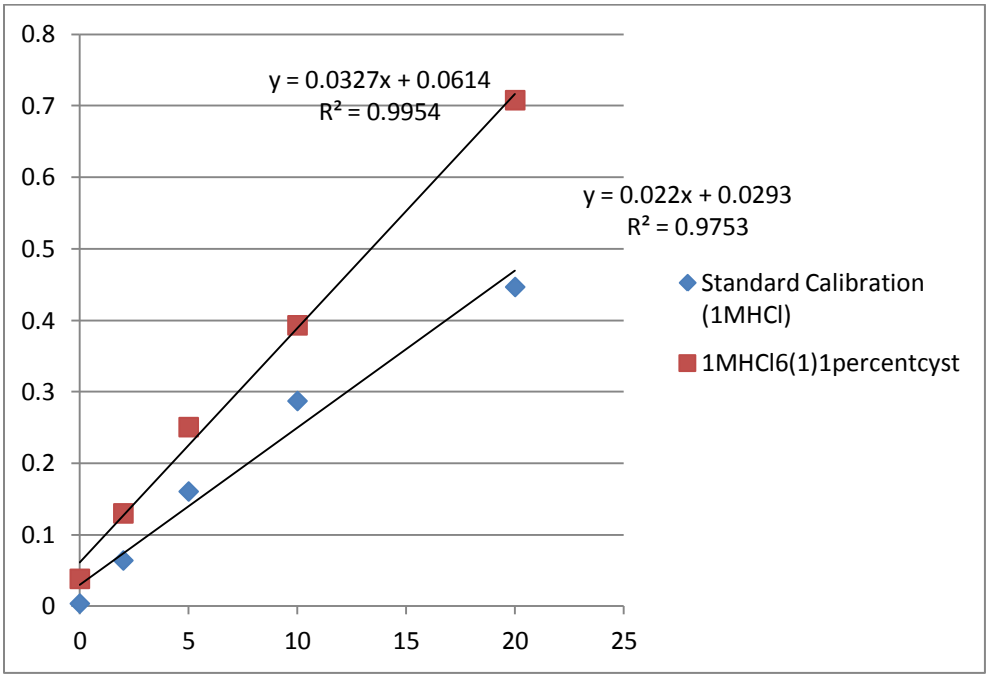


1M HCl step

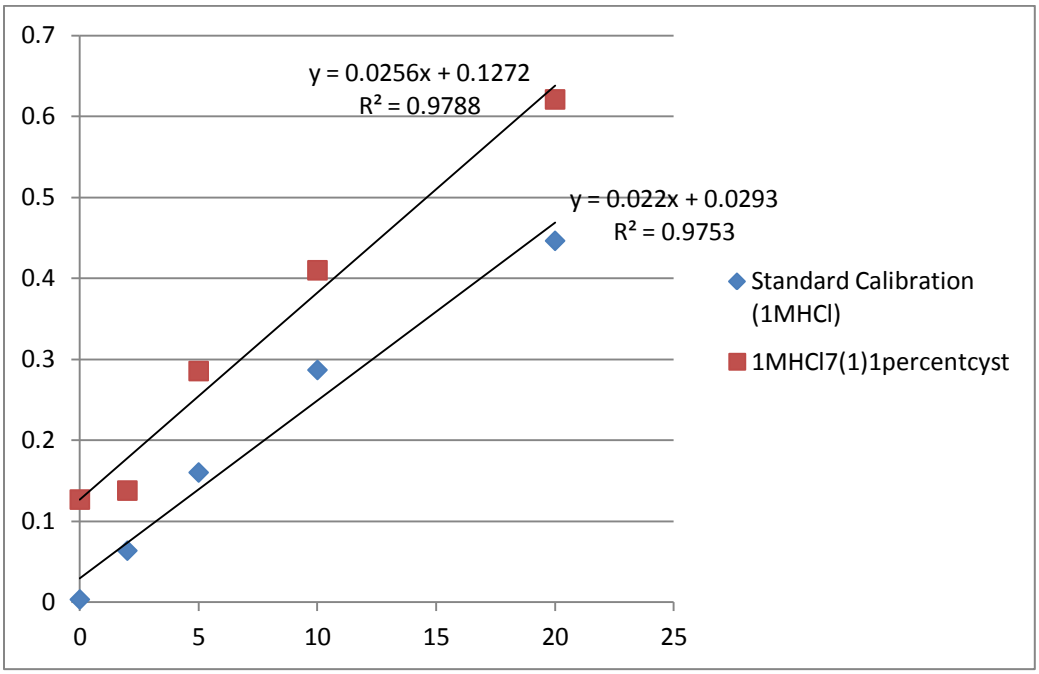
Graph plot AM



Graph plot AN

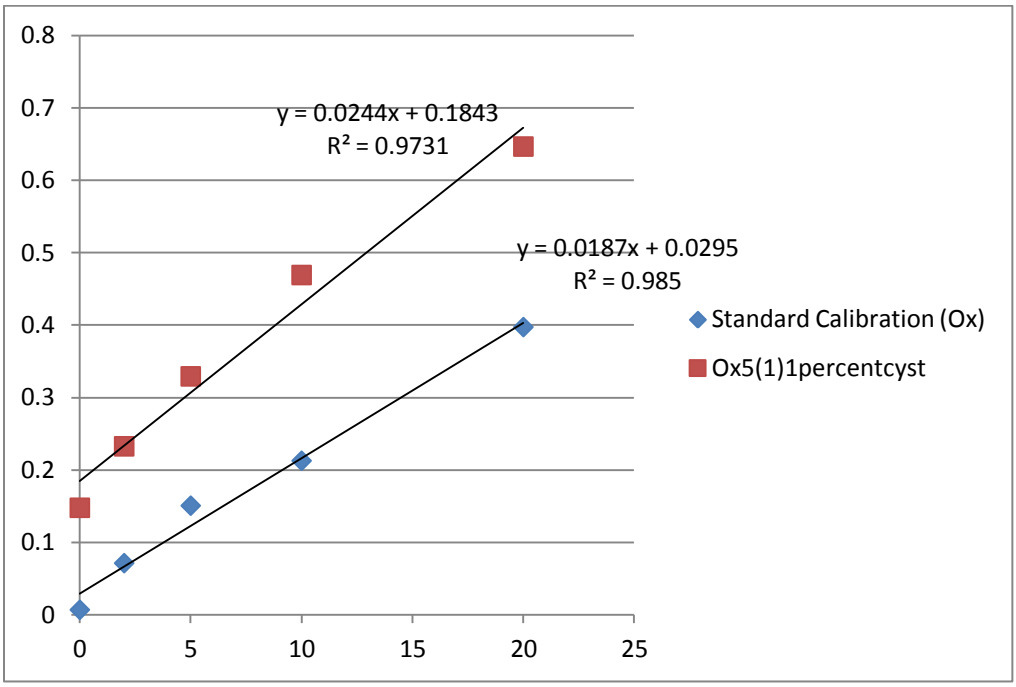


