POTENTIALLY TOXIC ELEMENTS IN AGRICULTURAL SOIL OF THE KURDISTAN REGION OF IRAQ AND IMPLICATIONS FOR HUMAN HEALTH

By

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Dedication

This work is dedicated to;

My parents for their encouragements

My wife for her patience

My daughter and son

Karzan

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Abstract

A rapidly increasing human population has resulted in the expansion of urban areas and an associated increase in the demand for food . Consequently, urban and peri-urban agriculture (UPA), using waste water as a source for irrigation, is increasingly common around the world, particularly in developing countries. Although UPA plays a crucial role in supplying food to urban populations, the quality of that food may be affected by accumulation of potentially toxic elements (PTEs) in the soil and the food chain.

The aim of this study was to assess potentially toxic element (PTE) contamination in soils and vegetables grown in the Kurdistan region of Iraq. Specific objectives included (i) to measure the total concentrations, mobility and bioavailability of PTEs using isotopic dilution approaches (E- and L-values) and single- and sequential-extraction procedures (ii) to compare these different metrics to determine the best assay for soils in Kurdistan and (iii) to investigate the potential human health risks from consumption of contaminated vegetables by estimating dietary intake and hazard quotients (HQs).

Overall, the concentration of PTEs were noticeably higher in waste disposal areas and progressively lower in urban, peri-urban and rural areas, with the exception of Ni concentrations which were high at all study sites, reflecting the geological background of the region. However, the total metal concentration does not represent the 'bioavailable' fraction of an element - chemical extractions such as DTPA, sequential extractions and measurements of isotopically-exchangeable metal may better represent bioavailable PTEs. DTPA-extractable and isotopically-exchangeable metals (E-value) were typically low for Ni (2.89, 0.629 mg kg^{-1}), Cu (4.76, 1.98 mg kg^{-1}), Zn (12.9, 9.92 mg kg^{-1}), Cd (0.144, 0.066 mg kg^{-1}) and Pb (5.03, 2.13 mg kg^{-1}), but the metals were more labile in soils in waste areas compared to urban, peri-urban and remote areas. Sequential extraction suggested that most PTEs were in the residual fraction with the exception of Se, Cd and Pb which were in the organic matter, carbonate and Fe/Mn oxide fractions, respectively.

PTE concentrations in the edible parts of vegetables collected from the study sites varied between vegetable types and site. Higher total concentrations of PTEs were measured in vegetables from the waste areas with decreasing concentrations in urban, semi-urban and rural areas. Concentrations of Ni and Cu exceeded recommended UK and WHO/EU limits (0.5 mg kg^{-1}Fw) in almost all vegetables except for tomato, okra and cucumber for Ni, while limits for As were exceeded in fruit vegetables from waste areas and leafy vegetables in waste, urban and peri-urban areas. Concentrations of Cd were above recommended limits in all vegetables except for cowpea and cucumber at all sites. The concentration of Pb exceeded the limits in okra, cow pea, leek, celery and chard in waste, urban and peri-urban areas.

An experiment growing vegetables in pots under controlled conditions was established to evaluate the ability of plants to accumulate PTEs by estimating the isotopically-exchangeable metal pool in plants (L-values). Results gave similar L-values for different vegetable types ranging from 7.70 mg kg^{-1} in chard to11.0 mg kg^{-1} in radish leaf for Ni, 44.2 mg kg^{-1} in lettuce to 51.8 mg kg^{-1} in celery for Zn and 0.0912 mg kg^{-1} in lettuce to 0.0992 mg kg^{-1} in chard for Cd. The L- values of trace elements in plant roots were higher than those obtained for the shoots in the vegetables. A comparison between DTPA, E- and L-values was made and the results demonstrated that L-values were higher.

Risks to human health were assessed using hazard quotients (HQ) assuming intakes of 0.187 kg FW d^{-1} for adults and 0.118 kg FW d^{-1} for children with body weights of 70 and 14.2 kg, respectively. Vegetable consumption showed no risks for adults while HQs ≥ 1 were observed for Ni, As and Cd for children. Although HQs for the vegetables suggest elevated risk for children these are likely to be lower when realistic dietary consumption levels are considered. Thus, more accurate estimates of daily intake of vegetables are recommended for future studies.

Conferences and meetings

1. 1st Kurdistan student's conference in Nottingham on 15 September 2013- Oral presentation
2. 2nd Kurdistan student's conference in Nottingham on 16 September 2014- head of organising committee-Poster presentation

3. East Midlands Universities Research Student Conference in Leicester on 18 September 2014- Oral presentation

4. Bill & Melinda Gates Foundation in Nottingham on 30 July 2014- Poster presentation

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6. Early Careers Researcher Conference (ECR) in York on 7-8 April 2015-Poster presentation

7. 6th International Conference on Medical Geology (MEDGEO2015) in Portugal-Aveiro 26 June to 2 July 2015-Oral presentation

8. Workshop: Early Career Researchers at the Bioscience Interface in Nottingham on 12 August 2015 -Oral presentation

Declaration

I hereby declare that the work presented in this thesis was carried out in accordance with the regulations of the University of Nottingham and it has not been submitted for any other degree. All sources of information have been acknowledged by reference to the authors.

Karzan Mohammed

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1 Introduction

1.1 Urban and peri-urban agriculture (UPA)

Global attention on urban and peri-urban agriculture (UPA) has been increasing for two decades (Yang et al., 2010). Boland (2005) defines *"urban and peri-urban agriculture as all kinds of agricultural production within or around a city, which mainly provides urban markets with food products for sale to consumers or for consumption by the city-dwelling growers themselves .* "Urban agriculture" encompasses all forms of agriculture, including horticulture, aquaculture, livestock production and forestry within a city. UPA has been growing throughout all socioeconomic groups around the world over the past two decades (Yang et al., 2010). In Italy for example, local governments offer urban allotment gardens to encourage low income senior citizens to practise their own agriculture and increase socioeconomic interaction (Tei et al., 2010).

UPA fulfils a variety of functions including food production and the building of communities; it may also help to reduce social, economic and environmental problems (Säumel et al., 2012). Urbanisation and industrialisation has increased agricultural production in many cities in developing countries as it is regarded as a primary source of livelihood by the population and it increases urban sustainability. In developed cities these activities may be done in specific areas, for example allotments, community vegetable gardens and roof top farms, whilst in developing cities it is mainly practised in informal areas including rear and front gardens and road verges (Nabulo et al., 2012). In developing countries UPA is the major strategy to obtain food security and food safety by increasing the quantity of food in the cities. Urban farmers generally have low incomes and need to practise urban agriculture and sell their produce as a source of income (FAO, 2010).

In addition to providing economic benefits for urban farmers, their communities and cities, UPA encourages efficiency in urban management and plays a crucial role in ensuring better public health. UPA has many physical, psychological and social benefits for both farmers and city dwellers, including provision of home-grown fresh fruit and vegetables, physical activity and outdoor interaction with "green space" in urban areas (Leake et al., 2009) (Adjia et al., 2008). It can also mitigate storm water runoff (Aubry et al., 2012) and encourage use of organic wastes thereby decreasing costs of waste management.

UPA can, however, also result in health risks to farmers, their communities and consumers because urban areas are characterised by high population, high energy use, consumption of resource and waste generation. The geographical concentration of resource use and generation of waste in and around a city can result in multiple exposure to contaminants. Exposure can be via direct and indirect routes (Leake et al., 2009) as UPA is likely to be practiced alongside areas where there is industrial contamination or waste discharge (Cole et al., 2006).

Anthropogenic activities, particularly motor vehicle emissions and domestic waste dumping and incineration, close to or around sites of cultivation, can increase levels of contaminants including potentially toxic elements (PTEs) and other organic and inorganic pollutants compared to rural agricultural sites (Alloway, 2004;Clark et al., 2006). For example, PTEs such as Cd can accumulate in soil and subsequently in vegetables and crops, possibly leading to development of chronic diseases in consumers (Lente et al., 2012). PTEs can also transfer in the food chain, accumulating at higher trophic levels (Cole et al., 2006). Consequently if UPA is practised on contaminated land using contaminated waste water for irrigation it may pose a risk to human health (Qadir et al., 2000;Anikwe and Nwobodo, 2002;Nabulo et al., 2010;Lente et al., 2012). Potential health hazards can be classified as physical, chemical, biological and/or psychological (see Table 1.1).

Table 1.1 Potential risks related to urban and peri-urban agriculture (UPA) (from Cole et al., 2006).

Type of hazard	Grouping of relevant exposure	Example
Physical	Internal	- frequent bending forward to weed plot
	External	- making noise from grinding equipment and using pointed farm tools
Chemical	Direct	- upstream waste discharges into irrigation water
	Indirect	- municipal waste disposes near UPA - toxic metals and polyaromatic hydrocarbons (PAHs) from automobile exhaust and waste disposal in vegetable farms
Biological	Directly transmitted via carrier	- swine fever among pigs, protozoa, viruses and parasitic worms - *Salmonella* species
	Vector borne	- malaria proliferation in water pools
Psychological	Overload	- working hard though out the days and carry out different demands
	Insecurity	- fear of theft or assault

1.1.1 Wastewater use in UPA

Waste water originates from a variety of sources including municipal waste water e.g. sewage, agricultural and industrial effluent and storm water. Rapid urbanization and industrialization generates a substantial volume of waste water that is increasingly used for irrigation, particularly in arid areas due to increasing problems of water shortages (Wang et al., 2012). For example, in Israel and Spain waste water comprises 70% and 88%, respectively, of water used for agricultural purposes (Lallana et al., 2001).

In many developing countries the vast majority of waste water flows directly into waterways and is not treated to remove contaminants including solids, oils, pathogens and PTEs (Kunhikrishnan et al., 2012) prior to being used for irrigation. For example, Ensink et al. (2004) estimated that in Pakistan 26% of national vegetable farming is irrigated with waste water and Assouline et al. (2002) noted that by 2020 the amount of sewage effluent used for irrigation in Israel will reach 65%. Other arid and semi-arid countries including Iraq, Tunisia and Jordan reclaim up to 78% of domestic waste water for agricultural irrigation.

Waste water irrigation has many positive benefits as well as risks (Yadav et al., 2002). It provides a reliable water resource to farmers that can supply appreciable amounts of essential plant nutrients and organic matter to the soil; consequently the application of chemical fertilizers is reduced or becomes unnecessary and pollution of surface water resources with artificial fertilizers can be reduced (Ensink et al., 2002;Liu et al., 2005). Detrimental effects of using waste water for irrigation include health hazards to the irrigator, accumulation of chemical pollutants such as PTEs including Pb, Cd, Ni, Zn and Cu in the soil, contamination of ground water and deterioration of food quality and safety (Khan et al., 2008b;Singh et al., 2010;Wang et al., 2012). For example, high concentrations of nitrogen in wastewater may lead to nitrate contamination of drinking water sources, particularly ground water, which can result in negative health impacts (Fewtrell, 2004). Wastewater can also contain a range of pathogenic microorganisms including viruses, bacteria and parasites such as protozoa and helminths (parasitic worms) which may pose risks to farmers, agricultural workers, crop harvesters and consumers (Blumenthal et al., 2000).

Transport and mobilization of PTEs into groundwater has been reported in areas which have been irrigated with waste water for a long time. For example, in irrigated agricultural soils in India and China, where untreated industrial waste waters are extensively used for irrigation purposes, Behbahaninia et al. (2010) and Tiwari et al. (2011) reported that Cr, Ni, As, Cd and Pb were retained by soil as a consequence of long- term irrigation. The authors also stated that the capacity of soil for PTE retention reduces as a result of continuous loading of pollutants and changes in soil properties particularly, pH. The presence of dissolved organic matter in wastewater will also influence PTE mobility, bioavailability, transport, adsorption, complexation and redox reactions in the soil (Figure 1.1) (Müller et al., 2007;Kunhikrishnan et al., 2012). Herre et al. (2004) assessed the effect of long term of waste water irrigation (90 years) on two soils, a Leptosol and a Vertisol, in the Mezquital valley in Mexico. The authors demonstrated that the quality of OM had changed significantly with increased carbon mineralization in the irrigated soil and, consequently, the concentration of dissolved organic matter (DOM) also increased. They stated this influence was more dominant in the Leptosol than in the Vertisol, indicating the importance of clay (Leptosols: 26–35%, Vertisols: 39–56%) in stabilizing SOM. Elevated DOM could be explained by the direct input of DOM from the irrigation water or through indirect solubilisation of SOM resulting from a change in pH. Organic matter can also affect the accumulation, mobility and bioavailability of PTEs in soils irrigated by waste water. Statistical analysis by Qishlaqi and Moore (2007) found that soils with high OM accumulated significantly higher concentrations of PTEs than those with low OM. Likewise, increased DOM in soil irrigated with waste water affects the mobility and bioavailability of PTEs (Bolan et al., 2011).

A strong, positive correlation has been observed between concentrations of DOM and Pb and Cu (Al-Wabel et al. (2002), suggesting creation of soluble Pb-DOM and Cu-DOM complexes. Kunhikrishnan et al. (2012), in a more detailed review on the influence of waste water irrigated soil on PTE dynamics, observed that waste water irrigation led to formation of soluble metal complexes resulting in decreasing PTE adsorption particularly for Cu, Cd and Pb. Insoluble metal–organic complexes can also be formed, resulting in reduced mobility of PTEs. Therefore, in OM-rich soils, including those subject to long-term waste water irrigation, manure amendment and pasture soil, only small amounts of PTEs are available (Herre et al., 2004). A number of investigations show the OM–rich soil encourages the reduction of certain PTEs in soil, especially Cr, As and Se (Losi et al., 1994;Frankenberger and Losi, 1995). For instance, application of manure to soils can facilitate volatilization of Se as a result of reduction to Se^0 (Ajwa et al., 1998). Some studies have reported the reduction of Cr^{6+} to less toxic Cr^{3+} in soils treated with cattle manure (Banks et al., 2006). Reduction of redox-sensitive PTEs in organic amended soils may be the result of providing carbon and protons as well as stimulation of microbial activity, which plays an important role in reduction of Cr^{6+} to Cr^{3+} (Losi et al., 1994). In contrast, it is believed that Mn oxides oxidise Cr^{3+} to highly toxic Cr^{6+} but this influence is attenuated if the oxide surface adsorbs other trace elements including Ni, Cu and Pb. Likewise, As^{3+} oxidation to As^{5+} on oxide surfaces leads to increased adsorption and results in lower potential risks (Young, 2013)

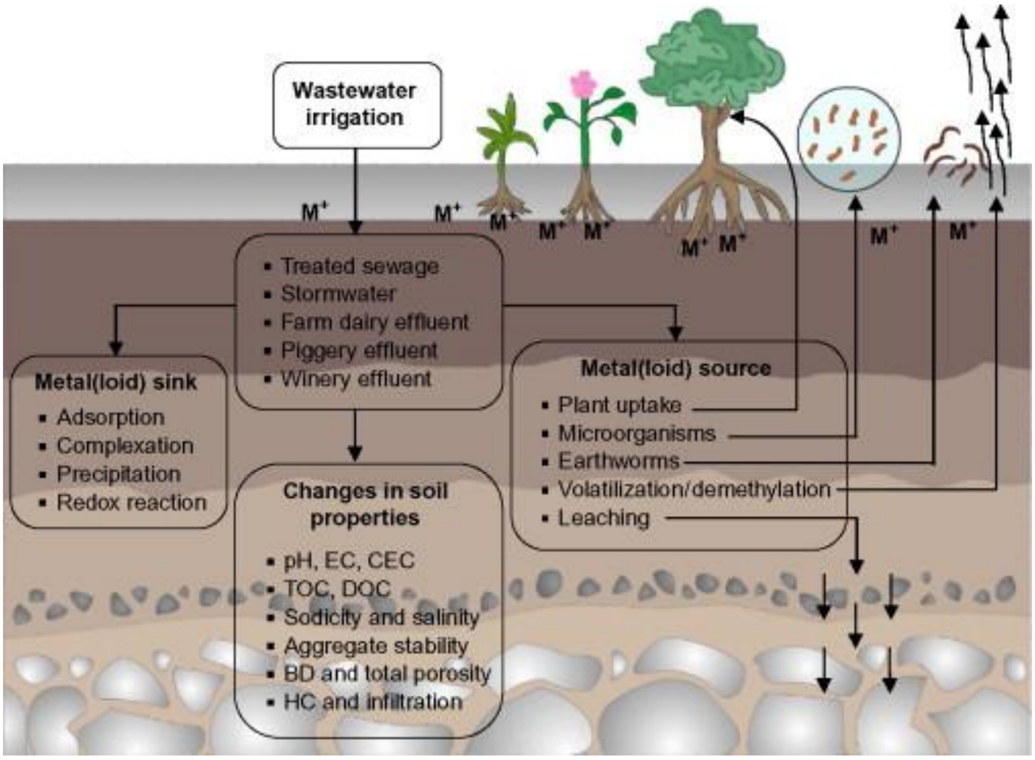


Figure 1.1 Schematic representation of wastewater irrigation and the impact on PTE transformation and behaviour in soils (Kunhikrishnan et al,. 2012).

Guideline values proposed by the World Health Organization (WHO) and the United Nations Environment Program (UNEP) advise using only treated waste water for irrigation of crops to remove pathogenic microorganisms and to decrease PTEs to safe limits (Blumenthal et al., 2000;Ensink et al., 2002).

1.1.2 Effect of municipal waste disposal on UPA

Handling and disposal of solid waste is a major environmental problem in many countries. Most waste is produced in urban areas of which between one third and one half is not properly treated (Pasquini and Alexander, 2004). Within limits, the organic portion of municipal waste (for example, food leftovers, rotten fruit, vegetables, leaves, crop residues, animal excreta and bones) can improve soil fertility in urban farming and develop the physical properties of soil (Asomani-Boateng and Murray, 1999;Anikwe and Nwobodo, 2002;Adjia et al., 2008). The production of compost from the organic components of domestic waste and its subsequent utilization in UPA may have a significant role in improving soil organic matter content and maintaining and improving the physical and biochemical properties of impoverished soil (Gigliotti et al., 1996).

Moreover, it is an alternative to incineration and dumping, reducing CO_2 and other atmospheric emissions (Baldantoni et al., 2010). Indiscriminate disposal and dumping of solid waste, however, may lead to accumulation of PTEs and other pollutants in soils, changes in soil physical and chemical properties and distortion of interactions between biological, chemical and physical soil functions (Anikwe and Nwobodo, 2002;Pasquini and Alexander, 2004;Adjia et al., 2008). Domestic solid waste can be considered a source of PTEs as it contains some of their main sources, for example, chemicals from household, packaging of food, batteries and electronic constituents, paints, ceramics, automotive components and oils, inks, plastics, debris from constructions and waste of hospitals (Nabulo et al., 2012). High concentrations of PTEs in composting materials have been reported (Kaschl et al., 2002;Baldantoni et al., 2010) which may accumulate in surface soils, thus posing a long term environmental hazard through absorption by plants, bioaccumulation through food webs or leaching through the soil to contaminate ground water (Karaca, 2004;Smith, 2009). Colloidal and dissolved organic matter in compost may also result in enhanced bioavailability and mobility of some elements, such as, Cr, Ni, Cu and Zn (Kaschl et al., 2002;Baldantoni et al., 2010).

1.2 Sources and behaviour of PTEs in the environment

Alloway (1995) defines soil as "*a fundamental and irreplaceable natural resource playing a role in food production, climate regulation and maintenance of biodiversity; it is the essential link between the geosphere, hydrosphere and atmosphere*". Natural processes may release large amounts of PTEs into the environment as a result of erosion and weathering, volcanic eruptions, geothermal activities, natural forest fires, wind-blown dust and sea salt spray (Alloway, 2004;Pekey, 2006). Trace elements can accumulate in soils contaminated as a results of fertilizer and pesticide application, wastewater irrigation, disposal of solid waste and atmospheric precipitation (Khan et al., 2008b) . Significant quantities of PTEs are also released annually from mining and energy generation (Pokhrel et al., 2009;Bhattacharya et al., 2007).

Soil is considered as a common reservoir for trace elements after they are discharged into the environment by anthropogenic activities. In contrast to organic pollutants, which are ultimately oxidized to carbon dioxide by the action of microbial communities, metals cannot be degraded by geological, chemical or biological processes (Kirpichtchikova et al., 2006). Although anthropogenically-sourced trace elements can remain in soil for a long time after their release, they may change their chemical form (speciation) and bioavailability (Raymond et al., 2011), a process which is controlled by many factors including pH, CEC and OM (Levy et al., 1992).

Chromium contamination can arise from industries including metal plating, alloying, tanning of animal hides, textile dyes and mordants, pigments, ceramic glazing, refractory brick manufacture and the disposal of Cr-containing wastes (Oliveira, 2012). Nickel and Cd are used in the production of alloys, in nickel-cadmium batteries and electrodes and as a component of catalysts (DEPA, 2005e). In addition they are used in metal plate, as dyes for printing textiles (Ni) and as pigments and stabilizers in plastics (Cd) (Manta et al., 2002;Nabulo et al., 2010). Copper contamination arises from electrical cable production. It is also used as a wood preservative, in anti-fouling paints, fungicides, algaecides, disinfectants and is present in phosphate fertilizers, nutritional supplements, printing inks and dyes (Nriagu, 1979). Zinc has been added to soils through anthropogenic activities such as mining and smelting for centuries. It is widely used in corrosion-resistant coatings for iron and steel, and can be mixed with other elements to produce alloys including brass and bronze. Zinc oxides are used in the formulation of paints, ceramics, rubber, and electrical products; it is also used to create dry cell batteries (Cynthia and David, 1997).

Lead is a widely distributed, ubiquitous element in the environment (Finster et al., 2004). Primary sources include smelting and mineral processing, battery manufacture, pigment and chemical production, incineration of wastes and waste disposal and combustion of leaded fuel. Lead accumulation in soil originates mainly from precipitation from the atmosphere, principally from traffic-related emissions. Wheeler and Rolfe (1979) found that the concentrations of Pb in vegetables and crops grown near to major roads were linearly related to traffic density. Nabulo et al. (2006) showed that Pb, Zn and Cd concentrations in surface soil samples and related vegetables increased with traffic density, but decreased with distance from the road. Other sources of PTEs include combustion of fuels to generate energy and smelting and refining operations.

Sewage sludge and effluent disposal can also be a source of PTEs to agricultural land. Other agricultural applications such as phosphate fertilizers, pesticides, herbicides and other agrochemicals, are considered the most significant sources of Zn, Cd and As contamination in agricultural soil (Alloway, 1995;Gregory et al., 1996).

Some trace metals including Cu, Zn, Fe and Mn, are essential for all living organisms but can pose non-carcinogenic risks including neurologic disorders, headaches, renal and liver diseases when ingested above their safe limits (USEPA, 2004). However, Cr, Ni, As, Cd and Pb are toxic thus can pose risks to human health because of their ability to transfer to human via various exposure pathways affect the central nervous system (CNS), endocrine system, hematopoietic function and normal cellular metabolism (Zhao et al., 2014a). Itoh et al. (2014) found that dietary Cd intake due to the ingestion of environmentally polluted rice and other vegetables was directly related to the incidence rate of postmenopausal breast cancer. Increasing life span risk of lung carcinoma death has been shown to result from occupational exposure to mists and dusts containing hexavalent chromium (Liu et al., 2013) and Zhoa et al. (2014b) concluded that there was a statistically significant correlation between topsoil Pb concentration and human gastric cancer and between Hg content of grain and liver cancer. It has been reported that children living in contaminated areas with heavy metals can have enlarged tonsils, lymphatic nodes and livers and acute lung injury (Prows et al., 2003) . Other acute toxic effects caused by exposure to PTEs include gastrointestinal symptoms such as loss of appetite, vomiting, diarrhoea and dysfunction of cardiovascular and nervous systems, including muscle cramps, heart complaints and eventually death (Rainbow, 2007).

1.3 Speciation and fractionation of PTEs in soils

There is a general consensus that the total concentration of PTEs in soil is inadequate to evaluate their biological availability, environmental accessibility, and potential risk to the environment and human health (Huang et al., 2011). Therefore, to account for more realistic exposure of biological communities to trace elements and assess risks arising from soil contamination it is important to consider metal bioavailability (Luo et al., 2011). Trace elements in soil occur in a range of chemical forms, distributed amongst solid and solution phases. Metal ions are bound to solid phases by precipitation, ion exchange or adsorption (Allen, 1993) and they vary in their chemical reactivity or degree of lability because of factors that influence their behaviour in the soil such as pH, redox potential, clay, organic matter and carbonate content. . Metal ions in the solution phase may occurs as free ions, form complexes with soluble organic or inorganic compounds or be bound with mineral colloids (Degryse et al., 2009;Alloway, 2013). In general, there are three trace element fractions in the solid phase: (i) inert forms which are strongly incorporated into the structure of minerals, (ii) non-labile forms i.e. elements that are strongly adsorbed or diffused into solid phase or suspended colloidal particles where the only way to be exchanged with the solution phase is through kinetically-moderated processes over long periods of time, and (iii) labile ions which react promptly in response to changes in soil equilibrium conditions (Young, 2013).

Different approaches have been applied to determine trace element reactivity and to quantify the physicochemically labile pool of metals in soil (Nolan et al., 2003). A commonly-used approach for assessing element bioavailability is the single or sequential extraction of metals from soil (Wragg and Cave, 2012). Single extractant procedures use weak ion-exchange extractants (e.g. $MgCl_2$, $CaCl_2$, NH_4NO_3), reductive extractants, weak acids (e.g. acetic acid), chelating agents (e.g. DTPA, EDTA), combined salt-acid extractants and strong acids (e.g. 0.43 M HNO_3) (Peijnenburg et al., 2007). Un-buffered salt solutions such as $CaCl_2$ and NH_4Cl are considered rapid and simple methods to extract bioavailable metals (Kashem et al., 2007) releasing into solution elements which are reversibly bound to exchange sites on the soil solid phase and which may represent a bioavailable fraction. The mobilized pool of trace elements is thought to reflect the fraction that that could be leached from soil to groundwater.

The choice of chemical extractant used to establish the 'available' metal fraction needs to be carefully considered. Natural salt solutions may be more effective in estimating exchangeable fractions of elements than chelating agents (Hammer and Keller, 2002). Many researchers have reported that easily exchangeable metals can be extracted with neutral solutions such as 0.01M $NaNO_3$ or 0.1M $CaCl_2$ (Houba et al., 2000;Menzies et al., 2007). Degryse et al. (2003) used 0.01 M $CaCl_2$ to predict Zn and Cd solubility in soil. Lindsay and Norvell (1978) developed a diethylenetriamine pentaacetic acid (DTPA) extractant (an aqueous mixture of 0.005 M of DTPA, 0.1 M tri ethanolamine (TEA) and 0.01 M $CaCl_2$) for measuring micronutrient metal availability in calcareous soils.

This extractant was strongly recommended for soils with pH > 7 where Cu, Fe, Mn and Zn are of interest as DTPA has a strong binding constant for these elements. TEA and $CaCl_2$ play an important role in buffering the system at pH 7.3 and they inhibit the dissolution of $CaCO_3$ (McLaughlin et al., 2000).

The most frequently applied SEP procedure is that proposed by Tessier et al. (1979) or modifications of this procedure (Li and Thornton, 2001). Tessier et al. (1979) used a series of chemical extractants with gradually increasing extraction power to partition elements into five operationally-defined geochemical fractions including: exchangeable; carbonates (acid-soluble); Fe and Mn oxides (reducible); organic matter (oxidisable) and; residual (insoluble) – see Figure 1.2. The objective of sequential extraction procedures (SEP) is different to single extractions in that they are used to discriminate trace elements held in different fractions in the soil rather than simply distinguishing between reactive and non-reactive forms of trace elements.

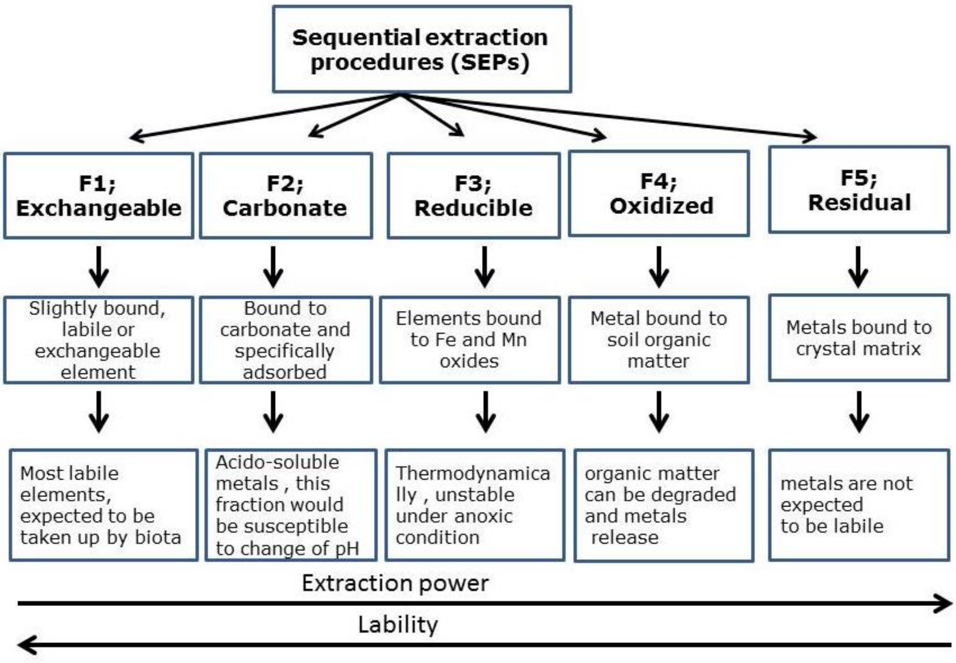


Figure 1.2 Schematic illustration of a typical Tessier-type SEP demonstrating the five operationally-defined fractions of trace elements in soil. The horizontal arrows denote the increasing strength of each extractant and the decreasing lability of extracted metals as the sequence moves from left to right. (adapted from Dean (2003).

Regardless of the extractant or extractants chosen, their suitability and applicability will differ for different elements (Garforth, 2014). Commonly applied extractants are either too weak to solubilise fully the bioavailable fraction of the PTE or too strong, resulting in removal of non-labile PTE into the solution (Young et al., 2000).

Isotopic dilution (ID) is an alternative approach to quantify the labile metal pool of an element in a soil. An aqueous soil solution is spiked with an isotope of the element of interest which enters into rapid equilibrium with the labile element already present in the system. By determining the amount of spike isotope that is able to mix with the labile element pool the 'E-value' (the amount of the element which is isotopically exchangeable with the solution phase in the soil suspension) can be determined. Assessing lability of elements using isotopic dilution can provide an exact estimation of the labile pool whereas some strong extractants such as DTPA are known to release some non-labile metal pool into the soil solution (Hooda, 2010). However, where extractants are carefully chosen similar results can be obtained for both approaches. For example, a comparison of the lability of Cd measured using 1 M $CaCl_2$ and isotopic dilution for 25 soils contaminated with sewage sludge and 41 mine-spoil soils demonstrated that $CaCl_2$ extraction was a good alternative to estimation of radiolabile Cd (Young et al., 2000).

Results from chemical extractions or E-value determinations can be used in statistical models in combination with other data such as major and minor cations, pH of the solution phase of the electrolyte suspension, Fe-Al oxides and LOI values, to predict the total element concentration in the solution phase that may be available to plants.

1.4 Uptake of PTEs by plants

Numerous studies have revealed that plants differ in their capacity to take up, accumulate and tolerate PTEs not only between different species, but also between parts of a given plant and between cultivars and varieties of the same species (Alexander et al., 2006;Rainbow, 2007;Säumel et al., 2012). For example, there is evidence that legumes accumulate low level of PTEs from soil, bulb vegetables such as onions accumulate moderate amounts, while leafy vegetables accumulate the highest concentrations of a given trace element when grown in the same soil (Kloke et al., 1984;Ge et al., 2000). Leafy vegetables are therefore sometimes described as accumulator crops (Alexander et al., 2006). In order to understand the transfer of trace elements into plants, the mechanisms of metal uptake by plants must be studied. Plant uptake of PTEs from soil is complex and includes transfer of the elements from soil solution to the root surface, movement inside the root cells and translocation of elements from the root to areal parts of the plant.

Uptake of elements by plants also occurs from atmospheric sources: the four major pathways of PTE uptake are shown in Figure 1.3. They include passive and active uptake via the root, gaseous and particulate deposition to aerial parts, and direct contact between soil and plant tissues (Reichman, 2002). There is still considerable uncertainty about the physiological mechanisms controlling these dissimilar forms of trace element uptake, root-to-shoot and shoot-to-fruit translocation and redistribution within vegetables (Murray et al., 2009). Metabolic differences amongst different plant genera and species of the same genus are suggested as an explanation for the differences (Ge et al., 2000).

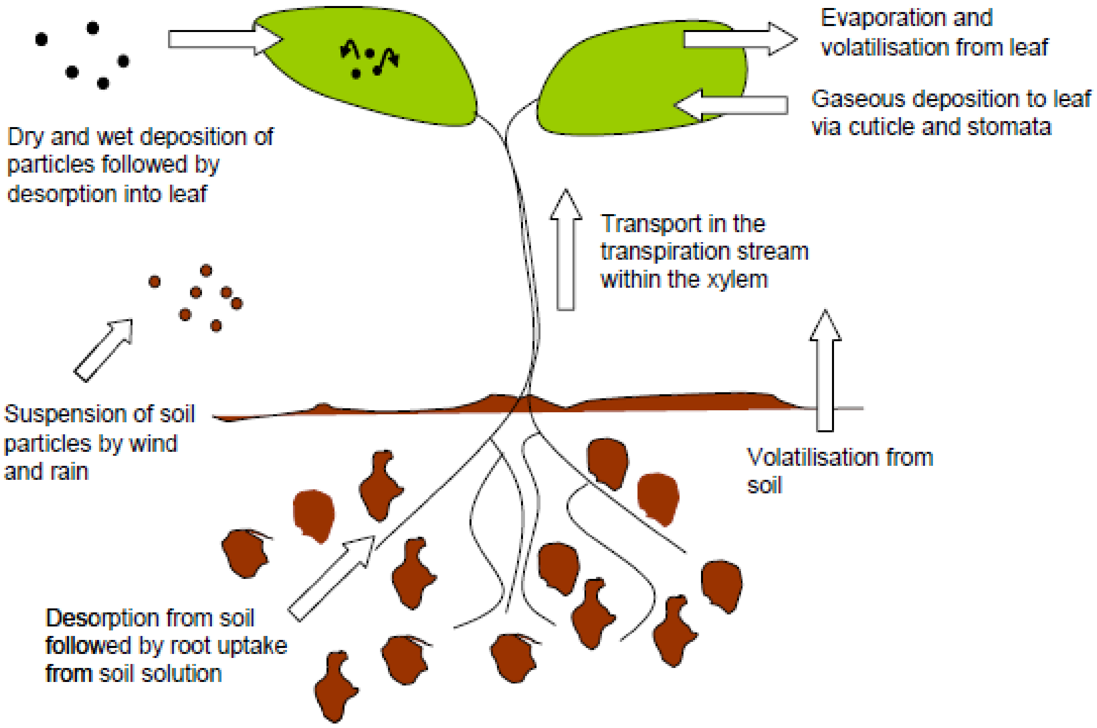


Figure 1.3 Plant uptake principal pathways (after Environment Agency, 2006)

Plants are highly selective in their uptake of some key elements and they have evolved highly specific and very efficient pathways to obtain essential micronutrients, present at low concentration, from their environment. Chelating agents, produced by plant roots, plant-induced pH changes and redox reactions are all able to solubilize micronutrients in the soil prior to root uptake. Plants have also developed very specific mechanisms to transfer and store micronutrients. These processes are also involved in the uptake, translocation and accumulation of toxic elements (Tangahu et al., 2011).

Jung et al. (1996) reported that many factors affect the transfer of elements into plants, some of which are inherent to the soil and some to the plant. Soil factors include pH, redox potential, organic matter content, fertiliser application, presence of Fe/Mn/Al oxides and hydroxides, cation exchange capacity, soil texture and the amount of other metals in the soil. Plant factors include plant species, cultivars and age. They reported that accumulation rates for Cd and Zn were much higher than those for Cu and Pb. However, this is not considered consistent for all kinds of soil and plant species since the level to which PTEs are mobile strongly depends on the elemental species, the degree of contamination and soil properties (Boshoff et al., 2014). For example, trace element uptake from low-pH soils may be greater than from calcareous soils. At high pH trace elements can be strongly absorbed onto organic matter including soluble compounds that maintain the elements in solution, or higher molecular weight humic compounds in the soil that retain them through chelation reducing bioavailability, while at low pH negatively charged sites are strongly protonated, thus reducing cation exchange and complexation of cationic elements subsequently increasing abailability of metals. Alloway & Jackson (1991) studied the effect of sewage sludge on accumulation of PTEs by plants and observed different uptake for different plants; for Cd, accumulation was in the order tobacco > spinach > celery > cabbage, for Pb it was kale > ryegrass > celery, for Cu sugar beet > barley, for Ni sugar beet > ryegrass > mangold > turnip and for Zn sugar beet > mangold > turnip.

1.5 PTEs and human health risk assessment

Although, some PTEs are considered beneficial as micronutrients for plants and animals at low concentration (e.g. Cr, Cu, Mn, Ni and Zn) others, including As, Cd and Pb, have no known health benefit at any concentration (Abrahams, 2002). Human are exposed to PTEs through inhalation, dermal absorption and oral ingestion (Peña-Fernández et al., 2014). Elevated concentrations of PTEs in the environment can result in irreversible adverse effects on human health especially for children because young organs tend to be more susceptible to contaminants and children are more likely to exhibit pica behaviour, hence are more likely to ingest soil directly (Landrigan et al., 2004;Egeghy et al., 2011).

Nickel has a significant role in the physiological function of both humans and animals but excessive intake over a long time may pose serious health risks. Children living in Ni contaminated areas have been reported to display hypertrophy of tonsils, enlarged lymphatic nodes, enlarged livers and acute lung injury (Prows et al., 2003). Long-term exposure to Cr^{6+} can result in renal failure, anaemia, haemolysis and liver failure, whereas Cr^{3+} is an essential element for humans and too little may lead to heart conditions and metabolic disruption . Chromium^{3+} can also cause skin rashes and allergic contact dermatitis (Bianchi and Levis, 1987). Bierkens et al. (2009) reported that the absorption rate of Pb from the environment for children is 40% higher than for adults because children are more exposed to toxic elements in many environments such as homes, streets, schools, play grounds, shops, recreation parks and picnic areas. Copper is needed in trace amounts by humans and animals to form haemoglobin and for carbohydrate metabolism. It is also important for resistance of disease and water regulation in plants, but it can cause damage to plants if it is present at too high a concentration, e.g. in sewage sludge applied to agricultural land.

PTEs may therefore be responsible for many types of adverse health effects, ranging from relatively minor symptoms such as nausea or skin eruption, to carcinogenic effects or even death (Satarug and Moore, 2004;Shi et al., 2011). It is therefore important to understand the sources, speciation, fractionation, distribution, bioavailability and bioaccessibility of toxic elements in the environment (Ge et al., 2000;Lucho-Constantino et al., 2005;Chen et al., 2008;Maas et al., 2010;Wang et al., 2011;Elbana et al., 2013;Hu et al., 2013;Xu et al., 2013;Huang et al., 2014). Most investigations focus on risk through ingestion of metal-contaminated soil, dust and vegetables. Health risks to populations from UPA can be calculated in many ways on the basis of degree of exposure and dose-response information. Risks of 'non-cancerous' diseases can be estimated by calculating target hazard quotients (THQ) which are ratios between the exposure and a reference dose (Han et al., 1998). A THQ less than 1 suggests that the predicted exposure is unlikely to pose significant health risks, whereas a THQ greater than 1 indicates a high probability of potential health effects (Lente et al., 2012). Alternatively, assessment of risk can be made using extraction techniques to simulate processes *in vitro* in the gastrointestinal tract (Intawongse and Dean, 2006;Hough et al., 2004).

1.5.1 Principles of risk assessment

In recent decades, not only scientists but also others within the regulatory communities, politicians, industries and the general public have paid more attention to the field of human health risk assessment. The IPCS (2004) defined human health risk assessment as:

> "*a process intended to estimate the risk to a given target organism, system or (sub)population, including the identification of attendant uncertainties, following exposure to a particular agent, taking into account the inherent characteristics of the agent of concern as well as the characteristics of the specific target system. It is the first component in a risk analysis process that also includes risk management and risk communication*".

Human health risk assessment is commonly divided into four steps; (i) hazard identification (problem definition), (ii) dose-response assessment, (iii) exposure assessment and (iv) risk characterization, according to the paradigm proposed by the US National Academy of Sciences (NAS, 1983;IPCS, 1999).

1.5.1.1 Hazard identification

Hazard identification can be defined as the qualitative assessment of the likelihood that a particular hazardous agent will have an adverse health effect. For instance, chemicals may be toxic, teratogenic, mutagenic, carcinogenic or allergenic. These classifications do not tell us if a chemical will be hazardous in all circumstances, but they identify the principal hazards which require further investigation in a risk assessment. Hazard identification is designed to answer two key issues: (i) whether an agent may potentially pose a health risk to human beings, and (ii) under what circumstances an identified hazard may become a risk to health. The result of the hazard identification is a scientific judgement whether the chemical assessed can, under certain exposure circumstances, cause a risk to human health.

1.5.1.2 Dose Response

Hazard characterization includes modification of the perspective of the hazards with specific reference to how the dose or extent of exposure affects the probability and severity of the health effect. It also involves obtaining insight into the mechanism of action which will inform the ultimate human risk assessment and may allow the derivation of Health Criteria Values (HCV) applicable to the human population.

The process involves characterising the quantitative relationships between the dose of the exposure, administered or received, and the probability of incidence of adverse health effects on an individual or in the population. In most kinds of adverse effects it is generally considered that there is a dose below which toxic effects will not be observed (threshold dose) but for other kinds of health adverse effects there is some probability of hazard at any dose of exposure (non-threshold).

1.5.1.3 Exposure assessment

The official ICPS (International Program on Chemical and Safety) definition of exposure is "*the concentration or amount of the particular agent that reaches the body in a specific frequency for a defined duration*" (IPCS, 1999;IPCS, 2004). Exposure is the contaminant mass entering the human body, per unit of body weight over time (Swartjes, 2011). Exposure can be considered 'internal' or 'external' exposure. Internal exposure is the concentration of contaminant that reaches specific target organs, i.e. the organs in which harmful effects occur via ingestion or inhalation. External exposure is the concentration of contaminant that crosses the 'outside border' of the human body via skin contact (IPCS, 1999).

In human exposure assessment three main exposure routes are recognised; dermal, oral and respiratory. The exposure medium refers to air, water, soil and food or products (consumer, commercial or industrial) which are believed to contain the contaminants (Figure 1.4). Ingestion exposure concerns contaminants in food, beverages and soil; inhalation exposure occurs when contaminants are present in air; dermal exposure requires contact between contaminants and skin.

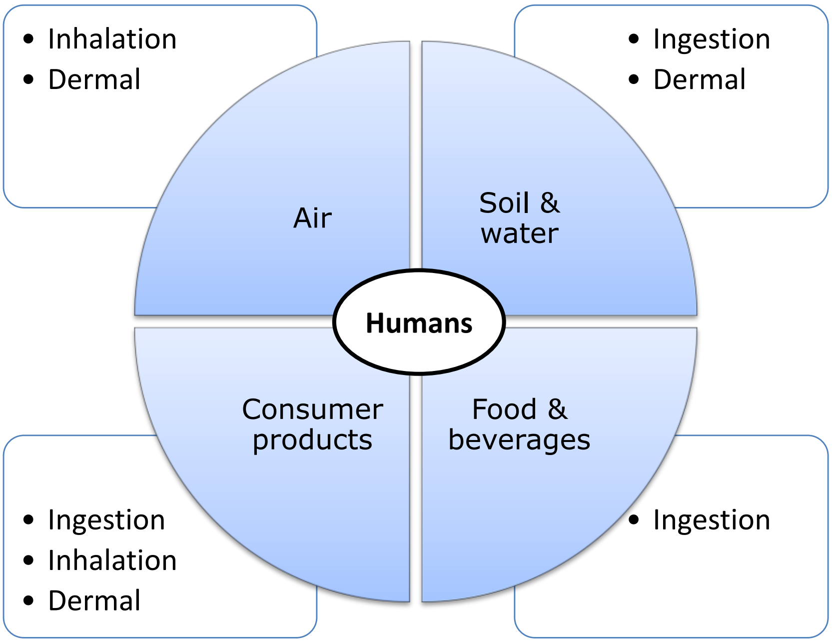


Figure 1.4 Exposure media and corresponding means of contact (IPCS, 2010)

Generally, the main source of PTE exposure to humans (excluding smokers) is via consumption of contaminated food (IPCS, 1999;Hough et al., 2004). Vegetable consumption is an important exposure route. For example, 70-90% of total Cd intake can be via this route (Swartjes et al., 1997;Sarwar et al., 2010b). When contaminated food is ingested contaminants may be absorbed via the lining of the mouth and gastrointestinal tract before absorption into the body and transport to the liver. Some chemicals are returned to the gastrointestinal tract through bile while others enter the circulatory system. Some or all the contaminants ingested may remain in the gut and be excreted

(Environment Agency, 2009a). The proportion of an ingested chemical, which is absorbed from the intestine into the body and reaches the circulation system, is considered to be the bioaccessible fraction and the resulting dose is known as a systemic dose, as illustrated in Figure 1.5. The bioaccessibility of a contaminant can therefore be between 0 (i.e. no contaminant is absorbed into the circulatory system) and 1 where all ingested contaminant reaches the circulatory system.

1.5.1.4 Risk characterization

Risk characterization is the final step of risk assessment. It involves a quantitative estimate of exposure relative to the most appropriate health-based guidance value. The information from the above steps is combined to reach a final risk decision. Risk is communicated as the chance of suffering as a consequence of exposure to a contaminant for a specified group of the population (Bennion et al., 2005).

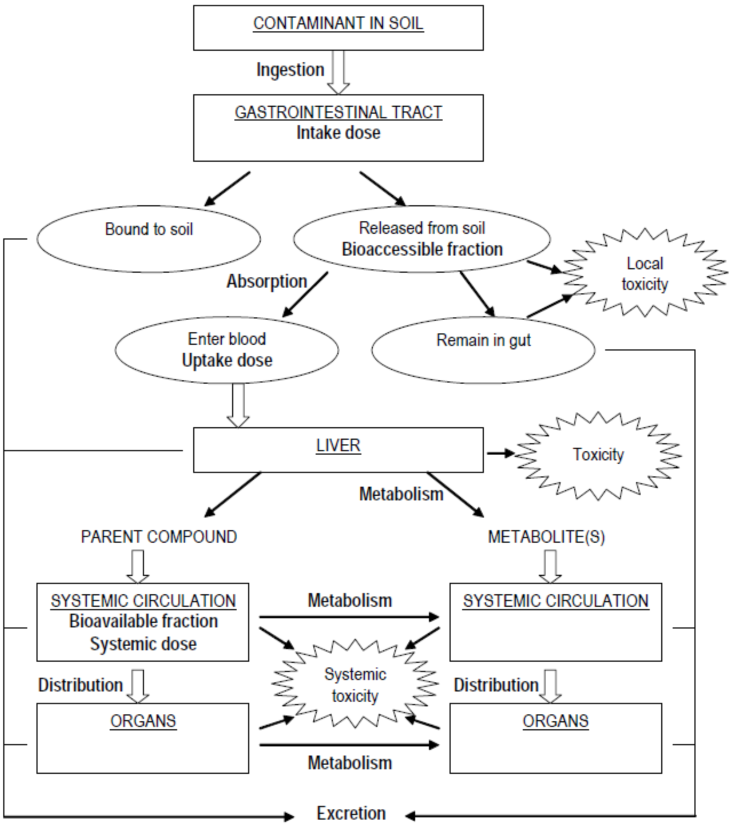


Figure 1.5 Schematic illustration for oral exposure pathway to chemicals (Environment Agency, 2009a)

1.6 Thesis background, aims and objectives

The aim of the work reported in this thesis was to investigate the nature and extent of PTE accumulation in soils in Sulaymaniyah province in the Kurdistan region of Iraq and to investigate if they have adversely impacted the safety of agricultural production in urban and peri-urban areas.

World population has being increasing, especially in developing countries which recorded an annual urban average growth rate of 3.6% between 1950 and 2005, compared to only 1.4% in developed countries (Aubry et al., 2012). This surge has led to increased demand for food, shelter and employment (Nafiu et al., 2011). The population of Iraq has tripled since 1970, growing from 10 to 30 million, with around 71% of people living in urban areas of which 47% currently live in slum-like conditions. It is predicted that the Iraqi population will increase to approximately 50 million by 2030 (UNCTI, 2010).

The Iraqi climate is arid and semi-arid - hot in summer, cold and moderately rainy in winter. The annual average rainfall is not more than 200 mm and more than 50% of Iraq is desert where rainfall is < 50 mm per year. Northern areas of Iraq are rainier with 300-550 mm per year and in the mountainous north-eastern area rainfall increases to 1000 mm per year (UNCTI, 2010).

Agricultural policy and strategy in Iraq, developed in the 1950's, aims to provide high levels of food quality and security for the population. This goal was achieved only during the period 1950-1960; after that the agricultural situation deteriorated due to involvement in military conflicts, particularly the 1980-88 Iran-Iraq War, the 1991 Gulf War and subsequent economic sanctions. In addition, after the toppling of Sadam Hussein's regime in 2003, agriculture suffered as a consequence of poor irrigation infrastructure resulting in degradation of fields and livestock pastures (Schnepf, 2004).

Iraq faces numerous environmental problems including drought, desertification, pollution from oil refineries, oil fires, discharge of raw sewage into rivers and the unregulated use of fertilizers and pesticides. There is also air pollution in urban areas and inefficient solid waste management (UNEP, 2003). UNCTI (2010) reported that 39% of agricultural land of Iraq suffers from decreasing areas for crop production.

In the Kurdistan region of Iraq, particularly in the study areas chosen for this investigation (Sulaymanyah province), solid wastes including domestic, hospital and industrial wastes are disposed of close to cities, where people practise many kinds of agriculture. In Sulaymanyah city, ~ 1 kg per capita per day of solid waste is produced and 1,000 tonnes of wastes are transferred every day by municipal vehicles (dumpers, tractors, trucks) to solid waste disposal areas (Rashid, 2010). The waste piles in disposal areas are frequently set on fire either by waste scavengers or by self-combustion; consequently pollutants may be released into the air. During the rainy seasons (winter and spring) leachate from the disposal areas flows into the Tanjaro river on which farmers depend for urban agriculture.

The quantity of water resources in Iraq are strictly linked with the amount of rainfall and snow in the main river basins and dams, consequently water resources fluctuate through time and from area to area. The predominant water sources of rural areas in Iraq are springs and wells while urban areas completely depend on ground and surface water and heavily extract them for domestic, irrigation and industrial purposes (Grego et al., 2004). Untreated but diluted waste water (waste water mixed with stream, spring and rain water) is frequently used for agricultural activities in urban areas due to the lack of alternative sources of irrigation water (Ormizyari, 2009).

UPA plays an important role in the provision of employment opportunities and provides fruit and vegetables to urban markets (Mahmood, 2002). It is estimated that about 1500-2000 vegetable and crop farms operate in and around Sulaymanyah city and the agricultural produce is sold as a component of daily meals eaten by more than 500,000 urban residents in and surrounding the city. The consequence of increased anthropogenic pollution on UPA has not previously been investigated in Iraq except for some research which has been conducted on drinking water contamination with some PTEs (Sulayvani and Mezuri, 2008;Hawrami and Mezuri, 2014).

In this investigation, UPA includes all vegetable farming which is practiced by dwellers within the city, in gardens or fenced vacant plots in the front of or close to their houses and production of crops and vegetables around cities. It is hypothesized that fruits and vegetables produced and consumed in Sulaymaniyah province are contaminated to some degree with PTEs and that different types of vegetables pose potential health risks via accumulation of different potentially toxic metals.

Specific objectives were to;

(i) Evaluate the concentrations and spatial distributions of PTEs in mainly urban soils in the Kurdistan region of Iraq.

(ii) Assess the potential health risks to adults and children posed by PTEs in soil via different routes of exposure; ingestion, inhalation and dermal contact.

(iii) Study the chemical fractionation of PTEs in these soils using a range of single and sequential extraction techniques and measure the isotopically exchangeable pool of metal (E-value) using stable metal isotopes; ^{62}Ni, ^{65}Cu, ^{70}Zn, ^{108}Cd and ^{204}Pb.

(iv) Assess transfer of PTEs from soil to plants by determining the concentrations of PTEs in the edible parts of different vegetables grown under field conditions in urban and peri-urban areas and associated soils.

(v) Establish whether washing vegetables before consumption results in any significant reduction in potential risk to human health.

(vi) Determine the carcinogenic and non-carcinogenic risks of toxic elements to adults and children from consumption of different vegetable types.

(vii) Establish the soil-plant transfer of Ni, Zn and Cd to five important vegetable crops through determination of ‘L-values’ in a pot experiment.

2 Materials and methods

Overview

This chapter comprises general description of the sampling and analytical approaches used throughout this work. Methods for the analysis of soil, water and plant samples are described.

2.1 Sample collection and characterisation

2.1.1 Soil Sampling

Five soils sub-samples were collected using a clean stainless steel trowel from randomly selected sites within a defined area (vegetable field) and combined to produce a composite sample for that area. Samples were sealed in plastic bags for transport to the Technical Institute of Halabja where they were air dried in aluminium trays, gently disaggregated using a pestle and mortar and then sieved to obtain a < 2 mm fraction. Approximately 25 g of each soil was then stored in a polyethylene tube for transport to the University of Nottingham, UK. A portion of each air dried, < 2 mm sieved soil was finely ground using an agate ball mill (Retsch, Model PM400) and stored in a polyethylene bag prior to analysis.

2.1.2 Plant Sampling

Plant samples were placed in clean paper bags and transported to the laboratory on the day of sampling. Fresh weights (FW) of the samples were recorded and approximately half of each sample was thoroughly washed with tap water and rinsed in distilled water to remove soil particles or dust adhering to the plant surface and other surface contamination before oven drying at 70°C for 72 h and reweighing. The other portion of the sample was dried and weighed with no washing. All plant samples were placed in separated, labelled paper bags for transport to the University of Nottingham’s laboratories for further analysis. Samples were milled in an ultra-centrifugal mill (Retsch, Model ZM200, Germany) fitted with a 0.5 mm titanium screen.

2.1.3 Water sampling

Water samples were immediately filtered in the field, through 0.45 µm cellulose acetate syringe filters into polyethylene bottles. The samples were acidified using 1 ml 25% (v/v) nitric acid and then stored at ambient temperature until laboratory analysis.

2.1.4 pH determination

Water pH was measured in the field and laboratory using a Hanna pH-209 pH meter with combined glass electrode (Ag/AgCl; PHE 1004) calibrated using pH buffers at pH 7.0 (3.9 g L^{-1} $NaHPO_4$ and 2.72 g L^{-1} KH_2PO_4) and pH 4.01 buffer (1.211 g L^{-1} $KHPO_4$). Soil pH was determined in the laboratory of the Technical Institute of Halabja. Exactly5 g of < 2 mm sieved air-dry soil was suspended in 12.5 mL of distilled water (1:2.5 ratio) and shaken on an orbital shaker (model SLM-INC-OS-16) at 40 rpm for 30 minutes before pH was measured in the resulting slurry. Five minutes was allowed for pH readings to stabilize before recording.

2.1.5 Loss on ignition(LOI)

Loss on ignition was used to estimate the percentage of organic carbon in the samples. A known weight of < 2 mm oven-dried soils was placed in a pre-weighed silica crucible in a muffle furnace (Gallenkamp size 3, Weiss-Gallenkamp, UK) overnight at 550°C to ignite the organic matter. The crucibles and soil were then placed in desiccators to cool to minimise moisture gain from the atmosphere. The weight loss was expressed as a percentage of soil organic matter as follows:

$$\%\,\mathrm{LOI} = \frac{(W_{ODS} - W_{IS}) \times 100}{W_{ODS}} \qquad \text{Eq. 2.1}$$

Where the W_{ODS} is the weight of oven-dry soil and W_{IS} the weight of ignited soil

2.1.6 Soil total carbon, nitrogen and sulfur content

Analysis of total carbon, nitrogen and sulfur was undertaken using a Flash EA1112 (CE Instruments) CNS analyser. Approximately 15-20 mg of dry, finely ground soil or certified soil reference standard was weighed into tin capsules and approximately 5 mg of vanadium pentoxide added. Capsules were carefully crimped, using tweezers, to avoid spillage. A capsule containing only vanadium pentoxide was used as a blank and certified soil standards (peat and sandy certified soil standards, Elemental Microanalysis; product codes B2176 and B2180) were used as a calibration standard. Samples were introduced from a MAS200 auto-sampler into a combustion tube packed with approximately 25 g copper oxide and 70 g electrolytic copper and heated to 900°C. The resulting gas was passed through an absorption filter containing magnesium perchlorate to remove water before passing through a PTFE separation column to a thermal conductivity detector in a helium carrier gas.

2.1.7 Chemical extraction procedures

2.1.7.1 DTPA extraction

Triplicate samples of air dried soil (c. 5.0 g < 2 mm sieved) were weighed into 50 ml polyethylene bottle and shaken with 10 ml of 0.005 mol L^{-1} DTPA (pH 7.0) on an end over end shaker 20 rpm for 2 hours at room temperature. The soil suspension were then centrifuged at 3000 rpm for 15 min and filtered immediately using 0.22 µm Millipore syringe filters and diluted 1 in 10 with MilliQ water before elemental analysis.

2.1.7.2 Mn and Fe(III) oxide concentrations

Triplicate samples (c. 0.25 g) of air dried finely ground soil were extracted in 20 ml of solution containing 0.07 mol L^{-1} Sodium citrate ($Na_3C_6H5O_7$), 0.3 mol L^{-1} Sodium bicarbonate ($NaHCO_3$) and 1 mol L^{-1} Sodium dithionate ($Na_2\ S_2O_6$) Samples were shaken in a water bath for 24 hr at 20°C, with loosened lids, before centrifugation at 2200 g for 15 min and filtration using 0.22 µm Millipore syringe filters. Solutions were diluted 1 in 10 with 2% HNO_3 before determination of Fe and Mn concentrations.

2.1.7.3 Sequential extraction procedure (SEP)

Sequential chemical extraction was carried out following the method described by Li and Thornton (2001), developed from that of Tessier et al. (1979). The extraction was carried out progressively, on an initial soil weight of 1.0 g, following the sequence listed below.

- ✓ *Exchangeable fraction*: The soil (1.0 g air dried, < 2 mm sieved) was extracted at room temperature for 20 minute with 8 ml of 0.5 M magnesium chloride ($MgCl_2$) with continuous agitation.
- ✓ *Carbonate-bound fraction*: The residue from the exchangeable fraction was leached with 8 ml 1 M sodium acetate (NaOAc) adjusted to pH 5.0 with HOAc for 5 hr at room temperature with continuous agitation.
- ✓ *Bound to Fe/Mn oxides*: Residual soil from the previous step was extracted with 20 ml 0.04 mol L^{-1} $NH_2OH.HCl$ in 25% (v/v) HOAc at 96 ^oC in a water bath for 6 hr with occasional agitation.
- ✓ *Bound to organic matter*: The remaining soil residue was extracted with 3 ml 0.02 M HNO_3 and 5 ml 30% H_2O_2 (adjusted to pH 2 with HNO_3); samples were heated to 85 °C in a water bath and maintained for 2 hr with occasional agitation before 3 ml of H_2O_2 was added and the mixture was heated again for 3 hr at 85 °C with intermittent agitation. After cooling 5 ml 3.2 M NH_4OAc in 20% HNO_3 (v/v) was added and the tubes were agitated for a further 30 min.
- ✓ *The Residual*: The residue from step 4 was acid digested with HNO_3, HF and $HClO_4$ (see Section 2.1.8).

2.1.8 Acid Digestion of Soils

Three replicates, approximatetely 250 mg, of finely ground soil were digested using 2.5 ml %70 HNO_3, Trace Analysis Grate (TAG), and 1 ml %70 $HCLO_4$ in a teflon-coated graphite Block Digestor (Analysco, UK) containing places for 48 PFA digestion vessels. The samples were heated at 80 °C and left overnight. Next day, 2.5 ml 40% HF was then put into the samples and then heated again at 120 °C for 10 hours. Further 2.5 ml of HNO3 and 2.5 ml of MQ water were added to the dry residue and the samples heated at 50°C for 30 minutes. Digested samples were diluted to 50 mL using Milli-Q water (18.3 MΩcm) and stored un-refrigerated in universal 25 ml plastic bottles (5% HNO_3) until elemental analysis. All digests were diluted at least 1 in 10 with Milli-Q water immediately prior to analysis.

For each digestion batch data were corrected using two blank samples and quality control was evaluated with two reference material samples (Standard Reference Material (SRM) 2711, Montana Soil, National Institute of Standards and Technology (NIST)). All elemental concentrations were converted to mg kg^{-1} dw according to Equation 2.2:

$$C_{soil} = \frac{(C_{sol} - C_{blank}) \times Vol}{W_{soil}} \qquad \text{Eq. 2.2}$$

Where C_{soil} is the elemental concentration (mg kg^{-1}) in the soil; C_{sol} and C_{blank} are the concentrations (μg L^{-1}) in the soil and blank digests, corrected for dilution, Vol is the digest volume (50 mL) and W_{soil} was the mass of soil digested (c. 250 mg).

2.1.9 Acid Digestion of Plant material

Milled plant materials (c. 200 mg) were digested in pressurised PFA vessels in 6.0 mL of 70% HNO_3 with microwave heating (Anton Paar 'Multiwave' fitted with a 48-place rotor). Digested samples were diluted to 20 mL using Milli-Q water (18.2 MΩ) and stored un-refrigerated (30% HNO_3) until elemental analysis. Straight before analysis, all samples were diluted about 1 in 10 with Milli-Q water.

2.1.10 Elemental Analysis

Elemental analysis was undertaken using ICP-MS, either a Model X-Series II or an iCAP-Q (both Thermo-Fisher Scientific). Samples were introduced from an auto-sampler (Cetac ASX-520 with 4 x 60-place sample racks) through a glass venturi nebuliser (flowrate 1~ mL min^{-1}). Internal standards were introduced to the sample stream via a T-piece and included Sc (100 ng mL^{-1}), Rh (20 ng mL^{-1}) and Ir (10 ng mL^{-1}) in 2% TAG HNO_3. External multi-element standards (Claritas-PPT grade CLMS-2, Certiprep/Fisher) were used in the range 0-100 μg L^{-1} for calibration. Sample processing was undertaken using Plasma lab software (version 2.5.4) or Qtegra (version 2.4 SP1). Polyatomic interferences were reduced using 7% H_2 in He (X-series) or He (iCAP-Q).

2.1.11 Isotopic dilution (ID)

2.1.11.1 Isotope stock solutions

Enriched stable isotopes with certified isotopic abundances (IA) (^{62}Ni, IA ≥ 98.2%; ^{65}Cu, IA ≥ 99.0%; ^{70}Zn, IA ≥ 92.7%; ^{108}Cd, IA ≥ 69.7%; and ^{204}Pb, IA ≥ 98.8%) were purchased as metal foil or oxide samples from ISOFLEX, San Francisco CA, USA. They were dissolved in HNO_3 (70%) before dilution with MilliQ water to give stock solutions with concentrations of ^{62}Ni (603.3 mg L^{-1}), ^{65}Cu (840.5 mg L^{-1}), ^{70}Zn (142.2 mg L^{-1}), ^{108}Cd (122.5 mg L^{-1}) and ^{204}Pb (441.8 mg L^{-1}) in 5% HNO_3 for preservation.

2.1.11.2 ID Assay

The ID assay used in this study was adapted from Mao et al. (2014). Six replicate soil samples (1 g, air dried < 2mm sieved) were pre-equilibrated in 30 ml 1 x 10^{-5} mol L^{-1} EDTA on an end-over-end shaker for 72 hr at room temperature after which three suspensions for each soil were spiked with 0.4 ml of a multi element isotopic spike solution (^{62}Ni, ^{65}Cu, ^{70}Zn, ^{108}Cd and ^{204}Pb) prepared from individual stocks diluted in Milli-Q water before addition to the suspension to minimise release of trace elements as a consequence of acid addition. For the purposes of spiking soil samples were separated into three groups based on their total elemental concentration and each group spiked with a unique spike solution designed to result in an ~ 20% increase in the isotopic abundance of the spike isotope. The remaining three suspensions were left as (un-spiked) controls.

After spiking the soil suspensions were shaken for further 72 hrs to obtain isotopic equilibrium before the supernatants were separated by centrifugation for 15 min at 2200 rpm and filtered (< 0.2 μm) and the isotopic ratios (^{62}Ni/^{60}Ni, ^{65}Cu/^{63}Cu, ^{70}Zn/^{66}Zn, ^{108}Cd/^{111}Cd, ^{204}Pb/^{206}Pb, ^{204}Pb/^{207}Pb, and ^{204}Pb/^{208}Pb) determined by quadrupole ICP-MS operated in 'collision cell mode' with kinetic energy discrimination' (KED) to reduce polyatomic interference, for example the ^{35}Cl-^{35}Cl interference on ^{70}Zn. It is known that the relative abundance of Pb isotopes vary according to the sources of Pb present in the soil. Therefore, instead of relying on relative abundances of naturally occurring isotopes, the isotopic ratio in un-spiked samples (blanks) were also determined for all five elements after appropriate dilutions to ensure the instrument detector operated throughout in pulse counting mode. Multiple runs (10*100 sweeps) were undertaken to give maximum precision. External mass discrimination correction was also applied by running a certified isotopic standard reference material (NIST SRM-981) as a drift correction every 10 samples, with ICP calibration standards for elements.

2.1.11.3 Calculation of *E value*

The isotopically exchangeable metal concentrations (*E values*) in soil solution in 1 x 10^{-5} mol L^{-1} EDTA were calculated from the ratio of main spike isotopes to one of the major background isotopes. The important measurement is the ratio of isotopic abundance (IA) in the spiked soil solution and in the un-spiked soil solution. For the studied trace elements assayed the ratio of isotopic abundances used was ^{62}Ni/^{60}Ni, ^{65}Cu/^{63}Cu, ^{70}Zn/^{66}Zn, ^{108}Cd/^{111}Cd, ^{204}Pb/^{206}Pb, ^{204}Pb/^{207}Pb, and ^{204}Pb/^{208}Pb. E value (mg/kg) was calculated from:

$$M_E = \left(\frac{AM_{soil}}{W}\right)\left(\frac{C_{spk}V_{spk}}{AM_{spk}}\right)\frac{\left({}^{204}IA_{spk} - {}^{208}IA_{spk}R_{ss}\right)}{\left({}^{208}IA_{soil}R_{ss} - {}^{204}IA_{soil}\right)} \qquad \text{Eq. 2.3}$$

where AM_{soil} and AM_{spk} is the average atomic mass of Ni, Cu, Zn, Cd and Pb in soils and spikes respectively, W is the weight of the soil (kg), C_{spk} is the gravimetric concentration of the metal in the spike solution, V_{spk} is the volume of spike added (L), IA is the isotopic abundance (mole) and Rss is the ratio of isotopic abundances, spiked (spk): background (bg), for the two isotopes in the spiked soil solution.

