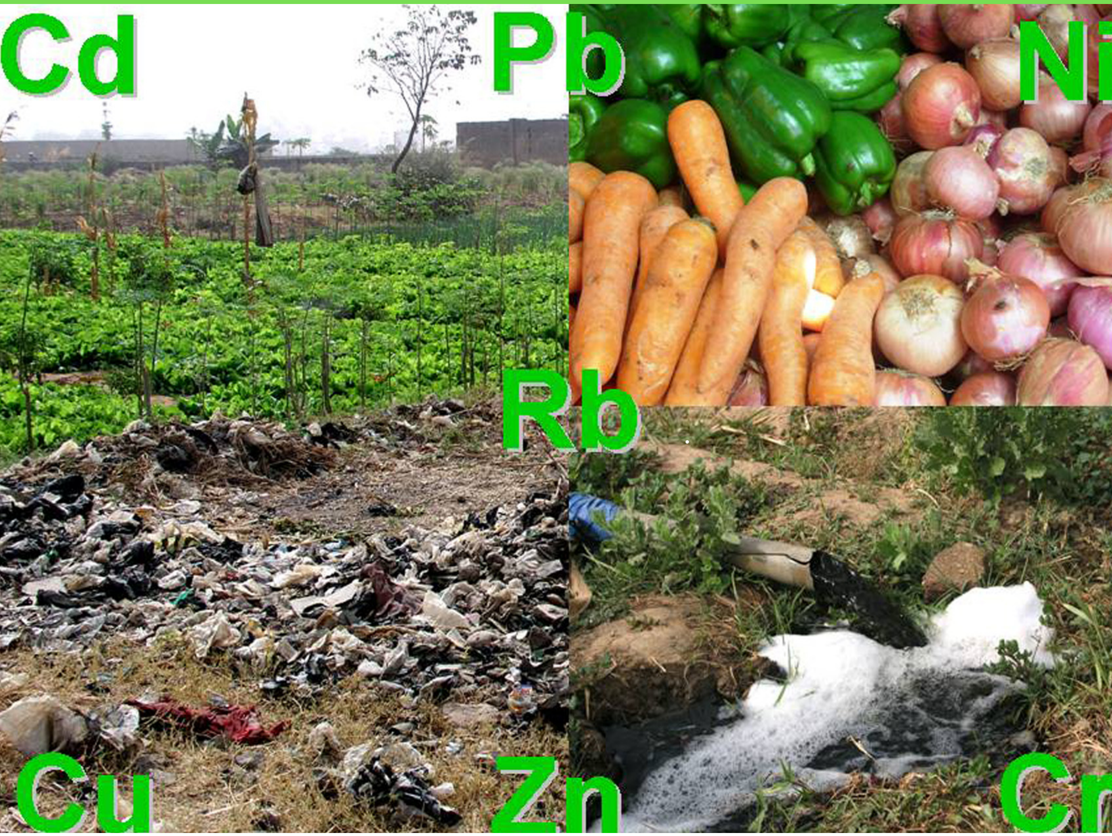
UNI KASSEL VERSITÄT

Ahmadu Bello University
Zaria - Nigeria

Nafiu Abdu

Availability, transfer and balances of heavy metals in urban agriculture of West Africa



VolkswagenStiftung

kassel
university
press

Nafiu Abdu

Availability, transfer and balances of heavy metals in urban agriculture of West Africa

kassel
university
press

This work has been accepted by the faculty of Organic Agricultural Sciences of the University of Kassel as a thesis for acquiring the academic degree of Doktor der Agrarwissenschaften (Dr. agr.).

Supervisor: Prof. Dr. Adreas Bürkert
Co-Supervisor: Prof. Dr. John O. Agbenin

Defense day: 24th June 2010

Bibliographic information published by Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at http://dnb.d-nb.de.

Zugl.: Kassel, Univ., Diss. 2010
ISBN print: 978-3-89958-956-6
ISBN online: 978-3-89958-957-3
URN: http://nbn-resolving.de/urn:nbn:de:0002-9574

© 2010, kassel university press GmbH, Kassel
www.upress.uni-kassel.de

Printed by: Unidruckerei, University of Kassel
Printed in Germany

Table of content

Dedication

To the memory of late Ja'afar Mahmud Adam who was brutally murdered by unknown assassins. May your gentle soul rest in perfect peace. Also to Al-Muhaddith Muhammad Auwal Adam Albani who always inspire me to learn.

Acknowledgments

My invaluable appreciation and immense gratitude go to Prof. (Dr.) Andreas Buerkert who despite his tight schedules did a painstaking supervision of my PhD research. You have certainly demonstrated a superb quality mentorship. Also to Prof. John O. Agbenin who was the foundation of my scientific career. Your constructive criticisms and helpful comments were also central to the success of this work. I am most grateful. I am also indebted to Prof. (Dr.) Eva Schlecht for her support, encouragement, care and understand. I acknowledge the funding of this research by the Volkswagen Foundation, Hannover, Germany.

My heartfelt gratitude to Professors Bashiru A. Raji and Joshua O. Ogunwole of the Department of Soil Science, Ahmadu Bello University, Zaria, Nigeria. Your fatherly advice was of paramount importance to the completion of this work. My sincere appreciation to Dr. Ludger Hermann for the tutorial on dust trapping and to Dr. Bettina Hausmann and Dr. Yeye of Plant Science Department for helping me with the transportation of mixed ion resins. I duly acknowledged the technical assistance of Malam Ilu Ibrahim, Messrs. Victor Odigie, Dashe, Anyawu, Bello, Jonathan, Joseph, Oshagbemi and Mrs. Cecilia of the Department of Soil Science laboratories, Ahmadu Bello University, Zaria.

Special thanks to Alhaji Ahmed Falaki of IAR, Kano and all his staff for providing me with office logistics and meteorological data during my stay in Kano. My sincere appreciation to a hardworking and polite young man, Jibril B. Jibril who was my field technician, I cherished your effort. To my cooperating farmers who were a pillar in this research, I say a million thanks.

I must not forget the management of Ahmadu Bello University, Zaria, Nigeria for granting me a study fellowship. I am extremely grateful.

To my colleague in the field, Aisha Abdulkadir, you have always been an excellent research associate and to your husband, Dr. Lawal Haliru for being a true friend I appreciate your support, prayers and encouragement. My colleagues in the ‘UrbanFood’ Hamadou Amadou, Desire Jean-Pascal Lompo, Sangare Khalil, Dr. Luc Hippolyte Dossa are worth mentioning. I also enjoyed the company of Mr. Konrad Siegfried, Jan Harndorf, Safi Zikrullah, Husam Al-Asfoor, Tilal Sayed Abdelhalim Musa, Munir Anjum, Muhidin Rabato, Dr. Martina Predotova and her family, Sahar Babiker, Ishtiag Abdalla, Khair Al-Busaidi, Drs. Katja Brinkmann and habil Jens Gebauer during my stay in Germany. Many thanks also to Mrs. Haber for her secretarial and administrative support. I am also grateful to Eva Wiegard and Claudia Thieme-Fricke.

I am especially grateful to Dr. Rodrigue Vivien Cao Diogo for introducing me to the use of SAS statistical package and SigmaPlot. Your all ever attention is duly appreciated.

I will like to thank the entire members of Daarul-Hadeeth Institute, Zaria, Nigeria for their spiritual support, prayers and encouragement. I am most thankful to Sheik Muhammad Auwal Adam Albani for being a mentor, a father and a gentle man. To my friends, Auwal Abubakar Maishago, Kabir Ameen Al-Asgar, Dawood Ibrahim Maiwada, Abdullahi Muhammad As-Salafy, Muhammad Baffah, Lukman Ibrahim, Aliyu Abdullahi Anchau, Dr. Ado A. Yusuf, Ibrahim Tanko, Adamu Aliyu, Dr. Bashir Zakariyyah, Abu Albani, Haruna Jibrin and others too numerous to mention.

I am short of words to express my sincere and well-deserved gratitude to my beloved parents, Hajia Sa’adatu Abdus-Salam and Alhaji Abdulganiyyi Raji and the entire members of the Abdulganiyyi family. Your prayers, inspiration, guidance, care and support were a ladder to my adulthood.

To my darling wife Muhibbat Alhaji Hamza, my little angels, Hafsah, Muneerah and Maryam your support is immeasurable. You are indeed an invaluable treasure to me. I am deeply grateful for your understanding and patient.

Summary

Urbanization and population surges are causing increasing demands for food; this is especially in developing countries. Consequently, the cultivation of horticultural surfaces within and outside the urban centers has been intensified. Urban agriculture (UA) therefore, plays a significant role in providing vegetables for urban consumption, whereby it is often associated with wastewater reuse leading to the accumulation of potentially toxic heavy metals in soil. A typical case of this is the northern Nigerian city of Kano, where quality irrigation water is scarce.

Little quantitative knowledge is available on the dynamics of heavy metal movement, bioavailability and the associated health risk for consumers from West Africa. To close this knowledge gap, this PhD research work aimed at investigating the distribution and movement of heavy metal (HM) in urban garden soils of Kano. It also assessed the extent of the food chain contamination and potential health risk to producers and consumers of UA produced vegetables. Results from Kano were compared with comparable datasets from the three West African cities of Bobo-Dioulasso (Burkina Faso) and Sikasso (Mali).

The distribution of heavy metals (cadmium, Cd; copper, Cu; lead, Pb; nickel, Ni; chromium, Cr and zinc, Zn) in five gardens in Kano and one each from Bobo-Dioulasso and Sikasso revealed that in the latter two cities HM concentration was below international critical threshold levels. Concentration of Cd (2.3-4.8 mg kg^{-1}) and Zn (13-285 mg kg^{-1}) in Kano were, however, near such levels. The concentrations of Cu (0.8-18 mg kg^{-1}), Cr (1.8-72 mg kg^{-1}), Ni (0-17 mg kg^{-1}), and Pb (0.6-46 mg kg^{-1}), were still within acceptable safety limits for agricultural soils. Kano urban soils were more loaded with HM than soils from Bobo-Dioulasso and

Sikasso, whereby soil Cd concentrations in Kano were 7-10 times higher than concentrations in Bobo-Dioulasso and Sikasso and Zn was 20 times higher in Kano than other cities. Heavy metal concentration across the three cities decreased with profile depth, which reflects its largely anthropogenic origin. Analysis of the HM balance indicated that irrigation water and fertilizer were the main sources of HM input. Irrigation water contributed annually 400-3700 g Cd ha^{-1} and 7200-22300 g Zn ha^{-1} and mineral fertilizer, 30-2100 g Cd ha^{-1} and 50-17600 g Zn ha^{-1}. Input from Harmattan dust, instead, only contributed 0.02-0.4 g Cd ha^{-1} and 40-200 g Zn ha^{-1}. Harvest of *Amaranthus* led to the highest annual exports of Cd and Zn, amounting to 0.7-2.0 g Cd ha^{-1} and 100-1700 g Zn ha^{-1} from a total dry matter (TMD) of 3.5-28 t ha^{-1}. Leaching of Cd estimated from resin extraction was 200-300 g ha^{-1} and of Zn 1100-2800 g ha^{-1}. Input-output calculations yielded an annual net positive balance of 700-3900 g Cd ha^{-1} and 9200-23400 g Zn ha^{-1}.

Fractionation of Cd and Zn into seven operationally defined pools in Kano urban soils indicated that the most labile and plant available fractions accounted for 29-42% of total Cd and 22-54% of total Zn. Correlation analysis revealed a significant negative correlation of total soil P with Mn oxide-bound Cd (-0.98; $P<0.01$), suggesting that Mn nodules (concretions) are significant Cd and P sinks in the soil. Soil OC correlated negatively with water-soluble Zn (-0.98; $P\leq0.01$) and positively with the Fe-oxide bound fraction (0.97; $P\leq0.05$), suggesting that decomposition of soil organic matter could reduce binding sites for the labile Zn fractions and can inhibit the crystallization of Fe thereby increasing the capability of Zn retention by Fe oxides. The mobility factors of Cd (31-42%) and Zn (22-54%) revealed high mobility of these HMs. The predominantly sandy nature of Kano soils with their high-metal mobility and high wastewater irrigation increases the risk of horizontal translocation of heavy metals especially for Cd that significantly correlated (0.41; $P<0.05$) with sand fractions.

DTPA-available Zn and Cd concentrations ranged from 18-66 mg kg^{-1} and 0.19-0.35 mg kg^{-1} in soils while total Zn and Cd were between 8.4-256 mg kg^{-1} and 0.04-1.7 mg kg^{-1} in shoot parts. Zinc concentrations in most of the vegetables studied were beyond the threshold safe limits of 60 mg kg^{-1} set by the WHO/FAO. Zn concentration in the edible leafy portion of amaranthus (*Amaranthus caudatus* L.) ranged from 13-128 mg kg^{-1} across the five locations while in roots, it ranged from 15-141 mg kg^{-1} on a dry-weight basis. In lettuce, however, Zn concentration by far exceeded the recommended threshold values of 60 mg kg^{-1} by a factor of four. Cadmium concentrations of *Amaranthus* ranged from 0.00–0.22 mg kg^{-1} in the leafy shoot parts and from 0.02 – 0.26 mg kg^{-1} in roots. Edible parts of lettuce (*Lactuca sativa* L.) had the highest Cd concentration (0.06-1.7 mg kg^{-1}) and root concentrations ranged from 0.1-0.24 mg kg^{-1}. Of all vegetables investigated, only carrot had Cd concentrations below the 0.2 mg kg^{-1} threshold for edible vegetables set by the WHO/FAO.

Metal transfer factor (MTF) ratios were higher in Zn (0.2-0.9) than in Cd (0.1-0.6). Translocation of Cd and Zn from the root to the shoot was high for both metals in all vegetables. Cadmium had a transfer factor (TF) of up to 4.1 while Zn recorded a maximum of 1.5. Lettuce showed a high translocation of Cd from the root to the shoot, while carrot (*Daucus carota* ssp. *sativus*) and parsley (*Petroselinum crispum*) had a similarly high translocation of Zn. Our result indicates that MTF values can be estimated for a given soil concentration of either total or DTPA-extractable metal. The estimated TF of Cd and Zn was negatively correlation with soil exchangeable bases and CEC (-0.99 at $P<0.01$). This may indicate that Cd and Zn uptake by the studied crops was not a diffusion-controlled mechanism but governed by the activity of competing ions in an active metabolic process.

A health risk assessment indicated the estimated dietary intake (EDI) of Cd and Zn through vegetable consumption in Kano is within the safe limit of 10-50 and 15000 µg day^{-1} for Cd and Zn respectively. The highest EDI recorded for Cd was 17 µg day^{-1} while, for Zn it was 6095 µg day^{-1}. Both, the average daily dose and target hazard quotient quantified through soil ingestion, and vegetable consumption indicated no apparent health hazard.

Zusammenfassung

Urbanisierung und Bevölkerungsanstieg in Entwicklungsländern führen zu erhöhtem Verbrauch an Nahrungsmitteln. Dies hat dazu geführt, dass im Umkreis und innerhalb urbaner Zentren vermehrt Landwirtschaft betrieben wird. Aufgrund dessen hat heute die urbane Landwirtschaft einen signifikanten Anteil an der städtischen Gemüseversorgung. Allerdings ist urbane Landwirtschaft in Entwicklungsländern durch intensive Kultivierung und extensive Verwendung von Abwässern zur Bewässerung geprägt, was zur Anreicherung potenziell toxischer Schwermetalle im Boden führt. Die beschriebene Situation ist typisch für die Stadt Kano mit begrenzten zur Verfügung stehenden Bewässerungsresourcen. Den Bauern bleibt keine andere Möglichkeit, als industrielle und städtische Abwässer zur Bewässerung zu nutzen. Es ist kaum etwas über Mengen und Dynamik der in den urbanen Böden Kanos angereicherten Schwermetalle und die damit verbundenen Risiken bekannt. Um diese Wissenslücke zu schließen, wurden in der vorliegenden Doktorarbeit die Verteilung und Bewegung von Schwermetallen in urbanen, landwirtschaftlich genutzten Böden der Stadt Kano untersucht. Ebenfalls wurden das Ausmaß der Kontamination in der Ernährungskette und potenzielle Risiken für Produzenten und Konsumenten bestimmt. Ein weiterer Teil der Arbeit bestand in einem Vergleich der Schwermetallverteilung in Böden von drei westafrikanischen Städten (Kano/Nigeria, Bobo-Dioulasso/Burkina Faso und Sikasso/Mali).

Die Schwermetallverteilung (Cd, Cu, Pb, Ni, Cr and Zn) in fünf Gärten in Kano und in jeweils einem Garten in Bobo-Dioulasso und Sikasso wurden im Jahr 2007 untersucht. Die ermittelte Schwermetallkonzentration in Bobo-Dioulasso und Sikasso lag unter den für eine Kontamination festgelegten Grenzwerten. Die in Kano festgestellten Werte für Cd (2,3-4.8 mg kg^{-1}) und Zn (13-285 mg kg^{-1}) lagen nahe am Kontaminationsgrenzwert. Die Konzentrationen von Cu (0,8-18 mg kg^{-1}), Cr (1,8-72 mg kg^{-1}), Ni (0-17 mg kg^{-1}), und Pb (0,6-46 mg kg^{-1}) lagen im Bereich der für landwirtschaftlich genutzte Böden gültigen Grenzwerte.

Urbane Böden in Kano waren stärker kontaminiert als Böden in Bobo-Dioulasso und Sikasso. Cadmium Konzentrationen in Kano waren sieben- bis zehnfach höher als in Bobo-Dioulasso und Sikasso während dagegen Zinkgehalte in Böden Kanos sogar zwanzigfach höher als in den anderen untersuchten Städten lagen. Die Tatsache, dass die mittleren Schwermetallkonzentrationen in den Böden der drei genannten Städte mit steigender Profiltiefe abnimmt, weist auf anthropogene Ursachen der Anreicherung hin. In der auf dem Input-Output Ansatz basierenden Schwermetallbilanz wurde deutlich, dass vor allem Bewässerungswasser und Dünger die Haupteingangsgrößen (Inputs) darstellten. Mit dem Bewässerungswasser wurden 400-3700 g Cd ha^{-1} a^{-1} zugeführt. Der Schwermetalleintrag mit dem verwendeten Dünger betrug 7200-22300 g Zn ha^{-1} a^{-1}, 30-2100 g Cd ha^{-1} a^{-1} und 50-17600 g Zn ha^{-1} a^{-1}. Die durch den ‚Harmattan dust‘ verursachten Einträge lagen dagegen nur bei 0,02-0,4 g Cd ha^{-1} a^{-1} und 40-200 g Zn ha^{-1} a^{-1}.

Jährliche Austräge von Cd und Zn in Form geernteten Amarandts waren mit 0,7-2,0 g Cd ha^{-1} a^{-1} und 100-1700 g Zn ha^{-1} a^{-1} bezogen auf eine Gesamttrockenmasse (TM) von 3,5-28 t ha^{-1} a^{-1} am höchsten. Mit Hilfe von Ionenaustauscherharzen bestimmte kumulative Sickerwasserausträge lagen bei 200-300 g Cd ha^{-1} a^{-1} und 1100-2800 g Zn ha^{-1} a^{-1}. Die Berechnung einer Bilanz aus Einträgen in Form von Dünger und Bewässerungswasser und Austrägen in Form geernteter Gemüsebiomasse und Sickerwasserverlusten ergab eine positive Nettobilanz von 700-3900 g Cd ha^{-1} a^{-1} und 9200-23400 g Zn ha^{-1} a^{-1}.

Die Fraktionierung von Cd und Zn in sieben operativ definierte Fraktionen in urbanen Böden Kanos zeigte, dass die am stärksten reaktiven, mit Ammoniumnitrat und Ammoniumacetat extrahierbaren labilen und pflanzenverfügbaren Fraktionen quantitativ einen Prozentanteil von 29-42% des gesamten Cadmium und von 22-54% des gesamten Zink ausmachten.

Eine Korrelationsanalyse ergab eine signifikante negative Korrelation von Phosphor mit an Manganoxid gebundenem Cadmium (-0,98; P<0,01), die nahelegt, dass Mangankonkretionen signifikante Cadmium- und

Phosphorsenken in den untersuchten Böden darstellen. Organisch gebundener Kohlenstoff zeigte negative Korrelation mit der in Wasser löslichen Zinkfraktion (-0,98; $P \leq 0,01$) und positive Korrelation mit der an Eisenoxide gebundenen Zinkfraktion (0,97; $P \leq 0,05$). Dies verdeutlicht, dass die Zersetzung organischer Substanz im Boden Bindungsstellen für labile Zinkfraktionen reduziert und über die Verhinderung der Reduktion von Eisenverbindungen die Kapazität für das Zink-Rückhaltevermögen durch Anbindung an Eisenoxide erhöht. Auch die negative Korrelation der austauschbaren Zinkfraktion mit der Kationenaustauschkapazität der Böden (-0,90; $P \leq 0,05$) zeigt, dass Zink wahrscheinlich auf spezifische Weise im Boden adsorbiert wurde.

Die potenzielle Mobilität von Cadmium und Zink wurde auf Basis der absoluten und relativen Gehalte der schwach gebundenen (F1 + F2) und der mäßig mobilen Fraktionen (F3) berechnet. Die Mobilitätsfaktoren von Cadmium (31-42%) und Zink (22-54%) zeigten die hohe Mobilität dieser Schwermetallelemente. Die hohe Mobilität der Metalle in sandigen Böden verdeutlichte das Risiko horizontaler Verlagerung von Schwermetallen besonders für Cadmium, das signifikant mit der Sandfraktion im Boden korrelierte (0,41; $P<0,05$). Dieses Schwermetall desorbiert relativ leicht von Bodenpartikeln in einfachen Ionenaustauschreaktionen. Das hohe Aufkommen an Abwasserbewässerung kann zur Umverlagerung von Schwermetallen in tiefere Horizonte des Bodenprofils durch Versickerung führen.

Der Tranfer von Cd und Zn vom Boden zur Pflanze wurde mit dem Metalltransferfaktor (MTF) auf der Grundlage des gesamten und DTPA-extrahierbaren Cd und Zn geschätzt. DTPA-verfügbarer Zink in den Böden lag im Bereich von 18 bis 66 mg kg^{-1} und DTPA-verfügbares Cadmium im Bereich von 0,19 bis 0,35 mg kg^{-1}. Gesamtgehalte von Zn und Cd in den Pflanzensprossteilen lagen im Bereich von 8,4-256 mg Zn kg^{-1} und 0,04-1,7 mg Cd kg^{-1}.

Zinkgehalte in den meisten untersuchten Gemüsesorten lagen über den von WHO/FAO festgelegten Grenzwerten von 60 mg kg^{-1}. Zinkkonzentrationen in den Blättern des Amarandts (Amaranthus caudatus L.) lagen im Bereich von 13-128 mg kg^{-1} in allen fünf Untersuchungsstandorten während Zinkkonzentrationen in den Wurzeln zwischen 15 und 141 mg kg^{-1} lagen. Im Kopfsalat wurde der empfohlene Grenzwert von 60 mg kg^{-1} für Zink um den Faktor vier überschritten. Die im Amarandt festgestellten Cadmiumkonzentrationen lagen im Bereich von 0,00–0,22 mg kg^{-1} in den Blättern und im Bereich von 0,02 – 0,26 mg kg^{-1} in den Wurzeln. Die höchsten Cadmiumkonzentrationen wurden beim Kopfsalat mit 0,06 bis 1,7 mg kg^{-1} im eßbaren Teil festgestellt während die in den Wurzeln vorgefundenen Konzentrationen mit 0,1 bis 0,24 mg kg^{-1} etwas geringer waren. Von allen untersuchten Gemüsearten wurden nur bei Karotte Cadmiumkonzentrationen unter dem von WHO/FAO festgelegtem Grenzwert von 0,2 mg kg^{-1} Cadmium in Gemüse festgestellt.

Metalltransferverhältnisse von 0,2 bis 0,9 für Zink waren im Mittel höher als mittlere Transferverhältnisse von Cadmium, die im Bereich von 0,1 bis 0,6 lagen. In allen untersuchten Gemüsearten war die Verlagerung von Zn und Cd von der Wurzel in den Sproß relativ hoch. Für Cadmium wurden Transferfaktoren von bis zu 4,1 ermittelt, bei Zink lag der Maximalwert bei 1,5. Im Kopfsalat wurden hohe Verlagerungsraten von Cadmium von der Wurzel in den Sproß festgestellt, während in Karotten und Petersilie ähnlich hohe Verlagerungsraten für Zink ermittelt wurden. Unsere Ergebnisse zeigen, dass Metalltransferfaktoren (MTF) von Böden entweder auf der Basis von gesamten Schwermetallgehalten oder auch anhand von DTPA-extrahierbaren Metallgehalten geschätzt werden können. Der geschätzte Transferfaktor (TF) von Cd und Zn korrelierte negativ mit austauschbaren Basen und der Kationenaustauschkapazität der Böden (-0,99, $P<0,01$). Das lies darauf schließen, dass die Cadmium- und Zinkaufnahme der von uns untersuchten Gemüsesorten nicht von Diffusionsmechanismen sondern dagegen vor allem durch die Aktivität von um Bindungsplätze konkurrierenden Ionen in aktiven Austauschprozessen beeinflusst wurde.

Eine Bewertung der gesundheitlichen Risiken zeigte, dass die geschätzte Aufnahme von Cd und Zn mit der Nahrung (EDI) in Form von Gemüse im für die Gesundheit nicht schädlichen Bereich von 10-50 µg Cd d^{-1} und 15000 µg Zn d^{-1} lag. Die höchsten festgestellten Werte des EDI lagen für Cd bei 17 µg d^{-1} und für Zn bei 6095 µg d^{-1}. Die Quantifizierung der mittleren täglichen Dosis und des Target Hazard Quotienten (THQ) über Bodenaufnahme und Gemüsekonsum ergab keine unmittelbare Gesundheitsgefährdung.

Chapter 1

General introduction, research objectives and hypotheses

1.0. General introduction

1.1. Urban agriculture

The surge in population and rapid urbanization especially in the developing countries has led to increasing demand for food, shelter and employment. In 1950 only 4.5% of people in Africa lived in urban centres, this rose to 11.7% in 2009 and by 2050, it is expected that 19.6% of Africans will live in cities (United Nations, 2010). This phenomenal growth is typical of sub-Saharan Africa (SSA) where annual population growth in cities is the highest (4 per cent) in the world (World Bank, 2009). Urban population of SSA has doubled to 290 million people from 1990 to 2007 (World Bank, 2009). In West Africa, where annual growth rate is 6.3% (Snrech, 1994), 63% of its population are expected to dwell in urban centres by 2020 (Drechsel et al., 2005).

Boland (2005) defined urban agriculture (UA) as all forms of agricultural production in or directly adjacent to the city, which mainly provide urban markets with food products for sale to consumers or for consumption by the city-dwelling growers themselves. It covers a range of production systems and techniques ranging from vegetable production, animal husbandry, aquaculture and horticulture. It plays an important role in ensuring constant supply of staple crop and animal products (Drechsel et al., 2007) within the proximity of urban spaces thus ensuring adequate family nutrition. It is used as a food security strategy by poor urban households (Klemesu and Maxwell, 2000; Nugent, 2000). It provides employment opportunity for economically and in some cases educationally disadvantaged and unemployed youths in cities (van Veenhuizen and Danso, 2007). UA also serves as an insurance against income losses especially on the side of female headed households (Mkwambisi et al., 2007). Drechsel et al. (2007) estimated a monthly income between US$ 40 - 1160 per farm under UA in Accra (Ghana), Bamako (Mali), Cotonou (Benin), Lagos (Nigeria), Niamey (Niger), and Ouagadougou (Burkina Faso).

Intensive use of resources like mineral and chemical fertilizers, pesticides, industrial and municipal waste, sludge which often contain hazardous toxic substances like heavy metals (HMs) (Binns et al., 2003) and pathogens (Keraita and Drechsel, 2002; Amoah et al., 2005) is raising a serious concern on sustainability of UA and environmental quality. There may be potential health risk for producers and consumers when faecal coliforms (Keraita and Drechsel, 2002; Amoah et al., 2005) and HMs (Mapanda et al., 2005; Agbenin et al 2009) are introduced into the food chain through wastewater irrigation. Wastewater irrigation has been identified as a major route of HM contamination of soil and groundwater (Zhang et al., 1996; Bassanino, 2007). Binns et al. (2003) observed high concentration of toxic HMs in irrigation water in Kano, Nigeria. Beside wastewater irrigation, anthropogenic source of heavy metals including battery dismantling, tire refuse, pesticide residues or textile colouring can also pollute urban gardens with HMs.

1.2. Wastewater use in urban agriculture

Increasing demand for irrigation water and organic fertilizers in urban centres to meet the demand of their rapidly growing population has led to the intensive use of organic waste products and wastewater in urban agriculture. Van der Hoek (2004) defines wastewater as domestic effluent consisting of black water (excreta, urine and associated sludge) and grey water (kitchen and bathroom wastewater). Wastewater reuse as a substitute for clean water irrigation has equally spread to areas downstream of urban centres (Scott et al., 2004). It has been estimated that about 20 Mio ha of land is under wastewater irrigation in over 50 countries (Hussain et al., 2001). Homsi (2000) reported that < 20% of these black waters receive treatment in developing countries. Wastewater irrigation plays a significant role in combating food shortages by supplying vegetables to meet the demand of the ever increasing population. Even though contaminated or polluted water used for irrigation may well contain essential plant nutrients (Ensink et al. 2002; Van der Hoek et al., 2002), it can also be a major source of heavy metal pollution for agricultural soils and its illicit use can have a detrimental effect on the surrounding environment including people living around the irrigated gardens, the gardener, his family and the eventual consumer of the produce.

In Kano, Nigeria, large amounts of industrial wastes, domestic and abattoir wastewater are discharged into city streams and used for irrigation, for which Binns et al. (2003) reported that they contained large amounts of toxic heavy metals. As a result of these irrigation practices and air-borne contamination, heavy metals such as cadmium (Cd), copper (Cu), zinc (Zn), lead (Pb), nickel (Ni), arsenic (As), chromium (Cr) and cobalt (Co) may have reached critical levels of which the plant availability and thus relevance for human health, however, is unknown for acid savannah soils, typical for this part of northern Nigeria.

Understanding the behaviour, movement, retention, mobilization and dynamic equilibria of heavy metals in a heterogeneous system like a soil is imperative to characterize its bioavailability and mobility (Gomes et al., 2001) and possible food chain contamination. Trace metal transport and availability in a competitive heterogeneous system between different soil components is a function of the interactions of the different chemical species of such metals present in the system, the soil conditions and the prevailing environmental conditions and not only a function of total metal content in the soil-solution or solid phase (He et al., 2004). Activity of heavy metals in a complex soil matrix is dependent on the chemical species of the metals present. Thus, knowledge about the chemical speciation of heavy metals provides information on the bioavailability and toxicity of such metals. The plant available heavy metals are the water soluble species which cause damage to human health through consumption of contaminated crops.

1.3. Heavy metals in the environment

Heavy metals are often referred to as trace or toxic elements because of the manifestation of their toxic effects in plants, animals and man (Doelsch et al., 2006) and herbal remedies (Obi et al., 2006). Heavy metals include As, Cd, Co, Cr, Cu, Pb, Zn, mercury (Ag), gold (Au), manganese (Mn), selenium (Se) and tin

(Sn). They exist in different forms and are associated with a range of soil components which determine their bioavailability and reactivity (Tack et al., 2006). They have variable oxidation states, exhibit paramagnetism and form coloured complex ions.

Heavy metals in soils may be of natural and anthropogenic origin. Pedogenesis is the major natural source of heavy metal contamination which may be overriding the effects of anthropogenic contamination wherever the parent material contains high levels of heavy metals (Brown et al., 1999). Minerals like galena, cerussite, cassiterite and arsenopyrite can undergo dissolution through chemical weathering thereby releasing heavy metals contained. Trace elements occur as constituents of primary and secondary minerals through the process of inclusion, adsorption, and solid solution formation termed as coprecipitation (Sposito, 2008). Atmospheric deposition as a result of acid rain and dew is another natural source of heavy metal pollution (Nriagu, 1990). Naidu et al. (1997) identified dust storms, wild forest fires and volcanic eruptions as natural sources of heavy metal contamination.