Graph plot AO

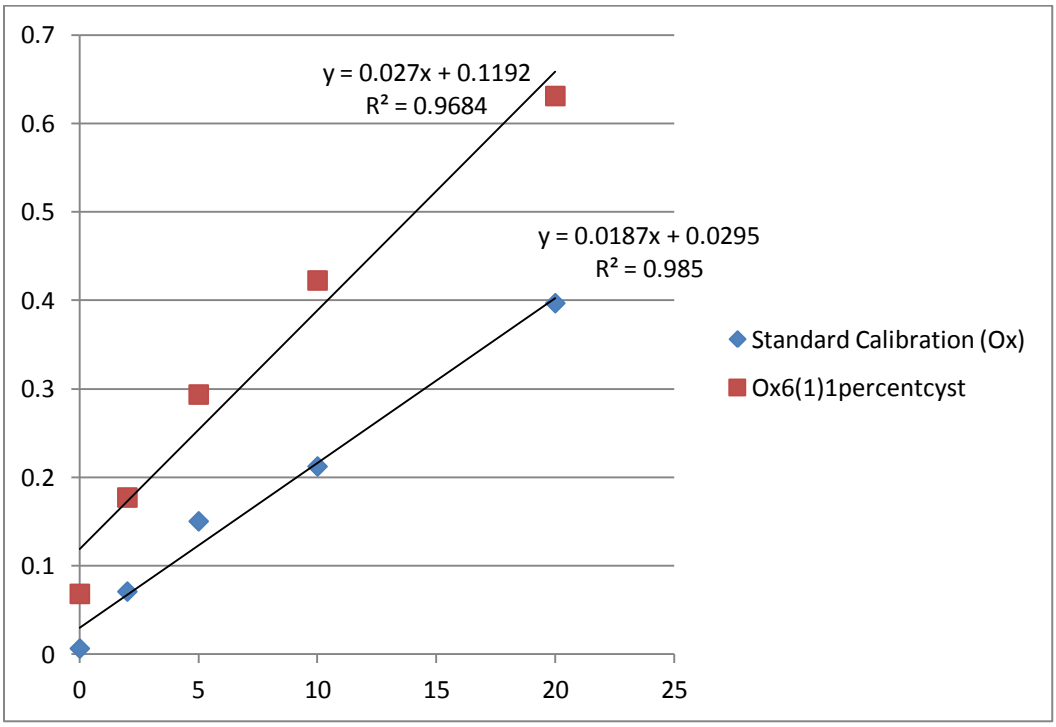


Ox step

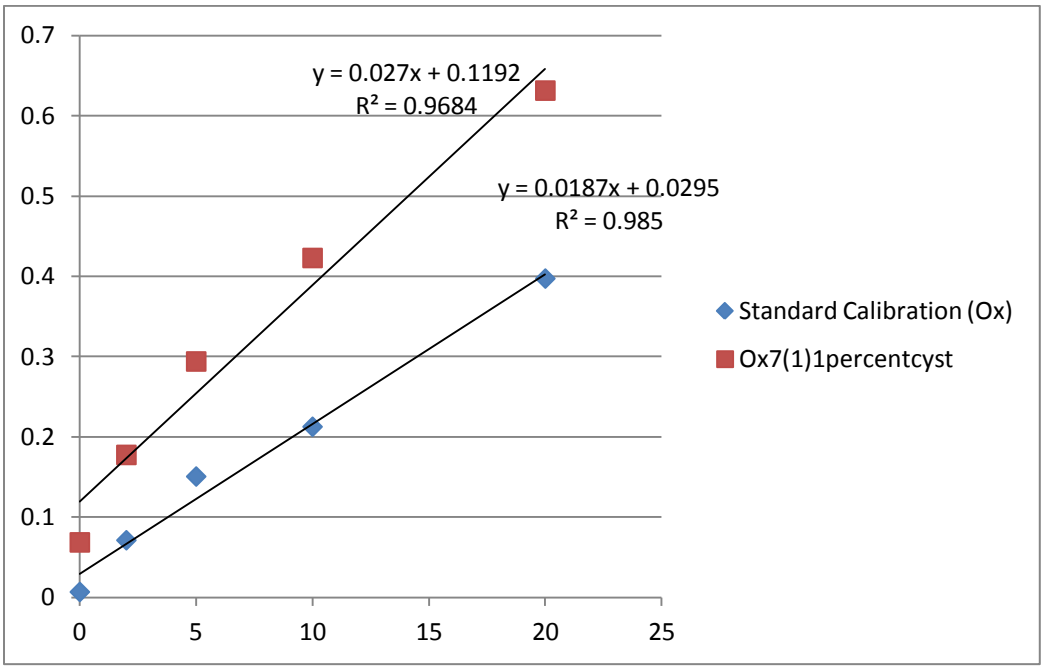
Graph plot AP



Graph plot AQ