2.2 Quality control

The Standard Reference Material (SRM 2711 Montana soil) and (SRM 1573a tomato leaf) were used as a reference standard alongside soil and plant samples to confirm data quality. Table 2.1 shows the % recovery of selected trace elements which have studied in this project

Table 2.1 % recovery of trace elements based on the standard material analysis (Montana soil and tomato leaf)

	Cr	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Cd**	**Pb**
Montana soil	89.4	96.5	110	125	113	152	123	124
Tomato leaf	104	102	87.3	88.6	96.2	101	99.6	

2.3 Statistical analysis

Descriptive statistics were presented as mean, median, standard error difference between means, minimum and maximum. A two way ANOVA was used to analyse the concentrations differences between groups. A Pearson correlation coefficient and linear regression were used to determine the relationship between total trace elements in soil and edible parts of vegetables. The data were statistically analysed using the packages SPSS 17.0 and MINITAB 16.0. A p value of <0.05 was considered to be statistically significant.

3 Concentration and Spatial Distribution of Potentially Toxic Elements (PTEs) in Irrigation water and Agricultural Soil in The Kurdistan Region of Iraq: A First comprehensive survey

3.1 An overview of the Kurdistan Region of Iraq

The Kurdistan region of Iraq comprises an area of approximately 165,000 km^2 where fertile plains meet the Zagros and Toros Mountains. It borders Syria to the west, Iran to the east and Turkey to the north (Figure 3.1). The geology is divided into three zones: a thrust zone, a highly folded zone and alluvial plains (the non-folded zone). All geological formations are sedimentary in origin with the rare exception of some rocks in the thrust zone (Buday, 1980). The region is traversed by the Tigris, Greater Zab and Lesser Zab rivers and divided into three governorates; Erbil, Sulaymanyah and Duhok.

Figure 3.1 Map of the Kurdistan region of Iraq showing Sulaymanyah Province.

Water resources and quantity in Iraq are strictly linked with the amount of rainfall and snow in the main river basins and dams, consequently water availability fluctuates through time and from area to area. The predominant water sources of rural areas in Iraq are springs and wells while urban areas completely depend on ground and surface waters; each source is heavily abstracted for domestic, irrigation and industrial purposes (Grego et al., 2004). Untreated but diluted waste water (waste water mixed with stream, spring and rain water) is frequently used for agricultural activities in urban areas due to the lack of alternative sources of irrigation water (Ormizyari, 2009).

The climate is arid and semi-arid: hot in summer, cold and moderately rainy in winter. The annual average rainfall is not more than 200 mm and more than 50% of Iraq is desert where rainfall is < 50 mm per year. Northern areas of Iraq are rainier with 300-550 mm yr^{-1} and in the mountainous north-eastern area rainfall increases to 1000 mm yr^{-1} (UNCTI, 2010). Temperatures are between 13-18°C in March rising to 40-48°C in July and August. Autumn is dry and mild, with average temperatures of 24-29°C in October, and winter temperatures 0-13°C .

World population is increasing, especially in developing countries where annual urban average growth rates of 3.6% were recorded between 1950 and 2005, compared to only 1.4% in developed countries (Aubry et al., 2012). This surge has led to increased demand for food, shelter and employment (Nafiu et al., 2011). The population of Iraq has tripled since 1970, growing from 10 to 30 million, with around 71% of people living in urban areas of which 47% currently live in slum-like conditions. It is predicted that the Iraqi population will increase to approximately 50 million by 2030 (UNCTI, 2010).

Agricultural policy and strategy in Iraq, developed in the 1950’s, aims to provide high levels of food quality and security for the population. This goal was achieved only during the period 1950-1960; after that the agricultural situation deteriorated due to involvement in military conflicts, particularly the 1980-88 Iran-Iraq War, 1991 Gulf War and subsequent economic sanctions. In addition, after the toppling of Sadam Hussein’s regime 1979 to 2003, agriculture suffered as a consequence of poor irrigation infrastructure resulting in degradation of fields and livestock pastures (Schnepf, 2004). The country faces environmental problems including drought, desertification, pollution from oil refineries, oil fires, factories, discharge of raw sewage into rivers, fertilizers and pesticides. There is also air pollution in urban areas and inefficient solid waste management (UNEP, 2003). UNCTI (2010) reported that 39% of agricultural land in Iraq suffered from decreasing areas for crop production.

This study covers Sulaymanyah province, located in northern Iraq. In general, the rocks are sedimentary and range from Cretaceous age to recent, consisting mostly of pelagic limestone and clastic rocks belonging to the Tanjaro and Kolosh formations (Upper Cretaceous and Paleocene in age) (Karim and Surdashy, 2006). Ali (2007) describes the area as covered by alluvial deposits up to about two metres in depth, consisting of a mixture of clasts mainly of limestone fragments.

Sulaymanyah is the largest inhabited Kurdish province with a population of 1,500,000 and a cultivated land area of 1,514,120 hectares. UPA plays an important role in the provision of employment opportunities and provides fruit and vegetables to urban markets (Mahmood, 2002). It is estimated that about 1500-2000 vegetable and crop farms operate in and around Sulaymanyah city and the agricultural produce is sold as a component of daily meals eaten by more than 500,000 urban residents in and around the city.

In the province, solid wastes including domestic, hospital and industrial wastes are disposed of close to the cities. In Sulaymanyah city, ~ 1 kg per capita per day of solid waste is produced and 1,000 tonnes of wastes per day are transferred by municipal vehicles (dumper, tractors, trucks) to solid waste disposal areas (Rashid, 2010). The waste piles in disposal areas are frequently set on fire either by waste scavengers or by spontaneous combustion; consequently pollutants may be released into the air. During the rainy seasons (winter and spring) leachate from the disposal areas flows into the Tanjaro river which farmers depend on for irrigation.

The consequence of increased anthropogenic pollution within UPA has not previously been investigated in Iraq except for some research which has been conducted on drinking water contamination with some PTEs (Sulayvani and Mezuri, 2008;Hawrami and Mezuri, 2014). In this investigation UPA includes all vegetable farming which is practiced by dwellers within the city, in gardens or fenced vacant plots in the front of or close to their houses, and production of crops and vegetables around cities. It is hypothesized that fruits and vegetables produced and consumed in Sulaymaniyah province may be contaminated to some degree with PTEs, and that different types of vegetables pose potential health risks via accumulation of different potentially toxic metals.

The principal objectives of the work presented in this chapter were to evaluate;

(i) The concentrations, spatial distribution and sources of PTEs in urban and peri-urban soils in the Kurdistan region of Iraq, and
(ii) Risk to the population from exposure to the soils via ingestion, inhalation and dermal adsorption.

3.2 Soil Survey of UPA sites in Sulaymanyah Province

A preliminary soil survey was conducted in Sulaymanyah province in November 2012; see Figure 3.2 where survey sites are indicated. Seven areas of five cities (Halabja, Sulaymanyah, Kalar, Sirwan and Khurmal) were selected as typical urban and peri-urban sites. Sample sites within each area were fields used to cultivate various species of leafy, root and fruit vegetables and crops for commercial use. Identification of fields was based on selection of sites where different historical and current irrigation practices operated but also included sites near a municipal waste disposal area where dumping occurred. Specific sampling sites are

described in detail below.

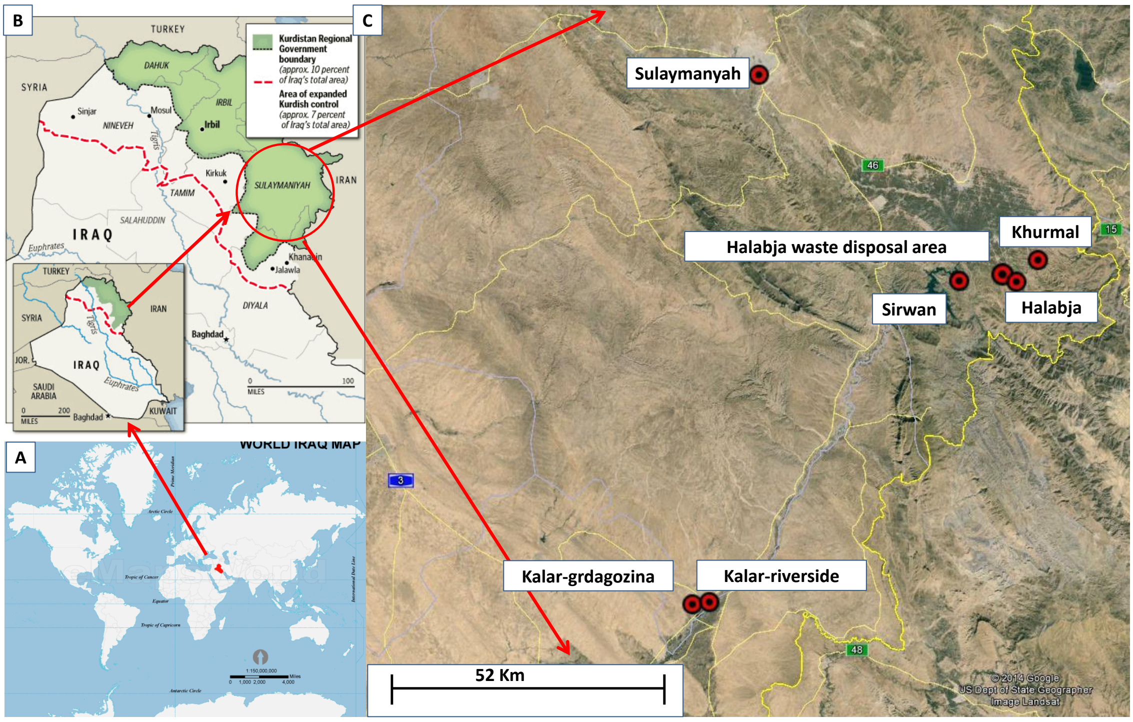


Figure 3.2 Map of Sulaymanyah Province showing selected areas in this survey

Halabja (HALU)

This is an urban area in the north of Halabja city, (Figure 3.3;, 35°11'25.75"N, 45°59'13.34"E) in a region where two waste water channels (from the eastern and southern areas of the city) flow through the site (Figure 3.3). The waste water channels collect water from industrial and domestic areas, including waste water discharge from the hospitals, and are the main source of irrigation water. Agricultural activities include cultivation of substantial pomegranate orchards in addition to a wide range of vegetables that are sold in Halabja city and surrounding districts. Use of pesticides is widespread. Approximately 25 soil samples were randomly sampled from fields and orchards in this area together with 7 samples of irrigation water (Figure 3.3).

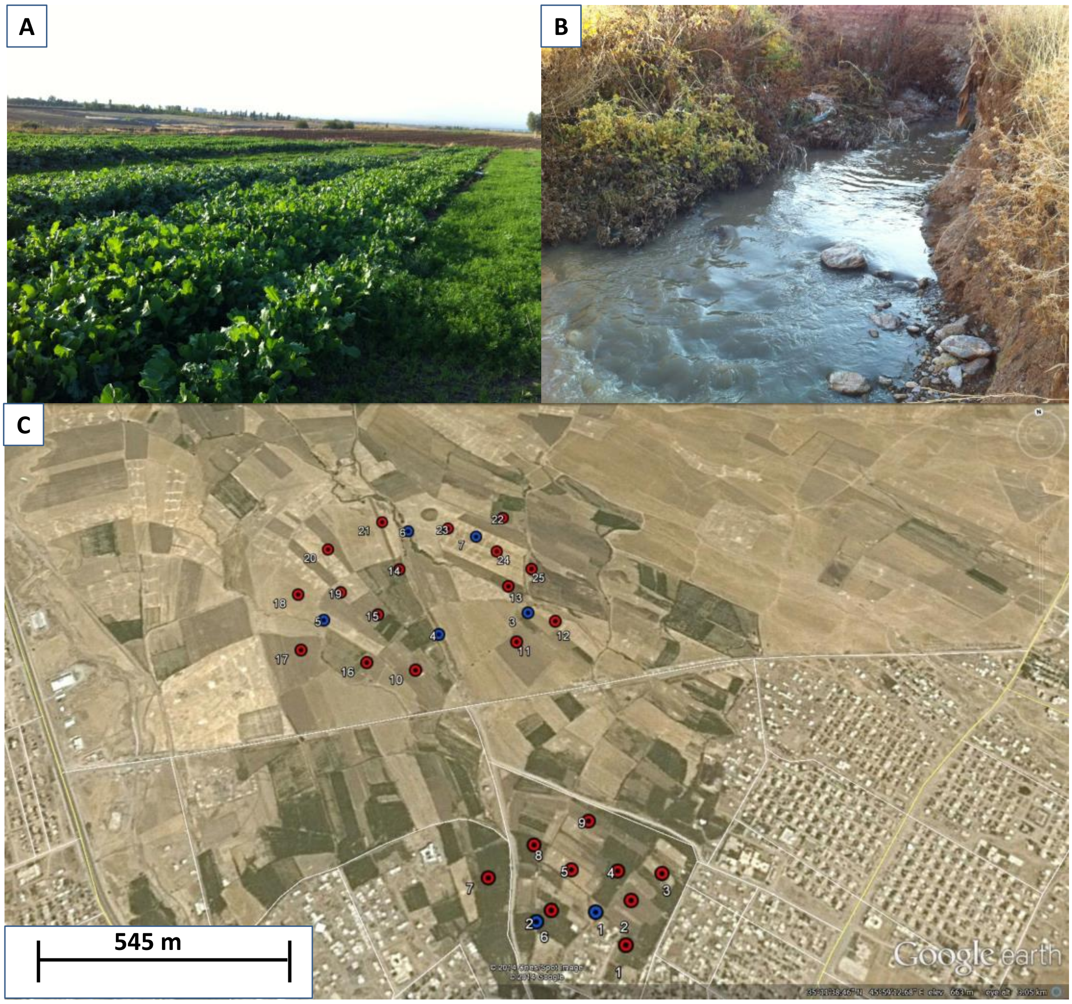


Figure 3.3 Photographs of a typical vegetable plot (a), waste water channel used for irrigation (b) and satellite image of the Halabja area (c) showing soil (red) and water (blue) sample sites.

Halabja waste disposal area (HALW & HALP)

This site to the north west of Halabja city (Figure 3.4; 35°12'28.08"N,45°56'57.65"E), is used by Halabja city council as a disposal site for municipal, hospital and industrial wastes (Figure 3.4a) and is in close proximity to areas used to grow commercial food crops. Wastes include plastic, glass, metal and batteries that are destroyed by burning (Figure 3.4b). Twelve soil samples were collected in and around the area (Figure 3.4 c). Those on the immediate edge of the waste area (3 samples) are termed 'HALW' whilst those further away are designated 'HALP' (9 samples).

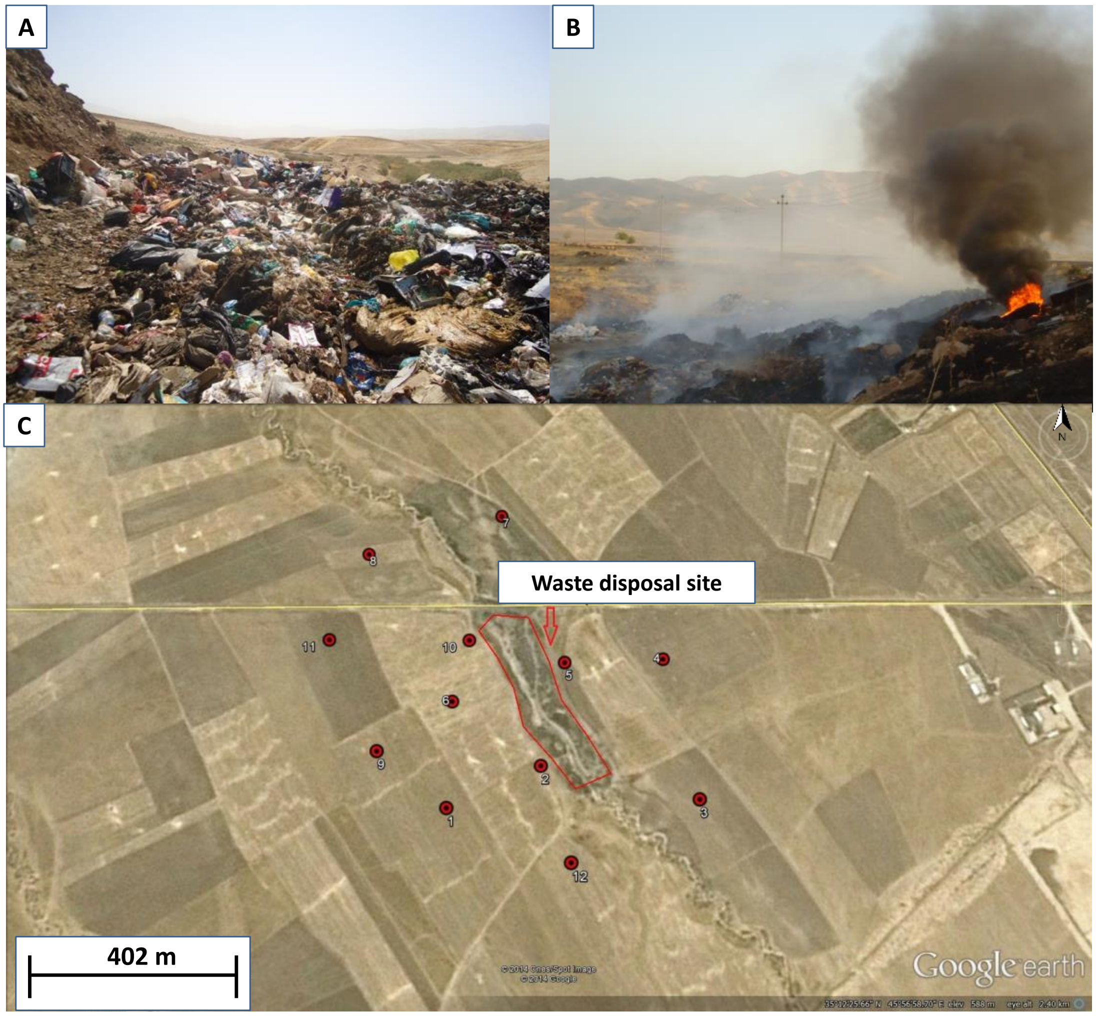


Figure 3.4 Halabja solid waste disposal site (a) where incineration of waste (b) is common. Satellite image of disposal area (c) surrounded by agricultural land showing soil sampling sites (red).

Sulaymanyah (SUL)

This site is to the south of Sulaymanyah city approximately 3 miles from the city centre (Figure 3.5;35°28'47.51"N45°25'28.36"E). Five sewage channels run through the site transporting household waste water to the Tanjaro River (Figure 3.5a & b). River water is used for irrigation and poultry manure is commonly used as an additional fertiliser. A broad range of agriculture activities are practiced alongside the river, with many varieties of fruits and root vegetables produced for commercial and subsistence purposes. This area is also close to the municipal waste disposal site for the city. During rainy seasons runoff from the site is washed into surrounding fields and ash generated as a result of waste incineration deposits on the fields. Several small-scale industries, metal workshops and car scrap yards are also located near the site. Twenty seven soil samples were randomly collected across the area with four samples of irrigation water (Figure 3.5c).

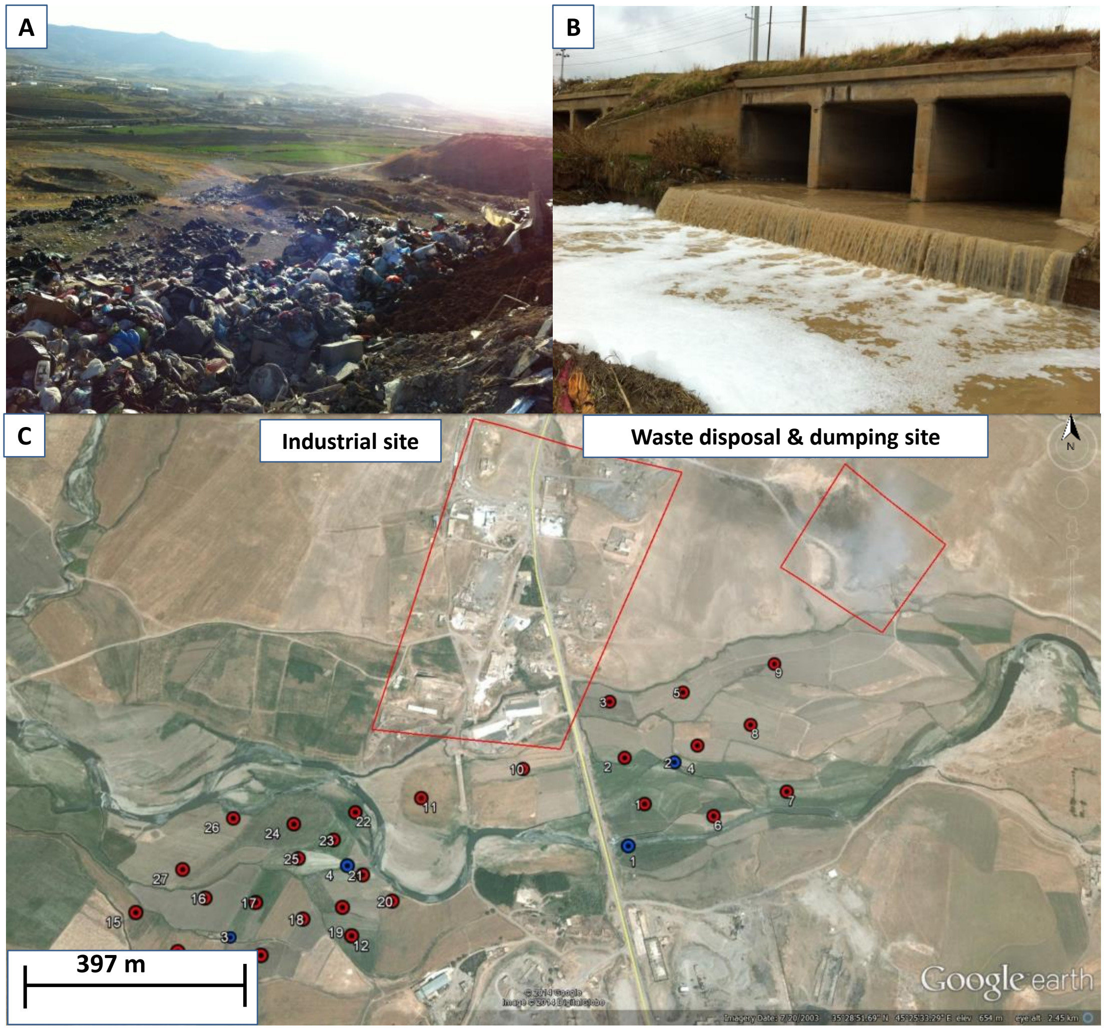


Figure 3.5 Sulaymanyah solid waste disposal and surrounding agricultural land (a) and un-treated waste water used for irrigation in the area (b). Satellite image (c) of Sulaymanyah area showing soil (red) and water (blue) sampling sites.

Sirwan River (SIR)

This site is a peri-urban area, located to the north west of Halabja and south of Saidsadaq city (Figure 3.6; 35°15'12.74"N, 45°51'31.72"E). The Sirwan river receives a combination of inputs from waste water channels from different cities and industrial areas with freshwater streams. During the rainy season (spring) the river floods the surrounding agricultural land (Figure 3.6c). Farming activity at this site begins in summer with a wide range of food crops and vegetables grown, particularly radish, turnip and water melon. Most of the vegetables are sold in the nearby cities. Twenty four soil samples and four irrigation water samples were collected in this area.

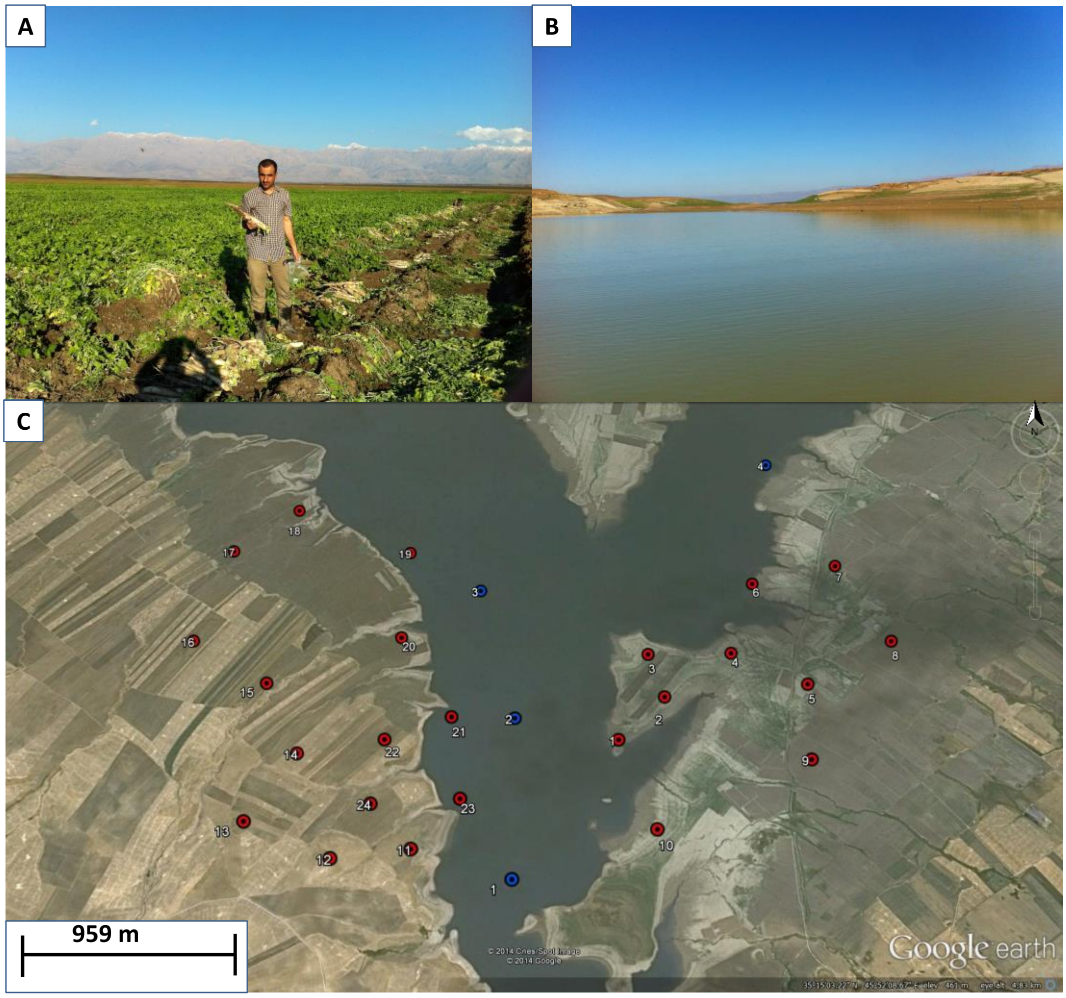


Figure 3.6 Field of radishes (a) alongside the Sirwan River (b) the source of irrigation water in the area. Satellite image of the Sirwan river area (c) showing soil (red) and water (blue) sampling locations.

Kalar Grdagozina (KALG)

This site is situated in a residential area in the south west of Kalar city (Figure 3.7; 34°35'02.44"N, 45°16'55.18"E). It is a relatively large area, about 200 ha, where a wide range of leafy vegetables are cultivated. The site is irrigated with clean (waterwheel) water and large quantities of manure are applied. Eleven soils and four water samples were collected from the area (Figure 3.7c).

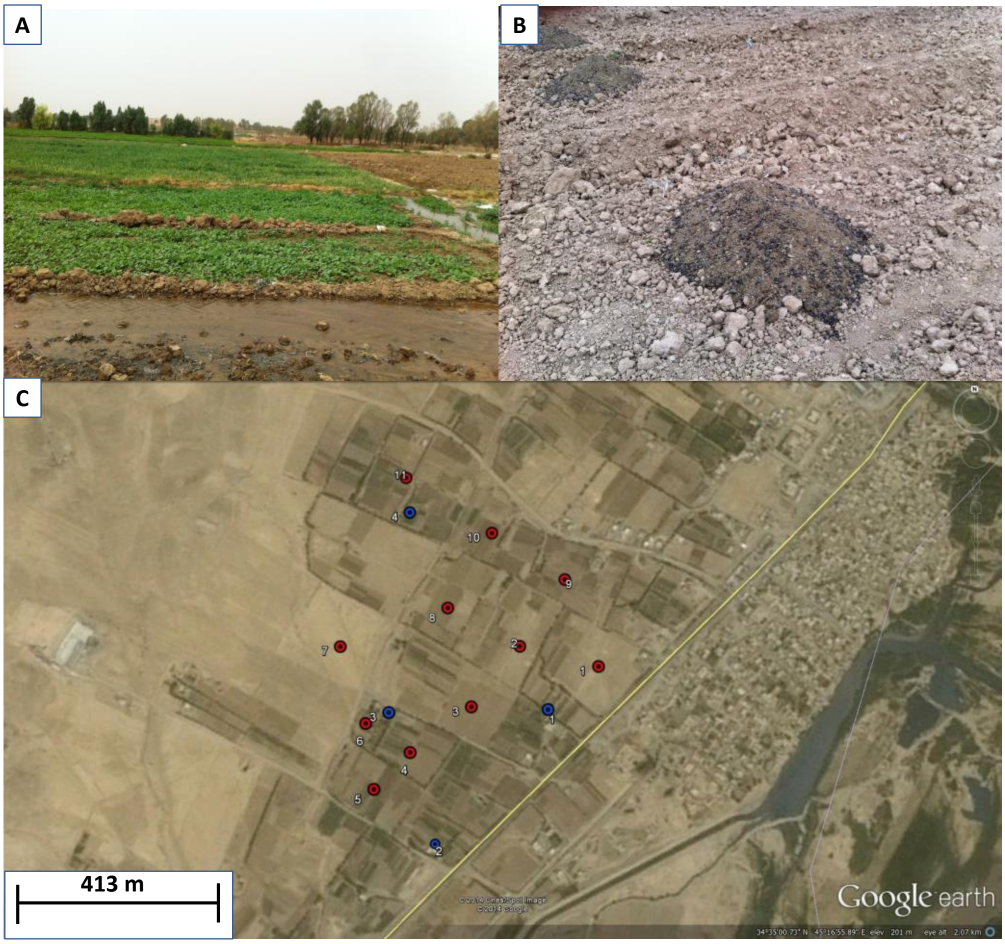


Figure 3.7 Vegetable fields (a) in the Kalar Gragozina area where manure (b) is regularly applied. Satellite image (c) of the area showing soil (red) and water (blue) sampling locations.

Kalar Riverside (KALR)

Located in the south of Kalar city, (Figure 3.8; 34°36'21.63"N, 45°19'04.63"E) this area is irrigated by the Sirwan River. A wide range of vegetable farming, particularly fruit crops and vegetables such as cow pea and okra are grown. Eleven soil samples and four water samples from the irrigation sources were collected (Figure 3.8c).

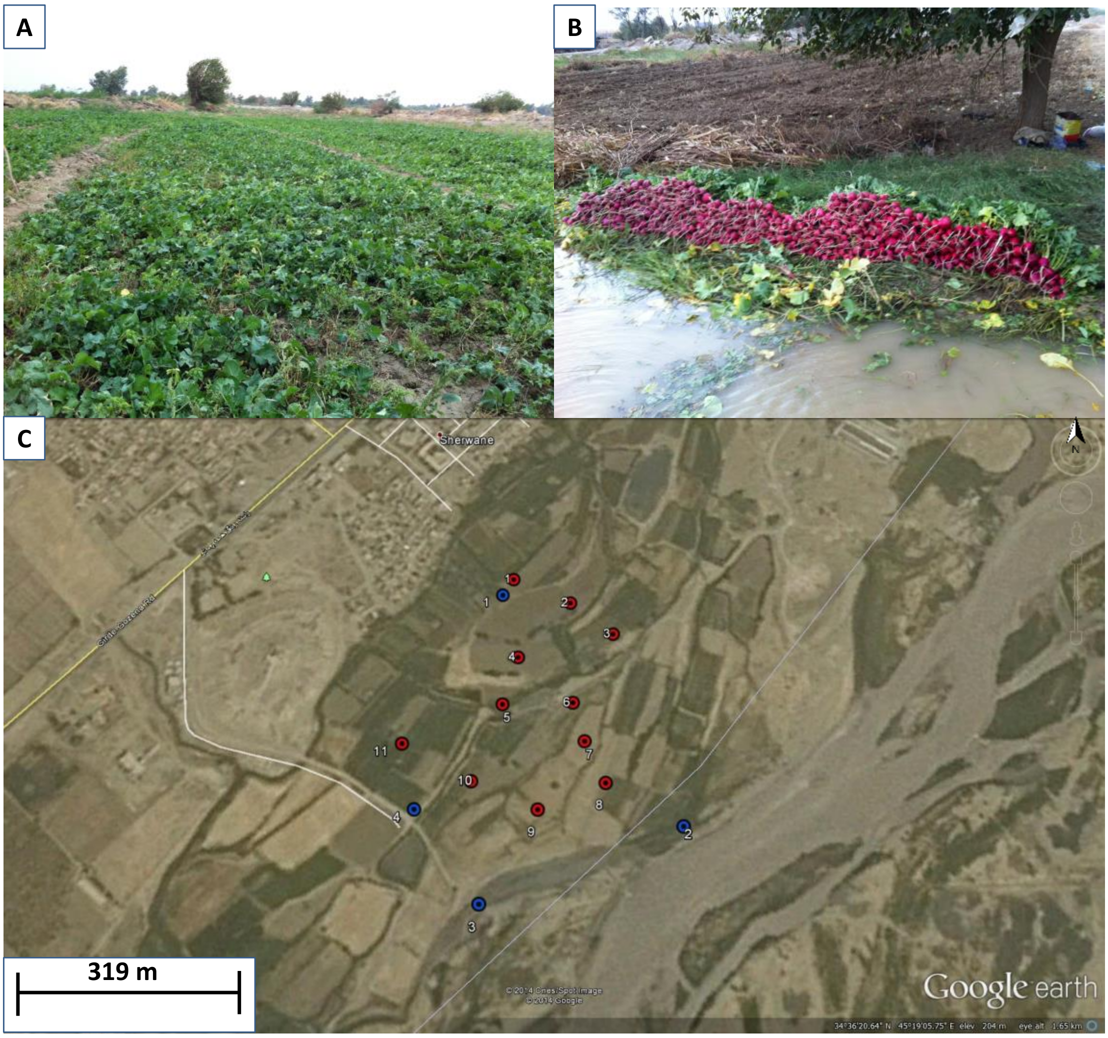


Figure 3.8 Vegetable farming around the Kalar Riverside area (a) where untreated but diluted waste water (b) is used for irrigation purposes. Satellite image (c) of the riverside area showing soil (red) and water (blue) sampling locations.

Khurmal (KHR)

This site is situated in the north west of Khurmal district (Figure 3.9; 35°18'15.83"N, 46° 1'29.88"E). Pomegranate orchards are the most common agriculture in the area (Figure 3.9a & b) although other vegetable types are also grown. There are two sources of water that are used for irrigation. First a freshwater spring which irrigates a few orchards (soil sampling locations 7 & 8) with the remainder irrigated by waste water, mainly sewerage (soil sampling sites 1-6) from the surrounding district (Figure 3.9c).

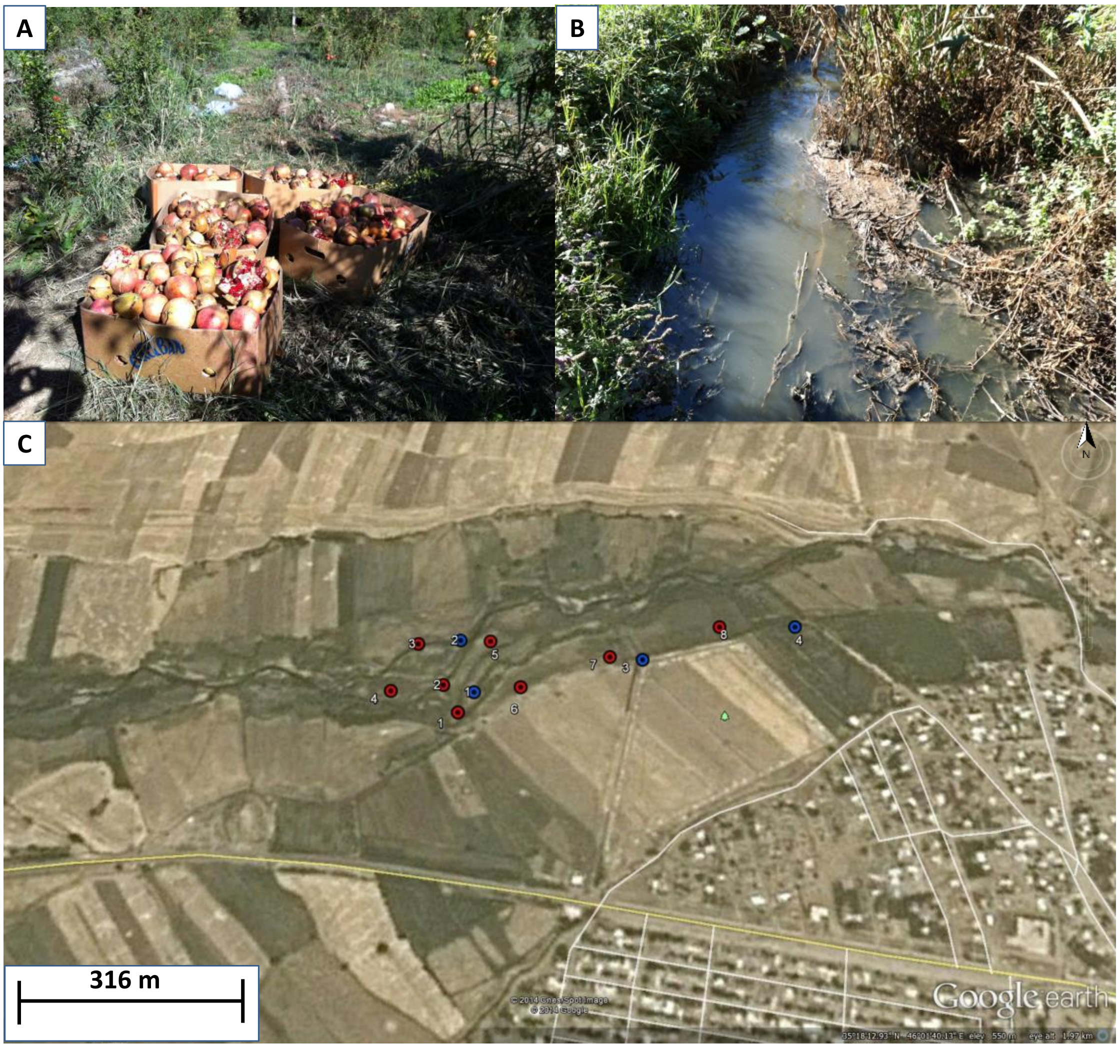


Figure 3.9 Pomegranate harvest (a) from orchards in the Khurmal area where sewage water (b) is used for irrigation. Satellite image (c) of the area showing soil (red) and water (blue) sampling sites.

3.3 Materials and methods

3.3.1 Water sampling

Water samples were taken and immediately filtered in the field through 0.45 µm cellulose acetate syringe filters into polyethylene bottles. Samples were then acidified to 2% HNO_3 and analysed by ICP-MS (see Sections 2.3.3 and 2.3.4).

3.3.2 Soil sampling

Composite top soil samples (0-20 cm depth, 117 samples) were collected from urban, peri-urban and rural areas across the province. Samples were placed in plastic bags and transported to the laboratory where they were air dried and sieved to obtain a <2 mm fraction see Section 2.1.1. Representative subsamples were then sampled using the coning and quartering technique and stored in polyethylene tubes for transport to the UK.

3.3.3 Soil characterisation and elemental analysis

Soil pH was measured in deionised water suspensions (1 : 2.5 soil : solution ratio) after 30 minutes shaking (see Section 2.3.4). Loss on ignition was used to estimate the percentage of organic carbon in the samples (see Section 2.3.5). A portion of each air dried < 2 mm sieved soil was finely ground using an agate ball mill (Retsch, Model PM400), and then stored in a polyethylene bag prior to acid digestion for elemental analysis. Approximately 250 mg of finely ground soil was digested using HF digestion method (see Section 2.3.8) and elemental analysis was undertaken using ICP-MS (see Section 2.3.10).

3.3.4 Exposure dose and health risk assessment model

In this study Cr, Ni, Cu, Zn. As, Cd and Pb were recognised as potentially toxic to human health (USEPA, 2006;USDOE, 2011) and their chronic daily intake (CDI) considered via three pathways: direct oral ingestion of soil particles (CDI_{ing}), inhalation of atmospheric particles (CDI_{inh}) and dermal absorption after adherance of soil particles to exposed skin

(CDI_{derm}). This approach is based upon the method developed by United State Environmental Protection Agency and United State Department of Energy and widely used by other authors (USEPA, 1989;USEPA, 2001b;USDOE, 2011;Luo et al., 2012;Olujimi et al., 2015;Wu et al., 2015).

Exposure dose was expressed in terms of chronic daily intake was calculated separately for each PTE and the various exposure pathways:.

$$CDI_{ing} = \frac{C \times R_{ing} \times EF \times ED}{BW \times AT} \times 10^{-6} \qquad \text{Eq 3.1}$$

$$CDI_{inh} = \frac{C \times R_{inh} \times EF \times ED}{PEF \times BW \times AT} \qquad \text{Eq 3.2}$$

$$CDI_{derm} = \frac{C \times SL \times SA \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \qquad \text{Eq. 3.3}$$

Where C is the exposure-point concentration (mg/kg), R_{ing} is ingestion rate (200 mg d^{-1} for children and 100 mg d^{-1} for adults (USDOE, 2011)), R_{inh} is inhalation rate (7.6 m^3 d^{-1} for children and 20 m^3 d^{-1} for adults (Li et al., 2013)), EF is exposure frequency (350 d yr^{-1} (Wu et al., 2015)), ED is exposure duration (6 yr for children and 24 yr for adults (USEPA, 2001b)), SA is exposed skin area (2800 cm^2 for children, 5700 cm^2 for adults), SL is a skin adherence factor (0.2 mg cm^{-2} d^{-1} for children and 0.7 mg cm^{-2} d^{-1} for adults (USEPA, 2001b), ABS is a dermal absorption factor (no unit) a value of 0.001 was used for all elements (Man et al., 2010), PEF is a particle emission factor PEF, developed by USEPA for the health risk assessment of soil and widely used to calculate the inhalation intake dose of pollutants in soil dusts (USEPA, 1989;Zheng et al., 2010) a value of 1.36×10^9 m^3 kg^{-1} was used (USEPA, 2001b). BW is average body weight, 15 kg for children and 70 kg for adults (Hamad et al., 2014). AT is the averaging time; for non-carcinogens this was equal to ED × 365 d; for carcinogens it is 70 × 365 = 25 550 days (Zheng et al., 2010;Li et al., 2013) .

3.3.5 Risk characterization

CDI for each metal and exposure pathway for potential nan-carcinogenic effect was subsequently divided by the reference dose (RfD) to obtain a Hazard quotient (HQ). It is reasonable to calculate the combined non-carcinogenic risk expressed as hazard index (HI) reflecting the sum of HQs from different exposure pathway (Li et al., 2013;Zhao et al., 2014b;Wu et al., 2015). Using the example of inhalation:

$$HQ_{inh} = \frac{CDI_{inh}}{RfD} \qquad \text{Eq. 3.4}$$

$$HI = \sum HQ = HQ_{ing} + HQ_{inh} + HQ_{derm} \qquad \text{Eq. 3.5}$$

Where HQ is the Hazard quotient based on non-carcinogenic risk, RfD (mg kg^{-1} d^{-1}) is a reference dose of potentially toxic elements via exposure pathways - an estimate of maximum permissible health risk to human via daily exposure through a life time. In this investigation RfDs for various exposure pathways were taken from USDOE (2011). HI is the sum of HQ in different exposure pathways. A value ≤1 denotes no adverse health effect whereas values >1 indicate possible adverse health effects (Li et al., 2013).

3.4 Results and discussion

3.4.1 Physico-chemical properties of waste and fresh waters

Physico-chemical properties of waste and fresh waters are listed in Table 3.1. Guideline values for irrigation water pH range from 6 to 9 (Patel et al., 2004) and all waters sampled are within these safe limits for irrigation purposes. It is not uncommon in the Iraqi Kurdistan region for the pH value of water to be characterized by a shift toward the alkaline side of neutral (above 7) because of the calcareous nature of the geology (Nabi, 2005). The EC of waste water effluents (635 $\mu S\ cm^{-1}$) was significantly higher than the fresh water (542 $\mu S\ cm^{-1}$) at all sampling sites except for Kalar (KAL).

The concentrations ($\mu g\ l^{-1}$) of trace metals in the waters are given in Table 3.1 alongside guideline values, where available. Elevated concentrations are generally observed in the waste waters compared to the fresh waters, although concentrations in both sources of irrigation water were within the permissible limits for their use as irrigation water. According to Pescod (1992) the maximum permissible concentrations of trace metals in irrigation water above which bioaccumulation in agricultural plants can occur are Zn (2000 mg L^{-1}), Cu (200 mg L^{-1}), Fe (5000 mg L^{-1}), Mn (200 mg L^{-1}), Ni (200 mg mg L^{-1}), Pb (5000 mg L^{-1}) and Cd (10 mg L^{-1}). These concentrations were not exceeded in this study. Arsenic concentrations in the waste waters were, however, of the same order of magnitude as the standard.

Lente et al. (2012) in a study in Ghana also found similar concentrations of trace metals in sewage water and ground water used for irrigation. It is normal to find this where the waste water is mixed (diluted) with some other clean sources such as streams, rain water and springs. Waters in several of the study areas (SUL, SIR and KAL) are subject to dilution by fresh water before use. Related studies on waste water in two cities of the Kurdistan region have shown similar trends (Duhoki, 1997;Shekha, 2008;Hamasalih, 2008).

Table 3.1 Concentrations of elements and physicochemical properties of irrigation water (waste and fresh) samples in Sulymanyah province with mean, SD and FAO/WHO guideline value. Values are given to three significant figures.

	HAL		SUL		SIR		KAL		KHUR		Mean		SD		WHO/FAO*
μg L-1	Waste	Fresh	Waste	Fresh	Waste	Fresh	Waste	Fresh	Waste	Fresh	Waste	Fresh	Waste	Fresh	
EC (μS cm-1)	946	604	652	557	620	520	453	603	505	427	635	542	172	66	**500**
pH	8.00	7.70	8.00	7.70	7.90	7.80	7.70	7.80	7.80	8.20	7.88	7.84	0.12	0.19	**7**
Na	66800	3830	23500	2460	12600	15000	10400	15500	24500	4470	27600	8240	22800	6420	
Mg	7200	11200	8220	10100	12600	13700	9690	15200	3880	6010	8320	11200	3210	3550	
K	10110	0890	5780	1560	2160	950	1860	900	4490	910	4880	1040	3350	290	
Ca	58800	72900	56300	59700	74.0	60900	50300	65400	49700	58000	57800	63300	9820	6000	
Al	40.5	20.1	13.8	28.3	11.4	21.9	56.1	11.2	18.2	13.0	28.0	18.8	19.5	6.97	
V	2.53	3.74	7.82	5.86	5.56	8.80	3.00	7.99	1.21	1.38	4.02	5.55	2.65	3.05	
Cr	3.07	2.49	2.30	2.35	1.59	1.02	2.94	3.92	6.86	5.52	3.35	3.67	2.05	1.30	**50**
Mn	124	13.2	276	20.4	37.6	2.03	6.76	0.90	70.4	1.34	103	7.60	106	8.80	**200^{1}**
Fe	57.5	26.6	26.7	31.5	19.4	18.9	82.5	10.6	49.4	33.0	47.1	24.1	25.3	9.30	**5000^{1}**
Co	0.62	0.13	1.51	0.25	0.39	0.04	0.14	0.03	0.36	0.06	0.60	0.10	0.53	0.09	**50**
Ni	5.78	2.58	10.0	4.16	4.11	1.23	2.91	0.85	4.91	4.00	5.54	2.56	2.71	1.53	**200^{1}**
Cu	2.66	0.79	1.25	1.27	0.65	0.60	0.81	0.34	1.47	4.02	1.37	1.40	0.80	1.50	**200^{1}**
Zn	60.8	65.0	20.8	37.1	17.4	15.5	19.9	15.1	37.9	27.5	31.3	32.0	18.4	20.5	**2000^{1}**
As	1.06	0.51	2.79	0.85	1.85	0.40	1.19	0.39	0.66	5.87	1.51	1.60	0.83	2.39	**10**
Se	0.73	0.91	0.37	1.08	0.56	0.49	0.48	0.58	0.18	0.16	0.46	0.64	0.21	0.36	
Sr	364	528	400	481	584	1320	607	1400	138	234	419	793	190	530	
Mo	7.41	10.8	2.73	14.8	2.44	2.82	2.77	2.34	3.24	2.37	3.72	6.64	2.08	5.83	
Cd	0.07	0.04	0.02	0.02	0.02	0.02	0.02	0.01	0.03	0.08	0.03	0.04	0.02	0.03	**10^{1}**
Cs	0.05	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.02	0.05	0.02	0.01	0.02	0.02	
Ba	106.1	124.6	73.8	86.3	94.2	50.3	74.5	57.1	28.1	32.2	75.0	70.0	30.0	36.0	
Pb	0.87	0.23	0.15	0.076	0.09	0.14	0.24	0.07	0.30	1.36	0.33	0.41	0.31	0.53	**5000^{1}**
U	0.44	0.98	0.44	1.02	0.64	1.60	0.48	1.82	0.24	0.34	0.45	1.15	0.14	0.58	

*FAO/WHO guideline values for PTEs in irrigation water. [1]concentrations leading to accumulation in the soil according to Pescod (1992)

3.4.2 Soil properties

Soil pH and organic matter are considered to be significant factors controlling trace element mobility, accumulation and bioavailability. At high pH the lability and bioavailability of trace elements decreases due to precipitation as carbonates and hydroxides, while their mobility increases when the pH decreases (Xu et al., 2010). The range of pH and organic matter (LOI %) values for all studied areas are given in Table 3.2. The mean soil pH values ranged from 7.94 in Khurmal (KHR) to 8.21 in Kalar (KALR), this narrow range of pH reflects the alkaline, calcareous nature of the soils (Rashid, 2010). The organic carbon content of the soils ranged from 6.62% at the Kalar Riverside area (KALR) to 13.67% at the Halabja waste disposal area (HALW). The highest value recorded at the Halabja waste disposal area is probably due to the influence of organic municipal waste disposal. Anikwe (2002) in a similar investigation recorded higher organic matter content at municipal waste dumping sites in Nigeria compared to non-dump sites. Many studies conducted at sites where there has been long term waste water irrigation of soils show higher soil organic matter contents in the topsoil compared to control sites (Gwenzy and Munodo, 2008;Qishlaqi et al., 2008;Xu et al., 2010).

3.4.3 Major and Trace Element Concentrations in Soils

Concentrations of major and trace elements are presented in Table 3.2. Major element chemistry reflects the calcareous geology of the area. Calcium is the dominant cation and present at significantly greater concentrations than the other base elements with mean concentrations ranging from 48800 mg kg^{-1} in the urban area of Halabja (HALU) to 129000 mg kg^{-1} at the Halabja waste disposal location (HALW). Other studies in calcareous areas have shown similar major elements profiles (Iqbal and Shah, 2011;Nazif et al., 2015).

Mean and trace element concentrations for soils in the different areas are presented in Table 3.2 and Fig. 3.10 together with available environmental standards. No local environmental standards exist for trace elements in soils in Iraq therefore concentrations were compared to

UK, European and WHO guidelines (EU/WHO). Large standard deviations for some elements demonstrate heterogeneity between soils within the same sampling area. Total concentrations of individual elements were also highly variable between study areas ($p<0.01$) suggesting localized contamination sources. With the exception of the HALW site, mean concentrations in each area were lower than UK and EU/WHO standards for all elements with the exception of Ni and Cr. Concentrations of Cr in all areas except KHR and KALG, and Ni in all areas, exceed EU standards (European Union, 2006). Cr concentrations ranged from 80.5 mg kg^{-1} at KHR to 128 mg kg^{-1} at HALU and Ni from 86.1 mg kg^{-1} at KHR to 185 mg kg^{-1} at KALR, respectively. The lowest Cr concentrations recorded was in soil 19 in the SIR area (59 mg/kg) (see Appendix Table A5).

Concentrations of Cr were above EU/WHO guideline and SGVs in most samples (see Appendix Tables A1-A8). In the HALU area all soil (n=24) Cr concentrations were above EU/WHO guidelines. Soils from KALG (n=11) had significantly lower Cr concentrations than the EU/WHO guideline (see Appendix Table A2 and A7 respectively) perhaps due to the geological background of this area. Chromium concentrations were in agreement with the study conducted in Damascus, Syria by Möller et al. (2005). They stated that the main sources of Cr in soils at their sampling sites was geogenic since the concentrations were in strong agreement with "pedogeochemical" background values . Nickel concentrations in all soils (n=117) exceed EU/WHO guidelines (50 mg kg^{-1}) but all were lower than the UK SGV of 250 mg kg^{-1}; again this may be a consequence of the background geology of the area. Nickel concentrations in this study are in agreement with those found by Habib et al. (2012). Their study was carried out in Baghdad city where 25 soil samples were analysed for trace elements including Ni. The authors reported high concentrations of Ni in all the soil samples, ranging between 105 - 210 mg kg^{-1} with little variation between the sites; this may also reflect geogenic sources of Ni in the Iraqi soil rather than anthropogenic sources.

Chromium concentrations were greatest in soils at HALW ranging from 106 - 175 mg kg^{-1} (Appendix Table A4) with a mean concentration of 135 mg kg^{-1}; this value exceeds both EU/WHO standards and SGVs (100 and 130 mg kg^{-1}, respectively) and is also significantly higher than Cr concentrations observed in other areas. This may therefore be attributed to the disposal of chromium–bearing wastes, particularly chemical pigments, leading to increased concentrations of Cr in the soils. By contrast, Ni was present at lower average concentration (74.9 mg kg^{-1}) than in other areas but still exceeded EU/WHO standards (50 mg kg^{-1}) perhaps due to being present at lower concentration in the waste components (Fig. 3.10b). The concentrations of Cr and Ni in the soils near the waste disposal site are in agreement with a study conducted by Beyene and Banerjee (2011). They sampled six soils near the municipal waste disposal area and reported soil concentrations of Cr of 178 mg kg^{-1} and Ni of 48 mg kg^{-1}.

Soil Cu and Zn concentrations ranged from 22 mg kg^{-1} at KALG to 37.0 mg kg^{-1} at HALU and 75 at SIR to 123 mg kg^{-1} at KALR, respectively. Zinc and Cu concentrations were below the UK Ministry of Agriculture Fisheries and Food (MAFF) threshold concentrations for the addition of sludge to agricultural soils in all areas where threshold levels (50 mg kg^{-1} Cu and 300 mg kg^{-1} Zn) were exceeded (MAFF, 1998). Significantly greater concentrations of Zn were measured in three soils in the SUL area (soils 3, 5 and 9 with 432, 356 and 278 mg kg^{-1}, respectively) (see Appendix Table A1). These are close to or exceed EU/WHO and SGV for sludge-amended soils. This increase in Zn concentration may be a consequence of their proximity to a municipal waste disposal area Figure 3.5 where leachate from the waste flows through the agricultural fields.

Concentrations of Cu and Zn at HALW were higher than in other areas (263 and 773 mg kg^{-1}, respectively) (Figs 3.10c and d). The values obtained for Cu and Zn at HALW were far above UK standards for soils amended with sludge. High concentrations of these elements may be expected if waste disposal is a source, although motor vehicle emissions may also be a significant contributor of Cu and Zn. Dao et al. (2014) conducted an investigation on 225 road side soils in Dublin and observed that concentrations of Cu and Zn decreased exponentially with increasing distance from the road.

Mean concentrations of As ranged from 4.74 mg kg^{-1} at SUL to 13.5 mg kg^{-1} at KHR and HALU. Se concentrations ranged from 0.690 at SIR to 1.47 at KHR. In all cases, As and Se concentrations were below soil guideline values (Environment Agency, 2009c). Wastewater irrigation is typically considered to be one of the main sources of As and Se (Harper and Kingham, 1992;Díaz et al., 1996). Analysis of the waste waters used for irrigation in these areas indicates that concentrations of As and Se are within those considered safe for irrigation water (Table 3.1). Variation in As and Se between areas may be due to local variation in the geology and the degree of weathering, in addition to anthropogenic activity (Bajaj et al., 2011). The highest As concentrations were observed in agricultural fields in the HALU, HALP and KHR areas which experience periodic flooding following heavy rain. Selenium concentrations are similar to those found in agricultural soils of other semi-arid regions (0.20–4.38 mg kg^{-1}) (Moreno et al., 2005;Roca-Perez et al., 2010) .The As and Se concentrations in the soils around the waste disposal site were 9.61 and 0.760 mg kg^{-1}, respectively. Unlike Cu and Zn, waste disposal did not appear to influence soil Se and As content since concentrations were similar to those of other areas.

Alloway (1995) observed that, in general, for top soils worldwide Cd concentrations do not exceed 1 - 1.1 mg kg^{-1}. Addition of Cd to soil can be from sources including agricultural applications, sewage sludge and atmospheric precipitation (Alloway, 2004). The concentrations of Cd in the studied areas (0.228-4.19 mg kg^{-1}) may reflect the local geology, low concentrations of Cd in the irrigation water and the lack of use of Cd-rich phosphate fertilizer in the area. The concentration of Cd at HALW (Figure 3.10g) was an order of magnitude higher than for other sampling sites, presumably a consequence of the waste disposal itself. Although there were small scale industrial and metal processing businesses near the SUL sampling area Cd concentration was low (0.32 mg kg^{-1}). Maas et al. (2010) recorded similar results for Cd in industrial areas of an Algerian city and suggested that this was due to low Cd emissions from the industries, high dispersion due to wind or low retention of Cd in the surface soil. Several previous studies have concluded that agricultural soils around municipal waste dumps and disposal sites may be significantly affected by waste leachate and/or precipitation of particulates from (Anikwe and Nwobodo, 2002;Beyene and Banerjee, 2011;Ali et al., 2014).

Table 3.2 Soil properties and total elemental concentrations (mg/kg) in selected urban and peri-urban soils in Sulaymanyah province with mean, SD and SGV. Values in bold denote those at or above relevant soil standards.

	SUL		**HALU**		**HALP**		**HALW**		**SIR**		**KHR**		**KALG**		**KALR**		**SGV[a]**	**EU/ WHO[c]**
	Mean	*±SD*	Mean	*±SD*	Mean	*±SD*	Mean	*±SD*	Mean	*±SD*	Mean	*±SD*	Mean	*±SD*	Mean	*±SD*		
n	26		27		8		3		25		11		11		8			
pH	8.08	*1.89*	8.04	*1.74*	8.11	*0.16*	8.10	*0.17*	8.15	*1.62*	7.94	*1.54*	8.01	*1.66*	8.21	*2.20*		
LOI%	8.81	*0.26*	11.0	*0.16*	11.1	*0.78*	13.7	*2.55*	8.55	*0.08*	9.23	*0.16*	8.76	*0.16*	6.62	*0.09*		
Na	2510	*270*	2550	*173*	2940	*557*	4620	*1640*	2350	*526*	2790	*186*	3530	*704*	6290	*1830*		
Mg	14700	*2710*	12500	*1170*	14800	*3120*	10300	*1070*	13900	*2122*	10513	*1830*	15300	*2020*	19500	*1690*		
K	7600	*1340*	11500	*533*	11200	*1840*	9390	*1700*	8260	*1760*	8770	*1700*	8530	*1000*	10600	*658*		
Ca	110000	*18800*	48800	*8310*	76500	*34500*	129000	*21700*	96300	*23100*	1270000	*49400*	111000	*16800*	11600	*6270*		
Al	32200	*4649*	41300	*3090*	47000	*9890*	31100	*3550*	34000	*7230*	36500	*8670*	31800	*3720*	42000	*3080*		
V	74.2	*5.52*	109	*5.43*	92.7	*14.7*	62.3	*7.90*	76.0	*11.5*	73.1	*14.8*	67.1	*5.02*	85.6	*3.61*		
Cr	**114**	*24.3*	**128**	*5.85*	**114**	*18.5*	**134**	*36.4*	**103**	*16.0*	80.5	*18.5*	81.3	*5.66*	**106**	*6.39*	**130**	**100**
Mn	590	*96.1*	879	*42.2*	726	*120*	651	*89.2*	548	*93.2*	614	*226*	539	*49.2*	563	*35.7*		
Fe	25000	*3090*	35000	*1200*	29400	*5000*	26800	*4300*	23800	*4230*	28107	*5540*	22016	*2380*	27738	*1790*		
Co	16.2	*2.51*	20.2	*0.94*	17.9	*3.05*	12.5	*1.41*	15.8	*2.48*	15.1	*3.54*	12.3	*1.25*	14.5	*1.39*		
Ni	**125**	*35.8*	**134**	*7.11*	**117**	*22.4*	**74.9**	*11.2*	**129**	*26.3*	86.1	*22.4*	**145**	*13.3*	**185**	*10.7*	**250**	**50**
Cu	29.0	*3.01*	37.0	*2.27*	30.8	*4.03*	**263**	*155*	27.8	*4.51*	29.5	*4.77*	22.0	*1.74*	26.3	*5.48*	**50[b]**	**100**
Zn	111	*94.4*	112	*35.9*	87.0	*9.38*	**773**	*192*	75.0	*13.9*	97.2	*15.5*	78.9	*6.94*	123	*53.8*	**300[b]**	**300**
As	4.74	*0.516*	13.5	*1.16*	10.4	*1.48*	9.61	*2.48*	5.70	*1.31*	13.5	*1.94*	6.43	*0.48*	5.90	*0.61*	**43**	
Se	0.9	*0.083*	1.38	*0.06*	0.94	*0.12*	0.76	*0.06*	0.69	*0.110*	1.47	*0.17*	0.926	*0.23*	1.17	*0.05*	**120**	
Sr	286	*40.0*	144	*18.4*	174	*47.3*	323	*43.5*	244	*54.3*	115	*10.8*	381	*31.4*	323	*14.6*		
Cd	0.32	*0.10*	0.57	*0.05*	0.422	*0.03*	**4.19**	*1.66*	0.34	*0.04*	0.36	*0.03*	0.23	*0.02*	0.24	*0.09*	**1.80**	**3.00**
Cs	2.64	*0.40*	3.42	*0.54*	3.99	*0.77*	2.45	*0.33*	2.83	*0.64*	3.45	*0.63*	2.47	*0.30*	2.81	*0.44*		
Ba	229	*23.1*	358	*17.1*	390	*40.4*	511	*126*	238	*47.2*	185	*51.0*	248	*18.5*	230	*9.54*		
Pb	12.1	*4.31*	15.5	*3.35*	13.1	*2.25*	**161**	*17.4*	21.7	*11.5*	17.1	*3.91*	44.4	*3.82*	63.0	*10.8*	**450**	**100**
U	1.13	*0.05*	1.72	*0.05*	1.42	*0.12*	1.20	*0.04*	1.23	*0.14*	1.17	*0.13*	1.19	*0.15*	1.16	*0.15*		

[a]Soil Guideline Values (SGVs)(Environment Agency, 2009c) [b]Cu and Zn (MAFF, 1998), [c] (European Union, 2006)

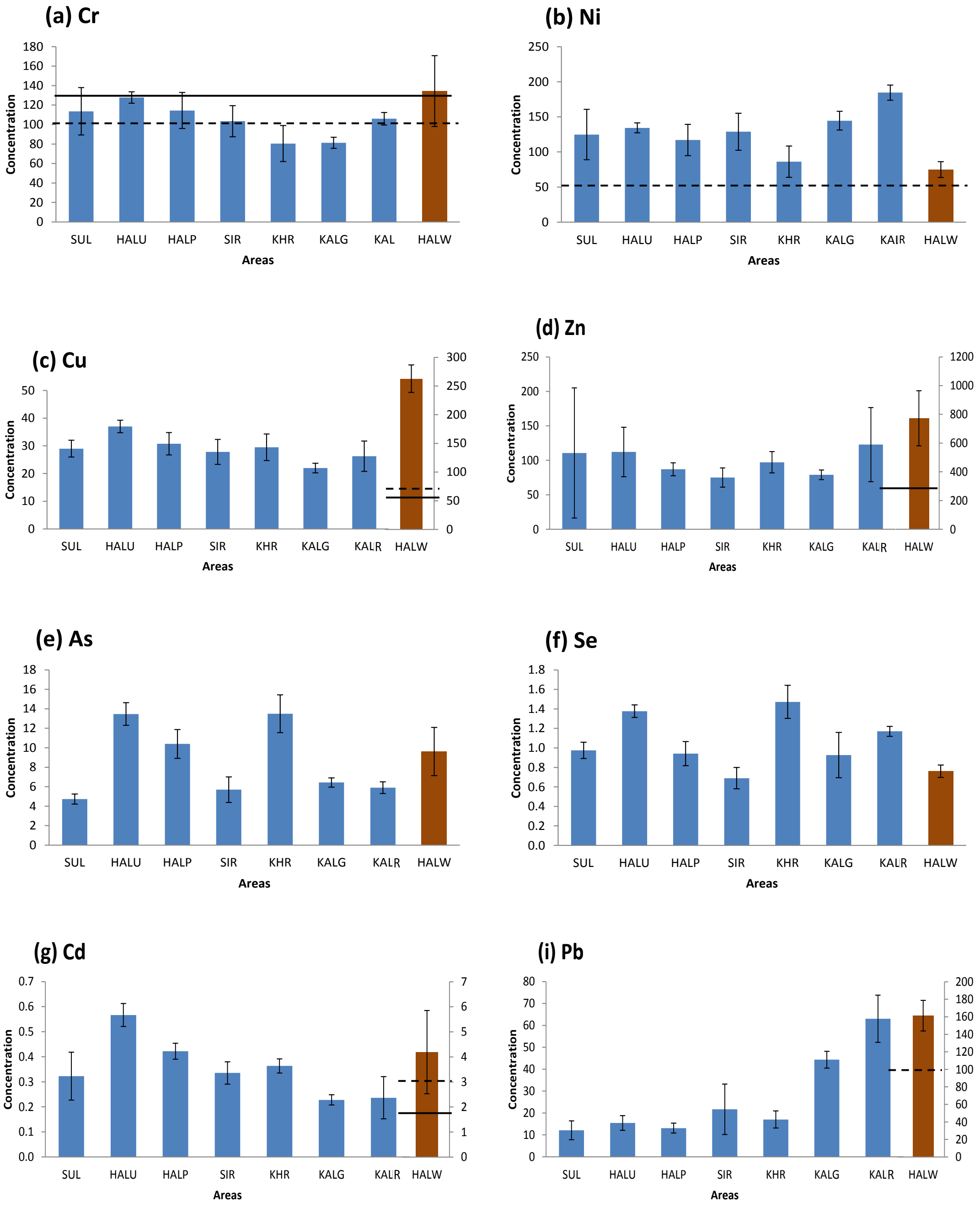


Figure 3.10 Mean concentrations of (a) Cr, (b) Ni, (c) Cu, (d) Zn, (e) As, (f) Se, (g) Cd and (i) Pb for all study sites (mg/kg). Vertical bars associated with each bar show standard deviations of concentrations at the different sites within one area. Dashed line denotes EU/WHO standards. The secondary axis relates only to the HALW data (column shown in brown).