Anthropogenic sources of heavy metal contamination are widespread. Agricultural activities such as pesticide and herbicide application, contaminated irrigation water, use of municipal waste for fertilization (Alloway and Jackson, 1991) and even mineral fertilizer containing traces of heavy metals (Gray et al., 1999) are major sources of enrichment. Direct deposition of waste by man on land (Merian et al., 2004), mining activities, use of lead as anti-nock in gasoline, traffic emission (Nriagu, 1990); building materials like paints, cigarette smoking, metallurgy or smelting, aerosol cans and sewage discharge, among others, are all anthropogenic sources of heavy metals. Even zero tillage may be contributing to the enrichment of atmosphere-deposited heavy metals as the mixing effects of ploughing are avoided (Düring et al., 2002). The atmosphere, in turn, may be loaded with heavy metals by the desintegration of applied waste materials which gradually release the heavy metals in them. Agbenin (2002) however, observed Pb accumulation in a Nigerian soil as a result of long-term cultivation. Anguelov and Anguelova (2009) reported a significant increase in the concentration of Zn in pasture fields as a result of manure application. Similarly, in soils of the Nigerian savannah, Agbenin (2001) reported addition of some trace metals through farmyard manure and mineral fertilizer application. Some authors (Sörme and Lagerkvist, 2002; Iijitima et al., 2007) identified heavy metal emissions from several sources such as wearing of automobile tires and brake linings in the traffic scenario, roofs and food remnants in the residential as well as other domestic by-products as diffuse. Heavy metals emanating from anthropogenic sources are more dangerous because of their instability and solubility leading to a typically high bio-availability.

1.4. Heavy metal availability in the soil

Tack et al. (2006) observed sesquioxides as major soil components contributing to heavy metal fractions in the soil environment. The amorphous and crystalline forms of these hydrous oxides have a large affinity for heavy metals and hence exert a major influence on heavy metal fixation and release in soils.

Organic matter is another soil component influencing the availability of heavy metals in soils through its binding effect on soil components (Naidu et al., 2003) and presence of weak functional groups that dissociate under alkaline condition (Fine at al., 2005). Metal binding in soil is common through interaction of humic substances with oxides of Al, Mn and Fe. These heavy metal fractions (Fe, Al and Mn oxides occluded and organic matter complexed) are regarded as the active fractions (Shuman, 1985). However, Kashem et al. (2007) reported water-soluble and exchangeable forms of heavy metals as the most active and bioavailable, while they described those associated with clay minerals as relatively inactive.

Soil solution chemistry is a key factor affecting heavy metal availability and mobility. A decrease in soil pH increases the mobility of positively charged heavy metals as a result of proton competition with these metals and decrease in negative binding sites (Horckmans et al., 2007). Under alkaline conditions, functional groups present in soil organic matter dissociate, thereby increasing the bio-availability of heavy metals that are bound to organic matter (Fine et al., 2005). Competition for metal cations by organic complexing ligands and soil surface at high pH also improves heavy metal movement and bio-availability in soils. This results mostly from pH-dependent dissolution/precipitation and oxidation/reduction of the hydrated oxides in soil (Tack et al., 2006).

1.5. Bioavailability and uptake of heavy metals by plants

Bioavailability is a term often used to describe the release of a chemical from a medium of concern to living receptors such as plant roots. Misra et al. (2009) defines metal bioavailability as the fraction of heavy metal in the soil that is accessible to the food chain and to the plants. Plants are known to accumulate heavy metals in their edible portion as a result of cropping contaminated fields. Such accumulation is greatly influenced by the concentration of the pollutant, chemical species of the pollutant in the soil, soil physicochemical properties as well as the plant’s growth characteristics (Dudka and Chlopecka, 1990). Repeated application of poor quality irrigation water can strongly influence the speciation of heavy metals, especially if the metal input is anthropogenic, reduce the soil sorption capacity for heavy metals and hence the metals eventually leached into soil solution making it more available for plant utilization and/or pollute the under ground water reserve (Sridhara Chary et al., 2008).

Heavy metals are mostly transported via the plant root through solute movement, mass flow and diffusion. Symbiosis with mycorrhizal fungi that increase the absorptive area of the root can play a significant role in the uptake of heavy metals as observed by Alloway (1995). Plant uptake of mobile ions present in the soil solution is largely determined by the total quantity of the ions in the soil solution, but in the case of strongly adsorbed ions, absorption seems to depend more upon the amount and surface area of roots produced (Wild, 1988). Roots excrete products like high molecular weight organic acids which form complexes and chelate with metal ions, thereby modifying heavy metal movement and fixation in soils (Wang et al., 2009). These authors observed heavy metals in plant roots to strongly correlate with all the metal fractions and total metal contents of their investigated soils and crops.

Kukier et. al (2004) and Basta et al. (2005) stated soil pH to be the most important property controlling heavy metal uptake by plants. Tsadiles et al. (2005) observed a negative linear correlation between pH and plant Cd contents which corrobates findings of Tudoreanu and Philips (2004). From a simulation study to model Cd transport in soils following a long-time sludge application, Bergkvist and Jarvis (2004) concluded that Cd loading was among the most important factors affecting leaching and crop uptake of Cd. Soil organic matter is another soil property that influences heavy metal availability in soils. Ge and Hendershot (2005) showed organic matter to be the primary accumulator of heavy metals especially of Cd in some temperate soils. Agbenin (2002) observed inhibitory effect of soil organic matter on crystallization of HM occluded in Mn and Fe oxides in soils of the Nigerian savannah. Other non-soil factors that influence heavy metals uptake by plants include (a) the concentration and speciation of the metal in the soil solution, (b) the movement of the metal from the bulk soil to the root surface, (c) the transport of the metal from the root surface into the root, and (d) metal translocation from the root to the shoot (Wild, 1988). Ageing of metal oxide is another factor affecting bioavailability of heavy metals. As a long-term chemical process it can decrease the bioavailability of heavy metals in soils with time (Lock and Janssen, 2003). This refers to dehydration and recrystalization of precipitates of hydrous metal oxides with time and hence reducing the mobility of the metal associated with these oxides with time.

Several methodological approaches have been employed to assess heavy metal availability in soils. The chemical reactivity and biological availability of a metal towards other components in a soil-solution matrix is characterized by its chemical species in the solution phase. Sequential extraction has been proposed by many authors (Chlopecka, 1996; Ma and Rao, 1997; Tipping et al., 2003; Lucho-Constantino et al., 2005). This method consists of partitioning heavy metals into five operationally defined fractions: exchangeable, carbonate, Fe-Mn oxide bound, organic and residual. Ma and Rao (1997) proposed that metals in non-residual fractions are more bioavailable than metals associated with the residual fractions. Therefore, metals in water-soluble and exchangeable fractions would contribute to the labile fractions, whereas metal ions in the residual fractions are tightly bound and are not expected to be released under natural conditions (Clevenger and Mullins, 1982; Xian, 1989). Silviera and Sommers (1977) suggested that sorbed metal fractions reflect potential mobility more than potential bioavailability in sludge amended soil. The major drawback of sequential extraction is the difficulty in interpreting its results with respect to availability (Degryse et al., 2004). These authors suggested isotopically exchangeable pools of heavy metals to well represent fractions in dynamic equilibrium with metals in the solution phase. Gray et al. (2005) employed this technique to assess Cd availability in soils. In a more recent study, Kirkham (2006) showed diffusive gradients in a thin film technique (DGT) to be a powerful method of determining the bioavailability of heavy metals. In the method as described by Kirkham (2006) ions are dynamically removed by their diffusion through a gel to a binding resin.

Kinetics and equilibria of metal release from the solid to the liquid phase has been related to the binding form of the metal in the solid phase which influences its remobilization and hence bioavailability (Tack and Verloo, 1995).

1.6. Health and risk assessment from heavy metal pollution

While soils serve as sinks for numerous waste products of natural and anthropogenic origins, they also are media for plant to grow and at the same time transmitters of pollutants to the environment, subsurface water and plants. Human health may be negatively affected by the consumption of crops grown on soils contaminated with heavy metals (Zheng et al., 2007) or through water supply (Lin et al., 2007). Wastewater has been linked to chronic health disorders such as diarrhea, cholera, typhoid and gastro-intestinal diseases (Scott et al., 2004). The use of wastewater for irrigation also leads to the risk of underground water pollution through leaching and sorption of heavy metals (Michel et al., 2007). Ingestion or inhalation of contaminated particles like dust directly exposes human to heavy metals.

The non-biodegradable nature of heavy metals and their long biological half-life make them a crucial environmental issue (Cui et al., 2005). Liu et al (2005) reported health damage to inhabitants of mine areas as a result of heavy metal pollution. Pruvot et al. (2006) showed French children living around a former smelter to have elevated blood Pb levels. Similar observations were made in Brazil by Bosso and Enzweiler (2008). It has been reported that soil contamination with Pb and Cd significantly reduced human life expectancy in Romania (Lăcătuşu et al., 1996). High prevalence of upper gastrointestinal cancer in the Van region of Turkey has been linked to heavy metal polltuion of soil, fruits and vegetables (Türkdoğan et al., 2003). Jarup (2003) reported Cd and Pb to be associated with the etiology of a number of cadiovascular, kidney, blood, nervous system and bone diseases.

Certain neurophysiologic disorders such as high prevalence of intrauterine growth retardation in man have been linked to the ingestion of heavy metals like As, Cd and Pb (Fu et al., 2008). Failure of hair pigmentation and liver damage has been attributed to excessive intake of Cu (Al-Subu et al., 2003). Lead accumulation can lead to distortion of haemoglobin and porphyries synthesis (Al-Subu et al., 2003). Possible effects of Zn on humans include nausea, weakness of the muscle, pain and irritability (AWWA, 1990).

There exists a plethora of literature (Audu and Lawal, 2006; Dawaki and Alhassan, 2007; Mashi and Alhassan, 2007; Tudunwada et al., 2007; Akan et al., 2008, 2009; Awode et al., 2008; Abdullahi et al., 2009) on HM contamination of urban gardens especially in Kano, Nigeria. These research works were merely based on the determination of HM concentration in soil, water and crop samples. None of them attempted to characterize HM dynamics, movement and transfer from soil to plant and subsequent translocation within the crop. Moreover, health risks associated with consumption of HM contaminated crops have not been previously studied in this region.

1.7. Research objectives

Based on the scarcity of information on heavy metal flow and dynamics and the potential health risk of heavy metal accumulation in soils of Kano urban gardens, this study was designed to:

(i) determine the dynamics and behaviour of HM transfer in soils;
(ii) determine the forms of HMs in soils and edible portions of vegetables and establish a relationship between soil concentration and plant uptake;
(iii) evaluate human health risks resulting from the cultivation and consumption of vegetables under waste water irrigation.

1.8. Research hypotheses

This PhD research aimed at testing the following research hypotheses:

(i) HM loads in urban arable soils of Kano depend to a larger degree on the use of contaminated irrigation water than on atmospheric deposition.
(ii) HM bio-availability is not only a function of the metal concentration, but equally depends on site-specific chemical species of these metals in the soil solid phase as affected by organic matter content and pH.
(iii) Given the prevailing soil pH, edible portions of vegetables cultivated under urban agriculture in Kano are contaminated by toxic HMs.

1.9. References

Abdullahi, M. S., Uzairu, A. and Okunola, O. J. 2009. Quantitative determination of heavy metal concentrations in onion leaves. International Journal of Environmental Research 3: 271-274.

Agbenin, J.O. 2001. The status and fluxes of some alkaline-earth metals in a savanna Alfisol under long-term cultivation. Catena 45: 313-331.

Agbenin, J.O. 2002. Lead in a Nigerian savanna soil under long-term cultivation. Science of the Total Environment 286: 1-14.

Agbenin, J.O., Danko, M. and Welp, G. 2009. Soil and vegetable compositional relationships of eight potentially toxic metals in urban garden fields from northern Nigeria. Journal of Science, Food and Agriculture 89: 49-54.

Akan, J.C., Abdulrahman, F.I. and Dimari, G.A. 2008. Physicochemical determination of pollutants in wastewater and vegetable samples along the jakara wastewater channel in Kano metropolis, Kano State, Nigeria. European Journal of Scientific Research 23: 122-133.

Akan, J.C., Abdulrahman, F.I., Ogugbuaja, V.O. and Ayodele, J.T. 2009. Heavy metals and anion levels in some samples of vegetable grown within the vicinity of challawa industrial area, Kano State, Nigeria. American Journal of Applied Sciences 6: 534-542.

Alloway, B.J. 1995. Heavy metals in soils. John Wiley and Sons. New York, USA.

Alloway, B.J. and Jackson, A.P. 1991. The behaviour of heavy metals in sewage-sludge amended soils. Science of the Total Environment 100: 151-176.

Al-Subu, M.M., Haddad, M., Mizyed, N., and Mizyed, I. 2003. Impacts of irrigation water containing heavy metals on soil and groundwater-A simulation study. Water, Air and Soil Pollution 146: 141-152.

Amoah, P., Drechsel, P., and Abaidoo, R.C. 2005. Irrigated urban vegetable production in Ghana: sources of pathogen contamination and health risk examination. Irrigation and Drainage 54: 49 – 61

Anguelov, G. and Anguelova, I. 2009. Assessment of land-use effect on trace elements concentrations in soil solution from Ultisols in North Florida. Agriculture, Ecosystems and Environment 130: 59–66

Audu, A .A. and Lawal, A .O. 2006. Variation in Metal Contents of Plants in Vegetable Garden Sites in Kano Metropolis Journal of Applied Science and Environmental Management. 10: 105 – 109.

Awode, U.A., Uzairu, A., Balarabe, M.L., Harrisson, G.F.S. and Okunola, O.J. 2008. Assessment of peppers and soils for some heavy metals from irrigated farmlands on the Bank of river Challawa, Northern Nigeria. Pakistan Journal of Nutrition 7: 244-248.

AWWA (American Water Works Association): 1990 Water Quality and Treatment: A Handbook for Community Water Supplies. 4th ed., McGraw Hill. USA.

Bassanino, M., Grignani, C., Sacco, D., and Allisiardi, E. 2007. Nitrogen balance at the crop and farm-gate scale in livestock farms in Italy. Agriculture, Ecosystems and Environment 122: 282 - 294.

Basta, N.T., Ryan, J.A. and Chaney, R.L. 2005. Trace elements chemistry in residual-treated soils: key concepts and metal bioavailability. Journal of Environmental Quality 34: 49-63.

Bergkvist, P. and Jarvis, N.J. 2004. Modeling organic carbon dynamics and cadmium fate in long-term sludge-amended soil. Journal of Environmental Quality 33: 181–191.

Binns, J.A., Maconachie, R.A. and Tanko, A.I. 2003. Water, land and health in urban and peri-urban food production: the case of Kano, Nigeria. Land Degradation and Development 14: 413-444.

Boland, J. 2005. Urban agriculture Growing vegetables in cities. Agromisa Foundation, Wageningen, 2005.

Bosso, S. T. and Enzweiler, J. 2008. Bioaccessible lead in soils, slag, and mine wastes from an abandoned mining district in Brazil. Environmental Geochemistry and Health 30: 219–229. doi:10.1007/s10653-007-9110-4.

Brown, G.K., MacCarthy, P. and Leenheer, J. A. 1999. Simultaneous determination of Ca, Cu, Ni, Zn and Cd binding strength with fulvic acid fractions. Analytical Chimica Acta 402: 169-181.

Chlopecker, A. 1996. Forms of Cd, Cu, Pb and Zn in soil and their uptake by cereal crops when applied jointly as carbonates. Water, Air and Soil Pollution 87: 297-309.

Clevenger, T.E. and Mullins, W. 1982. The toxic extraction procedure for hazardous waste. Trace substances in environmental health xvi .University of Missouri, Columbia, MO. pp 77-82.

Cui, Y., Zhu, Y. G., Zhai, R., Huang, Y., Qiu, Y. and Liang, J. 2005. Exposure to metal mixtures and human health impacts in a contaminated area in Nanning, China. Environment. International 31: 784–790.

Degryse, F., Buekers, J. and Smolders, E. 2004. Radio-labile cadmium and zinc in soils as affected by pH and source of contamination. European Journal of Soil Science 55: 113-121.

Doelsch, E., Van de Kerchove, V., and Saint Macary, H. 2006. Heavy metal contents in soils of Reunion (Indian Ocean). Geoderma 134: 119-134.

Drechsel, P., Giordano, M. and Enters, T. 2005. Valuing soil fertility change: Selected methods and case studies. In: Shiferaw, B., Freeman, H.A., Swinton, S.M. (eds) Natural resources management in agriculture; methods for assessing economic and environmental impacts. CAB International, Wallingford, UK, pp. 199 - 221.

Drechsel, P., Graefe, S., and Fink, M. 2007. Rural-urban food, nutrient and water flows in West Africa, IWMI Research Report 115, Colombo, Sri Lanka, 35 p.

Dudka, S. and Chlopecka, A. 1990. Speciation mobility and phytoavailability of trace metals in a sewage sludge amended soil. IUNG. Pulawy, Poland, R (270). pp 42.

Düring, R-A, Hoß, T and Gäth, S. 2002. Depth distribution and bioavailability of pollutants in differently tilled soils. Soil and Tillage Research 66: 183-195.

Ensink, J.H.J., Van der Hoek, W., Matsuno, Y., Munir, S. and Aslam, M.R. 2002. Use of untreated wastewater in peri-urban agriculture in Pakistan: risk and opportunities. Research Report 64. International Water Management Institute (IWMI), Colombo, Sri Lanka.

Fine, P., Scagnossi, A. Chen, Y. and Milgelgrin, U. 2005. practical and mechanistic aspects of the removal of cadmium from aqueous systems using peat. Environmental Pollution 138: 358-367.

Fu, G., Zhou, Q., Liu, J., Liu, W., Wang, T., Zhang, Q. and Jiang, G. 2008. High levels of heavy metals in rice (*Oryza sativa* L.) from a typical E-waste recycling area in southeast China and its potential risk to human health. Chemosphere 71: 1269-1275.

Ge, Y. and Hendershot, W. 2005. Modeling sorption of Cd, Hg and Pb in soils by the NICA [non-ideal competitive adsorption]-Donnan model. Soil and Sediment Contamination 14: 53-69.

Gomes, P.C., Fontes, M.P.F., da Silva, A.G., Mendonca, E.de S. and Netto, R.A. 2001. Selectivity sequence and competitive adsorption of heavy metals by Brazilian soils. Soil Science Society of America Journal 65: 1115-1125.

Gray, C.W., McLaren, R.G., Roberts, A.H.C., and Condron, L.M. 1999. The effect of long-time phosphatic fertilizer applications on the amounts and forms of cadmium in soils under pasture in New Zealand. Nutrient Cycling in Agroecosystems 54: 267-277.

Gray, C.W., McLaren, R.G. Gunther, D. and Sinaj, S. 2005. An assessment of cadmium availability in cadmium-contaminated soils using isotope exchange kinetics. Soil Science Society America Journal 68: 1210-1217.

He, Z.L., Zhang, M.K., Calvert, D.V., Stoffella, P.J., Yong, X.E. and Yu, S. 2004. Transport of heavy metals in surface runoff from vegetable and citrus field. Soil Science Society of America Journal 68: 1662-1669.

Homsi, J. 2000. The present state of sewage treatment. International Report. Water Supply 18: 325–327.

Horckmans, L., Swennen, R. and Deckers, J. 2007. Retention and release of Zn and Cd in spodic horizons as determined by pH_{stat} analysis and single extractions. Science of the Total Environment 376: 86 – 89.

Hussain, I., Raschid, L., Hanjra, M., Marikar, F. and van der Hoek, W. 2001. A Framework for Analyzing Socioeconomic, Health and Environmental Impacts of Wastewater Use in Agriculture in Developing Countries, Working Paper 26. International Water Management Institute (IWMI), Colombo, Sri Lanka, 31 pp.

Jarup, L. 2003. Hazards of heavy metal contamination. British Medical Bulletin 68: 167–182.

Iijima, A., Sato, K., Yano, K., Tago, H., Kato, M., Kimura, H. and Furuta, N. 2007. Particle size and composition distribution analysis of automotive brake abrasion dusts for evaluation of antimony sources of airborne particulate matter. Atmospheric Environment 41: 4908–4919

Kashem, M. A., Singh, B.R. and Kawai, S. 2007. Mobility and distribution of cadmium, nickel and zinc in contaminated soil profiles from Bangladesh. Nutrient Cycling in Agroecosystems 77: 187-198.

Keraita, B. and Drechsel, P. 2002. Waste water use in informal irrigation in urban and peri-urban areas of Kumasi, Ghana. Urban Agriculture Magazine 8: 11 - 13.

Kirkham, M.B. 2006. Cadmium in plants and polluted soils: Effects of soil factors, hyperaccumulation and amendments. Geoderma 137: 19-32.

Klemesu, M.A. and Maxwell, D. 2000. Accra: Urban agriculture as an asset strategy supplementing income and diets. In Nico Barker, Marielle Dubbelling, Sabine Gindel, Ulrich Sabel-Koschella and Henk de Zeeuw (eds), *Growing cities, growing food-Urban agriculture on the policy agenda*. DSE, Eurasburg, Germany, pp.183-208.

Kukier, U., Peters, C.A., Chaney, R.L. and Angle, J.S. 2004. The effect of pH on metal accumulation in two Alyssum species. Journal of Environmental Quality 33: 2090-2102.

Lacatusu R, Rauta C, Carstea S, and Ghelase I. 1996. Soil–plant–man relationships in heavy metal polluted area in Romania. Applied Geochemistry 11: 105– 7.

Li, Z. and Shuman, L.M. 1996. Heavy Metals movement in metal contaminated soil profiles. Soil Science 161: 656 – 666.

Lin, C., Wu, Y., Lu, W., Chen, A., and Liu, Y. 2007. Water chemistry and ecotoxicity of an acid mine drainage affected stream in subtropical China during a major flood event. Journal of Hazardous Materials 142: 199–207. doi:10.1016/j.jhazmat.2006.08.006.

Liu, H., Probst, A. and Liao, B. 2005. Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China). Science Total of the total Environment 339: 153–166.

Lock, K. and Jenssen, C.R. 2003. Influence of aging on metal availability in soils. Review of Environmental Contamination and Toxicology 178: 1-21.

Lucho-Contantino, C.A., Alvarez-Suarez, M., Beltran-Hernadez, R.I., Prieto-Gercia, F. and Poggi-Varaldo, H.M. 2005. A multivariate analysis of the accumulation and fractionation of major trace elements in agricultural soils in Hidalgo State, Mexico irrigated with waste water. Environmental International 31: 313-323.

Ma, Q.L. and Rao, G.N. 1997. Chemical fractionation of cadmium, copper, nickel and zinc in contaminated soils. Journal of Environmental Quality 26: 259-264.

Mansur U.D. and Jazuli A. 2007. Irrigation and Heavy Metals Pollution in Soils under Urban and Peri-Urban Agricultural Systems International Journal of Pure and Applied Sciences 1: 37–42.

Mapanda, F., Mangwayana, E.N., Nyamangra, J. and Giller, K.E. 2005. The effect of long-term irrigation using wastewater on heavy metal contents of soils under vegetables in Harare Zimbabwe. Agriculture, Ecosystems and Environment 107: 151-165.

Mashi, S.A. and Alhassan, M.M. 2007. Effects of wastewater discharge on heavy metals pollution in Fadama soils in Kano city, Nigeria. Biomedical and Environmental Science 20: 70-77.

Merian, E., Anke, M., Inhat, M. and Stoeppler, M. 2004. (Eds.). Elements and their compounds in the environment. Wiley VCH, Weinheim, Germany.

Michel, K., Roose, M. and Ludwig, B. 2007. Comparison of different approaches for modelling heavy metal transport in acidic soils. Geoderma 140: 207-214.

Misra, V., Tiwari, A., Shukla, B. and Seth, C.S. 2009. Effects of soil amendments on the bioavailability of heavy metals from zinc mine tailings. Environmental Monitoring and Assessment 155: 467–475.

Mkwambisi, D.D., Fraser, E.D.G. and Dougill, A.J. 2007. Urban agriculture and poverty reduction: Evaluating how food production in cities contributes to livelihood entitlements in Malawi No. 04 SRI PAPERS. Sustainability Research Institute (SRI) Sustainability Research Institute (SRI), School of Earth and Environment, The University of Leeds, Leeds, LS2 9JT, United Kingdom

Naidu, R., Kookana, R.S., Sumner, M.E., Harter, R.D. and Tiller, K.G. 1997. Cadmium sorption and transport in variable charged soils: A review. Journal of Environmental Quality 26: 602- 617.

Naidu, R., Oliver, D. and McConnell, S. 2003. Heavy metal phytotoxicity in soils. Proceedings of the fifth Natinal Workshop on the Assessment of Site Contamination. National Environmental Protection Council, Australia, pp 235-241.

Nriagu, J.O. 1990. The rise and fall of leaded gasoline. Science of the Total Environment 92:13-28.

Nugent, R. 2000. The impact of urban agriculture on the household and local economies. In Nico Barker, Marielle Dubbelling, Sabine Gindel, Ulrich Sabel-Koschella and Henk de Zeeuw (eds.), *Growing cities, growing food-Urban agriculture on the policy agenda*. DSE, Eurasburg, Germany, pp 67-97.

Obi, E., Dora, N. A. Ekpo, B. and Orish, E. O. 2006. Heavy metal hazards of Nigerian herbal remedies. Science of the Total Environment 369: 35-41.

Pruvot, C., Douay, F., Herve, F. and Waterlot, C. 2006. Heavy metals in soil, crops and grass as a source of human exposure in the former mining areas. Journal of Soils and Sediments 6: 215–20.

Scott, C.A., Faruqui, N.I and Raschid-Sally, L. Wastewater use in irrigated agriculture: Management challenges in developing countries. In: Scott et al. 2004, (eds). Wastewater use in irrigated agriculture: Confronting the livelihood and environmental realities. CABI International, Oxfordshire, UK.

Shuman, L.M. 1985. Fractionation method for soil microelements. Soil Science 140: 11-22

Silviera, D.J. and Sommers, L.E. 1977. Extractability of copper, zinc, cadmium and lead in soils incubated with sewage sludge. Journal of Environmental Quality 6: 47-52.

Snrech, S. 1994. Pour préparer l'avenir de l'Afrique de l'Ouest : une vision à l’horizon 2020. OCDE/BAD/CILSS. Cited in : Drechsel P, Quansah C, Penning De Vries F (1999) Stimulation of urban and peri-urban agriculture in West Africa: characteristics, challenges, need for action. In: Smith OB (ed) Urban Agriculture in West Africa. Contributing to Food Security and Urban sanitation, 2005. International Development Research Centre (IDRC), Ottawa, Canada and Technical Centre for Agricultural and Rural Cooperation (ACP-EU) Wageningen, Netherlands.

Sörme, L. and Lagerkvist, R. 2002. Sources of heavy metals in urban wastewater in Stockholm. Science of the Total Environment 298: 131–145.

Sposito, G. 2008. The chemistry of soils. 2nd edition: Oxford University press Madison Avenue, new York.

Sridhara Chary, N., Kamala, C.T., and Samuel Suman Raj, D. 2008. Assessing risk of heavy metals from consuming food grown on sewage irrigated soils and food chain transfer. Ecotoxicology and Environmental Safety 69: 513–524.

Tack, F. M G. and Verloo, M. G. 1995. Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. International Journal of Environmental Analytical Chemistry 59: 225–238.

Tack, F.M.G., Van Ranst, E. Lievens, C. and Vandenberghe, R.E. 2006. Soil solution Cd, Cu and Zn concentrations as affected by short-time drying or wetting: The role of hydrous oxides of Fe and Mn. Geoderma 137: 83-87.

Tipping, E., Rieuerts, J., Pan, G., Ashmore, M.R., Lofts, S., Hill, M.T.R., Farago, M.E. and Thornton, I. 2003. The solid-solution partitioning of heavy metals (Cu, Zn, Cd, Pb) in upland soils of England and Wales. Environmental Pollution 125: 213-225.

Tsadiles, C.D., Karaivazoglou, N.A., Tsotsolis, N.C., Stamatiadis, S. and Samaras, V. 2005. Cadmium uptake by tobacco as affected by liming, N form and year of cultivation. Environmental Pollution 134: 239-246.

Tudoreanu, L. and Philips, C.J.C. 2004. Modelling cadmium uptake and accumulation in plants. Advances in Agronomy 84: 121-157.

Tudunwada, I.Y., Essiet, E.U. and Mohammed, S.G. 2007. The effects of tannery sludge on heavy metals concentration in cereals on small-holder farms in Kano, Nigeria. Notulae Botanicae Horti Agrobotanici Cluj-Napoca 35: 55-60.

Türkdogan, M.K., Kilicel, F., Kara, K., Tuncer, I. and Uygan I. 2003. Heavy metals in soil, vegetables and fruits in the endemic upper gastrointestinal cancer region of Turkey. Environmental Toxicology and Pharmacology 13: 175–9.

UN, 2010. United Nations, Department of Economics and Social Affairs, Population Division, Population Estimates and Projections Section.

Van der Hoek, W., U.I., Hassan, M., Ensink, J.H.J., Feenstra, S., Raschid-Sally, L., Munir, S., Aslam, R., Ali, N., Hussain, R. and Matsuno, Y. 2002. Urban wastewater: A valuable resource for agriculture. A case study from Haroonabad, Pakistan. Research Report 63. International Water Management Institute (IWMI), Colombo, Sri Lanka.

Van der Hoek, W. 2004. A Framework for a global assessment of the extent of wastewater irrigation: The need for a common wastewater typology. In: Scott et al. 2004, (eds). Wastewater use in irrigated agriculture: Confronting the livelihood and environmental realities. CABI International, Oxfordshire, UK.

van Veenhuizen, R. and Danso, G. 2007. Profitability and sustainability of urban and peri-urban agriculture. Rome, FAO. Report 19, 95 p.

Wang, J., Zhang, C.B. and Jin, Z.X. 2009. The distribution and phytoavailability of heavy metal fractions in rhizosphere soils of Paulowniu fortunei (seem) Hems near a Pb/Zn smelter in Guangdong, PR China. Geoderma 148: 299-306.

Wild, A. 1988. Russell's soil condition and plant growth.11th edition. Longman, U. K.

World Bank. 2009. World Development Indicators database. World Bank.

Xian, X. 1989. Effect of chemical forms of cadmium zinc and lead in polluted soils on their uptake by cabbage plants. Plant Soil. 113: 257-264.

Zhang, W.L., Tian. Z.X., Zhang, N. and Li, X.Q. 1996. Nitrate pollution of groundwater in northern China. Agriculture, Ecosystems and Environment 59: 223 - 231.

Zheng, N., Wang, Q. C., and Zheng, D. M. 2007. Health risk of Hg, Pb, Cd, Zn, and Cu to the inhabitants around Huludao Zinc Plant in China via consumption of vegetables. Science of the Total Environment 383: 81–89. doi: 10.1016/j.scitotenv.2007.05.002.

Chapter 2

Vertical distribution of heavy metals in waste-water irrigated vegetable garden soils of three West African cities

Submitted:

Nutrient Cycling in Agroecosystems

Abstract

Application of untreated wastewater to irrigate urban vegetable gardens is raising serious concern about possible health risks associated with the consumption of these vegetables particularly with regard to the concentrations of heavy metals (HM) in their edible portions. The soil concentrations of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn), were investigated in seven vegetable gardens from the three West African cities of Kano (Nigeria), Bobo-Dioulasso (Burkina Faso) and Sikasso (Mali). Also determined were input–output balances of Cd and Zn from five vegetable gardens under long-term wastewater irrigation in Kano. There Cd (2.3-4.8 mg kg^{-1}) and Zn (13-285 mg kg^{-1}) concentrations throughout the profile attained unsafe levels. The concentrations of Cu (0.8-18 mg kg^{-1}), Cr (1.8-72 mg kg^{-1}), Ni (0-17 mg kg^{-1}) and Pb (0.6-46 mg kg^{-1}) were below the safety thresholds for arable soils. Overall, concentrations of Zn, Cd, Pb and Ni were generally higher in Kano than in Bobo-Dioulasso and Sikasso. Input-output analyses in Kano indicated that irrigation wastewater contributed annually 400-3,700 g Cd ha^{-1} and 7,200-22,300 g Zn ha^{-1}, fertilizer 30-2,100 g Cd ha^{-1} 50-17,600 g Zn ha^{-1}, harmattan dust 0.02-0.4 g Cd ha^{-1} and 40-200 g Zn ha^{-1} while 300-500 g Cd ha^{-1} and 2,700-4,700 g Zn ha^{-1} came from rainwater inputs. Input-output calculations subtracting the amounts of HM taken out in vegetable biomass and that lost to leaching from total inputs yielded an annual net positive balance of 700-4,160 g Cd ha^{-1} and 9,350-39,700 g Zn ha^{-1}. If such inputs remain unchanged for another 10-20 years vegetables raised in these garden fields are likely to be unsuitable for human consumption.