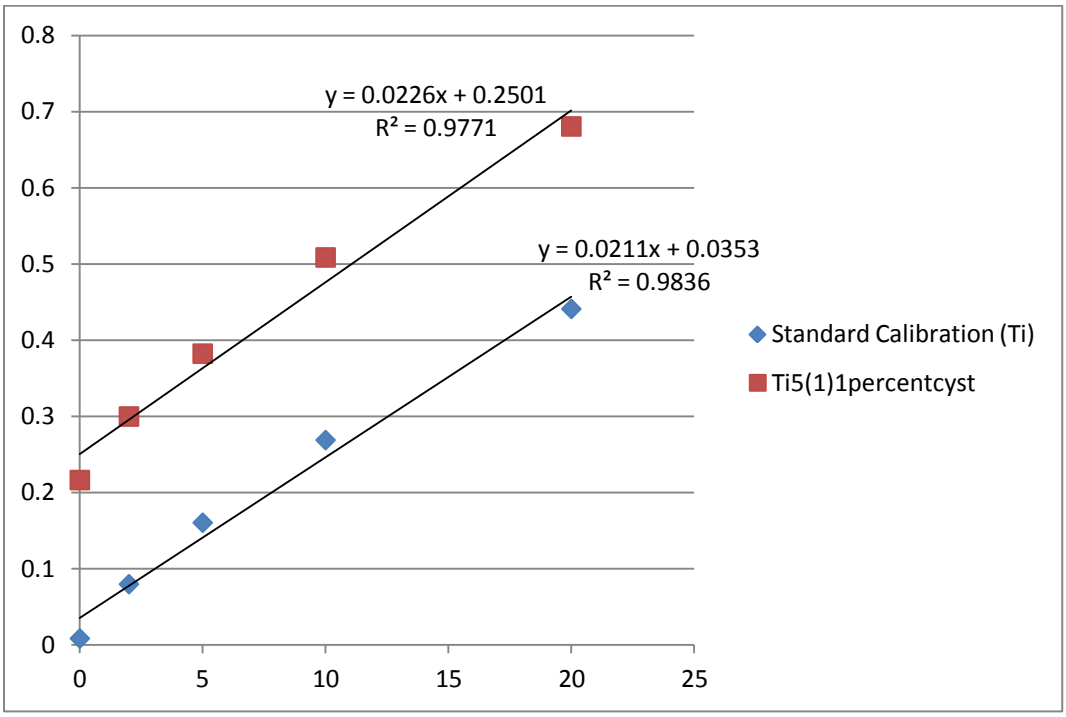


Graph plot AR

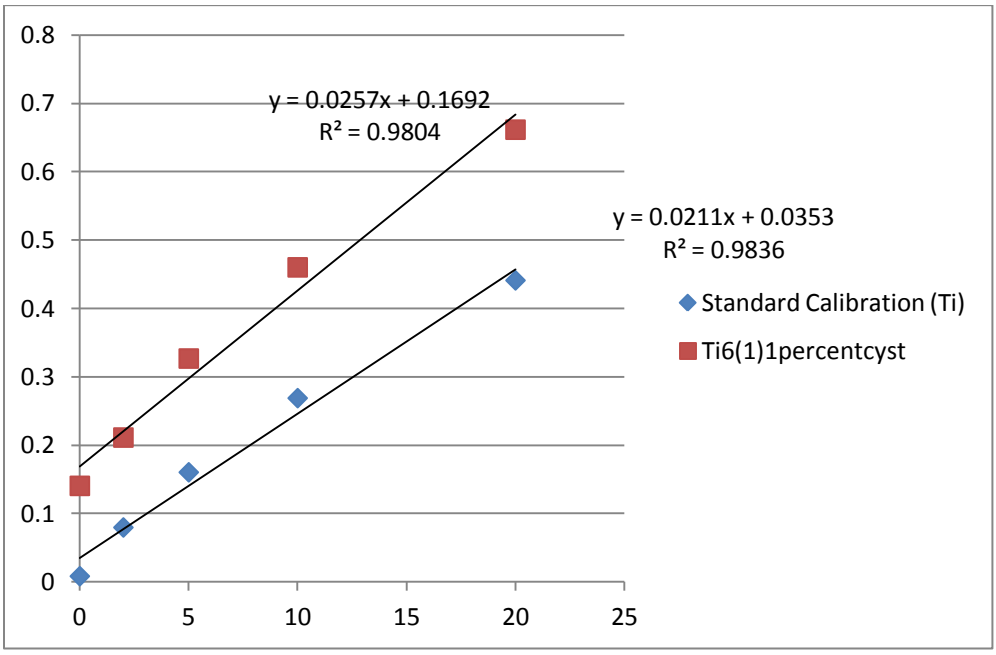


Ti step

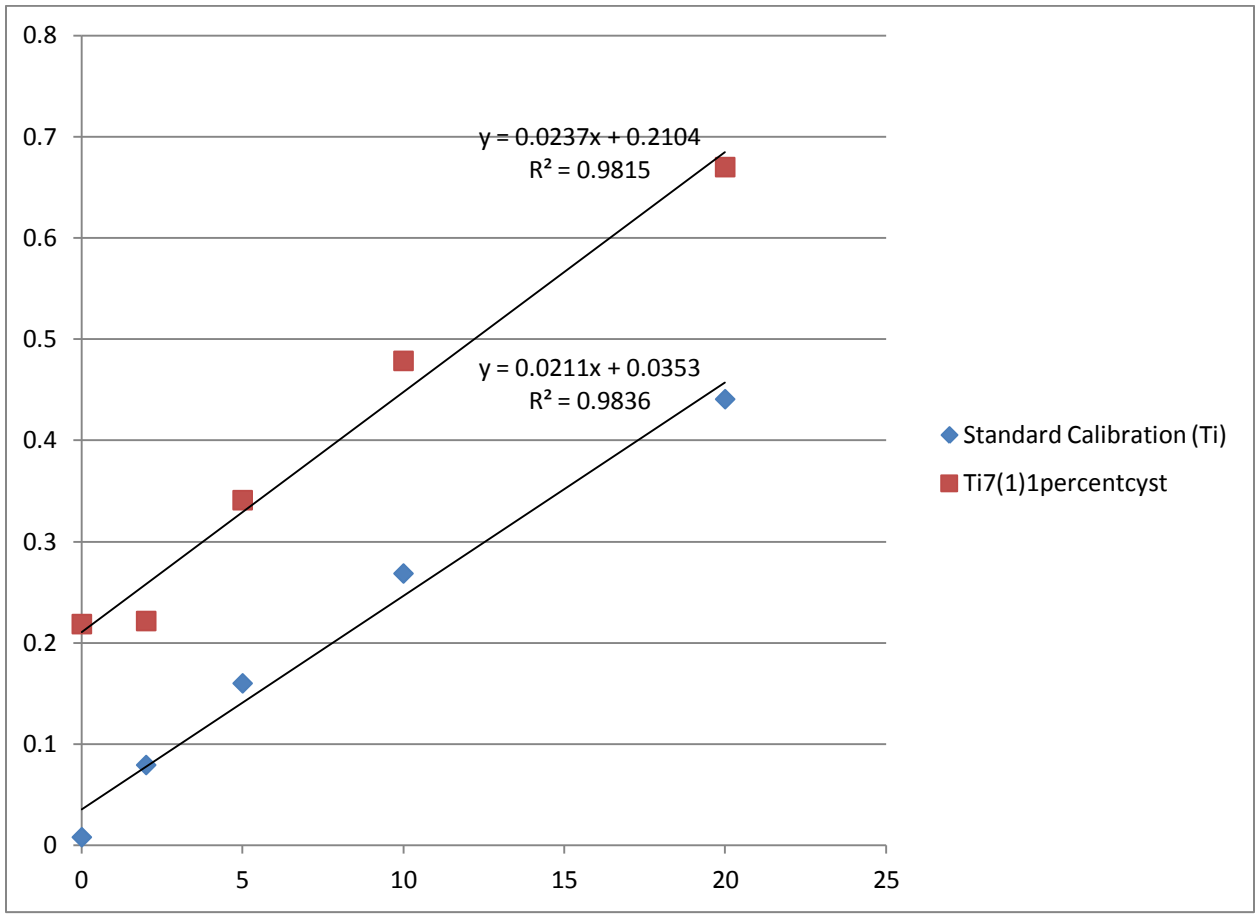
Graph plot AS



Graph plot AT