Total Pb concentrations ranged from 12.1 mg kg^{-1} in SUL to 63.0 mg kg^{-1} at KALR, excluding the concentration of 161 mg kg^{-1} recorded at HALW. An obvious increase in Pb concentration is observed at the KALG and KALR sites (Fig 3.10). This may be because soils from KALG and KALR are close to the main Kalar-Sulaymanyah road which has high traffic volumes while other sites are far away from main roads and therefore further away from traffic-related Pb emissions. In Iraq, leaded gasoline is widely used, for example in the Kurdistan region more than 82% of the gasoline consumption is leaded (Rashid, 2010).

A significantly higher concentration of Pb was observed at HALW compared to other sites. Pb-contamination sources in the area include a number of car-repair shops and the main Halabja-Sulaymanyah motorway. High concentrations of Pb in roadside verges are expected and have been reported in many previous studies (Cuny et al., 2001;Säumel et al., 2012;Aslam et al., 2013). Nabulo et al. (2006) conducted a study on 11 farming sites alongside main motorways around Kampala City and found that Pb, Zn and Cd concentrations in roadside soils increased significantly with proximity to highways. They concluded that the accumulation of Pb, Zn and Cd in the roadside samples decreased exponentially with distance from the main motorway.

A comparison between waste water and fresh water irrigated soils and soils at the waste site HALW is shown in Figure 3.11. Compared to the elevated PTE concentrations in the soils subject to waste disposal, no clear impact of waste water irrigation is observed. Slight increases in Cd, Cr, Ni, Cu, Zn and Pb are observed in the waste water irrigated soils, but this is insignificant compared to the impact of municipal waste disposal. Singh et al. (2010) and Nazif et al. (2015) also observed a similar pattern of trace elements in clean water and waste water irrigated soils with little effect of waste water irrigation.

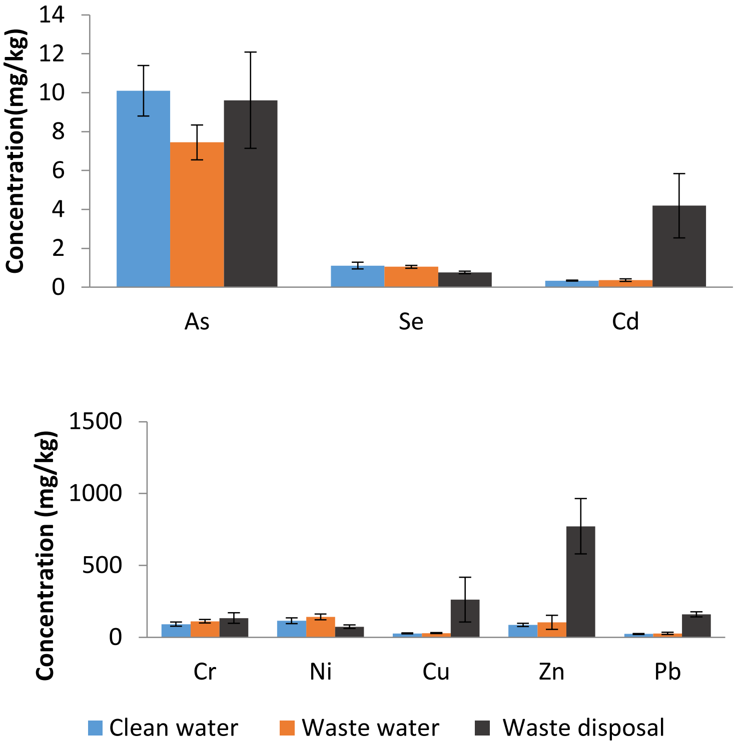


Figure 3.11 Mean concentration of PTEs in clean and waste water irrigated soil and waste disposal soils. Vertical bars associated with each bar show standard deviations of PTE concentrations at the different sites within one area.

3.4.4 Correlation analysis

Relationships between trace elements can provide information on their sources and pathways (Chen et al., 2008). Pearson correlation coefficients (r) were calculated in order to interpret and confirm relationships between trace elements and related soil properties (pH and organic matter) for the sampled areas (Table 3.3). Overall, negative relationships between pH and Ca, Mn, Cu, As and Cd were observed and positive, but very weak correlations, were observed between pH and Cr, Ni, Zn and Pb. This suggests that the narrow range of pH (7.9-8.3) of these soils limits interpretation of this relationship (Manta et al., 2002). In contrast, significant positive correlations were found between organic matter (LOI%) and elements including Cr, Mn, Co, Cu, Zn, As and Cd, which may reflect strong adsorption of these elements by organic matter.

Strong positive correlations ($p > 0.01$) were observed between Cr and Mn, Fe, Co, Ni and Cu when the entire dataset was considered. Cu, Zn, Cd and Pb were also highly correlated with each other Cu-Zn ($r=0.80$;

p>0.01), Cu-Cd (r=0.97; p>0.01), Cu-Pb (r=0.68; p>0.01), Zn-Cd (r=0.82; p>0.01), Zn-Pb (r=0.72; p>0.01) and Cd-Pb (r=0.70; p>0.01) suggesting common sources (Huang et al., 2013).

Correlations between elements are more variable when comparison is made on a site-by-site basis. For example, in HALP (n=8 soils) and KHR (n=11 soils) significant correlations were found between pH, LOI and trace elements (Al, V, Cr, Mn, Fe, Co, Ni, and As) (Appendix, Tables A11 and A14, respectively) but in other areas these correlations were weak. Strong significant relationships between essential elements (Na, Mg, K and Ca) and all trace elements except Pb and U were found in SUL soils (n=27) (Appendix Table A9); e.g. correlations with Cd were r= 0.99, 0.90, 0.98 and -0.97 at p<0.01, respectively. In contrast, for HALU soils (n=24) essential elements (Na, Mg, K and Ca) were weakly correlated with several trace elements; e.g. V, Mn, As and Ba.

In the HALP, SIR and KALG soils (n=8, 25 and 11), correlation coefficients indicated that Cu was significantly correlated with Mn (r=0.87, 0.55, 0.84), Zn (0.87, 0.90, 0.77) and Cd (r=0.56, 0.71, 0.44), respectively, suggesting probable adsorption of these metals on oxyhydroxides (Yan et al., 2010). Copper and Zn correlations varied from r = 0.91 at KALR to r = -0.14 at KHR. Cu and Cd correlations ranged from strongly positive (r = 0.98) to strongly negative (r = -0.97) at SUL and KALR, respectively. Correlations between Cu and Pb were significant in all areas except for SIR, KHR and KALG where very poor correlations were observed (r=0.07, r=-0.12 and 0.28 at p<0.01, respectively). Correlations of Zn with Cd and Pb also greatly varied between sampling areas. Strong positive correlations (p<0.01) of Zn-Cd and Zn-Pb were found in KALR and HALU while weak correlations were observed at KHR.

Table 3.3 Pearson correlation coefficients showing a number of significant positive and negative correlations between trace element concentrations and soil properties. Bold values denote significance at $p<0.01$.

	LOI	**pH**	**Na**	**Mg**	**K**	**Ca**	**Al**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Cd**	**Cs**	**Ba**	**Pb**	
pH	-0.16																						**pH**
Na	**-0.34**	0.23																					**Na**
Mg	-0.15	**0.34**	**0.46**																				**Mg**
K	**0.38**	0.12	**0.28**	0.26																			**K**
Ca	**-0.50**	-0.08	0.23	-0.04	**-0.68**																		**Ca**
Al	**0.36**	0.15	0.23	**0.47**	**0.86**	**-0.63**																	**Al**
V	**0.34**	0.06	0.01	0.12	**0.83**	**-0.84**	**0.76**																**V**
Cr	**0.48**	0.19	-0.06	**0.32**	**0.49**	**-0.64**	**0.53**	**0.63**															**Cr**
Mn	**0.39**	-0.03	-0.09	-0.14	**0.70**	**-0.74**	**0.57**	**0.84**	**0.49**														**Mn**
Fe	**0.49**	0.02	0.01	0.13	**0.85**	**-0.79**	**0.81**	**0.92**	**0.70**	**0.81**													**Fe**
Co	**0.44**	0.10	-0.25	0.18	**0.66**	**-0.85**	**0.71**	**0.87**	**0.80**	**0.72**	**0.88**												**Co**
Ni	-0.10	**0.30**	**0.39**	**0.82**	**0.34**	**-0.30**	**0.42**	**0.34**	**0.43**	0.02	**0.30**	**0.34**											**Ni**
Cu	**0.42**	-0.06	0.06	-0.22	0.04	0.05	-0.06	-0.10	**0.34**	0.10	0.09	-0.09	-0.26										**Cu**
Zn	**0.37**	0.02	0.15	-0.17	0.05	0.09	-0.04	-0.12	0.17	0.07	0.08	-0.15	-0.26	**0.80**									**Zn**
As	**0.43**	-0.19	-0.08	**-0.39**	**0.65**	**-0.55**	**0.50**	**0.70**	0.25	**0.75**	**0.74**	**0.54**	-0.16	0.10	0.07								**As**
Se	**0.29**	-0.18	0.12	**-0.01**	**0.57**	**-0.36**	**0.50**	**0.61**	**0.27**	**0.60**	**0.73**	**0.49**	0.14	-0.06	-0.04	**0.70**							**Se**
Sr	**-0.43**	0.06	**0.35**	**0.33**	**-0.49**	**0.64**	**-0.50**	**-0.65**	**-0.38**	**-0.58**	**-0.69**	**-0.70**	0.14	0.06	0.09	**-0.76**	**-0.49**						**Sr**
Cd	**0.44**	-0.06	0.06	**-0.28**	0.07	0.03	-0.06	-0.07	**0.33**	0.14	0.11	-0.07	**-0.30**	**0.97**	**0.82**	0.18	-0.05	0.02					**Cd**
Cs	**0.50**	-0.02	-0.11	0.22	**0.71**	**-0.62**	**0.89**	**0.66**	**0.43**	**0.56**	**0.75**	**0.70**	0.13	-0.06	-0.05	**0.58**	**0.48**	**-0.65**	-0.04				**Cs**
Ba	**0.67**	-0.06	-0.03	-0.13	**0.62**	**-0.59**	**0.51**	**0.58**	**0.58**	**0.63**	**0.61**	**0.48**	-0.06	**0.58**	**0.45**	**0.55**	0.24	**-0.34**	**0.61**	**0.49**			**Ba**
Pb	0.06	0.06	**0.54**	0.13	0.05	**0.30**	-0.08	-0.25	-0.01	-0.17	-0.13	**-0.41**	0.12	**0.68**	**0.72**	-0.09	-0.13	**0.43**	**0.70**	-0.24	0.24		**Pb**
U	**0.52**	-0.11	-0.23	-0.11	**0.74**	**-0.80**	**0.59**	**0.88**	**0.53**	**0.82**	**0.83**	**0.76**	0.13	0.05	0.00	**0.75**	**0.55**	**-0.60**	0.10	**0.61**	**0.69**	-0.19	**U**
	LOI	**pH**	**Na**	**Mg**	**K**	**Ca**	**Al**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Cd**	**Cs**	**Ba**	**Pb**	

3.4.5 Enrichment factor

Enrichment factors (EFs) are one approach to attempt to identify the addition of anthropogenic contaminants to a soil. They are based upon a comparison of an element, such as V, that is likely only to originate from the soil itself with an element that may have an anthropogenic source (Wu et al., 2010). Several investigations have been published in recent years that have used EFs to identify PTE additions to in soils e.g. (Iqbal and Shah, 2011;Hamad et al., 2014). The EF is calculated as:

$$\mathrm{EF} = \frac{(M_S/V_S)}{(M_B/V_B)} \qquad \text{Eq 3.6}$$

where M_s and V_s denote the actual concentration of trace elements and V in the soil samples, respectively, and M_B and V_B are the background concentrations of PTEs and V in a suitable reference material. In this case shale or carbonate rocks reflect the geology of the area. The background concentrations of PTE in Kurdistan region of Iraq have not been established yet, therefore background concentrations for soil were obtained from Turekian and Wedepohl (1961). These background concentrations have been widely used for the evaluation of soil pollution (Mohiuddin et al., 2010;Hamad et al., 2014). Levels of enrichment are typically grouped as shown in Table 3.4.

Table 3.4 Enrichment categories based on EF values (Wu et al., 2015)

EF value	**Enrichment category**
EF<2	Deficiency to minimal enrichment
2≤EF<5	Moderate enrichment
5≤EF<20	Significant enrichment
20≤EF<40	Very high enrichment
EF≥40	Extremely high enrichment

EF values calculated for all sites using typical carbonate and shale background elemental concentrations are presented in Figs. 3.12 and 3.13. This suggests that there is no significant enrichment of trace elements in the study sites if the waste area (HALW) is excluded (Figs. 3.12a and 3.13a). Moderate enrichment of Ni in the soils is suggested when using typical shale values as a reference but this is not supported by the EFs based on carbonate rocks (Fig. 3.13a). High EFs for Cu, Zn, Cd and Pb, regardless of the reference geology chosen, at the municipal waste disposal area (Figs. 3.12b and 3.13b) confirm the impact of the solid waste disposal area on the quality of soil at this site. (Anikwe and Nwobodo, 2002;Smith, 2009;Ali et al., 2014) also report that Cu, Zn, Cd and Pb were found to be the main pollutants in soils near municipal waste dumping and disposal area in their studies.

Although EFs calculated for all sites showed no significant anthropogenic contamination, selected sites showed a wider range of EF values for specific elements. For example, highly variable EF values were observed for Se in the KHR area compared to other areas (Appendix Fig A1f) which may be a consequence of the higher concentrations of soil Se in this area compared to other study areas. Higher EF values for Cr were also observed in the SUL area and for Ni in KALR (Appendix Fig. A1a and A1h).

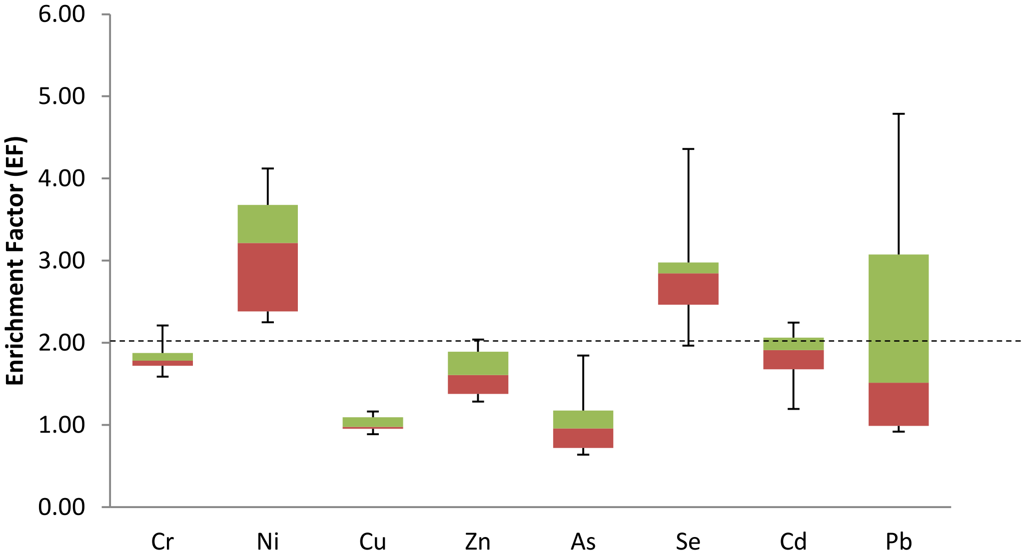
3.4.6 Principal Component analysis (PCA)

PCA is a method of multivariate analysis widely used in soil and contamination research. It can be an effective method to estimate anthropogenic influence on a specific spatial scale (Li and Feng, 2012). PCA is performed to understand the interrelationships of trace elements in the soil (Lucho-Constantino et al., 2005). Scree plots are used to detect the number of factors influencing a data set and correlations between trace elements can be identified using cluster analysis and dendrograms.

In this investigation three main components can be identified for the data set as a whole (n=117, Figure 3.14). These components are identified using a loading plot (Fig. 3.14a) and appear to be (i) the calcareous geology of the area illustrated by a grouping comprising Sr and Ca, (ii) elements associated with Fe and Mn oxides such as As, Cr, Mn, K, U Fe, Se, Al, Cs, V and Co, and (iii) anthropogenic activities indicated by the grouping of Pb, Zn, Cu and Cd. The first and second components explained % 62.2 of the variance. Results of Cluster Analysis (CA) shown in Figure 3.14b also indicate three distinct groupings. Cluster I includes Na-Mg-Ni-Ca-Sr , cluster II Cu-Cd-Zn-Pb-Mo and cluster III contains K-Al-Cs-V-Fe-Co-Mn-U-Cr-Ba-As-Se. Elements in cluster I seem to be strongly associated with soil parent material (alumino –silicate phases) indicating a natural origin for these elements (Salonen and Korkka-Niemi, 2007). Elements in cluster III may also be controlled by natural factors, particularly erosion and weathering (Chen et al., 2008), while elements in cluster II appear to be influenced by anthropogenic activities such as fertilizer and pesticide application, vehicle exhaust emissions, sewage irrigation and waste disposal (Chen et al., 2008;Lu et al., 2012). Figure 3.14c shows the scree plot in which values >2 indicate significant factors. Three significant values >2 are again indicated, in agreement with the other parts of the PCA analysis.

PCA analysis for individual study sites shows more variation, as would be expected given that there are fewer soils in each group (Appendix Figs. A3, A4 and A5). For example, analysis of the SUL area suggests 5 main groups (Appendix Figs. A3a and A4a) group (1) Ni, Cr, Mn and Co (2) Fe, Al, Cs and Se (3) V, K , Ba, Na and U (4) Cd, Pb, Zn, As and Mn (5) Sr and Ca. Groups 1, 2, 3 and 5 appear to originate from soil parent material (Chen et al., 2008;Salonen and Korkka-Niemi, 2007) with group 4 indicating anthropogenic contamination, possibly agrochemical application (Huang et al., 2007). However, the overall trends observed for the dataset as a whole are consistent with observations at individual sites.

(a) Urban area



(b) Waste area

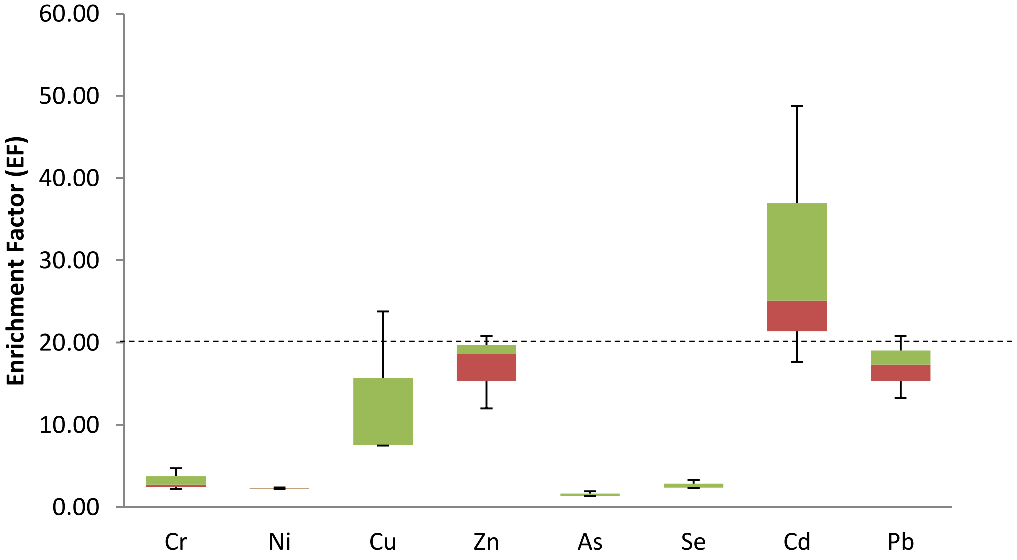
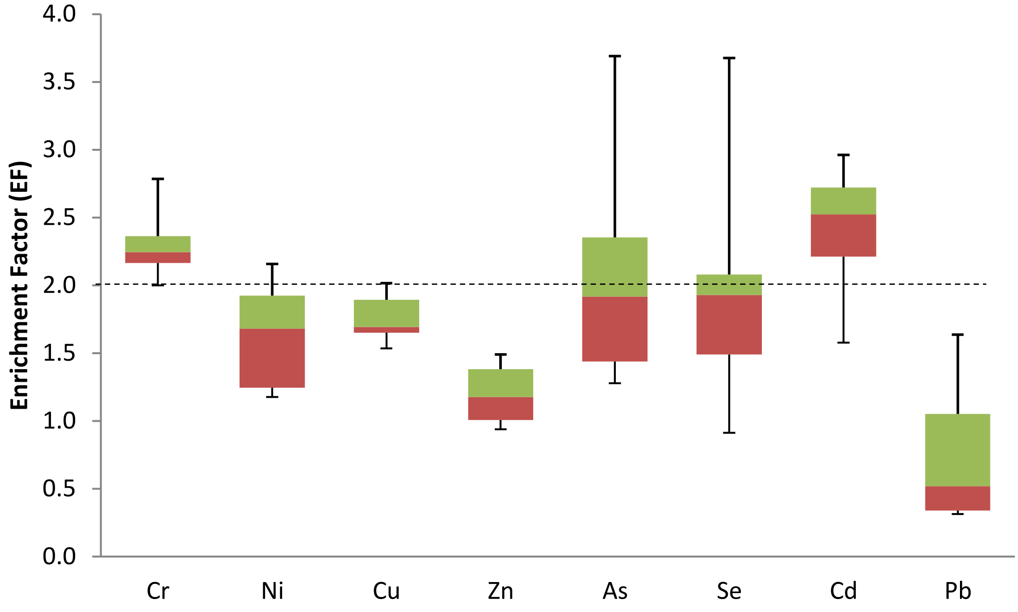


Figure 3.12: Mean enrichment factors (EF) of selected essential trace elements in some PTEs (a) urban areas (b) waste disposal area. Green: 75th percentile, red: 50th percentile with maximum and minimum bar. EFs were calculated based on shale

(a) Urban area



(b) Waste area

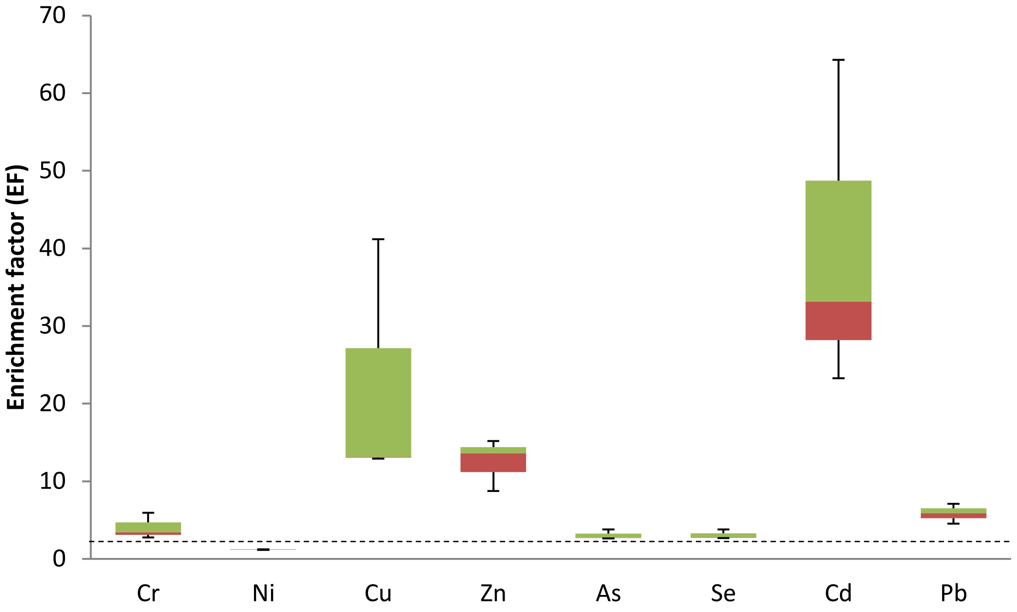


Figure 3.13: Mean enrichment factors (EF) of selected essential trace elements in some PTEs (a) urban areas (b) waste disposal area. Green: 75th percentile, red: 50th percentile with maximum and minimum bar. EFs were calculated based on carbonate rocks.

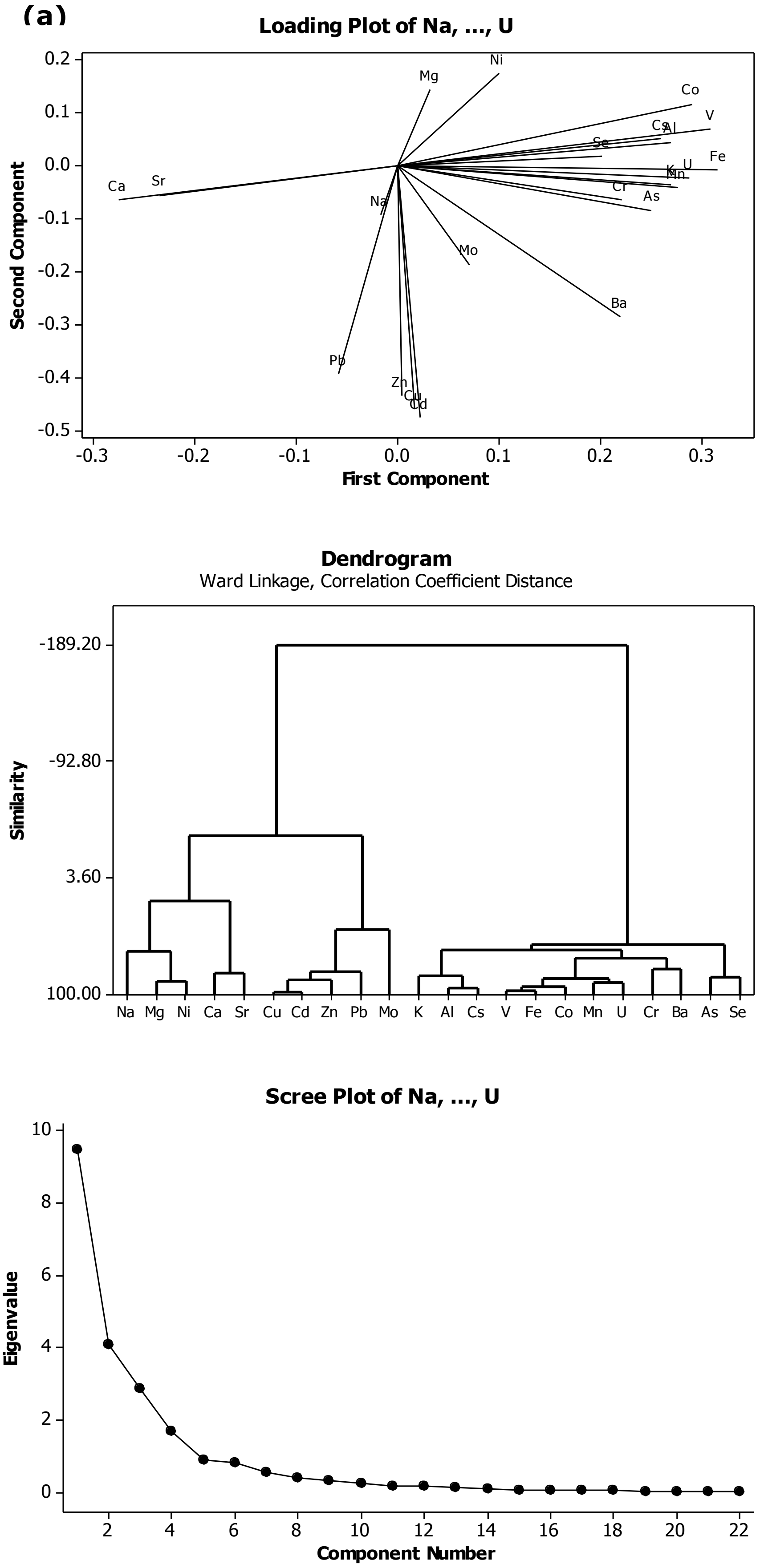


Figure 3.14 Principle component analysis of mean race elements in all all sampling sites. (a) loading plots for all elements (mg kg^{-1}) of soils (b) Dendrogram of elemental analysis on soils from samples areas (c) scree plots for all trace elements at all sampling

3.4.7 Risk Assessment from PTEs exposure

Table 3.5 and 3.6 show the results of health risk for non-carcinogenic effects on adults and children. It can be seen in the results; exposure by ingestion pathway appeared to be the main rout of exposure to soils and thus posed a higher health risk to both children and adults for all trace elements followed by dermal contact. This could be explained that adults have more daily outdoor activities such as having food outside, wiping sweat or having meals without washing hands, children have more recurrent hand to mouth activities. It is in agreement with some recent studies (Li et al., 2013;Olujimi et al., 2015).

The hazard indices (HI) of PTEs for adults increased in the order of Zn < Pb < Cu < Cd < Cr < As < Ni. The hazard risk for Ni was the highest (0.015) while, the lowest was Zn (0.001). Hazard quotient (HQ) values for all studied PTEs were far below the standard limit of 1, demonstrating that no adverse health due to exposure of urban and peri-urban soil. Compared to adults the HI of PTEs for children was higher. HI values were the same for that for adults, it increased in the order of Zn < Pb < Cu < Cd < Cr < As < Ni. The highest value was Ni (0.036) and the lowest value was Zn (0.002). High values were also far lower than the threshold level which means that no health risk for children has been found in the sampling areas due to PTEs. However, it is believed that the some PTEs in the urban area have an abroad impact on health of children such as (Cd, As and Pb) and a main source of their exposure for children are ingestion of contaminated soils (Hu et al., 2011). Moreover, by increasing the exposure frequency (EF) and the ingestion rate of both children and adults, the exposure of soil particles could increase potential health hazards.

The HQ and HI values in this study would not exhibit a serious health risk for the population due to exposure to soil particles. However, there is a kind of uncertainty of assessing health risk due to the calculation if average daily exposure of PTEs from different exposure pathways. This is because the assumptions were applied to this model appeared to be more ideal rather than practical and parameters of exposure and there were uncertainties of the elemental toxicity data. Although there is some vagueness regarding this model but it has proved to be a useful tool to estimate health risk of PTEs for the population and could help to give reliable information for the authority about health risk rises from PTEs exposure.

Table 3.5 Non carcinogenic risk of PTEs for Adults

		SUL	**HALU**	**HALP**	**HALW**	**SIR**	**KHR**	**KALG**	**KALR**
Cr	Ingestion	2.67E-02	3.00E-02	2.69E-02	3.16E-02	2.43E-02	1.89E-02	1.91E-02	2.49E-02
	Inhalation	1.18E-07	1.32E-07	1.19E-07	1.39E-07	1.07E-07	8.34E-08	8.42E-08	1.10E-07
	Dermal	4.26E-02	4.79E-02	4.29E-02	5.04E-02	3.88E-02	3.02E-02	3.05E-02	3.97E-02
	ΣHQ	**6.93E-02**	**7.79E-02**	**6.98E-02**	**8.20E-02**	**6.31E-02**	**4.91E-02**	**4.96E-02**	**6.46E-02**
Co	Ingestion	3.81E-02	4.75E-02	4.21E-02	2.93E-02	3.70E-02	3.55E-02	2.90E-02	3.40E-02
	Inhalation	3.29E-05	4.10E-05	3.64E-05	2.53E-05	3.19E-05	3.06E-05	2.50E-05	2.94E-05
	Dermal	1.52E-03	1.90E-03	1.68E-03	1.17E-03	1.48E-03	1.41E-03	1.16E-03	1.36E-03
	ΣHQ	**3.97E-02**	**4.94E-02**	**4.38E-02**	**3.05E-02**	**3.85E-02**	**3.69E-02**	**3.02E-02**	**3.54E-02**
Ni	Ingestion	7.99E-03	8.60E-03	7.50E-03	4.80E-03	8.25E-03	5.52E-03	9.25E-03	1.18E-02
	Inhalation	2.19E-04	2.35E-04	2.05E-04	1.31E-04	2.26E-04	1.51E-04	2.53E-04	3.23E-04
	Dermal	7.97E-03	8.58E-03	7.48E-03	4.78E-03	8.23E-03	5.50E-03	9.23E-03	1.18E-02
	ΣHQ	**1.62E-02**	**1.74E-02**	**1.52E-02**	**9.71E-03**	**1.67E-02**	**1.12E-02**	**1.87E-02**	**2.39E-02**
Cu	Ingestion	5.11E-04	6.51E-04	5.42E-04	4.63E-03	4.90E-04	5.19E-04	3.87E-04	4.63E-04
	Inhalation	7.51E-08	9.58E-08	7.97E-08	6.81E-07	7.21E-08	7.64E-08	5.69E-08	6.81E-08
	Dermal	2.04E-05	2.60E-05	2.16E-05	1.85E-04	1.96E-05	2.07E-05	1.55E-05	1.85E-05
	ΣHQ	**5.31E-04**	**6.78E-04**	**5.64E-04**	**4.82E-03**	**5.10E-04**	**5.40E-04**	**4.03E-04**	**4.81E-04**
Zn	Ingestion	2.60E-04	2.63E-04	2.04E-04	1.81E-03	1.76E-04	2.28E-04	1.85E-04	2.89E-04
	Inhalation	3.82E-07	3.87E-07	3.00E-07	2.67E-06	2.59E-07	3.36E-07	2.73E-07	4.24E-07
	Dermal	1.04E-05	1.05E-05	8.15E-06	7.24E-05	7.03E-06	9.11E-06	7.40E-06	1.15E-05
	ΣHQ	**2.71E-04**	**2.74E-04**	**2.13E-04**	**1.89E-03**	**1.83E-04**	**2.38E-04**	**1.93E-04**	**3.00E-04**
As	Ingestion	1.11E-02	3.16E-02	2.44E-02	2.26E-02	1.34E-02	3.17E-02	1.51E-02	1.39E-02
	Inhalation	3.27E-08	9.30E-08	7.18E-08	6.64E-08	3.94E-08	9.32E-08	4.44E-08	4.08E-08
	Dermal	4.44E-04	1.26E-03	9.74E-04	9.01E-04	5.34E-04	1.26E-03	6.03E-04	5.53E-04
	ΣHQ	**1.16E-02**	**3.29E-02**	**2.54E-02**	**2.35E-02**	**1.39E-02**	**3.29E-02**	**1.57E-02**	**1.44E-02**
Cd	Ingestion	2.27E-04	3.99E-04	2.97E-04	2.95E-03	2.36E-04	2.56E-04	1.61E-04	1.67E-04
	Inhalation	3.34E-09	5.87E-09	4.37E-09	4.34E-08	3.47E-09	3.77E-09	2.36E-09	2.45E-09
	Dermal	3.63E-04	6.37E-04	4.75E-04	4.71E-03	3.77E-04	4.09E-04	2.56E-04	2.66E-04
	ΣHQ	**5.90E-04**	**1.04E-03**	**7.72E-04**	**7.66E-03**	**6.13E-04**	**6.65E-04**	**4.17E-04**	**4.32E-04**
Pb	Ingestion	2.85E-05	3.63E-05	3.08E-05	3.79E-04	5.10E-05	4.01E-05	1.04E-04	1.48E-04
	Inhalation	1.47E-05	1.87E-05	1.58E-05	1.95E-04	2.62E-05	2.06E-05	5.36E-05	7.62E-05
	Dermal	9.74E-05	1.24E-04	1.05E-04	1.30E-03	1.74E-04	1.37E-04	3.56E-04	5.06E-04
	ΣHQ	**1.41E-04**	**1.79E-04**	**1.52E-04**	**1.87E-03**	**2.52E-04**	**1.98E-04**	**5.14E-04**	**7.31E-04**

Table 3.6 Non carcinogenic risk of PTEs for children

		SUL	**HALU**	**HALP**	**HALW**	**SIR**	**KHR**	**KALG**	**KALR**
Cr	Ingestion	6.23E-02	7.00E-02	6.27E-02	7.37E-02	5.67E-02	4.41E-02	4.46E-02	5.81E-02
	Inhalation	5.22E-08	5.87E-08	5.26E-08	6.17E-08	4.75E-08	3.70E-08	3.73E-08	4.87E-08
	Dermal	6.97E-03	7.84E-03	7.02E-03	8.25E-03	6.35E-03	4.94E-03	4.99E-03	6.50E-03
	ΣHQ	**6.92E-02**	**7.79E-02**	**6.97E-02**	**8.19E-02**	**6.30E-02**	**4.90E-02**	**4.95E-02**	**6.46E-02**
Co	Ingestion	8.89E-02	1.11E-01	9.83E-02	6.83E-02	8.63E-02	8.27E-02	6.76E-02	7.94E-02
	Inhalation	1.46E-05	1.82E-05	1.61E-05	1.12E-05	1.42E-05	1.36E-05	1.11E-05	1.30E-05
	Dermal	2.49E-04	3.10E-04	2.75E-04	1.91E-04	2.42E-04	2.32E-04	1.89E-04	2.22E-04
	ΣHQ	**8.92E-02**	**1.11E-01**	**9.86E-02**	**6.85E-02**	**8.66E-02**	**8.30E-02**	**6.78E-02**	**7.97E-02**
Ni	Ingestion	1.87E-02	2.01E-02	1.75E-02	1.12E-02	1.92E-02	1.29E-02	2.16E-02	2.76E-02
	Inhalation	9.70E-05	1.04E-04	9.10E-05	5.82E-05	1.00E-04	6.70E-05	1.12E-04	1.43E-04
	Dermal	1.31E-03	1.41E-03	1.22E-03	7.83E-04	1.35E-03	9.01E-04	1.51E-03	1.93E-03
	ΣHQ	**2.01E-02**	**2.16E-02**	**1.88E-02**	**1.20E-02**	**2.07E-02**	**1.38E-02**	**2.32E-02**	**2.97E-02**
Cu	Ingestion	1.19E-03	1.52E-03	1.26E-03	1.08E-02	1.14E-03	1.21E-03	9.04E-04	1.08E-03
	Inhalation	3.33E-08	4.25E-08	3.53E-08	3.02E-07	3.20E-08	3.39E-08	2.52E-08	3.02E-08
	Dermal	3.34E-06	4.26E-06	3.54E-06	3.03E-05	3.20E-06	3.39E-06	2.53E-06	3.02E-06
	ΣHQ	**1.20E-03**	**1.52E-03**	**1.27E-03**	**1.08E-02**	**1.15E-03**	**1.22E-03**	**9.06E-04**	**1.08E-03**
Zn	Ingestion	6.06E-04	6.14E-04	4.77E-04	4.23E-03	4.11E-04	5.32E-04	4.33E-04	6.73E-04
	Inhalation	1.69E-07	1.72E-07	1.33E-07	1.18E-06	1.15E-07	1.49E-07	1.21E-07	1.88E-07
	Dermal	1.70E-06	1.72E-06	1.33E-06	1.19E-05	1.15E-06	1.49E-06	1.21E-06	1.89E-06
	ΣHQ	**6.08E-04**	**6.16E-04**	**4.78E-04**	**4.25E-03**	**4.12E-04**	**5.34E-04**	**4.34E-04**	**6.75E-04**
As	Ingestion	2.60E-02	7.38E-02	5.70E-02	5.27E-02	3.12E-02	7.39E-02	3.52E-02	3.23E-02
	Inhalation	1.45E-08	4.12E-08	3.18E-08	2.94E-08	1.74E-08	4.13E-08	1.97E-08	1.81E-08
	Dermal	7.27E-05	2.07E-04	1.59E-04	1.48E-04	8.74E-05	2.07E-04	9.87E-05	9.05E-05
	ΣHQ	**2.60E-02**	**7.40E-02**	**5.71E-02**	**5.28E-02**	**3.13E-02**	**7.41E-02**	**3.53E-02**	**3.24E-02**
Cd	Ingestion	5.30E-04	9.31E-04	6.94E-04	6.89E-03	5.51E-04	5.97E-04	3.75E-04	3.89E-04
	Inhalation	1.48E-09	2.60E-09	1.94E-09	1.92E-08	1.54E-09	1.67E-09	1.05E-09	1.09E-09
	Dermal	5.94E-05	1.04E-04	7.77E-05	7.71E-04	6.17E-05	6.69E-05	4.20E-05	4.35E-05
	ΣHQ	**5.89E-04**	**1.04E-03**	**7.71E-04**	**7.66E-03**	**6.13E-04**	**6.64E-04**	**4.17E-04**	**4.32E-04**
Pb	Ingestion	6.65E-05	8.48E-05	7.18E-05	8.84E-04	1.19E-04	9.35E-05	2.43E-04	3.45E-04
	Inhalation	6.50E-06	8.29E-06	7.02E-06	8.64E-05	1.16E-05	9.14E-06	2.38E-05	3.38E-05
	Dermal	1.59E-05	2.03E-05	1.72E-05	2.12E-04	2.85E-05	2.24E-05	5.83E-05	8.29E-05
	ΣHQ	**8.89E-05**	**1.13E-04**	**9.61E-05**	**1.18E-03**	**1.59E-04**	**1.25E-04**	**3.25E-04**	**4.62E-04**

3.5 Conclusions

Use of wastewater and other industrial discharges for irrigation of agricultural areas is increasing in Iraq because it is a semi-arid country where availability of clean water has been declining for agricultural purposes. The current study examined the elemental composition of irrigation water and agricultural soils in Kurdistan region of Iraq.

In general, higher concentrations of elements were found in wastewaters compared to clean waters. An exception was in the Khurmal (KHUR) area where higher concentrations of Cu and As were measured in clean water compared to the wastewater. Agricultural soils in the region irrigated with waste water seem not to be significantly contaminated with trace elements. A slight increase in Cd, Cr, Ni, Cu, Zn and Pb is observed in the waste water irrigated soils but this is not significant when compared to the impact of municipal waste disposal with waste-affected soils, which have greater concentrations of Cr, Cu, Zn, Cd and Pb. Enrichment factors (EFs), calculated using typical shale and carbonate bedrock geologies, confirmed that there was typically no significant enrichment in trace elements above expected background concentrations except at the municipal waste disposal site (HALW). Principal component analysis (PCA) revealed that three principal components (calcareous geology, Fe-Mn oxides and anthropogenic contamination) accounted for the variation in trace elements in the soils. Whereas concentrations of PTEs were within ‘safe’ limits in the agricultural areas studied, prolonged application of sewage as irrigation water could lead to future problems, in particular with As because of its toxicity.

The main pathway of exposure to PTEs in soil in this study is ingestion followed by dermal adsorption and inhalation. For all the elements the non-carcinogenic risk calculated was lower than one, indicating that the risks through the exposure route is negligible and within world-wide acceptable limits. However the majority of the population will receive exposure to PTEs via the water they consume and their food. Risk associated with these routes of exposure can only be examined by a systematic investigation of vegetables and their associated soil to assess soil to plant transfer.

As total metal concentrations do not represent the ‘bioavailable’ fraction of PTEs that may be readily taken up into plants and into the human diet; fractionation and speciation of PTEs will be undertaken, in the next chapter, to examine their mobility and bioavailability in the soil.

4 Chemical Partitioning and Human Health Risks of PTEs in Agricultural Soil in The Kurdistan Region of Iraq

4.1 Introduction

The main purpose of extraction is to estimate the amount of an element bound to a specific soil fraction; the exchangeable metal pool where an element is held by electrostatic interaction, carbonate-bound, Fe-Mn oxide-bound, or the fraction associated with sulphide and/or organic matter (Ure, 1996). Determination of elemental fractionation can be through single or sequential extractions or an isotopic dilution technique. Extraction approaches can be argued to have greater toxicological, chemical and biological significance than measurement of total elemental concentrations (Manouchehri et al., 2014) as they may represent the pool of an element in the soil that is available to be taken up by a plant (see also Section 1.3). As such they may provide a better estimate for use in risk assessment models than total elemental concentrations (Yang et al., 2011;Luo et al., 2012).

Soil extraction approaches for trace element speciation have been used since the 1960s (Ure, 1996). The methods are typically uncomplicated and affordable. Air-dried soils are extracted using a chosen extractant at a specific soil-solution ratio, then after a set shaking and/or heating time the supernatant is separated from the solid residue by centrifugation and filtration for analysis. The amount of solubilised trace elements is practically defined since it depends on factors including the nature and power of the extractant, soil-solution ratio and time (Rauret, 1998;Young et al., 2005).   Single extractions are often used to estimate the size of the reactive metal pool in the soil. Common extractants include 0.005 M DTPA, 0.05 M EDTA, 1 M $CaCl_2$, and 0.43 M nitric or acetic acid (Quevauviller, 1998;Huang et al., 2011;Bakircioglu et al., 2011).

Sequential extractions are also frequently used e.g. Tessier et al. (1979), Quevauviller et al. (1997) and rely upon a sequence of increasingly powerful extractants to selectively remove elements associated with specific phases. The main problem with single and sequential extraction approaches is their lack of specificity and the potential for re-adsorption. Chelating agents, such as DTPA, act by creating soluble complexes and decreasing the activity of the soil solution encouraging desorption of ions from the surface of the solid phase of the soil (Silva et al., 2008).

A more limited number of studies have used an isotopic dilution techniques to determine exchangeable metal pool (Garforth, 2014). Comparisons of the extractable and exchangeable pool of an element established using isotopic dilution techniques have been made by a number of workers. For example, Echevarria et al. (1998) compared the pool of soil Ni that was isotopically exchangeable with DTPA extractable Ni and observed that DTPA extractable Ni was greater than the exchangeable Ni pool in a silty loam soil suggesting that DTPA might have released some non-isotopically exchangeable Ni into the solution. Gäbler et al. (1999) compared water, 1M NH_4NO_3 and 0.05 EDTA extracted Cr, Ni, Cu, Zn, Cd and Pb in uncontaminated soil with the isotopically exchangeable metal pool under extraction conditions. They observed that the concentration of isotopically exchangeable Ni, Cu, Zn, Cd and Pb, under the water, EDTA and NH_4NO_3 extractants conditions, were within the same order of magnitude. They also observed a difference of 1-2 orders of magnitude between the concentration of trace elemental extracted by EDTA and water, suggesting that extractants may alter the distribution of metal which are isotopically exchangeable between the soil-solution phase (Gäbler et al., 1999).

The main objective of this chapter was to investigate the chemical fractionation of PTEs in urban soil from the Kurdistan region of Iraq using single (DTPA) and sequential extraction approaches and to measure the isotopically exchangeable pool (E-value) of ^{62}Ni, ^{65}Cu, ^{70}Zn. ^{108}Cd and ^{204}Pb in the soils.

4.2 Material and methods

4.2.1 Extraction methodologies and isotopic dilution technique

Soils were extracted with DTPA as described by Lindsay and Norvell (1978) (Section 2.1.7.1) and sequentially extraction according to the approach described by Li and Thornton (2001), (Section 2.1.7.3).The isotope stock solution, isotopic dilution techniques and calculation of E values were described in chapter 2 , section 2.1.11

4.3 Result and discussion

4.3.1 Multi element fractionation in soil using SEPs

The average proportion of selected trace elements in the SEP fractions for all soil samples at all study sites are shown in Fig.4.1. Sequential extraction of soils from across the area indicated that most of the soil Cr (90%), Ni (80%), Cu (90%), Zn (80%) and As (80%) was associated with the residual fraction (F5) at all sampling sites. This suggests that the majority of these elements are held within the mineral lattices of primary and secondary minerals and therefore unlikely to be bioaccessible (Li et al., 2013). Typically a small proportion of the Cr, Ni, Cu, Zn and As (1% to 5%) was extracted in the carbonate (F2), Fe-Mn oxide (F3) and organic matter (F4) fractions. An exception to this was the waste disposal site (HALW) where 50% of Cu and 35% of Zn was extracted with the organic matter (F4) and Fe-Mn oxide (F3) fractions respectively, and at Kalar river side (KALR) where 40% of the Zn was extracted with Fe-Mn oxides (F3) (Fig. 4.1c and d). Cu has a high affinity for organic matter (Paradelo et al., 2011) and additions of large quantities of organic municipal waste at HALW may be responsible for this association; the highest soil organic matter content (13.7%) was also recorded at HALW (Table 3.2). The preference of Zn for oxide phases at both HALW and KALR sites is unclear. Siddiqui and Khattak (2010) in an investigation of the calcareous soil of Peshawar in Pakistan suggested that this was a result of the large surface area that sequisoxide phases provide for adsorption or occlusion.

Trace elements in the exchangeable fraction (F1) were generally present at concentrations below the limit of quantification. Generally the SEP fractions for these elements were in ascending order F1-F5 is believed that this order in agreement with the decreasing solubility and bioavailability of these metals in the soil (Lu et al., 2003).

Selenium fractionation was highly variable (Fig 4.1f); a substantial amount 30-50% of Se was associated with organic matter followed by the Fe-Mn oxides (25-35%), residual (20-30%) and carbonate (5-10%) fractions. Selenium is typically expected to be present in soils in an organic form but may also be associated with Fe-Mn oxide phases (Supriatin et al., 2015). They conducted a study of 42 grassland soils and 41 arable soils (pH range ~ 4-7) concluded that 82% of total Se in Dutch agriculture soil exists in organic form. The reduced association of Se in the soils in this study with organic matter may reflect the calcareous nature of the Kurdish soils (pH~8).

Cadmium fractionation was different from the other trace elements with >50% in the carbonate pool (F2) at all sites with exception of the HALW site where it was 30% and there was more oxide (F3) bound and residual Cd (F5) (Fig 4.1g). The high proportion of Cd in the carbonate phases probably reflects to ability of Cd^{2+} to substitute for Ca^{2+} in $CaCO_3$. The majority of Pb was in the oxide fraction (F3) which accounts for 40% to 60% of the total. A substantial proportion of Pb was also in the residual (F5) and organic matter (F4) fractions; 30-40% and 10-20% respectively. Oluwatosin et al. (2008) reported that c. 65% of Pb was associated with the residual fraction of soil in their investigation of sandy loam soils in urban areas of Nigeria whereas Pulford et al. (2009) observed 70% of Pb in mine contaminated sediment of a former Pb-Zn mine was associated with the carbonate fraction. This demonstrates the importance of the source of the Pb in controlling its fractionation in the soil.

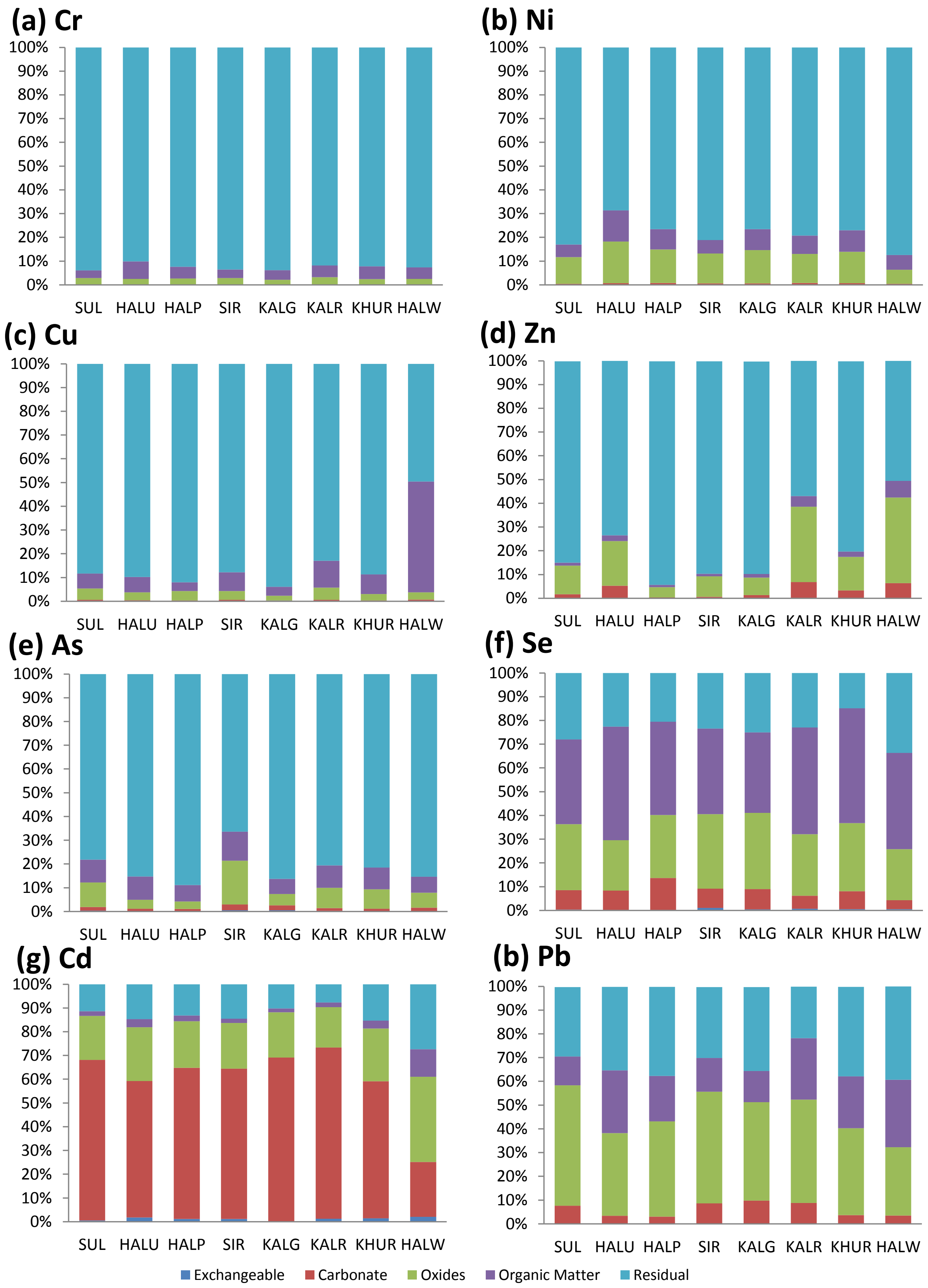


Figure 4.1: Average proportion (%) of (a) Cr, (b) Ni, (c) Cu, (d) Zn, (e) As, (f) Se, (g) Cd and (f) Pb in exchangeable, carbonate, oxides, organic matter, and residual fractions after sequential extraction.

Table 4.1: Distribution of trace elements (mg/kg) in each sequentially extracted fraction. Data is average for each area. The 'mobile phase' is the sum of first 3 fractions (Li et al., 2013).

Sites	Fractions	Cr	Ni	Cu	Zn	As	Se	Cd	Pb
SUL	F1	-0.005	0.005	0.066	-0.248	0.023	0.004	0.006	-0.071
	F2	0.168	0.823	0.212	1.77	0.109	0.102	0.727	1.83
	F3	4.97	20.8	2.02	12.8	0.744	0.346	0.200	12.2
	Mobile phase	**5.14**	**21.7**	**2.30**	**14.3**	**0.875**	**0.452**	**0.933**	**13.9**
	F4	5.89	9.74	2.64	1.37	0.687	0.446	0.020	2.91
	F5	171	154	37.5	90.2	5.59	0.349	0.123	7.02
HALU	F1	-0.004	0.038	0.060	0.004	0.022	0.004	0.023	-0.073
	F2	0.109	1.16	0.123	8.25	0.135	0.136	0.737	1.13
	F3	3.82	28.1	1.44	29.5	0.530	0.350	0.290	11.6
	Mobile phase	**3.92**	**29.3**	**1.63**	**37.8**	**0.684**	**0.495**	**1.05**	**12.6**
	F4	11.4	21.2	2.79	3.86	1.36	0.799	0.044	8.80
	F5	141	110	38.7	115	11.9	0.379	0.188	11.7
HALP	F1	-0.003	0.040	0.048	-0.227	0.013	0.004	0.013	-0.070
	F2	0.105	1.22	0.090	0.382	0.133	0.188	0.735	0.792
	F3	4.32	22.8	1.54	4.46	0.420	0.370	0.230	10.6
	Mobile phase	**4.42**	**24.1**	**1.67**	**4.61**	**0.568**	**0.565**	**0.975**	**11.3**
	F4	8.04	13.73	1.45	1.00	0.924	0.553	0.028	5.02
	F5	151	123	36.0	97.2	11.9	0.289	0.152	9.85
SIR	F1	-0.002	0.019	0.048	-0.253	0.036	0.014	0.013	-0.070
	F2	0.092	1.127	0.232	0.712	0.172	0.106	0.715	2.25
	F3	4.99	22.20	1.58	9.75	1.27	0.410	0.220	12.3
	Mobile phase	**5.08**	**23.3**	**1.86**	**10.2**	**1.48**	**0.529**	**0.945**	**14.5**
	F4	6.42	9.93	3.43	1.28	0.846	0.471	0.021	3.72
	F5	167	143	38.1	101	4.60	0.306	0.164	7.85
KHR	F1	-0.005	0.030	0.088	-0.212	0.031	0.008	0.017	-0.076
	F2	0.026	0.790	0.077	3.91	0.182	0.110	0.683	1.09
	F3	3.21	16.1	1.21	16.8	1.50	0.420	0.260	10.7
	Mobile phase	**3.23**	**16.9**	**1.37**	**20.5**	**1.71**	**0.537**	**0.963**	**11.7**
	F4	7.33	11.2	3.67	2.73	1.68	0.706	0.039	6.38
	F5	125	93.7	39.3	95.6	14.9	0.217	0.182	11.0
KALG	F1	-0.005	0.102	0.078	-0.261	0.049	0.005	0.000	-0.073
	F2	0.136	0.658	0.054	1.14	0.194	0.101	0.715	2.31
	F3	2.75	18.3	0.66	6.39	0.430	0.380	0.200	9.77
	Mobile phase	**2.88**	**19.1**	**0.79**	**7.27**	**0.677**	**0.484**	**0.913**	**12.0**
	F4	5.46	11.4	1.32	1.26	0.590	0.399	0.017	3.09
	F5	126	99.5	32.2	77.0	7.95	0.295	0.106	8.30
KAL	F1	0.003	0.019	0.075	-0.098	0.016	0.009	0.014	-0.072
	F2	0.217	1.003	0.165	11.1	0.083	0.069	0.774	3.81
	F3	4.13	15.7	1.95	51.1	0.590	0.320	0.180	18.9
	Mobile phase	**4.36**	**16.7**	**2.19**	**62.1**	**0.692**	**0.402**	**0.971**	**22.6**
	F4	6.89	9.85	4.29	7.22	0.653	0.562	0.022	11.2
	F5	126	101	31.5	91.7	5.60	0.288	0.082	9.41
HALW	F1	0.009	0.021	0.572	0.330	0.020	0.008	0.166	-0.059
	F2	0.228	0.579	2.73	62.7	0.186	0.051	1.859	8.15
	F3	5.99	7.75	13.7	355	0.790	0.290	2.89	66.8
	Mobile phase	**6.23**	**8.35**	**17.0**	**418**	**0.995**	**0.350**	**4.91**	**74.9**
	F4	12.3	8.01	209	68.8	0.836	0.550	0.937	66.0
	F5	231	114	223	498	10.7	0.457	2.20	91.5

Table 4.1 shows the 'mobile phase', the sum of exchangeable (F1), carbonate (F2) and Fe-Mn oxide (F3) fractions, is believed to represent the potentially labile and bioaccessible amount of the element (Feng et al., 2009;Li et al., 2013). The mobile phase for HALW was significantly greater than for other areas with Cu 7 times, Zn 6 times, Cd 4 times and Pb 3 times greater. There were similar or lower amounts of Ni, Se and As associated with the mobile phases at HALW compared to other sites.

4.3.2 DTPA-extractable PTEs

DTPA single extraction is commonly used to measure the availability of PTEs in soil, especially calcareous soils where alternative acidic extractants may solubilize the elements of interest and over-estimate the available pool (Meers et al., 2007). Results for a 0.005 M DTPA single extraction are shown in Table 4.2. In general, DTPA extractable concentrations are low for the majority of elements, particularly for Cr, Ni, Cu, Zn and As, when compared with the total concentration in the soil (see Chapter 3, Fig 3.10). Between 10-20% of the total Pb and 15-25% of total Cd was DTPA extractable. DTPA extractable concentrations were higher for the HALW area representing 11% of the total Cu, 16% of total Ni, 26% of total Cd and 15% of total Pb. Despite the greater total Cu, Cd and Pb concentrations at HALW DTPA extractable Cu, Cd and Pb were a similar proportion to that observed at other sites (10% Cu, 17% Pb and 26% Cd) suggesting that their geochemical behaviour may be controlled in a similar way at all the sites. This contrasts with the SEP results for HALW where the fractionation of Cu and Cd (and to some extent Pb) was different from other sites.

DTPA extractable concentrations of trace elements were significantly lower than the 'mobile phase' equivalent derived from sequential extraction with the exception of Cu. Copper concentrations were approximately twice as great in the DTPA extracts than in the SEP 'mobile phase'. This highlights the disadvantages of such extraction approaches where poor selectivity of the chemical reagents and redistribution of the elements during extraction can be problematic (Kim and Fergusson, 1991). For example, premature dissolution of a target phase during the extraction of a previous phase can leads to overestimation of the subsequent proportion of the element (Young et al., 2005). The high concentrations of Cu in DTPA extraction compared to the mobile phase of the SEP suggest that DTPA is able to extract some organically bonded Cu (Paradelo et al., 2011). Quevauviller (1998) also suggested that DTPA attacks not only the exchangeable, carbonate and oxide fractions but also organically-bonded elements.

Table 4.2 Average DTPA extractable trace elements in each study area with mean and standard deviation (±SD).

Area		DTPA (mg kg^{-1})							
		Cr	Ni	Cu	Zn	As	Se	Cd	Pb
SUL	Mean	0.020	1.81	3.89	3.70	0.048	0.045	0.056	2.73
	±SD	0.059	0.489	0.765	2.678	0.010	0.013	0.015	1.380
HALU	Mean	0.006	2.25	2.77	8.36	0.094	0.120	0.095	2.37
	±SD	0.007	0.535	0.780	2.657	0.012	0.021	0.022	1.209
HALP	Mean	0.075	2.36	2.38	0.895	0.126	0.101	0.067	1.45
	±SD	0.217	0.384	0.294	0.609	0.165	0.047	0.028	0.232
SIR	Mean	0.002	1.52	3.22	0.890	0.051	0.073	0.085	1.69
	±SD	0.002	0.423	0.795	0.397	0.018	0.032	0.019	0.431
KHR	Mean	0.001	1.38	2.99	4.26	0.058	0.077	0.065	1.63
	±SD	0.002	0.320	0.432	2.753	0.021	0.018	0.013	0.576
KALG	Mean	0.009	1.77	1.26	2.95	0.059	0.036	0.036	1.23
	±SD	0.003	0.371	0.250	1.594	0.017	0.010	0.010	0.238
KALR	Mean	0.004	1.04	2.30	6.09	0.029	0.031	0.046	3.67
	±SD	0.002	0.465	1.032	1.765	0.009	0.004	0.031	1.456
HALW	Mean	0.273	1.57	29.1	125	0.248	0.040	1.110	28.0
	±SD	0.423	0.542	18.745	31.672	0.344	0.015	0.509	15.475

4.3.3 E-value and %E-value

Exchangeable metal (E value) measured using an isotopic dilution technique may better represent the biologically available fraction of trace elements in the soil (Hamon et al., 2008). E-values (mg kg^{-1}) and %E values of Ni, Cu, Zn, Cd and Pb for a small selection of sixteen soils (chosen to cover the different areas and total element concentrations) are given in Table 4.3.

No clear trend in E-value or %E-value was observed in these soils probably due to the limited number of soils and their very narrow pH range. Typically E-value would decrease with increasing pH (Degryse et al., 2004;Marzouk et al., 2013). Percentage E-values were typically low; < 1% for Ni, <10% for Cu, Zn and Pb. Cadmium showed the greatest

%E-value 5-20% but the total labile Cd remains small as it is present in low concentrations in the soil. In general, the %E-values decreased in the order Cd>Pb>Cu>Zn>Ni which is in agreement with the findings of others e.g. Gäbler et al. (2007) and Mao et al. (2014). At HALW %E-values were greater for all five elements suggesting dumping of waste has increased both total metal and labile metal. In general the same trend in metal lability is observed in the HALW sample with the exception of Cu and Zn which are reversed.

Table 4.3 E-values and %E-values of selected soils from each sampling areas.