Keywords: Soil contamination; Urban agriculture; Heavy metal balance

2. Introduction

During the last decade the unique agroecological conditions of urban vegetable soils resulting from their input intensity, year-round vegetative cover, soil and hydrological characteristics and their spatial variability (Landsberg 1981; Witting 1991; Hollis 1992; Renger 1993; Businelli et al. 2009) have raised considerable research interests. This is especially so in developing countries where treatment of wastewaters is limited, thus raising concern about HM contamination of these soils when irrigated with untreated wastewater and subsequent accumulation in the food chain through plant uptake. Natural soils of the Nigerian savannah are characterized by low HM concentrations due to their high weathering intensity and long period of pedogenesis (Jones and Wild 1975; Agbenin and Latifatu 2004). However, with intensification of urbanization, agricultural activities and industrialization, the extent of HM accumulation has grown. Among such metals cadmium (Cd) and Zinc (Zn) are notoriously mobile and likely to move down through the soil profile to contaminate ground water (Citeau et al. 2003), even though they are easily intercepted by clay particles in subsurface horizons (Fernandez et al. 2007). Citeau et al. (2003) reported lead (Pb) to be largely stable with low solubility rate. Semlali et al. (2004) observed downward migration of Pb to be negligible. Agbenin (2002) reported lead to accumulate in insoluble forms in a Nigerian savannah soil after 50 years of continuous application of organic manure.

The West African cities of Kano (Nigeria), Bobo-Dioulasso (Burkina Faso) and Sikasso (Mali) are characterized by intensive urban production of vegetables. Even though the cities of Bobo-Dioulasso and Sikasso are less populated and industrialized compared to Kano, HM may as well be accumulated in the profiles of these urban garden soils owing to the quality of irrigation water, high inputs of mineral fertilizers (Diogo et al. 2010; Predotova et al. 2010) and pesticide application. While recent reports stressed the importance of HM loads in irrigation water and soils used for urban vegetable production in Kano (Binns et al. 2003; Abdu et al. 2010a), to our knowledge comparative studies of heavy metal pollution of urban vegetable gardens across West African cities are missing.

Balance or budget approaches have been used to assess HM flows in agricultural systems whereby nutrient budgets of the surface soil and farm-gate budgets are used most often (Bassanino et al. 2007). While the former addresses nutrient flows at the crop scale, the latter quantifies farm-inputs and outputs at the farm level (Velthof et al. 1996; Moolenaar and Lexmond 1998) or at the regional and national scales (Keller et al. 2001; Keller and Schulin 2003; Dach and Starmans 2005).

In view of the above this study aimed at determining the vertical distribution of Cd, Cr, Cu, Ni, Pb, and Zn in urban vegetable gardens of three West African cities. Given the elevated concentration of Cd and Zn in the Kano urban gardens input-output balances of these two metals (Cd and Zn) were monitored at the farm level.

2.1. Materials and methods

2.1.1. Description of the study areas and management practices

Seven urban vegetable gardens were selected for this study. They comprised five farmers' fields in Kano (Nigeria) and one field each in Bobo-Dioulasso (Burkina Faso) and Sikasso. Kano is located at 12° 00' N latitude and 8° 31' E longitude at 480 m above sea level in the Sudan savannah zone of Nigeria. Rainfall is seasonal and highly variable with an annual mean of 705 mm recorded during 2008 when this study was conducted. In Kano irrigation of vegetable gardens is intensively practiced along the major rivers which serve as effluent discharge routes for the municipal and industrial wastes produced by local industries. Management practices and garden sizes were similar across locations. Field plots were mostly between <0.1 ha to 0.4 ha and planted to fast growing vegetables such as (*Amaranthus caudatus* L.), lettuce (*Lactuca sativa* L.), parsley (*Petroselinum crispum*) and carrot (*Daucus carota* ssp. *sativus*) which is often intercropped with the former ones. Fertilizer use among farmers was only occasional whereby urea and NPK were the predominant fertilizer types used during the rainy season. However, one farmer (Zungeru) did not use fertilizer throughout the period of the study as he considered wastewater to contain sufficient nutrients for his crops.

Bobo-Dioulasso (11°10’ N, 4°19’ W, 432 m asl) has a typical southern Sudanian climate with the rainy season starting in April / May and lasting until October. Annual rainfall for the study year 2008 was 728 mm.

Sikasso (11° 19’ N, 5° 40’ W, 375 m asl) has a typi cal Guinean climate comprising two main periods: a 5-6 months rainy season from May / June to October and a subsequent 6-7 months long dry season. Annual rainfall during the study year 2008 was 1271 mm.

Selection of gardens was based on an in-depth survey comprising a GIS-based mapping and farmer interviews about the various sources of irrigation water and management practices across the cities. According to the farmers in Kano and Bobo-Dioulasso, the gardens selected have been under wastewater irrigation for decades while gardeners in Sikasso use mostly well water for irrigation.

In Kano the gardens of Koki, Zungeru, Kwakwaci, Gada and Katsina road were evenly distributed across the city and used different wastewater sources. A natural uncultivated reference / control site was selected for comparison of HM contamination in soil profiles. Another well water irrigated garden (‘Legal’) was also selected as a control in Kano for comparison of vegetable contamination. In Bobo-Dioulasso and Sikasso, all gardens suspected to be affected by high HM loads were located in the same area and irrigated with the same water source; therefore only one garden was selected from each city.

In Kano two of the three major industrial estates, Challawa and Sharada, comprise 115 industries ranging from tanneries, rubber and plastic factories, textile industries and units dedicated to food processing, metal and wood processing of which most discharge their untreated effluents into the city streams. Egboka et al. (1989) reported a severe contamination of boreholes in Kano with residues from food processing industries and Binns et al. (2003) reported Cd concentration as high as 30 mg l^{-1} in urban irrigation water.

2.1.2. Sampling strategy and analytical procedures

2.1.2.1. Soil and crop sampling

Five composite soil samples were taken from each profile in duplicate to a depth of 1.5 m in Kano, Nigeria. In Bobo-Dioulasso and Sikasso however, similar composite samples were taken to a depth of 0.8 and 0.7 meters owing to a hard pan and high water table, respectively. All samples were collected in 2007. The surface of the profile trench was cleaned with a sharp knife and samples were collected through the last layer from bottom upwards. Samples were taken at 0-15, 15-25, 25-35, 35-45, 45-75, 75-100 and 100-150 cm depth intervals. The samples were air-dried, crushed, and passed through a 2-mm mesh sieve prior to analysis.

In Kano at each location duplicate soil samples were taken in 2007 from 0-15, 15-25, 25-35, 35-45, 45-75, 75-100 and 100-150 cm depth. In Bobo-Dioulasso and Sikasso, however, sampling occurred only to depth of 0.8 and 0.7 m given occurrence of a hard pan and a high water table, respectively. All samples were air-dried, crushed, and passed through a 2-mm mesh sieve prior to analysis.

In Kano, where monitoring of farmers' activities such as planting date, frequency, date and duration of irrigation, type and date of fertilizer applied and date of harvest occurred, the year was divided into three seasons: the cold dry season (CDS), the hot dry season (HDS) and the wet season (WS). The CDS lasted from November to January, the HDS from February to May and the WS from June to October. Vegetable cropping was monitored throughout each season and crop and soil samples were collected at each harvest independently of whether a single or more crops were planted throughout the season. Additionally a composite soil sample consisting of 15-20 auger points was collected at 0-20 cm depth from each farmer's field. For the vegetable sampling, 20-25 sub-samples were taken in each of the five gardens just prior to farmers' harvest. The plant samples were washed with clean tap water to remove adhering soil particles. Subsequently, soil samples were air-dried and passed through a 2-mm sieve while vegetable samples were oven-dried to constant weight at 65℃. At

Bobo-Dioulasso and Sikasso soil and vegetable samples were only collected once, in November 2007.

2.1.3. Input sources of HM into the soil

2.1.3.1. Irrigation water sampling

At Kano, samples of wastewater used for irrigation were collected fortnightly from January 2008 to March 2009 into pre-washed 250 ml plastic containers. At each location monthly irrigation water samples were pooled per season yielding a total of three irrigation wastewater samples per year. Two drops of concentrated HCl were added to each sample to suppress microbial activity followed by refrigerator storage until analysis.

2.1.3.2. Atmospheric deposition and rain water collection

In Kano rain and dust samples were collected during the wet and dry seasons. To this end bulk deposition collectors were made of a 0.1 m^3 plastic container and mounted in each of the five gardens at 2 m above ground level as described by Drees et al. (1993) to minimize potential effects of human activities. The plastic containers were covered with a white cotton mesh to reduce contamination from bird droppings, trees and other unwanted materials. The dust in the trap was collected into a clean plastic bag using a clean brush after removing the cotton mesh. Dust samples were collected every week from December 2007 to April 2008 and monthly samples were pooled by season yielding three samples per year and location. Rain samples were collected immediately after each rainfall event during three rainy days in August 2008 yielding a total of three rainfall samples per year and mixed with two drops of concentrated HCl to suppress microbial activity prior to refrigeration until analysis.

2.1.3.3. Fertilizer sampling

Representative samples of fertilizer were collected at each application event in the specific gardens, ground and stored until analysis.

2.1.4. Output of HM

2.1.4.1. Estimating metal concentration in vegetable biomass

Harvested amaranthus, lettuce and parsley were typically packed in bundles and carrots in sacks prior to being taken to local markets. Total harvested biomass per unit area was estimated by measuring the dry weight of five bundles of amaranthus, lettuce and parsley and of five sacks of carrot. The average weight obtained was then multiplied by the total number of bundles or sacks harvested.

2.1.4.2. Leaching losses of metals

In all five gardens of Kano HM leaching was monitored by anion and cation exchange resin cartridges buried below the rooting zone at 60 cm depth. Amberjet 1200 Na^+ and Amberjet 4200 Cl^- acid anion and cation exchangers (Rohm and Hass, Philadelphia, PA, USA) were mixed with pre-washed fine sand and placed saturated with demineralized water into round PVC tubes of 230.6 cm^2 surface area and installed according to the guidelines of TerrAquat Consultancy (Stuttgart, Germany), the patent holder of this method. The tubes were equipped with a net of stainless steel to preserve the resins from falling and buried for ten months (December 2007-October 2008).

2.1.5. Chemical analyses

Particle size distribution was determined by the hydrometer method following dispersion of the soil with calgon solution (Gee and Bauder 1986) and cation exchange capacity (CEC) was determined by extracting the soil with silver-thiourea solution as described by van Reeuwijk (1993). Soil pH was measured in 1:2.5 soil:water suspension using a glass electrode pH meter and organic carbon (OC) content of the soil was determined by dichromate oxidation method (Nelson and Sommers, 1986). For total soil N and P, 1 g soil sample was digested with a mixture of H_2SO_4-salicylic acid-H_2O_2 using selenium as a catalyst. Total N was measured colorimetrically in the digest using the Bertholet reaction (Chaney and Marbach 1962) with an N-autoanalyzer (TECHNICON AAII, TechniCon Systems, Emeryville, CA, USA) and total P was determined by the molybdate-blue method of Lowry and Lopez using ascorbic acid as a reductant (van Reeuwijk 1993).

For heavy metal analysis, 1 g each of soil, plant, and dust samples was digested with concentrated HNO_3 (puriss, p.a. 65%; Sigma-Aldrich Corp., St. Louis, MO, USA) and HCl (37%, Sigma-Aldrich Corp.) at 80 ° C following the procedure described by Lim and Jackson (1986). Fertilizer samples were digested in a beaker with concentrated HNO_3 according to the procedure of the Association of Official Analytical Chemists (Williams 2000). The beakers were swirled gently until white fumes indicated full digestion. The digest was cooled to ambient temperature, filtered and adjusted to 50 ml with distilled water prior to analysis. The water samples were swirled with concentrated HNO_3 at 80 ° C until the solution turned white. Finally the digest was filtered through Whatman No. 42 and diluted to 50 ml with distilled water prior to analysis. Concentrations of Cd, Cr, Cu, Ni, Pb and Zn were determined by atomic absorption spectrophotometry (AAS; Model AA 6680, Shimadzu, Kyoto, Japan).

2.1.6. Resin extraction

After removal from the soil the resin-sand mixture in the cartridge was separated into four layers and a sub sample of exactly 30g was weighed from each layer into an extraction bottle and extracted four times by mechanical shaking with 100 ml of 2 M HCl for 16 hours. The solution was decanted into a beaker and the supernatant solution filtered into a plastic vial. Cadmium and Zn were determined by AAS.

2.1.7. Quantification of HM fluxes

Heavy metal balances were established for each garden based on inputs and outputs. Major sources of these inputs and outputs were irrigation water, fertilizer, rainwater, atmospheric dust, crop removal and leaching losses.

The quantity of irrigation water used throughout the life cycle of each crop was estimated based on the discharge rate of the irrigation pumps, length of irrigation per day and frequency of irrigation for the individual crops. The amount of water was multiplied by the concentration of Cd and Zn. Cadmium and Zn concentrations in rain water (mg l^{-1}) were converted to kg ha^{-1} by multiplication with the amount of annual rainfall. The Cd and Zn input through dust deposition were calculated by multiplying the concentration of dust in g by a yearly estimated dust input of 936 kg ha^{-1} dust from an average weekly dust deposition of 0.18 g collected per 0.1 m^2. The total metal content in the harvested biomass was estimated from the metal concentrations of the crops and the harvested dry matter.

2.1.8. Soil metal balance calculation

In this study, measured input variables were irrigation water and atmospheric deposition in the form of rainfall and dust (equation 1). As output consistend mainly of crop removal and leaching, no proxies for unmeasured input or output parameters had to be used:

$$\Delta SS_{HM} = [IW_{HM} + RW_{HM} + D_{HM}] - [CR_{HM} + L_{HM}] \qquad [1]$$

where ΔSS_{HM} is the balance of heavy metal (HM), IW_{HM}, RW_{HM} and D_{HM} are measured inputs of HM through irrigation water, rainwater and dust deposition, respectively; CR_{HM} is the measured crop removal of HM and L_{HM} denotes losses of HM through leaching. All data are in g ha^{-1} $year^{-1}$.

2.1.9. Statistical analysis

Computed metal balances for each crop were expresed on a hectare basis. Analysis of variance (ANOVA) was conducted and seasonal differences in HM concentration of soil and crop was determined using Least Significant Difference ($LSD_{0.05}$) tests. Simple correlation analysis was used to relate the change in HM content in each soil depth to the calculated HM budgets. All analyses were conducted using SAS 9.2 (SAS 2007) and Microsoft Excel (2003).

2.2. Results and discussion

2.2.1. Distribution of HM in the soil profiles

Heavy metal concentrations ranged from 2.3-4.0 mg kg^{-1} for Cd, from 2.6-50.1 mg kg^{-1} for Cr, from 4.9-13.6 mg kg^{-1} for Cu, from 3.3-12.4 mg kg^{-1} for Ni, from 1.7-16.5 mg kg^{-1} for Pb and from17.4-233 mg kg^{-1} for Zn (Figures 2.1 and 2.2) whereby concentrations of Cr, Cu, Ni, and Pb were below the threshold levels for agricultural soils as given by the EU and CCME (2001; Table 2.1. Across sites most HM concentrations decreased with profile depth, reflecting enrichment at the surface. Higher concentrations of some HM at lower profile depth likely reflected the effects of leaching-related translocation. Cadmium concentrations were with sometimes > 3 mg kg^{-1} at the bottom of the profile well above safety limits but lower than the 5.3 mg kg^{-1} reported by Awode et al. (2008) and far below the mean value of 10.3 reported by Mashi and Alhassan (2007) from Kano.

At the Gada site Cd concentration ranged from 3.7-4.8 mg kg^{-1} and Zn levels were with 233 mg kg^{-1} in the surface horizon surprisingly high (Figure 2.2). Affinity of metals to organic matter (Agbenin 2002) could be responsible for this surface enrichment because of the relatively high OC concentration in the topsoil.

In Bobo-Dioulasso and Sikasso the concentrations of HMs were often several times lower than in Kano. In the former city, Cd concentrations ranged from 0.35-0.46 mg kg^{-1} and 0.46-0.59 mg kg^{-1}, respectively, as compared to the lowest concentration value of 2.3 mg Cd kg^{-1} in Kano (Figure 2.1). Zinc concentrations were up to 20 times higher in Kano than in Bobo-Dioulasso and Sikasso (Figure 2.2). However, Cr concentration in the surface layer of the vegetable garden in Sikasso was with 67 mg kg^{-1} almost 25% higher than in Kano. As the few industries of Sikasso are dedicated to the processing and packaging of agricultural crops, oil and soap and unlike tanning and ginning enterprises do not produce Cr-rich waste, the high values in this Malian city are surprising. In Bobo-Dioulasso, the concentration of Cd and Zn decreased with profile depth (Figures 2.1 and 2.2). As this was similar for the other HMs it may again reflect the anthropogenic origin of the studied HMs in the surface soil. The high concentration of Cr observed in the control soil as well as in the soils from Bobo-Dioulasso and Sikasso likely reflects its association with the soil parent granite and ultramafic rocks. Changes in redox conditions and other chemical properties of the soil as a result of flooding during irrigation and modification of soil pH might have helped to change the oxidation state of Cr in the cultivated soil from the stable Cr (III) to highly mobile Cr (VI) leading to high mobility and hence low residual concentration of this metal. Binding to dissolved organic matter could also be responsible for low Cr concentration in the cultivated soil.

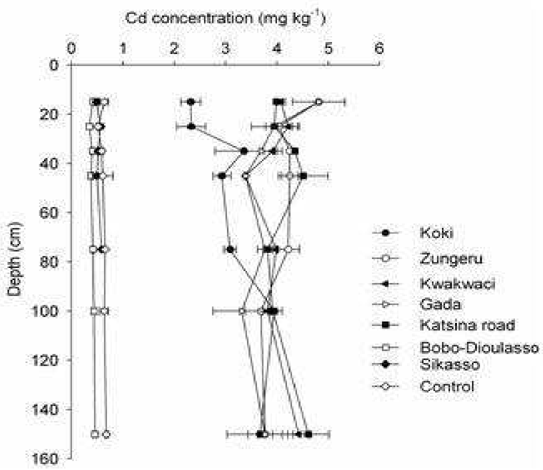


Figure 2.1. Distribution of cadmium (Cd) in soil profiles of wastewater irrigated vegetables gardens in three cities of West Africa (Kano, Bobo Dioulasso and Sikasso).

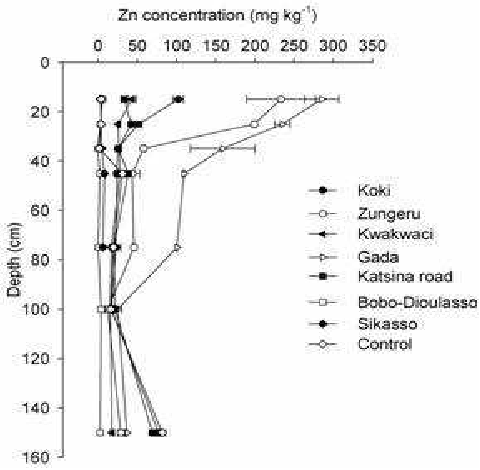


Figure 2.2. Distribution of zinc (Zn) in soil profiles of wastewater irrigated vegetables gardens in three cities of West Africa (Kano, Bobo Dioulasso and Sikasso).

2.2.2. Seasonal variation of heavy metals in Kano

Mean Cd concentration was with 1.4 mg kg^{-1} highest at the Zungeru site. Mean Zn concentration in the wastewater irrigated gardens ranged from 90–167 mg kg^{-1} with the highest and lowest concentrations observed in Gada and Kwakwaci respectively (Table 2.2). Concentrations of Cd and Zn in the well water irrigated garden soil (Legal) were 0.1 and 22.7 mg kg^{-1} Cd and Zn, respectively (Table 2.2). This indicates the effects of wastewater irrigation on Cd and Zn accumulation in the soil. The highest concentration of metals was observed in the CDS followed by HDS (Table 2.3). Irrigation was most intensive during these seasons given high evaporation rates and crop water demands. During the period from January/February to March vegetable production largely depends on wastewater, therefore it is not surprising that the concentration of both metals in the irrigation water was highest during this season and that the intensity of wastewater use for irrigation largely determines soil accumulation of HMs.

Table 2.1. International threshold values for heavy metals concentrations in soils (mg kg^{-1})

Heavy metal	Regulatory system EU	USA	Canada	UK
Cd	3.0	3.0	19.5	1.4
Zn	300	200-300	1400	200
Cr	180	400	1500	6.4
Cu	140	80-200	170	63
Pb	300	300	150	70
Ni	75	50-110	210	50

Source: CCME (2001)

Table 2.2. Concentration (mg kg^{-1}) of cadmium (Cd) and zinc (Zn) in five wastewater- and one wellwater-irrigated vegetable garden soils in Kano, Nigeria. Data show means ± one standard error.

Location	Cd	Zn
Koki (n=5)	0.7±0.2	136±21
Zungeru (n=5)	1.4±0.4	118±15
Kwakwaci (n=5)	0.5±0.2	90±32
Gada (n=5)	1.0±0.3	167±31
Katsina road (n=4)	1.2±0.5	110±21
Legal (n=4)	0.1±0.01	23±5

Table 2.3. Seasonal change of cadmium (Cd) and zinc (Zn) concentration (mg l^{-1}) in wastewater used to irrigate garden soils in Kano, Nigeria. Data show means ± one standard error.

Season	Cd	Zn
Cold dry season	1.1±0.2a[†]	118±17a
Hot dry season	0.9±0.2a	127±21a
Wet season	0.3±0.09b	68±21b

[†] Values followed by different letters are statistically different at P≤0.05.

2.2.3. Input sources of Cd and Zn to soils

2.2.3.1. Heavy metal concentration in irrigation water, fertilizer, rainfall and atmospheric dust

Gardening in Kano is characterized by very low inputs of mineral fertilizers. Irrigation water and atmospheric depositions were therefore, the major sources of Cd and Zn at all sites. Large seasonal concentration changes of HM in irrigation water, rain and dust and site specific differences were observed (Table 2.4). In the irrigation water average Cd concentration at the five sites in Kano was higher than the 0.01 mg l^{-1} threshold level set by the FAO. Zn concentrations were highest in Gada and lowest in Kwakwaci. Even though the mean concentration of 0.87 mg Zn l^{-1} in the irrigation water was less than half of the 2.0 mg l^{-1} threshold, high annual irrigation rates may have caused Zn enrichment as indicated by the significant correlation between irrigation water and soil Zn concentrations (r^2=0.45, $P < 0.05$). In rain water Zn ranged from 0.4-0.6 mg l^{-1} which is 2-3 fold lower than what was measured in the dry season. At the Gada location Zn concentration was highest (Table 2.4) and may reflect the effects of the high concentration of Zn (44-235 mg kg^{-1}) and Cd (0.02-0.45 mg kg^{-1}) in the dust. Fertilizers were major input sources of HMs to agricultural lands. Their concentration in NPK fertilizers was 16.5-17.7 mg Zn kg^{-1} and 0.16-0.22 mg Cd kg^{-1} while urea contained 0.03-0.1 mg Cd kg^{-1} and 0.13-0.85 mg Zn kg^{-1}. The rather high concentrations of HMs in NPK fertilizers may be reflect use of Cd-rich phosphate rocks.

Wastewater irrigation led to annual additions of 400-3,700 g Cd ha^{-1} and 7,200-22,300 g Zn ha^{-1} equivalent to 68% and 78% of the total respective inputs (Table 5). Fertilizer application contributed annually 30-2,100 g Cd ha^{-1} and 50-17,600 g Zn ha^{-1}. Atmospheric wet deposition from rainfall accounted annually for 250-500 g Cd ha^{-1} and 2700-4700 g Zn ha^{-1}. Cadmium and Zn inputs from the estimated 934 kg dust ha^{-1}, instead, were negligible (Table 2.5). In Kano total atmospheric deposition of Cd and Zn were thus 750- and 23-fold higher than the 0.5 g Cd ha^{-1} and the 160 g Zn ha^{-1} reported by Azimi et al. (2004) for Versailles, France.

While Cd concentrations in irrigation and rainwater were above the 0.01 mg l^{-1} FAO threshold level, Zn were below the 2 mg l^{-1} threshold but still higher than values reported by Akoto et al. (2008) for five polluted streams in Ghana. At the Gada site, construction activities at about 100 m from the sampling garden might have contributed to the high Zn concentration of 1.59 mg l^{-1} in the irrigation water (Table 4). Dust at this site also had Zn concentration of 207 mg kg^{-1}. The highest concentration of Cd (0.07 mg l^{-1}) and Zn (0.96 mg l^{-1}) was measured in irrigation water at Katsina road (Table 2.4) and might be caused by discharge from a seed and pesticide industry in the vicinity of the sampling site. Although the concentration of HM in the irrigation water may be low, continued use of this wastewater as practiced in Kano can lead to the build-up of HM in soils (Rattan et al. 2002).

2.2.4. Export of metals

Mean Cd concentration in vegetables ranged from 0.1-0.3 mg kg^{-1} while Zn export was between 11.5-163 mg kg^{-1}. Highest concentration of Cd and Zn was recorded in amaranthus and lettuce, respectively (Table 2.6). Amaranthus with its total dry matter (TDM) of 3.5-28 t ha^{-1} led to annual exports of 0.7-2.0 g Cd ha^{-1} and 100-1,700 g Zn ha^{-1} while such values were regligible for carrots with TDM yields of 1.8 and 3.0 t ha^{-1} in Kwakwaci and Koki, respectively (Table 2.6). The corresponding Cd and Zn export was equally low. Leaching of Cd estimated from resin extraction was 200-300 g ha^{-1} and of Zn 1,100-2,800 g ha^{-1}.

Table 2.4. Concentration of cadmium (Cd) and zinc (Zn) in irrigation wastewater (mg l^{-1}), rain water (mg l^{-1}) and atmospheric dust (mg kg^{-1}) in Kano, Nigeria. Data show means ± one standard error.

Location/Source	Cd	Zn
Koki		
Irrigation wastewater	0.05±0.01	0.7±0.02
Rain water	0.07±0.00	0.5±0.02
Atmospheric dust	0.28±0.02	266.8±18.4
Zungeru		
Irrigation wastewater	0.06±0.01	0.7±0.05
Rain water	0.04±0.01	0.6±0.01
Atmospheric dust	0.38±0.01	63.8±3.4
Kwakwaci		
Irrigation wastewater	0.07±0.02	0.4±0.02
Rain water	0.05±0.00	0.4±0.02
Atmospheric dust	0.47±0.01	87.6±6.80
Gada		
Irrigation wastewater	0.05±0.00	1.0±0.34
Rain water	0.05±0.00	0.6±0.04
Atmospheric dust	0.21±0.10	125.2±47.2
Katsina road		
Irrigation wastewater	0.07±0.01	0.7±0.14
Rain water	0.04±0.01	0.4±0.01
Atmospheric dust	0.31±0.16	132.7±42.5

Table 2.5. Annual balance of horizontal Zn and Cd fluxes for five vegetable gardens in Kano, Nigeria.

Location	**Source**	**Input-output (g ha^{-1} year^{-1})**	
		Cd	Zn
Koki	Irrigation water	1400	15700
	Fertilizer (NPK)	160	17600
	Dust	0.3	220
	Rainfall	300	4700
	Leaching losses	-300	-1500
	Amaranthus	-1.0	-600
	Carrot	-0.5	-300
	Total balance	**1560**	**35800**
Zungeru	Irrigation water	400	7200
	Dust	0.3	54
	Rainfall	500	3900
	Leaching losses	-200	-1800
	Amaranthus	-0.7	-100
	Parsley	-0.3	-100
	Total balance	**700**	**9154**
Kwakwaci	Irrigation water	3700	22300
	Fertilizer (NPK)	210	15470
	Fertilizer (urea)	50	770
	Dust	0.4	70
	Rainfall	500	3900
	Leaching losses	-300	-1100
	Amaranthus	-2.0	-1700
	Carrot	-0.2	-50
	Total balance	**4158**	**39660**
Gada	Irrigation water	700	20000
	Fertilizer (Urea)	80	210
	Dust	0.03	41
	Rainfall	400	4000
	Leaching losses	-200	-2100
	Amaranthus	-3.0	-1700
	Lettuce	-1.0	-500
	Total balance	**976**	**19950**
Katsina road	Irrigation water	840	13500
	Fertilizer (Urea)	30	50
	Dust	0.02	190
	Rainfall	500	2700
	Leaching losses	-200	-2800
	Parsley	-1.0	-900
	Lettuce	-1.0	-600
	Total balance	**1168**	**12140**

Table 2.6. Crop dry matter yield, cadmium (Cd) and zinc (Zn) concentration and annual removal of Cd and Zn in crops from five vegetable gardens in Kano, Nigeria. Data show means ± one standard error.

Location	Crop	Yield ($t\ ha^{-1}$)	Concentration ($mg\ kg^{-1}$)		Crop removal ($g\ ha^{-1}$)	
			Cd	Zn	Cd	Zn
Koki	Amaranthus (n = 8)	7.1	0.1±0.02	76±19	1.0	600.0
	Carrot (n = 2)	3.0	0.2±0.02	110±10	0.5	300.0
Zungeru	Amaranthus (n = 6)	3.5	0.3±0.13	47±11	0.7	100.0
	Parsley (n = 3)	1.7	0.2±0.08	79±5	0.3	100.0
Kwakwaci	Amaranthus (n = 10)	28.1	0.1±0.03	87±12	2.0	1,700.0
	Carrot (n = 2)	1.8	0.1±0.02	12±2	0.2	50.0
Gada	Amaranthus (n = 6)	25.8	0.2±0.03	67±25	3.0	1,700.0
	Lettuce (n = 4)	6.4	0.2±0.07	61±27	1.0	500.0
Katsina road	Parsley (n = 4)	8.1	0.1±0.01	112±27	1.0	900.0
	Lettuce (n = 2)	4.3	0.2±0.01	164±91	1.0	600.0

2.2.5. Input-output balances

High inputs of nutrients through wastewater irrigation have been reported for several studies from West African cities. Diogo et al. (2010) showed large nitrogen (N) surpluses as a result of N rich wastewater irrigation in Niamey, Niger. Similarly, Khai et al. (2007) reported large Zn inputs into vegetable gardens of Hanoi, Vietnam through wastewater irrigation. The net surplus of 9200-39700 g Zn ha^{-1} year^{-1} (Table 2.5) observed in our amaranthus gardens by far exceeded the 650-7700 g ha^{-1} reported by Khai et al. (2007). This largely reflects the level of contamination of the wastewater used for irrigation in Kano. With 9.2 kg ha^{-1} Zn surplus was lowest in the garden under parsley and lettuce. Gardens under amaranthus and carrot production, however, had highest values with 39700 kg Zn ha^{-1} and 4200 kg Cd ha^{-1} (Table 2.5). In the present study, leafy vegetables seemed to accumulate more HM than fleshy vegetables despite the fact that the fleshy vegetable (carrot) had a longer growing cycle (Table 2.6). The significance of correlations between the concentration of HMs and HM budgets decreased with soil depth (Table 2.7) reflecting the effects of anthropogenic activities. Such accumulations may in the long term cause environmental and human health risks even if at present those risks seem to be limited except for Cd and Zn.

Table 2.7. Relationship between profile distribution of Cd and Zn with HM budgets in wastewater irrigated vegetable gardens in Kano, Nigeria.