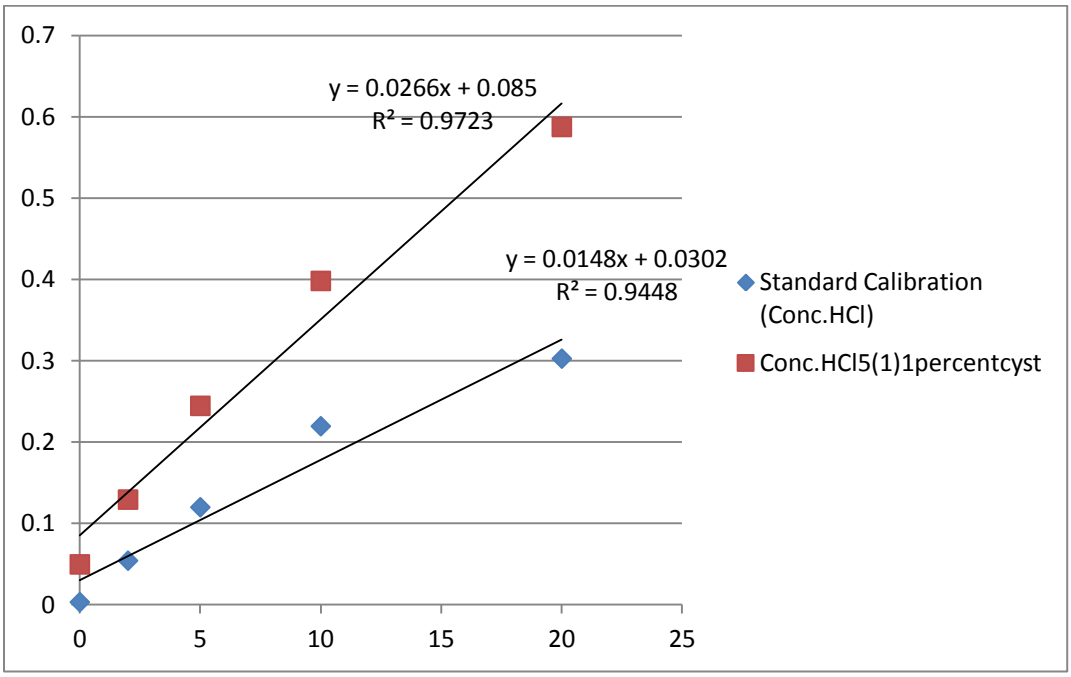


Graph plot AU

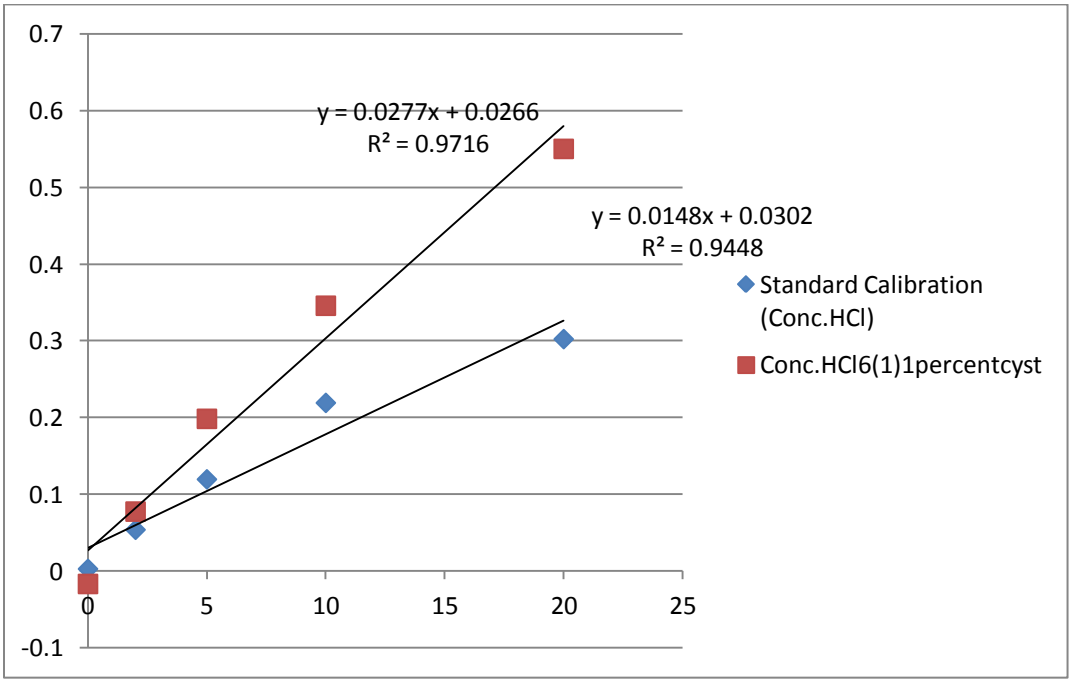


Conc. HCl step

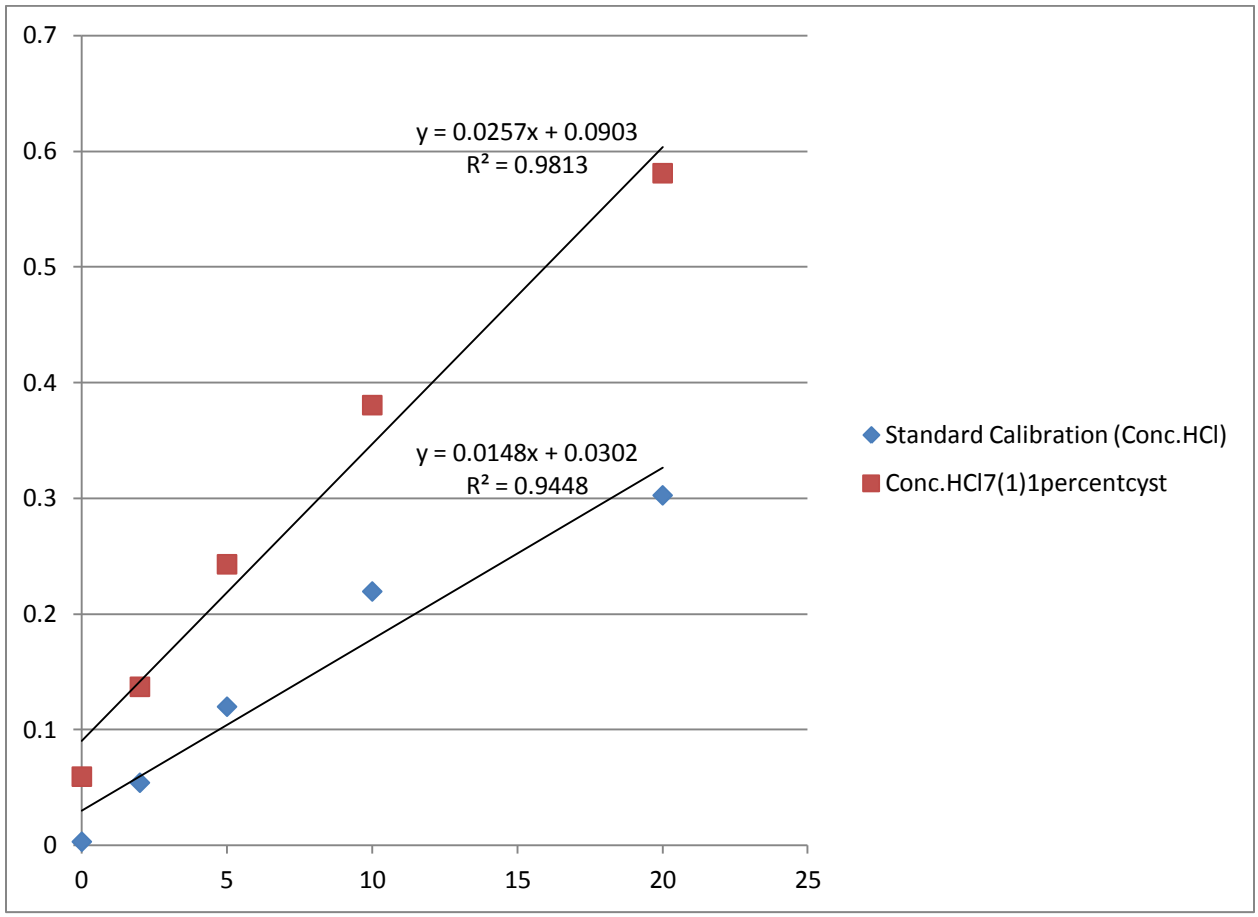