Site	Sample	E value(mg kg^{-1})					% E value				
	No	Ni	Cu	Zn	Cd	Pb	Ni	Cu	Zn	Cd	Pb
SUL	05	0.499	1.55	4.45	0.030	0.530	0.433	5.56	5.54	14.3	5.91
SUL	17	1.13	0.912	0.956	0.031	0.441	0.634	3.53	1.37	12.7	3.16
SUL	26	1.28	1.10	0.932	0.031	0.454	1.77	5.65	2.04	13.8	3.49
HALU	01	1.96	3.42	40.3	0.115	4.36	1.51	8.78	17.8	20.4	16.3
HALU	23	0.995	0.983	0.554	0.057	0.626	0.736	2.86	0.617	12.2	4.66
HALU	24	0.793	1.03	2.97	0.058	0.903	0.542	2.83	3.08	11.7	6.40
HALP	03	0.995	0.673	0.253	0.043	0.469	0.877	2.06	0.294	9.68	3.60
SIR	09	1.12	2.18	0.974	0.053	1.09	1.19	7.19	1.25	13.3	11.2
SIR	20	1.07	2.14	0.952	0.052	1.06	0.724	7.83	1.25	16.4	3.23
KALG	06	0.520	0.352	1.01	0.014	0.465	0.344	1.41	1.24	5.17	1.04
KALG	07	0.879	0.514	3.19	0.022	0.693	0.629	2.15	3.94	7.54	1.55
KALR	01	1.22	3.55	34.8	0.074	9.45	0.655	9.31	12.9	16.3	10.5
KALR	07	0.412	0.442	0.517	0.017	0.326	0.257	1.98	0.577	9.38	0.606
KHR	03	1.25	2.56	21.9	0.078	1.93	1.83	8.52	20.3	18.3	13.4
KHR	07	0.474	0.743	0.500	0.051	0.314	0.403	2.10	0.550	12.8	1.53
HALW	02	1.60	56.6	101	1.12	25.1	2.75	10.3	12.3	18.5	14.7

4.3.4 E-value and % E-value against soil pH and %LOI

Soil properties particularly, pH and organic matter are the important factors determine the mobility and solubility of trace element in the (McBride et al., 2006;Rodrigues et al., 2010). For example, when the pH increases the metal solubility and availability will decrease, this is partially because of the metal precipitation when the pH rises. Another possible reason because the amount of negative charge sites for metal adsorption increases on Fe/Mn oxides, organic matter carbonate and even clay mineral with increasing pH (McLean and Bledsoe, 1992).The correlation between E-values and % E-values with soil pH were not significant and very poor in these soils (n=16) (Fig 4.2 and 4.3) respectively. The results indicated that there was no correlations found between E-value and soil pH ($P<0.001$) for Ni ($R^2=0.007$), Cu ($R^2=0.0004$),Zn ($R^2=008$), Cd ($R^2=0.036$) and Pb ($R^2=0.001$) and relatively same pattern was found for the correlations between % E values and soil pH ($P<0.001$) for Ni ($R^2=0.048$), Cu ($R^2=0.031$),Zn ($R^2=098$), Cd ($R^2=0.001$) and Pb ($R^2=0.018$). These correlations were not expected because many studies found the negative correlations between Lability of trace elements and pH, it means increase metal lability with decreasing soil pH (Tye et al., 2003;Degryse et al., 2004). Lack of correlation between E-values and % E-values with soil pH may be related to the number of samples. In this preliminary experiment only 16 soils were examined for E-value test, two or three soils from each sampling areas. In the next chapter this correlation will be shown in details with a large number of soils. Another possible explanation is these samples had very narrow pH ranges from 7.59 to 8.35.

Similarly No or poor correlations were found between E-value and % E-value with %LOI (Fig 4.4 and 4.5). These figures indicated that there was no correlations found between E-value values and soil LOI ($P<0.001$) for Ni ($R^2=0.208$), Cu ($R^2=0.164$),Zn ($R^2=322$), Cd ($R^2=0.438$) and Pb ($R^2=0.145$) and relatively same pattern was found for the correlations between % E-values and soil LOI ($P<0.001$) for Ni ($R^2=0.188$), Cu ($R^2=0.121$),Zn ($R^2=316$), Cd ($R^2=0.166$) and Pb ($R^2=0.487$).

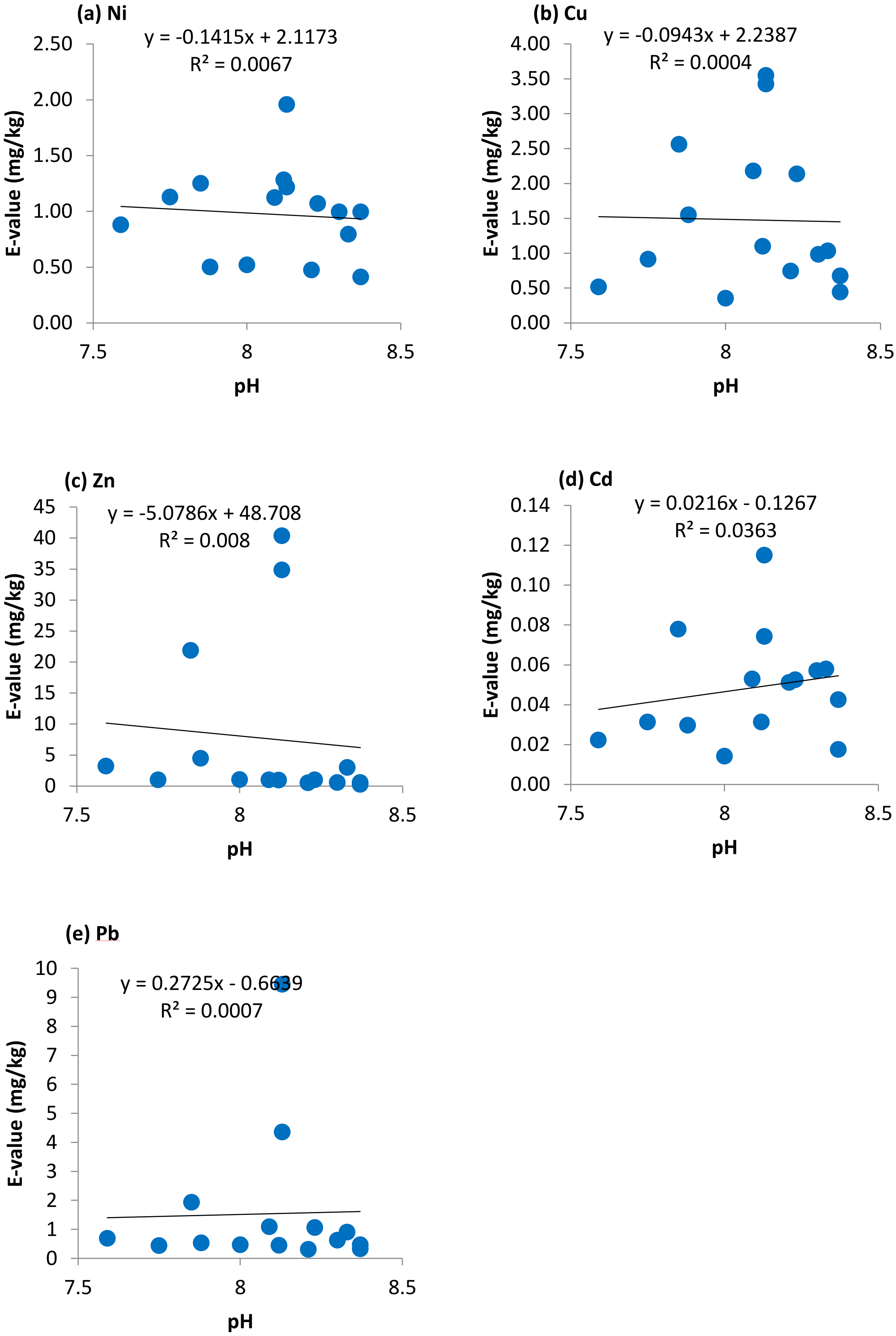


Figure 4.2 Correlation between E-value and pH for selected trace elements.

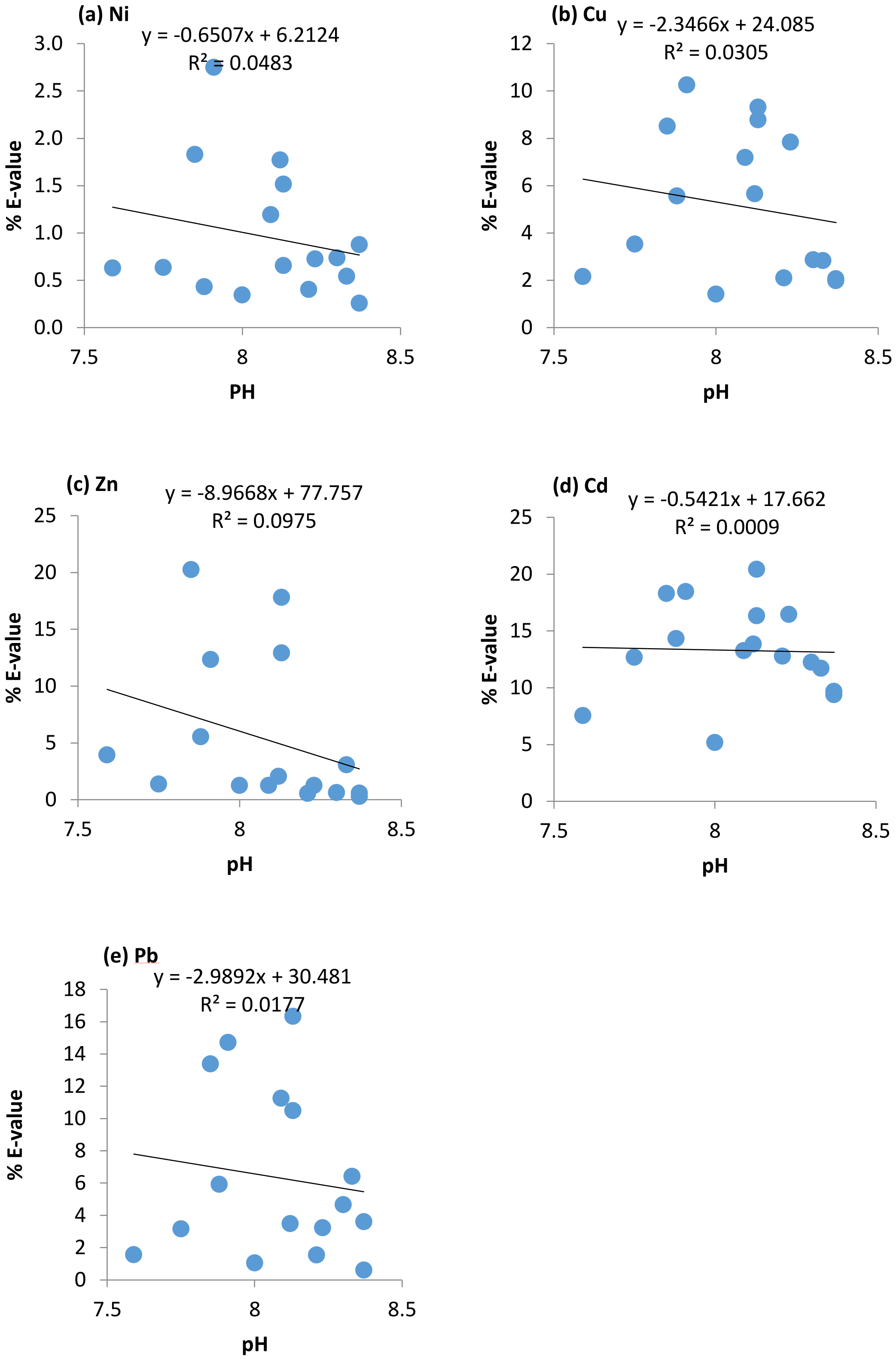


Figure 4.3: Correlation between %E value and pH for selected trace elements.

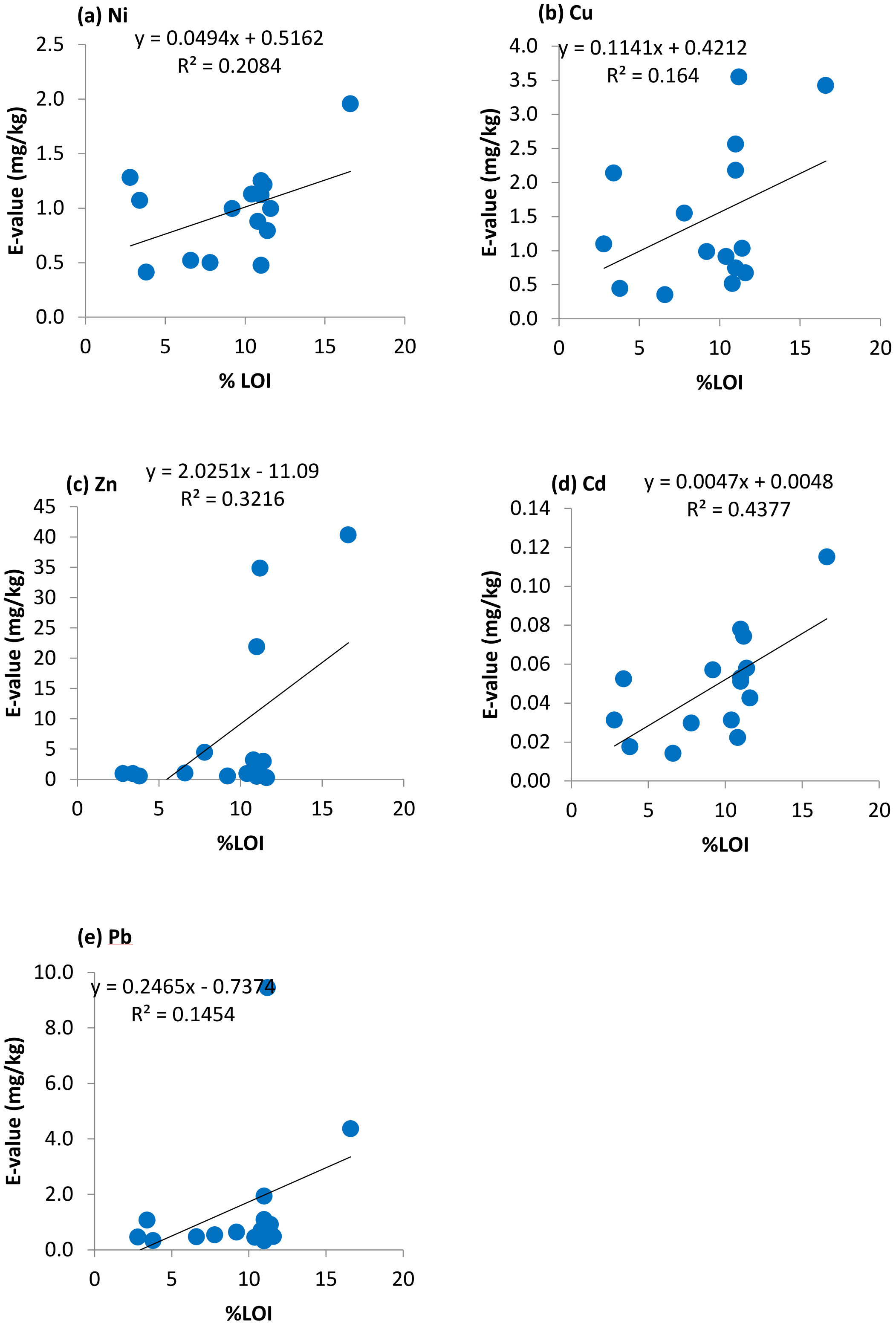


Figure 4.4: Correlation between E-value and %LOI for selected trace elements.

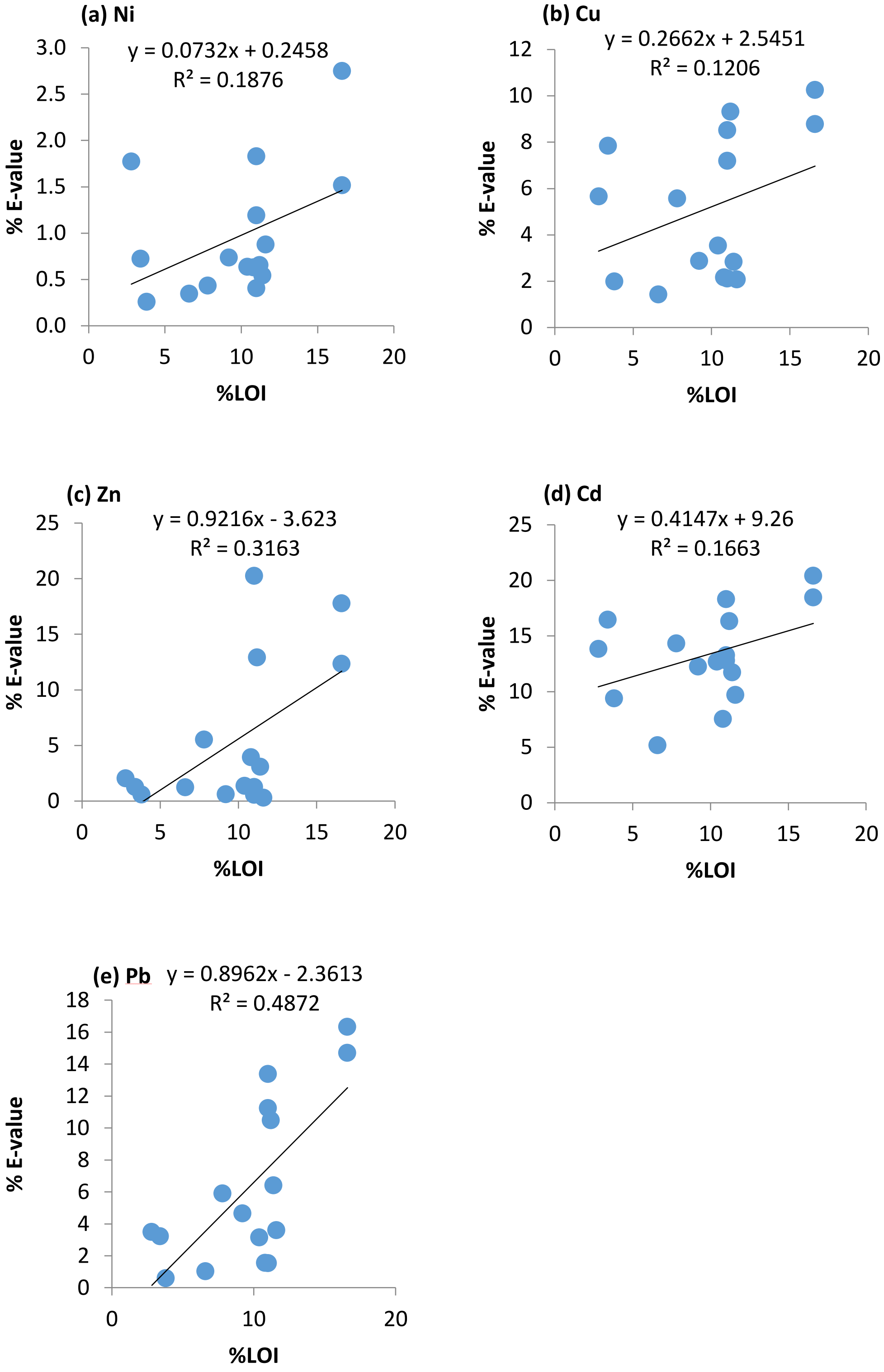


Figure 4.5: Correlation between %E-value and %LOI for selected trace elements.

4.3.5 Comparison of DTPA and E-value

Figure 4.6 compares DTPA extractable and E-value for the five metals. The results suggest that DTPA typically extracted more Ni, Cu, Cd and Pb than was isotopically exchangeable with the exception of Cu at HALW, Zn at HALU, KHR and KALR area and Pb at KALR (Fig 4.2b, c and e) where DTPA appears to underestimate lability. The capacity and efficiency of DTPA can be influenced by soil texture (Hooda and Alloway, 1994). Many studies have compared metals extracted by 0.005 M DTPA with E-value. For example, a study conducted on six soils by Lopez and Graham (1972) suggested that DTPA extractable Mn, Fe, Co, Cu and Zn were relatively similar to E-value. Other studies by Fujii and Corey (1986) and Echevarria et al. (1998) have however demonstrated that DTPA extractable Ni Cu, Zn and Cd underestimated exchangeable metal pool (E-values). In a recent study by Marzouk et al. (2013) DTPA extraction of Zn, Cd and Pb was also higher than E-values in acidic soils while relatively similar results were observed for calcareous soil in contrast to the findings in this study.

Significant correlations might be expected between SEP ‘mobile phase’ concentrations and those obtained for DTPA extractions and E value as all three approaches aim to evaluate the bioavailable fraction of trace elements in the soil (Gleyzes et al., 2002;Kashem et al., 2007;Silva et al., 2008;Huang et al., 2011). Although apparently good correlations are obtained when comparing SEP ‘mobile phase’ concentrations with DTPA extractable and E-values these are dominated by a single point for Ni, Cu and Cd which when removed show no relationship (Fig. 4.7 and 4. 8). Correlations for Zn, Cd and Pb are more convincing but the overall trend remains dominated by a few points.

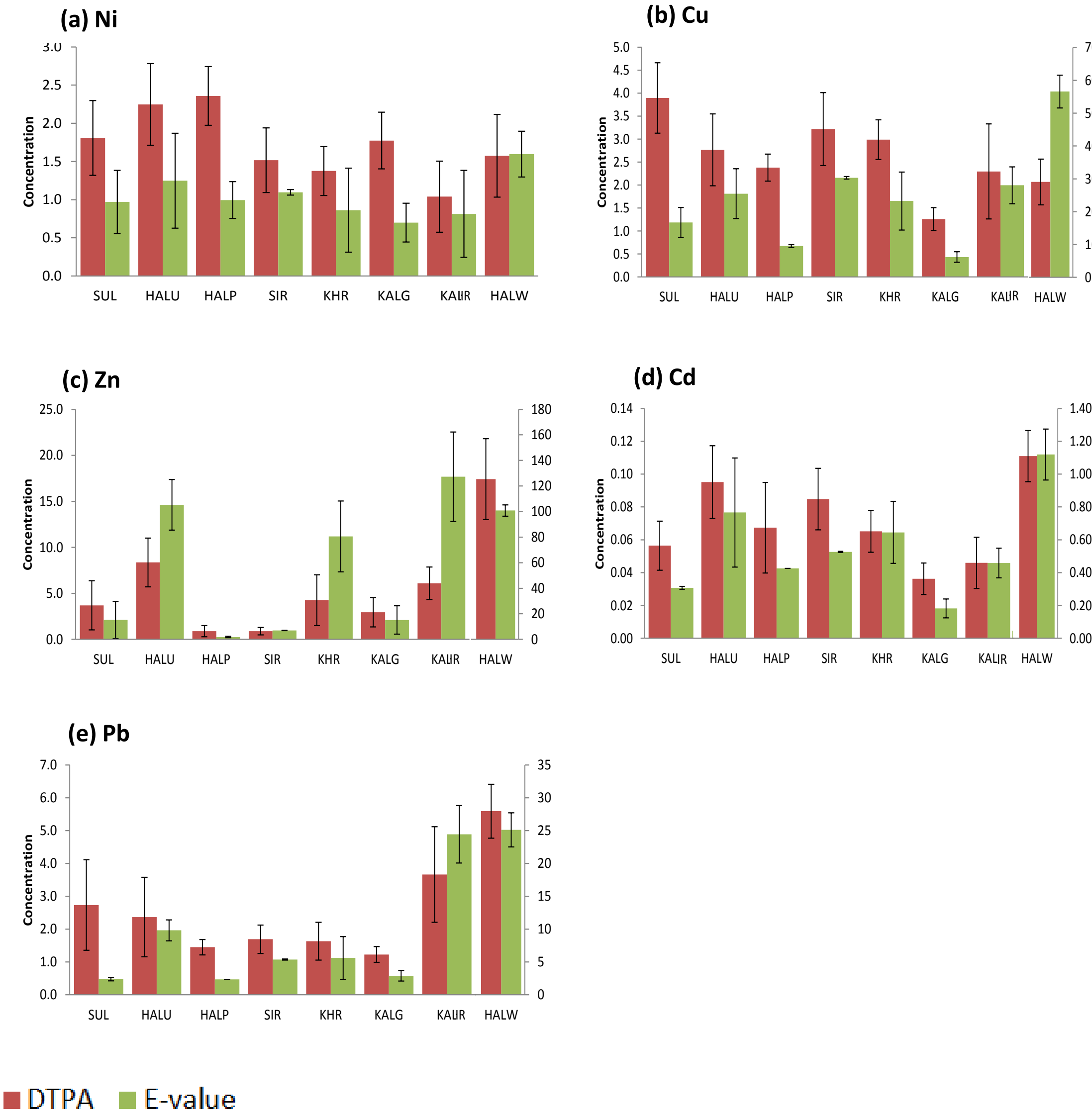


Figure 4.6: The DTPA extractable and E-value for (a) Cr, (b) Ni, (c) Cu, (d) Zn, (e) As, (f) Se,(g) Cd, (h) Pb at all study sites (mg kg^{-1}), vertical bars associated with each bar show Standard deviation of the different sites within one area. The secondary axis applied for the secondary axis applied for the HALW area

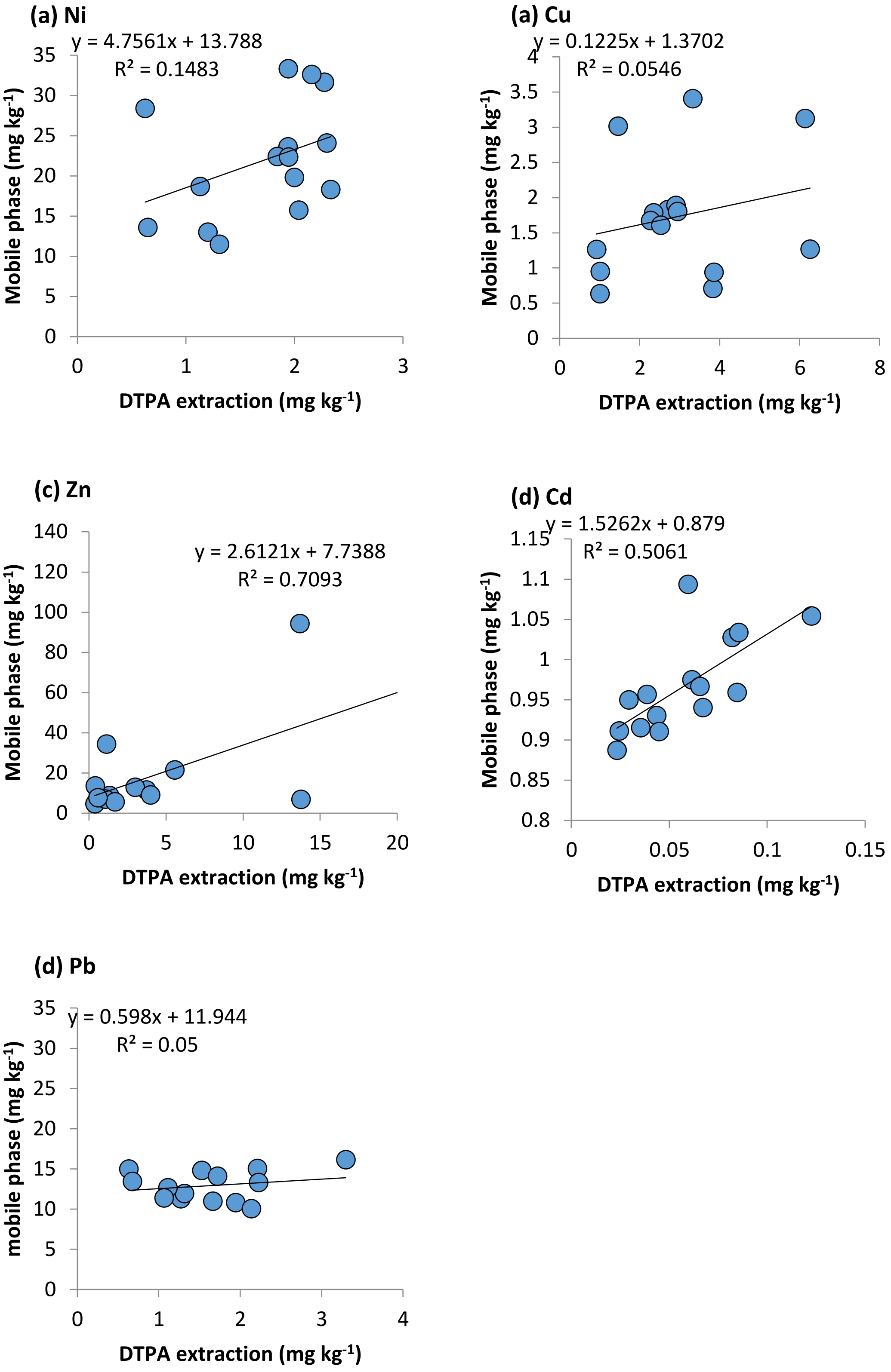


Figure 4.7 Linear correlation between SEP 'mobile phase' and DTPA extractable concentrations. Except Ni, the values were dominated by HALW10, which has been removed

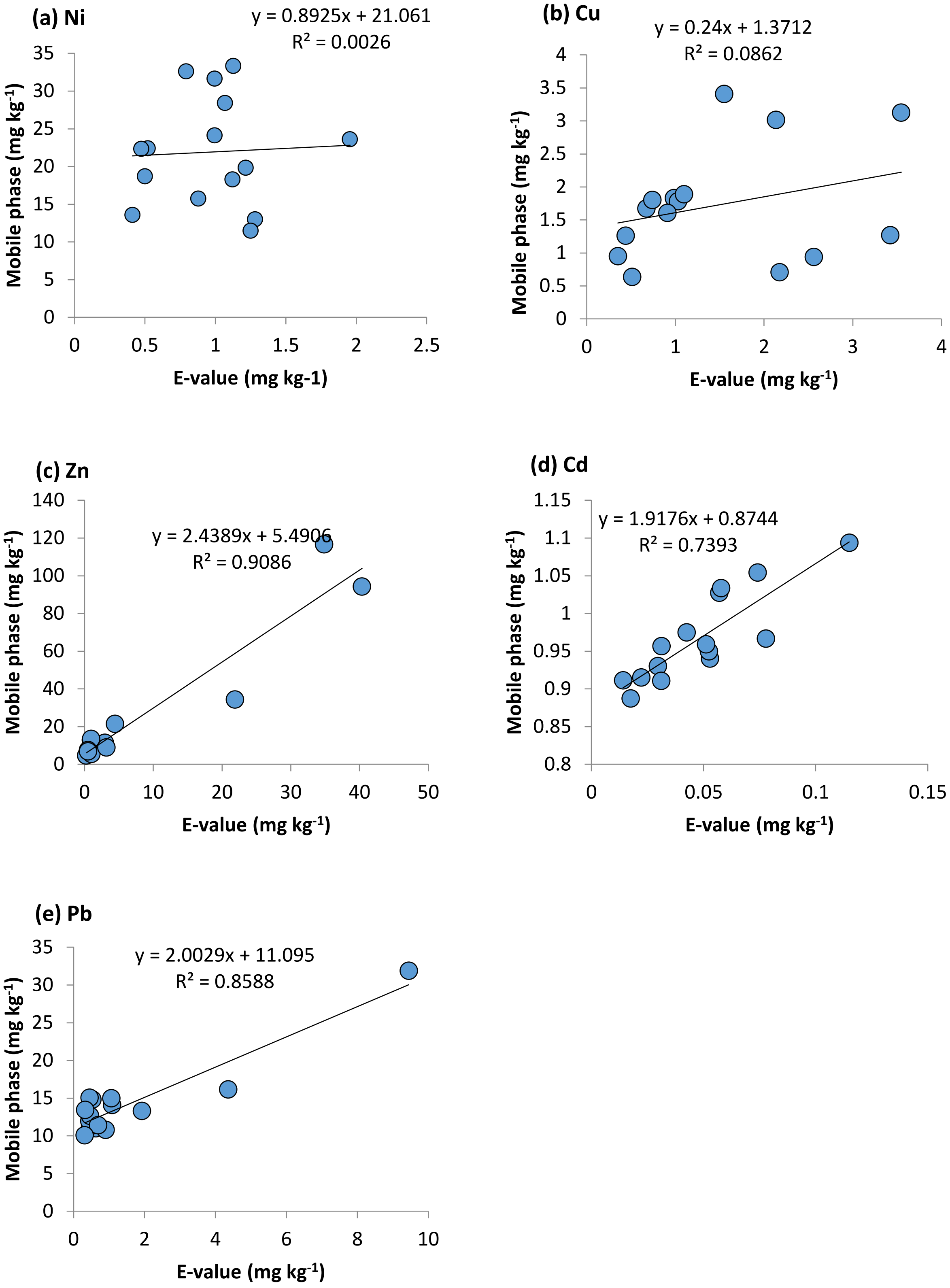


Figure 4.8: Linear correlation between SEP 'mobile phase' concentrations and E-values of selected trace elements. Except Ni, the values were dominated by HALW10, which has been removed

4.4 Conclusion

The geochemical fractionation of trace elements in the sampled soils showed that the SEP fractions of trace elements varied among the soils. Most of the PTEs such as Ni, Cu, Zn, As, were dominantly present in the residual fraction but the majority of Cd held within carbonate (F2) and Pb bound to Fe-Mn oxides (F3). DTPA extractions and isotopically exchangeable metal (E-value) also represent the bioavailable fractions of trace elements in the soil. The lability (DTPA extractable and isotopically exchangeable metals) varied among trace elements for some of them such as Ni, Cu and Zn were typically low if compared to the total concentrations but can be ~20% in the case of Cd and Pb. This is because the most trace elements in studied soils locked up in residual fractions of the soil as an inert form thus will not be available in a certain circumstances. However, highly greater values of DTPA extraction and E-values were found for the HALW sampling sites. Such results could be explained by the elevated concentration of trace elements in the HALW sites because of the waste disposal impacts. Although extraction methods solubilise non exchangeable metal pool into the solution, the extraction of trace elements using 0.005M DTPA seemed to be a good estimate of bioavailable elements in the soil because solubilisation of non-labile elements may compensate by incomplete mobilization of extraction-labile elements in the soil.

Neither mobile fractions from SEP (the sum of Exchangeable, carbonate and Fe/Mn oxides fractions) nor DTPA extractable metal pool provided consistently good estimation of E-values for Ni, Cu, Zn, Cd and Pb. For each trace element, there was a large difference in the values of chemical extractions (mobile phase, DTPA) and E-values with the ascending order of E-values<DTPA extractable< mobile phase. Perhaps this variation refers to the soil physicochemical characteristics and site specific sources of trace elements in the soil. The high values of mobile phase and DTPA extractions over E-values, it may refer to the power of extractants which were able to solubilize trace elements from non-isotopically exchangeable metal pool. The significant correlations were found between the mobile phase of trace elements and DTPA extraction and E-values of Cu, Zn, Cd and Pb but this correlation was highly poor in case of Ni.

In the next chapter soil to plant transfer will be investigated across a range of potentially contaminated and uncontaminated sites and the health risks to human from the consumption of vegetables will be assessed.

5 Risk Assessment of Potentially Toxic Elements (PTEs) from consumption of vegetables grown in and around urban areas in the Kurdistan region of Iraq

5.1 Introduction

Vegetables and crops grown in urban and peri-urban areas are more likely to be exposed to higher levels of PTEs and organic pollutants compared to those grown in rural areas. Vegetables have the ability to take up trace elements from contaminated soil. Some PTEs such as Cd are known to accumulate in fruits and vegetables and consequently have the potential to cause chronic disease in consumers (Clark et al., 2006;Wang et al., 2012).

Intake of PTEs from food is generally considered the most significant exposure pathway for the general population (Bacigalupo and Hale, 2012) if they do not smoke (Melo et al., 2012). More than 70% of Cd exposure is related to consumption of vegetables containing Cd (Swartjes, 2007;Sarwar et al., 2010a) whereas the main Pb source in the diet is from processing of food after harvesting rather than from Pb in the food itself (Bolger et al., 1996). Environmental agencies from various countries have therefore proposed permissible limits of trace elements in the human diet; where the PTEs exceed these limits they may pose risks to the consumer (European Commission, 2001).

In this study root and leaf vegetables and fruits were harvested from urban, peri-urban, rural and waste disposal sites in and around Sulaymanyah and Halabja cities (Iraq) together with associated soil samples. The objectives were to:

(i) Evaluate the PTE concentrations of the soils and edible parts of the associated plants.

(ii) Determine the lability of PTEs in the soils using DTPA extractions and isotopic dilution techniques and assess whether linear regression models can predict metal lability based on soil properties (pH and %LOI).

(iii) Determine if any potential health risks exist from consumption of the fruit and vegetables.

Sites	No	Classification	Description

5.2 Material and methods

5.2.1 Soil and plant sampling

Three areas (Kanikolka, Anab and Kani spi) in and around Halabja city and four areas (Tanjaro, Kanasura, Kanigoma and a waste disposal site,) in and around Sulaymanyah city were chosen for investigation. The locations were selected to cover urban, peri-urban and remote areas in addition to a waste disposal site. They represent typical areas where vegetables are grown and sold to the local population. Site descriptions and sampling locations are given in Table 5.1 and Figure 5.1.

Fifty-six composite soil samples from a depth of 1-15 cm (c. 1kg) were collected from different fields in each selected area (see Section 2.1.1). Plant samples were collected from individual plots within the area where a composite soil sample was collected. Twenty one fruit, leafy and root vegetable types were sampled (pepper, okra, tomato, eggplant, cowpea, cucumber, courgette, water melon, melon, leek, celery, parsley, purslane, spring onion, tarragon, chard, dill, cress, radish leaf, radish and onion). These represent the main species grown in the study area and those most commonly consumed by the local population. The edible parts of the plants were separated for drying and the rest discarded (see Section 2.1.2). Samples were transferred to the University of Nottingham (UK) for milling, digestion and multi-element analysis (see Sections 2.1.9 and 2.1.10).

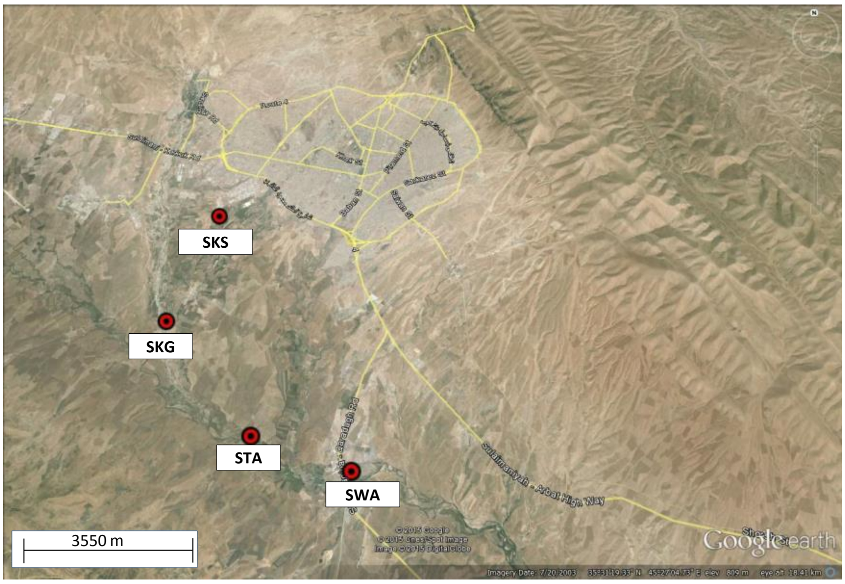
Sualaymanyah city	Waste site	5	Waste	Municipal waste disposal site located on the outskirts of the city close to agricultural fields. Leachates from the waste site can be seen flowing across the surrounding fields. Many kinds of waste are disposed of including, glass, metals, batteries, plastics and organic wastes.
	Tanjaro	11	Peri-urban	Located c. 10 km away from Sulaymanyah city centre. Most of the vegetables grown in this area are sold in the Sulaymanyah grocery market. Farmers used Tanjaro river as a main source for irrigation. Domestic waste water channels from the city flow in to the river.
	Kana sura	8	Urban	This area is located in a building area and waste water channel flows through the site and is used for growing some kinds of vegetables.
	Kani goma	6	Peri-urban	Close to the conurbation. A waste water channel from Sulaymanyah city runs through this site. Numerous orchards are found in the area and farmers grow vegetables between the trees.
Halabja city	Kanikolka	13	Urban	Located between domestic houses and a hospital. A waste water channel from Halabja city runs through this site which farmers use as a source of irrigation.
	Kanispi	5	Peri-urban	It is close to the city. Two waste water channels from Halabja city run through this site, which are used for irrigation.
	Anab	9	Rural	A village around 10 miles to the east of Halabja city. It is a wide plain mostly used for growing wheat and barley, although vegetables are also grown in this area. The main source of irrigation is spring and ground water.

Table 5.1 Description of sampling sites.

5.2.2 Soil characterization and elemental analysis

Soil pH was measured in deionised water suspensions (1 : 2.5 soil : solution ratio) after 30 minutes shaking (see Section 2.1.4). Loss on ignition was used to estimate the percentage of organic carbon in the samples (see Section 2.1.5). Analysis of total carbon was undertaken using a Flash EA1112 (CE Instruments) CNS analyser (see Section 2.1.6). A portion of each air dried < 2 mm sieved soil was finely ground using an agate ball mill (Retsch, Model PM400), and then stored in a polyethylene bag prior to acid digestion for elemental analysis. Approximately, 250 mg of finely ground soil was digested using an HF digestion method (see Section 2.1.8) and elemental analysis was undertaken using ICP-MS (see Section 2.1.10).

(a) Sulaymanyah



(b) Halabja

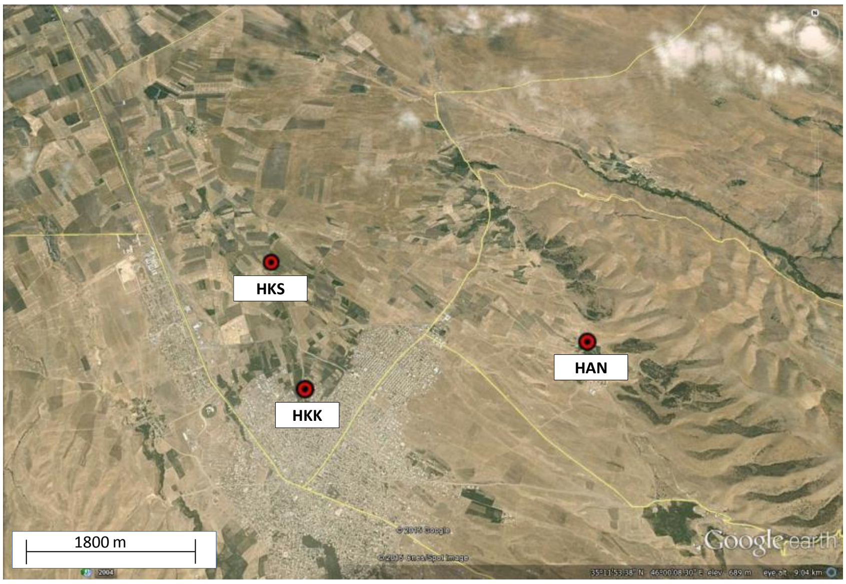


Figure 5.1: Map of sampling locations (a) Sulaimanyah city (b) Halabja city

5.2.3 DTPA extractions and isotopic dilution technique

Soils were extracted with DTPA as described by Lindsay and Norvell (1978) (Section 2.1.7.1). The isotopic dilution approach and calculation of E-values is described in Chapter 2 , Section 2.1.11.

5.2.4 Application of empirical model

Empirical models were tested for their ability to predict E-value and %E-value (%E-value) from observed soil properties. A linear multiple regression model was tested using variables that included pH, %LOI, inorganic carbon, DTPA-extractable metal (mg kg^{-1}) and total Ni, Cu, Zn, Cd, Pb concentrations (mg kg^{-1}). The significance of each variable was determined using Minitab vs 17 statistical software and only those variables which were significant ($p < 0.05$) were included, e.g.

$$\text{Predicted E-value} = k_0 + k_1\,(\text{pH}) + k_2\,(\%\text{LOI}) + k_3\,\text{DTPA extractable} \qquad \text{Eq 5.1}$$

5.2.5 Transfer factor

A transfer factor (TF) was calculated to indicate trace element transfer from soil to plant at each site according to;

$$TF = \frac{C_{plant}}{C_{soil}} \qquad \text{Eq 5.2}$$

Where C_{plant} and C_{soil} denote the concentrations of a trace element in the edible parts of the plant and soil, respectively, in the same units.

5.2.6 Risk assessment from PTEs in vegetable types

There are numerous pathways by which humans can be exposed to soil trace elements with the food chain as a main exposure route. A human health risk assessment method, including calculation of non-cancer and cancer risk, has been widely applied (USEPA, 2000). Non-cancer risk can be determined based on calculation of a target hazard quotient (THQ_m) and calculated according to the following equation (Nabulo et al., 2010):

$$THQ = \frac{ADD_M}{RfD} \qquad \text{Eq. 5.3}$$

Where:

$$\mathrm{ADD_M} = \frac{(\mathrm{DI} * \mathrm{M_{FW}})}{\mathrm{W_B}} \qquad \text{Eq 5.4}$$

In Eq.5.3 THQ denotes the 'target hazard quotient' from intake of trace elements via consumption of fruit and vegetables. $\mathrm{ADD_M}$ represents the average daily dose of the trace elements (mg $\mathrm{kg^{-1}\ d^{-1}}$) and RfD is the chronic reference dose for a trace element (mg $\mathrm{kg^{-1}\ d^{-1}}$) defined as the maximum tolerable daily ingestion of an element that will result in no adverse health impact (Hough et al., 2004). In Eq. 5.4, DI represents the daily intake of vegetables (kg $\mathrm{d^{-1}}$), $\mathrm{M_{FW}}$ is the concentration of the element in the vegetable tissue (mg $\mathrm{kg^{-1}}$ FW) and $\mathrm{W_B}$ is body weight (kg). The DI of fresh vegetables used in this calculation was 0.187 kg FW $\mathrm{d^{-1}}$ for adults and 0.118 kg FW $\mathrm{d^{-1}}$ for children with a $\mathrm{B_W}$ of 70 kg for an adult (Hamad et al., 2014) and 14.2 kg for a child (GEMS, 2000). The RfD values used were 1, 0.012, 0.04, 0.3, 0.0003, 0.00036 and 0.0035 mg $\mathrm{kg^{-1}\ d^{-1}}$ for Cr, Ni, Cu, Zn, As, Cd and Pb, respectively (WHO, 1982;IRIS, 2000;JECFA, 2006;Environment Agency, 2009b;Environment Agency, 2009c). Where the calculated THQ is less than 1, exposed consumers are unlikely to experience potential risk effects. If THQ is equal or higher than 1, this implies a potential hazard may exist to the health of the population.

Cancer Risk (CR) from consumption of food can be calculated according to the following equation (Liu et al., 2013) and evaluated using the method proposed by the USEPA Region III risk based concentration table (USEPA, 2006):

$$CR = CDI \times CSF \qquad \text{Eq 5.5}$$

Where CDI denotes the oral daily intake of carcinogens (mg $\mathrm{kg^{-1}\ d^{-1}}$) and CSF is the cancer slope factor. CSFs used were 0.5, 6.3, 0.085 and 1.5 mg $\mathrm{kg^{-1}day^{-1}}$ for Cr, Cd, Pb and As, respectively (Zhao et al., 2014b;USDOE, 2011). The tolerable risk for regulatory purposes is within the range of 10^{-6} to 10^{-4} (USEPA, 2001a).

5.3 Results and discussion

5.3.1 Soil characterization

Organic matter and pH are important factors which control trace element mobility, accumulation and bioavailability. At high pH the lability and bioavailability of trace elements decreases due to precipitation as carbonates or hydroxides or due to organic complex formation; their mobility increases when pH decreases (Xu et al., 2010). The values of pH and % LOI in soils from all sampling areas are presented in Table 5.2.

The highest pH values were recorded in spring water-irrigated fields in the Anab area (pH 8.07-8.36, n=9). Lower pH values were observed in waste water irrigated fields at Kani kolka. This difference may result from natural variation but some studies have also shown decreasing pH as a result of long-term wastewater irrigation (Rattan et al., 2005;Xu et al., 2010). For example, fields irrigated with waste water (pH 5.02) for 40 years resulted in a decrease in soil pH from 7.1 to 6.7 and from 6.2 to 5.9 at sampling depths of 0.1 and 1m, respectively (Rosabal, 2007). Xu et al., (2010) explained the lower soil pH of a long-term wastewater-irrigated soil as a result of the wastewater's acidity, while Angin et al. (2005) argued that the effect was a consequence of increasing mineralization of organic matter. In general, the effect of wastewater irrigation on soil pH depends on the wastewater pH and the capacity of the pH buffering of soil (Kunhikrishnan et al., 2012).

Loss-on-ignition (%LOI) is an estimate of the percentage of organic carbon in a soil. In the current study the lowest value (6.80%) was recorded in spring water irrigated fields at Anab (rural area) while the highest value (11.35%) was detected in fields near the municipal waste disposal site in Sulaymanyah city irrigated by diluted domestic waste water. Untreated waste water can add more organic matter to a soil than freshwater. Various studies have shown that farms irrigated over long periods with sewage effluent results in a significant increase in organic matter content of the top soil (Friedel, 2000;Rattan et al., 2005;Qishlaqi et al., 2008;Xu et al., 2010). Also, agricultural soils affected by municipal wastes may contain high OM (Rashid, 2010). Anikwe and Nwobodo (2002) conducted a study on the effect of long-term municipal waste disposal on soil physicochemical properties in Abakaliki, Nigeria. Soils were sampled at dump and non-dump sites to evaluate and compare the soil profiles. The authors reported that soil organic matter had increased substantially at the dump site compared to the non-dump site as a result of long term waste disposal because the waste disposed contained high amounts of municipal organic wastes. Heavy metals such as Cu, Zn, Pb were also increased in dumped sites compared to the control.

Table 5.2: Soil properties and mean (±SD) PTE concentrations (mg kg^{-1}) in soils at seven selected sites. Bold values indicate where soil trace element concentrations exceed Soil Guideline Values (SGV) and European Union standards (EU).

Sites	Code		pH	%LOI	Cr	Ni	Cu	Zn	As	Se	Cd	Pb
Waste area	SWA	Mean	7.92	11.4	**129**	**127**	**84.8**	262	8.17	0.236	0.467	35.8
		±SD	0.141	1.53	3.75	2.27	25.3	70.3	0.311	0.008	0.099	3.54
Tanjaro	STA	Mean	8.07	7.60	**137**	**156**	30.1	78.2	4.23	0.259	0.313	12.3
		±SD	0.101	1.29	3.37	3.02	0.746	2.17	0.156	0.004	0.021	0.36
Kana sura	SKS	Mean	7.86	8.89	**141**	**147**	34.4	94.5	8.59	0.253	0.423	14.8
		±SD	0.129	1.37	10.9	11.2	2.80	12.1	0.723	12.971	0.064	1.41
Kani goma	SKG	Mean	8.18	7.37	**108**	**109**	25.9	71.0	6.16	0.218	0.302	12.4
		±SD	0.137	1.17	3.19	3.19	0.943	2.40	0.316	3.108	0.026	0.332
Kani kolka	HKK	Mean	7.67	11.1	**114**	**132**	38.7	149	11.8	0.486	0.578	21.6
		±SD	0.319	1.74	5.80	7.06	1.98	10.7	0.777	0.006	0.048	1.27
Kani spi	HKS	Mean	7.69	9.56	**132**	**138**	35.0	122	12.2	0.441	0.560	18.8
		±SD	0.209	1.69	1.83	1.53	0.349	2.87	0.390	0.005	0.021	0.166
Anab	HAN	Mean	8.20	6.80	77.3	**81.0**	29.0	84.6	7.57	0.435	0.296	15.2
		±SD	0.117	0.385	2.37	2.70	0.984	3.64	0.321	0.026	0.022	0.476
SGV					[a]130	230[b]	50.0	300	43.0[c]		1.80[d]	450[a]
EU					100	50.0	100	300			3.00	100
P			NS	NS		*	*	*	*	*	*	*

[a](DEFRA and EA, 2002), [b](Environment Agency, 2009c), [c](Environment Agency, 2009b), [d](Environment Agency, 2009a).

5.3.2 Total metal concentrations in soil

The agricultural soils were collected from four areas across the Sulaymanyah province (Municipal waste site, Tanjaro, Kana sura and Kani goma) and three locations across Halabja city (Kani kolka, Anab and Kani spi). The descriptive statistics (mean and standard deviation) of the total concentrations of some PTEs at all sampling areas are shown in Table 5.2 and Fig. 5.2. Significant variation in concentrations of Cr, Ni, Cu, Zn, As, Se Cd and Pb was observed between sampling sites at $p<0.05$, suggesting localized differences in the soils.

Overall, a wide range of trace element concentrations were found across the studied areas in both Sulaymanyah and Halabja cities with Ni>Zn>Cr ≈ Cu> Pb>As>Cd>Se. Figure 5.2 compares concentrations based on land uses. Concentrations of Cu, Zn, Cd and Pb were generally greater and more variable in areas subject to waste disposal compared to other urban or rural areas (Fig. 5.2c, d, g and h). No increase was observed for Cr, Ni, As and Se (Fig. 5.2a, b, e and f). The lowest concentrations of all elements other than Se were recorded in the rural areas. Waste disposal and urban activity therefore appears to be increasing the concentrations of some PTEs in nearby agricultural soils.

The mean concentrations of Cr varied from 77.3 mg kg^{-1} at Anab (rural area, n=9) to 141 mg kg^{-1} at Kanasura (urban area, n=8) which exceeds the European Union standard of 100 mg kg^{-1} (European Union, 2006) and the SGV of 130 mg kg^{-1} (DEFRA and EA, 2002). Nickel concentrations varied from 81.0 mg kg^{-1} in rural Anab to 156 mg kg^{-1} at Tanjaro (peri-urban area, n=11) with concentrations exceeding the European Union standard of 50 mg kg^{-1} in all study areas. This may be a consequence of the calcareous nature of the soils or background geology of the area. High concentrations of Ni in calcareous soil were also found by Habib et al. (2012). They investigated 25 soil samples in Baghdad city in Iraq for trace element content. They reported high concentrations of Ni in all the soil samples, ranging between 105 - 210 mg kg^{-1} which may also suggest that Ni soils is highly dependent on the geological background of the areas in the Iraqi soil rather than anthropogenic sources. Nickel concentrations were found to be higher (up to 92 mg kg^{-1}) in calcareous soil compared to other types of soil which suggests that Ni in soils is highly linked to the soil parent material (Kabata-Pendias and Mukherjee, 2007).

Rahmatullah et al. (2001) reported high concentrations of Ni (up to 94 mg kg^{-1}) in nine calcareous soils and they concluded that up to 72% of total Ni is bound to residual fractions in the soils (see Section 4.3.1).

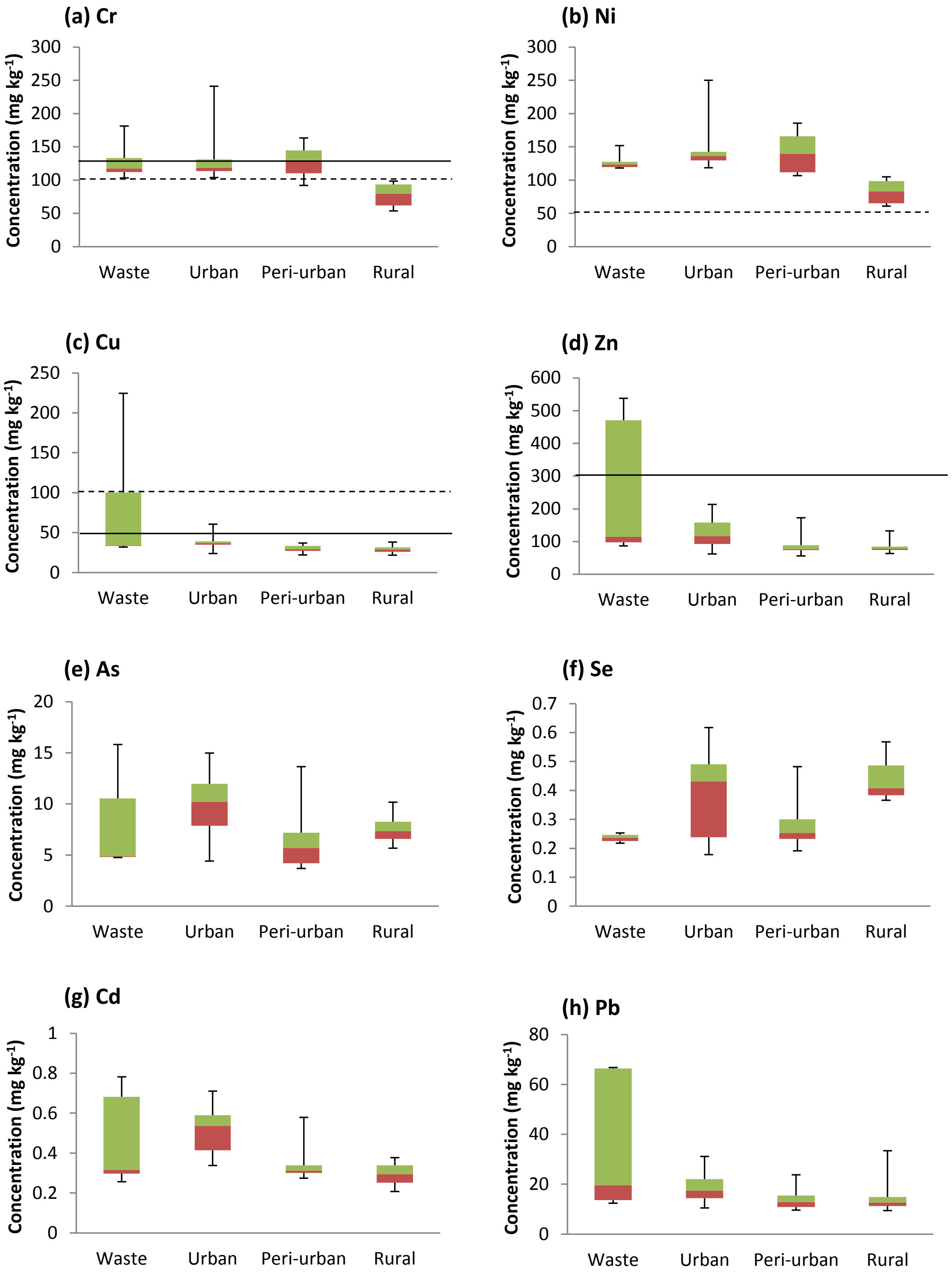


Figure 5.2: Mean concentration of (a) Cr, (b) Ni, (c) Cu, (d) Zn, (e) As, (f) Se, (g) Cd and (f) Pb for all study land uses. The boxes represent quartile values while the whiskers show maxima and minima. Solid and dashed lines denote the SGV and EU/WHO standards, respectively.

Copper and Zn concentrations were lower than the permitted UK sludge limits for agricultural soil (50 and 300 mg kg^{-1}) and European Union standards (100 and 300 mg kg^{-1}), respectively, except at the waste disposal site where higher mean concentrations were recorded (84.8 and 262 mg kg^{-1}), respectively. This may be due to the influence of the waste site with leachate and ash generated by waste incineration finding its way onto the surrounding land.

Concentrations of Se in locations closer to Halabja city (HKK, HAN, and HAN) were greater than at sites within and around Sulaymanyah (SWA, STA,SKS and SKG) (Table 5.2). This difference may be a consequence of differences in geology between the areas. Lower concentrations of Se were found in waste and urban areas compared to rural areas (Fig 5.2f).

Mean concentrations of other trace elements (As, Cd and Pb) were all below SGVs (43, 3 and 450 mg kg^{-1}, respectively). PTE concentrations in rural areas were typically lower than those in urban, peri-urban and waste sites and were within permissible limits given by various agencies (Environment Agency UK, UK sludge limits and European Union standards). By contrast, greater soil concentrations of PTEs were found around the waste disposal area in Sulaymanyah city, very probably due to the impact of the waste disposal in the area.

5.3.3 DTPA-extractable and E-values of PTEs in soil

The DTPA extraction was developed to assess nutrient deficiency in calcareous soils, thus it is not intended to dissolve carbonate phases which makes it a suitable extractant for calcareous soil (Hooda, 2010;Conesa and Faz, 2011). Likewise, determination of ‘E-values’ using stable isotopes offers an estimate of the labile metal pool in a soil because the technique uses the addition of a small volume of a spike isotope which distributes itself according to the natural solid–solution equilibrium without disturbing the solid phase (Ayoub et al., 2003;Hamon et al., 2008).

The DTPA extraction technique can be used to estimate the bioavailability of trace elements in the soil as easily-exchangeable and/or weakly adsorbed PTEs are solubilized by 0.005M DTPA (Lindsay and Norvell, 1978). For example, those elements bound to exchangeable, carbonate and Fe/Mn oxides fractions in the soil, and in some circumstances elements bound to organic matter, can be released by DTPA extraction (Quevauviller, 1998).

Figure 5.3 shows the amount of Ni, Cu, Zn, Cd and Pb extracted by DTPA for the waste, urban, peri-urban and rural areas and compares the results to E-values. The greatest mean DTPA-extractable metal pool for all metals was observed in the waste area (Ni 4.09 mg kg^{-1}, n=5; Cu 10.6 mg kg^{-1}, n=5; Zn 49.4 mg kg^{-1}, n=5; Cd 0.201 mg kg^{-1}, n=5; Pb 12. 9 mg kg^{-1}, n=5) followed by urban and peri-urban areas, with the lowest observed in rural areas (Ni 2.18 mg kg^{-1}, n=8; Cu 3.42 mg kg^{-1}, n=8; Zn 5.99 mg kg^{-1}, n=8; Cd 0.193 mg kg^{-1}, n=8; Pb 4. 9 mg kg^{-1}, n=8). This suggests the input of available forms of the elements into the surface soil is mainly from waste disposal but also from the urban and peri-urban activities.

In general, the % of the total element concentration that was DTPA-extractable was low for the Ni, Cu and Zn (see Fig 5.2 for total concentrations), but can be up to ~20% of the total concentration of Cd and Pb. This may suggest that Ni, Cu and Zn are primarily in less available phases than Cd and Pb. Although relatively low total concentrations of Ni were observed in the waste area compared to other areas, its extractability using DTPA is higher than other areas. This may reflect a more labile and soluble anthropogenic Ni component.

Measuring the exchangeable metal pool using isotopic dilution may better represent the labile fraction of an element in the soil (Hamon et al., 2008). Measured E-values (mg kg^{-1}) of selected trace elements are shown in Fig. 5.3. A similar trend to that given by DTPA extraction was observed with highest E-values in soils from the waste area and lowest from soils in rural areas. E-values were in general lower that DTPA-extractable metal concentrations.

This may be due to the DTPA extractant solubilising non-labile metal. It is believed that DTPA attacks not only the exchangeable metal pool but also metal-organic matter complexes, metal held within Fe/Mn oxides and/or bound to carbonates (Quevauviller, 1998). Comparing all the metals, DTPA-extractable Zn was closest to the E-values determined, probably because the majority of Zn was in the residual and Fe/ Mn oxide fractions. The greatest difference between DTPA-extractable metal and the corresponding E-value were observed for Cd. This suggests that non-labile Cd bound to the carbonate fraction (see Chapter 4, Fig 4.1) was mobilised by DTPA.

Many studies have compared the metal concentrations extracted by the 0.005 M DTPA and E-values. For example, a study conducted on six soils revealed that DTPA extraction of Mn, Fe, Co, Cu and Zn were relatively similar (about 80% to 100%) to E- values (Lopez and Graham, 1972). In contrast, studies by Fujii and Corey (1986) and Echevarria et al. (1998) demonstrated that the DTPA-extractable Ni, Cu, Zn and Cd underestimated exchangeable metal pools (E-values) in two soils. A recent study by Marzouk et al. (2013) demonstrated that DTPA extraction for Zn, Cd and Pb underestimated E- values in acidic soil whilst similar values were observed in calcareous soils. The capacity and efficiency of DTPA is also influenced by soil texture, with more extraction typically observed in sandy loam soils (Hooda and Alloway, 1994).

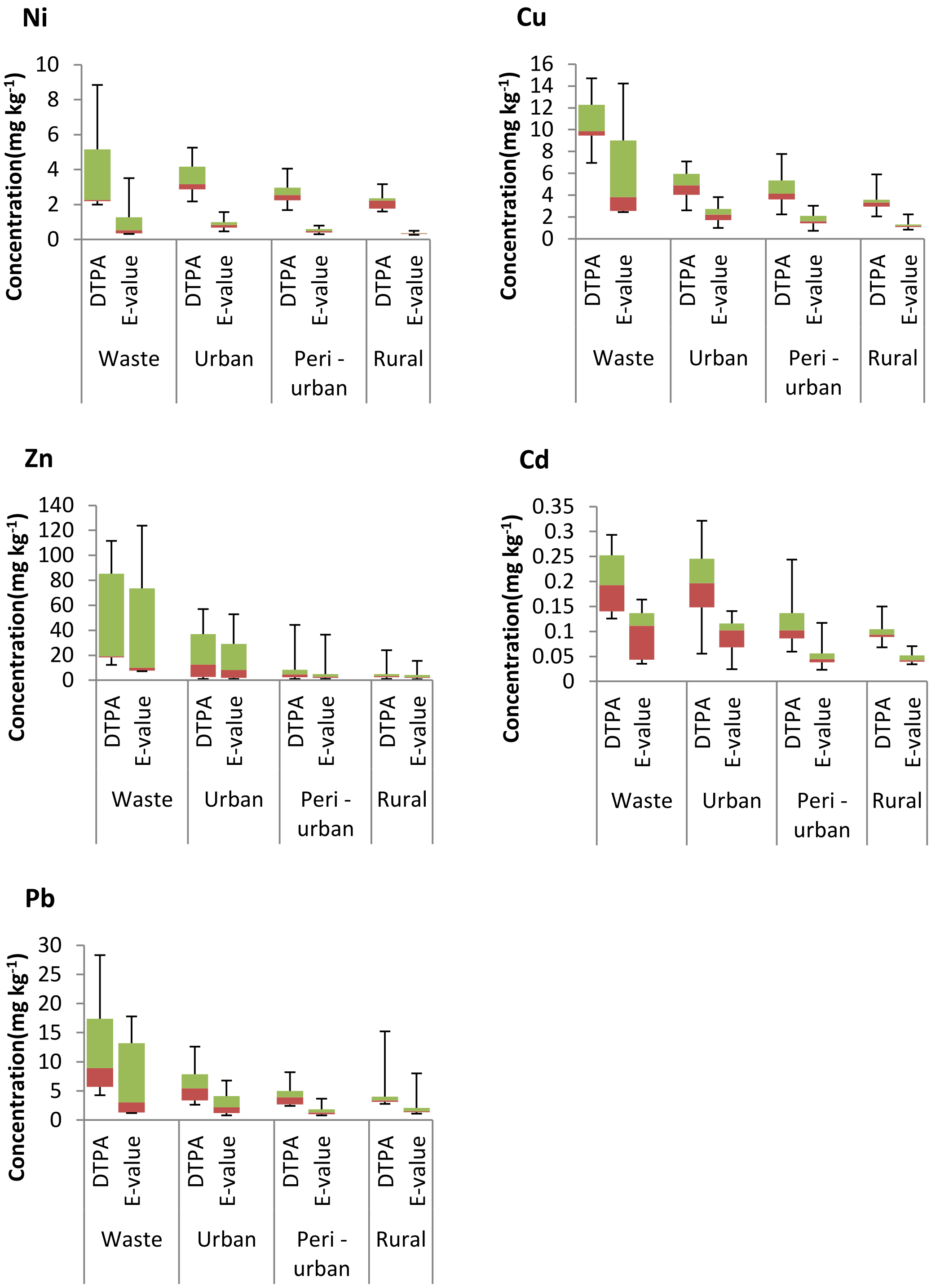


Figure 5.3: Comparison of DTPA extractable and E-value for Ni, Cu, Zn, Cd, Pb at all study sites (mg kg^{-1}). The boxes represent quartile values while the whiskers show maxima and minima.