Soil depth (cm)	Cd budget	Zn budget
	r^2 value	
0-15	0.99	0.98
15-25	0.96	0.51
25-35	0.93	0.32
35-45	0.80	0.26
45-75	0.99	0.48
75-100	0.33	0.56
100-150	0.43	0.17

2.3. Conclusions

Our study shows Cd and Zn accumulation in surface soils of vegetable gardens in Kano (Nigeria). Soil HM concentrations followed the sequence Kano >> Sikasso > Bobo-Dioulasso. Plot-based flux measurements of HM revealed that the major sources of Cd and Zn in Kano are wastewater irrigation, atmospheric deposition and NPK fertilizer wherever it was applied. Cadmium and Zn loads may lead to elevated concentrations in marketed vegetables and leach to the groundwater with negative consequences for human health. Legislation is needed to restrict HM loads and by limiting HM discharges from industries into wastewater that will continue to be used to irrigate urban vegetable gardens.

2.4. References

Abdu N., J.O. Agbenin and A. Buerkert. 2010a. Phytoavailability, human risk assessment and transfer characteristics of cadmium and zinc contamination from urban gardens in Kano, Nigeria. Journal of the Science of Food and Agriculture. (Submitted).

Agbenin, J.O. 2002. Lead in a Nigerian savanna soil under long-term cultivation. Science of the Total Environment 286:1-14.

Agbenin, J.O. and Latifatu, A.O. 2004. Competitive adsorption of copper and zinc by a Bt horizon of a savanna Alfisol as influenced by pH and selective removal of hydrous oxides and organic matter. Geoderma 119: 85-95.

Akoto, O., Bruce, T.N. and Darko, G. 2008. Heavy metals pollution profiles in streams serving the Owabi reservoir. African Journal of Environmental Science and Technology 2: 354-359.

Awode, U.A., Uzairu, A., Balarabe, M.L., Harrisson, G.F.S. and Okunola, O.J. 2008. Assessment of peppers and soils for some heavy metals from irrigated farmlands on the Bank of river Challawa, Northern Nigeria. Pakistan Journal of Nutrition 7: 244-248.

Azimi, S. Cambier, P., Lecuyer, I. and Thevenot, D. 2004. Heavy metal determination in atmospheric deposition and other fluxes in northern France agrosystems. Water Air, and Soil Pollution 157: 295-313.

Bassanino, M., Grignani, C., Sacco, D., Allisiardi, E. 2007. Nitrogen balance at the crop and farm-gate scale in livestock farms in Italy. Agriculture, Ecosystems and Environment 122: 282-294.

Binns, J.A., Maconachie, R.A. and Tanko, A.I. 2003. Water, land and health in urban and peri-urban food production: the case of Kano, Nigeria. Land Degradation and Development 14: 413-444.

Businelli, D., Massaccesi, L. & Onofri, A. 2009. Evaluation of Pb and Ni Mobility to Groundwater in Calcareous Urban Soils of Ancona, Italy. Water Air Soil Pollution 201: 185-193.

Canadian Council of Ministers for the Environment (CCME) 2001. Canadian water quality guidelines for the protection of aquatic life: summary table, Winnipeg, Canada.

Chaney, A.L. and Marbach, E.P. 1962. Modified reagents for determination of urea and ammonia. Clinical Chemistry 8: 130-132.

Citeau, L., Lamy, I., van Oort, F. Elsass, F. 2003. Colloidal facilitated transfer of metals in soils under different land use. Colloids and Surfaces A: Physicochemical Engineering Aspects 217: 11-19.

Dach, J. and Starmans, D. 2005. Heavy metals balance in Polish agronomy: Actual state and previsions for the future. Agriculture, Ecosystems and Environment 107: 309-316.

Diogo, R.V.C., Buerkert, A. and Schlecht, E. 2010. Horizontal nutrient fluxes and food safety in urban and peri-urban vegetable and millet cultivation of Niamey, Niger. Nutrient Cycling Agroecosystems 87:81–102.

Drees, L.R., Manu, A. and Wilding, L.P. 1993. Characteristics of Aeolian dust in Niger, West Africa. Geoderma 59: 213-233.

Egboka, B,C,E,, Nwankwor, G.I., Orajaka, I.P. and Ejiofor, A.O. 1989. Principles and problems of environmental pollution of groundwater resources with case examples from developing countries. Environmental Health Perspectives: Nigeria.

Fernandez, C., Labanowski, J., Cambier, P., Jongmans, A.G., and van Oort, F. 2007. Fate of airborne metal pollution in soils as related to agricultural management. 1. Zn and Pb distributions in soil profiles. European Journal of Soil Science 58: 547-559.

Gee, G.W., and Bauder, J.W. 1986. Particle-size analysis. p. 383–411. *In* A. Klute (ed.) Methods of soil analysis. Part 1. 2nd ed. Agronomy Monogram. 9. ASA and SSSA, Madison, WI.

Hollis, J.M., 1992. Proposal for the classification, description and mapping of soils in urban areas. English Nature, Peterborough.

Jones, M.J., and Wild, A. 1975. Soils of the West African Savanna, Commonwealth Bureau of Soils, Technical Communication, No. 55, Harpenden.

Keller, A and R. Schulin, R. 2003. Modelling heavy metal and phosphorus balances for farming systems. Nutrient Cycling in Agroecosystems 66: 271-284.

Keller, A., Steiger, B., Van der Zee, S. E. A. T. M. and Schulin, R. 2001. A stochastic empirical model for regional heavy metal balances in agroecosystems. Journal of Environmental Quality 30: 1976-1989.

Khai, N.M., Ha, P.Q. and Öborn, I. 2007. Nutrient flows in small-scale peri-urban vegetable farming systems in South Asia-A case study in Hanoi. Agriculture, Ecosystems and Environment 122: 192-202.

Landsberg, H.E., 1981. The urban climate. International Geophysics Series, vol. 28. Academic Press, London.

Lim, C.H. and Jackson, M.L. 1986**.** Expandable phyllosilicate reactions with lithium on heating. Clays and Clay Minerals 34: 346-352.

Mashi, S.A. and Alhassan, M.M. 2007. Effects of wastewater discharge on heavy metals pollution in Fadama soils in Kano city, Nigeria. Biomedical and Environmental Science 20: 70-77.

Moolenaar, S. W. and Lexmond, T. M. 1998. Heavy metal balances of agro-ecosystems in the Netherlands. Netherlands Journal of Agricultural Science 46: 171-192.

Nelson, D.W. and Sommers, L.M. 1986. Total carbon, organic carbon and organic matter, in Methods of Soil Analysis Part 2. Chemical methods, ed. by Sparks DL. American Society of Agronomy, Madison, WI, pp. 961-1010.

Predotova, M., Schlecht, E. and Buerkert, A. 2010. Nitrogen and carbon losses from dung storage in urban gardens of Niamey, Niger. Nutrient Cycling Agroecosystems 87:103–114.

Rattan, R.K., Datta, S.P., Chandra, S. and Saharan, N., 2002. Heavy metals and environmental quality: Indian scenario. Fertilizer News 47: 21-40.

Renger, M., 1993. In: Puskás, I. and Farsang, A. 2009. Diagnostic indicators for characterizing urban soils of Szeged, Hungary. Geoderma 148: 267-281.

Semlali, R.M., Dessogne, J.B., Monna, F., Bolte, J., Azimi, S., Navarro, N., Denaix, L., Loubet, M., Chateau, C., and van Oort, F. 2004. Modelling lead input and output in soils by using lead isotopic geochemistry. Environmental Science and Technology 38: 1513-1521.

Van Reeuwijk, L.P. 1993. Procedures for soil analyses; Technical paper No. 9. Fourth edition. International soil reference and information centre (ISRIC).

Velthof, G.L., van Erp, P.J. and Moolenaar, S.W. 1996. Optimizing fertilizer plans for arable farming systems, II. Effects of fertilizer choice on inputs of heavy metals. Meststoffen 1996: 74-80.

Williams, H. 2000. In: Kane PF (Ed). Official Methods of Analysis of AOAC International (17th Ed). Gaithersburg, Maryland, USA.

Witting, R., 1991. In: Puskás, I. and Farsang, A. 2009. Diagnostic indicators for characterizing urban soils of Szeged, Hungary. Geoderma 148: 267–281.

Chapter 3

Fractionation and mobility of cadmium and zinc in urban vegetable gardens of Kano, Northern Nigeria

Submitted:
Environmental Monitoring and Assessment

Abstract

Metal fractionation provides information on mobility and stability of various metal species which can be used to evaluate the movement of such metals in soils. The effect of waste water irrigation on the fractions, spatial distribution and mobility of cadmium (Cd) and zinc (Zn) was investigated in five urban gardens in Kano, Nigeria. Concentration of total Zn in the surface soils (0-20 cm) ranged from 121-207 mg kg^{-1} while Cd concentration was 0.3-2.0 mg kg^{-1}. Speciation of both heavy metals into seven operationally defined fractions indicated that the most reactive forms extractable with ammonium nitrate and ammonium acetate, also considered as the bioavailable fractions, accounted for 29-42% of total Cd and 22-54% of total Zn, respectively. The weakly bound fractions of Cd and Zn reached up to 50% of the total Cd and Zn concentrations in the soils. Such high proportions of labile Cd and Zn fractions are indicative of anthropogenic origins, arising from the application of wastewater for irrigation and municipal biosolids for soil fertility improvement. Thus, given the predominance of sandy soil textures, high concentrations of labile Cd and Zn in these garden soils represent a potential hazard for the redistribution and translocation of these metals into the food chain and aquifer.

Keywords: Heavy metals, Metal mobility, Metal speciation, Soil contamination

3. Introduction

As a result of year round cultivation of vegetables and water scarcity wastewater irrigation is increasing worldwide. In Kano, Nigeria large amounts of untreated industrial, domestic and abattoir wastewater discharged into city streams and used for irrigation contain large amounts of toxic heavy metals (Binns et al., 2003). Total soil concentration though it is an important parameter, does not allow assessing the availability and subsequent environmental impact of heavy metals (McLaughing et al., 2000; Kabala and Singh, 2001). Therefore, understanding the behaviour, movement, retention, mobilization and dynamic equilibria of heavy metals in a heterogeneous system such as a soil is imperative to characterizing their bioavailability, mobility (Gomes et al., 2001) and possible contamination of the food chain. Trace metal transport and availability in a competitive heterogeneous system also depends on the interactions of the different geochemical species of metals present in the system (He et al., 2004).

Heavy metals are usually characterized by their toxicity and complexity of chemical behaviour (Alloway, 1995). Thus, knowledge about the chemical speciation of heavy metals provides information on their bioavailability, mobility and toxicity. Williams et al. (1987) found a significant downward movement of Zn and Cd in soil profiles subjected to sewage sludge application for eight years. Kashem et al. (2007) reported Cd and Ni to accumulate in the surface horizons of soils in Bangledash but Dowdy et al. (1991) observed little translocation of Cd and Zn down a soil profile. Dowdy and Volk (1983) demonstrated movement of heavy metals through the profile of sandy, acidic soils, low in organic matter and subjected to intensive irrigation and/or rainfall. Similarly, Bhattacharyya et al. (2008) observed a degradation of soil quality as a result of long-term sewage water irrigation in India.

Sequential soil extraction of heavy metals allows characterization of lability and biological availability of a metal in a soil (Tessier et al., 1979; Chlopecka, 1996; Ma and Rao, 1997; Zeien and Brummer, 1998; Tipping et al., 2003; Lucho-Constantino et al., 2005) even if some authors report difficulties in interpreting results from sequential extraction procedure given the inability of most extractants to remove distinct solid-phase species of the metals from the soil matrix (Degryse et al., 2004; Fernàndez-Calviño et al., 2008). Given the lack of data on heavy metal fractions and mobility on intensively cropped urban garden soils of the Tropics, the primary objective of the present work was to investigate the occurrence and spatial distribution of geochemical species of Cd and Zn in irrigated soils of urban gardens in Kano, Nigeria and to investigate the influence of soil properties on Zn and Cd fractions.

3.1. Materials and methods

During June 2007, 15-20 soils samples were collected from 0-20 cm depth from five urban vegetable gardens in Kano, Nigeria. All gardens have been under wastewater irrigation for a long period of time. The soil is a well drained sandy loam that developed from basement complex rocks (Ahmed, 1987). Major vegetable produced in the city include amaranthus (*Amaranthus caudatus* L.), lettuce (*Lactuca sativa* L.), carrot (*Daucus carota* ssp. *sativus*), parsley (*Petroselinum crispum*), cabbage (*Brassica oleracea)*, tomato (*Lycopersicon esculentum*), and onion (*Allium cepa)* among others. Non-crop plants are predominantly herbaceous with scattered woody perennials dominated by *Adansonia digitata, Tamarindus indica* and *Moringa oleifera.*

The soil samples were bulked and sub-samples were air-dried, crushed, and passed through a 2-mm mesh sieve prior to storage for analysis. Soil physicochemical properties (Table 3.1) were measured according to standard analytical procedures. Particle size distribution was determined by the hydrometer method following dispersion of the soil with calgon solution (Gee and Bauder, 1986). Cation exchange capacity (CEC) was determined by extracting the soil with silver-thiourea solution (van Reeuwijk, 1993). Soil pH was measured in 1:2.5 soil/water suspension. Organic carbon content of the soil was determined by the dichromate oxidation method as described by Nelson and Sommers (1986). Total N was determined colorimetrically using the Bertholet reaction (Chaney and Marbach 1962) with an N-autoanalyzer (TECHNICON AAII, TechniCon Systems, Emeryville, CA, USA). Total P was determined by the molybdate-blue method of Lowry and Lopez using ascorbic acid as a reductant as described in van Reeuwijk (1993).

Total concentration of Cd and Zn in the soil was determined by AAS (Model AA 6680, Shimadzu, Kyoto, Japan) following aqua regia (HNO_3 and HCl) digestion of a ground soil sample (Lim and Jackson, 1986).

Table 3.1. Physicochemical properties of five vegetable garden soils in Kano, Nigeria.

Location	Total N (g kg^{-1})	Total P (g kg^{-1})	OC (g kg^{-1})	CEC ($cmol_{(+)}$ kg^{-1})	pH	Total Zn (mg kg^{-1})	Total Cd (mg kg^{-1})	Clay (g kg^{-1})	Sand (g kg^{-1})	Silt (g kg^{-1})	Texture
Koki	1.4	0.7	11.0	8.8	6.9	161	1.0	150	550	300	Sandy loam
Zungeru	1.5	1.0	10.1	11.5	7.1	121	2.0	130	630	240	Sandy loam
Kwakwaci	1.3	1.0	11.0	10.0	6.6	138	0.9	110	770	120	Sandy loam
Gada	1.3	0.7	14.0	9.0	6.6	207	1.3	110	710	180	Sandy loam
Katsina road	0.6	0.3	5.2	7.4	7.4	181	1.4	170	610	220	Sandy loam

3.1.1. Sequential extraction of metals

Operationally defined fractions of Cd and Zn were determined using the extraction scheme developed by Zeien and Brummer (1989) and their lability or mobility was interpreted in terms of mildness of the extractant and the relative concentration of the metal in the sequence of extraction. This fractionation method was developed for aerated soils with very low carbonate concentrations (Lair et al., 2007) which are similar to the soils of this study. The method partitions heavy metals into seven operationally defined fractions as follows:

Readily soluble (F1): Two grams of soil sample were weighed into a pre-weighed 80 ml centrifuge tube and 50 ml unbuffered 1 M NH_4NO_3 was added and shaken for 24h. The suspension was centrifuged at 3500 rpm for 15 min and filtered through a Whatman No. 42 filter paper into a clean plastic vial. This represents the water soluble and highly mobile fraction.

Specifically adsorbed and weakly bound (F2): The soil residue from above was sequentially extracted with 50 ml of 1 M NH_4OAc at pH 6.0 by shaking the suspension for another 24h, centrifuged at 3500 rpm for 15 min and filtered through a Whatman No. 42 filter paper into a clean plastic vial. This was termed as the exchangeable fraction.

Bound to Mn oxides (F3): Residue from F2 was extracted with a mixture of 0.1 M NH_2OH, 0.1 M HCl and 1 M NH_4OAc, in equal ratio at pH 6.0 and the suspension shaken for 30 min. The suspension was centrifuged at 3500 rpm for 15 min and filtered through a Whatman No. 42 filter paper into a clean plastic vial.

Organically bound (F4): The residue from the above extraction was extracted by adding 50 ml of 0.025 M NH_4EDTA at pH 4.6 and shaken for 90 min. The suspension was centrifuged at 3500 rpm for 15 min and filtered through a Whatman No. 42 filter paper into a clean plastic vial. This was named as the organically bound fraction.

Incorporated in amorphous and poorly crystalline Fe oxides (F5): 50 ml of 0.2 M NH_4oxalate at pH 3.25 was added to the residue from the organically bound fraction and extracted by shaking for 4h in the dark. The suspension was centrifuged at 3500 rpm for 15 min and filtered through a Whatman No. 42 filter paper into a clean plastic vial. This was called the amorphous and poorly crystalline Fe oxide fraction.

Incorporated in crystalline iron oxides (F6): This fraction was extracted by shaking the residue from above with 0.1 M ascorbic acid in 0.2 M NH_4oxalate, pH 3.25 for 30 min at 95^0C in a water bath. This was followed by centrifugation at 3500 rpm for 15 min and filtered through a Whatman No. 42 filter paper into a clean plastic vial.

Residual (F7): The residual fraction was determined by transferring the residue from the crystalline iron oxide fraction into a digestion tube and digested with concentrated HNO_3 and $HClO_4$ at a ratio 4:1 on a digestion block. The digestion was completed on the appearance of white fumes. The suspension was equally centrifuged at 3500 rpm for 15 min and filtered through a Whatman No. 42 filter paper into a clean plastic vial.

The individual metal fractions from all the extracts were determined by AAS (Model AA 6680, Shimadzu, Kyoto, Japan).

3.1.2. Data analysis

Cadmium and Zn mobility was assessed based on the absolute and relative content of the weakly bound (labile or mobile: F1 + F2) and the moderately mobile (F3) fractions (Kabala and Singh, 2001). The relative mobility index was calculated as a mobility factor (MF) (Salbu et al., 1998; Kabala and Singh, 2001; Kashem et. al., 2007) using the following equation:

$$MF = \frac{(\mathrm{F1} + \mathrm{F2} + \mathrm{F3})}{(\mathrm{F1} + \mathrm{F2} + \mathrm{F3} + \mathrm{F4} + \mathrm{F5} + \mathrm{F6} + \mathrm{F7})} \times 100$$

The numerator represents the mobile to moderately mobile fractions which included the water or readily soluble, the exchangeable and the Mn oxide-bound fractions. Depending on the prevailing soil conditions, metals occluded in Mn nodules and concretions can be very active and bioavailable and can transform to the acid soluble fraction when the pH of the soil increases (Li et al., 2010). In the present study, manganese oxide bound (F3) fractions of the fractionation scheme of Zeien and Brummer (1989) are less mobile than F1 and F2 fractions and as such, the index used gives the potential mobility as observed by Salbu et al. (1998).

3.2. Results and discussion

3.2.1. Soil physicochemical properties and total metal content

All garden soils were slightly acidic to neutral and predominantly sandy loamy in texture (Table 3.1). Soil organic carbon (OC) was low (5-14 g kg^{-1}), but still higher than values found in soils of the Nigerian savannah (that would range from 0.8-2.9 g kg^{-1} (Jones, 1973; Jones and Wild, 1975). Cation exchange capacity ranged from 7.4-11.5 $cmol_{(+)}$ kg^{-1} which is much higher than values reported by Abdu et al. (2007) for soils of the Nigerian savannah. Total metal concentration in the soils ranged from 121-207 mg kg^{-1} for Zn and 0.9-2.0 mg kg^{-1} for Cd. These values though lower than the threshold value of 3 mg Cd kg^{-1} and 300 mg Zn kg^{-1} set by the EU, Zn concentrations are still higher than the 52-158 mg Zn kg^{-1} reported by Agbenin et al. (2009) for similar garden soils in the Nigerian savannah.

3.2.2. Cadmium and zinc speciation

3.2.2.1. Cadmium fractions

In the Koki soil 28% of the total Cd was in the crystalline Fe oxide fraction. However, Cd mobility in this soil could be high as the next most important fraction was the readily soluble one which comprised 22% of total Cd (Figure 3.1). Organically bound Cd was far lower than the other fractions. In the Kwakwaci and Gada soils, in contrast, the organically bound fraction was the most important one, followed by the carbonate bound fraction. In these soils, Cd bioavailability has been reported (Abdu et al., 2010b) thereby representing potential phytotoxic and human health hazards (Udom et al., 2004). The relatively high percentage of mobile and more labile fractions (26 to 42%) of Cd observed in these soils is an indication of its anthropogenic source. Similar findings were reported by Chlopecker (1996), Kabala and Singh (2001) and Kashem et al. (2007).

At all locations except Zungeru and Katsina road (Figure 3.1), crystalline Fe oxide fractions were more important Cd stores than amorphous Fe oxides. Similar results were reported by Wilcke et al. (1998) and underline the importance of Fe oxide as a sorbent for Cd, particularly at Koki and Zungeru. The relatively high percentage of carbonate-bound Cd fractions at Katsina road is probably due to Cd being held by (exchangeable) electrostatic adsorption and that specifically adsorbed (Christensen and Huang, 1999) which may be plant available when it undergoes solubilization (Kabala and Singh, 2001; Kashem et al., 2007).

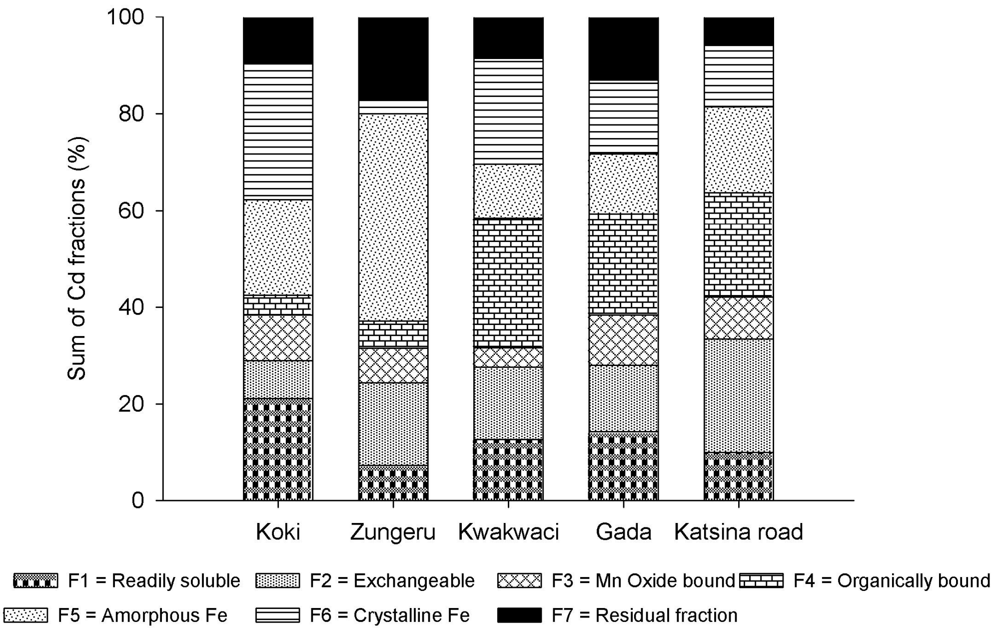


Figure 3.1. Distribution of Cd in the different geochemical fractions in five urban vegetable garden soils of Kano, Nigeria.

Correlation analysis between Cd fractions across all sites (Table 3.2) revealed that the water soluble fraction correlated significantly with the crystalline Fe oxide bound fraction (0.96; $P \leq 0.05$), and the Mn-oxide Cd fraction also correlated significantly with amorphous Fe oxide fraction. Though not shown in Table 3.2, total soil P correlated negatively with Cd occluded in Mn-oxide (-0.98; $P<0.01$), probably suggesting Mn nodules/concretions are significant Cd and P sinks in these garden fields. Likewise, soil CEC correlated negatively (data not shown) with residual Cd (-0.95; $P \leq 0.05$), probably suggesting that not all specifically sorbed Cd was removed in the extraction sequence from F1 to F6.

3.2.2.2. Zinc fractions

At Koki, Zungeru and Gada organically bound Zn accounted for 27-40% of total Zn (Figure 3.2) indicating the strong ability of Zn to form complexes with organic matter thereby reducing its mobility and phytotoxicity (Kashem et al., 2007). At Koki, Kwakwaci and Katsina road 41, 53 and 54% of total Zn, respectively were associated with the weakly bound fractions (F1 + F2 + F3). Microbial metabolic processes occurring under low oxygen supply such as in a flood-irrigated soil can lead to the degradation of complex organic compounds (Sposito, 2008) releasing these weakly bound metals into the soil solution.

Though Zn bound to Mn oxide has been reported to be another important source of heavy metals under reducing condition (Chao, 1972), in the present study this fraction only prevailed at Kwakwaci where it accounted for 40% of the total extractable amount. Several other studies have reported association of Zn with Fe-Mn oxide (Ma and Rao, 1997; Wilcke et al., 1998; Kashem et al., 2007) whereby the latter authors suggested that the association of Zn with the oxide fraction reflects the high stability constant characteristic for Zn oxides. Metals in this fraction though immobile, can easily go into solution when a soil is subjected to irrigation because of the high susceptibility of Mn oxide to reduction followed by Mn release into the soil pore water.

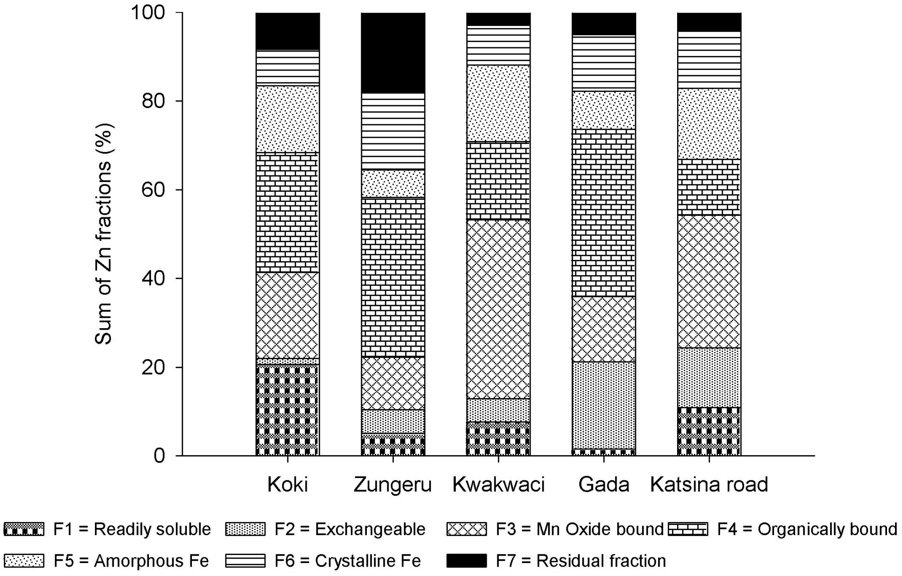


Figure 3.2. Distribution of Zn in the different geochemical fractions in five urban vegetable garden soils of Kano, Nigeria.

The higher proportion of moderately soluble fractions (F2 to F6) in the surface soils as opposed to the residual and readily soluble fractions indicates anthropogenic rather than geogenic origin of Zn in these garden fields. Long-term waste water irrigation has probably led to mobilization of Zn by increasing the soil organic carbon pool and reducing conditions that enhance the solubility and mobility of Zn. Alloway (1995) reported that low-molecular weight organic compounds forms soluble complexes and chelates with Zn, thereby increasing its mobility in soil.

The water soluble Zn fraction (F1) was negatively correlated with crystalline iron oxides (F6) indicating that the latter may suppress the availability of the water soluble fractions thereby reducing the risk of plant uptake. The Mn oxide bound fraction also correlated significantly with the amorphous iron oxide fraction while the organically bound Zn fractions were positively correlated with the crystalline iron oxide fraction (P≤0.05; Table 3.2). When the various fractions were correlated with soil properties, organic carbon correlated negatively with water soluble Zn (-0.98; P≤0.01) and positively with the crystalline Fe oxide fraction (0.97; P≤0.05). Soil organic carbon may thus play a dual role in these soils: its negative correlation with the water soluble fraction implies that decomposition of soil organic matter could release binding sites for the highly mobile Zn fraction while the positive association with the Fe-oxide bound fraction indicates the role of soil organic carbon in the inhibition of Fe crystallization thus increasing the surface area of Fe oxides for Zn retention /occlusion. The exchangeable fraction of Zn was negatively correlated (-0.90; P≤0.05) with soil CEC, probably indicating specific Zn adsorption.

Table 3.2. Correlations between different Zn and Cd fractions from vegetable garden soils in Kano, Nigeria.

	F1	F2	F3	F4	F5	F6	F7
F1		0.13	0.77	0.08	0.62	0.96*	0.69
F2	-0.76		0.60	0.82	0.37	0.11	0.20
F3	-0.02	0.12		0.46	0.71	0.62	0.80
F4	-0.84	0.82	-0.10		-0.11	0.09	0.40
F5	0.04	0.25	0.96*	-0.04		0.38	0.51
F6	-0.99**	0.79	-0.04	-0.88*	0.01		0.52
F7	-0.56	0.02	-0.58	0.46	-0.74	0.57	

The left lower part is correlation coefficient for Zn; the right upper part is correlation coefficient for Cd; *, Significant at P ≤ 0.05; ** Significant at P ≤ 0.01

3.3. *Mobility of Zn and Cd in soils*

With 31-42% for Cd and 22-54% for Zn heavy metal mobility expressed by the mobility factor indicated high Zn and Cd availability and thus potential for food chain and ground water contamination (Figure 3.3). These results are consistent with those of Ma and Rao (1997) but in contrast with those of Kashem et al. (2007) who observed the mobility index to be higher for Cd than for Zn. The result of this investigation suggests that on all soils studied the risk of horizontal translocation of Cd and Zn is high. This is further aggravated by the predominantly sandy texture of the studied soils. Cadmium is known to be very toxic to human health (USEPA, 2005) and has a high potential to be released from the soil by simple ion exchange reactions (Rogan et al., 2009). Results from several other studies (Kuo et al., 1983; Szerszen et al., 1993; Kabala and Singh, 2001) have shown that metal mobility calculated on the basis of weakly adsorbed fractions in surface horizon does not represent metal redistribution to lower horizons. In our study, the significant correlation between Cd and sand fractions (0.41; $P<0.05$) coupled with intensive irrigation in Kano could lead to Cd being redistributed to the deeper layers of the soil profile, particularly under reducing conditions when the garden soil is flooded. Further studies on metal redistribution in various horizons of the soil profiles are, however, required to support this notion. The relatively high proportion of Cd and Zn in the more mobile fractions, likely reflecting its anthropogenic origin and the high mobility index is a further indication that metals of anthropogenic origin are more mobile and phytoavailable than those from pedogenic origin. Similar conclusions were made by Kabata-Pendias (1993), Kashem et al. (2007) and Oyeyiola et al. (2010).

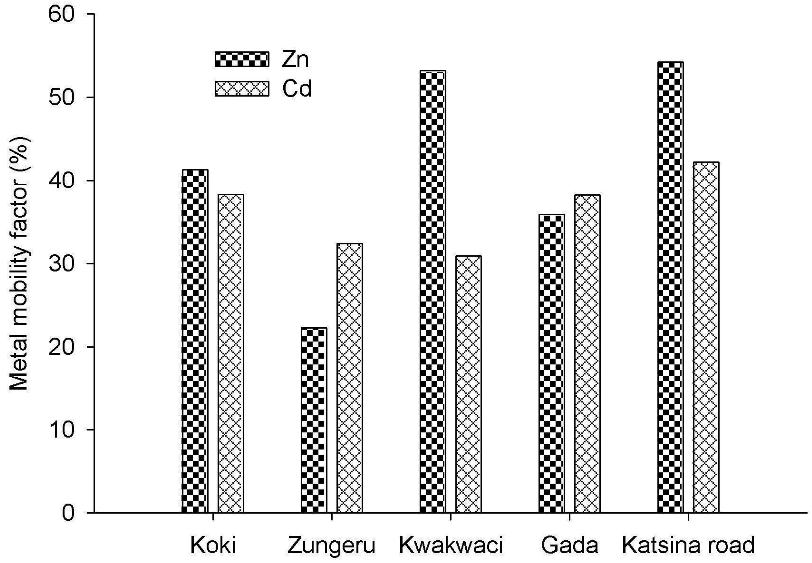


Figure 3.3. Mobility factors for Zn and Cd in the surface soils of vegetable gardens in Kano, Nigeria.