Graph plot AV



Graph plot AW



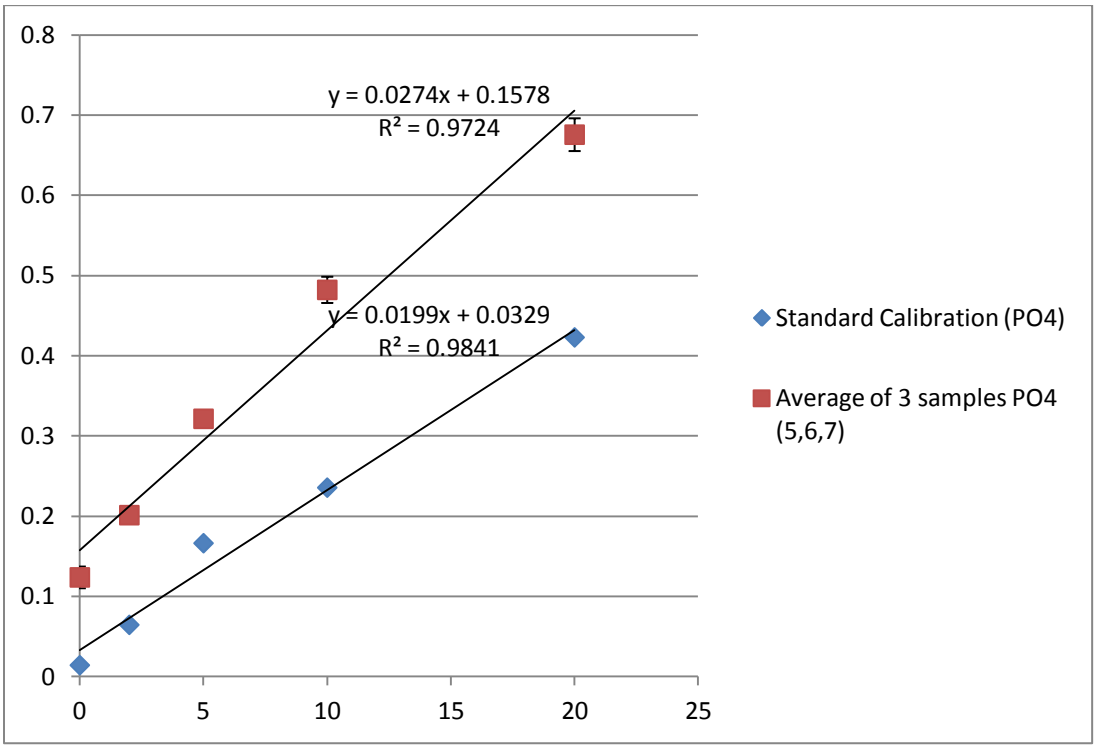
Graph plot AX



(9.2.3) As (Standard addition graph plot with 1% cysteine added to each sample)