5.3.4 Correlation between DTPA, E value and % E value

Figure 5.4 shows the correlation between DTPA-extractable and the exchangeable metal pool in the soil. Significant positive correlations were observed between E-values and DTPA-extractable concentrations for Cu (R^2=0.715), Zn (R^2=0.884), Cd (R^2=0.873) and Pb (R^2=0.778) but DTPA-extractable Ni, Cu, Cd and Pb concentrations were greater that the corresponding E-values. Reasonably good agreement was seen for Zn with most values on a 1:1 line. Sinaj et al. (1999) conducted an investigation on six polluted and six unpolluted soils. They also found good agreement between DTPA-extractable concentration and the E value for Zn.

Figure 5.5 shows the correlation between total concentrations and E values for Ni, Cu, Zn, Cd and Pb. Even though only a small proportion of each element was labile, there was a consistent positive correlation; Cu (R^2=0.873), Zn (R^2=0.803), Cd (R^2=0. 848) and Pb (R^2=0.893). Izquierdo et al. (2013) conducted an investigation of 43 soils comparing E-values and total concentrations of selected metals. They found that the E-values of Zn, Cd and Pb were highly correlated with the corresponding total concentrations with correlation coefficients (r) of 0.97, 0.95 and 0.84, respectively. A significant positive correlation was also observed between E-value and total Cd by Sterckeman et al. (2009) for 29 soils with different Cd sources (r = 0.76; (Sterckeman et al., 2009). However, they did not find a relationship between total concentration of Ni and its E-value, possibly due to a large proportion of non-labile Ni in some calcareous soils.

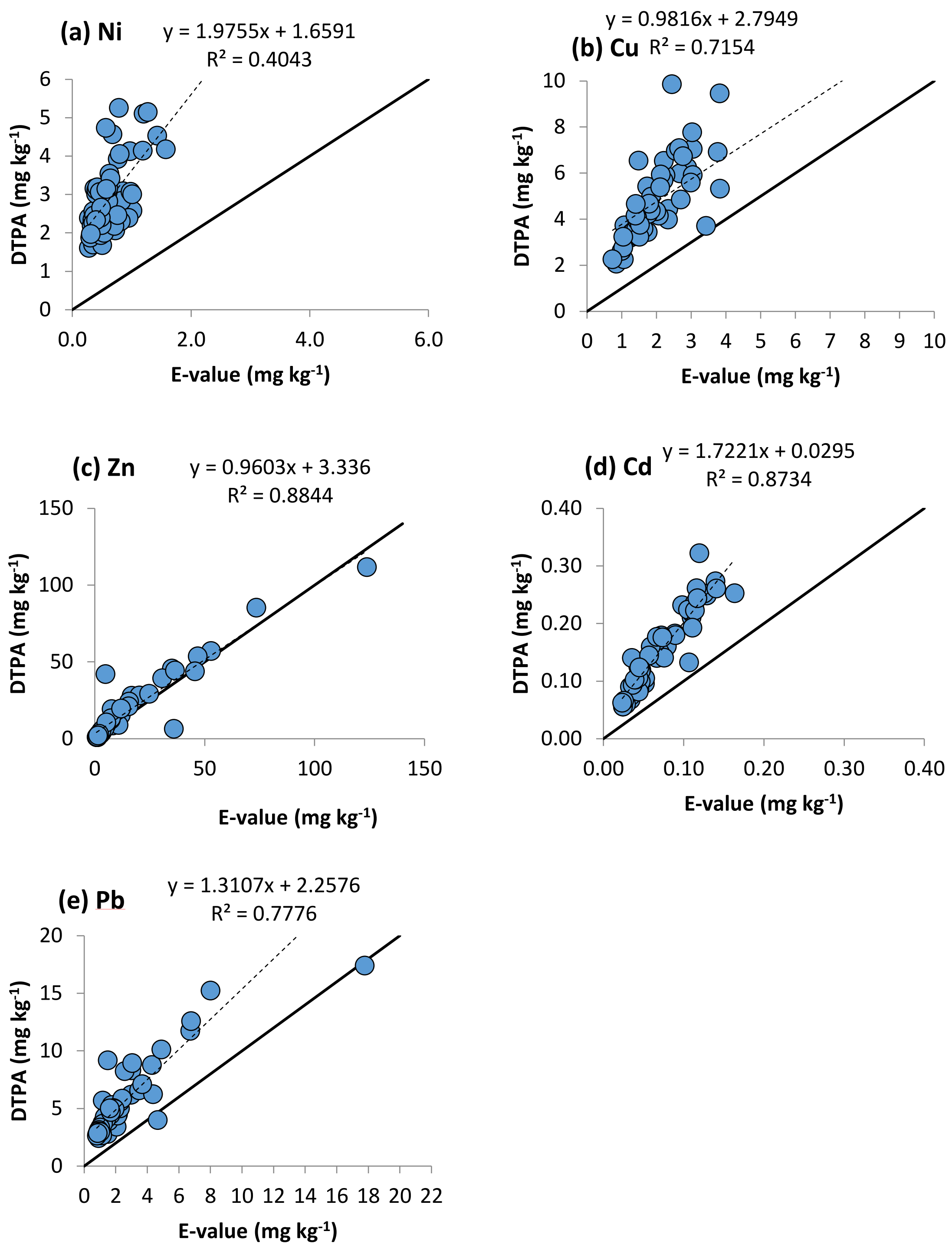


Figure 5.4: Correlation between DTPA-extractable concentrations of trace elements and the exchangeable metal pools (E-values) for (a) Cu, (b) Zn, (c) Cd and (d) Pb.

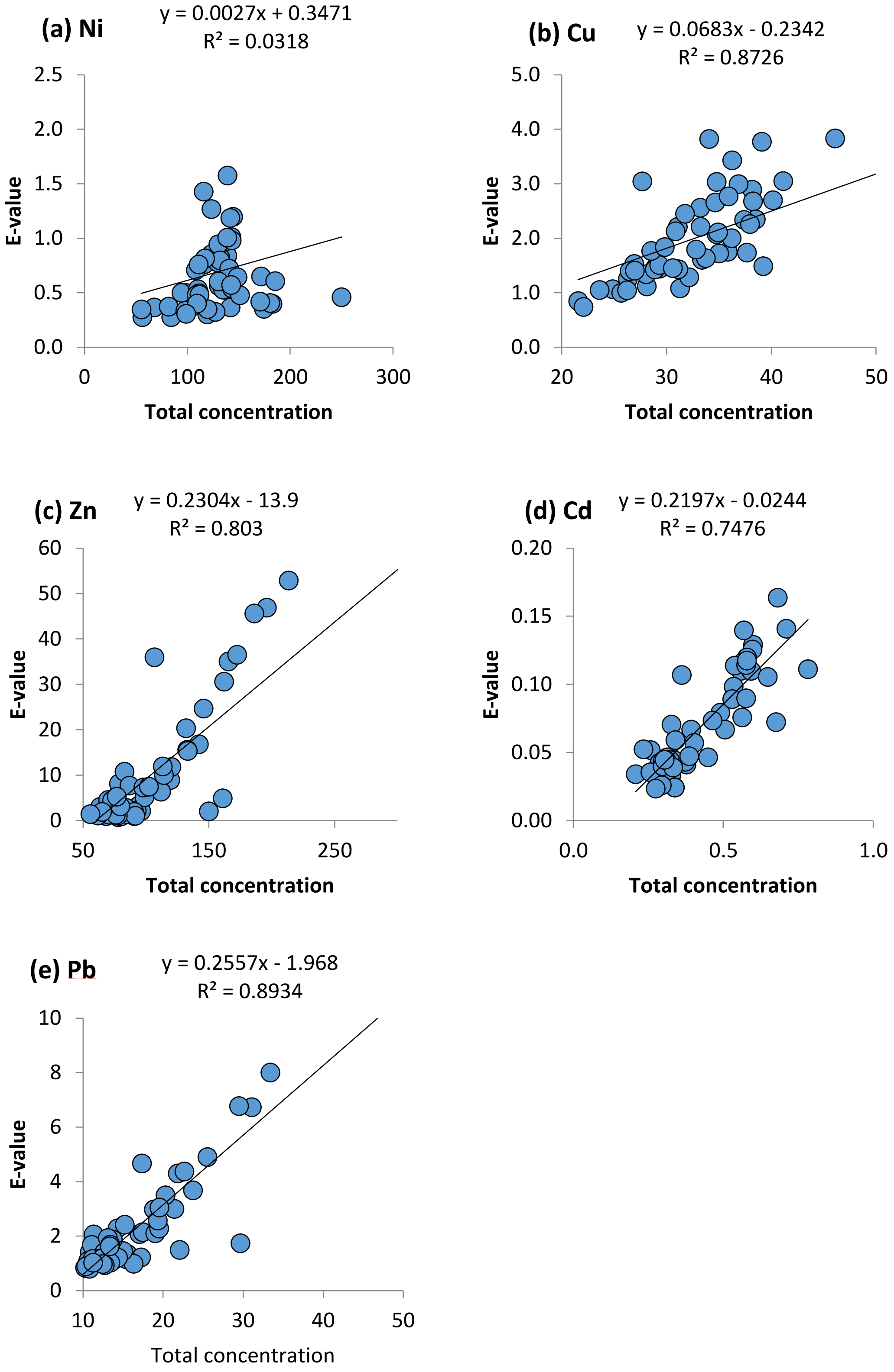


Figure 5.5: Correlation between total concentrations of trace elements and exchangeable metal pools (E-values) (with mg kg^{-1}) for (a) Ni, (b) Cu, (c) Zn, (d) Cd and (e) Pb.

5.3.5 Impact of soil pH and organic matter on metal lability

Soil properties, particularly pH and organic matter, are considered to be important factors which govern the behaviour of trace elements in the soil (Gäbler et al., 1999). In this study, despite a narrow pH range, negative linear correlations were observed between DTPA-extractable concentrations or E-values and pH (Fig 5.6). Ni, Cu, Zn, Cd and Pb in lower pH soils are, therefore, more likely to be extractable and exchangeable than soils with high soil pH. Similar correlations have been demonstrated in many studies e.g. Clemente et al. (2005);Degryse et al. (2004), Martínez and Motto, (2000), Tye et al. (2003). Yoo and James (2002) investigated factors affecting Zn extractability. They showed that increasing pH leads to increased sorption of Zn on organic carbon and Fe/Mn oxides and they stated that pH and redox potential controlled the solubility of Zn bound to Fe/Mn hydroxides through precipitation, reduction and complexation. Thus, reduced and solubilised Fe^{2+} and Mn^{2+} combined with high pH decreased the solubility of Zn. Small changes in pH can result in precipitation or dissolution of Fe oxides, if pH decreases trace elements are released into the soil solution whereas, as pH increases, metals precipitate (Adamo et al., 2002). When the pH increases the bonds between oxygen atoms and metal ions in the soil solid phase are more likely to be stronger (Crout et al., 2006). Another possible mechanism that decreases lability of metals as soil pH increases is a change in metal fractionation, for example a change from organic matter-bound to Fe/Mn oxide-bound forms (Marzouk, 2012).

Organic matter is a crucial soil component that also controls the mobility and solubility of trace elements (Ottosen et al., 2009). Soluble organic species can retain trace elements in the soil solution whereas humic compounds with high molecular weights are able to retain the trace elements in the solid phase via chelation, thus reducing bioavailability (Clemente et al., 2005). This interaction of trace elements and organic matter is entirely pH-dependent.

Figure 5.7 shows the correlations between DTPA, E-value and %LOI. These were results very weak for Ni (R^2=0.338, 0.003), Cu (R^2=0.025, 0.014,), Zn (R^2=0.069, 0.036,), Cd (R^2=0.032, 0.028,) and Pb (R^2=0.338, 0.021,), respectively. The correlation of metal mobility with organic matter is affected by pH; increased pH increases the negative charge on sites leading to increased adsorption of trace elements (McLean and Bledsoe, 1992). Garrido et al. (2012) showed that Cu sorption increased in soils amended with sewage sludge, attributing this to an increase in the number of elemental sorption sites due to the addition of organic matter. In this study, more Zn was extracted and exchangeable with increasing organic matter because it is believed that Zn sorption on organic matter unpredictably decrease with addition of sewage sludge, which riches with organic matter, (Tsadilas et al., 2009;Shaheen et al., 2013). This reveals that Zn is strongly associated with the inorganic phase rather that organic matter (Degryse et al., 2009). This explanation is in complete agreement with Chaney et al. (2010) who suggest that Zn is well known to specifically bind to inorganic components of the soil.

However, the impact of organic matter on some trace elements including Zn is not clear and it has been suggested that it is difficult to distinguish between the effects of organic matter and pH as both are related to each other (Shaheen et al., 2013). Furthermore, pH also has an important role in increasing metal extractability and changing the sorption status of elements in soil. Many investigations have observed that the sorption of PTEs is pH-dependent (Spark et al., 1995;Mustafa et al., 2006). Pagnanelli et al. (2003) reported that increased organic matter may lead to decreased pH; subsequent metal extractability will increase because of decreasing metal sorption.

Figure 5.8 shows the correlations between %E-value and pH for Ni, Cu, Zn, Cd and Pb. A weak negative correlation with %E-value for all five elements exists. (Degryse et al., 2004) reported a highly negative correlation between Zn %E-values and pH in 99 European soils covering a wide range of pH (3.3-7.5). This is perhaps partially due to precipitation as hydroxide, oxide, carbonate and phosphate phases at high pH (McLean and Bledsoe, 1992). Sterckeman et al. (2009) reported that %E-value of Cd was negatively correlated with pH values in 29 soils.

Mao (2013) found that the %E-values of Ni, Cu, Zn, Cd and Pb were correlated negatively with pH in 50 urban soils in Nottinghamshire and Wolverhampton. Marzouk et al. (2013) reported negative correlation between %E-values of Zn, Cd and Pb and pH in 246 soils in Pb/Zn mine contaminated soil with a wide range of pH from 2.6 to 7.6. Young et al. (2007) also noticed decreasing Zn and Cd %E-values with increasing pH in 23 soils, with pH range 3.3-7.6, incubated with metal salts for 818 days.

A positive but poor correlation was found between %LOI and %E-value, for Ni (R^2=0.015), Cu (R^2=0.003), Zn (R^2=0.181), Cd (R^2=0.303) and Pb (R^2=0.132) (Figure 5.9), reflecting the binding of the elements to organic matter including humic and fulvic acids (Belaid et al., 2012). The soils are calcareous and, consequently, show low trace element lability particularly for Ni, Cu and Zn. This may be due to the effects of soil properties on trace element dynamics in the soil. For example, some trace elements are retained in the soil by adsorption onto organic matter in the soil surface. The soil pH also plays an important role here and has a crucial impact on metal bioavailability in soil (Quevauviller et al., 1997). Marzouk et al. (2013) reported a poor correlation between %E-value of Cd and Pb and %LOI in 246 soils with a wide pH range (2.6-7.6). The authors suggested poor correlation in some soils might have been influenced by the low pH.

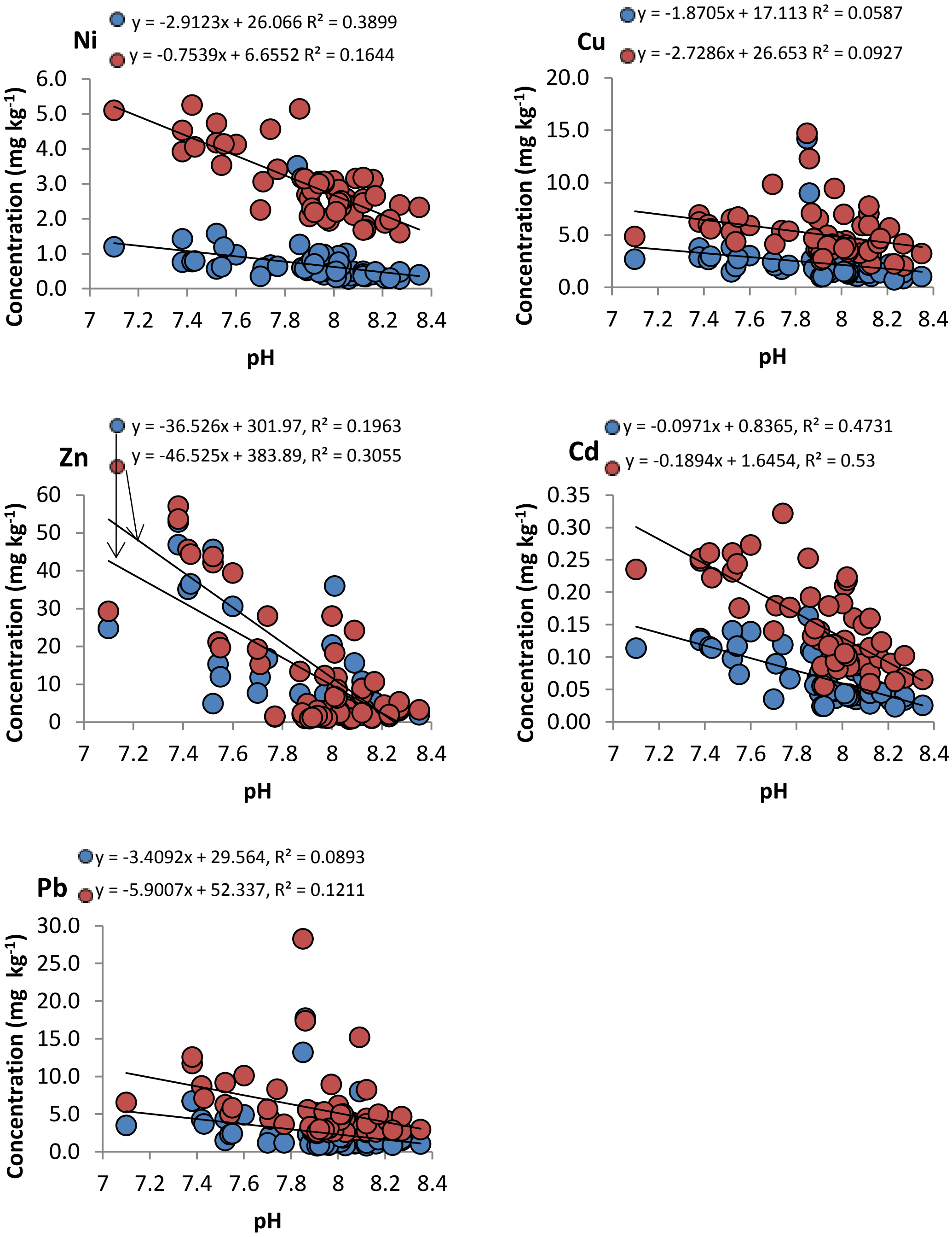


Figure 5.6 Correlations between DTPA-extractable (red), exchangeable metal pool (blue) and pH for selected trace elements.

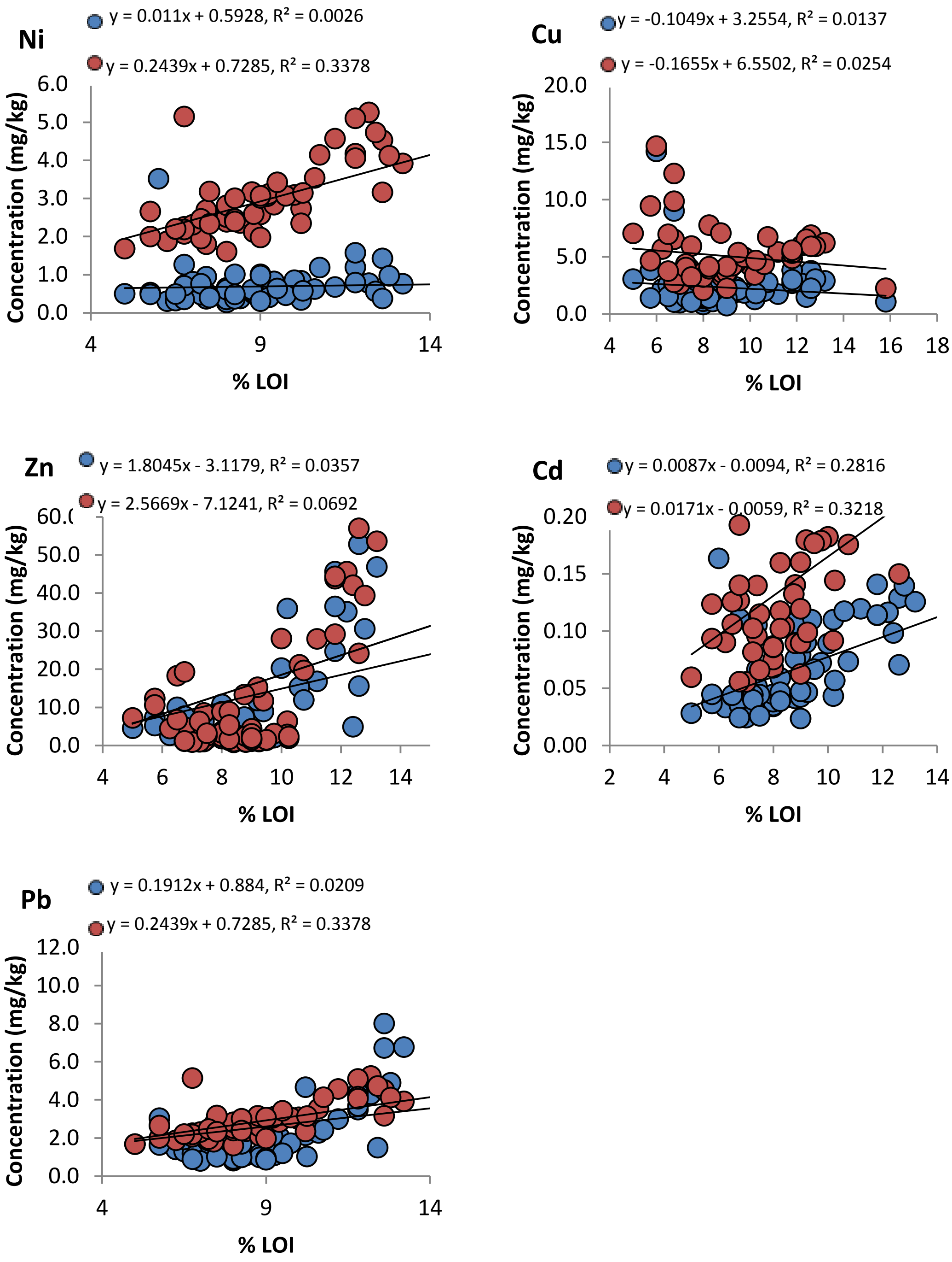


Figure 5.7 Correlations between DTPA-extractable (red), exchangeable metal pool (blue) and %LOI for selected trace elements.

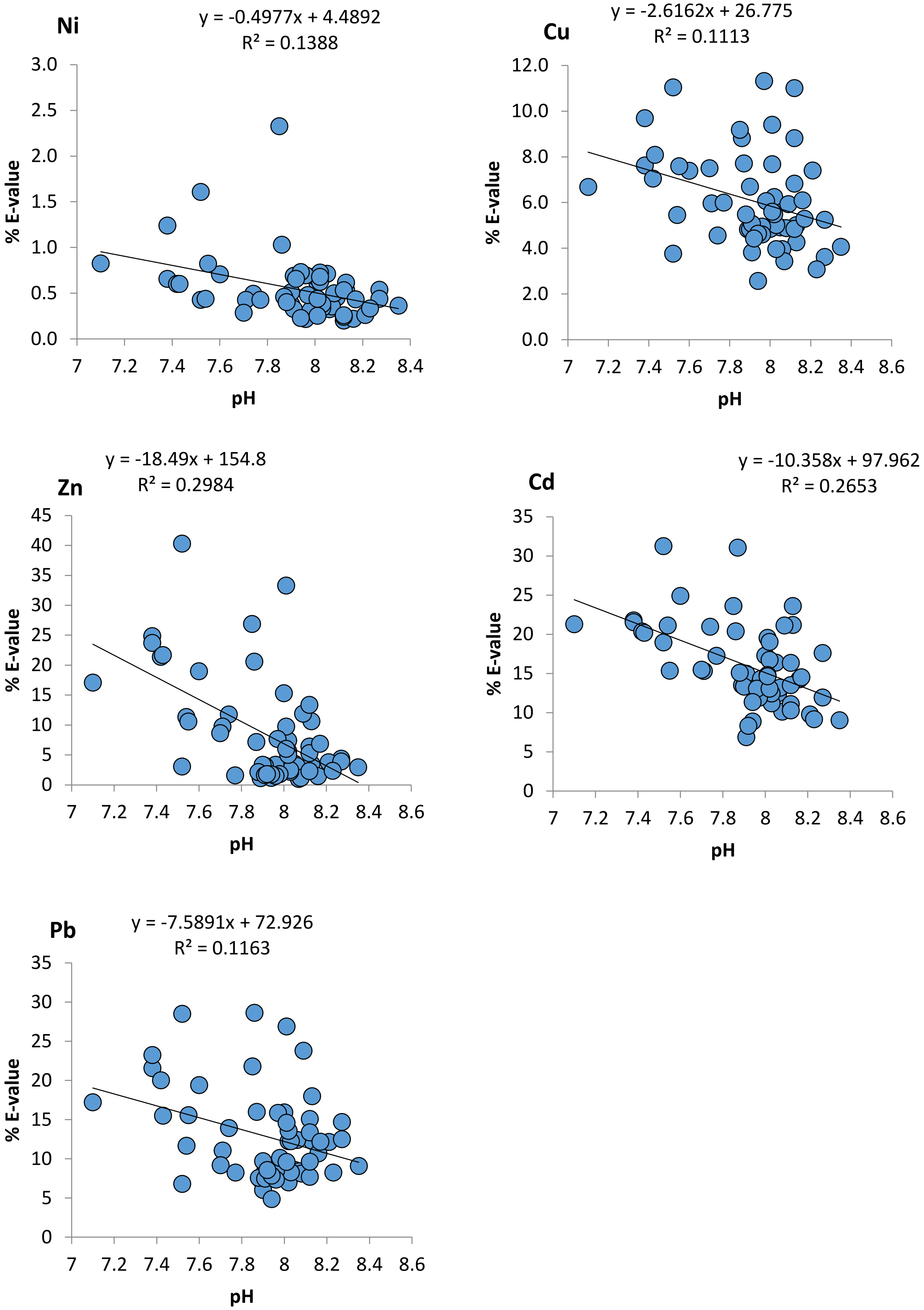


Figure 5.8 Correlations between %E-values and pH for selected trace elements.

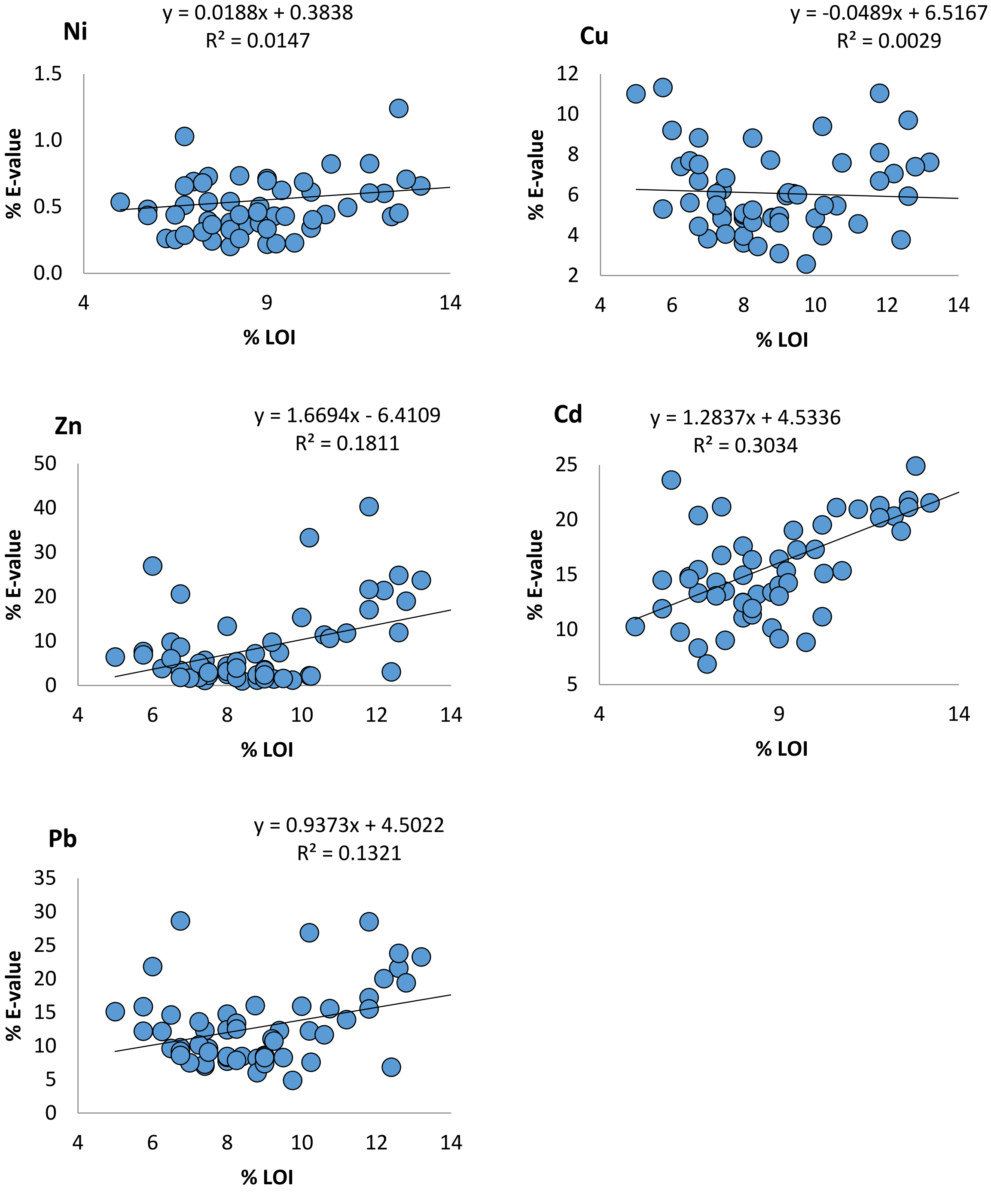


Figure 5.9 Correlations between %E-values and %LOI for selected trace elements.

5.3.6 Application of empirical model to predict E-value and %E-value

Fig. 5.10 and Table 5.3 give the results of multiple linear regression modelling based on Equation 5.1. Variables included pH, %LOI and DTPA-extractable metal pool, but other variables including Fe-Mn oxide, cation exchange capacity (CEC) and % clay content could also be included (Tipping et al., 2003;Groenenberg et al., 2012).

The majority of variation in E value for each trace element was explained by the DTPA-extractable metal pool; this explained a total variation of 65.2 %, 71.5 %, 82.4 %, 87.3 % and 77.8 % in the E value for Ni, Cu, Zn, Cd and Pb, respectively. Soil pH and %LOI improved the prediction of E-value for some metals. For Zn, pH accounted for 6.9% of the total variance in E-value whereas for Ni %LOI was important, accounting for 4.8% of the total variance. Fig. 5.11 shows the comparison between modelled and measured %E values. Again, DTPA-extractable metal explained the majority of the total variation of 48.6 %, 45.6 %, 57 %, 51 % and 48.3 % in the %E value for Ni, Cu, Zn, Cd and Pb, respectively.

Other soil properties (pH and %LOI) explained >10% in the Zn, Cd and Pb models. The results were less successful than prediction of E-value. A limited number of investigations have tried to predict %E- values from physico-chemical properties of the soil, especially pH, LOI, extractable and total concentrations of metals in the soil. Marzouk et al. (2013) reported the prediction of % E-values of Zn, Cd and Pb, from pH, LOI and total metal concentrations using multiple linear regression for 246 mine spoil contaminated soils. The authors found that 80%, 53% and 66% of the variation in the Zn, Cd and Pb %E-values, respectively, might be related to the soil properties. Likewise, in a study conducted on 23 soils amended with metal salts, using multiple linear regression to predict %E-values of Ni, Cu, Zn, Cd and Pb from pH, Fe/Mn/Al oxide concentrations, clay content and total metal concentrations, significant predictions were obtained for Ni, Zn and Cd while predictions for Cu and Pb were less successful (Mao, 2013).

Table 5.3: Linear regression coefficients (see Eq. 5.1) (a) for E-value prediction (b) for % E-value prediction. Values in brackets are the % of total variation. *N.S:* not significant

(a)

	k_0	k_{pH}	k_{LOI}	k_{DTPA}	RSD	R^2
Ni	-0.33	NS	-0.0482 (4.80)	0.357 (65.2)	0.381	70.1
Cu	-6.04	NS	NS	0.752 (71.5)	1.30	71.8
Zn	-58.1	7.29 (6.90)	NS	0.971 (82.4)	7.12	89.3
Cd	-0.0093	NS	NS	0.508 (87.3)	0.02	87.3
Pb	-8.79	NS	NS	0.605 (77.8)	1.43	78.2

(b)

	k_0	K_{pH}	K_{LOI}	K_{DTPA}	RSD	R^2
Ni	-0.510	NS	NS	0.219 (48.6)	0.400	50.8
Cu	16.4	NS	NS	0.525 (45.6)	1.82	47.9
Zn	20.6	NS	-7.22 (4.11)	0.240 (57.0)	5.38	60.2
Cd	-6.60	NS	0.573 (5.9)	46.6 (51.8)	3.93	52.0
Pb	-7.60	0.380 (2.40)	0.780 (3.20)	0.802 (48.3)	4.44	48.4

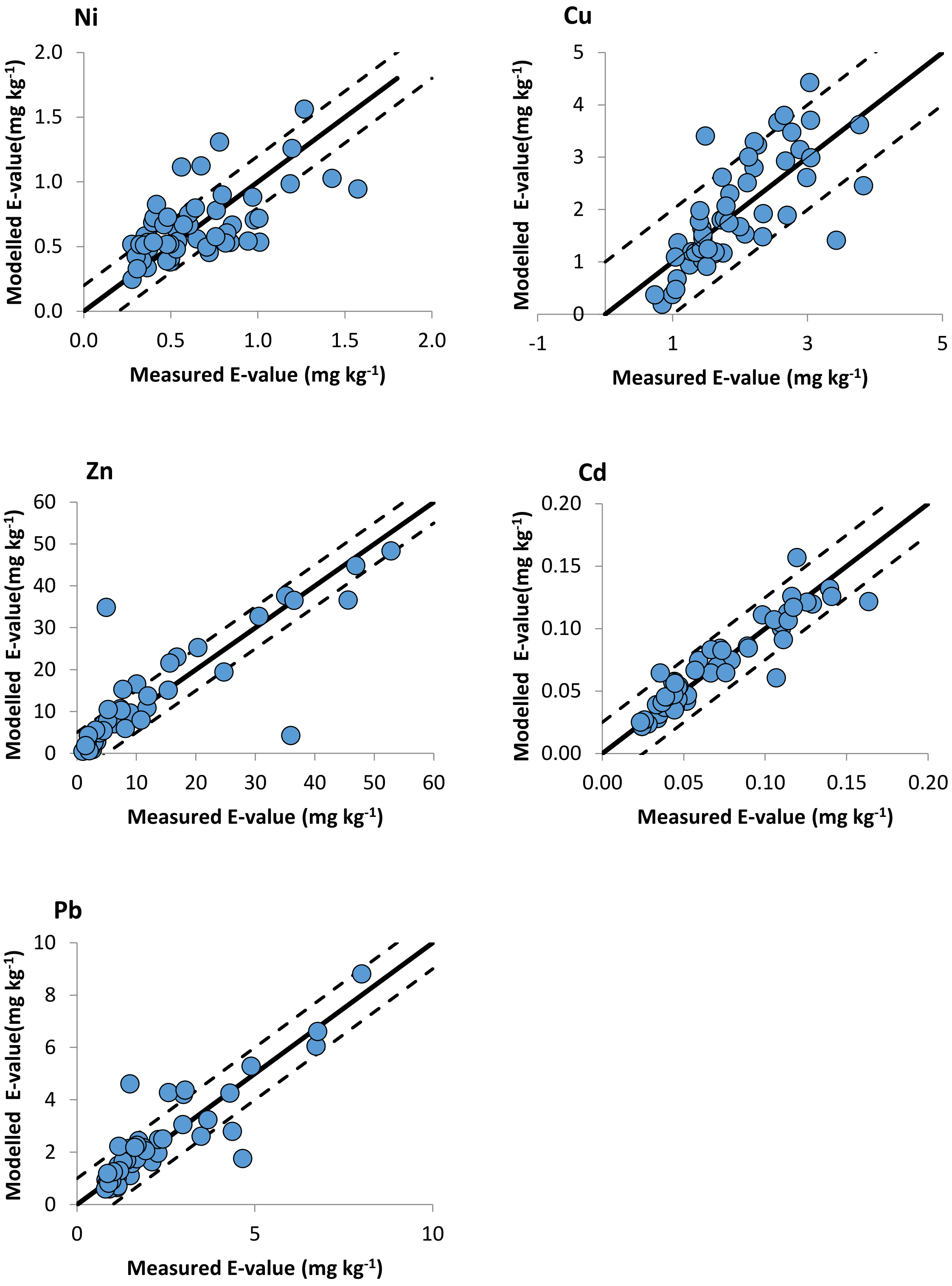


Figure 5.10 Comparison of measured and modelled E-values (mg kg^{-1}) using a multiple linear regression model (Eq 5.1) for agricultural soils. The solid line is the 1:1 line. Dashed lines represent ±1 RSD for the model fit.

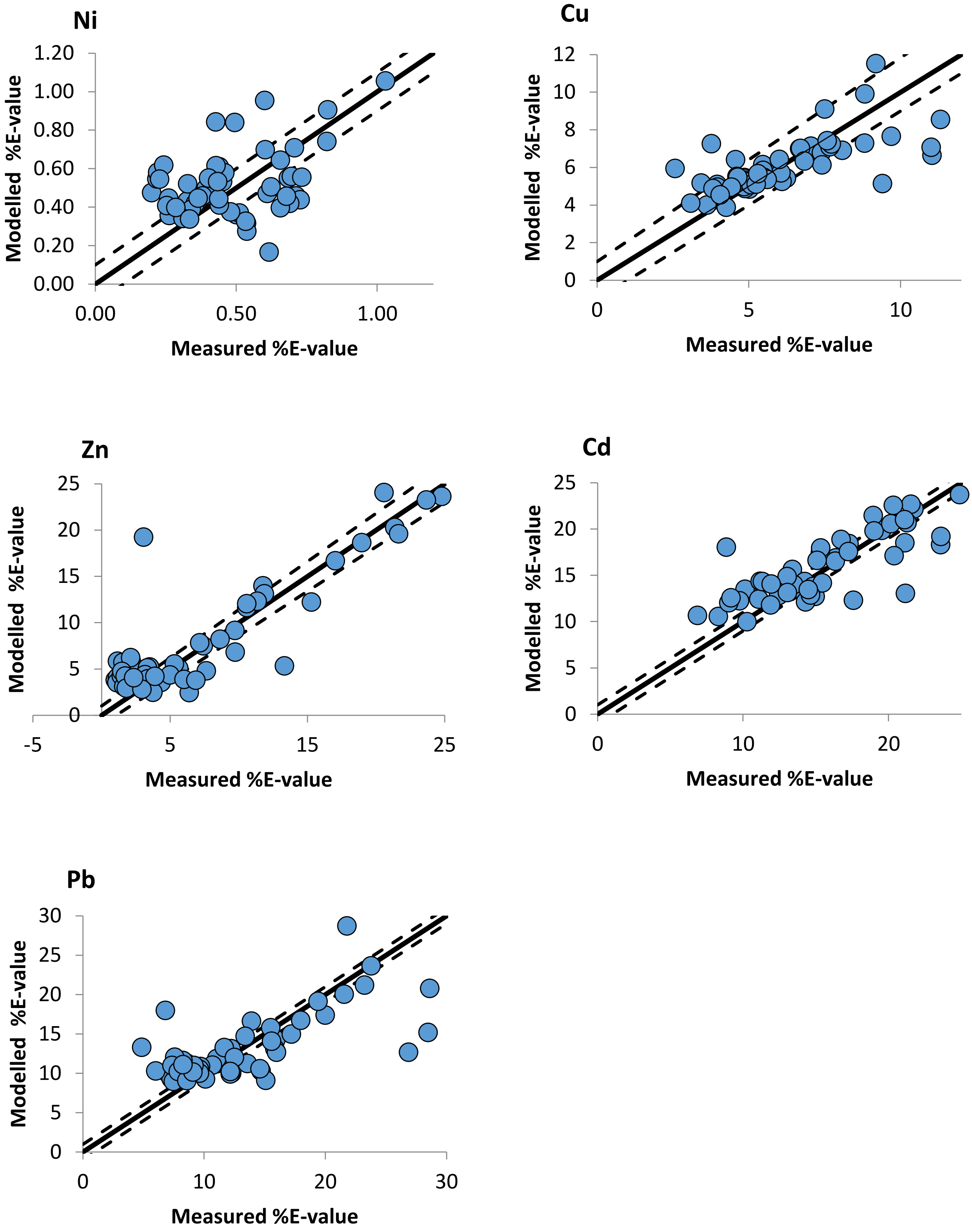


Figure 5.11 Comparison of measured and modelled % E-values using a multiple linear regression model (Eq 5.1) for agricultural soils. The solid line is the 1:1 line. Dashed lines represent ±1 RSD for the model fit.

5.3.7 Accumulation of trace elements in the vegetables

Mean concentrations of PTEs determined in washed and unwashed vegetable samples are compared in Figure 5.12. This suggests that, with a few exceptions, no difference is observed between the concentrations in washed and unwashed samples. The greatest deviation from the 1:1 line found for As and Pb (Fig.5.12e and h) suggests a contribution from airborne or soil particles containing As and Pb, especially at higher total concentrations. Many authors have reported that washing such foods in the home plays an important role in minimizing trace element concentrations in the vegetables grown in/around cities and near the verges of main roads (Qadir et al., 2000;Itanna, 2002;Sharma et al., 2008;Nabulo et al., 2010;Ali and Al-Qahtani, 2012;Kumar, 2013). Although unwashed samples may be contaminated with soil dust, washing also has the potential to introduce contaminants. Given the generally good agreement between the concentrations in washed and unwashed samples only unwashed concentrations are subsequently considered.

The mean concentrations of PTEs in 21 types of unwashed vegetables are presented in Table 5.4. A significant variation between PTEs in all plant types was clear at $p<0.05$. The highest concentrations based on the dry weight of unwashed tissues were Cr (3.49 mg kg^{-1}) in dill, Ni (10.6 mg kg^{-1}) in radish leaf, Cu (17.0 mg kg^{-1}) in tarragon, Zn (53.0 mg kg^{-1}) in okra, As (0.456 mg kg^{-1}) in cress, Se (0.283 mg kg^{-1}) radish leaf, Cd (0.627 mg kg^{-1}) in tarragon and Pb (0.711 mg kg^{-1}) in cress. Mean concentrations in the most common and frequently consumed vegetables (pepper, okra, tomato, eggplant, cowpea, cucumber, leek, celery, parsley, purslane and chard) are presented in Figures 5.13 and 5.14, grouped according to land use (waste, urban, peri-urban or rural) at the sites where the samples were collected. All vegetable types are widely grown. Purslane is a wild vegetable that grows on the farms and provides a supply of vegetable for poor families. Most of the vegetables can be consumed directly after harvest and served as salad or added to soups (e.g.celery) but some are cooked or steamed before eating e.g. okra and eggplant.

Table 5.3 Trace element concentrations (mg kg^{-1} dw) in the edible fruits and leafy vegetables (unwashed) from all selected sites. The mean concentrations and standard deviations (SD) are shown. *denotes significant difference ($p<0.05$) between certain PTEs in vegetable types.

Vegetables	**n**		**Cr**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Cd**	**Pb**
Pepper	16	Mean	0.449	3.57	12.9	26.1	0.021	0.062	0.122	0.048
		±SD	0.309	2.15	2.06	3.43	0.017	0.064	0.047	0.030
Okra	19	Mean	0.551	3.14	10.5	53.0	0.031	0.034	0.178	0.071
		±SD	0.283	1.58	1.91	7.11	0.038	0.030	0.098	0.044
Tomato	15	Mean	0.312	1.31	9.32	25.8	0.006	0.090	0.177	0.045
		±SD	0.109	0.519	2.06	4.84	0.014	0.064	0.069	0.040
Eggplant	11	Mean	0.305	0.797	10.5	23.2	0.015	0.056	0.096	0.034
		±SD	0.133	0.190	1.36	4.35	0.033	0.072	0.071	0.019
Cow pea	18	Mean	0.378	6.39	11.0	42.9	0.012	0.113	0.010	0.047
		±SD	0.211	1.59	1.55	7.19	0.021	0.098	0.007	0.034
Cucumber	9	Mean	0.498	2.40	8.95	41.3	0.196	0.100	0.046	0.073
		±SD	0.356	0.593	1.22	4.88	0.104	0.088	0.031	0.068
Courgette	4	Mean	0.504	3.98	10.9	29.7	0.013	0.048	0.030	0.066
		±SD	0.376	2.08	2.58	3.62	0.015	0.028	0.018	0.033
Water melon	4	Mean	0.400	2.55	5.04	19.3	0.040	0.075	0.101	0.064
		±SD	0.087	1.86	3.57	11.9	0.044	0.069	0.054	0.030
Melon	3	Mean	0.415	1.62	1.97	8.50	0.057	0.043	0.102	0.113
		±SD	0.128	1.06	0.515	1.64	0.024	0.042	0.077	0.020
Leek	12	Mean	1.40	2.16	9.28	41.0	0.166	0.143	0.142	0.322
		±SD	0.525	0.520	1.43	13.5	0.063	0.095	0.048	0.248
Celery	11	Mean	2.52	4.02	8.64	38.3	0.197	0.156	0.146	0.500
		±SD	1.06	1.36	1.36	10.8	0.098	0.129	0.052	0.262
Parsley	5	Mean	2.23	4.30	7.65	33.0	0.168	0.092	0.052	0.346
		±SD	1.20	2.05	1.46	6.46	0.125	0.090	0.047	0.143
Purslane	18	Mean	1.89	5.32	11.3	39.4	0.119	0.031	0.145	0.277
		±SD	1.54	2.04	3.86	15.8	0.098	0.018	0.076	0.166
Spring onion	3	Mean	1.28	2.57	5.75	39.4	0.117	0.129	0.217	0.173
		±SD	0.852	0.119	0.009	13.5	0.063	0.075	0.083	0.113
Tarragon	4	Mean	1.39	5.11	17.0	52.4	0.128	0.113	0.627	0.310
		±SD	0.164	0.954	0.084	6.95	0.005	0.065	0.328	0.092
Chard	19	Mean	2.00	2.83	10.1	21.5	0.150	0.069	0.242	0.482
		±SD	0.989	1.04	2.23	5.72	0.069	0.071	0.111	0.226
Dill	1	Mean	3.49	4.75	9.03	40.0	0.221	0.138	0.122	0.692
		±SD								
Cress	1	Mean	3.14	9.45	6.84	49.6	0.456	0.041	0.396	0.711
		±SD								
Radish leaf	4	Mean	2.20	10.6	3.62	48.7	0.368	0.283	0.518	0.643
		±SD	0.464	9.46	0.329	3.35	0.095	0.068	0.010	0.212
p<0.05			*	*	*	*	*	*	*	*

The different fruit and vegetable types had different abilities to accumulate trace elements from the soil (Figure 5.13). Higher concentrations were typically observed in fruits and vegetables grown in the waste area with progressively lower concentrations in in urban, peri-urban and rural areas. The interaction between vegetable and land use and the vegetable×land use interaction were all significant ($p < 0.001$; Table 5.4; Fig. 5.13 a and 5.14 a).

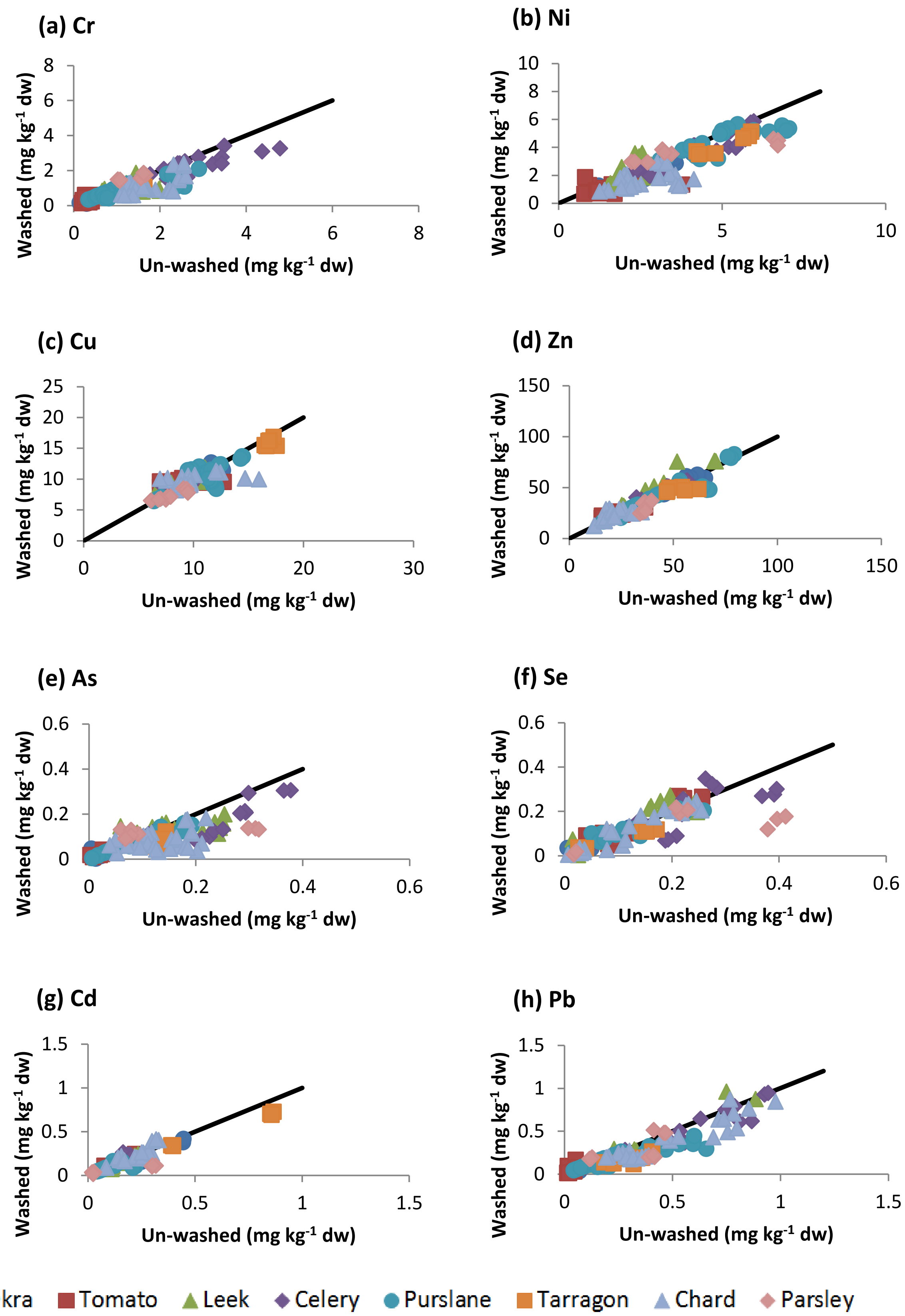


Figure 5.12 Correlations between trace element concentrations in unwashed and washed vegetable types (mg kg^{-1} dw) for (a) Cr, (b) Ni , (c) Cu , (d) Zn , (e) As , (f)Se, (g) Cd, (h) Pb at all study sites. The solid line shows the 1:1 relationship.

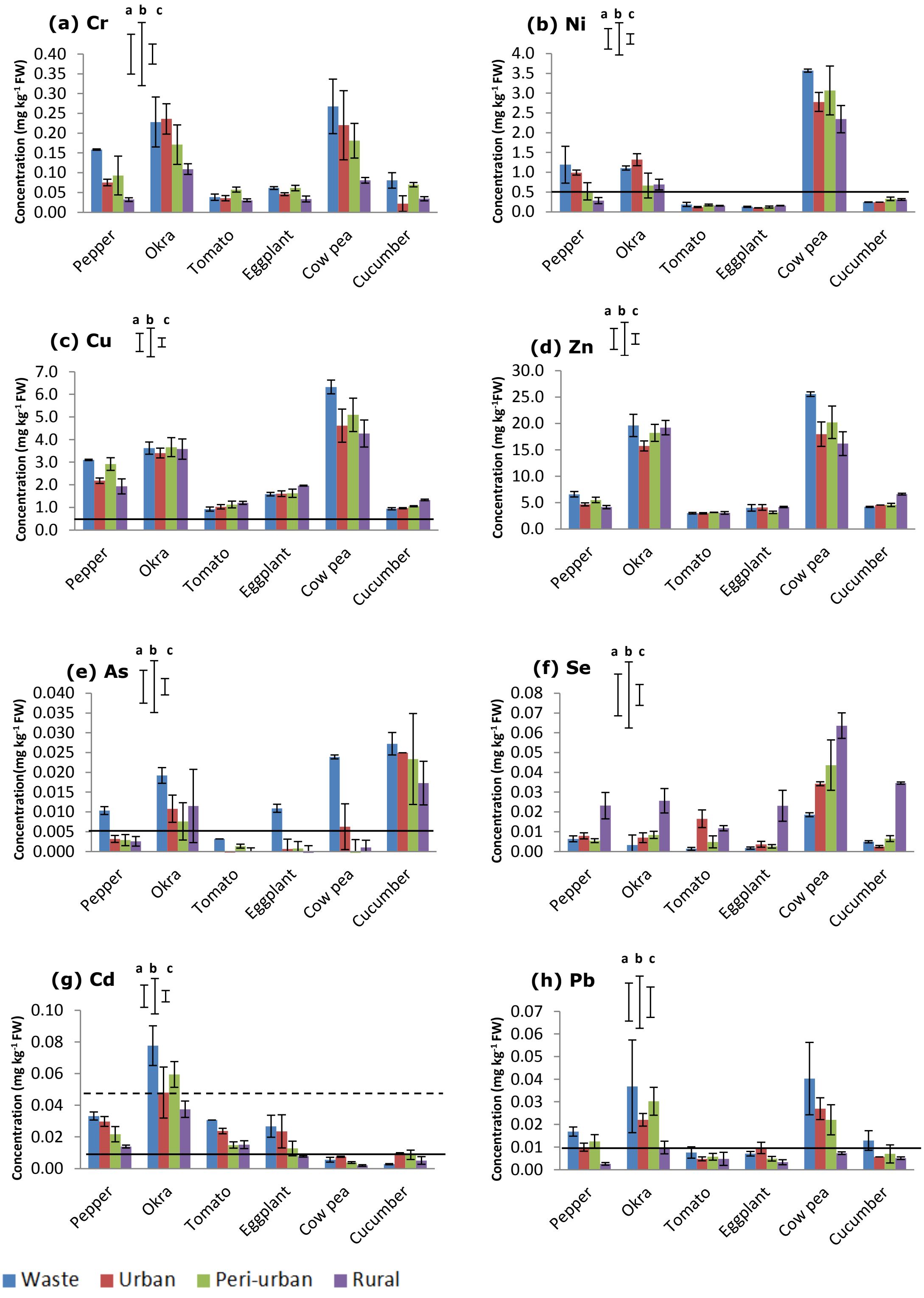


Figure 5.13: Mean concentrations of Potentially Toxic Elements (PTEs) for pepper, okra, tomato, eggplant, cowpea and cucumber grown in waste, urban, peri-urban and remote areas in both Halabja and Sulaymanyah cities. Vertical bars related with each histogram show standard errors of the means (n=3). SED values a, b and c show the standard error of the difference between means for comparing vegetable, soil and interaction between vegetable and soil type. The solid and dashed lines denote UK and WHO/EU standards, respectively.

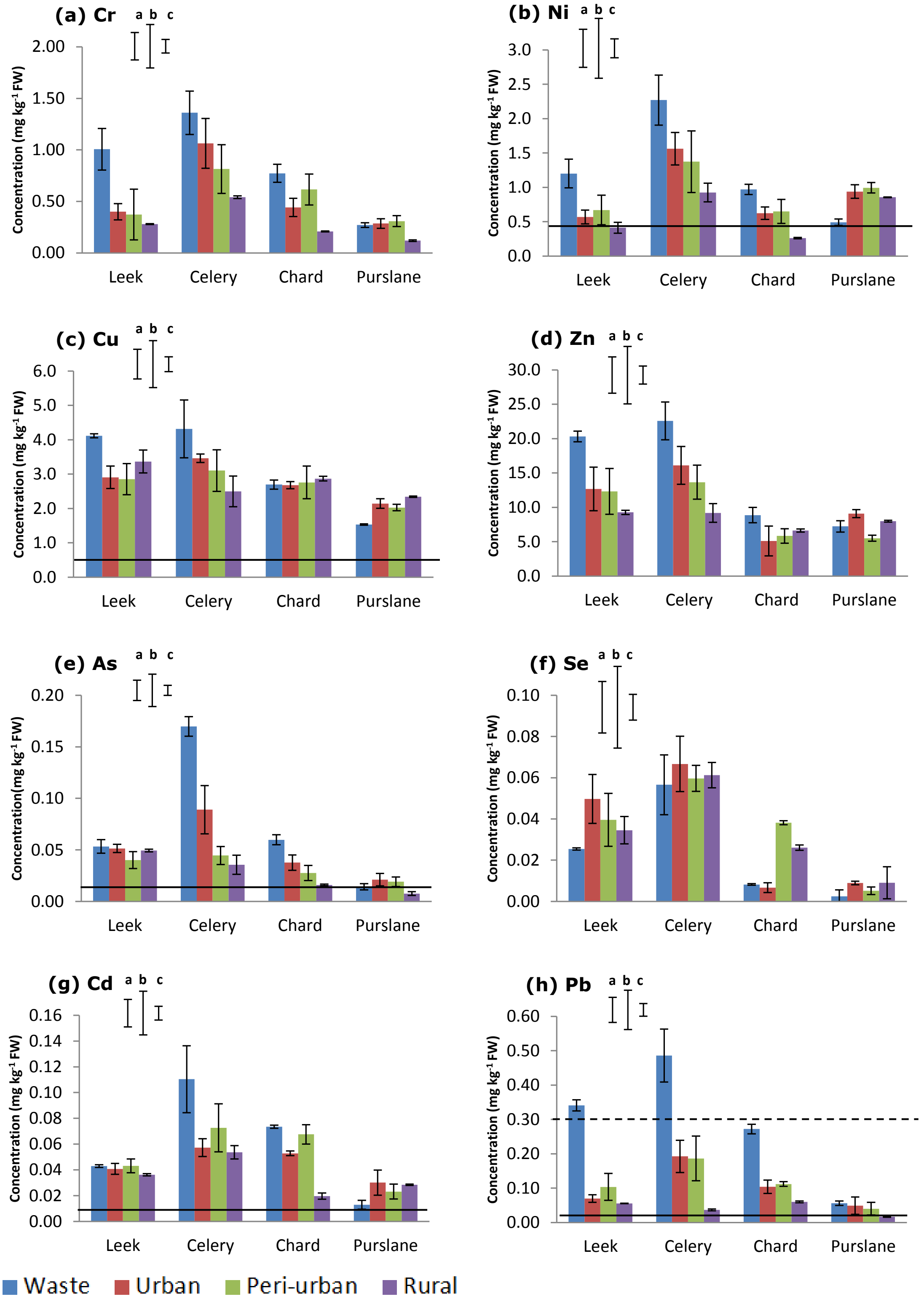


Figure 5.14: Mean concentrations of potentially toxic elements (PTEs) for leek, celery, chard and purslane grown in waste, urban, peri-urban and remote areas in both Halabja and Sulaymanyah cities. Vertical bars related with each histogram show standard errors of the means (n=3). SED values a, b and c show the standard error of the difference between means for comparing vegetable, soil and interaction between vegetable and soil type. The solid and dashed lines denote UK and WHO/EU standards, respectively.

Table 5.4: Sources of variation of PTE concentrations in the edible parts of leafy and fruit vegetables grown on study sites as determined by ANOVA (n=4).

Source of difference	Cr		Ni		Cu		Zn		As		Se		Cd		Pb	
	P	**SED**	**P**	**SED**	**P**	**SED**	**P**	**SED**	**P**	**SED**	**P**	**SED**	**P**	**SED**	**P**	**SED**
Vegetables	**p<0.001**	0.089	**p<0.001**	0.206	**p<0.001**	0.324	**p<0.001**	1.641	**p<0.001**	0.007	**p<0.001**	0.011	**p<0.001**	0.007	**p<0.001**	0.027
Land use	**p<0.002**	0.141	p<0.084	0.326	p<0.362	0.513	p<0.369	2.595	**p<0.016**	0.010	p<0.087	0.018	**p<0.001**	0.011	**p<0.001**	0.043
vegetables * land use	**p<0.049**	0.045	p<0.711	0.103	p<0.432	0.162	p<0.246	0.821	**p<0.036**	0.003	**p<0.001**	0.006	**p<0.001**	0.004	**p<0.029**	0.014

Concentrations of Cr were all below the 'safe limit' of 2.3 mg kg^{-1} FW based on the FAO/WHO standard(FAO/WHO, 2001).

Nickel and Cu in all vegetable types were higher than UK recommended values of 0.2 and 0.5 mg kg^{-1} FW, respectively (UK Food Standard Agency, 2009), at all study areas, with the exception of Ni in tomato, eggplant and cucumber. Concentrations of Ni and Cu in the current study are higher than those reported in calcareous soils by Al-Ansari et al. (2013) in Jordan and Mahmood et al. (2014) in Pakistan. Ni and Cu concentrations in this study are similar to results reported for edible parts of vegetables in a Libyan study (Elbagermi et al., 2012).

Concentrations of As, Cu, Cd and Pb also exceeded UK standards in many fruits and vegetables. Arsenic concentrations in leafy vegetables (leek, celery and chard) were higher than the recommended values for all land uses. As concentrations in pepper, okra, eggplant and cowpea only exceeded the UK FSA limit of 0.005 mg kg^{-1} FW in the waste area, except for okra grown in the rural areas which also exceeded the limit. In this study the concentrations of As were lower than the values reported by Nazemi (2012) in vegetables grown in long term waste water irrigated fields in Iran. Cadmium concentrations exceeded UK limits in all vegetables (except for cowpea and cucumber) for all land uses. Okra concentrations in the waste and peri-urban areas were also higher than European standards for non-leafy vegetables of 0.05 mg kg^{-1} FW. (European Commission, 2004). Alloway et al. (1990) conducted a study of Cd accumulation in cabbage, carrot, lettuce and radish in soils with different properties. They found that soil properties including pH, organic matter and inorganic carbon had a direct impact on Cd accumulation. Yang et al. (2009) conducted a study on Cd accumulation in leek, pak choi, carrot, radish, tomato and cucumber grown on Cd-contaminated soils in a field-trial. They found that Cd concentrations varied from 0.01 to 0.1 mg kg^{-1} FW, which is a similar range to that observed in this study. The highest level of Cd accumulation was observed in a sample of celery (0.110 mg kg^{-1} FW) and the lowest in samples of cowpea and cucumber (0.002 and 0.003 mg kg^{-1} FW, respectively). In general, Pb concentrations were significantly above the UK limit of 0.01 mg kg^{-1} FW in okra, cowpea, leek, celery and chard in waste, urban and peri-urban areas. Pb concentrations were noticeably greater in vegetables grown in the waste area where EU standards for leafy vegetables were also exceeded.

Typically, lower concentrations of trace elements were detected in fruiting vegetables compared to leafy vegetables. This finding is in agreement with studies elsewhere. For example, Gebrekidan et al. (2013) found higher accumulation of Cr, Ni and Cd in chard and lettuce compared to tomato and green pepper. Variations in element concentrations between the vegetable types implied that the ability to accumulate trace elements varies between different species of plants and/or among different plants of the same species (Säumel et al., 2012;Xu et al., 2013). In a study conducted to assess risks of urban horticulture in the city of Berlin, Säumel et al. (2012) found that leaf vegetables had higher concentrations of Cu, Zn, Ni or Cr compared to fruit, stem and root vegetables.

Selenium concentrations were different from the patterns observed for the other trace elements with higher concentrations particularly in fruiting vegetables in samples from rural areas. The likely reason for this difference is the slightly higher pH values (all soils >8) in the rural soils (Table 5.2) (Hurst et al., 2013).

Overall, greater accumulation of PTEs was observed in vegetables grown around the waste and urban areas and is probably related to the availability of trace elements which were higher in the waste and urban areas and low in, peri-urban and remote areas (see Section 5.3.3).

5.3.8 Transfer Factor

Transfer factor (TF) is defined as a ratio of element concentrations in the vegetables to those in the corresponding soils in order to assess plant uptake of trace elements across the sampling areas (Belaid et al., 2012). Plants possess highly specialized mechanisms to promote metal mobility in the rhizosphere and to induce uptake into the roots (McGrath et al., 2001;Hammer and Keller, 2002). Different vegetable species accumulate different trace elements depending on environmental conditions, the type of element and plant-available forms of trace elements (Tiwari et al., 2011).

The TF for any element or plant is a primary factor contributing to dietary exposure and risk to consumers, including humans (Zhuang et al., 2009;Avci and Deveci, 2013). Significant differences in TF were found between PTEs and vegetable types ($p<0.001$; (Table 5.5).

The mean TF for each vegetable type and for each trace element in waste, urban and peri-urban areas varied in the order Cd> Zn> Cu> Se>Ni>Pb>As>Cr while in rural areas the order was Se>Zn>Cu> Cd>Ni>Pb>As>Cr. This suggests that vegetables had higher potential for accumulation of Cd followed by Zn and Cu in waste, urban and peri-urban areas compared to other trace elements.