3.4. Conclusions

Distribution of chemical species of heavy metals in the studied surface soils of intensively managed vegetable gardens revealed the major role of mobile fractions. Between 29 and 42% of total Cd and 22-54% of total Zn were in the most reactive and presumably mobile fractions (F1 + F2 + F3) indicating anthropogenic origin of these metals. At all study locations, potential mobility of Zn and Cd was around 50%. Positive correlations between Cd and sand fractions coupled with a high mobility index strongly suggest that these metals could be translocated from the surface to subsurface horizons and be easily available for uptake by vegetables leading to potential human health hazards as a result of continued irrigation with contaminated waste water.

3.5. References

Abdu N., J.O. Agbenin and A. Buerkert. 2010b. Phytoavailability, human risk assessment and transfer characteristics of cadmium and zinc contamination from urban gardens in Kano, Nigeria. Journal of the Science of Food and Agriculture. (Submitted).

Abdu, N., Yusuf, A.A., Abdulkadir, A., Arunah, U.L., Chude, V.O. and Pam, S.G. 2007. Zinc soil test calibration based on 0.1N HCl extractable zinc and cation exchange CAPACITY from upland soils of Northern Nigeria. Journal of Agronomy 6: 179-182.

Agbenin, J.O., Danko, M. and Welp, G. 2009. Soil and vegetable compositional relationships of eight potentially toxic metals in urban garden fields from northern Nigeria. Journal of Science, Food and Agriculture 89: 49-54.

Ahmed, K. 1987. Erosion hazard assessment in the Savannah: The Hadejia-Jama'are River Basin: In Mortimore, M. Olofin, E.A. Clinecole, R.A, and Abdulkadir A. (eds), Perspective on land Administration and Development in Northern Nigeria, Proceedings of the Workshop on Land Resources, Department of Geography, Bayero Univeristy, Kano pp 234-247.

Alloway, B.J. 1995. Heavy metals in soils. John Wiley and Sons. New York, USA.

Binns, J.A., Maconachie, R.A. and Tanko, A.I. 2003. Water, land and health in urban and peri-urban food production: the case of Kano, Nigeria. Land Degradation and Development 14: 413-444.

Bhattacharyya, P., Tripathy, S., Chakrabarti, K., Chakraborty, A. and Banik, P. 2008. Fractionation and bioavailability of metals and their impacts on microbial properties in sewage irrigated soil. Chemosphere 72: 543-550.

Chaney, A.L. and Marbach, E.P. 1962. Modified reagents for determination of urea and ammonia. Clinical Chemistry 8: 130–132.

Chao, T.T. 1972. Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. Soil Science Society America Journal 36: 764-768.

Chlopecker, A. 1996. Forms of Cd, Cu, Pb and Zn in soil and their uptake by cereal crops when applied jointly as carbonates. Water, Air and Soil Pollution 87: 297-309.

Christensen, T.H., and Huang, P.M. 1999. Solid phase cadmium and the reactions of aqueous cadmium with soil surfaces. p. 65–96. *In:* McLaughlin, M.J, and Singh, B.R., (Eds) Cadmium in soils and plants. Kluwer Academic Publications, Dordrecht, the Netherlands.

Degryse, F., Buekers, J. and Smolders, E. 2004. Radio-labile cadmium and zinc in soils as affected by pH and source of contamination. European Journal of Soil Science 55: 113-121.

Dowdy, R.H. and Volk, V.V. 1983. Movement of heavy metals in soils. in chemical mobility n sol systems. D.W. Nelson et al. (Eds), SSSA special publication. Madison W. USA. pp. 227-240.

Dowdy, R.H., Latterell, J.J., Hinesly, T.D., Grussman, R.B. and Sullivan, D.L. 1991. Trace metal movement in an Aeric Ochraqualf following 14 years of annual sludge applications. Journal of Environmental Quality 20: 119-123.

Fernandez, C., F. Monna, J. Labanowski, M. Loubet and F. van Oort. 2008. Anthropogenic lead distribution in soils under arable land and permanent grassland estimated by Pb isotopic compositions. Environmental Pollution 156: 1083–1091.

Gee, G.W., and Bauder, J.W. 1986. Particle-size analysis. p. 383–411. *In* A. Klute (Ed) Methods of soil analysis. Part 1. 2nd ed. Agronomy Monogram. 9. ASA and SSSA, Madison, WI.

Gomes, P.C., Fontes, M.P.F., da Silva, A.G., Mendonca, E.de S. and Netto, R.A. 2001. Selectivity sequence and competitive adsorption of heavy metals by Brazilian soils. Soil Science Society of America Journal 65: 1115-1125.

He, Z.L., M.K. Zhang, D.V. Calvert, P.J. Stoffella, X.E. Yang, S. Yu. 2004. Transport of heavy metals in surface runoff from vegetable and citrus fields. Soil Science Society of America Journal 68:1662–1669.

Jones, M. J. 1973. The organic matter content of the savanna soils of West Africa. Journal of soil Science 24: 42-53.

Jones. M. J. and Wild. A. 1975. Soils of the West African Savanna, Commonwealth Bureau of Soils, Technical Communication, No. 55, Harpenden.

Kabala, C. and Singh, B.R. 2001. Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter. Journal of Environmental Quality 30: 485–492.

Kabata-Pendias, A. 1993. Behavioural properties of trace metals in soils. Applied Geochemistry, Supplementary Issue 2: 3–9.

Kashem, M. A., Singh, B.R. and Kawai, S. 2007. Mobility and distribution of cadmium, nickel and zinc in contaminated soil profiles from Bangladesh. Nutrient Cycling in Agroecosystems 77: 187-198.

Kuo, S., Heilman, P.E. and Baker, A.S. 1983. Distribution and forms of copper, zinc, cadmium, iron, and manganese in soils near a copper smelter. Soil Science 135: 101–109.

Lair, G.J., Gerzabek, M.H., and Haberhauer, G. 2007. Retention of copper, cadmium and zinc in soil and its textural fractions influenced by long-term field management. European Journal of Soil Science 58: 1145–1154

Li, X.H., Tang, Z.L., Chu, F.Y. and Yang, L.Y. 2010. Characteristics of distribution and chemical speciation of heavy metals in environmental mediums around Jinchang mining city, Northwest China. Environmental Earth Science DOI 10.1007/s12665-009-0438-1

Lim, C.H. and Jackson, M.L. 1986**.** Expandable phyllosilicate reactions with lithium on heating. Clays and Clay Minerals 34: 346-352.

Lucho-Constantino, C.A., M. Alvarez-Suarez, R.I. Beltran-Hernadez, F. Prieto-Gercia and H.M Poggi-Varaldo. 2005. A multivariate analysis of the accumulation and fractionation of major trace elements in agricultural soils in Hidalgo State, Mexico irrigated with waste water. Environment International 31:313-323.

Ma, Q.L. and Rao, G.N. 1997. Chemical fractionation of cadmium, copper, nickel and zinc in contaminated soils. Journal of Environmental Quality 26: 259-264.

McLaughlin, M.J., Hamon, R.E., McLaren, R.G., Speir, T.W. and Rogers, S.L. 2000. Review: a bioavailability-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. Australia Journal of Soil Research 38: 1037–1086.

Nelson, D.W. and Sommers, L.M. 1986. Total carbon, organic carbon and organic matter, in Methods of Soil Analysis Part 2. Chemical methods, (Ed). by Sparks DL. American Society of Agronomy, Madison, WI, pp. 961–1010.

Oyeyiola, A.O., Olayinka, K.O. and Alo, B.I. 2010. Comparison of three sequential extraction protocols for the fractionation of potentially toxic metals in coastal sediments. Environmental Monitoring and Assessment. DOI 10.1007/s10661-010-1336-4.

Rogan, N., Dolenec, T., Serafimovski, T., Tasev, G. and Dolenec, M. 2009. Distribution and mobility of heavy metals in paddy soils of the Kočani field in Macedonia. Environmental Earth Science. DOI 10.1007/s12665-009-0405-x.

Salbu, B., T. Krekling, and D.H. Oughton. 1998. Characterization of radioactive particles in the environment. Analyst 123: 843–849.

Sposito, G. 2008. The chemistry of soils. 2nd edition: Oxford University press Madison Avenue, New York.

Szerszen, L., T. Chodak, and A. Karczewska. 1993. Areal, profile and time differentiation of heavy metal content in soils in the vicinity of copper smelters in LGOM, Poland. p. 279–281. In: H.J.P. Eijackers (Ed) Integrated soil and sediment research. Kluwer Academic Publications, Dordrecht, the Netherlands.

Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry 51: 844–851.

Tipping, E., Rieuerts, J., Pan, G., Ashmore, M.R., Lofts, S., Hill, M.T.R., Farago, M.E. and Thornton, I. 2003. The solid-solution partitioning of heavy metals (cu, Zn, Cd, Pb) in upland soils of England and Wales. Environmental Pollution 125: 213-225.

Udom, B.E., Mbagwu, J.S.C, Adesodun, J.K. and Agbim, N.N. 2004. Distribution of zinc, copper, cadmium and lead in a tropical Ultisol after long-term disposal of sewage sludge. Environment International 30: 467–470.

USEPA. 2005. Guideline for carcinogen risk assessment: Risk assessment forum, U.S. Environmental Protection Agency, Washington, DC.

Van Reeuwijk, L.P. 1993. Procedures for soil analyses; Technical paper No. 9. Fourth edition. International soil reference and information centre (ISRIC).

Wilcke, W., Kretzschmar, S., Bunt, M., Saboro, G. and Zech, W. 1998. Aluminum and heavy metal partitioning in A horizons of soils in Costa Rican coffee plantations. Soil Science 163: 463-471.

Williams, D.E., Vlamis, J., Pukite, A.H. and Corney, J.E., 1987. Metal movement in sludge amended soils: a nine year study. Soil Science 143: 124–131.

Zeien, H. and Brümmer, G.W. 1989. Chemische Extraktion zur Bestimmung von Schwermetallbindungsformen in Böden. (in German) Mitteilgn. Dtsch. Bodenkundl. Gesellsch 59: 505-510.

Chapter 4

Phytoavailability, human risk assessment and transfer characteristics of zinc and cadmium loads in urban gardens in Kano, Nigeria

Submitted:
Journal of the Science of Food and Agriculture

Abstract

Quantitative data about soil concentrations, phytoavailability and transfer into consumed plant parts for heavy metals in intensively managed urban vegetable production areas of sub-Saharan Africa are scarce. To close this knowledge gap, we studied the transfer of zinc (Zn) and cadmium (Cd) from soil to the root and subsequent translocation to edible portions of amaranthus, lettuce, carrot and parsley. To this end samples were collected from garden soils (0-20 cm depth) of five garden sites (Katsina road, Koki, Gada, Kwakwaci and Zungeru) and the corresponding marketable vegetable crop samples in Kano, Nigeria. Air-dried soil samples were analyzed for total and DTPA-extractable Zn and Cd and plant samples for total Zn and Cd. While respective DTPA-available Zn and Cd concentrations ranged from 18-66 mg kg^{-1} and 0.19-0.35 mg kg^{-1} in soils, total Zn and Cd were between 8.4-256 mg kg^{-1} and 0.04-1.7 mg kg^{-1} in shoot parts. Metal transfer factor (MTF) ratios were higher in Zn (0.2-0.9) than in Cd (0.1-0.6). Our data suggest that total Zn concentration in soil is a reliable indicator to assess its transfer from soil to crop in lettuce, carrot and parsley, while for Cd DTPA-extractable concentration may be used to estimate soil-crop transfer of Cd in amaranthus and carrot. For Cd root-shoot translocation was highest in lettuce while carrot had the highest translocation factor for Zn. Overall, Cd was more easily translocated to the edible plant parts than Zn. Across the locations the exposure for Zn was in the order Katsina road ≈ Koki ≈ Gada > Kwakwaci > Zungeru. Although the calculated target hazard quotient exceeded the international recommended safe limit, average daily dietary intake of Zn and Cd from urban vegetables was within the safe limit. However, the use of untreated wastewater for irrigation should call for action to avoid possible health risk to consumers of urban vegetables in Kano on the long-run.

Keywords: Health risk; root-shoot translocation; heavy metals; vegetables; soil pollution

4. Introduction

Access to high-quality irrigation water in urban agriculture of sub-Saharan Africa is a major limitation to sustainable production modes (WHO, 2006) given repeated reports about risks of food contamination by fecal pathogens (Diogo et al., 2010) and heavy metals (Binns et al., 2003). Although Zn is a micronutrient for plants and essential for human nutrition, its accumulation in the soil and transfer to edible plant parts may in high concentration harm consumers. Cadmium, a non essential element for plants and humans has been identified as the most mobile and easily bio-accumulating metal by green plants (Li et al., 2006).

In Kano, northern Nigeria, large amounts of untreated industrial and municipal waste effluents is used for year round irrigation of vegetables. Such waste water usually contains besides plant nutrients (Ensink et al., 2002; Van der Hoek et al., 2002) often also harmful heavy metals that accumulate in the soil. The use of such untreated waste water has been reported to cause contaminations of the food chain (Wang et al., 2004; Mapanda et al., 2005). Repeated application of poor quality irrigation water can reduce a soil’s retention capacity for heavy metals leading to metals being plant available in the soil solution and/or polluting drinking water reserves (Sridhara Chary et al., 2008).

Given the scarcity of fresh water in this Sahelian environment, farmers in Kano have no alternative but to use contaminated waste water for year round vegetable production in order to meet the demand for such crops. These waters have been reported to contain large amount of toxic heavy metals which may lead to health disorders in humans depending on the uptake and translocation of these metals into plant parts consumed by animals or humans (Binns et al., 2003; Bakare et al., 2004; Oluwatosin et al., 2005; Bosso and Enzweiler, 2008; Fu et al., 2008; Lim et al., 2008; Agbenin et al., 2009).

Consumption of metal contaminated crops may lead to a weakened immune system, intra-uterine growth retardation, impaired psycho-social behavior, high prevalence of upper gastrointestinal cancer and other disorders typically associated with malnutrition (Arora et al., 2008). Anemia and pulmonary disease, edema, pneumonitis, an impaired endocrine system, defects in sensory function, and bone damage have all been attributed to Cd ingestion (USEPA, 2005).

In view of the above the objectives of this study were to determine the concentration of Zn and Cd in soil and vegetables grown in urban gardens and to assess the potential health risk by estimating dietary intake and target hazard quotients of heavy metals via consumption of contaminated crops.

4.1. Materials and methods

4.1.1. Description of the study area

This study was conducted in the city of Kano (12^0 00'N, 8^0 31' E, 476 m asl, ≈4 Mio inhabitants) the industrial node in the Sudan savannah zone of northern Nigeria. Local rainfall is mono-modal and highly variable with an annual mean of 801 mm (1988-2001). The soils in the study area were classified as either Typic Ustropepts or Eutric Cambisols (FAO/UNESCO, 1974). They are well-drained and predominantly have a sandy loamy texture, and they are underlain by basement material comprising of crystalline igneous, metamorphic and younger granite rocks (Ahmed, 1987). Irrigation development is well advanced along the major rivers of the city (Gari, Thomas, Jakara, Challawa and Kano). These waterways consist of numerous tributaries draining the entire surrounding basin throughout the year except between January and March when the rate of water flow is greatly reduced. Most rivers serve as discharge avenues for wastewaters of urban dwellers as well as of the city's proliferating industrial estates.

Vegetable production within the city limits is a lucrative business for thousands of resource-poor farmers and hence, takes place throughout the year except during the rainy season when some of the farmers allocate portions of their garden to rain-fed crop production. The most common irrigation system of the largely resource-poor farmers is surface flooding of the entire garden through channels built by accumulating soils into ridges. All farmers selected for this study used motorized pumps to pump water from the waste water streams into the gardens. Given their higher profitability most farmers prefer to cultivate fast growing crops like lettuce and amaranthus rather than slow growing ones such as carrots, which are often intercropped with the former ones.

Five locations under waste water irrigation (Koki, Zungeru, Kwakwaci, Gada and Katsina road), representing the dominant management systems were identified based on an in-depth survey and GIS mapping between March and May, 2007. One garden (Legal) under clean well water irrigation was selected as a control. The total area of gardens and the individual plot sizes were determined using a hand-held differential Global Positioning System (GPS; Trimble Pro XR, Sunnyvale, CA, USA). These data were imported into a detailed map produced from a 2005 Google Earth satellite image with 15 m resolution using ArcView 3.2 (Redlands, CA, USA; Figure 4.1).

4.1.2. Sample collection and treatment

Composite soil samples consisting of 15-20 auger points at 0-20 cm depth were collected in 2008 at the time farmers were harvesting their crops of amaranthus (*Amaranthus caudatus* L.), lettuce (*Lactuca sativa* L.), carrot (*Daucus carota* ssp. *sativus*) or parsley (*Petroselinum crispum* var *crispum*) for the market. Gardens were <0.1 ha subdivided into sub-plots (beds) of about 1m^2 each. Soil samples were air-dried, crushed, and passed through a 2-mm mesh sieve prior to storage for analysis.

For vegetables, 20-25 sub-samples were taken in each of the five gardens and pooled. Care was taken to sample in all sampling locations the same crop varieties at the same physiological age when farmers were harvesting them for sale. The samples were washed using clean tap water to remove any adhering soil particles. Subsequently, shoots were severed from the roots using a sharp knife to determine Zn and Cd concentrations in the edible and inedible parts of the crop. Shoot and the root parts were separately oven-dried at 65^{o}C to constant weight and crushed with a porcelain mortar grinder to pass a 2-mm mesh sieve. All plant material was stored in clean polythene bags at ambient temperature prior to chemical analysis. Fresh sub-samples of each vegetable were taken and weighed immediately after sampling to determine the fresh weight followed by oven drying and dry weight measurement.

4.1.3. Soil and plant analysis

Soil physicochemical properties were measured according to standard procedures (Table 4.1). Particle size was determined by the hydrometer method following dispersion of the soil with calgon solution (Gee and Bauder, 1986). Cation exchange capacity (CEC) and exchangeable cations of the soil were measured by extracting the soil with silver-thiourea solution as described in van Reeuwijk (1993). Soil pH was determined in a 1:2.5 soil:water suspension using a glass electrode pH meter and organic carbon content by the dichromate oxidation method as described by Nelson and Sommers (1986). Total N was determined colorimetrically using the Bertholet reaction (Chaney and Marbach, 1962) with an N-autoanalyzer (TECHNICON AAII, Ontario, Canada). Total P was measured by the molybdate-blue method of Lowry and Lopez using ascorbic acid as a reductant (van Reeuwijk, 1993).

For determination of Cd and Zn concentrations, 1 g of air-dried and finely ground soil and 0.5 g of plant material were weighed into separate glass beakers and digested with a 5:1 mixture of HNO_3 and HCl at 80°C following the procedure described by Lim and Jackson (1986). The beakers were swirled gently and digested on a digestion block until brown fumes appeared which subsequently turned white indicating full digestion. The digested plant and soil samples were set aside to cool and filtered through Whatman No. 42 filter paper and diluted to 50 ml with distilled water in clean plastic vials prior to analysis. Concentrations of Zn and Cd in the digest were determined with an Atomic Absorption Spectrophotometer (AAS: Model AA 6680, Shimadzu, Kyoto, Japan).

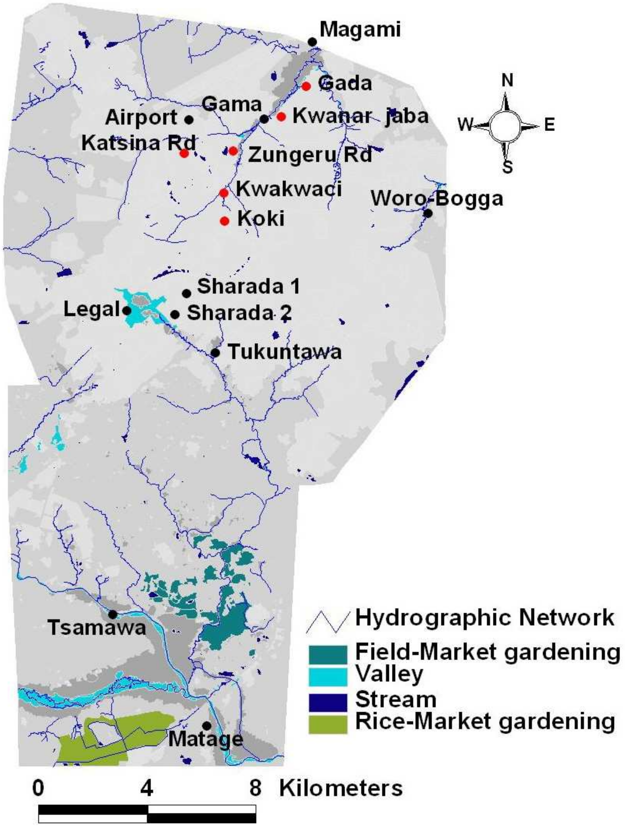


Figure 4.1. Map showing the locations of the sampled vegetable gardens in Kano, Nigeria. (Author: Ibrahima Kadaoure).

The di-ethylene-triamine-penta-acetic acid (DTPA) chelation method of Lindsay and Norvell (1978) was used to determine the concentration of extractable or labile Zn and Cd concentrations in the soil samples. Fifty grams of 2-mm sieved soil were weighed into polystyrene flask and 100 ml of 0.005 M DTPA solution was added and shaken for 2 hours. The suspension was filtered through Whatman No. 42 filter paper into 100-ml volumetric flask. Extractable Cd and Zn in the extract were determined as above.

Table 4.1. Mean and standard error of selected characteristics of urban garden soils collected from the study area in Kano, Nigeria.

	Locations				
Soil properties	Koki	Zungeru	Kwakwaci	Gada	Katsina road
pH	6.7±0.2	6.8±0.2	6.4±0.2	6.6±0.06	7.3±0.2
O C (g kg^{-1})	11.8±0.2	12.3±0.2	13.2±0.3	11.1±0.2	6.7±0.2
CEC (cmol kg^{-1})	8.8±0.2	11.7±0.5	9.9±0.1	9.2±0.3	7.6±0.2
Total N (g kg^{-1})	1.4±0.03	1.4±0.03	1.1±0.01	1.1±0.01	0.7±0.01
Total P (g kg^{-1})	0.9±0.01	1.2±0.01	1.3±0.03	1.1±0.01	0.4±0.01
Clay (g kg^{-1})	150	130	110	110	170

4.1.4. *Data analysis*

4.1.5. *Average daily doses of heavy metal*

Average daily dose of Zn and Cd (ADD) was quantified from the intake by the most likely pathways using the following equation (Lee et al., 2006),:

$$ADD = \frac{(C \times IR \times ED \times EF)}{(BW \times AT \times 365)} \quad [1]$$

where C = Concentration of a contaminant in the environmental sample (e.g. soil, water, air in mg kg^{-1}, mg L^{-1}); IR = Ingestion rate per unit time (kg day^{-1}, L day^{-1});

ED = Duration of exposure (years); EF = Exposure frequency (days per year); BW = Body weight of the receptor (kg); AT = Averaging time (years).

In this study, the major pathway for oral intake of heavy metal was assumed to be soil ingestion through agricultural activities. All parameters and factors used were based on information obtained from farmers indicating the duration of their exposure to farming activities and compared with international standards.

4.1.6. Metal transfer factor (MTF)

The metal transfer factor, also referred to as 'bio-accumulation factor', an index of the ability of a vegetable to accumulate a particular metal as a function of its concentration in the soil (Ghosh and Singh, 2005) was calculated from the following equation:

$$MTF = \frac{C_{plant}}{C_{soil}} \qquad [2]$$

where C_{plant} and C_{soil} were the Zn and Cd concentrations in edible portions of vegetables and in soils, respectively, on a dry weight basis. To also calculate the transfer factor of the plant available heavy metal concentration, MTF was also calculated as a ratio of plant concentration of Zn and Cd and the respective DTPA extractable concentrations in the soil.

4.1.7. Metal translocation

Translocation of metals from one part of a vegetable to another is a function of root-shoot or shoot-shoot transport. It can be expressed as the translocation factor (TF), (Gosh and Singh, 2005):

$$TF = \frac{C_{shoot}}{C_{root}} \qquad [3]$$

where in our study C_{shoot} was the concentration of Zn and Cd in the aboveground portion of the vegetable and C_{root}, their concentration in the belowground portion.

4.1.8. Oral intake of heavy metals from vegetables

The estimated daily intake (EDI) of Cd and Zn through vegetable consumption was calculated by the following equation (Cui et al., 2004):

$$EDI = D \times M \qquad [4]$$

where D is the daily vegetable consumption (g day^{-1}) and M is the mean concentration of metal in contaminated crop (mg kg^{-1}, on fresh weight basis). Based on the survey of Kushwaha et al. (2007), inhabitants of Kano city have an average leafy and root vegetable consumption of 255 g day^{-1} (fresh weight).

4.1.9. Target hazard quotient (THQ)

As a ratio of determined dose of pollutant to a reference dose level (RfD), the THQ has been widely employed in estimating and evaluating the associated risk with consumption of contaminated crops (Rupert et al., 2004; Lee et al., 2006; Sridhara Chary et al., 2008; Zhuang et al., 2009). It is usually calculated according to the equation of Chien et al. (2002):

$$THQ = \frac{(EFr \times ED \times FI \times MC)}{(RfD \times BW \times AT)} \times 0.001 \qquad [5]$$

where *EFr* is the exposure frequency (per 365 days); *ED* is exposure duration over 60 years; *FI* is food ingestion (g $person^{-1}$ day^{-1}); *MC* is the heavy metal concentration in food (µg g^{-1} on a fresh weight basis); *RfD* is the oral reference dose (mg kg^{-1} day^{-1}); *BW* is body weight for an adult (60 kg); *AT* is the averaging time for non-carcinogens (given as 365 days $year^{-1}$ multiplied by the number of exposure years). Based on the survey of Kushwaha et al. (2007), inhabitants of Kano city have an average vegetable consumption of 255 g day^{-1} (fresh weight). Oral reference doses were based on values provided by USEPA (1997) for Zn (3×10^{-1}) and Cd (1×10^{-3}). The concentrations of Zn and Cd in the oven dried crops were converted to fresh weight concentration by dividing the value for each element by a moisture adjustment factor calculated from the difference between the fresh and oven dried vegetables. If the ratio of exposure or average intake of hazardous substances to the corresponding reference dose exceeded unity, the overall intake of heavy metals reached toxic levels.

For the computation of F- and t-tests, data were subjected to the corresponding analyses within SAS 9.1 (SAS Institute, USA, 2003). Figures are drawn with SigmaPlot 10.0 (Systat Software Inc., Chicago, IL, USA).

4.2. Results

4.2.1. Zinc and Cd concentrations in soils and vegetables

Total concentration of Zn and Cd in soil samples from all locations is presented in Table 4.2. Total Zn concentrations in vegetable soils ranged from 39-228 mg kg^{-1} with the highest and lowest concentrations observed in Katsina road and Kwakwaci, respectively. Total Cd concentrations in the soils were with 0.24-2.4 mg kg^{-1} low. Concentration of DTPA-extractable heavy metals ranged between 18-66 and 0.19-0.35 mg kg^{-1} for Zn and Cd, respectively. Highest concentration of extractable Zn and Cd was observed in Gada study site.

Zinc concentrations (dry weight) in most of the vegetables studied from the contaminated gardens far exceeded the threshold levels of 50 mg kg^{-1} set by the EU (Table 4.3). Concentration of Zn in the edible portion of amaranthus (*Amaranthus caudatus* L.) ranged from 13-128 mg kg^{-1} across the five locations, while in roots it ranged from 15-141 mg kg^{-1} on a dry weight basis. Zinc concentration in the edible parts of carrot ranged from 14-86 mg kg^{-1}. In lettuce Zn levels exceeded threshold values of 50 mg kg^{-1} by five-fold. Generally, plant Zn concentrations increased with the Zn level in the soil. Cadmium levels in amaranthus ranged from 0.00–0.22 mg kg^{-1} and 0.02–0.26 mg kg^{-1} in the edible and root compartments of the crop, respectively, with the highest shoot and root concentrations in Zungeru and Gada, respectively. Lettuce had with 0.06-1.7 mg kg^{-1} in the edible portion and 0.1-0.24 mg kg^{-1} in the root highest Cd levels. Of all vegetables investigated, only carrot had Cd concentrations below the 0.2 mg kg^{-1} threshold limit for edible vegetables set by the EU. This reflects a low transfer index of Cd from the soil to the plant (Table 4.3). The roots of parsley accumulated Cd concentrations of up to 0.9 mg kg^{-1} at the Katsina road site. Unlike what was observed with Zn, root Cd concentrations were significantly higher than shoot concentrations in most crops across locations (Table 3). Such a trend was also reported by McKenna et al. (1993) and Shentu et al. (2008). The lowest concentration of Zn (5.0 mg kg^{-1}) and Cd (0.03 mg kg^{-1}) observed in vegetable tissues were from the reference garden.

Table 4.2. Total concentration (range, mean and standard error, mg kg^{-1}) of Zn and Cd in urban garden soils of Kano, Nigeria

Location		Zn	Cd
Koki	(n = 5)	64.8 – 186.3 (136.2 ± 21.0)	0.24 - 0.69 (0.7 ± 0.2)
Zungeru	(n = 5)	77.7 – 159.0 (118.0 ± 15.0)	0.46 - 2.40 (1.4 ± 0.4)
Kwakwaci	(n = 5)	38.6 – 213.9 (90.1 ± 32.0)	0.09 - 0.99 (0.5 ± 0.2)
Gada	(n = 5)	52.4 – 226.4 (167.4 ± 31.0)	0.11 - 1.63 (1.0 ± 0.3)
Katsina road	(n = 4)	(121.7 ± 227.5) (154.7 ± 30.2)	0.38 - 2.40 (1.2 ± 0.5)
Legal	(n = 4)	11.2 - 38.7 (22.9 ± 5.7)	0.07 – 0.10 (0.09 ± 0.01)

Table 4.3. Zinc (Zn) and Cadmium (Cd) concentrations (mg kg^{-1}) in roots and shoots (DW) of selected vegetables under wastewater irrigation in Kano, Nigeria

Location	Crop	Part	Zinc	Cadmium
Koki	Amaranthus	Shoot	20 ± 11.2$_a$	0.20 ± 0.0$_a$
		Root	22 ± 7.0$_a$	0.21 ± 0.0$_a$
	Carrot	Shoot	100 ± 0.7$_a$	0.16 ± 0.0$_a$
		Root	90 ± 0.0$_a$	0.15 ± 0.0$_a$
Zungeru	Amaranthus	Shoot	42 ± 24.5$_b$	0.15 ±0.1$_a$
		Root	67 ± 22.0$_a$	0.58 ± 0.4$_b$
	Carrot	Shoot	102 ± 0.4$_a$	0.05 ± 0.0$_a$
		Root	30 ± 0.1$_b$	0.06 ± 0.0$_a$
	Parsley	Shoot	89 ± 14.2$_a$	0.26 ± 0.0$_a$
		Root	92 ± 8.3$_a$	0.15 ± 0.1$_b$
Kwakwaci	Amaranthus	Shoot	16 ± 7.2$_b$	0.05 ± 0.0$_a$
		Root	26 ± 8.7$_a$	0.13 ± 0.1$_b$
	Carrot	Shoot	9 ± 0.1$_b$	0.15 ± 0.0$_a$
		Root	86 ±0.0$_a$	0.23 ± 0.0$_b$
Gada	Amaranthus	Shoot	14 ± 1.8$_b$	0.15 ± 0.0$_a$
		Root	116 ± 25.0$_b$	0.21 ± 0.1$_a$
	Lettuce	Shoot	120 ± 7.4$_a$	0.68 ± 0.5$_a$
		Root	75 ± 16.0$_b$	0.18 ± 0.0$_a$
Katsina road	Amaranthus	Shoot	62 ± 0.0$_a$	0.09 ± 0.0$_a$
		Root	30 ± 0.0$_b$	0.13 ± 0.0$_b$
	Parsley	Shoot	140 ± 43.6$_a$	0.12 ± 0.0$_a$
		Root	84 ± 29.0$_b$	0.08 ± 0.0$_b$
Legal	Carrot	Shoot	5 ± 0.6$_a$	0.04 ± 0.03$_a$
		Root	10 ± 0.8$_b$	0.03 ± 0.01$_a$

† Values indicate means and one standard error; values in column followed by the same letter are not statistically different at $P > 0.05$; Threshold for Cd and Zn in vegetable crops are 0.2 and 60 mg kg^{-1} (DW) respectively (WHO/FAO, 1993)

4.2.2. Heavy metal translocation

The MTF value based on both the total and extractable metal contents was higher for Zn than for Cd. For Zn MTF_{total} values ranged from 0.2 to 0.9 and that of Cd from 0.1 to 0.6 (Figure 4.2). Root-shoot translocation was high for both metals in all vegetables. When the aboveground concentration of a heavy metal is higher than the belowground concentration, the plant has a high capacity to transport this element from root to shoot. In the present study, Cd had a TF of up to 4.1 compared to Zn with a maximum of 1.5 (Figure 4.3). Lettuce showed a high translocation of Cd from the root to the shoot while carrot and parsley had a similarly high translocation of Zn (Figure 4.3).