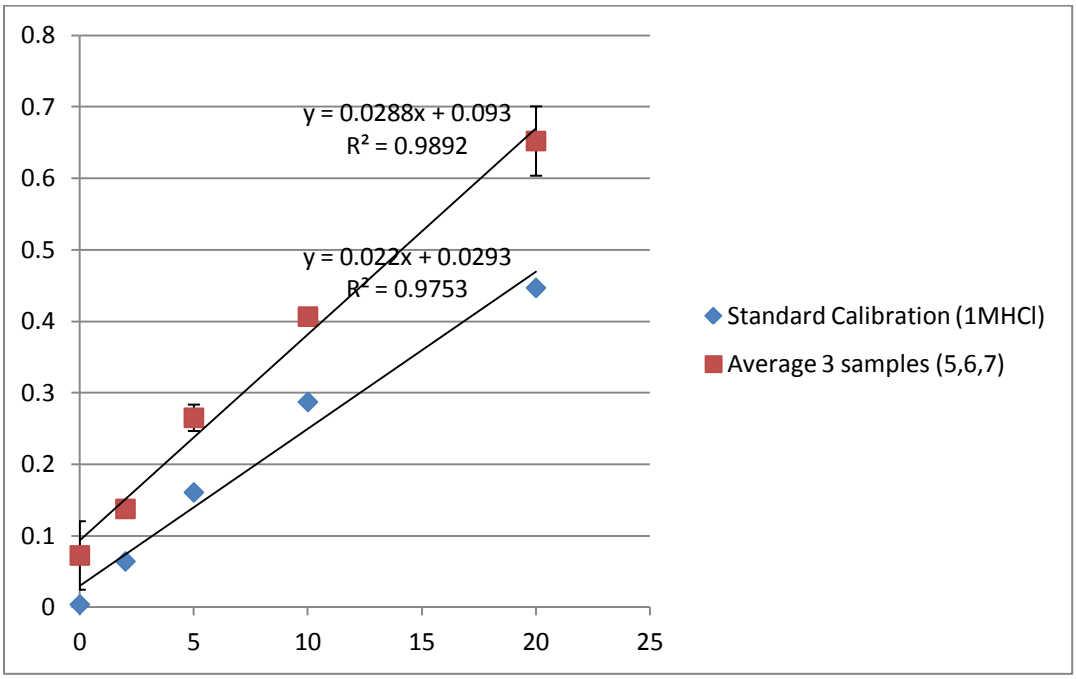
PO4 (Average of 3 sub-samples) step

Graph plot AY



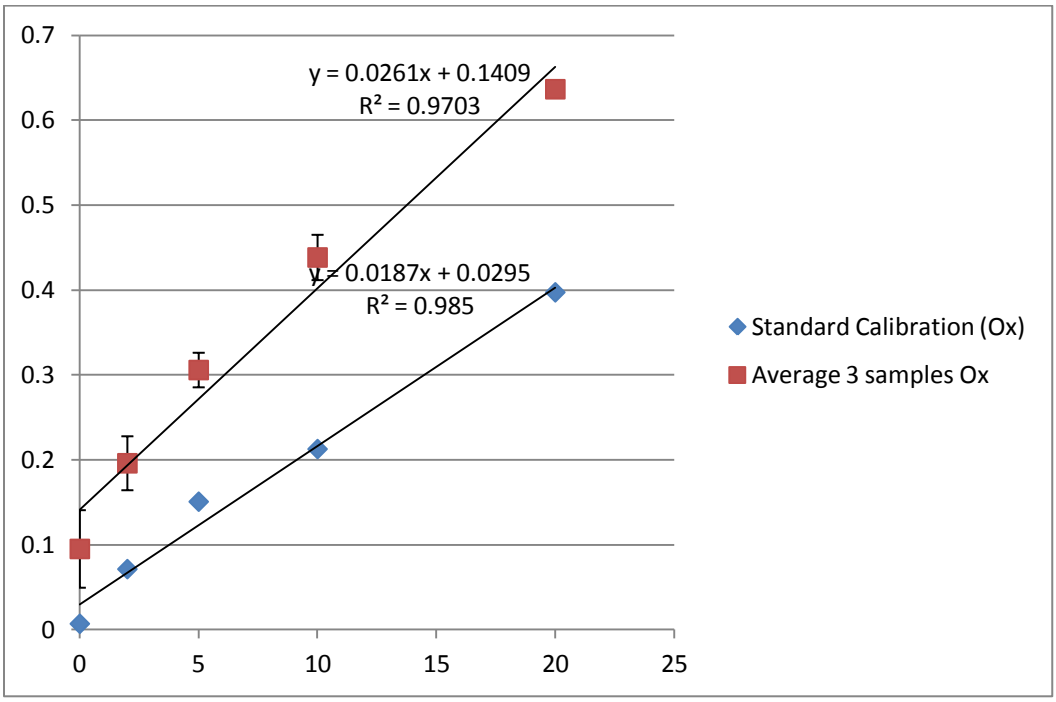
1M HCl (Average of 3 sub-samples) step

Graph plot AZ



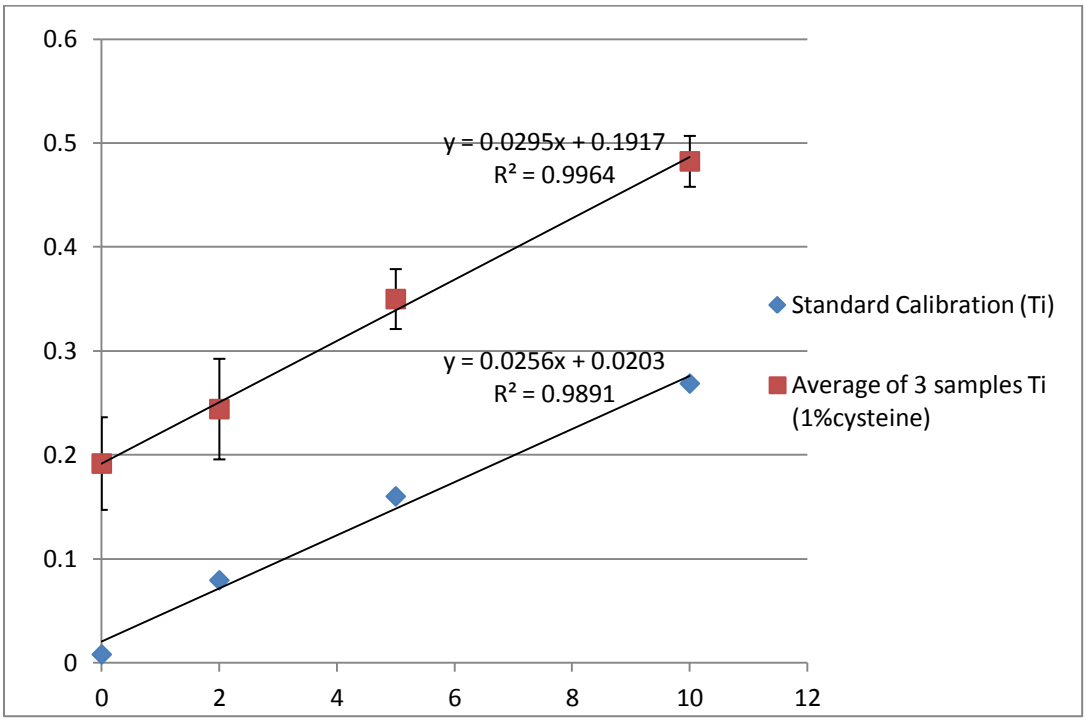
Ox (Average of 3 sub-samples) step

Graph plot BA



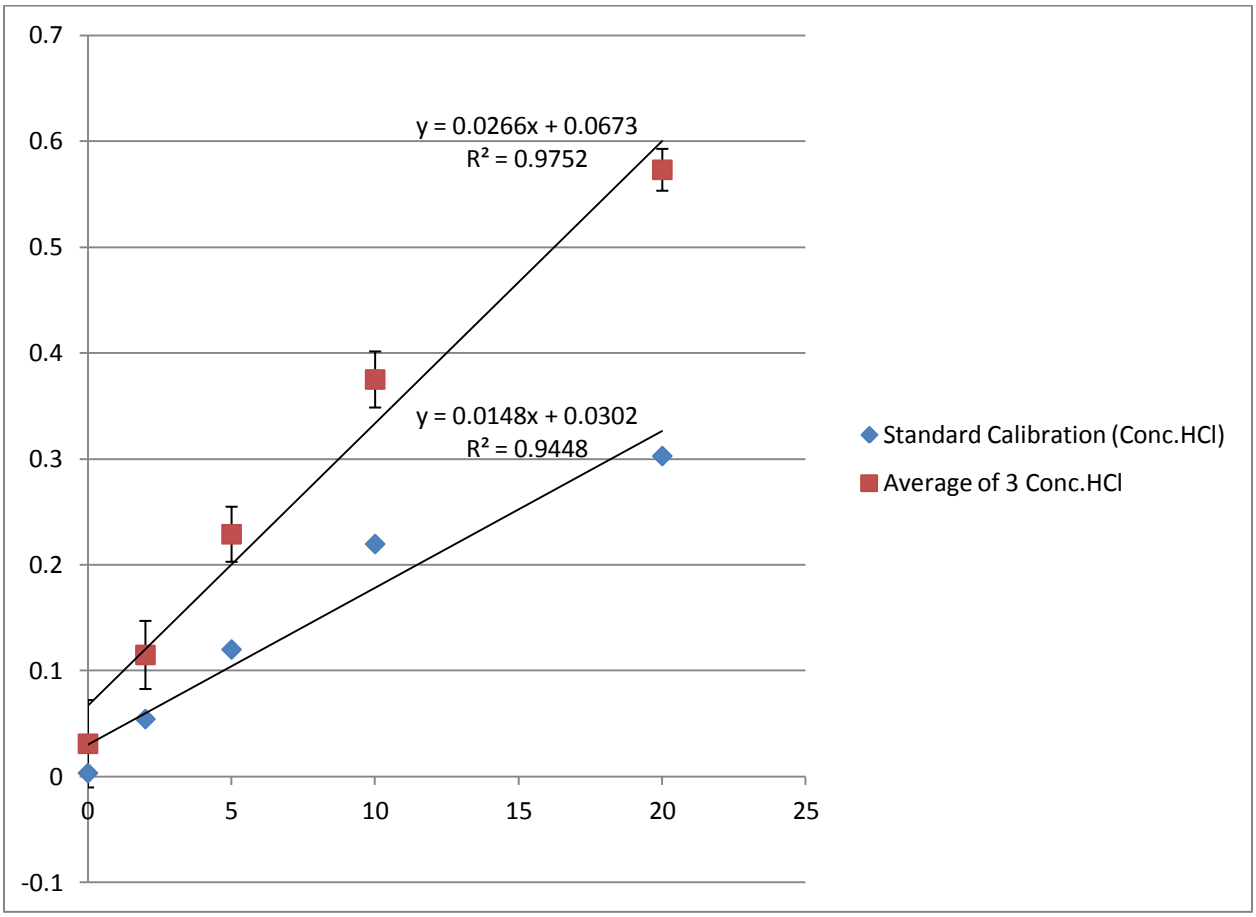
Ti (Average of 3 sub-samples) step

Graph plot BB



Conc. HCl (Average of 3 sub-samples) step

Graph plot BC



(9.3) Appendix C

(9.3.1) Instrumentation

(1) Atomic absorption spectroscopy :

Varian SpectrAA-300, PSC-56 Programmable Sample Changer, GTA-96 Graphite Tube Atomizer, $NaBH_4$, flow-rate 1.2 ml/min; sample flow-rate 11.0 ml/min

Table (9.3.1.1): Parameters of hydride generation pump of HG-AAS

Hydride generation pump	Varian VGA-76
Inert gas	300-400 kPa
Power	20VA, only 50/60 Hz
Sample collection tube	Tygon 2.29ID, R3607, wall 0.86
Sample collection rate	7ml/min
Reagent collection tube	Tygon 0.76ID, R3607, wall 0.86
Reagent collection rate	1ml/min

Table (9.3.1.2): Parameters of AAS instrument (Arsenic)

	Working conditions (fixed)
Lampe current	10 mA
Fuel	Acetylene
Support	Air