Table 5.5 Transfer factors (TF) of trace element accumulation in various vegetable types grown in waste, urban, peri-urban, rural areas. Data are given to three significant figures.

	land use	Cr	Ni	Cu	Zn	As	Se	Cd	Pb
Pepper	Waste	0.00345	0.0445	0.287	0.184	0.00680	0.120	0.371	0.00385
	Urban	0.00322	0.0207	0.312	0.190	0.00143	0.0960	0.279	0.00272
	Peri urban	0.00560	0.0359	0.467	0.336	0.00214	0.0937	0.576	0.00482
	Rural	0.00252	0.0209	0.406	0.299	0.00217	0.351	0.278	0.00105
Okra	Waste	0.00554	0.0167	0.213	0.364	0.00804	0.0414	0.275	0.00246
	Urban	0.00463	0.0274	0.330	0.470	0.00373	0.0635	0.494	0.00475
	Peri urban	0.00523	0.0293	0.369	0.672	0.00338	0.0952	0.530	0.00730
	Rural	0.00401	0.0216	0.332	0.646	0.00432	0.173	0.331	0.00164
Tomato	Waste	0.00313	0.0166	0.101	0.061	0.00327	0.0680	0.208	0.00124
	Urban	0.00265	0.0076	0.237	0.217	0.00220	0.343	0.363	0.00236
	Peri urban	0.00322	0.0088	0.311	0.319	0.00244	0.151	0.690	0.00409
	Rural	0.00304	0.0150	0.315	0.285	0.00990	0.220	0.398	0.00179
Egplant	Waste	0.00358	0.0075	0.201	0.140	0.0111	0.0500	0.356	0.00143
	Urban	0.00214	0.0041	0.228	0.167	0.00200	0.0459	0.218	0.00265
	Peri urban	0.00354	0.0065	0.369	0.287	0.00266	0.0579	0.211	0.00259
	Rural	0.00215	0.0092	0.337	0.257	0.00177	0.279	0.129	0.00113
Cow pea	Waste	0.00461	0.0638	0.290	0.332	0.00812	0.169	0.0293	0.00411
	Urban	0.00320	0.0489	0.278	0.292	0.00327	0.258	0.038	0.00326
	Peri urban	0.00369	0.0418	0.345	0.475	0.00523	0.243	0.024	0.00355
	Rural	0.00259	0.0679	0.346	0.455	0.00770	0.375	0.019	0.00125
Cucumber	Waste	0.00520	0.0183	0.125	0.197	0.0315	0.224	0.058	0.00324
	Urban	0.00184	0.0180	0.253	0.314	0.0209	0.0508	0.165	0.00261
	Peri urban	0.00405	0.0180	0.263	0.410	0.0213	0.180	0.254	0.00489
	Rural	0.00306	0.0267	0.304	0.554	0.0155	0.560	0.120	0.00280
Leek	Waste	0.0204	0.0211	0.306	0.597	0.0270	0.229	0.317	0.0561
	Urban	0.0111	0.0135	0.254	0.353	0.015	0.379	0.242	0.0127
	Peri urban	0.0119	0.0240	0.414	0.782	0.0272	0.301	0.522	0.0242
	Rural	0.00594	0.0144	0.286	0.364	0.0097	0.648	0.455	0.00776
Celery	Waste	0.0204	0.0295	0.237	0.490	0.0233	0.376	0.600	0.0590
	Urban	0.0225	0.0270	0.228	0.336	0.0187	0.610	0.350	0.0286
	Peri urban	0.0270	0.0488	0.392	0.508	0.0342	0.159	0.654	0.0422
	Rural	0.0109	0.0180	0.196	0.266	0.0089	0.398	0.278	0.00621
Chard	Waste	0.0132	0.0198	0.037	0.059	0.0117	0.113	0.241	0.0127
	Urban	0.0110	0.0163	0.349	0.239	0.0134	0.0928	0.630	0.0320
	Peri urban	0.0177	0.0166	0.308	0.255	0.0144	0.336	0.630	0.0281
	Rural	0.0112	0.0140	0.331	0.219	0.00944	0.201	0.263	0.00788
Pursulane	Waste	0.0121	0.0254	0.162	0.215	0.00867	0.0781	0.215	0.0116
	Urban	0.0157	0.0384	0.284	0.349	0.0144	0.0906	0.330	0.0173
	Peri urban	0.0099	0.0587	0.479	0.569	0.0249	0.0887	0.561	0.0203
	Rural	0.0219	0.0433	0.437	0.364	0.0161	0.135	0.391	0.0211

Low TFs were found for Cr and Pb because they have very low solubility in the soils and, even if they could accumulate in plant roots, they are not readily translocated to the aerial parts of plants (Tiwari et al., 2011). TFs for fruiting vegetables were lower than leafy vegetables, which agrees with other findings in the literature where the highest TFs are seen in root vegetables, then leafy vegetables with the lowest TFs in fruit vegetables (Bose and Bhattacharyya, 2008;Tiwari et al., 2011).

5.3.9 Correlation matrix between PTE in plants and soil

Table 5.6 gives Pearson correlation coefficients for PTEs in plant and total, DTPA-extractable, E-value and %E-value of PTEs in soil. Significant positive correlations were observed between total concentrations of Cr, Zn, and Cd and their concentrations in fruiting vegetables. Total Se in soil was correlated positively with Se in leafy vegetables (leek, celery, chard and purslane). However, in general, total concentrations of trace elements in soil were poorly correlated with the corresponding trace element concentrations in the plant when compared to correlations with DTPA-extractable concentrations and E-values, indicating that the total concentrations of an element in soil is a poor predictor of metal availability (Menzies et al., 2007). Sauvé et al. (1998) concluded that the availability of trace elements in soil has a stronger correlation with the free metal ion activity in the soil solution than the total concentration in a soil. Murray et al. (2000) also reported that the concentrations of trace elements in plants are not affected by their total concentrations in the soil, especially for Ni, Cu, Zn, Cd and Pb.

Trace elements in the vegetables were more strongly correlated with DTPA-extractable trace element concentrations in soil than total concentrations. Many authors have reported that the extraction of trace elements with DTPA correlates with observed plant uptake, particularly for Ni, Zn and Cd (Cajuste et al., 2000;Simmons and Pongsakul, 2005;Menzies et al., 2007). In general, DTPA-extractable metal concentrations in the soil were better correlated with plant metal uptake compared to E-values, especially for Zn, As, Cd and Pb. This may reflect the action of root exudates in the rhizosphere. Collins et al. (2003a) suggested that plant roots absorb not only from the exchangeable metal pool but also, in some circumstances, are able to access the non-labile metal pool in the soil because root exudates (e.g. organic acids) encourage trace element lability from the non-labile pool by releasing organic chelating chemicals or by change the soil properties in some other way.

Table 5.6: Pearson correlation coefficients for the relationships between trace element concentrations in vegetable types and total, DTPA-extractable, E-values and %E-values of trace elements in soil. Bold values denote significant relationships at $p<0.05$.

PTEs	Pepper	Okra	Tomato	Eggplant	Cow pea	Cucumber	Leek	Celery	Chard	Purslane
Cr$_{Total}$	**0.548**	**0.626**	**0.683**	**0.71**	**0.526**	**0.886**	-0.053	-0.511	0.414	0.338
Ni$_{Total}$	0.391	0.359	0.362	-0.096	0.173	0.627	-0.196	-0.682	0.361	-0.041
Cu$_{Total}$	0.048	-0.153	0.36	0.394	0.335	0.603	0.001	-0.479	-0.282	-0.078
Zn$_{Total}$	**0.506**	**0.506**	**0.675**	**0.849**	**0.601**	**0.496**	-0.039	0.04	-0.088	0.351
As$_{Total}$	-0.065	-0.225	-0.115	-0.228	-0.041	**0.728**	0.107	0.034	0.403	0.222
Se$_{Total}$	0.224	0.292	0.261	0.525	0.319	0.249	**0.680**	**0.817**	**0.577**	**0.704**
Cd$_{Total}$	**0.741**	**0.553**	**0.758**	**0.829**	**0.572**	**0.503**	0.443	0.385	0.020	0.039
Pb$_{Total}$	0.093	**0.466**	**0.583**	0.442	0.285	**0.84**	-0.022	0.238	**0.491**	0.387
Cr$_{DTPA}$	-0.059	**0.535**	0.309	**0.489**	0.22	**0.791**	-0.229	-0.339	0.102	-0.11
Ni$_{DTPA}$	0.122	0.013	**0.49**	0.114	0.038	0.137	-0.53	-0.038	0.221	-0.184
Cu$_{DTPA}$	0.006	-0.189	**0.458**	0.131	**0.708**	**0.694**	-0.167	-0.41	-0.265	-0.145
Zn$_{DTPA}$	**0.458**	-0.016	**0.66**	**0.854**	**0.56**	**0.54**	-0.153	0.148	**0.439**	**0.478**
As$_{DTPA}$	**0.469**	0.121	**0.49**	**0.739**	**0.646**	**0.846**	**0.450**	**0.535**	**0.546**	**0.473**
Se$_{DTPA}$	-0.382	-0.334	-0.050	-0.422	-0.266	**-0.809**	0.176	**0.522**	0.237	0.033
Cd$_{DTPA}$	**0.861**	**0.715**	**0.522**	**0.602**	**0.862**	**0.606**	-0.026	**0.812**	-0.201	-0.113
Pb$_{DTPA}$	0.046	0.326	**0.438**	**0.447**	0.357	0.308	**0.847**	**0.654**	**0.475**	**0.725**
Ni$_{E\ value}$	0.41	-0.01	0.473	0.055	-0.042	0.184	-0.226	-0.609	0.319	-0.22
Cu$_{E\ value}$	-0.078	-0.171	0.364	0.339	0.389	0.611	0.200	-0.418	-0.277	-0.078
Zn$_{E\ value}$	0.355	-0.001	**0.592**	**0.863**	**0.563**	0.298	-0.067	0.205	0.391	0.33
Cd$_{E\ value}$	**0.850**	**0.613**	**0.465**	**0.681**	**0.731**	**0.820**	0.172	0.313	-0.263	-0.016
Pb$_{E\ value}$	0.117	**0.503**	**0.594**	0.429	0.251	**0.845**	0.038	0.427	0.424	0.468
Ni %$_{E\ Value}$	0.273	-0.245	0.431	0.118	-0.201	0.115	-0.204	-0.553	0.293	-0.225
Cu %$_{E\ Value}$	-0.077	-0.241	0.213	-0.01	0.469	0.585	0.315	-0.421	-0.223	-0.118
Zn %$_{E\ Value}$	0.096	0.148	0.249	**0.724**	0.309	0.331	0.013	0.227	0.432	0.417
Cd %$_{E\ Value}$	**0.653**	0.256	-0.136	0.499	0.230	-0.038	0.055	0.475	-0.431	0.125
Pb %$_{E\ Value}$	-0.001	0.312	**0.561**	0.448	0.097	**0.780**	0.151	0.504	0.255	0.426

5.3.10 Health risk assessment

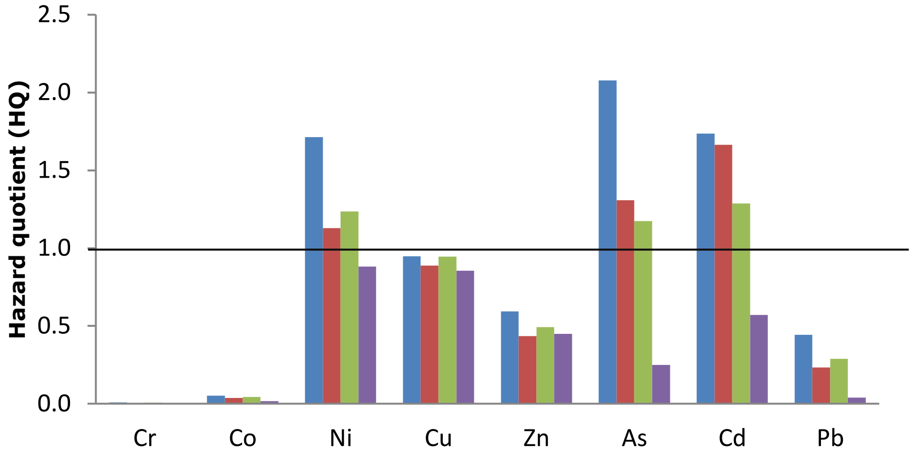
In general, all trace elements in this study can pose a risk to human health and some of them are considered to be carcinogenic e.g. As, Cd and Pb (WHO, 2011). Non-carcinogenic risk from consumption of vegetable types was assessed using a Hazard Quotient (HQ) calculated by Eq 5.4. Values of element-specific HQs were calculated for the 10 commonly-consumed vegetables, such as tomato, okra, eggplant, cow pea, cucumber, leek, celery, chard, cress and dill. An equal contribution from each vegetablewas assumed at waste, urban, peri-urban and rural areas for both adults and children.

Calculated HQs were higher for plants that were grown in the waste area and progressively lower for urban, peri-urban and rural areas, suggesting a clear influence of municipal waste and urban pollution on the agricultural fields in these areas (Figure 5.15a and b). HQ values for adults for all PTEs were lower than the threshold value of 1.0 (Fig. 5.15b). HQs for children, however, exceeded 1.0 for Ni, As and Cd for waste, urban and peri-urban soils (Fig. 5.15a). This indicates that risks may be greater to children because of their (assumed) higher rate of vegetable consumption relative to their body weight.

Cancer risks for individual elements are presented in Table 5.7. In this study As seemed to be the predominant element that resulted in a relatively higher cancer risk for the local population, followed by Cd. Carcinogenic risks, calculated for all vegetable types, varied from a minimum of 6.7×10^{-7} for Pb in a rural area to a maximum value of 2.41×10^{-3} for As in the waste area. The carcinogenic risk values were within the safe range from 10^{-6} to 10^{-4} with the exception of As and Cd for children in the waste and urban areas. This suggests that farmers and local people may be exposed to undesirable levels of PTEs in their diets, but further investigation would be needed to confirm the actual risk to these consumers.

Non-cancer and cancer risk in this study might be overestimated. To be more precise, we need to know the exact contribution of specific vegetable types to an individual's dietary consumption in the Kurdistan population. In this study we assumed "equal contributions" because of the lack of a local dietary survey in the region. To minimize the error and to be more realistic only the 10 most common types of vegetables were used for risk calculation.

(a) Child



(a) Adult

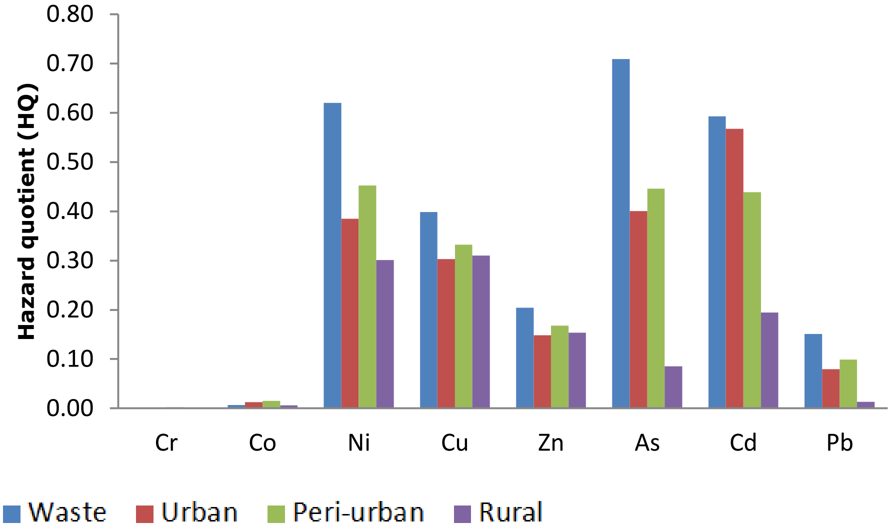


Figure 5.15: Mean Hazard Quotients (HQ) for PTEs from consumption of vegetables by (a) children and (b) adults, assuming equal contributions from most common vegetables studied to dietary PTE loading. *HQ ≥1,* implies a potential hazard to the population.

Table 5.7: Mean cancer risk values for 16 different vegetable types grown at all study areas. Bold values indicate where cancer risk values exceed the USEPA limit which is 10^{-6} to 10^{-4}.

Sites		Cr	As	Cd	Pb
Waste	Adult	1.08E-04	9.12E-04	6.13E-04	5.78E-06
	Child	3.39E-04	**2.41E-03**	**4.69E-03**	1.81E-05
Urban	Adult	8.47E-05	8.40E-04	5.06E-04	2.90E-06
	Child	2.66E-04	**2.68E-03**	**5.51E-03**	9.10E-06
Periurban	Adult	7.36E-05	2.11E-04	9.87E-04	3.70E-06
	Child	2.31E-04	6.61E-04	3.10E-05	1.16E-05
Rural	Adult	2.17E-05	6.06E-05	5.72E-04	6.71E-07
	Child	6.82E-05	1.90E-04	1.30E-05	2.10E-07

5.4 Conclusion

Water treatment is a priority and key concern for developing countries. Most of them do not have adequate facilities to treat wastewater. Thus, wastewater and industrial effluents in an incompletely treated, diluted, or untreated form is discharged and used as a reliable source for irrigation of urban and peri-urban agriculture to grow a wide variety of vegetables and crops . It can be concluded that the municipal waste disposal in urban and peri urban agriculture fields are the major sources of PTE accumulation in the vegetables at the study area because PTEs in waste disposal area found to be higher than the standard values for one or more toxic elements.

DTPA-extractable and isotopically-exchangeable metal pools in soils are considered to be the most reliable measures of plant available trace elements. In this investigation the labile fractions vary among trace elements and across the different land uses. For example, the labile fractions of Ni, Cu, Zn were typically low if compared to the total concentrations because the majority of these trace elements were locked up in residual fractions of the soil as inert forms, unavailable for plant uptake. The labile Cd and Pb can be ~25% if compared to the total concentration because the majority of Cd is bound to the carbonate fraction and Pb is mostly held by Fe/Mn oxides; metals bound in these two fractions can easily be released using chelating agents. From the comparison between DTPA-extractable and the exchangeable metal pool it can be concluded that DTPA extracted a higher proportion of metal than the isotopically exchangeable fraction. This is probably because

DTPA not only extracts the exchangeable metal pool but is also able to attack the metals bound to carbonates, Fe/Mn oxides and/or even organic matter. The lability of metals differs significantly among different land uses. The metal in the waste area appeared to be more labile then in other sampling sites, progressively reducing in urban, peri-urban and rural areas. This variance appears to depend on the total metal concentration loading in the study areas. Consequently, vegetable crops grown on waste and urban fields contained higher concentrations of PTEs than crops in the peri-urban and rural areas. Vegetables in rural areas most of the PTEs were found to be within standard limits.

Consumption of vegetables grown around municipal waste disposal sites appears to pose a health risk from dietary exposure to PTEs. Carcinogenic and non-carcinogenic risk assessment of the vegetables demonstrates that As has the highest non-cancer and cancer effects followed by Cd and Ni. Therefore, further attention should be given to control Cd, As, and Ni contamination in the study areas because the population may currently be exposed to a potential health risk due to the consumption of contaminated vegetables in the area.. However, calculation of risks from consumption of vegetables in this study could be improved since, currently, it depends on an assumption of 'equal contribution' of different vegetable types in the diet, rather than a detailed breakdown of daily dietary intake. Estimating local daily intake of vegetables by the population is strongly recommended in future work in order to assess realistic risks from vegetables and other dietary sources in the Kurdistan region of Iraq.

The effect of soil properties on the prediction of E-values and %E-values of Ni, Cu, Zn, Cd and Pb was evaluated, using 117 soils with a broad range of pH (7.2-83), a wide range of %LOI (5-13.4), total concentrations and DTPA-extractable concentrations of metals It can be concluded from this study that the DTPA-extractable metal concentrations are the only important parameter that influence the E-values for all trace elements. The regression modelling for some PTEs using four soil chemical properties (pH, %LOI, total metal concentrations, DTPA-extractable metal concentrations) gave very good predictions of E-values but less successful predictions for % E-values.

Accordingly, a systematic investigation of agricultural soil contamination with PTEs and an associated assessment of human health risk is recommended to help manage the potential intake of PTEs in local diets and, ultimately, to improve health in the local population. Conducting further investigation is also strongly recommended in order to assess more precisely the toxic element intakes from specific vegetable types by the local population. In the next chapter the potential ability of the most common vegetables (celery, chard lettuce, radish and spring onion) to take up three specific PTEs (Ni, Zn and Cd) will be examined under growth room conditions. The exchangeable metal pool in plant tissue (L-values) will be measured and compared to other mesures of metal bioavailability, such as DTPA extraction and E values.

6 Assessing the transfer of PTEs from soil to plant

6.1 Introduction

PTEs are taken up by plants through pathways including root uptake from soil solution and atmospheric deposition. The ability of plants to absorb metals and metalloids from the soil differs between species. Some species have been recognised as hyperaccumulators which can take up very high concentrations of toxic trace elements from soil, sediment and water, particularly Ni, Zn, As, Cd and Pb. The ability of different plant species to take up a wide range of trace elements in the environment was reviewed by Tangahu et al. (2011).

Numerous investigations have evaluated plant uptake of trace elements using approaches including growth rooms, green houses, field trials and field surveys. For example, Intawongse and Dean (2006) conducted an experiment on soil-plant uptake of trace elements to evaluate the accumulation of Zn and Cd in vegetable plants including lettuce and radish. The experiment was established in a greenhouse under controlled environmental conditions using soil spiked with metals at low, medium and high concentrations, plus control (uncontaminated) soil. The results of this experiment showed the difference in the ability of different plants to take up specific trace elements. For example, spinach accumulated high concentrations of Mn and Zn compared to other vegetables (Intawongse and Dean, 2006).

A wide range of investigations have been conducted to investigate soil-plant uptake of PTEs in pot-culture and field-culture experiments using spiked soil with different levels of trace elements in order to assess PTE uptake by different plant species. For example, the plant uptake of Cd, Cr and Pb (Khan et al., 2008a), Zn (Moynier et al., 2009) and ^{109}Cd and stable Cd (Rosén et al., 2012) has been the subject of numerous studies. Most investigations have assessed lability of trace elements using a range of approaches, including single or sequential extraction or E-value determination (see Chapter 4 and 5), whereas relatively few studies have used isotopic dilution techniques to measure trace element transfer to plants (L-value) in combination with single and sequential extraction procedures to obtain further information about the interaction behaviour of trace elements in the soil.

Ahnstrom and Parker (2001) conducted an investigation using isotopic dilution in combination with a five step sequential extraction procedure on four soils spiked with ^{111}Cd. These authors measured the ^{111}Cd/^{110}Cd ratio in all five fractions following a wide range of contact times from 2 hours to 59 weeks. At the shortest contact time (2 hours) ^{111}Cd was measured in all fractions while, even after the longest contact time (59 weeks), they noticed the ^{111}Cd/^{110}Cd ratio measured in the exchangeable fraction was still higher than the ^{111}Cd/^{110}Cd in all other fractions (F1 to F5) indicating the presence of non-isotopically exchangeable Cd in F2 - F5 (Ahnstrom and Parker, 2001).

The pool of trace elements that is isotopically exchangeable can be determined by growing plants on a soil spiked with isotopic tracers. The labile pool of trace elements obtained after plant analysis is identified as the “L value”, which is a biological estimate of the exchangeable pool of trace elements available in soil to a plant (Hamon et al., 1997;Smolders et al., 1999). The L-value is considered to be the most precise approach to estimate the labile pool of trace elements in a soil it is calculated from direct measurement of the labile portion of metal in the plant. Plants can also be ideal indicators of bioavailable trace elements in soils (Stanhope et al., 2000;Almas and Singh, 2001). Previously the L-value approach has been used to determine the labile phosphorus (P) pool in agricultural plants (Fried, 1964) while, more recently, determination of labile metal pool in the plant using the L-value approach has been extended to a wide variety of trace elements such as Ni (Echevarria et al., 1998), Cd (Hutchinson et al., 2000;Guerra et al., 2014), Zn (Sinaj et al., 2004) and Pb (Tongtavee et al., 2005).

The isotopically exchangeable pool in the plant (L-value) should be similar to the corresponding isotopic exchangeable pool determined in the soil soilution (E-value) as plants are not able to distiguish between the different isotopes. If L-values are smaller than E-values this would be because the plants take up trace elements from the non-exchangeable pool in the soil (Sinaj et al., 2004); if L values are greater than E values that would be due to element fixation in the soil.

Echevarria et al. (1998) conducted an investigation on two soils, a silty loam and a clay, to determine the bioavailabilityof Ni in the soil using isotopic dilution. The L-value was determined on the soils after spiking with ^{63}Ni. After growing the plants, a 0.005 M DTPA extraction of the soil was also undertaken. Their study revealed that the exchangeable Ni pool in the soil soilution was identical to the isotopic composition of Ni in the plant tissues suggesting the plants took up Ni only from the exchangeable Ni pool. Also, DTPA extraction gave a reasonable estimate of the phytoavailabilityof Ni in the soil (Echevarria et al., 1998).

Ayoub et al. (2003) measured the lability of Zn and Cd in two contrasting UK soils; a sewage-amended soil and an arable soil. They used different lability assays, including isotopic dilution, to determine the exchangeable pool of Zn and Cd in the soil and plant (E-values and L-values, respectively) and a variety of chemical extractants including 0.01 M $CaCl_2$, 0.43 M CH_3COOH and 0.05 M EDTA. The soil was spiked with ^{67}Zn and ^{114}Cd before growing the plants. The exchangeable metal pool in soil (E-value) was determined in the soil solution at 13 times from 1 hour to 50 days. The exchangeable metal pool in plants (L-value) was determined in alpine penny cress, dandelion and spring barley. The authors observed that the L-values were similar for the different plant species and that generally they were slightly (but not significantly) lower than the E-values. They concluded that determination of the isotopically exchangeable pool provided a precise and alternative estimate to determination of the extractable pool using chemical extraction methods (Ayoub et al., 2003).

Sinaj et al. (2004) conducted a study to compare E- and L-values in seven contaminated and non-contaminated soils covering a range of physico chemical properties using rye-grass as the expermental plant. DTPA and EDTA extractions were also undertaken and compared to the L-values obtained. The authors concluded that isotopically exchangeable

Zn in the soil was the only source of plant Zn and that the isotopic dilution technique was the best assay to determine Zn lability in the soil and plant. Chemically determined extractable isotopic composition was different from the measured E- and L-values, suggesting that DTPA and EDTA extractions represented neither the soil available Zn nor plant available Zn (Sinaj et al., 2004).

The main objectives for this chapter were to: (i) determine isotopically-exchangeable Ni, Zn and Cd for different vegetable types, (ii) evaluate different approaches to estimate the labile metal pool in the soil by comparing labile pools of metals using DTPA, E-values and L-values.

6.2 Materials and methods

6.2.1 Pot experiment for determination of L-values

6.2.1.1 Sampling procedure

The soil used in this experiment was surface agricultural soil (0–15 cm) collected in the Tanjaro area of Sulaymanya City, northern Iraq (35°28'46.12"N, 45°25'29.85"E, 652 m elevation) in August 2013. The site is located approximately 10 km to the south of the city centre and used for local agriculture with many kinds of leafy and fruit vegetables grown. The fields are irrigated with waste water. The soil selected for this experiment was from an area of low PTE contamination (Table 6.1). The soil was air-dried, homogenised and sieved (< 2 mm) to remove debris and stones at the Technical Institute of Halabja before shipping to the University of Nottingham. A portion (50g) of air dried, < 2 mm sieved soil was finely ground using an agate ball mill (Retsch, Model PM400) and digested for elemental analysis (see Section 2.1.8).

6.2.1.2 Soil preparation and spiking using stable isotopes

The experiment was undertaken in a growth room in which the climate was set to mimic that of northern Iraq. The soil (< 2 mm sieved) was moistened and kept in a cold room for three days before being spiked with a solution of ^{62}Ni, ^{70}Zn and ^{108}Cd 5.306 μg ml^{-1}, 2.506 μg ml^{-1} and 0.300 μg ml^{-1}, respectively. Sufficient spike solution was added to produce a change in the natural isotopic ratio of ~ 20% (see Section 2.1.11). The impact of the added spike on the total elemental concentration of the soil was small. Soil and spike were mixed together thoroughly using a food processor and the soil was equilibrated for 7 d before placing into pots, after which the moisture content was increased to around 60% of field capacity using deionized water. Pots were labelled and organized in a randomised block design containing 12 replicates of each treatment (vegetable types). Prior to seeding, the pots were left for several days to estimate the water lost per day under the selected conditions.

Table 6.1 Soil properties, total and DTPA-extractable concentrations of trace elements (mg kg^{-1}) in pot experiment soil before growing the vegetables. Showing means of 12 replicates ±SD.

Pot soil	pH	LOI %	Cr		Ni		Cu		Zn		As		Se		Cd		Pb	
		%	Total	DTPA	Total	DTPA	Total	DTPA	Total	DTPA	Total	DTPA	Total	DTPA	Total	DTPA	Total	DTPA
Rep 1	7.95	7.71	67.4	0.00680	67.1	2.02	29.8	6.58	117	21.5	4.72	0.0385	0.245	0.00757	0.356	0.0833	22.1	4.87
Rep 2	7.90	7.75	70.2	0.00206	69.4	1.76	32.6	6.02	122	21.5	4.78	0.0354	0.242	0.00677	0.374	0.0770	23.1	4.84
Rep 3	7.95	7.65	67.9	0.00449	68.7	1.43	30.3	4.94	100	19.5	4.54	0.0403	0.227	0.00732	0.402	0.0689	23.1	4.30
Rep 4	7.93	7.75	85.2	0.00392	80.0	2.20	34.7	7.26	116	30.0	4.92	0.0561	0.247	0.01143	0.41	0.1059	25.8	6.89
Rep 5	7.95	7.81	88.2	0.00385	83.7	1.97	42.1	6.44	115	26.1	6.31	0.0460	0.294	0.00930	0.802	0.0952	34.9	5.76
Rep 6	7.88	7.75	52.3	0.00306	50.5	1.34	25.0	4.52	71.1	21.3	3.7	0.0348	0.162	0.00598	0.263	0.0618	18.2	4.06
Rep 7	7.95	7.72	68.2	0.00328	68.5	2.43	31.2	8.14	95.0	31.3	4.93	0.0483	0.246	0.01065	0.39	0.115	24.4	7.19
Rep 8	7.89	7.75	68.1	0.00216	67.2	1.80	31.3	6.20	91.4	26.2	4.76	0.0423	0.245	0.00802	0.392	0.0849	31.8	5.40
Rep 9	7.95	7.73	70.6	0.00415	69.3	1.88	34.8	6.80	93.9	27.0	5.14	0.0551	0.237	0.00924	0.376	0.0906	31.8	6.31
Rep 10	7.95	7.85	72.0	0.00548	72.3	1.83	36.5	6.70	96.6	25.1	5.32	0.0535	0.232	0.00835	0.382	0.0853	25.2	5.53
Rep 11	7.97	7.74	75.7	0.00371	73.6	1.79	33.0	5.88	97.0	23.4	5.01	0.0446	0.238	0.00819	0.358	0.0808	20.9	5.47
Rep 12	7.94	7.75	74.3	0.00682	72.1	1.77	32.3	6.29	94.8	23.7	5.03	0.0490	0.242	0.00823	0.385	0.0840	21.7	5.20
Mean	**7.93**	**7.75**	**71.7**	**0.00415**	**70.2**	**1.85**	**32.8**	**6.31**	**101**	**24.7**	**4.93**	**0.045**	**0.238**	**0.008**	**0.408**	**0.086**	**25.3**	**5.49**
±SD	**0.03**	**0.05**	**9.12**	**0.00156**	**8.04**	**0.295**	**4.15**	**0.958**	**14.3**	**3.62**	**0.594**	**0.0073**	**0.029**	**0.0015**	**0.130**	**0.0146**	**5.048**	**0.952**
SGV			**130**		**250**		**50.0**		**300**		**43.0**		**120**		**1.80**		**450**	

6.2.1.3 Vegetable Sowing

Five vegetable types (leafy and root) were chosen for this experiment (Fig. 6.1) based on Kurdish genotypes. The main criterion used to select the vegetables were that they were amongst the most popular vegetables varieties grown and consumed in the Kurdistan region of Iraq. According to this criterion, celery, chard, lettuce, radish and spring onion were selected.

The seeds were sown just below the surface layer of the soil with a density 0.5 gram of seeds per pot. To minimise contamination of shoots with soil during watering, and to reduce evaporation of water, the soils were covered with a thin layer (>1 cm) of perlite. In order to give seedlings sufficient room for growth the plants were thinned after germination to 2 lettuce, 2 chard, 2 radish, 10 celery and 10 spring onion plants per pot. The plants were grown in controlled conditions for up to three months. Environmental conditions were initially 25/15°C, 14 h day/10 h night at 50 % atmospheric humidity. After two weeks the conditions were changed to 28/18°C, 14h day/10h night at 25% humidity (Fig 6.2 and 6.3), the photon flux was 650 μmol m^{-2} s^{-1} during the light period.

Figure 6.1 Vegetable types grown in the pot experiment.

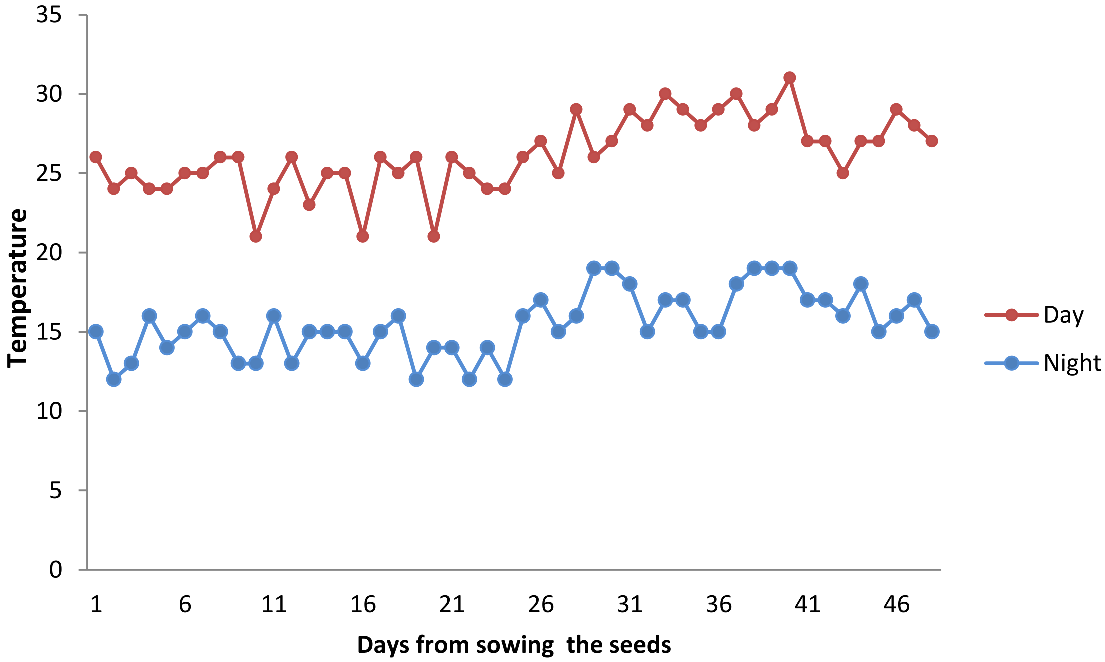


Figure 6.2 Mean day and night temperatures (°C) during the period of the experiment.

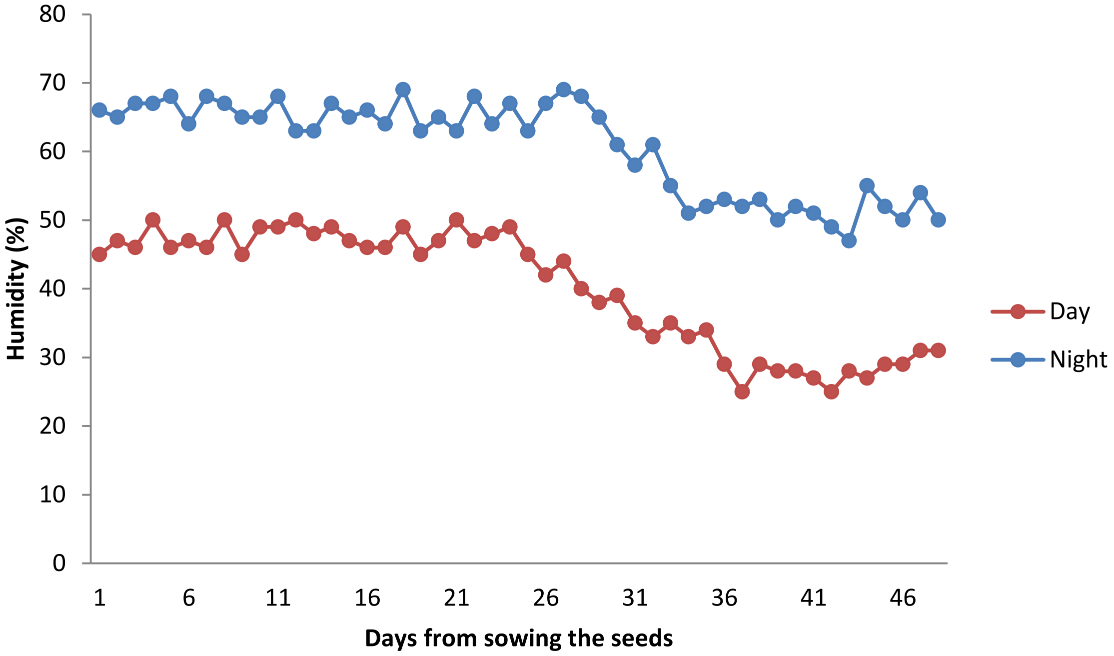


Figure 6.3 Mean day and night humidity (%) during the period of the experiment.

The water required for each vegetable throughout the growth period was different for each species; 1.76 L for spring onion, 2.21 L for celery, 3.08 L for chard, 3.09 L for lettuce and 3.16 L for radish. Watering was estimated by weight and adjusted with daily watering using deionized water. After three weeks of growth, the vegetables were fertilized with the equivalent of 50 kg ha^{-1} nitrogen as KNO_3 and phosphorus using $[(NH_4)_2 HPO_4]$.

6.2.1.4 Plant Harvesting

Shoots were harvested by excising just above the surface of the perlite, using stainless steel scissors. Care was taken during the cutting process to avoid contamination of the shoots by soil particles and perlite. The shoots were weighed immediately after harvest to estimate their fresh weight before placing into paper bags. The roots and bulbs were washed clean of soil using tap water and then rinsed in deionized water to remove all remaining adhering soil particles, dried with absorbent paper and put into paper bags prior to oven drying.

6.2.2 Soil and plant preparation and analysis

Following harvesting and cleaning, plant samples were oven dried at 40°C for 72 hrs then the shoot biomass weighed to obtain a dry shoot weight using a precision analytical balance (Precisa 125 A). Samples were then milled in an ultra-centrifugal mill (Retsch, Model ZM200, Germany) fitted with a 0.5 mm titanium screen. The milled material (c. 200 mg) was digested in pressurised PFA vessels with 6.0 mL of 70% TAG HNO_3 with microwave heating (Anton Paar 'Multiwave' fitted with a 48-place rotor) (see Section 2.1.9).

Approximately 250 mg of finely ground soil was digested using the HF digestion method (see Section 2.1.8). Total elemental analysis and isotopic ratios for Ni^{62}/Ni^{60} , Zn^{70}/Zn^{66} and Cd^{108}/Cd^{111} were determined using ICP-MS (Model X-SeriesII, Thermo-Fisher Scientific, Bremen, Germany - see Sections 2.3.10 and 2.3.11 for a full description). Soils were extracted with DTPA as described by Lindsay and Norvell (1978) (see Section 2.1.7.1) and sequentially extracted (see Section 2.1.7.3).

6.2.3 L value calculation

The isotopically exchangeable metal concentration (L-value) was calculated from the ratio of main spike isotopes to major isotopes. For the studied trace elements the ratio of isotopic abundances used was $^{62}Ni/^{60}Ni$, $^{70}Zn/^{66}Zn$, $^{108}Cd/^{111}Cd$. The L- value (mg/kg) for each element was calculated from:

$$L_{value} = R\left(\frac{AM_{soil}}{AM_{spk}}\right)\frac{\left(IA_{spk} - IA_{meas}R_{ss}\right)}{\left(IA_{meas}R_{ss} - IA_{nat}\right)} \qquad \text{Eq. 6.1}$$

where AM_{soil} and AM_{spk} are the average atomic masses of Ni, Zn or Cd in soils and spikes, respectively. IA_{spk} is the isotopic abundance ratio of $^{62}Ni/^{60}Ni$, $^{70}Zn/^{66}Zn$, $^{108}Cd/^{111}Cd$ in spike solution (mole), IA_{meas} is the measured abundance ratio of $^{62}Ni/^{60}Ni$, $^{70}Zn/^{66}Zn$, $^{108}Cd/^{111}Cd$ in plant tissue, $IA_{nat\ is\ the}$ natural abundance ratio of $^{62}Ni/^{60}Ni$, $^{70}Zn/^{66}Zn$, $^{108}Cd/^{111}Cd$ in plant tissue (from control pots) and Rss is the ratio of isotopic abundances in plant. Spiked (spk): measured (meas) and natural (nat).

6.3 Result and discussions

6.3.1 Soil analysis

6.3.1.1 Soil properties and multi elemental analysis

Table 6.1 gives the soil properties (pH and %LOI), total and DTPA-extractable concentrations of trace elements in the soil used for the pot experiment before growing the vegetables. The results show that the mean soil pH values for 12 replicates were 7.93. The organic carbon content of the soil was 7.75%. The mean concentrations of Cr, Ni, Cu, Zn, As, Se, Cd and Pb in the pot experiment soil were lower than the UK soil SGVs. The percentages of DTPA-extractable trace elements were Cr 0.01%, Ni 2.64%, Cu 19.2%, Zn 24.5%, As 0.920%, Se 3.54%, Cd 21.1% and Pb 21.7%.

6.3.1.2 Combined isotopic ratio and sequential extraction procedures in soil

After adding isotopes of ^{62}Ni, ^{70}Zn and ^{111}Cd then growing the selected vegetables under growth room conditions for 8 weeks, the uncontaminated and spiked soils were analysed to determine the isotopic ratios ^{62}Ni/^{60}Ni, ^{70}Zn/^{66}Zn and ^{108}Cd/^{111}Cd in sequentially extracted fractions. Results for each fraction are shown in Fig.6.4 and can be used to investigate the fractionation of the added spike. For Ni, the greatest displacement from the expected ratio (the ratio in the control soil is 0.14) was detected in F1 (exchangeable fraction) with progressively less displacement in the subsequent fractions F2> F3> F4 > F5 (Fig.6.4a). This suggests that, for Ni, the majority of the spike isotope was present in the exchangeable fraction, i.e. the fraction generally most easily taken up by plants (Øygard et al., 2008).

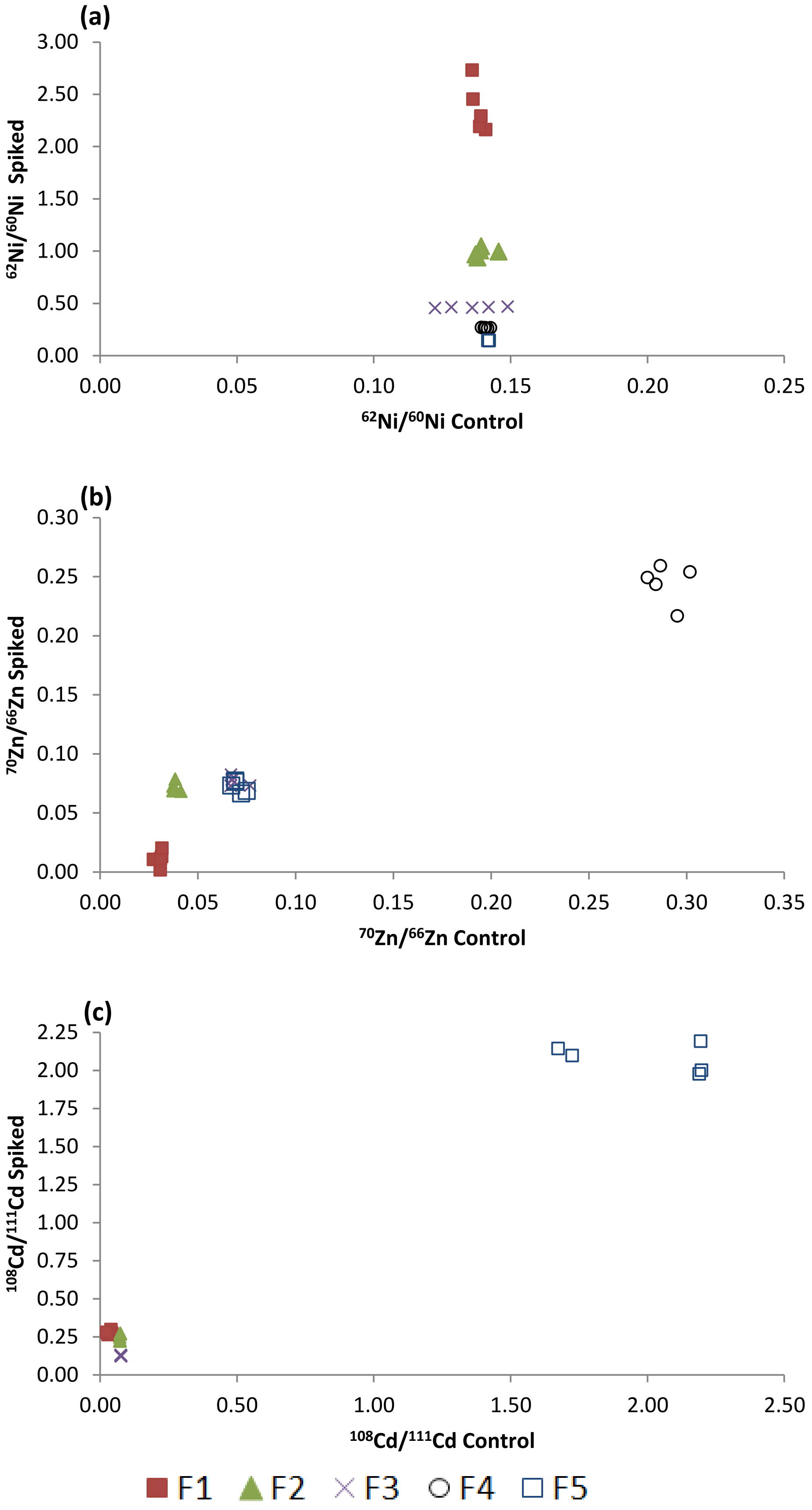


Figure 6.4 Comparison of isotopic ratios in sequentially extracted fractions of spiked and uncontaminated soil from the pot experiment

The isotopic ratios for Cd and Zn isotopes in some fractions of the control soil (oxides, carbonate and residual for Zn and residual for Cd) deviated significantly from the expected values (0.022 and 0.07 for ^{70}Zn/^{66}Zn and ^{108}Cd/^{111}Cd respectively). This is unlikely to be a genuine result and may have occurred due to errors in technique or instrumentation or possibly contamination of samples during preparation while the Ni data did not seem to be affected by these erroneous results.

The greatest displacement of the ^{70}Zn/^{66}Zn ratio from the expected value was observed in the organic matter fraction (F4) and the greatest displacement of the ^{108}Cd/^{111}Cd ratio was detected in the residual fraction (F5, Fig.6.4b and c). Ratios in the other fractions were close to the expected ratios. This result is also unexpected and not consistent with the study conducted by Riise et al. (1994) who observed the ratio of ^{109}Cd/^{stable}Cd in exchangeable (F1) and carbonate (F2) followed by the Fe/Mn oxide (F3) and organic matter (F4) fractions with percentages of 25% and 60%, 10% and 2%, respectively. This result is also different from that found by Ahnstrom and Parker (2001), who conducted a similar investigation combining isotopic dilution with SEP for Cd. They measured ^{111}Cd/^{110}Cd in four spiked soils, with ^{111}Cd, in each fraction from SEP using a wide range of contact times (2 hours to 59 weeks). The ratio of ^{111}Cd/^{110}Cd was found to be significantly greater in the exchangeable fraction (F1) compared to other fractions (F2-F4). A high ^{108}Cd/^{111}Cd ratio in the residual fraction could be explained by migration of the spike isotope into the residual fraction over time.

Ahnstrom and Parker (2001) reported that, with increasing incubation duration, migration of ^{111}Cd/^{110}Cd into the organic matter and residual fraction increased. Another possible explanation could be the redistribution of the tracer into the residual fraction during SEP because studies have observed that redistribution of trace elements in this way can be expected (Ahnstrom and Parker, 1999).

6.3.2 Plant analysis

6.3.2.1 Trace element concentrations in the vegetables

The concentrations of trace element isotopes in the roots and shoots of the vegetables are given in Figure.6.5. Figures for the spiked soil include the metal isotope derived from both soil sources and the added spike combined. The concentrations of ^{62}Ni in the vegetable shoots ranged from 0.0153 mg kg ^{1} in radish leaves grown in un-spiked soil to 0.216 mg kg^{-1} in celery grown in spiked soil. The ^{62}Ni concentration in celery was greater than in the other vegetables whereas relatively similar concentrations were found in chard, lettuce, radish and spring onion (Fig 6.5a). The concentration of ^{62}Ni in the roots of the vegetables was much greater than in the shoots, especially in spiked soils. For example, root concentrations ranged from 0.312 mg kg^{-1} in lettuce grown in un-spiked soil to 1.47 mg kg^{-1} in radish grown in spiked soil. Accumulation of ^{62}Ni in chard and radish roots was significantly greater than in celery, lettuce and spring onion roots (Fig 6.5d). By contrast, the ^{62}Ni concentration in radish bulbs grown in un-spiked and spiked soil were 0.0232 and 0.0683 mg kg^{-1}, respectively, much lower than its concentration in radish root and shoots, indicating translocation of ^{62}Ni from bulb to shoot.

Concentrations of ^{70}Zn in shoots varied from 0.201 mg kg^{-1} in radish grown in un-spiked soil to 0.550 mg kg^{-1} in chard grown in spiked soil (Fig 6.5b). Concentrations in roots ranged from 0.329 mg kg^{-1} in lettuce grown in un-spiked soil to 0.887 mg kg^{-1} in spring onion grown in spiked soil (Fig 6.5e), which were much greater than those found in vegetable shoots. The Zn concentration in radish bulbs grown in un-spiked and spiked soil were 0.0207 and 0.0386 mg kg^{-1}respectively, significantly lower than the Zn concentrations in shoots and roots.

The concentrations of ^{108}Cd in shoots ranged from 0.00082 mg kg^{-1} in radish grown in un-spiked soil to 0.00340 mg kg^{-1} in chard grown in spiked soil (Fig 6.5c). Concentrations in celery, chard and lettuce were significantly greater than radish and spring onion. In common with the other trace elements, the concentrations of Cd in roots were greater than those in the shoots, ranging from 0.0029 mg kg^{-1} in lettuce grown in un-spiked soil to 0.0140 mg kg^{-1} in spring onion grown in spiked soil (Fig 6.5f). The concertations of Cd in radish bulbs grown in un-spiked and spiked soil were 0.000451 and 0.000942 respectively, also much smaller than its concentration in shoot and roots. In general, the concentrations of ^{62}Ni, ^{70}Zn and ^{108}Cd were different between vegetable types grown in spiked soil, and also varied between plant tissues and organs (shoot, root and bulb). This difference has commonly been reported by other authors (Kloke et al., 1984;Turner, 1994;Alexander et al., 2006;Khan et al., 2008a;Murray et al., 2011). Ge et al. (2000) reported that metabolic variation between plant species is a reliable reason to explain such variation in the accumulation of trace elements in different plant species and parts of plants.

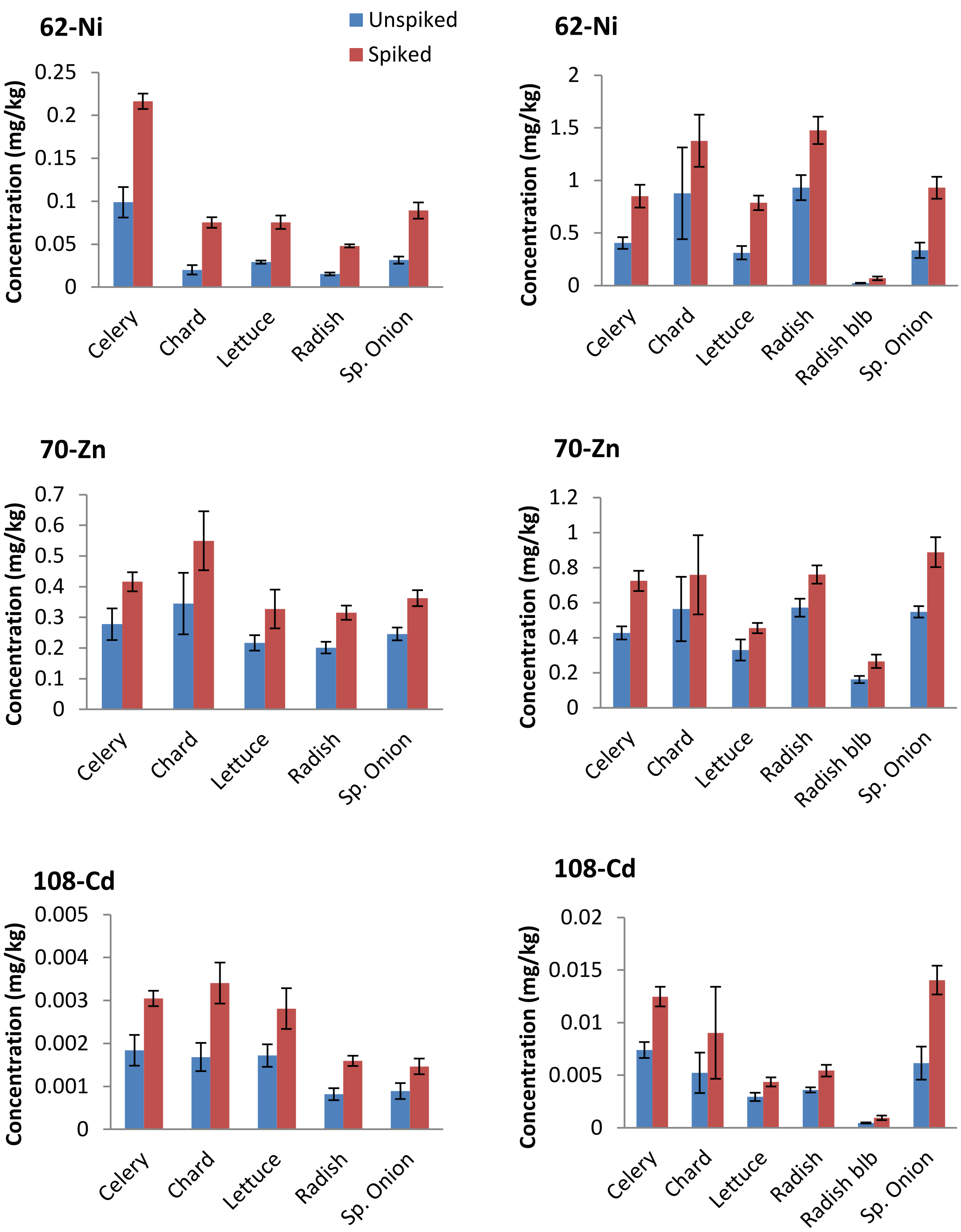


Figure 6.5 The mean concentrations of (a) ^{62}Ni, (b) ^{70}Zn and (c) ^{108}Cd in the shoots, and (d) ^{62}Ni, (e) ^{70}Zn and (f) ^{108}Cd roots and bulbs of all vegetable types grown on un-spiked and spiked soil. The error bars show the standard error of the mean (±SEM).

The distribution of Ni, Zn and Cd in spiked soil between shoot, root and bulb for each vegetable type is shown in Figure 6.6. In general, higher trace element concentrations were found in the roots with much lower concentrations in the shoots or radish bulb. The greater concentrations of Ni, Zn and Cd in roots compared to shoots and the radish bulb may indicate a physiological limit to the degree of translocation of trace metals from root to shoot tissues. Plants have the ability to take up trace elements and translocate them to the aerial parts of the plant (McGrath et al., 2001;Ozturk et al., 2003). However, the solubility and speciation of trace elements directly affects the transfer of trace elements from the rhizosphere to the roots and the translocation from root to shoot. It is believed that, even if the low-solubility trace elements are apparently absorbed by roots, they are not significantly translocated to the upper parts of the plant (Tiwari et al., 2011). However, in interpreting root concentrations of trace metals it cannot be ruled out that not all soil particles were washed off the root before processing despite the care taken to do this.

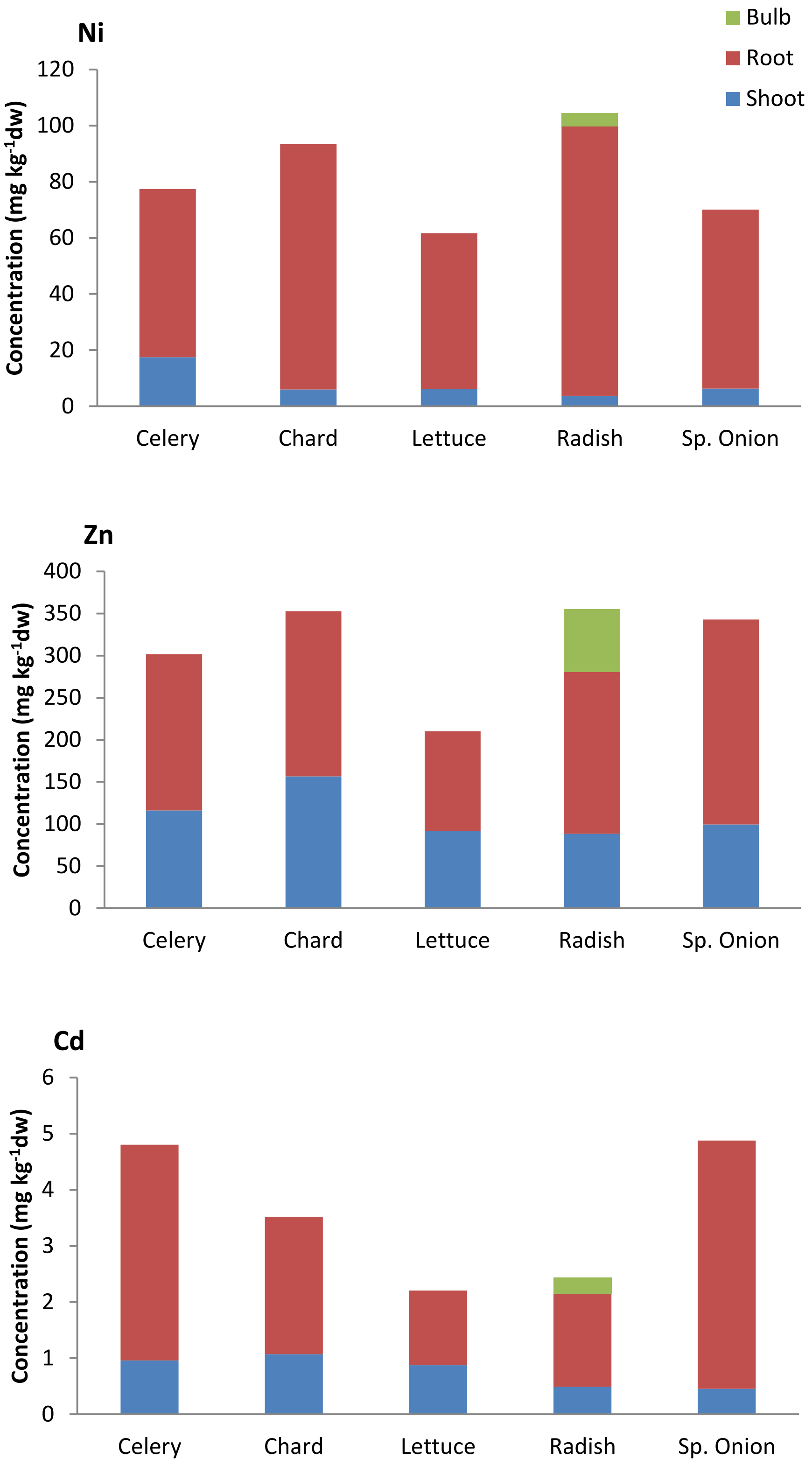


Figure 6.6 Distribution of Ni, Zn and Cd concentrations in different parts of the vegetable types (shoot, root and bulb).

6.3.3 Transfer factor (TF)

A comparison of TFs (defined in the Section 5.3.8) for shoots of vegetables grown on uncontaminated and spiked soils is given in Fig. 6.7. In general, the TFs of spiked ^{62}Ni, ^{70}Zn and ^{108}Cd were significantly greater than the TF of native Ni, Zn and Cd in the soil at $p<0.001$ (Fig. 6.7). This can be ascribed to the greater bioavailability of the freshly added 'spike' isotopes compared to the native isotopes which may be present in inert and residual fractions of the soil. A difference in TFs of trace elements between vegetable types grown on spiked soil compared with controls has also been reported by Alexander et al. (2006).

TFs were significantly different ($p<0.001$) between vegetable types and TFs varied in the order of Cd> Zn> Ni suggesting that all the vegetables studied had higher potential for accumulation of Cd. The same order was found for the same vegetables grown in the field (see Chapter 5, Section 5.3.4). Furthermore, it can be clearly seen from Fig. 6.7 that the differences between TFs for native Ni and spiked Ni are greater than the difference of native Zn, Cd and spiked Zn and Cd. Mean TFs of spiked Ni in all vegetable types were ten times greater than the mean TFs for native Ni, while the mean TFs of spiked Zn and ^{108}Cd were only 2 and 3 times greater, respectively. This may be due to the observed retention of the majority of spiked ^{62}Ni in the exchangeable fraction of the soil compared to the ^{70}Zn which was mostly bound to the organic matter and ^{108}Cd which further migrated to the residual fraction (see Section 6.3.1.2).

Figure 6.7 also shows the TFs for roots of vegetables grown on uncontaminated and spiked soils. Generally, the TFs for both native and spiked trace elements were higher in roots compared to shoots. For example, the mean root TFs for native Ni in all vegetable types was 80 times higher than that recorded for shoots, but the TF for spiked Ni was only seven times higher than the TF for spiked Ni in the shoots. Likewise, the mean TF of Zn in roots was two times higher than the mean TF for Zn in the shoots, while similar spiked Zn TFs were observed in shoots and roots. In the case of native Cd and spiked Cd, the mean TFs in all vegetable roots were 2 and 3 times greater than TFs in shoots. There is not a general consensus to demonstrate that TFs for roots are greater than TFs for shoots. In some studies, the TF for roots is reported to be greater than that for shoots but this is not generally applicable to all vegetable types grown in different soils (Hossain et al., 2007;Tiwari et al., 2011;Yashim et al., 2014).

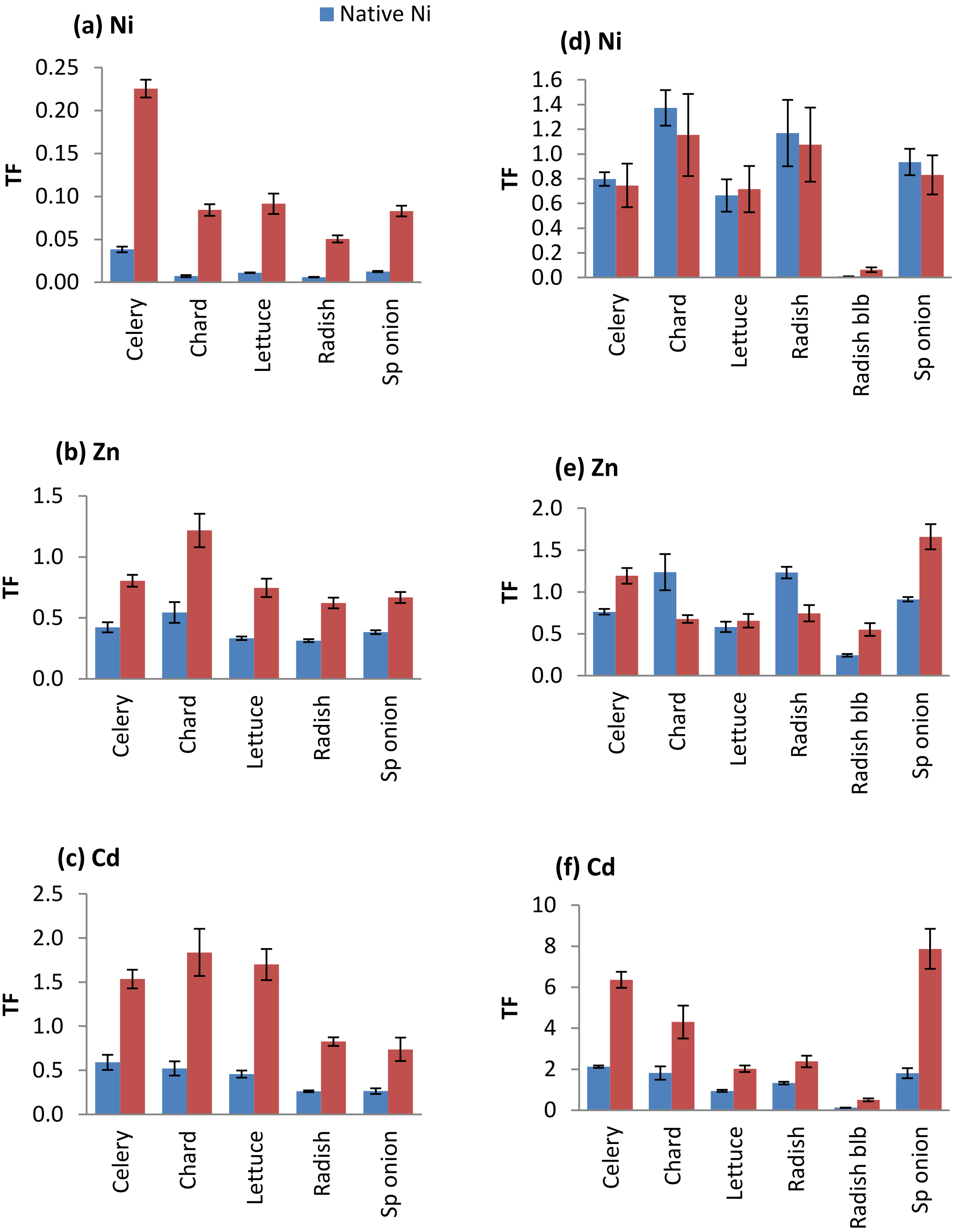


Figure 6.7 The mean transfer factors (TF) of (a) Ni, (b) Zn and (c) Cd in shoots, and (d) Ni, (e) Zn and (f) Cd in roots and bulbs of all vegetable types grown on uncontaminated and spiked soils. The error bars show the standard error of the mean (±SEM).