4.2.3. Heavy metal exposure and hazard index

The estimated dietary intake of heavy metals through vegetable consumption ranged from 1268-6095 µg day^{-1} for Zn and 3-17 µg day^{-1} for Cd in the wastewater irrigated gardens (Table 4.4). The highest EDI of Zn (6095 µg day^{-1}) for the inhabitants of Kano was observed in Katsina road while highest Cd intake was through lettuce consumption from Gada. Estimated dietary intake of Zn and Cd from the reference garden is 5-22 and 1-6 times respectively lower than the EDIs from contaminated gardens (Table 4.4). Average daily dose of Zn and Cd taken in by human through the soil pathway in Kano is presented in Table 4.4. Estimated daily intake of Zn was between 9.4×10^{-10} to 1.2×10^{-9} g d^{-1} while Cd has a daily dose of between 8.0×10^{-12} to 1.2×10^{-11}. The THQ values of amaranthus at all the five contaminated gardens varied from 0.35 to 0.91 for Zn and 0.2 to 0.65 for Cd. Lettuce had high Cd and Zn THQ values in the gardens of Gada and Katsina road, respectively. As a non leafy vegetable, carrot exhibited lowest THQ values (Figure 4.4).

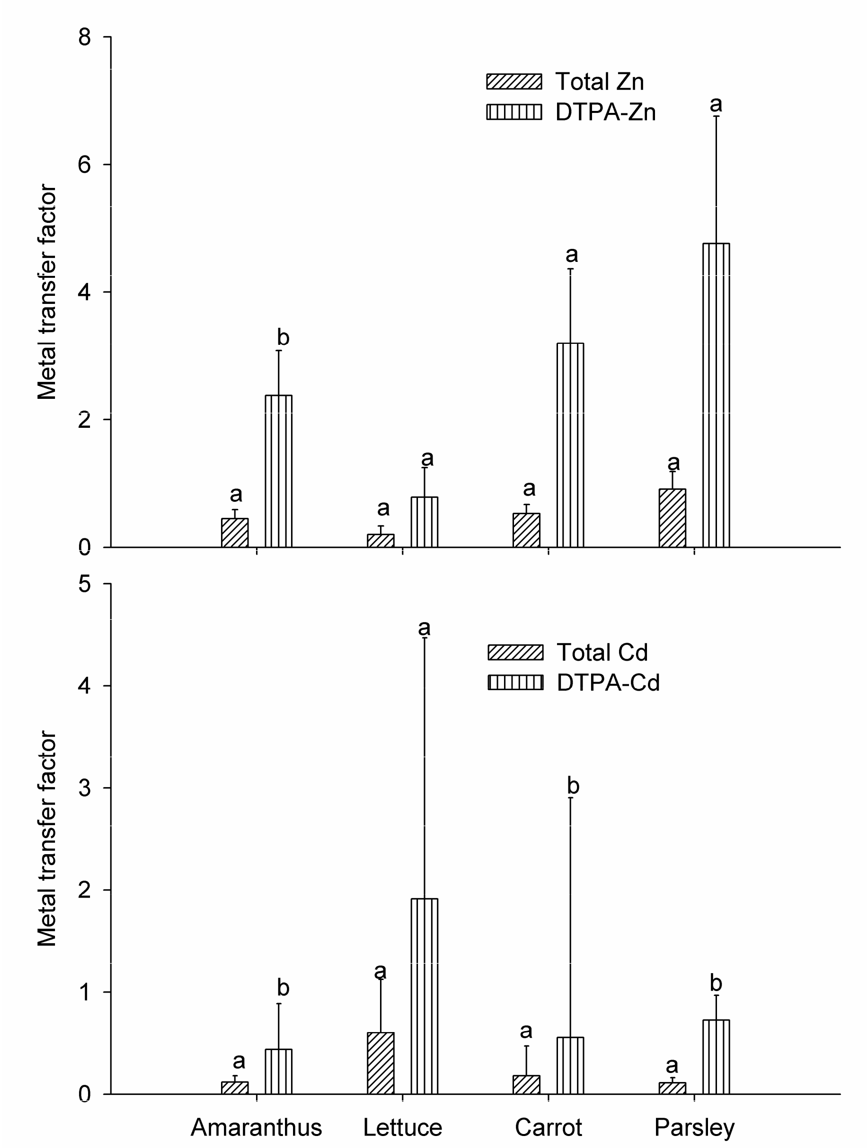


Figure 4.2. Metal transfer factor of Zn and Cd from soil to vegetables based on total and DTPA-extractable Zn. Bars followed by similar letter are statistically similar.

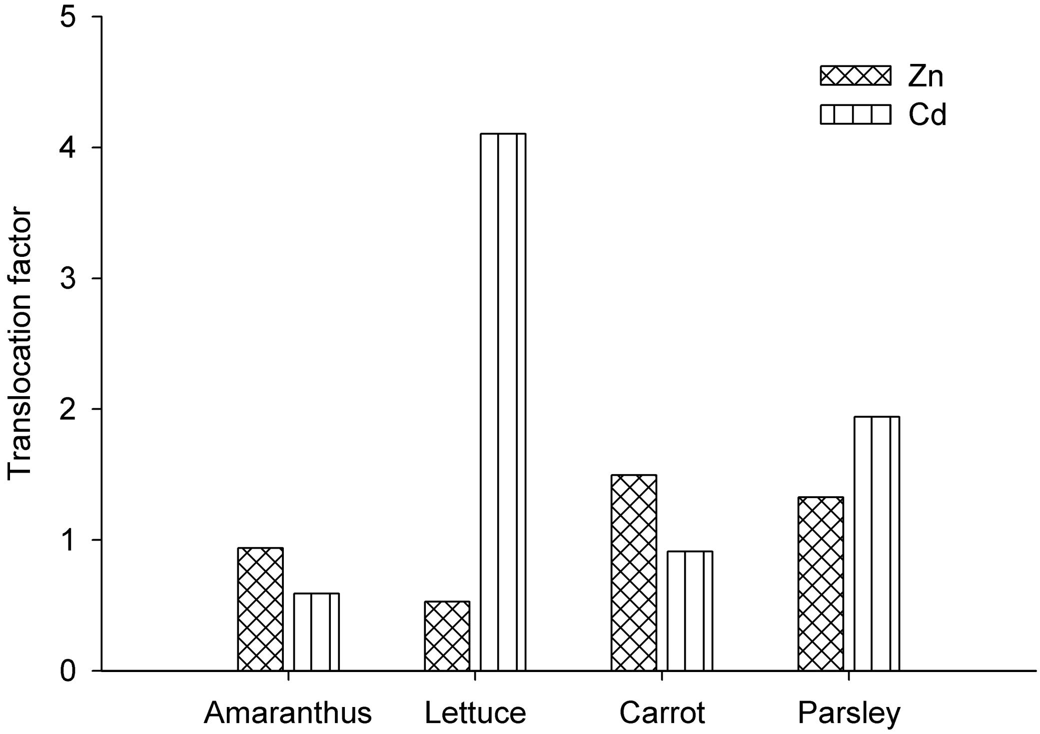


Figure 4.3. Translocation factor of Zn and Cd from the root to the shoot of the crops studied

Table 4.4. Average daily dose (ADD, mg $kg^{-1}day^{-1}$) and estimated dietary intake (EDI, µg g^{-1}) of Zn and Cd taken up by consumers through soil ingestion and vegetable consumption respectively, in Kano, Nigeria.

	ADD				EDI	
Location	Zn	RfD†	Cd	RfD†	Zn	Cd
Koki	1.3×10^{-9}	3.0×10^{-1}	6.6×10^{-12}	5.0×10^{-4}	2646.2	7.0
Zungeru	9.4×10^{-10}		1.3×10^{-11}		2916.3	6.9
Kwakwaci	7.2×10^{-10}		4.5×10^{-12}		1268.3	3.1
Gada	1.6×10^{-9}		8.0×10^{-12}		1909.8	16.6
Katsina road	1.2×10^{-9}		1.2×10^{-11}		6095.2	5.5
Legal	2.2×10^{-10}		8.1×10^{-13}		283.2	2.7

RfD† is the oral reference dose (US-EPA IRIS database)

4.3. Discussion

4.3.1. Contamination of soils and vegetables with Zn and Cd

The concentration of Zn and Cd reported in this study were considerably higher than those reported for similar irrigated garden soils in Northern Nigeria by Agbenin et al. (2009) but still below the threshold limit for agricultural soils as set by the European Union (McGrath et al. 1994). However, Agbenin et al. (2009) argued that the limits set by the EU may not be well adapted for weathered tropical soils which are predominantly sandy in texture with relatively low cation or metal retention capacity. The maximum concentration of Cd (2.4 mg kg^{-1}) observed at Zungeru and Katsina road approached the EU limit of 3.0 mg kg^{-1} for agricultural soils and far exceeded the maximum limit of 1.5 mg kg^{-1} set for German agricultural soils (Agbenin et al., 2009). Superficial enrichment of these metals may, however, reach potentially toxic levels if illicit application of waste water for irrigation continues.

The concentration of heavy metals present in plant tissues as a fraction of total metal concentration in the soil reflects its bioavailability (Misra et al., 2009). High concentration of Zn observed in amaranthus (*Amaranthus caudatus* L.) is in consistence with values reported by Romer and Keller (2001) and Mattina et al. (2003) who identified this crop to greatly uptake Cu, Cd and Zn from soils into the shoot. Ogundiran and Osibanjo (2008) reported Zn concentration >1000 mg kg^{-1} for plants grown on contaminated soil in south-western Nigeria. The higher mean concentrations of Zn in the edible plant parts were consistently higher than root concentrations for all the crops investigated except for amaranthus at Zungeru and Gada which a had higher proportion of Zn in the roots. At these locations (Zungeru and Gada) only a fraction of Zn might have passed through the xylem vessels and translocated to the shoot. Amaranthus shoot may have a selective preference for Zn which is associated with an antagonistic effect on Cd given the chemical similarity between both heavy metals (Rainbow, 1997; Daka and Hawkins, 2005). Such a mitigating effect of Zn on Cd in the edible portion of vegetable may decrease Cd toxicity.

High concentration of chloride salt in a soil together with low pH might lead to high Cd accumulation in plants. Norvell et al. (2000) and Khoshgoftar et al. (2004) observed an increased phytoavailability of Cd in durum wheat grain (*Triticum turgidum* subsp. *durum*) as a result of increased NaCl concentration in the soil. The soil of this location (Zungeru) had with 0.92, 7.9 and 1.5 cmol kg^{-1} the highest concentration of exchangeable K, Ca, and Mg, respectively, of all sites which may be accumulated in the soil as chlorides as a result of high irrigation with poor quality water and, thus increasing the total salt content of the soil.

4.3.2. Heavy metal transfer from soil to vegetables

It has been argued by several authors (Lindsay and Norvell 1978; Gray et al., 1999; McBride et al., 2003; Wang et al., 2006) that for heavy metals DTPA-extractable levels better reflect their plant availability than total concentration. The DTPA-extractable MTF values of Zn for the four crops were seven times higher than those of Cd, reflecting that Zn is more easily translocated from the soil to the plant than Cd. The overall high MTF observed in this study underlines the importance of the soil-plant-human pathway for heavy metal transfer into the food chain whereby the relative similar MTF values of amaranthus and carrot for Cd (Figure 4.2) is an indication that the two crops may have similar uptake and translocation capability for this metal. The high metal accumulation index observed may be related to the low organic carbon content of the soils under study. Our results are not consistent with the observations of McBride et al. (2003), Liu et al. (2005) and Zhuang et al. (2009) who reported higher MTF values for Cd than for Zn.

Plant species, physiological stage, uptake capability as well as growth rate are major determinants of metal transfer from a soil to the crop (Cui et al., 2004). The overall high MTF values reported in this study are consistent with values reported by Khan et al. (2008) and Zhuang et al. (2009) for leafy vegetables. Zinc and Cd similarly affect nucleic acid metabolism (Zhuang et al., 2009) and our results may suggest that Zn binds more efficiently with enzymes instead of Cd when they simultaneously entered plant cells, which is in contrast with the conclusions reached by Gu et al. (2005). The MTF values obtained from total and DTPA-extractable Zn were statistically similar for all the vegetables except for amaranthus. Transfer of Cd from the soil to the plant, however, was different for total and extractable concentrations in the studied crops except for lettuce (Figure 4.2). However, only MTF_{total} was significantly related to total and extractable soil-Zn concentration for all crops investigated (Table 4.5). This suggests that total soil Zn may be a better indicator to assess Zn transfer risks from soil to crop in lettuce, carrot and parsley, while DTPA-extractable Zn may be a better predictor of soil-crop transfer of Zn in amaranthus. For Cd, however, our data indicate that DTPA-extractable soil Cd was a better criterion to predict the soil-crop transfer of Cd in amaranthus and carrot while total soil Cd content should be used to assess the soil-crop transfer of Cd in lettuce and parsley (Table 4.6). Our results corroborated the recommendations of Wang et al. (2006) that MTF values can be estimated at a given soil concentration of either total or DTPA-extractable metal.

Correlation of Cd and Zn transfer factors with soil properties revealed a negative relationship between Zn and Cd transfer factor and soil exchangeable calcium (-0.99; $P<0.01$) at Zungeru. Likewise, in Katsina road Cd transfer factor correlated negatively with Ca (-0.99; $P<0.01$). At Gada, Zn transfer factor was also negatively correlated with soil CEC (-0.99; $P<0.05$). In other locations, strong but non-significant correlations (>0.90) exist between metal transfer factor and soil exchangeable cations (Ca, Mg and Na) and CEC. Correlations observed may be related to the competition between these heavy metals and soil cations in the soil exchange site. Thus Cd and Zn transport from this soil to vegetables is probably governed and inhibited by the activity of competing cations. Antagonistic effects of Ca and Mg on heavy metals has been reported (Kabata-Pendias, 2001). It can thus be inferred that Cd and Zn uptake by crops in this soil is probably not limited by diffusion flux (Degryse et al., 2009), and accordingly controlled by metabolic processes within roots (Kabata-Pendias, 2001).

Table 4.5. Relationship between the metal transfer factor (MTF) of Zn (y) and the DTPA-extractable and total Zn concentrations in urban vegetable soils (x) in Kano, Nigeria.

Crop	Equation for MTF_{DTPA}	Equation for MTF_{Total}
Amaranthus	$y = 0.0027x^2 + 0.164x + 2.41$ $r^2 = 0.99^*$	$y = 2.097e^{-0.0113x}$ $r^2 = 0.626^*$
Lettuce	$y = 0.0035x^2 - 0.388x + 11.23$ $r^2 = 0.163^{NS}$	$y = 1.58 - 0.0092x$ $r^2 = 0.937^*$
Carrot	$0.746x - 0.009x^2 - 8.23$ $r^2 = 0.60^{NS}$	$y = - 0.0002x^2 + 0.043x - 1.74$ $r^2 = 0.992^*$
Parsley	$0.009x^2 - 0.8x +18.1$ $r^2 = 0.33^{NS}$	$y = 2.79 - 0.013x$ $r^2 = 0.94^*$

* Statistically significant at the 5 % level; NS = not significant

Table 4.6. Regression analysis between the metal transfer factor of Cd (y) and DTPA-extractable and total Cd concentrations in urban vegetable soils (x) of Kano, Nigeria.

Crop	Equation for MTF_{DTPA}	Equation for MTF_{Total}
Amaranthus	$y = 1.746 – 4.177x$ $r^2 = 0.99^*$	$y = 0.4478x – 0.2414$ $r^2 = 0.54^*$
Lettuce	$y = 2.362 – 3.22x$ $r^2 = 0.01^{NS}$	$y = 1.24x2 – 2.83x – 1.65$ $r^2 = 0.99^*$
Carrot	$y = 3.3x – 0.31$ $r^2 = 0.77^*$	$y = 0.223x^{– 1.764}$ $r^2 = 0.69^*$
Parsley	$y = 37.79x – 71.36x^2 – 4.05$ $r^2 = 0.96^{NS}$	$y = 0.218 – 0.107x$ $r^2 = 0.96^*$

* Statistically significant at the 5 % level; NS = not significant

4.3.3. Metal translocation from root to shoot

The higher translocation of Cd relative to Zn observed in this study is consistent with the observations of Kumar et al. (2009). It is well established that transpiration is a major driver of heavy metal transport from the root to the shoot (Shentu et al., 2008). Lettuce which had the highest biomass of all studied vegetables might also have the highest transpiration rate and hence a high shoot accumulation of Cd. Uraguchi et al. (2009) stated that transpiration and xylem transport are major driving forces for Cd translocation. The high biomass and water content of lettuce may, however, help to dilute tissue concentration of Cd in the fresh matter to below threshold levels (Shentu et al., 2008). Zhao et al. (2002) proposed that Ca and Mg transport pathways are also responsible for Cd transport in *Thlaspi caerulescens* using *ZNTI* as a carrier. The relatively moderate concentration of Cd observed in the shoot of other crops may be related to competition between Zn and Cd for uptake by roots and subsequent translocation from roots to shoots, which limit Cd accumulation.

4.3.4. Average daily dose of heavy metals

In our study, the major intake pathway for Zn and Cd was assumed to be vegetable consumption and soil ingestion through agricultural activities. Threat of Cd toxicity from vegetable consumption in Kano is limited. The highest estimated dietary intake (17 µg day^{-1}) is within the limit of 10-50 µg day^{-1} recommended as safe by the WHO. Values reported here were also lower than what was reported in other studies (Cui et al., 2004; Zhuang et al., 2009) for Chinese soils but by far exceeded the 0.05 µg kg^{-1} day^{-1} reported for Iranian soils (Aghili et al., 2009).

Zinc intake through vegetable consumption also poses no health risk to inhabitants of Kano. Daily recommended Zn intake for adult is 15000 µg day^{-1} (Food and Nutrition Board, 1974). The maximum intake of Zn via vegetable consumption was 6095 µg day^{-1} in this study. No standard exposure factors and input parameters were available for Nigerian farmers from previous studies and therefore these were based on information obtained from farmers indicating the duration of their exposure to farming activities and compared with international standards (Table 4.4 and 4.7).

Across the locations the exposure to Zn was in the order Katsina road ≈ Koki ≈ Gada > Kwakwaci > Zungeru. For Cd, Katsina road still had the highest ADD, closely followed by that of Zungeru, while Gada had the lowest ADD. The quantified ADD through soil ingestion was lower than the recommended reference dose (Table 4.7). Overall our data suggest that farmers and vegetable consumers in Kano are presently not at risk of taking up toxic levels of Zn and Cd and hence no negative consequences for their health are to be feared.

Table 4.7. Average daily dose (ADD, mg $kg^{-1}day^{-1}$) of Zn and Cd taken up by inhabitants of Kano, Nigeria through the soil pathway.

Location	Zn	Cd
Koki	1.31×10^{-9}	6.64×10^{-12}
Zungeru	9.43×10^{-10}	1.30×10^{-11}
Kwakwaci	7.20×10^{-10}	4.51×10^{-12}
Gada	1.61×10^{-9}	8.02×10^{-12}
Katsina road	1.19×10^{-9}	1.18×10^{-11}

4.3.5. Target hazard quotient (THQ)

Across locations the THQ of the studied heavy metals through vegetable consumption was higher for Zn than for Cd and mostly below 1.0 except for parsley that exceeded 1.0 wherever it was cultivated (Figure 4.4). Even if both, Zn and Cd may be contributing to health risks in Kano, Horiguchi et al. (2004) argued that the ingested dose of heavy metals is not equal to the body-absorbed dose as an unknown fraction of the ingested metal may be excreted and only the rest accumulates in the human body posing possible health risks.

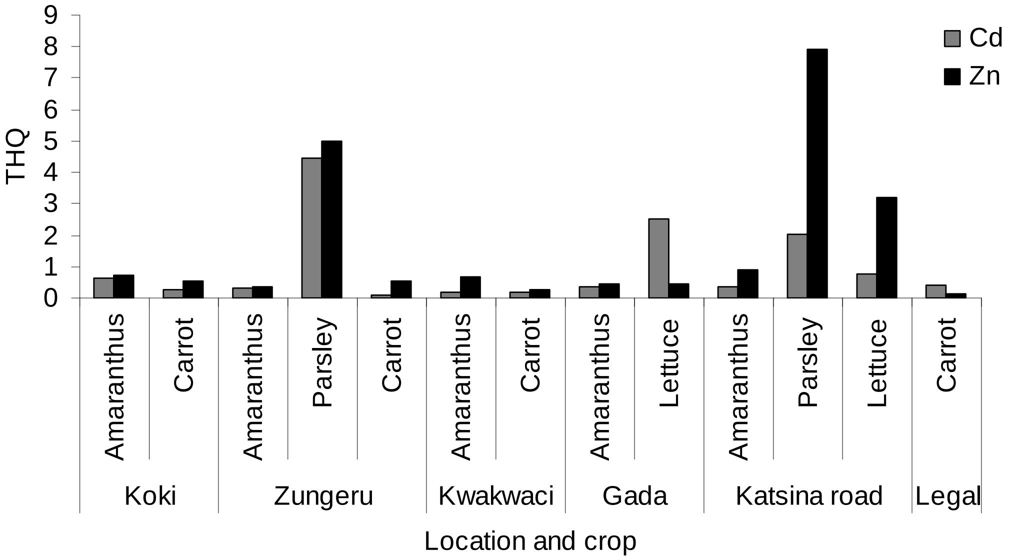


Figure 4.4 Zinc and Cd target hazard quotient (THQ) values through consumption of vegetables in Kano, Nigeria

4.4. Conclusions

Long-term wastewater irrigation in Kano may cause health risks to producers and consumers alike. Even though there are no legal thresholds for heavy metal contamination for the local soil conditions, the concentrations measured in soils and vegetable crops give rise to concerns especially in view of the sandy nature of the soils that allows easy movement of solutes. The studied vegetables showed a high translocation of Cd from the root to the edible portion of the shoot which has important consequences for the contamination of the food chain.

4.5. References

Agbenin, J.O., Danko. M. and Welp, G. 2009. Soil and vegetable compositional relationships of eight potentially toxic metals in urban garden fields from northern Nigeria. Journal of Science Food and Agriculture 89: 49-54.

Aghili, F., Khoshgoftarmanesh, A.H., Afyuni, M. and Mobli, M. 2009. Relationships between fruit mineral nutrients concentrations and some fruit quality attributes in greenhouse cucumber. Journal of Plant Nutrition 32:1994-2007.

Ahmed, K. 1987. Erosion hazard assessment in the Savannah: The Hadejia-Jama'are River Basin. In: Mortimore M, Olofin EA, Clinecole RA, Abdulkadir A (eds), Perspective on land administration and development in northern Nigeria, Proceedings of the workshop on land resources, Department of Geography, Bayero Univeristy, Kano, pp 234-247.

Arora, M., Kiran, B., Rani, S., Rani, A., Kaur, B. and Mittal, N. 2008. Heavy metal accumulation in vegetables irrigated with water from different sources. Food Chemistry 111: 811–815.

Bakare, S., Denloye, A.A.B. and Olaniyan, F.O. 2004. Cadmium, lead and mercury in fresh and boiled leafy vegetables grown in Lagos, Nigeria. Environmental Technology 25: 1367–1370.

Binns, J.A., Maconachie, R.A. and Tanko, A.I. 2003. Water, land and health in urban and peri-urban food production: the case of Kano, Nigeria. Land Degradation and Development 14: 413-444.

Bosso, S.T. and Enzweiler, J. 2008. Bioaccessible lead in soils, slag and mine wastes from an abandoned mining district in Brazil. Environmental Geochemistry and Health 30: 219-229.

Chaney, A.L. and Marbach, E.P. 1962. Modified reagents for determination of urea and ammonia. Clinical Chemistry 8: 130–132.

Chien, L.C., Hung, T.C., Choang, K.Y., Choang, K.Y., Yeh, C.Y., Meng, P.J., Shieh, M.J. and Han, B.C. 2002. Daily intake of TBT, Cu, Zn, Cd and As for fishermen in Taiwan. Science of the Total Environment 285: 177–85.

Codex Alimentarius. 1984. Commission, Contaminants. Joint FAO/WHO Food Standards Program. vol. XVII, First ed.

Cui, Y.J., Zhu, Y.G., Zhai, R.H., Chen, D.Y., Huang, Y.Z., Qui, Y., Ling and J.Z. 2004. Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China. Environment International 30: 784-790.

Daka, E.R. and Hawkins, S.J. 2005. Interactive effects of copper, cadmium and lead on zinc accumulation in the Gastropod Mollusc *Littorina saxatilis.* Water, Air and Soil Pollution 171: 19–28.

Degryse, F., Smolders E., Zhang, H. and Davison, W. 2009. Predicting availability of mineral elements to plants with the DGT technique: a review of experimental data and interpretation by modelling. Environmental Chemistry 6:198-218.

Diogo, R.V.C., Buerkert, A. and Schlecht, E. 2010. Horizontal nutrient fluxes and food safety in urban and peri-urban vegetable and millet cultivation of Niamey, Niger. Nutrient Cycling Agroecosystems 87:81–102.

Ensink, J.H.J., Van der Hoek, W., Matsuno, Y., Munir, S. and Aslam, M.R. 2002. Use of untreated wastewater in peri-urban agriculture in Pakistan: risk and opportunities. Research Report 64. International Water Management Institute (IWMI), Colombo, Sri Lanka.

FAO/UNESCO. 1974. Soil map of the world. 1:5,000,000, ten volumes, UNESCO-Paris.

Fu, G., Zhou, Q., Liu, J., Liu, W., Wang, T., Zhang, Q. and Jiang, G. 2008. High levels of heavy metals in rice (*Oryza sativa* L.) from a typical E-waste recycling area in southeast China and its potential risk to human health. Chemosphere 71: 1269-1275.

Food and Nutrition Board. 1974. Recommended Dietary Allowances. 8th Ed. National Academy of Sciences, National Research Council, Washington, DC.

Gee, G.W. and Bauder, J.W. 1986. Particle-size analysis. In: Klute A (Ed) Methods of soil analysis, part 1. 2nd edn. Agronomy Monogram. 9. ASA and SSSA, Madison, WI, pp. 383–411.

Ghosh, M. and Singh, S.P. 2005. A comparative study of cadmium phytoextraction by accumulator and weed species. Environmental Pollution 133: 365-371.

Gu, J.G., Lin, Q.Q., Hu, R., Zhuge, Y.P., Zhou, Q.X. 2005. Translocation behavior of heavy metals in soil–plant system: a case study from

Qingchengzi lead–zinc mine in Liaoning Province. In: Zhuang et al (2009). Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China. Science of the Total Environment 407: 1551-1561.

Gray, C.W., McLaren, R.G., Roberts, A.H.C. and Condron, L.M. 1999. Cadmium phytoavailability in some New Zealand soils. Australian Journal of Soil Research 37: 461-477.

Horiguchi, H., Oguma, E., Sasaki, S., Miyamoto, K., Ikeda, Y., Machida, M. and Kayama, F. 2004. Dietary exposure to cadmium at close to the current provisional tolerable weekly intake does not affect renal function among female Japanese farmers. Environmental Research 95: 20–31.

IRIS (Integrated Risk Information System), http://www.epa.gov/ngispgm3/iris (23 April, 2010).

Kabata-Pendias A. 2001. Trace elements in soils and plants. Third Edition, CRC Press, NY.

Khan, S., Cao, C., Zheng, Y.M., Huang, A. and Zhu, Y.G. 2008. Health risks of heavy metals contaminated soils and food crops irrigated with waste water in Beijing, China. Environmental Pollution 152: 686-692.

Khoshgoftar, A.H., Shariatmadari, H., Karimian, N., Kalbasi, M., van der Zee, S.E.A.T.M. and Parker, D.R. 2004. Salinity and zinc application Effects on phytoavailability of cadmium and Zinc. Soil Science Society America Journal 68: 1885–1889.

Kumar, N., Soni, H., Kumar, R.N., Bhatt, I. 2009. Hyperaccumulation and mobility of heavy metals in vegetable crops in India. The Journal of Agriculture and Environment 10: 29–38.

Kushwaha, S., Sen, C. and Yakasai, M.T. 2007. Current trends in Vegetable consumption in Nigeria: Case Study of consumption pattern in Kano State. Paper prepared for presentation at the I Mediterranean Conference of Agro-Food Social Scientists. 103rd EAAE Seminar ‘Adding Value to the Agro-Food Supply Chain in the Future Euro Mediterranean Space’. Barcelona, Spain, April 23rd - 25th, 2007.

Lee, S.G., Lee, B.T., Kim, J.Y., Kim, K.W. and Lee, J.S. 2006. Human risk assessment for heavy metals and As contamination in the abandoned metal mine areas, Korea. Environmental Monitoring and Assessment 119: 233–244.

Li, S.T., Liu, R.L., Wang, M., Wang, X.B., Shan, H. and Wang, H.T. 2006. Phytoavailability of cadmium to cherry-red radish in soil applied composted chicken or pig manure. Geoderma 136: 260-271.

Lim, C.H. and Jackson, M.L. 1986. Expandable phyllosilicate reactions with lithium on heating. Clays and Clay Minerals 34: 346-352.

Lim, H.S., Lee, J.S., Chon, H.T., and Sager, M. 2008. Heavy metal contamination and risk assessment in the vicinity of the abandoned Songcheon Au-Ag mine in Korea. Journal of Geochemical Exploration 96: 223-230.

Lindsay, W.L. and Norvell, W.A. 1978. Development of a DTPA Soil Test for Zinc, Iron, Manganese, and Copper. Soil Science Society America Journal 42:421-428.

Liu, W.H., Zhao, J.Z., Ouyang, Z.Y., Soderlund, L. and Liu, G.H. 2005. Impact of sewage irrigation on heavy metals distribution and contamination in Beijing, China. Environment International 31: 805-812.

Mapanda, F., Mangwayana, E.N., Nyamangara, J. and Giller, K.E. 2005. The effect of long-term irrigation using wastewater on heavy metal contents of soils under vegetable s in Harare, Zimbabwe. Agriculture Ecosystem and Environment 107: 151-165.

Mattina, M.I., Lannucci-Berger, W., Musante, C. and White, J.C. 2003. Concurrent plant uptake of heavy metals and persistent organic pollutants from soil. Environmental Pollution 124: 375–378.

McBride, M.B., Nibarger, E.A., Richards, B.K. and Steenhuis, T. 2003. Trace metal accumulation by red clover grown on sewage sludge-amended soils and correlation to Mehlich 3 and calcium chloride-extractable metals. Soil Science 168: 29-38.

McGrath, S.P., Chang, A.C., Page, A.L. and Witter, E. 1994. Land application of sewage sludges: Scientific perspectives of heavy metal loading limits in Europe and United States. Environmental Review 2: 108–118.

McKenna, I.M., Chaney, R.L. and Williams, F.M. 1993. The effect of cadmium and zinc interactions on the accumulation and tissue distribution of zinc and cadmium in lettuce and spinach. Environmental Pollution 79: 113–120.

Misra, V., Tiwari, A., Shukla, B. and Seth, C.S. 2009. Effects of soil amendments on the bioavailability of heavy metals from zinc mine tailings. Environmental Monitoring and Assessment 155: 467–475.