Flame stoichiometry	
Acetylene flow rate	1.5 litres/min
Air	3.5 litres/min

Wavelength (nm)	Slit width (nm)	Optimum working range µg/mL
193.7	0.5	3-150

Table (9.3.1.3): Parameters of AAS instrument (Iron)

	Working conditions (fixed)
Lampe current	5 mA
Fuel	Acetylene
Support	Air
Flame stoichiometry	Oxidizing
Air	3.5 litres/min

Wavelength (nm)	Slit width (nm)	Optimum working range µg/mL
372.0	0.2	1-100

Table (9.3.1.4): Parameters of AAS instrument (Manganese)

	Working conditions (fixed)
Lampe current	5 mA
Fuel	Acetylene
Support	Air
Flame stoichiometry	Oxidizing
Air	3.5 litres/min

Wavelength (nm)	Slit width (nm)	Optimum working range µg/mL
403.1	0.2	0.5-60

Table (9.3.1.5): Parameters of AAS instrument (Copper)

	Working conditions (fixed)
Lampe current	4 mA
Fuel	Acetylene
Support	Air
Flame stoichiometry	Oxidizing
Air	3.5 litres/min

Wavelength (nm)	Slit width (nm)	Optimum working range µg/mL
327.4	0.2	0.1-24

(2) X-ray fluorescence analysis:

Fa. Philips, Baujahr 2002, RFA-Spectrometer MagiXPRO, ionization energies maximum 4.0kW

(3) Disposable sterile centrifuge tube:

VWR, polypropylene, 50ml

(4) Centrifuge instrument:

Table (9.3.1.5): Parameters of centrifuge instrument

Heraeus Instruments Megafage 1.0	D-37520 Osterode Germany
Baujahr	1997
kin energie	26 kNm
Max. Drehzahl	Siehe rotor
Spannung	N/PE 230V~
Frequency	50/60 Hz
Strom	4.5A
Leistung	700W
Fabr.-Nr	256267
Bestell-Nr	75003490

(5) Filter paper:

Sartorius, Polycarbonate Track-Etch Membrane, Sartorius AG-37075, Goettingen-Germany

(6) Milli-Q water system:

SG Water, Barsbuttel, Germany

(7) Oven

MMM oven, Medcenter Einrichtungen GmbH, MMM-Group, Venticell

(8) Instrument for loss of ignition (LOI)

Arnold Schröder, Nabertherm, 1000^{o}C, Program Controller S27

(9) Inductive coupled plasma mass spectrometry (ICP-MS)

Table (9.3.1.6): Instrumental parameters of ICP-MS system

Model	HP 4500 (Agilent Technologies)	
Plasma	Radio frequency (RF) power	1200 W
	Auxiliary gas flow	1.0 L/min
	Plasma gas flow	16 L/min
	Carrier gas flow	0.9 L/min
	Nebulizer	Burington
	Spray chamber	Scott type
	Sampler cone	Ni, 1.0 mm orifice
	Skimmer cone	Ni, 0.7 mm orifice
Acquisition	Mode	Spectrum
	Replicates	10
	Isotopes monitored	^{203}Tl, ^{205}Tl, ^{103}Rh
Plasma source	Argon gas 99.996 Vol-%	Westfalen AG, Münster, Germany

COSHH Assessment

1) Supra pure concentrated hydrochloric acid 30%, Merck, corrosive H2
2) Titanium chloride ($TiCl_3$,15%) in 10% HCl for synthesis, Merck, corrosive H2
3) Sodium borohydride ($NaBH_4$), pro analysis, Merck, H2
4) Potassium Iodide (KI), pro analysis, Merck, H2
5) Ascorbic acid (L+), Merck, corrosive H2
6) Sodium hydroxide (NaOH), pro analysis, Merck, irritant H2
7) Ethylenediaminetetraacetic acid (EDTA), in tetrasodium salt dehydrate, Fluka, irritant H2
8) Hydroxylamine hydrochloride, p.a. > 99.0%, Fluka, harmful H2
9) Sodium phosphate, Acro's monobasic for analysis, anhydrous, Acros organics, H2
10) Citric acid, anhydrous for synthesis, Merck, corrosive H2
11) Ammonium oxlate, pro analysis, Merck, H2
12) Oxalic acid, pro analysis, Merck, H2
13) Sodium dithionite, pro analysis, Merck, H2
14) Ammonium nitrate, pro analysis, Merck, H2
15) Arsenic solution standard, 1000 mg/l, Merck, toxic H2
16) Manganese solution standard (in $MnCl_2 \cdot 4H_2O$), 1000 mg/l, Riedel-de Häen, H2
17) Iron solution standard (in $FeCl_2 \cdot 2H_2O$), 1000 mg/l, Riedel-de Häen, H2
18) Copper solution standard (in $CuCl_2 \cdot 2H_2O$), 1000 mg/l, Riedel-de Häen, H2
19) Thallium solution standard, 1000 mg/l, Merck, toxic H2
20) Rhodium solution standard 1000 mg/l, Merck, toxic H2

(10.0) Curriculum vitae (CV)

Personal details

Name: Mr. Ka Hei Lui

Date of birth: 29/05/1979

Nationality: Hong Kong

Tel: (+49)-(0)-160-9974-6317

Email: lui@uni-mainz.de

Address: Wittichweg 45, Zimmer 212, 55128 Mainz, Germany

Education background

2008-2011 PhD in Geochemistry

University of Mainz, Germany

PhD thesis: Speciation of Metals in Agricultural Lime and Contaminated Soil

2006-2007 MSc Master of Science in Chemical Process Engineering

UCL, University of London, U.K.

2000-2004 MChem (Hons) Master of Environmental Chemistry with Industrial Experiences

University of Edinburgh, U.K.

Professional Memberships

Royal Society of Chemistry (RSC), UK – Associate Member (Pending)

Institution of Chemical Engineers (IChemE), UK – Affiliate Member (Pending)

Peer-refereed publications

(1) Gerald T. Schmidt, Ka Hei Lui, Michael Kersten, 2009. Speciation and mobility of arsenic in agricultural lime. Journal of Environmental Quality 38, 2058-2069

(2) Michael Kersten, Tatiana Y. Reich, Ka Hei Lui, Gerald T. Schmidt, Jörg Göttlicher. Speciation of copper enriched in agricultural lime. Soil Science Society of America Journal Vol. 75, No.2, 509-520, March-April, 2011

Report case studies

(1) To: "An das Oberlandesgericht Hamm, z.H. Herrn Richter Serwe, Heßlerstr. 53, 59065 Hamm, Deutschland. Sachverständigengutachten, im Rechtsstreit Kohnhorst ./. Dyckerhoff AG, Geschäftsnummer: I-24 U 131/07.

(2) To: "An das Landgericht Münster, z.H. Herrn Richter Dr. Terhan, Am Stadtgraben 10, 48143 Münster, Deutschland. Sachverständigengutachten, im Rechtsstreit Meyer ./. Dyckerhoff AG, Geschäftsnummer: 011-O-530/04.

Presentations

(1) G. T. Schmidt, K. H. Lui, M. Kersten. Speciation and mobility of arsenic in agricultural lime. Journal of Environmental Quality. Oral presentation in Ebernburg GRK 826/3 meeting, November 2008, Mainz, Germany.

(2) Michael Kersten, Tatiana Y. Reich, Ka Hei Lui, Gerald T. Schmidt, Jörg Göttlicher, 2010. Speciation of copper enriched in agricultural lime. Soil Science Society of America Journal. Oral presentation in Ebernburg GRK 826/3 meeting, November 2009, Mainz, Germany.

Employment

Apr 08-Apr 11	Research Chemist
	German Science Foundation (DFG-GRK 826)
Sept 05-Sept 06	Laboratory Attendant
	Island School, The English School Foundation, Hong Kong
Sept 04-Sept 06	Sales Executive
	Euro Sofa Mondo, Hong Kong
Aug 02-Aug 03	Research Chemist
	Syngenta, Grangemouth Manufacturing Centre, Scotland
Jun-Sept 01& 04	Personal Assistant Fiona Paton Design, Hong Kong

Languages

Fluent in Cantonese and English. Average and basic skills in Mandarin and German.