When considering the TFs for Ni and Zn in the roots of each vegetable type, no significant difference was observed between spiked and non-spiked values. Native TFs were slightly greater than spiked TFs for chard, lettuce, radish and spring onions. This might be related to soil contamination of the roots because these vegetables have dense roots that may have retained small particles during root cleaning. By contrast, root TFs for spiked Cd were significantly higher than those for native Cd (6.36, Fig 6.7).

6.3.4 Isotopic ratio of trace elements in soil and plant

6.3.4.1 Comparison of plant isotopic ratios with DTPA extraction of associated soil

To investigate plant uptake, isotopic ratios $^{62}Ni/^{60}Ni$, $^{70}Zn/^{66}Zn$ and $^{108}Cd/^{111}Cd$ were determined in both soil DTPA extracts and plants and compared (Table 6.2). The vegetable types give relatively similar isotopic ratios to the ratios extracted by DTPA, particularly for $^{108}Cd/^{111}Cd$. This may be because the main source of trace element in the plant was readily extractable by DTPA from the soil. The plants are not generally able to distinguish between different isotopes of an element during uptake. Therefore, the ratio between trace elements could be expected to be similar in shoot tissues and the corresponding fraction within the soil that the plant is accessing. Measured isotopic ratios in the roots were lower than in the soil DTPA extractions. This is perhaps because plants will absorb metals from the labile pool over their entire growing period whereas the DTPA extraction is a single measurement at the end of the experiment when more of the metal is likely to have become fixed in the soil.

Table 6.2 Isotopic ratios of selected trace elements in the vegetable types and in the soil after DTPA extraction at harvest

Vegetable types	^{62}N1/^{60}Ni		^{70}Zn/^{66}Zn		^{108}Cd/^{111}Cd	
	Plant	soil (DTPA)	Plant	Soil (DTPA)	Plant	Soil (DTPA)
Shoot						
Celery	1.23	1.32	0.0629	0.0766	0.301	0.306
Chard	1.28	1.33	0.0646	0.0806	0.294	0.302
Lettuce	1.45	1.38	0.0640	0.0819	0.311	0.317
Radish leaf	1.14	1.40	0.0663	0.0817	0.321	0.323
Sp onion	0.97	1.33	0.0585	0.0772	0.319	0.306
Root						
Celery	0.655	1.32	0.0523	0.0766	0.283	0.306
Chard	0.590	1.33	0.0509	0.0806	0.235	0.302
Lettuce	0.823	1.38	0.0516	0.0819	0.286	0.317
Radish	0.614	1.40	0.0480	0.0817	0.284	0.323
Radish bulb	0.962	1.40	0.0632	0.0817	0.309	0.323
Sp onion	0.695	1.33	0.0578	0.0772	0.318	0.306

Figure 6.8 compares the isotopic ratios of trace elements in the shoots and roots of the vegetables with those in the DTPA extract of soil. Lower ^{62}Ni/^{60}Ni ratios in the plants (particularly the spring onions) compared to the ratio in the DTPA extracts were observed. This is perhaps due to the growth profile of the individual plants. For example, spring onions were slower to germinate and grow than the other vegetables and, therefore, more of the spike may have been fixed before they went through their main growth period compared to other vegetables. The ^{62}Ni will be most available to the plant in the earlier stages of growth and later in the growth period the plant will be accessing less spike isotope.

Another possible explanation for this difference is an increase in the DTPA extracted ratios in soils where spring onion has grown (i.e. DTPA extracted more ^{62}Ni in spiked soil solution compared to ^{60}Ni). This is possible because spiked ^{62}Ni tended to be more labile than native ^{60}Ni in the soil. In this case, the first explanation would be more realistic because all the vegetables, except spring onions, had relatively similar isotopic ratios of ^{62}Ni/^{60}Ni compared with DTPA extracted ratios. In contrast, spring onion, for some physiological reason, has taken up less ^{62}Ni in the soil, thus the ratios have decreased. With regard to the ^{70}Zn/^{66}Zn ratios (Fig 6.8b), the ratios were displaced from the 1:1 line in both spiked and uncontaminated soil. This is perhaps because DTPA might have attacked some native element in addition to the spike leading to increased DTPA-extractable ratios. . The ^{108}Cd/^{111}Cd ratios in all vegetables were very similar to the ratios recorded in the DTPA extract from spiked soil. Figure 6.8c reveals that all ratios in plant tissues and DTPA extracts fall along the 1:1 line.

Figure 6.8d shows that there was a decrease in ^{62}Ni/^{60}Ni ratios in all vegetable roots. This may be because of continuous transfer of ^{62}Ni from root to shoot, leading to very low concentrations of ^{62}Ni in the root subsequently. Another reason could be contamination of the roots and radish bulb with soil particles as it is difficult to clean the roots completely of small particles.

The ^{70}Zn/^{66}Zn ratios in roots (Fig 6.8e) also deviated from the 1:1 line for both spiked and uncontaminated systems. This may be a combination of decreasing ratios in the root with ongoing plant growth and continuing spike fixation, or a large proportion of ^{70}Zn may have been extracted by DTPA because it may have attacked non-labile metal in the soil. The ^{108}Cd/^{111}Cd ratios in different roots and radish bulb are shown in (Fig 6.8f). Like the ^{108}Cd/^{111}Cd ratios in vegetable shoots, the ^{108}Cd/^{111}Cd in DTPA extracts and root tissues all fall on the 1:1 line except one replicate of chard root in which the ratios decreased; this may be due to one of the above-mentioned reasons or soil contamination.

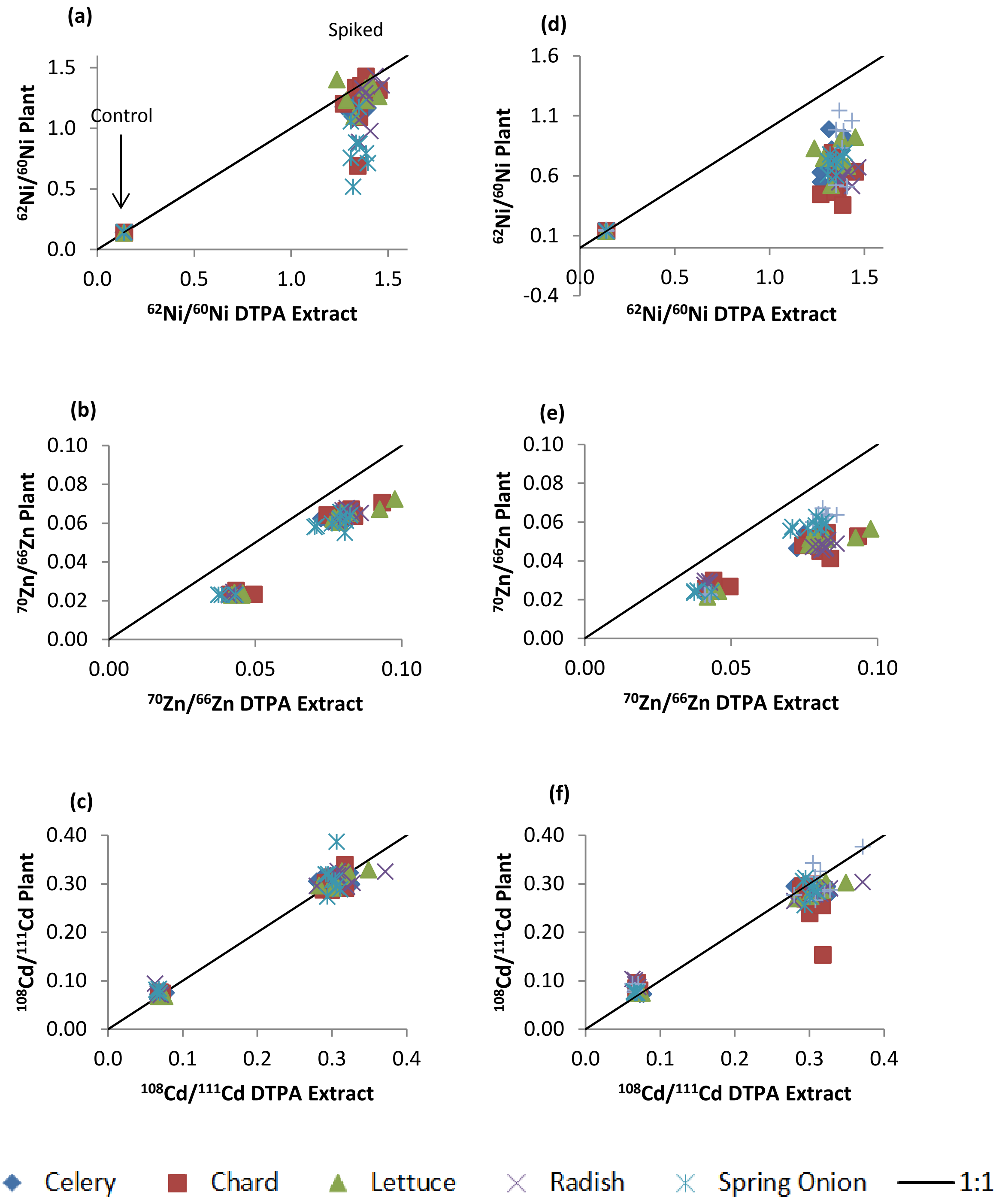


Figure 6.8 Correlations between the isotopic ratios of ^{62}Ni/^{60}Ni, ^{70}Zn/^{66}Zn and ^{108}Cd/^{111}Cd in vegetable shoots (a, b, c) and roots (d,e,f) with soil DTPA extracts. The solid line is the 1:1 relationship.

6.3.4.2 Comparison of isotopic ratios in plants and sequentially-extracted fractions

Sequential extraction has been used in an attempt to understand the mechanisms of plant uptake. The isotopic ratios of ^{62}Ni/^{60}Ni, ^{108}Cd/^{111}Cd and ^{70}Zn/^{66}Zn in different soil fractions after spiking and those in the vegetables are shown in Figures 6.9, 6.10 and 6.11, respectively. The greatest ratios of ^{62}Ni/^{60}Ni in soil samples were found to be in the exchangeable fraction (2.37) which was significantly higher than the ratios in other fractions - carbonate (0.976), Fe/Mn oxide (0.462), organic matter (0.266) and residual (0.145). The plant ratios of ^{62}Ni/^{60}Ni in celery, chard, lettuce, radish and spring onion were 1.23, 1.28, 1.45, 1.14 and 0.970, respectively. Comparing the expected ratio for the whole soil with ratios in plants and sequentially-extracted fractions it can be seen that the total soil ratio falls between the ratios in the carbonate (F2) and exchangeable (F1) fractions. The results suggest that all the vegetable types may have accessed trace element isotopes associated with both exchangeable (F1) and carbonate (F2) fractions. This was expected since the spiked tracer in the soils is supposed to be more labile than native Ni. Sungur et al. (2014) suggested trace elements such as Ni, Zn and Cd bound to F1 and F2 were more likely to be accessible for plants (Sungur et al., 2014).

The largest ratio of ^{70}Zn/^{66}Zn was found in the organic matter fraction (0.244) which was significantly higher than the ratios in other fractions: this is perhaps because soil organic matter provides the ultimate sink for the added ^{70}Zn isotope. The ratios in all plants were smaller than ratios found in the organic matter. The whole soil ratio was close to other soil fractions (Fig 6.10). This reveals that the plants might have accessed the metals bound to the resistant fractions. The greatest ratios of ^{108}Cd/^{111}Cd were observed in the residual soil fraction (2.081) which is much larger than ratios observed in different plants (0.291 in chard to 0.321 in radish). The whole soil ratios were again located between exchangeable /carbonate and residual fractions (Fig 6.11). According to this finding the plants might have been able to absorb elements found in exchangeable and other fractions. These isotopic ratios observed for ^{70}Zn/^{66}Zn and

$^{108}Cd/^{111}Cd$ may be explained if spiked elements have migrated to soil fractions that are more resistant given the relatively long contact time between spiked isotopes and soil (see Section 6.3.1.2). Riise et al. (1994) conducted a study on two soils which were spiked with ^{109}Cd and sequentially extracted to investigate the distribution of spiked ^{109}Cd between the soil fractions for a wide range of soil-spike contact times (5 to 221 days) . These authors found that the majority of spiked ^{109}Cd was present in the carbonate fraction, F2 (60 %), followed by 25% found in the exchangeable fraction, F1 and 10% and 2 % in F3 and F4, respectively, even after 221 days.

This finding disagrees with the current study. The authors explained this as a consequence of the contact time between spiked trace elements and soil. They reported that ^{109}Cd had not efficiently equilibrated with non-labile native Cd in the soil after 221 days of contact time (Riise et al., 1994). By contrast, in the current study the higher ratios of $^{70}Zn/^{66}Zn$ and $^{108}Cd/^{111}Cd$ found in the fractions F4 and F5, respectively, rather than in the F1 and F2 may be because of migration of the spiked isotopes into organic matter and residual fractions.

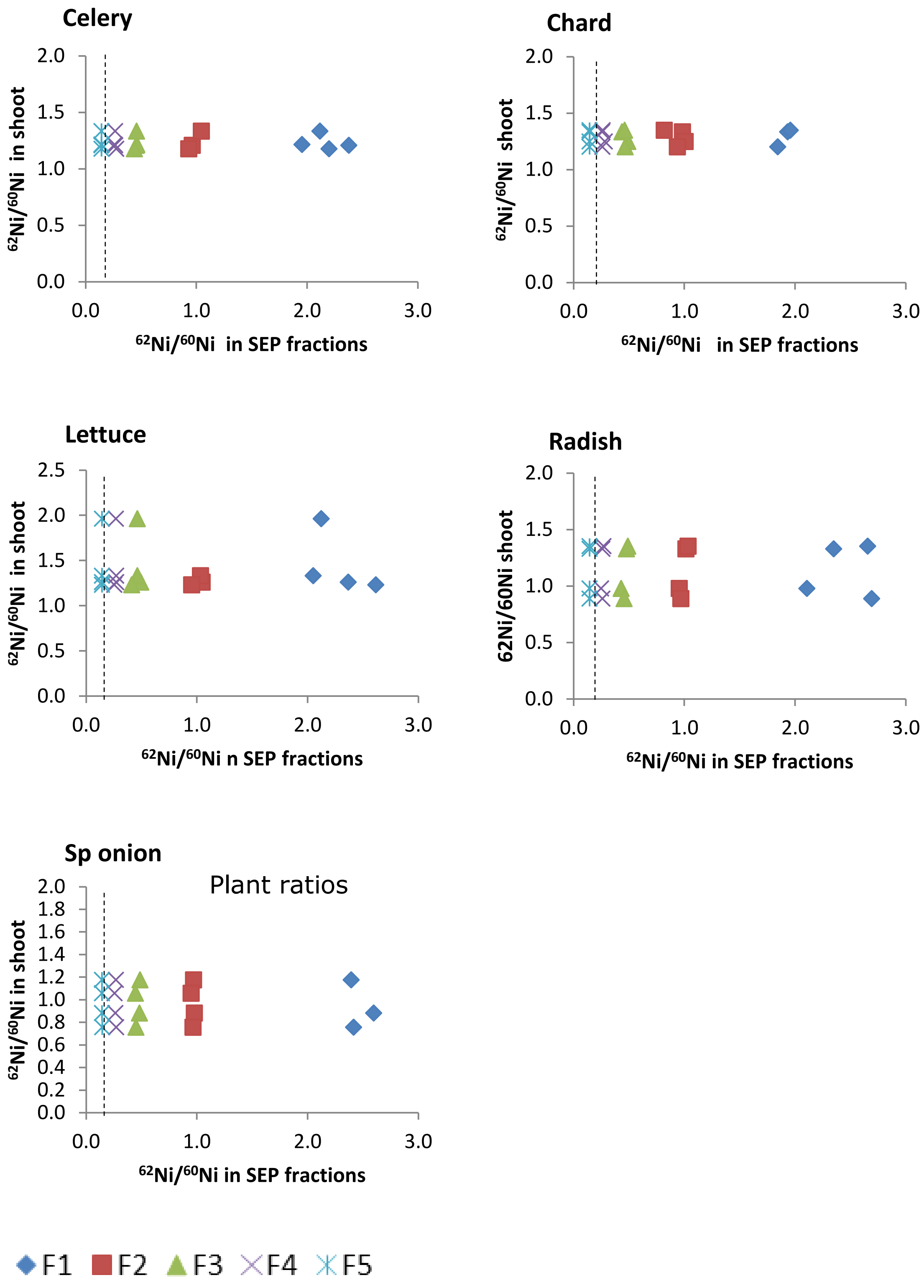


Figure 6.9 Comparison of isotopic ratios of ^{62}Ni/^{60}Ni in different vegetables and sequentially-extracted soil fractions. The vertical dashed line denotes the whole soil isotopic ratio (0.14).

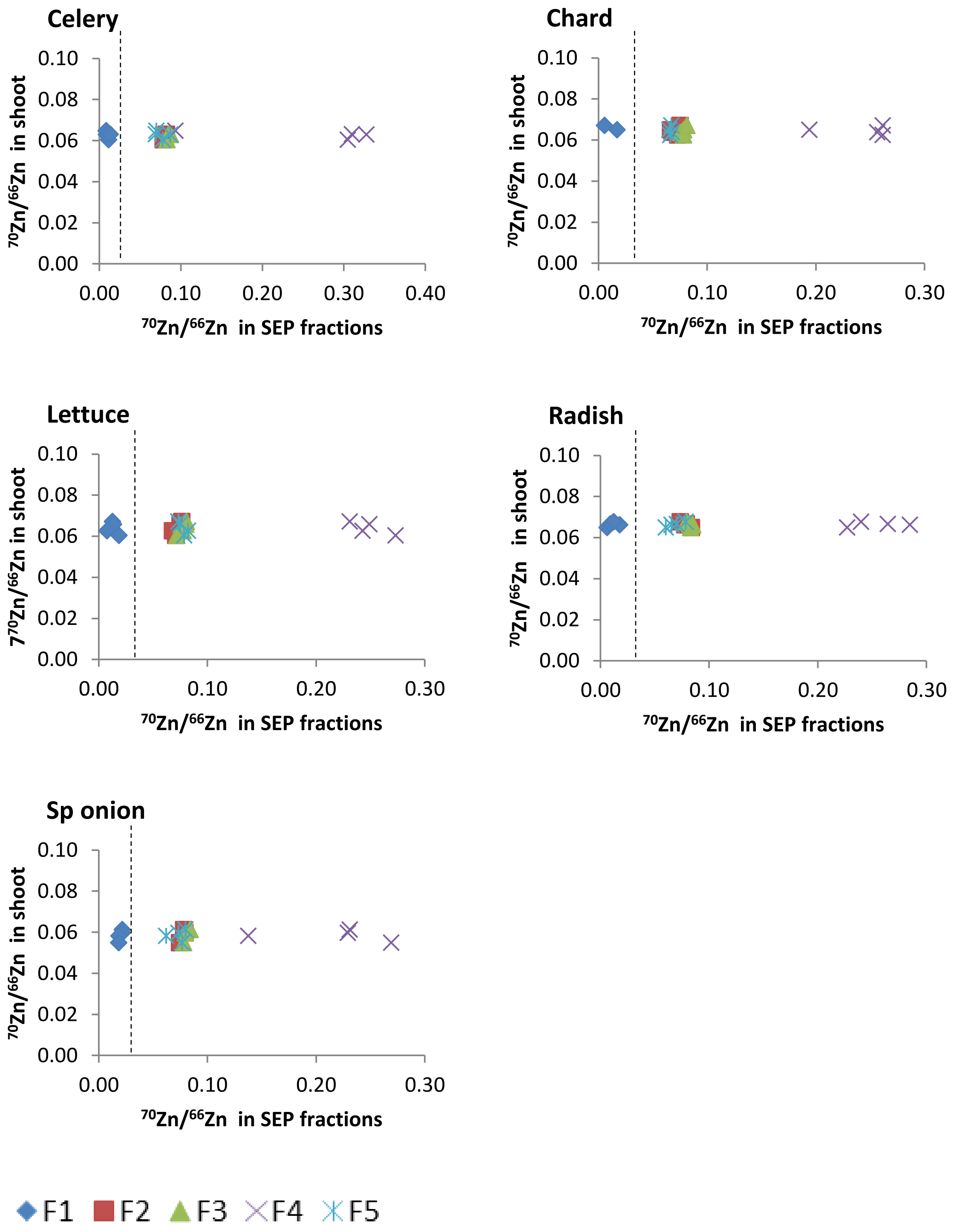


Figure 6.10 Comparison of isotopic ratios of ^{70}Zn/^{66}Zn in different vegetables and sequentially-extracted soil fractions. The vertical dashed line is denotes to the whole soil isotopic ratio (0.022).

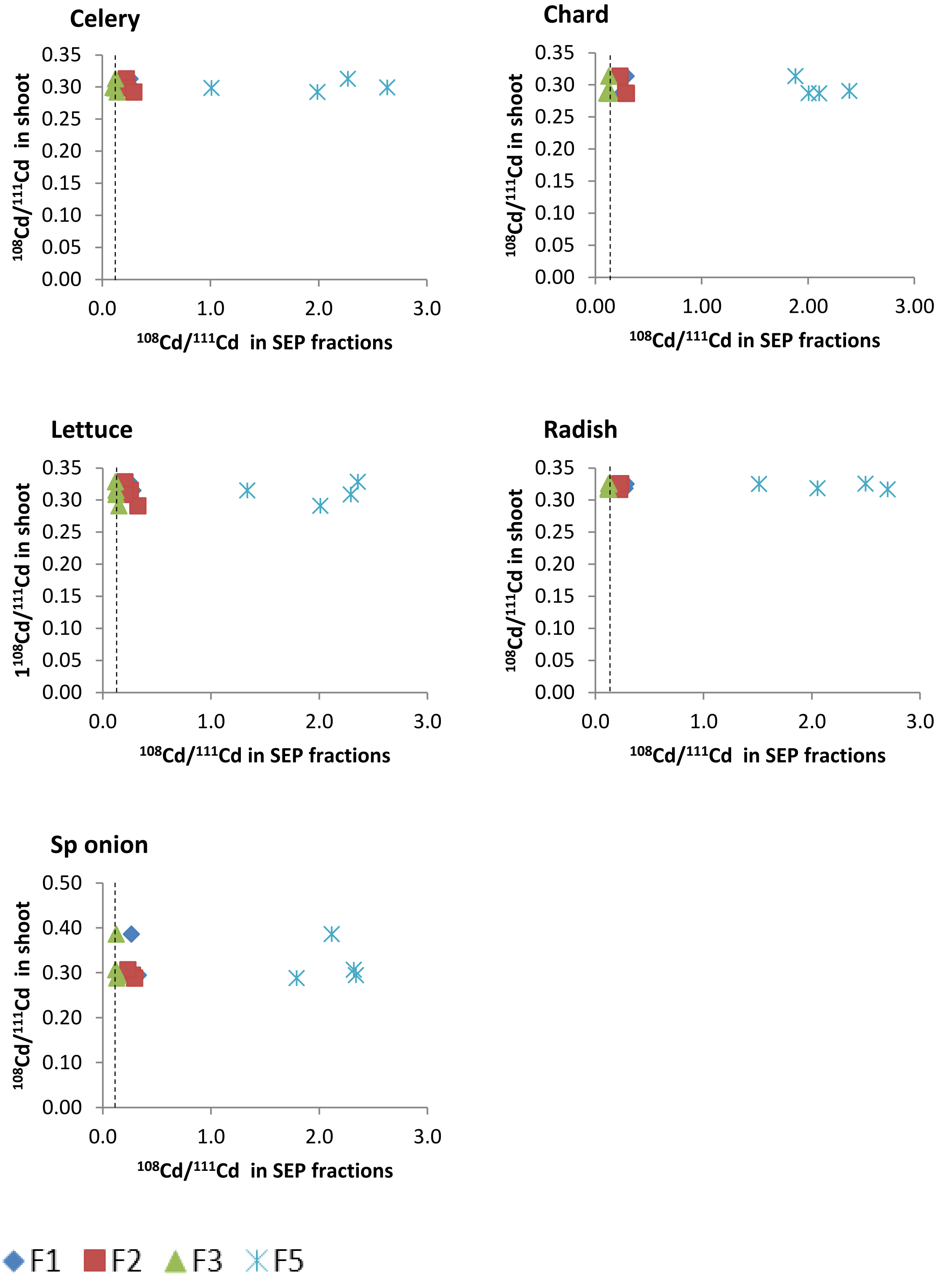


Figure 6.11 Comparison of isotopic ratios of ^{108}Cd/^{111}Cd in different vegetables and sequentially-extracted soil fractions. The vertical dashed line denotes the whole soil isotopic ratio (0.07).

6.3.5 Comparison of L-values with DTPA-extractable metal and E-values

Measured L-values for Ni, Cd and Zn are compared with total metal content, DTPA-extractable metal and E-values in Table 6.3. Differences between mean L-values for the different vegetable types were not significant (Fig 6.7a,b,c). The similarity of L-values for different plant species is expected and has been reported in previous studies (Gérard et al., 2000). Hamon et al. (1997) also observed similar L-values for Cd and Zn in a range of plant species with the exception of *Canola* which, the authors suggested, was not able to access the labile pool of Cd and Zn. The authors believed that this may reflect different metal uptake strategies among plants and perhaps the role of plant roots in changing the pH of the rhizosphere with consequent changes in the status of organic ligands (Hamon et al., 1997).

The L-values calculated for roots were significantly different between vegetable types. For example, the mean L-value for Ni ranged from 11.8 mg kg^{-1} in lettuce to 22.6 mg kg^{-1} in celery. The L-value for Zn varied from 53.5 mg kg^{-1} in spring onion to 109 mg kg^{-1} in chard and for Cd the L-values were 0.0996 mg kg^{-1} in spring onion and 0.207 mg kg^{-1} in chard. The L-values for radish bulb were 25.5 mg kg^{-1}, 47.6 mg kg^{-1} and 0.0974 mg kg^{-1} for Ni, Zn and Cd, respectively. Root L-values were markedly different from the L-values measured for shoots of the same vegetables for a given element (Table 6.3). This may be due to the higher accumulation of trace elements in the roots rather than shoots (Fig 6.7d,e,f), or may be due to contamination of the roots by soil particles.

Mean L-values can also be compared to the amount of labile Ni, Zn and Cd estimated using other assays, specifically DTPA extractions and isotopically-exchangeable metal pools (E-values) (Table 6.3). Overall, L-values were significantly greater than corresponding DTPA and E-values. For example, Ni L-values were 8 to 11 times greater than DTPA-extractable Ni and 16 to 22 times greater than the E-value measured in the soil used for this experiment. Differences between Zn L-values and DTPA-extractable Zn were not as great; the L-value was approximately double the DTPA-extractable Zn pool and 10 times greater than the E-value. Cadmium L-values were not significantly different from DTPA-extractable Cd but were c. 3 times greater than the E-value.

The L- Value results of previous studies were not consistent, although some agree with the findings of this investigation. For example, Tongtavee et al. (2005) demonstrated that, in some uncontaminated soil, L-values were greater than chemically-extractable metal and E -value because of progressive trace element fixation in the spiked soil. Another possible explanation was that their results reflected further isotopic mixing during the growth period of the plant. Rhizosphere dynamics can also contribute to differences between L-values and E-values through the action of root exudates.

Contact time between isotope spikes and soil solution is likely to be another significant explanation for the overestimation of L-values. The contact time for the E–value calculation was 3 days (see Section 2.1.11) whereas the growth period of plants was 42 days. This difference is very likely to have significantly affected the comparison of E-values and L-values. Ahnstrom and Parker (2001) reported increasing E-values for Cd from 5% to 20% (of total Cd) over 57 weeks of contact time, suggestion time-dependent migration of trace elements into less labile pools of trace metal (Ahnstrom and Parker 2001). Oliver et al. (2006) studied the effect of contact time on E and L values for Cu isotopes. They confirmed that the spike isotope contact time with soil significantly affected the measured E-value with greater equilibration times leading to larger E-values.The E-value and L-value measurement are affected by contact time for both stable and radioisotopic investigations (Fardeau, 1993;Massoura et al., 2004;Oliver et al., 2006).

Some other studies report that E- and L-values produce a range of estimates of labile metal in the soil and plant. For example Smolders et al. (1999) reported greater L-values than E-values in wheat (*Triticum aestivum*) for Zn and Cd in a wide range of Belgian soils. The authors attributed the variation between E- and L-values to rhizosphere dynamics such as release of plant exudates that encourage trace element release from the non-labile pool of metal by releasing organic chelating agents or changing soil properties such as pH (Collins et al., 2003a;Collins et al., 2003b). Gérard et al. (2000) reported that difference between E- and L-values could reflect the inaccessibility of trace elements present in soil aggregates. Other studies have also reported that E- and L-values can be similar indicating that the main source of trace elements to the plants is the isotopically-exchangeable metal in the soil (Tiller et al., 1972;Smolders et al., 1999;Sinaj et al., 2004).

Table 6.3 Comparison of mean total, DTPA-extractable, E- and L-values of Ni, Zn and Cd.

Trace elements	**Total (mg kg^{-1})**	**DTPA (mg kg^{-1})**	**E-value (mg kg^{-1})**	**plant parts**	**L- value (mg kg^{-1})**				
					Celery	**Chard**	**Lettuce**	**Radish**	**Sp. Onion**
Ni	70.2	1.85	0.499	Shoot	8.62	7.7	8.177	11	8.92
				Root	22.6	14.2	11.8	18.7	15.6
				Bulb				25.2	
Zn	101	24.7	4.45	Shoot	51.6	48	44.2	46.5	50.3
				Root	67.3	109	68.5	88.7	53.5
				Bulb				47.6	
Cd	0.408	0.086	0.03	Shoot	0.096	0.0992	0.0912	0.0948	0.0982
				Root	0.103	0.207	0.106	0.121	0.0996
				Bulb				0.0974	

Some studies reported a convergence between E-values and corresponding L-values of trace elements. For example, Echevarria et al. (1998) conducted an investigation on Ni phytoavailability. Their results showed that isotopically-exchangeable Ni in the soil was in a very good agreement with isotopically-exchangeable Ni taken up by plants. They also found that the DTPA extraction was a very good method to measure the phytoavailability of Ni in the soil. In addition, Ayoub et al. (2003) reached a similar conclusion for Zn and Cd E- and L-values in two soils for the plant species *Thlaspi caerulescens, Taraxacum officinale and Hordeum vulgare*.

L-values measured for vegetable roots were much greater than bioavailable metal estimated by DTPA extraction or E-value. Specifically, labile Zn concentrations in roots varied from 53% to 108% of total metal concentration in the soil (Table 6.3), although this may be due to contamination of the roots with spiked soils as mentioned above.

6.4 Conclusion

Determination of isotopic ratios in sequentially-extracted fractions has demonstrated that the majority of Ni spike isotope was detected in the exchangeable fraction, F1. Also, ratios for ^{70}Zn/66Zn and ^{108}Cd/^{111}Cd suggested that the spike may have migrated to the organic matter and residual fraction of the soil over the duration of the experiment (c. 3 months).

Vegetables grown on spiked soil are able to take up higher concentrations of spiked trace elements (Ni, Zn and Cd) than those grown on uncontaminated soils. Some ^{70}Zn and ^{108}Cd was found to be bound to organic matter and residual fractions suggesting that the contact time between spiked elements and soil solution affect the measured ratios. Roots also appeared to play an important role in changing the availability of trace elements in the soil through root exudates. Spiked ^{62}Ni, ^{70}Zn and ^{108}Cd are the main source of trace elements accumulated in the vegetables grown on the spiked soil, since TFs of the spiked trace elements were higher than the TFs of the native trace elements.

The isotopic ratios of ^{62}Ni/^{60}Ni, ^{70}Zn/^{66}Zn and ^{108}Cd/^{111}Cd in shoots of vegetable types were higher than the roots, suggesting translocation of the majority of spiked trace element isotopes (^{62}Ni, ^{70}Zn and ^{108}Cd) from root to the upper parts of the plant. Moreover, the isotopic ratios of ^{62}Ni/^{60}Ni and ^{108}Cd/^{111}Cd obtained from the DTPA extraction were in a very good agreement with corresponding ratios in the plant shoots while significantly lower ratios were recorded in roots, particularly for ^{62}Ni/^{60}Ni ratios.

Despite the difference in trace element concentrations in the plants, the variation in L-values is not significant for different vegetable shoots for certain trace elements. The Ni and Zn L-values in roots of different vegetables were higher than L-values estimated for shoots of the same vegetables for Ni and Zn, but not Cd. This is ascribed to the greater accumulation of metals in the roots compared to the shoots, or may be due to contamination of the roots by small soil particles during separation from the soil.

It can be concluded that the Ni and Zn and Cd L-values of the vegetable types are greater than the corresponding DTPA-extractable concentrations and E-values. This may be because the vegetable rhizospheres affected the lability of trace elements in the soil. However, the nature and amount of root exudates could be plant species- specific or may depend on environmental factors.   The impact of exudates may also be different for different elements.

7 Conclusions

7.1 An overview

Waste water irrigation and waste disposal lacks regulatory control or supervision in the Kurdistan region of Iraq. The majority of waste water flows through agricultural fields in peri-urban areas and is directed into waterways without treatment. Some local farmers used this untreated water for irrigation because it is easy to access, contains nutrients and it compensates for a lack of clean water alternatives, particularly during dry seasons. Assouline et al. (2002) classified Iraq as a semi-arid country which depends on domestic waste water for 78% of agricultural irrigation. Municipal waste is disposed close to cities, adjacent to agricultural land growing vegetables for economic and subsidence purposes. Waste piles are subject to frequent burning by waste scavengers or self-combustion; consequently, pollutants may be released into the air and deposited on the surrounding areas. During rainy seasons (winter and spring) leachate from the disposal areas flows into the Tanjaro river which farmers use for urban agriculture.

This investigation was an attempt to evaluate the extent of PTE contamination in this setting and to understand risks to human health from consumption of vegetables grown in the Kurdistan region of Iraq. The main objectives were to (i) assess the concentrations of PTEs in the soils of the Kurdistan region , (ii) evaluate the mobility and availability of PTEs using various lability assays, such as single and sequential extractions and isotopic dilution techniques, (iii) assess the PTE content of the edible parts of common vegetable varieties grown in the area, (iv) assess risks to human health from consumption of vegetables and (v) assess the transfer of Ni, Zn and Cd to plants by determining L-values for common vegetables .

7.2 Soil contamination with PTEs

In general, the soils were calcareous with pHs from 7.9 to 8.2 and organic matter contents between 6.6% and 13.7%. The highest organic matter value was recorded close to a waste disposal area, perhaps due to the influence of organic municipal waste. PTE results indicated that total concentrations were highly variable between study areas ($p<0.01$) which may result from differences in background concentrations, use of different types of irrigation water quality or localized contamination sources. Excluding the waste disposal area, mean PTE concentrations in each area were lower than UK and EU/WHO standards for all elements with the exception of Ni and Cr. Mean concentrations of Cr in all areas, except KHR and KALG, exceed EU standards. Soils from KALG (n=11) had significantly lower Cr concentrations compared to other areas, perhaps because of the geological background of this area. Ni concentrations in all soils (n=273) exceeded EU/WHO guidelines (50 mg kg^{-1}) but were all lower than the UK SGV of 250 mg kg^{-1}. Again, the elevated concentrations may be a consequence of the nature of the calcareous soils.

Elevated Zn concentrations were present in soils near the waste disposal site. Selenium and As were both below SGVs and EU/WHO guidelines in both soil and water. Although waste water concentrations of As are within those considered safe for irrigation water, accumulation of As may be possible if the soil continues to be irrigated by wastewater for extended periods. Increased Pb concentrations were observed at the KALG and KALR sites. This may be because soils from KALG and KALR are close to the main Kalar-Sulaymanyah road which has high traffic volumes compared to other sites that are away from main roads and, therefore, further away from traffic-related Pb emissions.

The concentration of trace elements, particularly Cr, Cu, Zn, Cd and Pb in the waste disposal sites, were greater than found in other urban, peri-urban and rural areas demonstrating that the waste contaminated surrounding land. This area may also be impacted by other sources of metal contamination which include the presence of a number of car-repair shops . The lowest PTE concentrations were found in rural areas. If comparison is made between waste water-irrigated, fresh water-irrigated soils and soils affected by waste, it can be seen that PTE concentrations in the soils subject to waste disposal are more contaminated than waste water-irrigated soils. Slight increases in Cd, Cr, Ni, Cu, Zn and Pb concentrations were observed in waste water-irrigated soils, but this is not significant compared to the impact of municipal waste disposal.

The complex relationship between trace elements was investigated using principal component analysis (PCA) and cluster analysis (CA). Three main components/clusters can be recognised in the data. First, elements associated with soil parent material (Na, Mg, Sr and Ca) indicating a natural origin for these elements. Second, elements bound to Fe and Mn oxides such as As, Cr, Mn, K, U Fe, Se, Al, Cs, V and Co. Finally, elements controlled by anthropogenic activities such as fertilizer and pesticide application, vehicle exhausts, sewage irrigation and waste disposal, illustrated by the grouping of Pb, Zn, Cu and Cd.

7.3 Lability of PTEs in Kurdish soils

Sequential extraction of soils from across the area showed that, typically, in 80% to 90% of soils Cr, Ni, Cu, Zn and As was associated with the residual fraction (F5) at all sampling sites, suggesting that these elements are locked within the mineral lattices of primary and secondary minerals that are resistant to other extraction steps. Smaller proportions of these elements (1% to 5%) were held in carbonate (F2), Fe-Mn oxide (F3) and organic matter (F4) fractions. Fractionation of Se was different from other elements; a greater amount is bound to organic matter with progressively lower amounts in Fe/Mn oxides, residual and carbonate fractions.

The fractionation of Cd differed from other trace elements with 70% bound in the carbonate pool (F2) at all sites with the exception of the waste site where it was 30%. Measureable Cd was also determined in the exchangeable (F1) fraction. The high proportion of Cd in the carbonate phase probably reflects the ability of Cd^{2+} to substitute for Ca^{2+} in $CaCO_3$. Only 10-15% of Cd was in the residual fraction indicating potentially high bioavailability of Cd. Lead was predominantly held in the Fe/Mn oxide fraction (F3) which accounted for 40% to 60% of the total. The remainder was in residual (F5) and organic matter (F4) fractions (30-40% and 10-20%, respectively).

Extractable metal was typically low for the majority of elements, particularly for Cr, Ni, Cu, Zn and As, whereas it was ~20% of total Cd and Pb. This confirms that most elements (e.g. Cr, Ni, Cu, Zn and As) were bound within the residual fraction (F5) of the soil and, therefore, unlikely to be mobile. In contrast, DTPA extracted higher concentrations of elements from soils collected from the waste disposal area. This was clearly seen for Cu, Zn, Cd and Pb and suggests that these elements may pose a greater risk in these areas.

Isotopically-exchangeable metal (E-value) was very low compared to the total concentrations of corresponding trace elements, ranging from 3.52 to 0.277 mg kg^{-1} for Ni, 14.2 to 0.738 mg kg^{-1} for Cu, 124 to 0.781 mg kg^{-1} for Zn, 0.164 to 0.0235 mg kg^{-1} for Cd and 17.8 to 0.799 mg kg^{-1} for Pb. Based on the percentage of total metal concentration, Cd was the most labile metal and Ni was the least labile. The high concentration of Ca may also play an important role in decreasing the bioavailability of Ni (Wu and Hendershot, 2010).

Comparison of DTPA-extractable metal and the mobile phase of trace elements from SEP (F1-F3) shows that, for the majority of trace elements, the DTPA-extractable metal was greater than the mobile phase of the corresponding trace element from SEP. DTPA-extractable metal was generally greater than the E-value; this may reflect the power of DTPA as an extractant since it has been shown that DTPA is able to extract metals not only bound to exchangeable fractions but also carbonate, Fe/Mn oxide and even organic matter fractions. Typically element concentrations are in the order E values< mobile phase < DTPA extractable. DTPA, SEP and E-values were correlated for all elements except Ni.

Soil physical and chemical properties were used to attempt to predict E-values and %E-values for five elements (Ni, Cu, Zn, Cd and Pb). Regression modelling using soil chemical properties (pH, %LOI, total concentration, DTPA-extractable metal) gave relatively good predictions of E-values with R^2 values between modelled and measured values of 0.70, 0.72, 0.89, 0.87 and 0.78 for Ni, Cu, Zn, Cd and Pb respectively. Prediction of %E values was less successful.

7.4 Plant uptake of PTEs

PTE concentrations varied between vegetable types, typically in the order Zn>Cu>Ni>Cr> As> Pb Cd>Se. Generally, vegetables grown in the waste area contain higher concentrations of PTEs with progressively lower concentrations observed in vegetables grown in urban, peri-urban and rural areas. This confirms that the greater lability of PTEs in the waste area does result in increased PTE contents of vegetables grown in this area. Thus, the handling and disposal of municipal waste should be monitored and controlled to avoid contamination of surrounding agricultural land. The authorities should also recommend to avoid farming in the immediate vicinity of waste disposal sites or to cultivate vegetable types which accumulate low PTE concentrations, such as fruiting vegetables.

The accumulation of trace elements in different vegetables can be influenced by soil type, degree of contamination, plant species. Furthermore, different concentrations may be observed in different parts of the plant. Trace elements such as Cr and Pb have lower accumulation in plants because of their low solubility. Alse Tiwari et al. (2011) reported that Cr and Pb could not translocate to aerial parts of plants in certain circumstances. In this study, accumulation of PTEs in leafy vegetables such as leek, celery, chard and purslane was higher than in the fruiting vegetables eggplant, pepper, okra, tomato, cowpea and cucumber. Similar patterns of accumulation have also been observed by other authors (Bose and Bhattacharyya, 2008;Tiwari et al., 2011;Säumel et al., 2012).

Comparison of plant uptake of PTEs under field and controlled environmental conditions indicated that the vegetables grown in the field accumulated more PTEs in their tissues than vegetables grown in the pot trial (Fig. 7.1). This may be a consequence of stresses on the plants in the pot trial, principally relatively small pot sizes and high water losses. Other studies have demonstrated that water stress significantly reduces plant uptake of trace elements (Nahar and Gretzmacher, 2002;Keller, 2015). Limited space for root development may have affected the growth and subsequent uptake of trace elements.

7.5 Risk assessment

Human exposure to soil via ingestion, dermal exposure or inhalation did not pose a risk; all non-carcinogenic risks were estimated to be lower than 1 and within safe limits.

Non-carcinogenic and carcinogenic health risks were assessed for selected vegetables in this study. In general, HQ values were greater for plants grown adjacent to the waste disposal area and were progressively lower in urban, peri-urban and rural areas. Specifically, Ni, As, Cd may pose a health risk to children from consumption of vegetables grown in waste disposal, urban and peri urban areas while no risks were established for all PTEs for adults since the HQ values were <1. It is worth noting that the approach used to calculate risks in this study assumes an ‘equal contribution’ of each vegetable type, which may be greater than the normal daily intake of the vegetables by the local population. Hence, HQs for vegetables may have been overestimated.

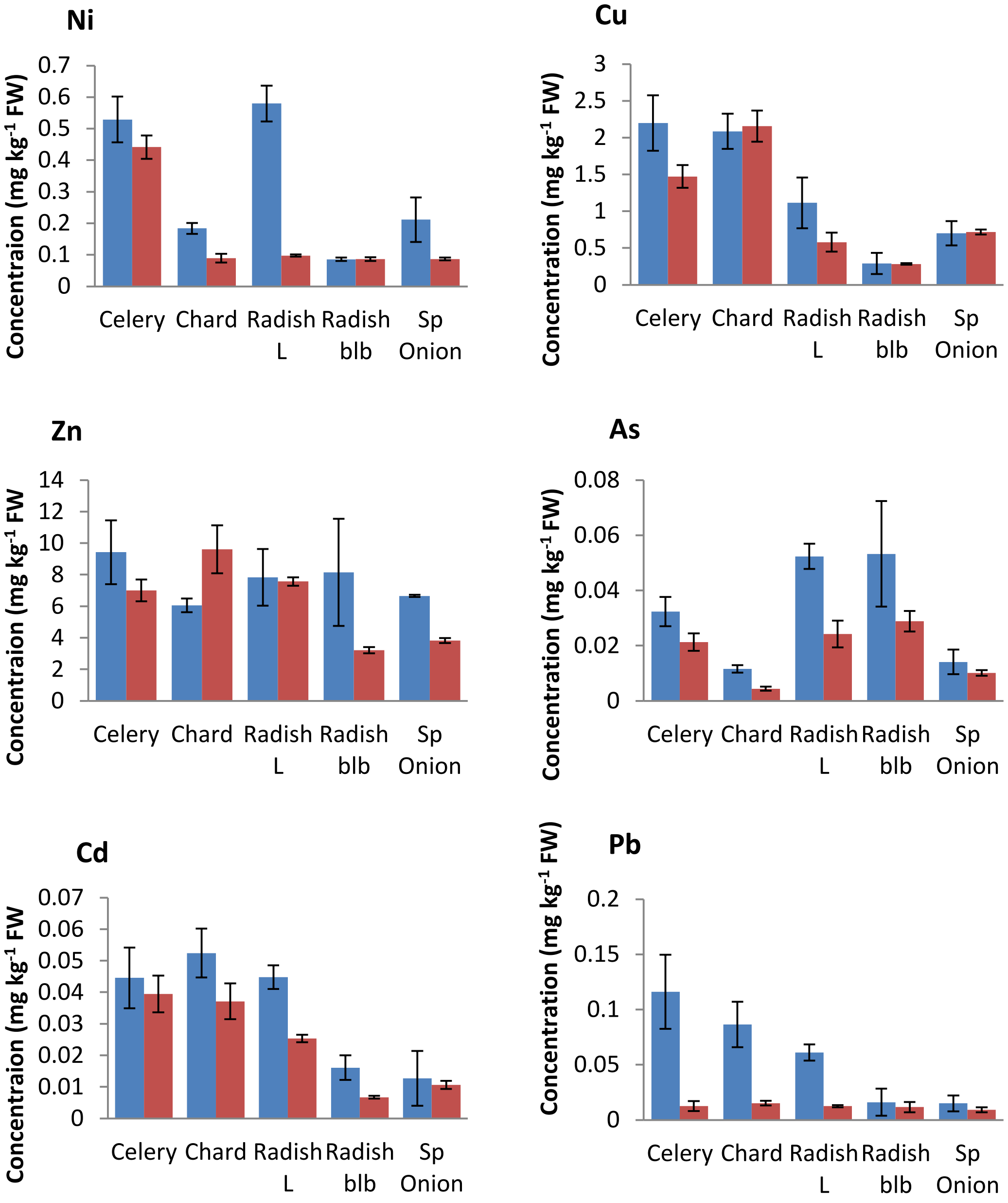


Figure 7.1 Mean concentrations of PTEs in vegetables grown in the field (blue) and in a growth room (red). The vertical bar on each histogram denotes the standard error around each mean.

7.6 Future work

Although this investigation was for one province of three in the Kurdistan region of Iraq it is reasonable to assume that the findings are applicable to other provinces because farming and waste disposal practices are similar.

The lack of local dietary information, including average daily intake for adults and children, percentage contribution of each vegetable to total dietary intake and actual body weights, is a shortcoming of this study. Actual dietary intake of foods, including vegetables, could be determined in wider dietary studies to enable future dietary exposure studies to be more precise.

Other dietary sources also need to be investigated in terms of toxicity and deficiency of trace elements. For example, rice is common in the daily diet in Kurdistan and approximately 95% of all rice is imported; thus it is important to understand whether rice consumption contributes to As exposure. Zinc and Se deficiency could also be investigated using a market basket-type survey including both imported and local foods.

Soil guideline values (SGVs) and recommended limits for PTEs in soils and vegetables used in this study may not be applicable to the Kurdish situation where the soils are calcareous and elements such as Ni exceed standards but are generally unavailable to plants. It would of significant future benefit to the population of Kurdistan to develop SGVs or similar values specific to the soils and dietary characteristics of the region, perhaps with an emphasis on calcareous soils.

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Appendices

Table A1 Soil properties and total elemental concentrations (mg kg^{-1}) in soils in Sulaymanyah (SUL) with EU/WHO and SGVs.

SUL	**LOI**	**pH**	**Na**	**Mg**	**K**	**Ca**	**Al**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Cd**	**Cs**	**Ba**	**Pb**	**U**
SOIL 1	10.0	7.33	2172	12621	7884	104956	33231	76.6	92.9	532	24731	14.3	99.0	32.3	106	4.92	0.951	267	0.387	2.91	287	12.8	1.23
SOIL 2	7.4	7.91	2215	11677	6053	130189	26529	66.9	91.2	560	21351	13.4	88.2	29.8	173	4.74	0.866	325	0.388	2.11	227	19.3	1.10
SOIL 3	10.2	8.05	2379	14001	7499	102589	33909	77.8	105	681	26457	15.8	106.5	36.8	432	5.62	0.982	263	0.389	2.77	250	22.8	1.19
SOIL 4	7.4	8.18	2854	14006	7626	102367	32770	77.1	100	672	25100	16.2	109.1	31.5	112	5.11	1.065	289	0.757	2.67	244	10.7	1.11
SOIL 5	7.8	7.88	2946	13738	7621	103206	31867	77.6	103	642	24524	16.1	109.3	29.3	79.0	4.96	0.971	290	0.238	2.56	238	9.43	1.08
SOIL 6	9.4	8.18	1784	10671	6209	108798	26784	62.6	81.1	494	20863	12.0	80.5	28.4	356	4.86	0.846	264	0.338	2.31	207	11.3	0.98
SOIL 7	7.4	8.27	2463	13958	7610	106241	32956	75.1	98.3	641	24769	15.5	106.7	29.0	136	4.89	0.949	288	0.287	2.82	234	11.8	1.10
SOIL 8	8.2	8.2	2899	14536	13164	99589	34545	80.3	108	674	25887	16.6	113.8	30.5	77.6	5.02	1.004	285	0.285	2.84	245	12.1	1.17
SOIL 9	7.6	8.33	2502	15854	8034	97961	37307	83.3	117	566	27691	16.9	116.9	31.1	278	5.80	0.985	256	0.308	3.10	250	15.2	1.20
SOIL 10	7.2	7.54	2488	11691	6356	131434	25618	66.7	96.0	550	20858	13.4	88.3	31.5	81.3	4.24	0.838	328	0.304	2.00	219	22.8	1.06
SOIL 11	8.2	8.25	2597	11372	6875	134517	27093	67.7	89.6	595	21045	13.2	88.0	28.8	81.2	4.87	0.857	327	0.358	2.15	230	13.1	1.14
SOIL 12	11.2	8.07	2531	18270	8040	88625	37063	78.6	153	471	28439	19.8	180.4	26.4	61.8	4.38	1.087	232	0.314	2.97	228	11.3	1.14
SOIL 13	10.6	8.06	2472	18536	7830	88015	36788	78.7	154	490	28385	19.9	181.8	26.7	62.3	4.71	1.061	232	0.303	2.98	224	8.03	1.13
SOIL 14	10.0	8.22	2675	18033	7855	91576	36084	76.7	149	484	27601	19.3	174.3	26.5	60.2	4.28	1.032	238	0.299	2.85	223	9.09	1.12
SOIL 15	11.0	8.81	2360	19794	7779	90842	36528	77.7	158	434	28617	20.0	193.8	27.2	61.9	3.95	1.024	243	0.287	2.95	226	7.23	1.13
SOIL 16	11.0	7.98	2280	17446	7593	100982	35929	74.4	133	492	27582	18.1	160.9	26.9	65.6	4.14	1.019	268	0.290	3.06	240	8.60	1.10
SOIL 17	10.4	7.75	2395	18112	7693	96489	37315	75.7	143	520	28535	19.1	170.4	26.8	69.0	4.23	1.038	254	0.283	3.09	243	10.1	1.13
SOIL 18	10.2	8.04	2505	17821	8053	92008	36714	72.9	145	557	28391	19.1	170.6	27.0	72.5	3.80	1.037	247	0.285	3.00	239	8.18	1.13
SOIL 19	10.8	8.23	2494	17745	8191	92742	36983	74.7	142	505	28481	18.8	166.6	28.0	71.6	3.73	1.038	255	0.324	3.09	240	8.08	1.16
SOIL 20	10.0	8.02	2841	15504	8355	93709	35776	80.4	119	639	27260	17.7	130.6	34.9	97.3	4.84	1.109	265	0.332	2.99	248	16.9	1.24
SOIL 21	9.2	8.08	2800	14242	7531	108004	31578	77.2	109	607	24846	16.1	115.6	32.6	78.8	5.23	1.025	299	0.278	2.60	229	14.8	1.18
SOIL 22	8.4	8.05	2600	13986	7258	116479	29831	74.5	103	613	23900	15.3	112.2	27.7	62.1	5.25	0.967	320	0.267	2.49	210	8.88	1.10
SOIL 23	8.4	8.09	2571	14082	7719	111572	31300	74.4	105	892	24834	16.4	119.5	28.0	69.1	5.15	0.974	305	0.268	2.68	229	10.0	1.16
SOIL 24	6.6	8.13	2609	13484	7202	120694	29189	73.5	98.0	700	23361	15.2	107.9	27.6	63.3	4.94	0.913	320	0.255	2.40	209	9.03	1.10
SOIL 25	6.6	8.15	2654	13214	6925	125069	28017	72.7	97.7	654	22759	14.7	104.6	27.9	60.2	5.03	0.963	332	0.255	2.29	201	8.88	1.14
SOIL 26	2.8	8.12	1972	9385	5096	172505	19467	59.4	74.7	643	16713	10.7	67.8	21.7	47.9	4.40	0.767	402	0.305	1.57	158	16.2	1.10
SOIL 27	10.0	8.23	2717	13461	7103	124964	27261	70.1	102	625	22487	14.8	106.3	28.0	72.7	4.86	0.952	325	0.323	2.14	201	10.8	1.12
Mean	8.8	8.08	2510	14713	7598	108745	32164	74.2	114	590	25017	16.2	124.8	29.0	110.7	4.74	0.975	286	0.322	2.64	229	12.1	1.13
Median	9.2	8.09	2505	14006	7621	103206	32956	75.1	105	595	24846	16.1	112.2	28.0	72.7	4.86	0.982	285	0.303	2.77	229	10.8	1.13
SGV									**130**				**250**	**50**	**300**	**43**	**120**		**1.8**			**450**	
EU/WHO									**100**				**50**	**100**	**300**				**3**			**100**	

Table A2 Soil properties and total elemental concentrations (mg kg-1) in soils in Halabja urban (HALU) with EU/WHO and SGVs.

HALU	LOI	pH	Na	Mg	K	Ca	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Cd	Cs	Ba	Pb	U
SOIL 1	16.6	8.13	2799	14269	11414	44502	46481	99.7	118.4	898	34263	18.8	123.1	40.3	225	11.57	1.533	150	0.610	4.41	363	26.1	1.71
SOIL 2	12.0	7.85	2246	13577	11005	62245	45012	101.8	113.9	966	33263	18.6	122.4	33.4	118	12.73	1.360	183	0.603	4.32	363	17.7	1.72
SOIL 3	11.2	7.81	2681	15242	11799	46174	49662	110.8	126	900	36222	20.3	135.2	35.9	97	13.36	1.468	143	0.558	4.80	367	15.1	1.66
SOIL 4	10.0	8.13	2599	14589	11620	56301	47898	107.5	125	915	35099	19.7	131.8	35.8	141	12.71	1.416	180	0.605	4.62	375	17.0	1.70
SOIL 5	12.4	8.11	2403	11595	11660	44264	40195	110.2	127	903	35279	20.5	137.0	39.9	121.9	13.22	1.354	139	0.607	3.25	365	16.24	1.73
SOIL 6	10.2	8.07	2651	12171	11805	34033	40175	115.3	133.4	889	36387	21.6	144.2	38.8	96	14.23	1.331	115	0.554	3.36	363	14.1	1.67
SOIL 7	11.8	7.91	2445	11295	11239	36716	37904	114.0	132.9	867	35770	21.3	143.3	39.4	101	13.72	1.291	117	0.560	3.10	356	14.3	1.64
SOIL 8	11.0	8.02	2480	12215	11325	36024	40014	112.9	132	870	35998	21.2	141.6	37.1	101.2	13.60	1.273	120	0.534	3.33	359	14.4	1.67
SOIL 9	10.6	7.99	2528	11625	11632	37798	38889	114.4	133	870	36177	21.4	145.2	38.4	101	13.90	1.242	122	0.550	3.11	361	14.5	1.66
SOIL 10	14.0	8.13	2526	10935	10428	61060	37615	96.1	114.8	773	31463	17.7	115.9	42.2	206.4	11.52	1.437	164	0.703	3.09	350	24.4	1.73
SOIL 11	10.0	8.09	2354	11247	11186	55292	38934	107.6	123.1	890	33490	20.2	133.6	34.6	86.9	13.88	1.353	145	0.544	3.04	339	12.6	1.68
SOIL 12	10.8	7.92	2432	12768	11433	46721	42431	115.4	131	950	35974	20.9	138.1	35.2	88.9	15.02	1.441	134	0.566	3.44	352	13.4	1.71
SOIL 13	10.0	8.05	2415	11758	11349	51070	40284	114.2	133	911	35765	21.2	140.9	40.0	86.2	14.45	1.386	130	0.562	3.11	347	13.04	1.69
SOIL 14	9.0	8.03	2477	11332	11170	56587	38511	108.9	127	877	33821	20.4	132.4	37.4	86.6	13.67	1.335	150	0.554	2.99	337	12.70	1.76
SOIL 15	13.0	8	2464	12903	11416	44770	41526	109.5	130	890	35278	20.1	134.6	38.5	137.1	13.61	1.431	139	0.568	3.41	370	16.36	1.73
SOIL 16	10.0	7.59	2474	11781	11002	52934	40521	111.8	128	857	35065	20.1	132.8	35.3	103.0	14.55	1.418	151	0.572	3.20	384	14.67	1.80
SOIL 17	11.8	8.17	2551	12579	11597	38644	40675	110.8	134	862	36069	20.4	135.6	37.3	136.6	14.00	1.421	133	0.594	3.40	377	17.5	1.76
SOIL 18	9.6	7.93	2597	11022	10979	55687	38664	110.6	127	885	34650	19.8	130.2	35.9	94.7	15.30	1.397	159	0.610	3.02	377	14.09	1.84
SOIL 19	10.2	8.04	2351	11694	10600	49015	40184	116.7	133	893	35967	20.7	138.7	36.5	90.5	15.66	1.363	143	0.594	3.11	390	13.85	1.76
SOIL 20	9.4	8.15	2619	13458	11423	55918	42274	108.2	126	875	34738	19.8	131.7	33.8	100.8	13.09	1.396	151	0.538	3.46	347	14.2	1.71
SOIL 21	9.4	8.13	2714	13428	12120	56350	41404	105.8	126	869	34732	20.0	131.3	35.0	91.5	12.33	1.365	152	0.517	3.34	345	14.0	1.73
SOIL 22	9.8	8.14	2972	13301	12537	52733	41240	104.1	130	804	34616	20.1	133.4	36.5	90.5	11.78	1.361	160	0.496	3.20	328	13.92	1.74
SOIL 23	9.2	8.3	2900	12462	12515	54364	39454	101.9	127	801	33777	19.6	129.2	34.7	90.8	11.47	1.336	159	0.485	2.93	322	13.1	1.73
SOIL 24	11.4	8.33	2542	12446	12351	41202	40227	114.8	137.0	880	36112	21.2	141.3	35.8	98.3	13.83	1.344	121	0.515	3.12	346	13.80	1.64
Mean	11.0	8.04	2551	12487	11484	48767	41257	109.3	127.8	879	34999	20.2	134.3	37.0	112.1	13.47	1.377	144	0.567	3.42	358	15.47	1.72
Median	10.4	8.06	2527	12331	11419	50043	40256	110.4	127.6	882	35188	20.3	134.1	36.5	99.4	13.64	1.364	144	0.561	3.23	360	14.24	1.72
SGV									**130**				**250**	**50**	**300**	**43**	**120**		**1.8**			**450**	
EU/WHO									**100**				**50**	**100**	**300**				**3**			**100**	

Table A3 Soil properties and total elemental concentrations (mg kg^{-1}) in soils in Halabja peri-urban (HALP) with EU/WHO and SGVs.

HALP	**LOI**	**pH**	**Na**	**Mg**	**K**	**Ca**	**Al**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Cd**	**Cs**	**Ba**	**Pb**	**U**
SOIL 1	10.8	8.15	3457	19505	13251	61788	60644	106.0	130.1	840	33512	20.2	136.4	33.8	93	11.45	1.047	152	0.454	5.08	401	14.3	1.51
SOIL 2	11.6	8.37	2960	15522	11205	83959	50019	97.8	122.3	739	30275	18.6	118.9	29.9	83	10.54	0.942	172	0.383	3.97	426	12.5	1.44
SOIL 3	11.6	8.28	2951	15674	12112	53198	52955	102.8	128	814	32750	19.9	132.2	33.5	98	11.59	1.066	142	0.440	4.33	448	14.7	1.50
SOIL 4	11.4	8.16	2985	15977	11982	42852	50771	101.0	126	803	32548	20.4	134.0	33.3	93	11.40	0.979	126	0.437	4.50	391	13.8	1.49
SOIL 5	10.6	8.11	3592	16147	12462	66802	48587	96.5	118	755	31601	18.9	123.7	30.9	87.0	10.56	1.065	155	0.408	4.14	342	12.40	1.44
SOIL 6	11.0	7.83	3133	15999	11885	51940	49998	99.0	123.7	791	31628	19.7	128.6	33.2	87	10.88	0.965	134	0.422	4.29	369	13.1	1.48
SOIL 7	12.6	8.08	3068	13616	10765	73793	45064	91.7	110.9	731	28837	17.3	114.6	31.5	95	10.99	0.908	194	0.475	3.80	432	16.2	1.47
SOIL 8	10.2	8.02	2655	13151	9833	97852	38847	80.7	99	588	25429	15.4	99.5	30.1	79.5	9.23	0.695	212	0.393	3.47	331	13.0	1.33
SOIL 9	10.2	7.99	1656	8054	7035	156558	25637	58.7	73	471	17774	11.0	65.9	20.8	68	6.92	0.810	275	0.386	2.34	374	8.0	1.15
Mean	11.1	8.11	2940	14849	11170	76527	46947	92.7	114	726	29373	17.9	117.1	30.8	87	10.40	0.942	174	0.422	3.99	390	13.1	1.42
Median	11.0	8.11	2985	15674	11885	66802	49998	97.8	122	755	31601	18.9	123.7	31.5	87	10.88	0.965	155	0.422	4.14	391	13.1	1.47
SGV									**130**				**250**	**50**	**300**	**43**	**120**		**1.8**			**450**	
EU/WHO									**100**				**50**	**100**	**300**				**3**			**100**	

Table A4 Soil properties and total elemental concentrations (mg kg^{-1}) in soils in Halabja waste disposal (HALW) with EU/WHO and SGVs.

HALW	**LOI**	**pH**	**Na**	**Mg**	**K**	**Ca**	**Al**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Cd**	**Cs**	**Ba**	**Pb**	**U**
SOIL 1	12.0	8.13	6189	10398	9510	152785	31317	64.3	121.9	564	22592	11.9	74.1	168.6	563	12.28	0.690	345	3.726	2.49	442	171.3	1.17
SOIL 2	12.4	8.25	4748	11354	11031	110039	34608	69.0	106.0	742	31254	14.1	86.5	178.7	940	9.20	0.778	273	2.812	2.76	433	141.2	1.18
SOIL 3	16.6	7.91	2911	9217	7636	124981	27522	53.6	175	649	26508	11.5	64.1	441.5	815	7.37	0.814	351	6.033	2.11	656	171.4	1.24
Mean	13.7	8.10	4616	10323	9393	129269	31149	62.3	134	651	26785	12.5	74.9	262.9	773	9.61	0.761	323	4.190	2.45	511	161.3	1.20
Median	12.4	8.13	4748	10398	9510	124981	31317	64.3	122	649	26508	11.9	74.1	178.7	815	9.20	0.778	345	3.726	2.49	442	171.3	1.18
SGV									**130**				**250**	**50**	**300**	**43**	**120**		**1.8**			**450**	
EU/WHO									**100**				**50**	**100**	**300**				**3**			**100**	

Table A5 Soil properties and total elemental concentrations (mg kg^{-1}) in soils in Sirwan (SIR) with EU/WHO and SGVs.