Nelson, D.W. and Sommers, L.M. 1986. Total carbon, organic carbon and organic matter. In: Sparks DL (ed) Methods of Soil Analysis Part 2. Chemical methods, American Society of Agronomy, Madison, WI, pp 961–1010.

Norvell, W.A., Wu, J., Hopkins, D.G. and Welch, R.M. 2000. Association of cadmium in durum wheat grain with soil chloride and chelate-extractable soil cadmium. Soil Science Society of America Journal 64: 2162–2168.

Oluwatosin, G.A., Jaiyeoba, O.M., Banjoko, V.A., Aikore, O.D. and Akinbola, G.E. 2005. Heavy metals in an urban valley bottom soil in south-western Nigeria. Discovery and Innovation 17: 85–93.

Ogundiran, M.B., and Osibanjo, O. 2008. Heavy metal concentrations in soils and accumulation in plants growing in a deserted slag dumpsite in Nigeria. African Journal of Biotechnology 7: 3053-3060.

Rainbow, P.S. 1997. Trace metal accumulation in marine invertebrates: Marine Biology or Marine. Chemistry. Journal of Marine Biological Association 77: 195–210.

Römer, W. and Keller, H. 2001. Exudation of organic acids by spinach and the mobilization of Cu, Zn and Cd in soil. In: Horst WJ (Ed) Plant Nutrition: Food Security and Sustainability of Agroecosystems. Kluwer Academic, the Netherlands, pp 556–557.

Rupert, L.H., Neil, B., Scott, D.Y., Neil, M.J.C., Andrew, M.T., Ann, M.M. and Iain, T. 2004. Assessing potential risk of heavy metal exposure from consumption of home-produced vegetables by urban populations. Environmental Health Perspective 112: 215–221.

Shentu, J., He, Z., Yang, X.E. and Tingqiang, L.I. 2008. Accumulation properties of cadmium in a selected vegetable-rotation system of Southeastern China. Journal of Agricultural and Food Chemistry 56: 6382–6388.

Sridhara Chary, N., Kamala CT, Samuel Suman Raj D. 2008. Assessing risk of heavy metals from consuming food grown on sewage irrigated soils and food chain transfer. Ecotoxicology and Environmental Safety 69: 513–524.

Uraguchi, S., Mori, S., Kuramata, M., Kawasaki, A., Arao, T. and Ishikawa, S. 2009. Root-to-shoot Cd translocation via the xylem is the major process determining shoot and grain cadmium accumulation in rice. Journal of Experimental Botany 60: 2677–2688.

USEPA, 2005. Guideline for carcinogen risk assessment: Risk assessment forum, U.S. Environmental Protection Agency, Washington, DC.

USEPA, 1997. Exposure factors handbook (EPA/600/P-95/002Fa) (Update to Exposure factors handbook (EPA/600/8–89/043), Environmental Protection Agency Region I, Washington, D.C., USA.

Van der Hoek, W., Hassan, M., Ensink, J.H.J., Feenstra, S., Raschid-Sally, L., Munir, S., Aslam, R., Ali, N., Hussain, R. and Matsuno, Y. 2002. Urban wastewater: a valuable resource for agriculture. A case study from Haroonabad, Pakistan. Research Report 63. International Water Management Institute (IWMI), Colombo, Sri Lanka.

van Reeuwijk, L.P. 1993. Procedures for soil analyses; Technical paper No. 9. Fourth edition. International soil reference and information centre (ISRIC).

Wang, G., Su, M.Y., Chen, Y.H., Lin, F.F., Luo, D. and Gao S.F. 2006. Transfer characteristics of cadmium and lead from soil to the edible parts of six vegetable species in southeastern China. Environmental Pollution 144: 127-135.

Wang, X.P., Shan, X.Q., Zhang, S.Z. and Wen, B. 2004. A model for evaluation of the phytoavailability of trace elements to vegetables under field conditions. Chemosphere 55: 811–822.

World Health Organization (WHO). 1993. Evaluation of Certain Food Additives and Contaminants. Technical Report Series, Number 837, World Heath Organisation, Geneva.

World Health Organization (WHO). 2006. WHO Guidelines for the safe use of wastewater, excreta and greywater. Volume 2: Wastewater use in agriculture. World Health Organization, Geneva.

Zhao, F.J., Hammon, R.E., Lombi, E., McLaughin, M.J. and McGrath, S.P. 2002. Characteristics of cadmium uptake in two contrasting ecotypes of the hyperaccumulator Thlapsi caerulescens. Journal of Experimental Botany 53: 535–543.

Zhuang, P., McBride, M.B., Xia, H., Li, N. and Li, Z. 2009. Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China. Science of the Total Environment 407: 1551-1561.

Chapter 5

Geochemical assessment, distribution and dynamics of trace elements in contaminated urban soil under long-term wastewater irrigation in Kano, northern Nigeria

Submitted:
African Journal of Earth Science

Abstract

This study was conducted to evaluate the distribution and origin of trace elements (TEs; Ti, Fe, Nb, Pb, Rb, Sr, Y, and Zr) in five representative long-term wastewater irrigated urban vegetable gardens of Kano. Surface soil concentrations (0-15 cm) of Ti (4,600-14,300 mg kg^{-1}), Fe (4,000-31,800 mg kg^{-1}), Pb (96-355 mg kg^{-1}), and Y (33-98 mg kg^{-1}) where high compared to mean concentrations in soils worldwide. Soil pollution assessment; however, yielded no evidence of anthropogenic input of the TEs studied. Indices such as the enrichment factor (EF), the contamination factor (CF) and the geoaccumulation index (I_{geo}) revealed little to no contamination with TEs. The I_{geo} calculated for these metals varied across locations between 0.00-0.12 with Nb having the highest I_{geo} value. Similarly, CF was low for all metals with the exception of Fe reaching a CF of 4.2 at one location. Geochemical balance evaluations showed depletion of all TEs except for Fe which was 176% higher than in a natural uncultivated und unirrigated reference soil. Correlation and factor analyses showed that all determined TEs likely originated from the same natural sources which probably are the soil parent material and atmospheric depositions.

Keywords: atmospheric deposition, contamination indices, heavy metals, parent material

5. Introduction

The origin and properties of pedogenic materials and the often interacting mineralization processes in a soil determine its natural distribution of TEs and radionuclides (Maþvila et al., 2001). Radionuclides are generally known to be toxic and harmful to the ecosystem irrespective of their level or concentration in the environment. In contrast soil TEs may be beneficial to crops, animals and man but beyond a given threshold, they can also have detrimental effects. In addition to their pedogenic origin, trace elements can also be released into the environment through anthropogenic activities such as agriculture, mining, industrial processes and combustion of fossil fuels (Nriagu, 1990). During the last years in many countries point source pollution of the environment with TEs has been reduced, but emissions from the transportation sector can still be worrisome (Takamatsu et al., 2010). The city of Kano with its population of about 4 Mio inhabitants is an example of an agglomeration characterized by high density of vehicular traffic, an inefficient traffic infrastructure and predominance of old vehicles. Thus environmental contamination with TEs through fuel combustion (Wang et al., 2003), abrasion and wearing of automobile parts (Boulay and Edwards, 2000; Kock and Rotard, 2000; Sörme and Lagerkvist, 2002; Iijitima et al., 2007) is likely to occur. TEs emanating from anthropogenic sources are considered to be more dangerous because of their instability and solubility leading to their often high bio-availability. In a recent study Abdu et al. (2010b) observed an annual atmospheric dust deposition of up to 200 g Zn ha^{-1} in Kano. Inhalation of dust particles that are associated with TEs and radionuclides during the “Harmattan” period may contribute to cancer development and miscarriages that were recently reported from Nigeria by Lar and Tejan (2008).

Ewa et al (1999) and Agbenin and Felix-Henningsen (2001) observed accumulation of radioactive elements in soils of the Nigerian savannah. The former authors attributed this to long-term fertilization with organic fertilizers in the form of manure, thereby supporting similar speculations of Dach and Starmans (2005). Quantitative data about TM contamination of urban garden soils in Kano are readily available (Mashi and Alhassan, 2007; Awode et al., 2008; Abdu et al., 2010a; Abdu et al., 2010b). However, little attention has been paid to the quantification of radioactive trace elements in this city even if these elements may accumulate in the soil from natural and anthropogenic sources. The objective of this study therefore was to determine the status and distribution of Fe, Nb, Pb, Rb, Sr, Y, and Zr in waste-water irrigated vegetable gardens from Kano and to explore their likely origin.

5.1. Materials and methods

5.1.1. Study location

All five sampled vegetable gardens were located in Kano, northern Nigeria (12° 00^{l} N, 8° 31^{l} E, 476 m asl) in the Sudan savannah ecological zone of West Africa. Even if there is a large variation in the age, composition and structure of the underlying geology of the soils of the Nigerian savannah (Jaiyeoba, 1995), these soils could be classified as Typic Ustropepts or Eutric Cambisols (FAO/UNESCO, 1974). They are well-drained, predominantly sandy loamy in texture and underlain by Precambrian basement complex rocks comprised of crystalline igneous, metamorphic and younger granite rocks with a marked differentiation of horizons (Ahmed, 1987). Cassiterite/columbite mineralization in association with U- and Th-bearing minerals such as monazite, zircon, pyrochlore, thorite and fergosonite as well as sulphide minerals such as galena, sphalerite, molybdenite, pyrite, arsenopyrite, and chalcopyrite are associated mainly with younger granites (Lar and Tejan, 2008). The five sites selected for the study were characterized by heavy wastewater irrigation throughout the year except during the 4-months rainy season. High levels of zinc (Zn) and cadmium (Cd) have been previously reported from these locations (Abdu et al., 2010a). A natural uncultivated soil was also sampled as a control unaffected by waste-water irrigation.

5.1.2. Profile sampling

At each location an approximately 1 m wide trench was dug to a depth below 1.5 m. The surface of the trench was cleaned with a sharp knife and five sub-samples were each collected in duplicate at profile depth intervals of 0-15, 15-25, 25-35, 35-45, 45-75, 75-100 and 100-150 cm. The sub samples were bulked together to make composite samples which were air-dried, crushed and sieved to 2-mm prior to storage for analysis. For bulk density determination according to Blake and Hartge (1986), additional undisturbed core samples were collected using a hand-held hammer driven cylindrical core sampler (Soil Moisture Equipment Co., CA, USA).

5.1.3. Soil analysis

Particle size distribution was determined according to Gee and Bauder (1986) following dispersion of the soil with a calgon solution. Soil pH was determined in a 1:2.5 soil/water suspension using a pH meter. Subsequently, all soil samples were ground in an agate mortar with a pestle to a mean particle diameter of 50 µm. An aliquot of the powdered sample was moistened with four drops of 10% PVC in toluene, thoroughly homogenised and allowed to dry. Samples were then pelleted with a hydraulic press and the concentration of Fe, Nb, Pb, Rb, Sr, Ti, Y, and Zr determined from the pellet using radioisotope excited X-ray fluorescence at the Centre for Energy Research, Ahmadu Bello University, Zaria, Nigeria.

5.2. Data analyses

5.2.1. Geochemical balance evaluation

Calculation of mass balances are often used to evaluate soil metal pools as they combine their mobility, distribution, flows and soil retention characteristics. They are also useful to evaluate gains and losses of elements as a result of management or land use patterns (Agbenin, 2001; Shotbolt et al., 2008) and of weathering processes (Ndjigui et al., 2008). Several methods have been applied to study element balances in soils and geologic material. In the present study, we evaluated gains and losses as a result of soil management using the immobile-element approach (Agbenin, 2001; Moroni et al., 2001; Ndjigui et al., 2008; Takamatsu et al., 2010). To this end the percentage gain or loss in the concentration of each element in the studied wastewater irrigated soil profile samples were compared with its concentration in an unirrigated reference soil using equation 1 of Ndjigui et al. (2008):

$$\% \text{ change} = [((X_a/I_a) / (X_u/I_u) - 1)] \times 100 \qquad [1]$$

where Xa and Xu are the element concentration of the likely contaminated profile sample and of the reference profile sample, respectively; Ia and Iu are the concentrations of the immobile element in the likely contaminated profile sample and in the reference profile sample, respectively. We used Titanium (Ti) as a reference element because of its insignificant anthropogenic origin and the fact that it has been previously demonstrated to have a consistent concentration throughout the profiles of similar soils in the Nigerian savannah (Agbenin and Felix-Henningsen, 2001). It has a naturally uniform concentration (Daskalakis and O'Connor, 1995) and is mainly derived from weathering of crustal rock minerals (Schütz and Rahn, 1982). Furthermore, this element is associated with many rock-forming minerals such as anatase and rutile (TiO_2), ilmenite ($FeTiO_2$), sphene ($CaTiSiO_5$) and zirconolite ($CaZrTi_2O_7$).

5.2.2. Metal enrichment factor (EF)

The enrichment factor for each metal was calculated by normalizing its concentration against that of the immobile reference element (Ti; equation 2).

$$EF = \frac{M_c / Ti_c}{M_{ref} / Ti_{ref}} \qquad [2]$$

where M_c and Ti_c are the concentrations of the element and the reference element in the contaminated soil, and M_{ref} and Ti_{ref} are the concentrations of the element and the reference element in the reference soil. EF values close to unity indicate that the metal is of crusted origin, values <1 indicates mobilization or depletion of the metal, and values >1 suggests anthropogenic enrichment (Bhuiyan et al., 2010).

5.2.3. Metal contamination factor (CF)

The CF value describes the ratio between the metal concentration in the polluted soil and in the reference unpolluted soil (Bhuiyan et al., 2010). The intensity of contamination is reflected on a scale with zero indicating no contamination, 1 none to medium, 2 moderate, 3 moderate to strong, 4 strong, 5 strong to very strong, and 6 high contamination (Muller, 1969).

5.2.4. Geoaccumulation index (I_{geo})

This term allows the assessment of metal contamination through a comparison of the metal concentration in the contaminated soil with its concentration prior to contamination (Loska et al., 1997; equation 3):

$$I_{geo} = \frac{\log 2(Cm)}{1.5(Bm)} \qquad [3]$$

where *Cm* is the concentration of the metal *m* in the polluted soil and *Bm* is the geochemical background concentration of the metal *m* (Muller, 1979). The factor 1.5 was introduced as a correction factor to normalize the background metal concentration for lithospheric (Bhuiyan et al., 2010) and anthropogenic effects (Loska et al., 1997). Muller (1981) distinguished the following seven classes or grades of the geoaccumulation index:

Class 0; $I_{geo} \leq 0$ = unpolluted
Class 1; $0 < I_{geo} < 1$ = unpolluted to moderately polluted
Class 2; $0 < I_{geo} < 2$ = moderately polluted
Class 3; $2 < I_{geo} < 3$ = moderately to highly polluted
Class 4; $3 < I_{geo} < 4$ = highly polluted
Class 5; $4 < I_{geo} < 5$ = highly to extremely polluted
Class 6; $5 < I_{geo} < 6$ = extremely polluted

5.2.5. Statistical analysis

Simple correlation analysis was used to evaluate the geochemical association of trace elements with soil constituents. The correlation matrix obtained was subjected to factor analysis to assess the relationship, behavior and source of pollution using the Varimax rotation (Kleinbaum et al., 1988).

5.3. Results and discussion

5.3.1. Element analysis

Across locations most analyzed elements were regularly distributed throughout the profiles (Table 5.1). Titanium concentration ranged from 4,600-14,300 mg kg^{-}

^{1} whereby the fairly uniform distribution of this element down the profile suggests that this element is most likely derived from anatase and rutile minerals; its decomposition during carbonization processes could release Ti in the form of oxides (Xing and Dudas, 1993; Sakurovs et al., 2007; Bhuiyan et al., 2010). A similar distribution of this element was observed by Agbenin and Felix-Henningsen (2001) in long-term cultivated soils from the Nigerian savannah. Titanium may replace Al during isomorphous substitution in the tetrahedral site of the clay mineral (Deer et al., 1962) as this element has a strong affinity for aluminosilicates (Goodarzi, 1988). Values reported in our study are higher than those given by Agbenin and Felix-Henningsen (2001) for cultivated soils from the Nigerian savannah but close to concentrations reported by Bhuiyan et al. (2010) for polluted soils from Bangladesh.

Iron showed the highest concentration of all the studied metals, ranging from 4,000 to 31,800 mg kg^{-1} in the soils with a noticeable decrease in concentration with depth. Highest concentrations were observed in the surface layers (0-25 cm) indicating possible enrichment. A similar trend of Fe distribution was observed by Zaccone et al. (2007) in peat bog. In most cases Fe is of lithogenic or pedogenic origin (Fischer et al., 2008) but input of atmospheric particulate fallout from anthropogenic sources or precipitation of Fe^{3+} oxide in the oxic horizon may also cause Fe accumulation in soils (Evans and Heller, 1994; Zaccone et al., 2007). It is also associated with coarse atmospheric dust particles (Al-Khashman and Shawabkeln, 2006).

Niobium occurs mainly as columbite, a mineral with a ratio of Nb_2O_5:Ta_2O_5. Its concentration in our study soils ranged from 23-83 mg kg^{-1} with a fairly uniform distribution across the soil profiles. This reflects its relative immobile nature (Åström et al., 2008) and its association with stable soil minerals. It is generally regarded as little health-relevant (Schroeder et al., 1970), but very little research was conducted on its toxicity in man. The primary exposure route of humans to Nb is again through dust inhalation (Dias Da Cunha et al., 2001; Juliao et al., 2007). The Nb concentrations observed in our soils was 4 to 5 times lower than those (85 to 138 mg kg^{-1}) reported by Ogunleye et al. (2006) in granitic material

Table 5.1. Concentrations of trace elements (mg kg^{-1}) in five waste-water irrigated vegetable garden soils and one uncultivated control soil of Kano, northern Nigeria.

Site	Depth (cm)	Ti	Fe	Nb	Pb	Rb	Sr	Y	Zr
1	0-15	11,600	6,200	54	355	93	82	82	1020
	16-25	12,800	16,600	83	263	132	79	73	1040
	25-35	13,600	20,600	47	255	124	92	65	790
	35-45	12,400	29,500	51	318	92	92	77	856
	45-75	11,600	22,600	50	315	90	89	80	722
	75-100	11,200	14,100	64	285	91	108	74	837
	>100	14,300	14,300	65	238	96	89	98	871
2	0-15	8,340	19,800	36	167	90	137	59	616
	15-25	7,480	17,300	38	170	74	84	63	623
	25-35	8,120	23,600	42	201	71	65	76	585
	35-45	9,990	16,200	37	208	81	90	90	598
	45-75	6,920	6,990	40	164	70	65	46	720
	75-100	4,620	4,060	26	96	54	41	39	440
	>100	5,320	4,070	29	124	49	47	33	439
3	0-15	5,360	10,900	29	143	55	37	44	446
	15-25	6,870	16,300	31	185	62	55	50	456
	25-35	5,960	8,520	23	106	40	40	34	389
	35-45	7,760	9,890	34	164	55	52	60	504
	45-75	6,640	6,880	28	121	46	45	38	467
	75-100	10,300	6,260	46	183	69	79	91	719
	>100	7,860	12,800	37	179	69	56	73	600
4	0-15	8,170	19,800	46	185	82	69	65	529
	15-25	8,140	22,500	54	191	71	68	68	638
	25-35	7,820	16,300	44	197	70	61	54	622
	35-45	6,890	10,800	34	202	70	54	48	617
	45-75	5,050	7,280	24	110	54	49	33	474
	75-100	11,200	4,970	35	146	54	50	43	616
	>100	8,990	16,500	49	256	71	73	63	537
5	0-15	5,070	31,800	46	124	48	42	36	626
	15-25	9,020	19,500	44	171	75	75	64	620
	25-35	6,590	11,100	30	135	68	46	43	399
	35-45	6,930	11,300	26	105	93	43	41	435
	45-75	8,580	18,300	43	223	84	73	59	582
	75-100	5,700	7,140	28	205	68	38	32	597
	>100	5,060	5,550	25	100	42	63	34	633
Control	0-15	8,160	21,000	45	194	115	74	59	748
	15-25	8,770	19,000	39	193	87	115	54	532
	25-35	7,900	10,600	42	174	72	78	53	656
	35-45	7,920	9,370	37	173	89	61	53	738
	45-75	7,030	5,440	32	350	52	46	50	548
	75-100	9,190	6,720	34	150	59	80	58	660
	>100	7,220	11,500	35	170	81	56	50	501

from the Nigerian savannah but within the range of 25-120 mg kg^{-1} reported by Bhuiyan et al. (2010) in Bangladeshi soils.

Lead has been considered as the most widespread contaminant of the metals studied (Oliver, 1997). Its concentration ranged from 96-355 mg kg^{-1} and was thus 3-9 times higher than the 28-45 mg kg^{-1} reported by Agbenin (2002) in soils of the same region and 6-24 times higher than the average Pb concentration in the earth's crust (15 mg kg^{-1}; Kabata-Pendias, 2001). Its fairly uniform distribution in the soil profiles reflects its relative immobility. This result is consistent with Agbenin (2002) who observed limited Pb movement in soils of the Nigerian Savannah. Lead is primarily of pedogenic origin but elevated concentrations may reflect anthropogenic pollution. It is naturally inherited from soil parent material such as galena which slowly oxidizes during weathering (Kabata-Pendias, 2001). Secondary Pb has been attributed to radioactive decay of uranium (U) and Thorium (Th) (Kabata-Pendias, 2001). The high Pb concentration reported in this study may apart from vehicular emission be due to the deposition of aeolian dust particles rich in U, which may have originated from neighboring Niger Republic which has important U-mining activities (Agbenin and Felix-Henningsen, 2001). High Pb concentrations in soils may lead to its ingestion through dust inhalation and plant uptake near unpaved roads, causing subsequent health problems such as brain damage in children (Pocock et al., 1994). It may also cause dysfunction of the central nervous and the reproductive system (Landrigan, 1989).

Rubidium is generally associated with claystones and siltstones (Hower and Robertson, 2003) and also has affinity for aluminosilicates such as in the case of Ti (Goodarzi, 1988). Its concentration in Nigerian savannah soils ranged from 40-132 mg kg^{-1} with highest concentrations near the surface. Our concentrations are in the range of those reported by Sposito (1989) but 2-3 times lower than concentrations shown by Bhuiyan et al. (2010) in mine contaminated soils from Bangladesh. Our values are, however; lower than those reported by Agbenin (2001) in long-term cultivated savannah soils from northern Nigeria. The fairly uniform distribution of this metal in the profile with a tendency of higher concentration in surface layers is in contrast to findings of Agbenin (2001).

Strontium showed a fairly erratic distribution with soil depth. Its concentration ranged from 37-137 mg kg^{-1}. This value is 2-4 times lower than those reported by Bhuiyan et al. (2010) in contaminated Bangladesh soils. Higher concentrations observed in the surface layer may be related to the recirculation and deposition of Sr by plant litter and atmospheric deposition (Miller et al., 1993). Silicate minerals are the primary soil-born source of this alkaline-earth metal (Tyler, 2004) which may also be present as phosphate and carbonate in soils (Mejeed, 1997). The geochemical and biochemical properties of this element are similar to those of Ca (Kabata-Pendias, 2001). The toxicity of Sr is often assessed by a soil's Ca:Sr ratio whereby a ratio < 8 indicates an unsafe Sr accumulation (Kabata-Pendias, 2001).

Yttrium concentration in the studied soils ranged from 33-98 mg kg^{-1} whereby the lowest values were higher than the 25 mg kg^{-1} reported as world average Y concentration in soils (Sposito, 1989). Agbenin and Felix-Henningsen (2001) reported similar Y concentrations in soils of the Nigerian savannah and pointed out the human health relevant toxicity of this element. The fairly uniform Y concentration in the soil profiles indicates its association with resistant soil mineral fractions (Xing and Dudas, 1993). The ease at which this element can replace Ca^{2+} in the soil exchange site adds to its toxicity risk (Deuber and Heim, 1991). Dust inhalation is the major ingestion route of Y in humans and animals (Agbenin and Felix-Henningsen, 2001) which during the Harmattan season (November to March) may be of concern.

Zirconium occurs in soils mainly as zircon (Sakurovs et al., 2007) and its concentration in the studied soils ranged from 435-1,040 mg kg^{-1}. A fairly uniform concentration of this element was observed throughout the soil profiles except for site 1 where it was found to decline with depth. The uniform distribution observed in other profiles could be related to its occurrence in zircon which is a mineral that is highly resistant to dissolution (Milnes and Fitzpatrick, 1989) and the very low solubility of zircon in aqueous solution (Brookins, 1988).

5.3.2. Evaluation of contamination

The contamination factor of most studied elements was below 2 and of many below 1, indicating no to medium contamination (Table 5.2 and 5.3; Muller, 1969). Only Fe had a contamination factor that ranged from 0.4-4.2 with values above 1 found only at site 1. Similarly, at site 5 at a depth below 50 cm, the contamination factor for Fe was >3 indicating moderate to strong contamination (Muller, 1969). The higher contamination factors for Fe were all observed at lower profile depths which preclude anthropogenic Fe input from the surface.

The geoaccumulation index also showed that concentrations of all elements were below critical levels (Table 5.4). None of the geoaccumulation indices approached 1. For Fe the geoaccumulation factor was zero across locations and depths indicating that the elevated contamination factor at site 1 is insufficient to prove Fe contamination. The enrichment factor calculated for this element, however, suggests an anthropogenic contamination of Fe at this site. With a few exceptions enrichment factors were for all elements only slightly above unity. The EF calculated for Nb (0.7-1.7), Rb (0.6-2.2), Sr (0.5-1.8) and Y (0.6-1.4; Table 5.3) suggests that these elements originated mainly from the parent rock in the earth’s crust. Values <1 indicate mobilization or depletion of an element whereas EF >1 indicate effects of anthropogenic inputs (Bhuiyan et al., 2010) which may only have been the case for Fe.

Mass balance calculations revealed depletion of most elements. Only Fe and Pb showed sizeable accumulations. The accumulation of Pb in the surface layer of the profiles at site 1, 3 and 5 was 29%, 12% and 3% (Table 5.5) which may be attributed to vehicular emissions. Enrichment of Fe was between 0 and 176% further suggesting anthropogenic accumulation of this element. Negative values may reflect aging effects of the soil minerals and a possible transfer of elements into immobile forms.

Table 5.2. Contamination factors (CF) for trace elements in five waste-water irrigated vegetable garden soils of Kano, northern Nigeria.

Site	Depth (cm)	Ti	Fe	Nb	Pb	Rb	Sr	Y	Zr
1	0-15	1.4	0.8	1.2	1.8	0.8	1.1	1.4	1.4
	16-25	1.5	0.9	2.1	1.4	1.5	0.7	1.4	2.0
	25-35	1.3	1.9	1.1	1.5	1.7	1.2	1.2	1.2
	35-45	1.6	3.2	1.4	1.8	1.0	1.5	1.5	1.2
	45-75	1.7	4.2	1.5	0.9	1.7	2.0	1.6	1.3
	75-100	1.2	2.1	1.9	1.9	1.5	1.4	1.3	1.3
	>100	1.0	1.2	1.8	1.4	1.2	1.6	2.0	1.7
2	0-15	1.0	0.9	0.8	0.9	0.8	1.9	1.0	0.8
	15-25	0.9	0.9	1.0	0.9	0.9	0.7	1.2	1.2
	25-35	1.0	2.2	1.0	1.2	1.0	0.8	1.4	0.9
	35-45	1.3	1.7	1.0	1.2	0.9	1.5	1.7	0.8
	45-75	1.0	1.3	1.2	0.5	1.3	1.4	0.9	1.3
	75-100	0.5	0.6	0.7	0.6	0.9	0.5	0.7	0.7
	>100	0.7	0.4	0.8	0.7	0.6	0.8	0.7	0.9
3	0-15	0.7	0.5	0.7	0.7	0.5	0.5	0.8	0.6
	15-25	0.8	0.9	0.8	1.0	0.7	0.5	0.9	0.9
	25-35	0.8	0.8	0.6	0.6	0.6	0.5	0.6	0.6
	35-45	1.0	1.1	0.9	1.0	0.6	0.9	1.2	0.7
	45-75	0.9	1.3	0.9	0.4	0.9	1.0	0.8	0.9
	75-100	1.1	0.7	1.3	1.2	1.2	1.0	1.6	1.1
	>100	1.1	1.4	1.1	1.1	0.9	1.0	1.5	1.2
4	0-15	1.0	0.9	1.0	1.0	0.7	0.9	1.1	0.7
	15-25	0.9	1.2	1.4	1.0	0.8	0.6	1.3	1.2
	25-35	1.0	1.5	1.1	1.1	0.9	0.8	1.0	1.0
	35-45	0.9	1.2	0.9	1.2	0.8	0.9	0.9	0.8
	45-75	0.7	1.3	0.8	0.3	1.0	1.1	0.7	0.9
	75-100	1.2	0.7	1.0	1.0	0.9	0.6	0.8	0.9
	>100	1.3	1.4	1.4	1.5	0.9	1.3	1.3	1.1
5	0-15	0.6	1.5	1.0	0.6	0.4	0.6	0.6	0.8
	15-25	1.0	1.0	1.1	0.9	0.9	0.7	1.2	1.2
	25-35	0.8	1.1	0.7	0.8	1.0	0.6	0.8	0.6
	35-45	0.9	1.2	0.7	0.6	1.1	0.7	0.8	0.6
	45-75	1.2	3.4	1.3	0.6	1.6	1.6	1.2	1.1
	75-100	0.6	1.1	0.8	1.4	1.2	0.5	0.6	0.9
	>100	0.7	0.5	0.7	0.6	0.5	1.1	0.7	1.3

Table 5.3. Enrichment factors (EF) for trace elements in five waste-water irrigated vegetable garden soils of Kano, northern Nigeria.

Site	Depth (cm)	Fe	Nb	Pb	Rb	Sr	Y	Zr
1	0-15	0.5	0.8	1.3	0.6	0.8	1.0	1.0
	16-25	0.6	1.5	0.9	1.0	0.5	0.9	1.3
	25-35	1.1	0.7	0.9	1.0	0.7	0.7	0.7
	35-45	2.0	0.9	1.2	0.7	1.0	0.9	0.7
	45-75	2.5	0.9	0.5	1.0	1.2	1.0	0.8
	75-100	1.7	1.5	1.6	1.3	1.1	1.1	1.0
	>100	0.6	0.9	0.7	0.6	0.8	1.0	0.9
2	0-15	0.9	0.8	0.8	0.8	1.8	1.0	0.8
	15-25	1.1	1.2	1.0	2.2	0.7	1.4	1.7
	25-35	2.2	1.0	1.1	1.3	0.8	1.4	0.9
	35-45	1.2	0.8	1.0	0.9	1.2	1.4	0.6
	45-75	1.3	1.3	0.5	1.1	1.4	0.9	1.3
	75-100	1.2	1.5	1.3	1.3	1.0	1.4	1.3
	>100	0.5	1.1	1.0	1.3	1.1	0.9	1.2
3	0-15	0.8	1.0	1.1	0.7	0.8	1.1	0.9
	15-25	1.1	1.0	1.2	0.9	0.6	1.2	1.1
	25-35	1.1	0.7	0.8	0.8	0.7	0.9	0.8
	35-45	1.1	0.9	1.0	0.6	0.9	1.2	0.7
	45-75	1.3	0.9	0.4	0.9	1.0	0.8	0.9
	75-100	0.8	1.2	1.1	1.0	0.9	1.4	1.0
	>100	1.0	1.0	1.0	0.8	0.9	1.3	1.1
4	0-15	0.9	1.0	1.0	0.7	0.9	1.1	0.7
	15-25	1.3	1.5	1.1	0.9	0.6	1.4	1.3
	25-35	1.6	1.1	1.1	1.0	0.8	1.0	1.0
	35-45	1.3	1.1	1.3	0.9	1.0	1.1	1.0
	45-75	1.9	1.0	0.4	1.4	1.5	0.9	1.2
	75-100	0.6	0.8	0.8	0.8	0.5	0.6	0.8
	>100	1.2	1.1	1.2	0.7	1.0	1.0	0.9
5	0-15	2.4	1.7	1.0	0.7	0.9	1.0	1.4
	15-25	1.0	1.1	0.9	0.8	0.6	1.2	1.1
	25-35	1.3	0.9	0.9	1.1	0.7	1.0	0.7
	35-45	1.4	0.8	0.7	1.2	0.8	0.9	0.7
	45-75	2.8	1.1	0.5	1.3	1.3	1.0	0.9
	75-100	1.7	1.3	2.2	1.9	0.8	0.9	1.5
	>100	0.7	1.0	0.8	0.7	1.6	1.0	1.8

Table 5.4. Geoaccumulation indices (I_{geo}) of trace elements in five waste-water irrigated vegetable garden soils of Kano, northern Nigeria.