SIR	**LOI**	**pH**	**Na**	**Mg**	**K**	**Ca**	**Al**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Cd**	**Cs**	**Ba**	**Pb**	**U**
SOIL 1	9.8	8.14	2612	15141	10076	93811	38572	84.6	109.6	562	26389	17.2	121.4	29.8	75	6.29	0.694	237	0.346	3.18	259	10.7	1.26
SOIL 2	7.8	8.21	2600	14655	8835	110178	35902	77.6	100.1	577	24466	16.0	108.3	24.2	63	7.12	0.595	227	0.324	3.01	251	17.3	1.18
SOIL 3	10.0	8.15	3396	15501	11930	51871	47727	92.9	126	659	31345	19.6	134.9	32.8	84	8.15	0.788	167	0.314	3.87	320	13.3	1.43
SOIL 4	10.8	8.19	3288	15430	12452	33476	49645	100.3	135	794	33177	21.1	141.6	34.6	86	9.75	0.847	121	0.361	3.96	344	12.9	1.40
SOIL 5	9.0	8.13	2069	15669	9267	103204	40965	86.1	111	542	26595	16.5	120.9	31.1	80.8	5.82	0.759	261	0.430	3.48	249	11.92	1.34
SOIL 6	7.4	8.25	2143	14111	7420	131277	38913	70.1	96.8	568	24193	15.7	105.8	24.0	58	6.18	0.641	221	0.342	3.31	214	7.9	1.12
SOIL 7	8.8	8.18	2754	13501	9751	86635	37057	74.0	99.0	508	24973	15.9	103.9	27.1	69	6.19	0.659	214	0.341	3.31	285	9.9	1.28
SOIL 8	8.8	8.04	1714	11109	6302	147184	26032	55.8	74	354	17458	11.2	74.5	20.8	52.2	3.27	0.835	403	0.279	2.41	247	7.0	1.09
SOIL 9	11.0	8.09	2613	12902	9347	88944	34390	68.4	94	449	23282	14.8	98.5	29.1	77	5.06	0.841	262	0.352	3.18	306	9.9	1.30
SOIL 10	7.6	8.12	2594	14504	7884	98219	32869	76.2	102.4	564	23221	15.8	111.6	28.4	68.6	5.07	0.662	255	0.346	2.73	220	10.2	1.24
SOIL 11	8.4	8.17	2564	15343	7907	108689	33560	77.0	107.4	505	23283	15.7	115.6	27.8	70.4	4.23	0.629	285	0.311	2.65	223	10.5	1.23
SOIL 12	8.4	8.21	2484	15520	8212	96169	35040	79.4	108	567	24671	16.2	121.0	30.1	73.7	5.72	0.645	258	0.341	2.87	234	11.2	1.25
SOIL 13	8.4	8.17	2328	16369	8789	97156	37780	85.0	115	564	26387	17.1	163.4	34.2	96.7	5.91	0.671	258	0.376	3.15	245	35.10	1.32
SOIL 14	9.4	8.17	1999	14366	8859	81499	35435	84.1	111	547	25932	17.3	153.7	32.4	91.6	5.76	0.700	224	0.399	3.03	239	32.08	1.41
SOIL 15	8.6	7.88	1800	12613	7325	98780	30871	71.7	92	515	22007	14.7	126.5	25.8	75.3	5.39	0.748	283	0.311	2.68	229	26.60	1.20
SOIL 16	10.0	8.15	1982	12148	8034	82755	34483	78.4	101	569	23857	17.0	141.9	30.4	83.6	5.47	0.858	201	0.366	2.77	237	30.20	1.25
SOIL 17	6.8	8.17	1492	9133	6630	74171	27714	65.9	80	442	19583	13.0	112.1	24.7	68.2	4.93	0.648	154	0.298	2.25	186	28.1	1.00
SOIL 18	9.2	8.2	1927	13734	8120	92595	32591	78.6	105	553	24336	16.3	152.6	29.4	86.3	6.04	0.717	262	0.352	2.84	239	32.09	1.28
SOIL 19	9.6	8.2	1310	7890	4337	106588	15995	44.9	59	356	12634	8.5	95.4	15.7	42.8	4.37	0.340	213	0.200	1.25	123	28.64	0.79
SOIL 20	3.4	8.23	2611	14234	6998	111439	27292	71.8	108	543	21051	15.4	152.6	26.0	75.2	4.37	0.610	284	0.285	2.11	205	32.9	1.13
SOIL 21	7.0	8.14	2943	14443	6573	115664	25267	68.8	112	660	19740	14.6	137.5	23.3	63.5	5.22	0.596	257	0.335	1.79	177	29.5	1.14
SOIL 22	6.8	8.22	2900	14543	6469	114350	25730	68.5	111	655	19791	14.5	142.5	23.9	66.4	5.32	0.638	258	0.338	1.86	178	31.17	1.16
SOIL 23	10.2	8.08	2050	16370	8630	89058	37849	83.9	118	558	26948	17.4	183.4	32.7	100.8	5.99	0.699	251	0.367	3.26	248	42.4	1.37
SOIL 24	8.0	8.12	2286	15494	8078	98383	34389	79.0	110.3	537	24862	16.5	171.9	29.6	91.4	5.13	0.727	286	0.335	2.95	243	39.58	1.32
Mean	8.6	8.15	2353	13947	8259	96337	34003	76.0	103.5	548	23758	15.8	128.8	27.8	75.0	5.70	0.690	244	0.335	2.83	238	21.70	1.23
Median	8.7	8.17	2406	14474	8099	97688	34436	77.3	107.6	555	24265	15.9	123.9	28.7	75.2	5.59	0.683	256	0.341	2.91	239	21.93	1.25
SGV									**130**				**250**	**50**	**300**	**43**	**120**		**1.8**			**450**	
EU/WHO									**100**				**50**	**100**	**300**				**3**			**100**	

Table A6 Soil properties and total elemental concentrations (mg kg-1) in soils in Khurmal (KHR) with EU/WHO and SGVs

KHR	LOI	pH	Na	Mg	K	Ca	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Cd	Cs	Ba	Pb	U
SOIL 1	7.2	7.94	2712	9197	7590	166257	30575	63.6	66.2	558	24239	13.1	84.1	24.0	69	15.40	1.316	124	0.340	3.09	151	20.0	1.03
SOIL 2	10.0	7.9	2924	9994	8205	149685	34133	69.7	75.1	488	26275	13.6	94.6	26.6	105	14.88	1.494	125	0.361	3.26	167	24.3	1.16
SOIL 3	11.0	7.85	2847	10144	8585	150825	34624	70.2	78	513	26768	14.0	78.8	28.4	110	13.81	1.540	120	0.383	3.39	171	17.2	1.15
SOIL 4	8.2	7.8	2384	8431	6520	169178	26262	54.9	59	334	21894	10.7	57.0	24.2	114	10.21	1.226	122	0.321	2.76	125	14.3	1.01
SOIL 5	7.4	7.77	2845	9332	7666	156877	30698	62.1	68	449	24310	13.0	64.0	28.0	109.7	11.73	1.359	119	0.353	3.10	154	13.71	1.08
SOIL 6	8.8	7.9	2871	10539	9156	121006	36822	74.4	82.3	677	28325	15.6	76.9	33.6	89	12.10	1.468	109	0.368	3.11	185	12.6	1.20
SOIL 7	11.0	8.21	2975	13807	11382	55124	50966	95.5	108.4	943	36390	20.3	112.0	35.2	87	15.53	1.741	100	0.367	4.43	254	15.3	1.34
SOIL 8	10.2	8.13	2718	12659	11056	45840	48077	94.9	107	946	36653	20.5	121.9	35.9	94.3	14.27	1.634	98	0.415	4.43	270	19.0	1.36
Mean	9.2	7.94	2785	10513	8770	126849	36520	73.1	80	614	28107	15.1	86.1	29.5	97.2	13.49	1.472	115	0.363	3.45	185	17.1	1.17
Median	9.4	7.9	2846	10069	8395	150255	34379	69.9	76	536	26522	13.8	81.5	28.2	99.5	14.04	1.481	119	0.364	3.18	169	16.2	1.15
SGV									**130**				**250**	**50**	**300**	**43**	**120**		**1.8**			**450**	
EU/WHO									**100**				**50**	**100**	**300**				**3**			**100**	

Table A7 Soil properties and total elemental concentrations (mg kg-1) in soils in Kalar-Grdagozina (KALG) with EU/WHO and SGVs

KALG	LOI	pH	Na	Mg	K	Ca	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Cd	Cs	Ba	Pb	U
SOIL 1	8.0	8.13	2961	13993	7826	97758	28766	65.5	81.6	482	19918	12.5	132.2	21.6	72	6.22	0.564	361	0.214	2.51	242	38.3	1.17
SOIL 2	7.2	8.09	3254	13457	7542	88229	28143	63.9	81.0	510	19880	12.4	137.6	21.4	73	6.37	0.599	338	0.228	2.47	248	42.0	1.16
SOIL 3	9.8	7.92	2961	13478	7185	90875	28348	59.9	74	476	18842	11.3	128.2	20.6	72	6.07	0.593	352	0.239	2.48	243	41.1	1.12
SOIL 4	10.6	8.05	3431	15464	8814	100348	31661	65.7	81	546	22089	12.4	139.8	22.4	80	6.53	1.025	363	0.248	2.51	242	42.7	1.11
SOIL 5	10.0	8.03	3170	15681	7842	110093	29221	66.5	81	560	22404	12.7	143.7	22.1	79.7	6.71	1.037	411	0.218	2.37	241	43.16	1.15
SOIL 6	6.6	8	2796	15934	8477	101776	33306	70.8	85.3	590	24663	13.9	155.8	23.6	81	7.20	1.037	363	0.232	2.91	268	44.5	1.45
SOIL 7	10.8	7.59	3097	15084	8540	112375	33041	69.4	79.4	551	23293	12.7	146.8	22.8	82	7.06	1.105	420	0.265	2.65	274	44.2	1.44
SOIL 8	5.8	8.17	3680	15632	8375	125736	32676	66.8	82	527	22289	11.9	140.8	20.5	73.2	6.37	0.990	369	0.216	2.27	227	43.3	1.08
SOIL 9	9.6	7.93	4735	16510	9067	140216	34450	69.6	81	550	22508	11.6	150.3	22.8	90	6.02	1.128	439	0.235	2.25	235	48.9	1.15
SOIL 10	8.8	8.04	4865	13174	9392	128070	29681	61.4	74.3	496	19541	9.8	137.3	18.7	74.0	5.53	0.899	385	0.187	1.83	225	48.1	0.96
SOIL 11	9.2	8.15	3854	20349	10810	123237	40798	78.4	95.2	643	26750	14.5	177.0	25.3	91.4	6.65	1.208	395	0.226	2.87	282	51.6	1.31
Mean	8.8	8.01	3528	15342	8534	110792	31826	67.1	81.3	539	22016	12.3	144.5	22.0	78.9	6.43	0.926	381	0.228	2.47	248	44.4	1.19
Median	9.2	8.04	3254	15464	8477	110093	31661	66.5	81.0	546	22289	12.4	140.8	22.1	79.7	6.37	1.025	369	0.228	2.48	242	43.3	1.15
SGV									**130**				**250**	**50**	**300**	**43**	**120**		**1.8**			**450**	
EU/WHO									**100**				**50**	**100**	**300**				**3**			**100**	

Table A8 Soil properties and total elemental concentrations (mg/kg) in soils in Kalar-Riverside (KALR) with EU/WHO and SGVs.

KALR	**LOI**	**pH**	**Na**	**Mg**	**K**	**Ca**	**Al**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Cd**	**Cs**	**Ba**	**Pb**	**U**
SOIL 1	11.2	8.13	4589	20588	11318	102204	44603	84.2	111.3	605	29800	15.5	191.4	37.0	269	5.41	1.274	306	0.415	3.26	257	89.4	1.46
SOIL 2	7.6	8.14	4794	21820	11626	112392	46240	89.2	112.6	547	30141	16.2	196.7	28.3	127	5.50	1.171	318	0.261	3.37	230	62.7	1.27
SOIL 3	8.2	8.3	6034	21597	11047	114814	46692	91.8	111	544	29527	15.5	192.3	26.1	114	5.49	1.190	315	0.248	3.22	225	63.9	1.19
SOIL 4	5.8	8.33	6841	19721	10325	115118	43425	84.5	100	545	27366	13.9	178.7	23.3	96	5.82	1.115	316	0.208	2.80	226	57.1	1.11
SOIL 5	4.8	8.15	7397	17678	9797	114467	39489	81.9	97.0	510	25646	12.8	166.8	22.9	103.9	4.75	1.094	339	0.194	2.41	224	55.97	1.11
SOIL 6	6.6	8.13	5367	18663	10285	125162	38723	79.3	100.2	600	26146	14.0	182.2	25.5	102	6.09	1.205	344	0.241	2.71	227	56.8	1.23
SOIL 7	3.8	8.37	8183	17412	9789	118572	38415	84.5	102.6	562	26098	13.0	172.2	21.2	90	6.05	1.134	328	0.167	2.23	223	57.2	0.99
SOIL 8	6.0	8.28	7948	17655	10216	123463	38767	83.8	102	591	25976	13.2	175.9	22.1	89.8	6.35	1.153	332	0.156	2.31	227	57.5	1.04
SOIL 9	4.6	8.25	8262	18211	10376	118948	40104	85.0	103	592	26573	13.6	181.6	22.3	92	6.75	1.148	330	0.161	2.44	230	58.0	0.99
SOIL 10	5.2	8.16	7289	19367	10697	117427	41799	88.8	108.1	589	28003	14.7	191.6	24.1	98.3	6.79	1.160	329	0.184	2.77	231	57.1	1.03
SOIL 11	9.0	8.11	2460	21488	11543	110660	43512	88.1	116.9	503	29843	17.0	200.6	36.1	170.2	5.92	1.225	294	0.365	3.44	232	77.7	1.29
Mean	6.6	8.21	6288	19473	10638	115748	41979	85.6	106.0	563	27738	14.5	184.5	26.3	122.9	5.90	1.170	323	0.236	2.81	230	63.0	1.16
Media	6.0	8.16	6841	19367	10376	115118	41799	84.5	103.0	562	27366	14.0	182.2	24.1	101.9	5.92	1.160	328	0.208	2.77	227	57.5	1.11
SGV									**130**				**250**	**50**	**300**	**43**	**120**		**1.8**			**450**	
EU/WHO									**100**				**50**	**100**	**300**				**3**			**100**	

Table A9 correlation coefficients between trace element concentrations and soil properties in Sulaymanyah (SUL), bold values denote significance at the level p<0.01.

	LOI	**pH**	**Na**	**Mg**	**K**	**Ca**	**Al**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Mo**	**Cd**	**Cs**	**Ba**	**Pb**	**U**
LOI																								
pH	0.04																							
Na	0.20	**0.25**																						
Mg	-0.20	**0.22**	**0.86**																					
K	**0.26**	**0.25**	**0.98**	**0.82**																				
Ca	-0.10	**-0.27**	**-0.96**	**-0.94**	**-0.94**																			
Al	0.00	-0.21	**-0.95**	**-0.93**	**-0.93**	**0.94**																		
V	-0.09	0.18	**0.91**	**0.95**	**0.86**	**-0.94**	**-0.94**																	
Cr	0.19	**0.25**	**0.99**	**0.88**	**0.99**	**-0.97**	**-0.97**	**0.91**																
Mn	-0.06	-0.21	**-0.95**	**-0.94**	**-0.93**	**0.97**	**0.97**	**-0.94**	**-0.97**															
Fe	0.00	-0.21	**-0.96**	**-0.93**	**-0.93**	**0.95**	**1.00**	**-0.94**	**-0.97**	**0.98**														
Co	0.21	**0.25**	**0.94**	**0.83**	**0.91**	**-0.93**	**-0.87**	**0.89**	**0.92**	**-0.90**	**-0.87**													
Ni	**0.28**	-0.12	**-0.63**	**-0.69**	**-0.62**	**0.61**	**0.78**	**-0.66**	**-0.67**	**0.66**	**0.78**	**-0.43**												
Cu	-0.05	**-0.27**	**-0.96**	**-0.94**	**-0.94**	**0.98**	**0.98**	**-0.94**	**-0.97**	**0.99**	**0.98**	**-0.91**	**0.67**											
Zn	0.00	-0.03	**-0.71**	**-0.67**	**-0.68**	**0.68**	**0.69**	**-0.67**	**-0.69**	**0.70**	**0.69**	**-0.68**	**0.35**	**0.75**										
As	-0.13	**0.22**	**0.90**	**0.99**	**0.86**	**-0.96**	**-0.96**	**0.97**	**0.92**	**-0.96**	**-0.96**	**0.87**	**-0.71**	**-0.96**	**-0.68**									
Se	-0.14	-0.08	**-0.30**	**-0.27**	**-0.32**	**0.29**	**0.30**	-0.22	**-0.32**	**0.30**	**0.30**	**-0.27**	0.22	**0.30**	0.21	**-0.27**								
Sr	-0.10	**-0.26**	**-0.96**	**-0.94**	**-0.94**	**1.00**	**0.95**	**-0.94**	**-0.97**	**0.98**	**0.96**	**-0.93**	**0.63**	**0.98**	**0.67**	**-0.96**	**0.30**							
Mo	**0.23**	0.12	**0.92**	**0.81**	**0.92**	**-0.90**	**-0.90**	**0.85**	**0.94**	**-0.91**	**-0.90**	**0.86**	**-0.63**	**-0.89**	**-0.63**	**0.85**	**-0.29**	**-0.91**						
Cd	0.15	**0.23**	**0.99**	**0.90**	**0.98**	**-0.97**	**-0.97**	**0.93**	**1.00**	**-0.97**	**-0.98**	**0.93**	**-0.67**	**-0.98**	**-0.69**	**0.93**	**-0.31**	**-0.98**	**0.93**					
Cs	-0.13	0.13	**0.79**	**0.88**	**0.75**	**-0.85**	**-0.83**	**0.86**	**0.80**	**-0.84**	**-0.84**	**0.84**	**-0.53**	**-0.84**	**-0.59**	**0.88**	**-0.30**	**-0.85**	**0.75**	**0.83**				
Ba	-0.03	**-0.27**	**-0.96**	**-0.94**	**-0.94**	**0.97**	**0.99**	**-0.95**	**-0.98**	**0.99**	**0.99**	**-0.90**	**0.70**	**0.99**	**0.70**	**-0.97**	**0.30**	**0.98**	**-0.89**	**-0.98**	**-0.84**			
Pb	-0.25	-0.25	-0.18	-0.29	-0.05	**0.46**	-0.29	-0.18	-0.22	0.14	-0.22	-0.29	**-0.33**	**0.56**	**0.38**	0.14	-0.29	**0.37**	0.01	-0.01	**-0.32**	0.04		
U	0.19	-0.09	0.31	**0.41**	0.30	-0.13	**0.60**	**0.71**	0.32	0.28	**0.60**	**0.43**	0.29	**0.53**	0.01	**0.54**	**0.42**	-0.08	**0.44**	0.08	**0.61**	**0.83**	0.16	

Table A10 correlation coefficients between trace element concentrations and soil properties in Halabja urban (HALU), bold values denote significance at the level p<0.01.

	LOI	**pH**	**Na**	**Mg**	**K**	**Ca**	**Al**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Mo**	**Cd**	**Cs**	**Ba**	**Pb**	**U**
LOI																								
pH	0.04																							
Na	-0.05	**0.39**																						
Mg	0.15	0.03	**0.46**																					
K	**-0.23**	**0.47**	**0.68**	**0.42**																				
Ca	-0.23	-0.04	0.02	0.09	-0.22																			
Al	0.22	-0.15	**0.26**	**0.94**	0.21	0.13																		
V	**-0.38**	**-0.25**	**-0.32**	-0.17	0.05	**-0.58**	-0.12																	
Cr	**-0.38**	0.11	0.07	-0.14	**0.40**	**-0.65**	**-0.24**	**0.84**																
Mn	0.04	**-0.32**	**-0.45**	**0.36**	-0.12	-0.05	**0.51**	**0.43**	0.04															
Fe	-0.18	-0.12	0.03	**0.24**	**0.34**	**-0.69**	0.22	**0.86**	**0.83**	**0.43**														
Co	**-0.41**	-0.05	-0.11	-0.16	**0.32**	**-0.68**	-0.19	**0.91**	**0.90**	**0.27**	**0.85**													
Ni	**-0.36**	-0.05	-0.14	-0.16	**0.30**	**-0.72**	-0.18	**0.91**	**0.89**	**0.25**	**0.85**	**0.98**												
Cu	**0.36**	0.07	0.06	-0.13	-0.07	-0.19	-0.09	0.05	0.12	-0.06	0.09	0.10	0.12											
Zn	**0.87**	0.16	0.13	0.19	**-0.27**	0.06	**0.25**	**-0.59**	**-0.54**	-0.14	**-0.39**	**-0.64**	**-0.60**	**0.37**										
As	**-0.34**	**-0.42**	**-0.54**	**-0.35**	**-0.35**	**-0.29**	-0.21	**0.85**	**0.56**	**0.46**	**0.57**	**0.63**	**0.60**	-0.04	**-0.50**									
Se	**0.41**	-0.08	0.20	**0.45**	-0.12	**0.26**	**0.52**	**-0.29**	**-0.32**	0.14	-0.11	**-0.44**	**-0.45**	0.04	**0.50**	-0.13								
Sr	-0.02	-0.04	0.17	**0.35**	-0.12	**0.88**	**0.39**	**-0.68**	**-0.71**	0.01	**-0.61**	**-0.77**	**-0.79**	-0.17	**0.28**	**-0.44**	**0.35**							
Mo	0.23	-0.12	**-0.35**	-0.14	**-0.46**	0.19	-0.02	-0.12	**-0.27**	0.09	**-0.27**	**-0.28**	**-0.28**	0.14	**0.24**	0.09	**0.28**	0.10						
Cd	**0.51**	-0.18	**-0.33**	-0.14	**-0.62**	0.20	0.05	-0.21	**-0.39**	0.12	**-0.26**	**-0.41**	**-0.39**	**0.50**	**0.64**	0.04	**0.34**	**0.28**	**0.45**					
Cs	**0.35**	-0.20	0.15	**0.86**	0.06	0.09	**0.95**	-0.21	**-0.38**	**0.49**	0.11	**-0.29**	**-0.26**	-0.07	**0.38**	**-0.26**	**0.48**	**0.39**	0.04	0.18				
Ba	0.22	**-0.47**	**-0.33**	0.09	**-0.44**	-0.20	**0.26**	**0.37**	0.11	**0.40**	**0.39**	0.09	0.12	0.14	0.20	**0.52**	0.21	0.00	0.08	**0.49**	**0.31**			
Pb	**0.86**	0.09	0.13	0.22	**-0.28**	0.09	**0.29**	**-0.60**	**-0.58**	-0.11	**-0.38**	**-0.66**	**-0.62**	**0.35**	**0.97**	**-0.50**	**0.49**	**0.31**	**0.25**	**0.65**	**0.42**	0.20		
U	-0.12	**-0.18**	0.14	-0.01	-0.18	**0.47**	0.02	-0.12	-0.12	0.00	-0.14	**-0.28**	**-0.35**	0.11	0.09	0.15	**0.30**	**0.50**	0.02	**0.35**	-0.07	**0.33**	0.09	

Table A11 correlation coefficients between trace element concentrations and soil properties in Halabja peri-urban (HALP), bold values denote significance at the level $p<0.01$.

	LOI	**pH**	**Na**	**Mg**	**K**	**Ca**	**Al**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Mo**	**Cd**	**Cs**	**Ba**	**Pb**	**U**
LOI																								
pH	**0.41**																							
Na	0.34	0.37																						
Mg	0.32	**0.43**	**0.87**																					
K	0.38	0.45	**0.91**	**0.97**																				
Ca	**-0.47**	**-0.41**	**-0.78**	**-0.85**	**-0.92**																			
Al	**0.40**	**0.48**	**0.82**	**0.98**	**0.97**	**-0.88**																		
V	**0.46**	**0.50**	**0.83**	**0.94**	**0.97**	**-0.94**	**0.98**																	
Cr	**0.44**	**0.50**	**0.81**	**0.94**	**0.96**	**-0.94**	**0.97**	**1.00**																
Mn	**0.46**	**0.45**	**0.80**	**0.92**	**0.96**	**-0.94**	**0.97**	**0.99**	**0.98**															
Fe	**0.43**	**0.47**	**0.88**	**0.94**	**0.98**	**-0.95**	**0.96**	**0.99**	**0.99**	**0.98**														
Co	**0.44**	**0.46**	**0.81**	**0.93**	**0.96**	**-0.97**	**0.95**	**0.99**	**0.99**	**0.98**	**0.99**													
Ni	**0.43**	**0.45**	**0.82**	**0.94**	**0.97**	**-0.97**	**0.96**	**0.99**	**0.99**	**0.99**	**0.99**	**0.99**												
Cu	**0.44**	0.38	**0.73**	**0.82**	**0.87**	**-0.92**	**0.85**	**0.89**	**0.88**	**0.87**	**0.88**	**0.89**	**0.91**											
Zn	**0.52**	**0.39**	**0.70**	**0.73**	**0.81**	**-0.87**	**0.81**	**0.85**	**0.83**	**0.88**	**0.85**	**0.83**	**0.87**	**0.87**										
As	**0.52**	**0.47**	**0.82**	**0.87**	**0.93**	**-0.95**	**0.92**	**0.97**	**0.96**	**0.96**	**0.97**	**0.96**	**0.96**	**0.91**	**0.93**									
Se	0.20	0.16	**0.70**	**0.56**	**0.64**	**-0.50**	**0.58**	**0.57**	**0.57**	**0.61**	**0.64**	**0.56**	**0.57**	**0.40**	**0.54**	**0.60**								
Sr	**-0.41**	**-0.41**	**-0.77**	**-0.87**	**-0.92**	**0.97**	**-0.88**	**-0.94**	**-0.95**	**-0.94**	**-0.96**	**-0.98**	**-0.97**	**-0.86**	**-0.78**	**-0.91**	**-0.57**							
Mo	0.15	0.20	**0.40**	**0.39**	**0.43**	-0.31	**0.39**	0.36	0.35	0.36	0.37	0.34	0.35	**0.42**	0.36	**0.43**	**0.40**	-0.30						
Cd	0.23	0.04	**0.40**	0.35	**0.41**	**-0.46**	**0.41**	**0.41**	**0.38**	**0.48**	**0.42**	**0.39**	**0.43**	**0.56**	**0.70**	**0.56**	**0.43**	-0.34	**0.48**					
Cs	0.35	**0.41**	**0.81**	**0.98**	**0.96**	**-0.90**	**0.98**	**0.96**	**0.95**	**0.96**	**0.95**	**0.95**	**0.97**	**0.86**	**0.80**	**0.91**	**0.54**	**-0.90**	0.37	**0.43**				
Ba	**0.43**	0.36	0.07	0.19	0.22	-0.26	0.38	**0.38**	**0.39**	**0.43**	0.32	0.32	0.33	0.24	**0.54**	**0.45**	0.31	-0.22	0.12	**0.41**	0.28			
Pb	**0.56**	**0.44**	**0.63**	**0.64**	**0.69**	**-0.78**	**0.71**	**0.75**	**0.72**	**0.74**	**0.73**	**0.71**	**0.75**	**0.85**	**0.91**	**0.84**	0.24	**-0.63**	0.34	**0.65**	**0.70**	**0.46**		
U	**0.47**	**0.43**	**0.77**	**0.88**	**0.91**	**-0.94**	**0.92**	**0.96**	**0.95**	**0.96**	**0.94**	**0.95**	**0.96**	**0.91**	**0.90**	**0.96**	**0.46**	**-0.89**	0.29	**0.51**	**0.92**	**0.42**	**0.84**	

Table A12 correlation coefficients between trace element concentrations and soil properties in Halabja waste disposal (HALW), bold values denote significance at the level p<0.01

	LOI	**pH**	**Na**	**Mg**	**K**	**Ca**	**Al**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Mo**	**Cd**	**Cs**	**Ba**	**Pb**	**U**
LOI																								
pH	**-0.91**																							
Na	**-0.92**	**0.69**																						
Mg	**-0.80**	**0.93**	0.60																					
K	**-0.83**	**0.97**	0.61	**0.99**																				
Ca	-0.24	-0.18	0.59	-0.18	-0.23																			
Al	**-0.80**	**0.94**	0.59	**1.00**	**1.00**	-0.22																		
V	**-0.89**	**0.96**	**0.72**	**0.99**	**0.99**	-0.06	**0.98**																	
Cr	**0.94**	**-0.97**	**-0.75**	**-0.84**	**-0.90**	0.08	**-0.86**	**-0.90**																
Mn	0.05	0.36	-0.37	0.51	0.50	**-0.88**	0.52	0.37	-0.21															
Fe	0.02	0.39	-0.36	0.52	0.51	**-0.90**	0.53	0.39	-0.24	**1.00**														
Co	-0.53	**0.82**	0.22	**0.90**	**0.90**	-0.58	**0.91**	**0.83**	**-0.70**	**0.82**	**0.83**													
Ni	**-0.76**	**0.95**	0.51	**0.98**	**0.99**	-0.33	**0.99**	**0.96**	**-0.86**	0.60	0.62	**0.95**												
Cu	**0.94**	**-0.87**	**-0.85**	**-0.77**	**-0.80**	-0.18	**-0.77**	**-0.85**	**0.86**	0.02	-0.02	-0.53	**-0.74**											
Zn	0.27	0.16	-0.59	0.28	0.28	**-0.95**	0.30	0.13	-0.02	**0.97**	**0.97**	0.66	0.39	0.21										
As	**-0.83**	0.52	**0.97**	0.40	0.42	**0.72**	0.39	0.54	-0.62	-0.57	-0.56	0.00	0.31	**-0.75**	**-0.75**									
Se	**0.68**	-0.40	**-0.81**	-0.26	-0.28	-0.64	-0.24	-0.37	0.51	0.57	0.56	0.11	-0.17	0.51	**0.70**	**-0.82**								
Sr	0.48	**-0.80**	-0.12	**-0.77**	**-0.82**	**0.71**	**-0.80**	**-0.71**	**0.71**	**-0.78**	**-0.82**	**-0.92**	**-0.86**	0.50	**-0.68**	0.09	-0.07							
Mo	0.44	-0.31	-0.48	-0.30	-0.28	-0.34	-0.28	-0.35	0.23	0.24	0.19	-0.08	-0.22	**0.69**	0.33	-0.47	0.16	0.03						
Cd	**0.94**	**-1.00**	**-0.73**	**-0.91**	**-0.95**	0.11	**-0.92**	**-0.95**	**0.98**	-0.28	-0.32	**-0.77**	**-0.92**	**0.90**	-0.08	-0.58	0.46	**0.76**	0.34					
Cs	**-0.87**	**0.99**	0.64	**0.96**	**0.99**	-0.22	**0.97**	**0.97**	**-0.94**	0.44	0.46	**0.87**	**0.97**	**-0.83**	0.23	0.46	-0.33	**-0.82**	-0.28	**-0.98**				
Ba	**0.99**	**-0.95**	**-0.87**	**-0.83**	**-0.87**	-0.12	**-0.83**	**-0.90**	**0.97**	-0.04	-0.08	-0.60	**-0.81**	**0.94**	0.16	**-0.75**	0.63	0.59	0.41	**0.97**	**-0.91**			
Pb	0.42	**-0.76**	-0.06	**-0.73**	**-0.78**	**0.75**	**-0.76**	-0.66	0.66	**-0.80**	**-0.84**	**-0.90**	**-0.83**	0.44	**-0.72**	0.15	-0.13	**1.00**	0.01	**0.71**	**-0.78**	0.53		
U	**0.77**	-0.65	**-0.72**	-0.48	-0.55	-0.22	-0.51	-0.56	**0.76**	0.21	0.17	-0.26	-0.47	0.64	0.33	**-0.68**	0.66	0.35	0.13	**0.69**	-0.60	**0.78**	0.31	

Table A13 correlation coefficients between trace element concentrations and soil properties in Sirwan (SIR), bold values denote significance at the level $p<0.01$

	LOI	pH	Na	Mg	K	Ca	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Mo	Cd	Cs	Ba	Pb	U
LOI																								
pH	**-0.29**																							
Na	-0.01	**0.25**																						
Mg	0.02	0.10	**0.64**																					
K	**0.50**	0.03	**0.64**	**0.59**																				
Ca	**-0.46**	-0.05	**-0.35**	**-0.15**	**-0.70**																			
Al	**0.42**	0.05	**0.54**	**0.70**	**0.91**	**-0.56**																		
V	.296*	0.07	**0.56**	**0.77**	**0.88**	**-0.63**	**0.88**																	
Cr	0.09	0.16	**0.74**	**0.87**	**0.74**	**-0.49**	**0.74**	**0.90**																
Mn	0.02	**0.26**	**0.75**	**0.64**	**0.60**	**-0.48**	**0.59**	**0.75**	**0.86**															
Fe	**0.39**	0.06	**0.58**	**0.75**	**0.94**	**-0.64**	**0.96**	**.964***	**0.85**	**0.69**														
Co	**0.27**	0.11	**0.63**	**0.75**	**0.88**	**-0.62**	**0.87**	**0.97**	**0.91**	**0.80**	**0.96**													
Ni	-0.06	0.06	0.17	**0.54**	0.23	**-0.34**	**0.26**	**0.55**	**0.66**	**0.51**	**0.44**	**0.55**												
Cu	**0.38**	-0.03	**0.40**	**0.68**	**0.79**	**-0.63**	**0.78**	**0.90**	**0.79**	**0.55**	**0.87**	**0.87**	**0.60**											
Zn	**0.29**	-0.13	0.20	**0.61**	**0.58**	**-0.54**	**0.59**	**0.77**	**0.71**	**0.43**	**0.72**	**0.75**	**0.82**	**0.90**										
As	**0.40**	0.21	**0.56**	**0.43**	**0.81**	**-0.69**	**0.76**	**0.76**	**0.65**	**0.77**	**0.80**	**0.78**	**0.27**	**0.55**	**0.39**									
Se	**0.38**	**-0.36**	0.19	0.22	**0.54**	**-0.26**	**0.50**	**0.47**	**0.34**	**0.27**	**0.51**	**0.51**	0.10	**0.54**	**0.45**	**0.30**								
Sr	**-0.24**	**-0.38**	**-0.26**	0.02	**-0.44**	**0.79**	**-0.41**	**-0.39**	**-0.28**	**-0.45**	**-0.42**	**-0.40**	-0.15	**-0.28**	-0.17	**-0.66**	0.10							
Mo	-0.02	-0.11	-0.04	**0.28**	-0.10	0.06	0.00	0.17	**0.28**	**0.29**	0.08	0.15	**0.49**	0.18	**0.32**	0.02	0.10	0.09						
Cd	**0.24**	0.00	**0.24**	**0.63**	**0.54**	**-0.24**	**0.60**	**0.69**	**0.64**	**0.48**	**0.65**	**0.67**	**0.40**	**0.71**	**0.64**	**0.37**	**0.49**	-0.10	**0.35**					
Cs	**0.49**	-0.05	**0.41**	**0.63**	**0.89**	**-0.50**	**0.97**	**0.81**	**0.62**	**0.43**	**0.92**	**0.80**	0.19	**0.76**	**0.58**	**0.70**	**0.56**	**-0.31**	-0.04	**0.60**				
Ba	**0.54**	-0.15	**0.53**	**0.46**	**0.92**	**-0.55**	**0.82**	**0.72**	**0.56**	**0.40**	**0.83**	**0.74**	0.08	**0.69**	**0.52**	**0.66**	**0.71**	-0.19	-0.18	**0.45**	**0.87**			
Pb	-0.21	-0.03	**-0.29**	-0.03	**-0.32**	-0.06	**-0.32**	-0.04	0.07	0.04	-0.17	-0.05	**0.76**	0.07	**0.43**	-0.15	-0.18	-0.01	**0.41**	-0.02	**-0.35**	**-0.39**		
U	**0.39**	-0.12	**0.51**	**0.77**	**0.82**	**-0.48**	**0.80**	**0.88**	**0.82**	**0.56**	**0.88**	**0.87**	**0.52**	**0.89**	**0.81**	**0.56**	**0.62**	-0.11	0.21	**0.75**	**0.81**	**0.78**	-0.03	

Table A14 correlation coefficients between trace element concentrations and soil properties in Khurmal (KHR), bold values denote significance at the level p<0.01

	LOI	**pH**	**Na**	**Mg**	**K**	**Ca**	**Al**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Mo**	**Cd**	**Cs**	**Ba**	**Pb**	**U**
LOI																								
pH	**0.57**																							
Na	**0.45**	0.34																						
Mg	**0.70**	**0.93**	**0.53**																					
K	**0.69**	**0.90**	**0.55**	**0.99**																				
Ca	**-0.61**	**-0.91**	-0.34	**-0.96**	**-0.96**																			
Al	**0.69**	**0.93**	**0.51**	**1.00**	**0.99**	**-0.97**																		
V	**0.69**	**0.93**	**0.50**	**0.98**	**1.00**	**-0.97**	**1.00**																	
Cr	**0.70**	**0.91**	**0.50**	**0.99**	**1.00**	**-0.98**	**1.00**	**1.00**																
Mn	**0.54**	**0.94**	**0.44**	**0.95**	**0.97**	**-0.96**	**0.97**	**0.97**	**0.97**															
Fe	**0.68**	**0.92**	**0.45**	**0.98**	**0.99**	**-0.99**	**0.99**	**1.00**	**1.00**	**0.97**														
Co	**0.62**	**0.92**	**0.47**	**0.97**	**0.99**	**-0.98**	**0.99**	**0.99**	**0.99**	**0.99**	**1.00**													
Ni	**0.55**	**.792**	**0.36**	**0.74**	**0.76**	**-0.74**	**0.77**	**0.79**	**0.77**	**0.76**	**0.78**	**0.77**												
Cu	**0.52**	**0.66**	**0.46**	**0.82**	**0.85**	**-0.83**	**0.82**	**0.83**	**0.85**	**0.81**	**0.83**	**0.84**	**0.55**											
Zn	0.16	**-0.51**	-0.22	-0.29	-0.32	0.26	-0.31	-0.32	-0.27	**-0.48**	-0.29	-0.35	-0.20	-0.14										
As	**0.45**	**0.68**	**0.59**	**0.56**	**0.55**	**-0.41**	**0.57**	**0.58**	**0.53**	**0.57**	**0.53**	**0.53**	**0.65**	0.23	**-0.59**									
Se	**0.82**	**0.79**	**0.67**	**0.92**	**0.92**	**-0.83**	**0.92**	**0.91**	**0.92**	**0.83**	**0.90**	**0.88**	**0.73**	**0.77**	-0.14	**0.60**								
Sr	**-0.49**	**-0.80**	-0.24	**-0.88**	**-0.90**	**0.96**	**-0.90**	**-0.89**	**-0.91**	**-0.91**	**-0.91**	**-0.92**	**-0.61**	**-0.83**	0.23	-0.21	**-0.72**							
Mo	-0.07	0.02	0.19	0.05	0.11	-0.02	0.05	0.07	0.07	0.12	0.05	0.08	-0.10	**0.45**	-0.27	-0.03	0.08	-0.08						
Cd	**0.59**	**0.51**	**0.43**	**0.66**	**0.72**	**-0.67**	**0.69**	**0.72**	**0.73**	**0.67**	**0.72**	**0.71**	**0.62**	**0.75**	-0.02	0.38	**0.74**	**-0.59**	0.13					
Cs	**0.68**	**0.92**	**0.42**	**0.96**	**0.95**	**-0.94**	**0.97**	**0.96**	**0.96**	**0.93**	**0.97**	**0.96**	**0.78**	**0.74**	-0.25	**0.59**	**0.88**	**-0.84**	-0.08	**0.71**				
Ba	**0.64**	**0.91**	**0.43**	**0.96**	**0.98**	**-0.99**	**0.98**	**0.99**	**0.99**	**0.97**	**1.00**	**1.00**	**0.78**	**0.83**	-0.29	**0.52**	**0.87**	**-0.92**	0.04	**0.74**	**0.97**			
Pb	0.12	0.09	0.06	-0.01	-0.01	0.03	0.01	0.03	0.01	-0.01	0.01	0.00	**0.63**	-0.12	0.18	0.32	0.10	0.14	-0.24	0.14	0.04	0.02		
U	**0.74**	**0.85**	**0.50**	**0.96**	**0.97**	**-0.96**	**0.97**	**0.98**	**0.98**	**0.92**	**0.98**	**0.97**	**0.76**	**0.87**	-0.17	**0.47**	**0.91**	**-0.89**	0.08	**0.78**	**0.93**	**0.97**	0.03	

Table A15 correlation coefficients between trace element concentrations and soil properties in kalar-Grdagozina (KALG), bold values denote significance at the level $p<0.01$

	LOI	**pH**	**Na**	**Mg**	**K**	**Ca**	**Al**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Mo**	**Cd**	**Cs**	**Ba**	**Pb**	**U**
LOI																								
pH	**-0.57**																							
Na	0.09	0.13																						
Mg	0.09	0.16	0.19																					
K	0.14	0.14	**0.61**	**0.75**																				
Ca	0.05	-0.01	0.82	**0.50**	**0.69**																			
Al	0.05	0.03	0.30	**0.93**	**0.79**	**0.58**																		
V	0.00	0.03	0.10	**0.93**	**0.74**	**0.45**	**0.88**																	
Cr	-0.17	0.33	-0.01	**0.88**	**0.65**	0.25	**0.78**	**0.92**																
Mn	0.08	0.03	0.08	**0.90**	**0.72**	**0.39**	**0.81**	**0.92**	**0.86**															
Fe	0.02	-0.02	0.04	**0.92**	**0.70**	**0.43**	**0.88**	**0.95**	**0.86**	**0.96**														
Co	-0.08	0.08	**-0.50**	**0.68**	0.28	-0.17	**0.53**	**0.78**	**0.84**	**0.77**	**0.77**													
Ni	0.02	0.06	0.20	**0.88**	**0.79**	**0.45**	**0.83**	**0.92**	**0.84**	**0.94**	**0.90**	**0.69**												
Cu	0.17	-0.08	-0.21	**0.79**	**0.46**	0.09	**0.68**	**0.86**	**0.83**	**0.84**	**0.82**	**0.88**	**0.77**											
Zn	**0.37**	-0.17	0.33	**0.81**	**0.71**	**0.55**	**0.76**	**0.80**	**0.63**	**0.82**	**0.78**	**0.49**	**0.85**	**0.77**										
As	-0.01	-0.28	**-0.60**	**0.41**	0.04	-0.21	0.32	**0.55**	**0.50**	**0.62**	**0.65**	**0.80**	**0.46**	**0.67**	0.32									
Se	0.25	-0.20	**0.37**	**0.73**	**0.72**	**0.69**	**0.72**	**0.72**	**0.52**	**0.81**	**0.82**	**0.36**	**0.74**	**0.55**	**0.80**	**0.40**								
Sr	**0.50**	**-0.47**	**0.48**	**0.45**	**0.44**	**0.75**	**0.45**	**0.45**	0.15	**0.42**	**0.44**	0.01	**0.42**	0.32	**0.70**	0.08	**0.71**							
Mo	0.28	0.08	0.03	**0.37**	0.34	0.05	0.31	0.30	0.31	0.34	0.28	0.28	**0.38**	**0.38**	**0.42**	0.07	0.28	0.15						
Cd	**0.41**	**-0.61**	**-0.38**	0.17	-0.09	-0.19	0.19	0.23	0.08	0.23	0.28	**0.36**	0.11	**0.44**	0.30	**0.52**	0.23	0.18	0.07					
Cs	-0.02	-0.10	**-0.58**	**0.57**	0.11	-0.30	**0.55**	**0.62**	**0.65**	**0.58**	**0.64**	**0.86**	**0.51**	**0.78**	**0.38**	**0.74**	0.20	-0.07	0.22	**0.50**				
Ba	0.17	-0.33	**-0.39**	**0.57**	**0.36**	-0.14	**0.57**	**0.70**	**0.65**	**0.69**	**0.69**	**0.81**	**0.68**	**0.80**	**0.52**	**0.71**	**0.35**	0.14	0.32	**0.48**	**0.84**			
Pb	0.15	-0.01	**0.64**	**0.57**	**0.76**	**0.66**	**0.62**	**0.50**	**0.36**	**0.57**	**0.51**	0.07	**0.75**	0.28	**0.74**	-0.07	**0.66**	**0.53**	0.34	-0.11	-0.01	0.24		
U	0.03	**-0.47**	**-0.49**	**0.43**	0.14	-0.13	**0.45**	**0.62**	**0.51**	**0.59**	**0.65**	**0.75**	**0.55**	**0.74**	**0.46**	**0.82**	**0.36**	0.20	0.14	**0.54**	**0.82**	**0.89**	0.10	

Table A16 correlation coefficients between trace element concentrations and soil properties in Kalar Riverside (KALR), bold values denote significance at the level p<0.01

	LOI	**pH**	**Na**	**Mg**	**K**	**Ca**	**Al**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Mo**	**Cd**	**Cs**	**Ba**	**Pb**	**U**
LOI																								
pH	**-0.49**																							
Na	**-0.82**	**0.65**																						
Mg	**0.70**	-0.33	**-0.71**																					
K	**0.79**	**-0.50**	**-0.78**	**0.89**																				
Ca	**-0.66**	0.32	**0.53**	**-0.40**	**-0.51**																			
Al	**0.59**	-0.15	**-0.48**	**0.94**	**0.76**	**-0.37**																		
V	0.25	0.07	-0.21	**0.72**	**0.65**	-0.17	**0.76**																	
Cr	**0.68**	**-0.36**	**-0.68**	**0.81**	**0.91**	**-0.44**	**0.69**	**0.75**																
Mn	0.00	0.05	0.33	-0.21	-0.08	0.31	-0.15	-0.19	-0.11															
Fe	**0.76**	**-0.35**	**-0.70**	**0.96**	**0.95**	**-0.54**	**0.90**	**0.75**	**0.90**	-0.13														
Co	**0.77**	**-0.49**	**-0.86**	**0.90**	**0.97**	**-0.51**	**0.72**	**0.65**	**0.92**	-0.22	**0.93**													
Ni	**0.48**	-0.32	**-0.52**	**0.62**	**0.62**	-0.27	**0.52**	**0.44**	**0.65**	-0.03	**0.63**	**0.65**												
Cu	**0.92**	**-0.63**	**-0.89**	**0.67**	**0.80**	**-0.70**	**0.51**	0.23	**0.74**	-0.11	**0.76**	**0.81**	**0.52**											
Zn	**0.87**	**-0.50**	**-0.66**	**0.48**	**0.61**	**-0.78**	**0.42**	0.07	**0.55**	0.08	**0.61**	**0.57**	**0.40**	**0.91**										
As	**-0.35**	0.20	0.32	-0.21	-0.08	**0.51**	-0.25	0.09	0.01	**0.56**	-0.17	-0.11	0.09	-0.28	**-0.35**									
Se	**0.64**	**-0.36**	**-0.51**	**0.52**	**0.57**	-0.17	**0.45**	0.25	**0.56**	0.30	**0.57**	**0.53**	**0.52**	**0.65**	**0.61**	0.02								
Sr	**-0.67**	0.12	**0.67**	**-0.56**	**-0.65**	**0.78**	**-0.44**	**-0.39**	**-0.65**	**0.40**	**-0.65**	**-0.72**	**-0.43**	**-0.71**	**-0.61**	0.19	-0.24							
Mo	0.14	-0.17	-0.05	-0.05	0.03	0.02	-0.09	-0.29	-0.11	**0.53**	-0.04	-0.01	-0.06	0.11	0.17	0.32	0.16	0.06						
Cd	**0.93**	**-0.57**	**-0.87**	**0.64**	**0.74**	**-0.72**	**0.49**	0.16	**0.65**	-0.11	**0.71**	**0.75**	**0.41**	**0.97**	**0.92**	**-0.39**	**0.63**	**-0.69**	0.10					
Cs	**0.82**	**-0.49**	**-0.85**	**0.97**	**0.92**	**-0.53**	**0.86**	**0.59**	**0.82**	-0.22	**0.95**	**0.94**	**0.64**	**0.81**	**0.62**	-0.27	**0.56**	**-0.64**	0.02	**0.78**				
Ba	**0.71**	**-0.44**	**-0.40**	**0.41**	**0.56**	**-0.53**	**0.43**	0.13	**0.50**	**0.42**	**0.56**	**0.44**	0.32	**0.74**	**0.87**	-0.07	**0.65**	-0.32	0.29	**0.72**	**0.49**			
Pb	**0.79**	**-0.39**	**-0.63**	**0.50**	**0.58**	**-0.66**	**0.44**	0.16	**0.60**	0.00	**0.61**	**0.57**	**0.71**	**0.84**	**0.89**	-0.24	**0.64**	**-0.63**	0.05	**0.80**	**0.61**	**0.73**		
U	**0.91**	**-0.60**	**-0.83**	**0.69**	**0.72**	**-0.59**	**0.58**	0.13	**0.59**	-0.03	**0.71**	**0.70**	**0.41**	**0.89**	**0.85**	-0.49	**0.63**	**-0.48**	0.13	**0.92**	**0.80**	**0.72**	**0.72**	

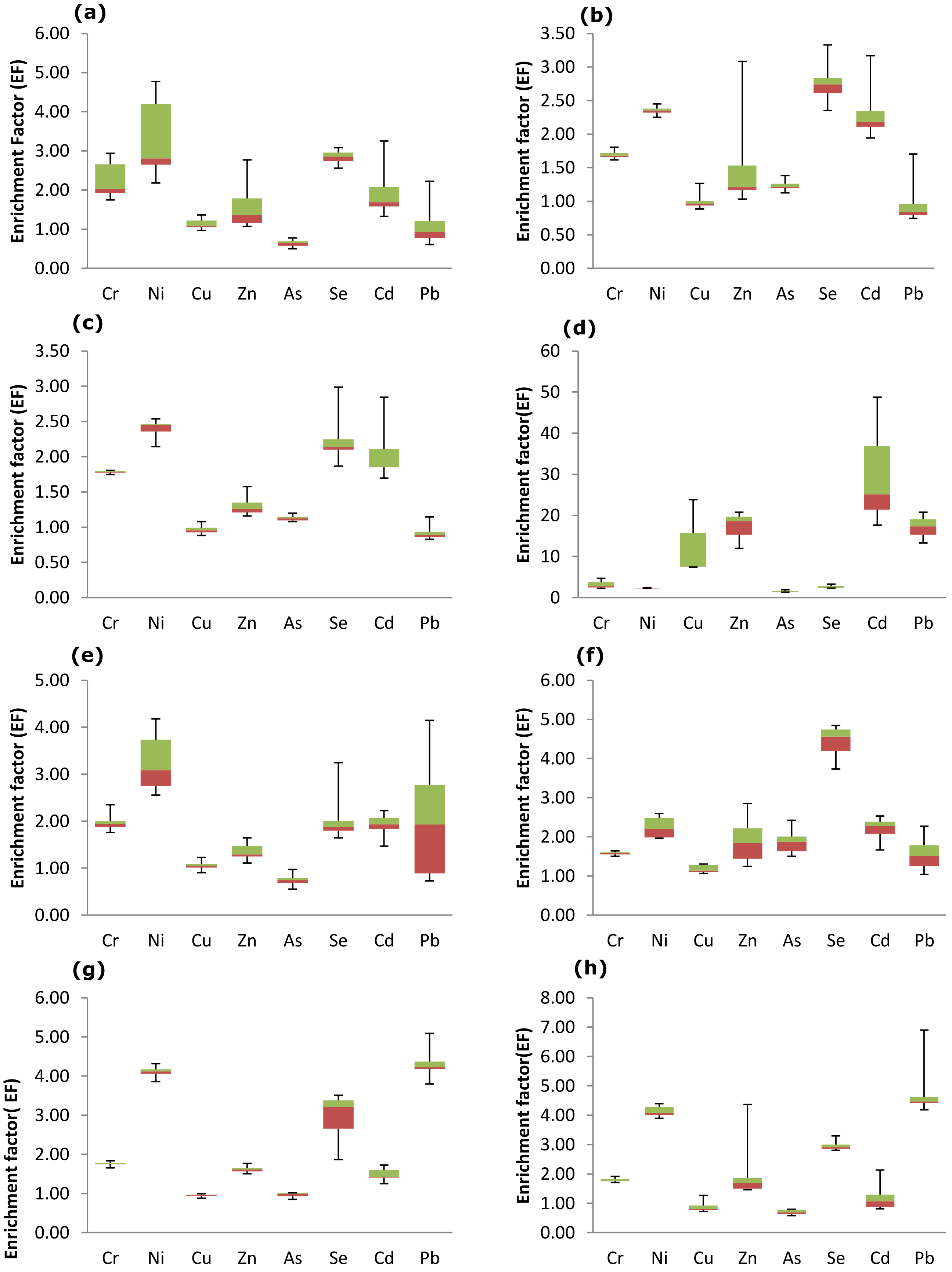

Figure A1 Mean enrichment factors (EFs) of selected essential trace elements in some PTEs based on shale at (a) SUL, (b) HALU, (c) HALP, (d) HALW, (e) SIR (f) KHR , (g) KALG and (g) KALR

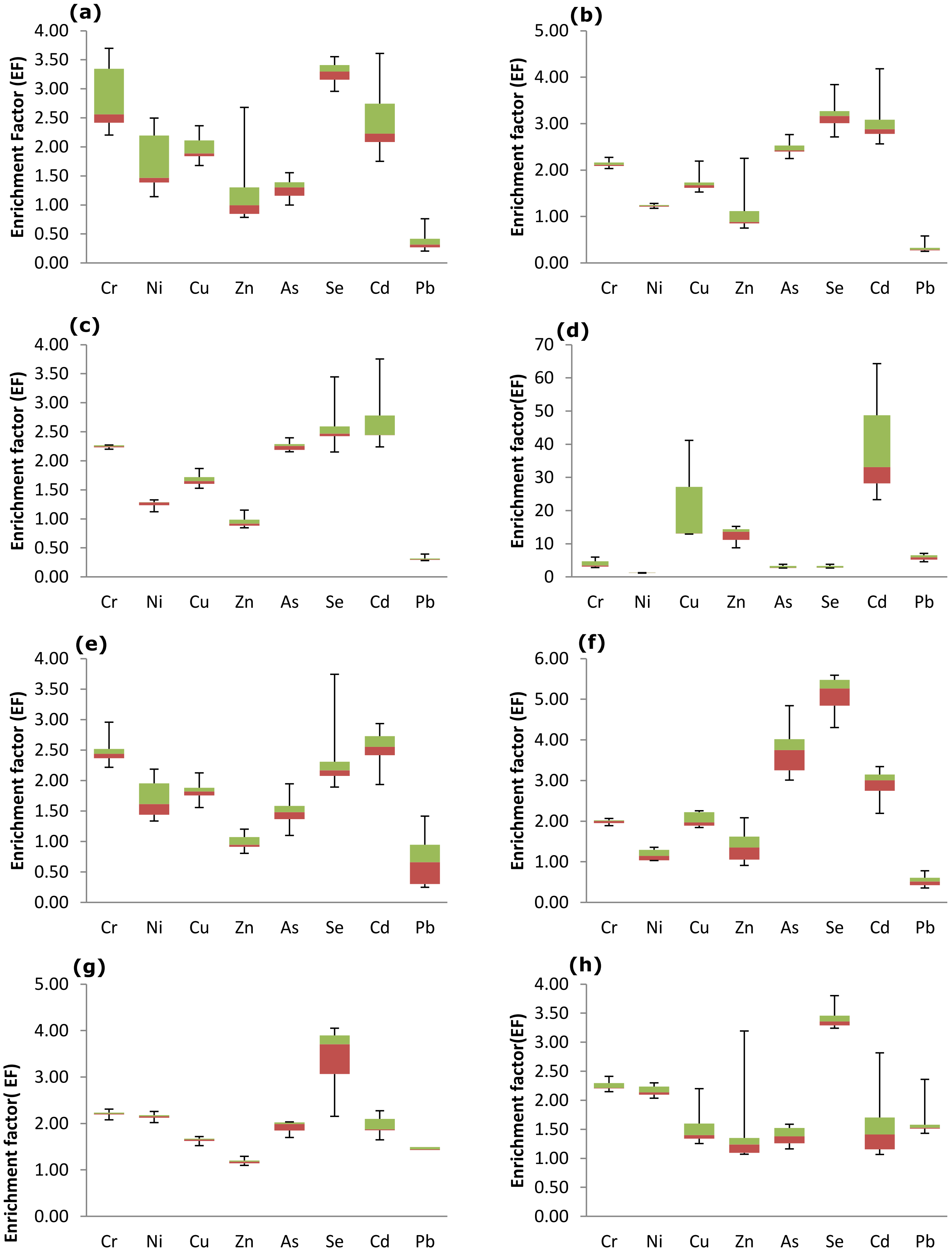

Figure A2 Mean enrichment factors (EFs) of selected essential trace elements in some PTEs based carbonate rocks at (a) SUL, (b) HALU, (c) HALP, (d) HALW, (e) SIR (f) KHR , (g) KALG and (g) KALR

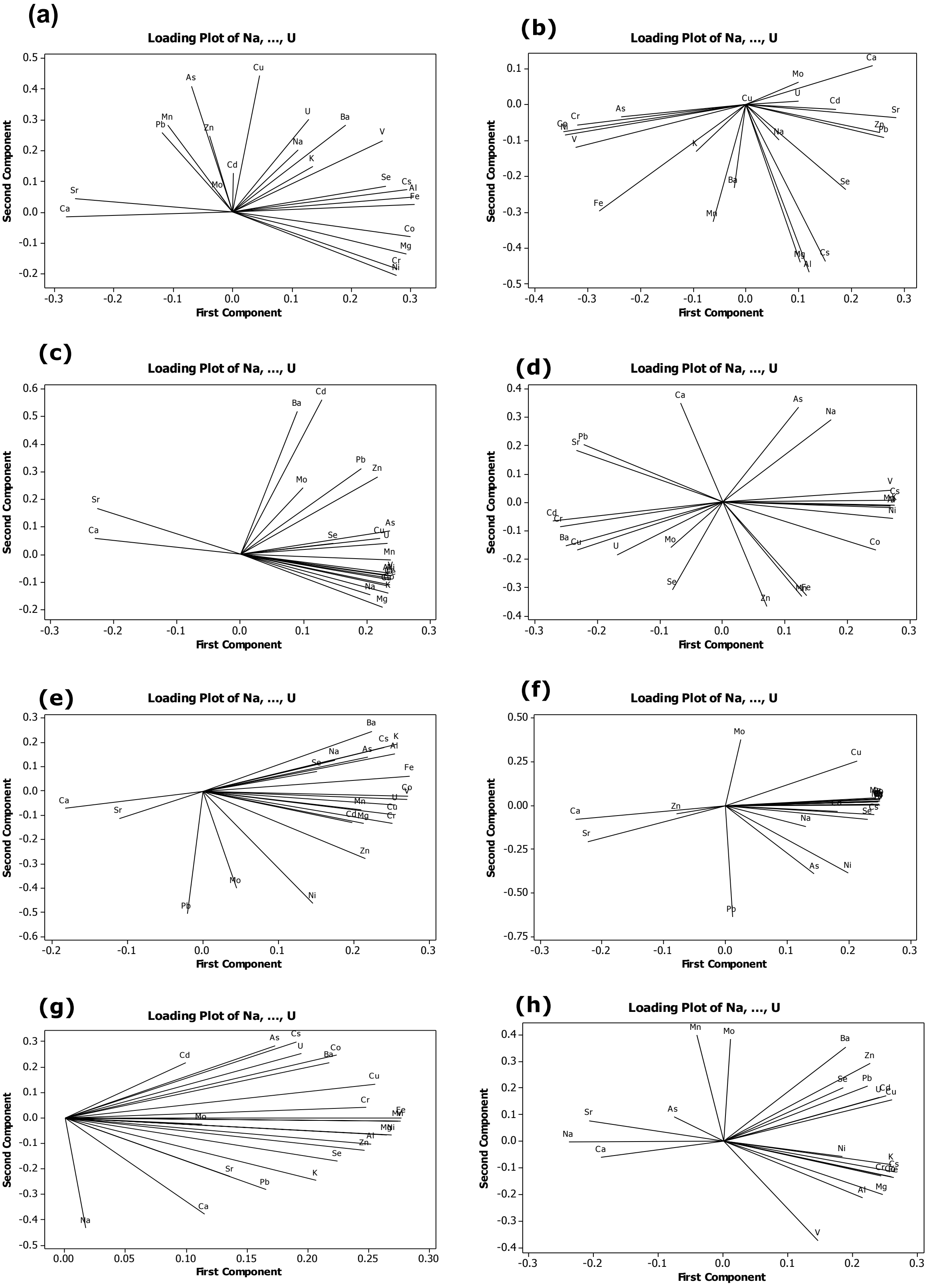

Figure A3 Principle component analysis for trace elements in soil samples uaing loading plots for different components at (a) SUL, (b) HALU, (c) HALP, (d) HALW, (e) SIR (f) KHR , (g) KALG and (g) KALR

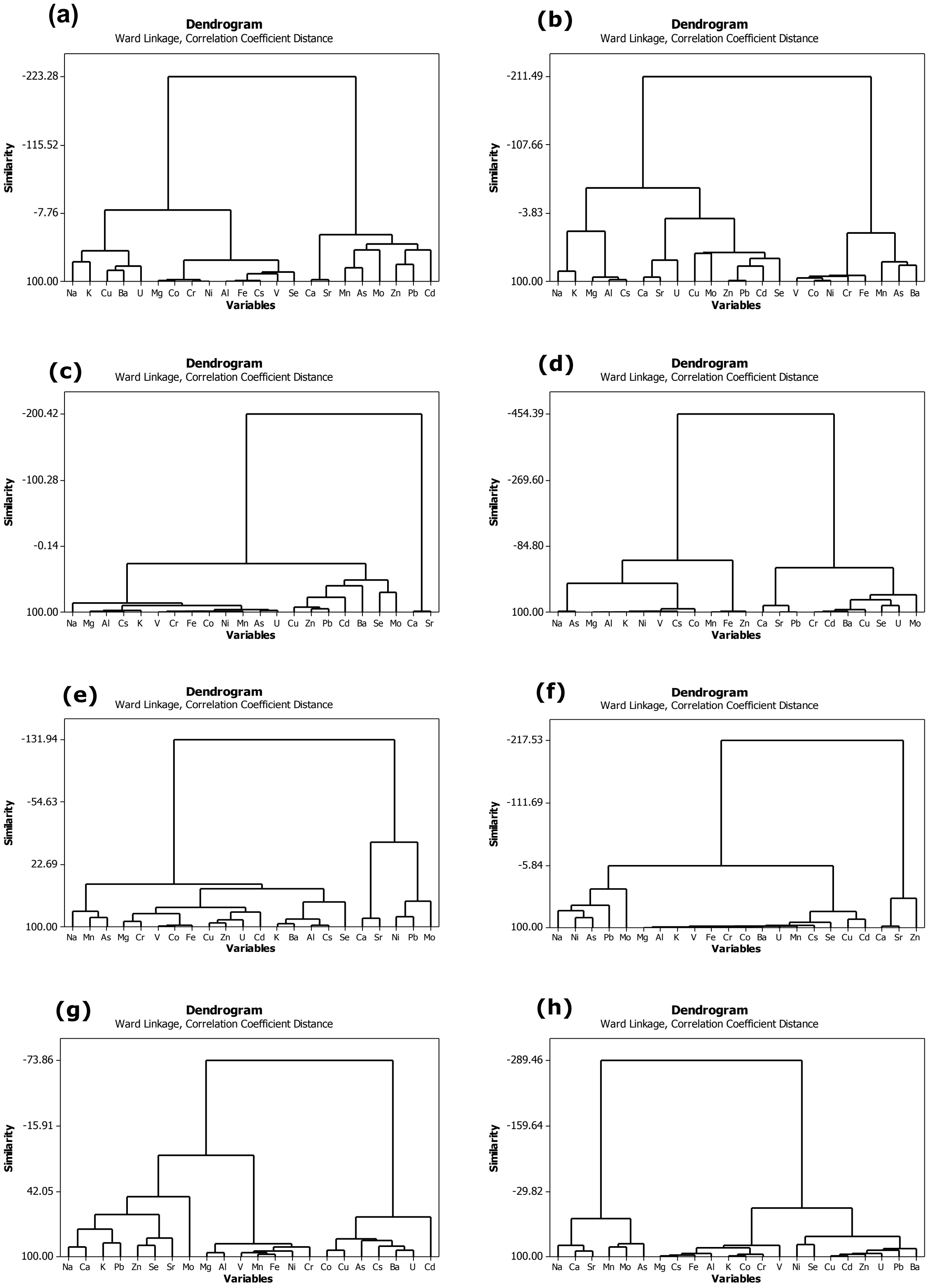

Figure A4 Principle component analysis for trace elements in soil samples using dendogram showing cluster analysis for (a) SUL, (b) HALU, (c) HALP, (d) HALW, (e) SIR (f) KHR , (g) KALG and (g) KALR

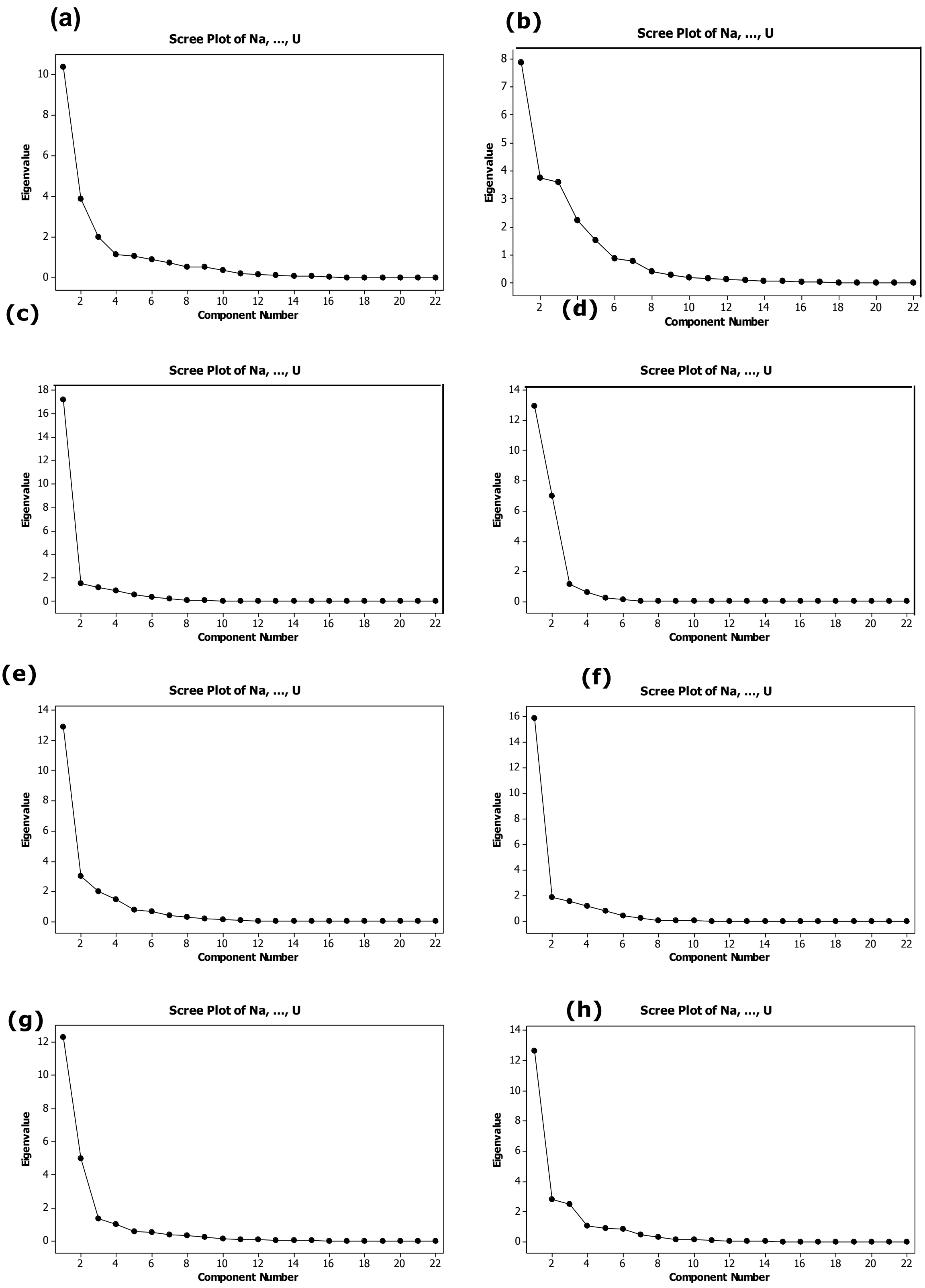

Figure A5 Principle component analysis for trace elements in soil samples using scree plots showing Eigen values determining dominant factors which controlling the elemental association in the soil for (a) SUL, (b) HALU, (c) HALP, (d) HALW, (e) SIR (f) KHR , (g) KALG and (g) KALR