Site	Depth (cm)	Ti	Fe	Nb	Pb	Rb	Sr	Y	Zr
1	0-15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	16-25	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.04
	25-35	0.06	0.05	0.06	0.06	0.08	0.07	0.05	0.04
	35-45	0.07	0.09	0.08	0.08	0.06	0.08	0.07	0.08
	45-75	0.08	0.07	0.09	0.12	0.09	0.09	0.11	0.10
	75-100	0.12	0.11	0.01	0.01	0.01	0.01	0.01	0.01
	>100	0.01	0.03	0.02	0.03	0.03	0.03	0.03	0.04
2	0-15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	15-25	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.04
	25-35	0.06	0.05	0.06	0.05	0.08	0.06	0.05	0.04
	35-45	0.07	0.09	0.07	0.08	0.04	0.07	0.07	0.08
	45-75	0.07	0.06	0.09	0.11	0.07	0.08	0.09	0.09
	75-100	0.09	0.09	0.01	0.01	0.01	0.01	0.01	0.01
	>100	0.01	0.03	0.01	0.03	0.03	0.03	0.03	0.03
3	0-15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	15-25	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.03
	25-35	0.05	0.04	0.05	0.05	0.07	0.07	0.05	0.03
	35-45	0.06	0.08	0.07	0.08	0.05	0.07	0.06	0.06
	45-75	0.07	0.08	0.07	0.10	0.08	0.07	0.08	0.09
	75-100	0.11	0.10	0.01	0.01	0.01	0.01	0.01	0.01
	>100	0.01	0.02	0.01	0.03	0.03	0.03	0.03	0.03
4	0-15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	15-25	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.04
	25-35	0.06	0.05	0.06	0.05	0.07	0.07	0.05	0.04
	35-45	0.06	0.08	0.08	0.07	0.05	0.07	0.07	0.07
	45-75	0.07	0.06	0.09	0.09	0.08	0.08	0.10	0.09
	75-100	0.10	0.11	0.01	0.01	0.01	0.01	0.01	0.01
	>100	0.01	0.03	0.01	0.03	0.03	0.03	0.03	0.03
5	0-15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	15-25	0.00	0.00	0.05	0.05	0.00	0.00	0.03	0.06
	25-35	0.08	0.07	0.06	0.04	0.05	0.04	0.05	0.09
	35-45	0.06	0.07	0.06	0.09	0.07	0.07	0.08	0.08
	45-75	0.08	0.09	0.01	0.01	0.11	0.09	0.01	0.01
	75-100	0.01	0.01	0.03	0.03	0.02	0.03	0.03	0.01
	>100	0.00	0.00	0.09	0.03	0.04	0.07	0.07	0.01

Table 5.5. Geochemical balance (G_{bal}) of trace elements in five waste-water irrigated vegetable garden soils of Kano, northern Nigeria.

Site	Depth (cm)	Ti	Fe	Nb	Pb	Rb	Sr	Y	Zr
1	0-15	0.0	-46.0	-15.0	29.0	-43.0	-23.0	-2.0	-4.0
	16-25	0.0	-40.0	45.0	-7.0	4.0	-53.0	-7.0	34.0
	25-35	0.0	13.0	-34.0	-15.0	1.0	-32.0	-29.0	-30.0
	35-45	0.0	101.0	-12.0	17.0	-33.0	-3.0	-6.0	-26.0
	45-75	0.0	152.0	-7.0	-45.0	5.0	18.0	-4.0	-20.0
	75-100	0.0	72.0	53.0	56.0	27.0	11.0	6.0	4.0
	>100	0.0	-37.0	-7.0	-29.0	-40.0	-20.0	-1.0	-12.0
2	0-15	0.0	-8.0	-22.0	-16.0	-24.0	81.0	-2.0	-19.0
	15-25	0.0	7.0	15.0	3.0	0.0	-14.0	36.0	37.0
	25-35	0.0	117.0	-2.0	12.0	-4.0	-20.0	39.0	-13.0
	35-45	0.0	37.0	-19.0	-5.0	-28.0	17.0	35.0	-36.0
	45-75	0.0	31.0	25.0	-52.0	36.0	43.0	-6.0	33.0
	75-100	0.0	20.0	47.0	160.0	81.0	2.0	35.0	33.0
	>100	0.0	-52.0	12.0	-1.0	-18.0	12.0	-10.0	19.0
3	0-15	0.0	-21.0	-1.0	12.0	-27.0	-23.0	14.0	-9.0
	15-25	0.0	10.0	1.0	22.0	-9.0	-39.0	20.0	9.0
	25-35	0.0	7.0	-26.0	-19.0	-25.0	-32.0	-15.0	-21.0
	35-45	0.0	8.0	-6.0	-3.0	-37.0	-12.0	17.0	-30.0
	45-75	0.0	34.0	-10.0	-63.0	-7.0	3.0	-21.0	-10.0
	75-100	0.0	-17.0	18.0	9.0	4.0	-11.0	41.0	-3.0
	>100	0.0	2.0	-2.0	-3.0	-22.0	-9.0	34.0	10.0
4	0-15	0.0	-6.0	2.0	-5.0	-29.0	-7.0	10.0	-29.0
	15-25	0.0	28.0	50.0	7.0	-12.0	-37.0	36.0	29.0
	25-35	0.0	55.0	7.0	14.0	-1.0	-22.0	2.0	-4.0
	35-45	0.0	32.0	6.0	34.0	-9.0	3.0	6.0	-4.0
	45-75	0.0	86.0	4.0	-56.0	43.0	48.0	-8.0	20.0
	75-100	0.0	-39.0	-17.0	-20.0	-25.0	-49.0	-39.0	-23.0
	>100	0.0	15.0	11.0	21.0	-30.0	3.0	1.0	-14.0
5	0-15	0.0	144.0	65.0	3.0	-33.0	-9.0	-2.0	35.0
	15-25	0.0	0.0	9.0	-14.0	-16.0	-37.0	16.0	13.0
	25-35	0.0	26.0	-13.0	-7.0	14.0	-29.0	-3.0	-27.0
	35-45	0.0	38.0	-19.0	-31.0	20.0	-19.0	-12.0	-33.0
	45-75	0.0	176.0	8.0	-48.0	32.0	31.0	-5.0	-13.0
	75-100	0.0	71.0	30.0	120.0	85.0	-23.0	-10.0	46.0
	>100	0.0	-31.0	1.0	-16.0	-27.0	59.0	-5.0	80.0

5.3.3. Correlation analysis and origin of trace elements

Pearson correlation coefficients indicated that all metals were highly correlated with each other ($P \leq 0.01$; Table 5.6). Such strong inter-element correlation is an indication that the elements originated from similar sources possibly subjected to the same mineralization processes. The strong positive correlations observed between these metals are consistent with the reports of Dragovič et al. (2008) and Bhuiyan et al. (2010). We therefore speculate that these metals largely originated from native columbite, phosphate and sulfide minerals such as galena, monazite, fergosonite which are part of the parent rock underlying the soils of the study locations. The significant correlation between soil pH and TEs in this study is contrary to the results obtained by Manta et al. (2002), Tume et al. (2006) and Bhuiyan et al. (2010). It may indicate that release of TEs through pedogenesis is in our soils a pH-dependent process which is consistent with the observations of Lindroos et al. (2003). Positive correlations observed between Fe, Rb, Pb and clay fraction indicate a high affinity of these metals for clays.

Factor analysis (FA) on the correlated TEs and soil properties using Varimax rotation to maximize the sum of the variance of the factor coefficients (Gotelli and Ellison, 2004) showed two factors with eigenvalues > 1 that explained 74% of the variation in the data set (Table 5.7). Factor 1 accounts for 58% of the total variance and is dominated by all TEs and pH. This factor may reflect the pedological accumulation of these metals through weathering in the form of dissolution and hydrolysis as affected by pH. The very high loadings (0.50-0.91) obtained are a strong indication that these metals originated from the same or a similar source and thus further support the results of the correlation analysis. Factor 2 is dominated by OC, CEC and Fe with high positive loadings. Given its high OC loading which affects soil CEC factor 2 may reflect organic colloids. It may thus be concluded that the high level of Fe observed in the soil might be a result of decomposition of organic matter releasing Fe into the soil solution.

Table 5.6. Pearson correlation matrix for trace elements and soil properties in five waste-water irrigated vegetable garden soils of Kano, northern Nigeria.

Parameter	Ti	Fe	Nb	Pb	Rb	Sr	Y	Zr	CEC	Clay	pH
Ti	1										
Fe	0.38*	1									
Nb	0.78**	0.52**	1								
Pb	0.74**	0.46**	0.70**	1							
Rb	0.78**	0.45**	0.73**	0.68**	1						
Sr	0.68**	0.46**	0.58**	0.58**	0.65**	1					
Y	0.80**	0.44*	0.71**	0.70**	0.62**	0.69**	1				
Zr	0.78**	0.36**	0.84**	0.75**	0.71**	0.61**	0.65**	1			
CEC	0.01	0.47**	0.06	-0.14	0.14	0.18	0.06	-0.07	1		
Clay	0.30	0.36*	0.21	0.29	0.40*	0.22	0.28	0.13	0.33*	1	
pH	0.58**	0.35*	0.57**	0.57**	0.54**	0.53**	0.49**	0.45**	0.06	0.06	1

* Significant P< 0.05; ** Significant at P< 0.01

Iron has been observed to displace several other TEs from organic sorption sites which reflect the role of OC in the complexation and chelation of Fe with organic ligands and the ease with which Fe substitutes for cations like Mg and Al at soil exchange sites (Agbenin et al., 1999; Syrovetnik et al., 2008).

Table 5.7. Rotated component matrix for trace elements and soil properties in five waste-water irrigated vegetable garden soils of Kano, northern Nigeria (loadings factors > 0.4 are shown in bold).

Parameter	Factor 1	Factor 2
CEC	0.028	**0.778**
Clay	0.368	0.190
OC	-0.116	**0.735**
pH	**0.646**	0.118
Ti	**0.906**	-0.062
Fe	**0.495**	**0.598**
Nb	**0.865**	0.137
Pb	**0.842**	-0.123
Rb	**0.838**	0.126
Sr	**0.753**	0.139
Y	**0.836**	0.017
Zr	**0.855**	-0.097
Eigenvalue	5.844	1.582
% of variance	57.899	16.361
Cumulative %	71.480	90.830

5.4. Conclusions

Based on the calculated metal enrichment factor, geoaccumulation index and contamination factor, there seems to be no apparent contamination of the garden soils with the studied metals (Nb, Pb, Rb, Sr, Ti, Y and Zr). Such indices of pollution and mass balance calculations can be used to identify likely sources of

TM contamination in soils of the Nigerian savannah. Of all elements studied only Fe had at one location CF and EF values above unity suggesting anthropogenic input of this element while mass balance calculations indicated depletion of all metals except of Fe and Pb. The concentrations of the monitored TEs were apparently largely governed by pedogenic rather than anthropogenic factors.

5.5. References

Abdu, N., Abdulkadir, A., Agbenin, J.O. and Buerkert, A. 2010a. Vertical distribution of heavy metals in wastewater-irrigated vegetables garden soils of three West African cities. Nutrient Cycling in Agroecosystems (submitted).

Abdu, N., Agbenin, J.O. and Buerkert, A. 2010b. Phytoavailability, human risk assessment and transfer characteristics of cadmium and zinc contamination from urban gardens in Kano, Nigeria. Journal of the Science of Food and Agriculture (submitted).

Agbenin, J.O., De Abreu, C.A., and van Raij, B., 1999. Extraction of phytoavailable trace metals from tropical soils by mixed ion exchange resin modified with inorganic and organic ligands. The Science of the Total Environment 227: 187-196.

Agbenin, J.O. 2001. The status and fluxes of some alkaline-earth metals in a savanna Alfisol under long-term cultivation. Catena 45: 313-331.

Agbenin, J.O. and Felix-Henningsen, P. 2001. The status and dynamics of some trace elements in a savanna soil under long-term cultivation. The Science of the Total Environment 277: 57-68.

Agbenin, J.O. 2002. Lead in a Nigerian savanna soil under long-term cultivation. The Science of the Total Environment 286: 1-14.

Ahmed, K. 1987. Erosion hazard assessment in the Savannah: The Hadejia-Jama’are River Basin. In: Mortimore M., Olofin E.A., Clinecole R.A. and Abdulkadir A. (Eds), Perspective on land administration and development in northern Nigeria, Proceedings of the workshop on land resources, Department of Geography, Bayero Univeristy, Kano, pp 234-247.

Al-Khashman, O. A. and Shawabkeln, R. A. 2006. Metals distribution in soils around the cement factory in southern Jordan. Environmental Pollution 140: 387–394.

Åström, M.E., Peltola, P., Virtasalo, J.J., Kotilainen, A.T. and Salminen, R. 2008. Niobium in boreal stream waters and brackish-water sediments. Geochemistry: Exploration, Environment, Analysis 8: 139-148.

Awode, U.A., Uzairu, A., Balarabe, M.L., Harrisson, G.F.S. and Okunola, O.J. 2008. Assessment of peppers and soils for some heavy metals from irrigated farmlands on the Bank of river Challawa, Northern Nigeria. Pakistan Journal of Nutrition 7: 244-248.

Bhuiyan, M.A.H., Parvez, L., Islam, M.A., Dampare, S.B. and Suzuki, S. 2010. Heavy metal pollution of coal mine-affected agricultural soils in the northern part of Bangladesh Journal of Hazardous Materials 173: 384-392.

Blake, G.R. and Hartge, K.H., 1986. Bulk density. In: Klute A, (Ed). Methods of soil analysis. Part 1. Physical and mineralogical methods. Madison, WI: American Society of Agronomy, pp 363-377.

Boulay, N. and Edward, M. 2000. Copper in the Urban Water Cycle. Critical Reviews in Environmental Science and Technology 30: 297-326.

Brookins, D.G. 1988. Eh-pH Diagrams for Geochemistry. Springer-Verlag, New York, N.Y.

Dach, J. and Starmans, D. 2005. Heavy metals balance in Polish and Dutch agronomy: Actual state and previsions for the future. Agriculture, Ecosystem and Environment 67: 121-131.

Daskalakis, K.D. and O’Connor, T.P. 1995. Normalization and elemental sediment contamination in the Coastal United States. Environmental Science Technology 29: 470-477.

Deer, W.A., Howie, R.A. and Zussman, J. 1962. Sheet Silicates, Longmans Green and Co. Ltd., London, UK.

Deuber, R. and Heim, T. 1991. “Yttrium”. In: Marian, E. (Ed) Metals and their compounds in the environment: Occurrence, analysis and biological relevance, VCH, Weinheim; Germany, pp 1299-1308.

Dias Da Cunha, K., Lipsztein, J.L., Azeredo, A.M., Melo, D., Julião, L.M.Q.C., Lamego, F.F., Santos, M. and Barros Leite, C.V. 2002. Study of worker’s exposure to thorium, uranium and niobium mineral dust. Water, Air, and Soil Pollution 137: 45-61.

Dragovic, S., Mihailovic, N. and Gajic, B. 2008. Heavy metals in soils: distribution, relationship with soil characteristics and radionuclides and multivariate assessment of contamination sources. Chemosphere 72: 491-495.

Evans, M.E. and Heller, F. 1994. Magnetic enhancement and palaeoclimate: Study of a loess/paleosol couplet across the Loess Plateau of China. Geophysical Journal International 117: 257-264.

Ewa, I.O.B., Oladipo, M.O.A. and Dim, L.A. 1999. Horizontal and vertical distribution of selected metals in the Kubani River, Nigeria as determined by neutron activation analysis. Communication Soil Plant Analysis 30: 1081-1090.

FAO/UNESCO., 1974. Soil map of the world. 1:5,000,000, ten volumes, UNESCO-Paris, France.

Fischer, H., Luster, J. and Gehring, A.U. 2008. Magnetite weathering in a Vertisol with seasonal redox-dynamics. Geoderma 143: 41-48.

Gee, G.W. and Bauder, J.W. 1986. Particle-size analysis. In: Klute, A., (Ed) Methods of soil analysis, part 1. 2nd edn. Agronomy Monogram. 9. ASA and SSSA, Madison, WI, USA, pp. 383-411.

Goodarzi, F. 1988. Elemental distribution in coal seams at the fording coal mine, British Columbia, Canada, Chemical Geology 68: 129-154.

Gotelli, N.J. and Ellison, A.M. 2004. A primer of ecological statistics. First edition, Sinauer Associates, Sunderland, MA, USA, 492 pp.

Hower, J. and Robertson, J.D. 2003. Clausthalite in coal, International Journal Coal Geology 53: 219-225.

Iijima, A., Sato, K., Yano, K., Tago, H., Kato, M., Kimura, H. and Furuta, N., 2007. Particle size and composition distribution analysis of automotive brake abrasion dusts for evaluation of antimony sources of airborne particulate matter. Atmospheric Environment 41: 4908-4919.

Jaiyeoba, I.A. 1995. Variation of soil chemical properties over Nigerian savanna. Singapore Journal of Tropical Geography 16: 141-157.

Juliao, L.M.Q.C., Melo, D.R., Sousa, W.O., Santos, M.S., Fernandes, P.C. and Godoy, M.L.D.P. 2007. Exposure of workers in a mineral processing industry in Brazil. Radiation Protection Dosimetry. 125: 513–515.

Kabata-Pendias, A. 2001. Trace elements in soils and plants. CRC Press LLC, Boca Raton, FL, USA.

Kleinbaum, D.G., Kupper,L. L. and Muller, K. E. 1988. Applied regression analysis and other multivariable methods (2nd edn). PWS-Kent, Boston, MA, USA.

Koch, M. and Rotard, W. 2000. On the contribution of background sources to the heavy metal content of municipal sewage sludge. Water Science and Technology 43: 67-74.

Landrigan, P.J. 1989. Toxicity of lead at low dose. British Journal Industrial Medicine 46: 593-596.

Lar, U. A. and Tejan, A. B. 2008. Highlights of some environmental problems of geomedical significance in Nigeria. Environmental Geochemistry and Health 30: 383-389.

Lindroos, A.J., Brügger, T., Derome, J. and Derome, K. 2003. The weathering of mineral soil by natural soil solutions. Water, Air, and Soil Pollution 149: 269-279.

Loska, K., Cebula, J., Pelczar, J., Wiechula, D. and Kwapulinski, J. 1997. Use of enrichment, and contamination factors together with geoaccumulation indexes to evaluate the content of Cd, Cu, and Ni in the Rybnik water Reservoir in Poland. Water Air and Soil Pollution 93: 347-365.

Maþvila, J., Adomaitis, T. and Eitmanavièius, L. 2001. Heavy metals in Lithuanian soils and plants. Kaunas 92-111.

Manta, D.S., Angelone, M., Bellanca, A., Neri, R. and Sprovieri, M. 2002. Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. Science of the Total Environment 30: 229-243.

Mashi, S.A. and Alhassan, M.M. 2007. Effects of wastewater discharge on heavy metals pollution in Fadama soils in Kano city, Nigeria. Biomedical and Environmental Science 20: 70-77.

Mejeed, S.Y. 1997. Trace element distribution among the components of soils in Zitny Ostrov Region, southwestern Slovakia. Geology Carpath 48: 63-68.

Miller, E.K., Blum, J.D. and Friedland, A.J. 1993. Determination of soil exchangeable cation loss and weathering rates using strontium isotopes. Nature 362: 438-441.

Milnes, A.R. and Fitzpatrick, R.W. 1989. Titanium and zirconium minerals. In Minerals in Soils Environments, Dixon, J.B., Weed, S.B. (Eds). Soil Science Society America, Madison, WI, pp 1131-1205.

Moroni, M., Girardi, V.A.V. and Ferrario, A. 2001. The Serra Pelada Au-PGE deposit, Serra dos Caraja´s (Para´ State, Brazil): geological and geochemical indications for a composite mineralizing process. Mineral Deposita 36: 768–785.

Muller, G. 1969. Index of geoaccumulation in sediments of the Rhine River. Geojournal 2: 108-118.

Muller, G. 1979. Schwermetalle in den sedimenten des Rheins - Veränderungen seit 1971, Umschau 79: 778–783.

Muller, G. 1981. Die Schwermetallbelastung der sedimente des Neckars und seiner Nebenflüsse: Eine Bestandsaufnahme. Chemiker - Zeitung 105: 157-164.

Ndjigui, P.A., Bilong, P., Bitom, D. and Dia, A. 2008. Mobilization and redistribution of major and trace elements in two weathering profiles developed on serpentinites in the Lomie´ ultramafic complex, South-East Cameroon. Journal of African Earth Sciences 50: 305-328.

Nriagu, J.O. 1990. The rise and fall of leaded gasoline. Science of the Total Environment 92: 13-28.

Ogunleye, P.O., Garba, I. and Ike, E.C. 2006. Factors contributing to enrichment and crystallization of niobium in pyrochlore in the Kaffo albite arfvedsonite granite, Ririwai Complex, Younger Granites province of Nigeria. Journal of African Earth Sciences 44: 372-382.

Oliver, M.A. 1997. Soil and human health. a review. European Journal of Soil Science 48: 573-592.

Pocock, S.J., Smith, M. and Baghurst, P. 1994. Environmental lead and children’s intelligence: a systematic review of the epidemiological evidence. British Medical Journal 309: 1189-1197.

Sakurovs, R., French, D. and Grigore, M. 2007. Quantification of mineral matter in commercial cokes and their parent coals. International Journal Coal Geology 72: 81-88.

Schütz, L. and Rahn, K.A. 1982. Trace-element concentrations in erodible soils. Atmospheric Environment 16: 171-176.

Shotbolt, L. A. Rothwell, J. J. and Lawlor, A. J. 2008. A mass balance approach to quantifying Pb storage and fluxes in an upland catchment of the Peak District, north-central England. Earth Surface Processes and Landforms 33: 1721-1741.

Schroeder, H.A., Mitchener, M. and Nason, A.P. 1970. Zirconium, Niobium, Antimony, Vanadium and Lead in Rats: Life term studies. Journal of Nutrition 100: 59-68.

Sörme, L. and Lagerkvist, R. 2002. Sources of heavy metals in urban wastewater in Stockholm. Science of the Total Environment 298: 131-145.

Sposito, G. 1989. The chemistry of soils. Oxford University Press, New York, NY, USA.

Syrovetnik, K., Malmström, M.E. and Neretnieks, I. 2008. Modelling retention of heavy metals in the Oostriku peat bog, Estonia: Comparison of predicted and observed results. Applied Geochemistry 23: 1498-1512.

Takamatsu, T., Watanabe, M., Koshikawa, M.K., Murata, T., Yamamura, S. and Hayashi, S. 2010. Pollution of montane soil with Cu, Zn, As, Sb, Pb, and nitrate in Kanto, Japan. Science of the Total Environment 408: 1932-1942.

Tume, P., Bech, J., Longan, L., Tume, L., Reverter, F. and Sepulveda, B. 2006. Trace elements in natural surface soils in Sant Climent (Catalonia, Spain). Ecological Engineering 27: 145-152.

Tyler, G. 2004. Vertical distribution of major, minor, and rare elements in a Haplic Podzol. Geoderma 119: 277-290.

Wang, Y.F., Huang, K.L., Li, C.T., Mi, H.H., Luo, J.H. and Tsai, P.J. 2003. Emissions of fuel metals content from a diesel vehicle engine. Atmospheric Environment 37: 4637-4643.

Xing, B. and Dudas, M.J. 1993. Trace and rare-earth element content of white clay soils of the Three River Plain Heilangjiang Province, PR China. Geoderma 58: 181-199.

Zaccone, C., Cocozza, C., Cheburkin, A.K., Shotyk, W. and Miano, T.M. 2007. Enrichment and depletion of major and trace elements, and radionuclides in ombrotrophic raw peat and corresponding humic acids. Geoderma 141: 235-246.

Chapter 6

General discussion and conclusions

6.1. Heavy metal pollution of soils under urban agriculture in Kano (Nigeria), Sikasso (Mali) and Bobo-Dioulasso (Burkina Faso)

Despite the opportunities of supplementing plant nutrient demand and ensuring year round cultivation that is associated with wastewater irrigation in urban centers, environmental contamination with potentially toxic heavy metals still remains a potential hazard for soil quality and human health. The challenge of ecosystem contamination and associated health risk are obvious in Kano. Assessment of heavy metal pollution during the course of this research work corroborated previous research works (Binns et al., 2003; Mashi and Alhassan, 2007; Awode et al., 2008) on heavy metal pollution in this industrial center of northern Nigeria. Prior to this study, comparative data on heavy metal contamination of urban gardens in Sikasso (Mali) and Bobo-Dioulasso (Burkina Faso) were unavailable.

Heavy metal accumulation in vegetable garden soils form Kano revealed the effects of Cd and Zn accumulation in excess of permissible threshold values by the FAO. In Sikasso and Bobo-Dioulasso, however, heavy metal pollution was still uncritical. The uncontrolled proliferation of poorly managed industrial estates coupled with more than 3 Mio inhabitants shows the potential of conflicts between the different interests of consumers and producers of heavy metals. Analysis of heavy metal balances using the input-output approach (Mercuri et al., 2006; Bassanino et al., 2007; Khai et al., 2007) indicated a net positive balance of Cd and Zn. The results of the present study may serve as a starting point for further studies on toxic metal balances in soils of the Nigerian savannah. In the past solid nutrient budget data from urban agriculture in the West African sub-region were only available for the major elements (N, P, K and C) (Graefe et al., 2008; Predotova et al., 2010; Diogo et al., 2010). A long-term study of heavy metal and nutrient balance is however, required for adequate assessment of changes in the soil nutrient pool.

Geochemical assessment of trace metals (Fe, Ti, Nb, Pb, Rb, Sr, Y and Zr) in Kano irrigated gardens indicated that concentrations of Fe, Pb, Ti and Y where higher than mean soil concentration worldwide. The origin of these metals was attributed to weathering of parent material and atmospheric deposition.

6.2. Mobility and plant availability of HM

Chemical fractionation is often used to characterize plant available portions, mobility and origin of HM in soil (McBride, 1994). However, certain soil processes control and influence HM solubility and bioavailability in soils. The most important in soil solution is pH-dependant protonation or hydrolysis reaction (Hayes and Traina, 1998). HM are mostly soluble and available at low pH. Brummer and Herms (1983) reported Zn, Cd, Cu and Pb solubility to be higher at pH range 4-5 than at pH 5-7. Similarly, Christensen (1984) observed a threefold increase in Cd sorption for each unit of pH increase from 4.0-4.7. In acid soils with $pH < 6$, retention and mobility of heavy metals are mainly dictated by adsorption/desorption reactions. Cadmium, Zn, Ni and Cr are relatively mobile at low pH (Kabata-Pendias and Pendias, 1992) but Cu and Pb are slowly mobile, whereas at $pH > 6.5$, Cd and Zn could still be moderately mobile, while Cu and Pb are less mobile (Fuller, 1977). Similar observation on Cu adsorption was made by Agbenin and Atin (2003) in soils of the Nigerian savannah. In the present study, no inference could be made from soil pH on metal mobility due to lack of meaningful correlation between pH and metal fractions. The persistence and mobility of Cd, Cu, Zn and Pb in highly weathered tropical soils are dictated by their strength of adsorption to the solid phases components. Several studies (Icopini and Long, 2002; Dijkstra et al., 2004; Fest et al., 2008) have shown mobility and solubility of heavy metals to be highly dependent on complexation with dissolved organic matter. The binding strength of metals to soils is strongly related to its pH and ionic strength (Naidu et al., 1997) which in turn depends on level of soil contamination (Karpukhin and Ladonin, 2008).

Cadmium and Zn in this study were both found to have a high mobility factor (chapter 3) which reflects their potential to be easily plant available. Heavy metals are mostly transported via the plant root through solute movement, mass flow and diffusion. Plant uptake of mobile ions present in the soil solution is largely determined by the total quantity of the ions in the soil solution, but in the case of strongly adsorbed ions, absorption seems to depend more upon the amount and surface area of roots produced (Wild, 1988). Translocation and transfer factors determined for both Cd and Zn (chapter 4) showed a high risk of metal movement from the soil to the root and eventually to the shoot. Several authors (Gray et al., 1999; McBride et al., 2003; Wang et al., 2006) underscored the importance of soil metal fraction to be used in assessing metal transfer from soil to crop. Our data also showed that Zn is more easily translocated from soil to crop than Cd in Kano urban soils.

Heavy metal movement and exposure to contaminants uses the solution phase as its gateway which requires the metal to be in the soluble phase or associated with mobile particulates that are in equilibrium with the pore water. The soil pore water is directly or indirectly influenced by soil properties like organic matter (OM), cation exchange capacity (CEC) and soil reaction. These soil characteristics exert a profound influence on the sorptive capacity of the soil (Bradl, 2004; Sipos et al., 2008). In this study, however, when metal fractions were related to soil properties, soil organic carbon was negatively correlated with the mobile fraction of Zn. This observation is contrary to the study of Karpukhin and Ladonin (2008) who observed an abrupt decrease in the capacity of a soil to adsorb heavy metals following removal of organic matter from the soil. Therefore, movement, sorption/desorption of heavy metals is essentially related to physicochemical forms of the metals in soil and prevailing soil properties, because varying forms of metals have different potentials for mobilisation by inorganic or organic ligands in the soil solution (Li and Shuman, 1996). At pH above 7, solubility of OM increases which inherently increase the solubility of OM-bound HM (You et al., 1999). Soil total P and CEC were negatively correlated with Cd fractions implying that these soil properties might decrease Cd mobility in this soil. This may be as a result of saturating the exchange site of the soil with this particular metal originating from soil contamination (Karpukhin and Ladonin, 2008).

The first three fractions which we referred to as “labile” due to their mobility under slightly changing soil conditions like pH dominated the fractions of Zn and Cd in this study indicating anthropogenic input of Zn and Cd. The dominance of soluble and available fractions of Cd and Zn in the sandy soil of Kano underscores the importance of anthropogenic HM input.

6.3. Health and risk assessment from heavy metal pollution

Vegetables produced within the city make up a major part of vegetables consumed in Kano. Accumulation of HMs in the urban soils used for the production of these vegetables may have elevated concentration of HMs due to anthropogenic activities like wastewater irrigation. Soil-to-plant transfer of heavy metals therefore remain the major pathway of human exposure to soil contamination (Cui et al., 2005). Renal dysfunction has been linked with Cd contamination (Ryan et al., 1982; Cai et al., 1990; Young, 1997; Watanabe et al., 2000). Lettuce and radish have been observed to be more responsible than other vegetable for transfer of HMs to human (Intawongse and Dean, 2006). In our present study however, vegetables were contaminated with HM but health risk assessment revealed no potential health hazard through vegetable consumption.

In this study, health risk assessment was based on (a) soil-root-shoot transfer of metal (b) average daily dose of heavy metal intake and (c) target hazard qoutient. Even though Zn transfer from soil to root was higher than Cd, there was higher translocation of Cd from the root to the shoot in the studied crops, which is consistent with the observations of Kumar et al. (2009). Lettuce was observed to have the highest accumulation of Cd in the shoot which was attributed to its high biomass when compared with other crops.

Data obtained from the average daily dose and target hazard qoutients indicated that farmers and vegetable consumers are currently not at risk of heavy metal intake beyond permissible levels and soil/plant uptake was found to be the major exposure route.

6.4. A critical review of the methodological approaches

Assesment of HM pollution and environmental quality demands intensive study of the distribution and dynamics of metal pollutants in soil. Distribution of HM in soils from Kano (chapter 2) followed similar pattern of results from other studies in similar locations (Awode et al., 2008; Agbenin et al., 2009). Lack of literature on HM contents of agricultural soils from Bobo-Dioulasso and Sikasso makes comparison difficult. Similarly, HM balance based on the input-output approach (Mercuri et al., 2006; Khai et al., 2007) followed trends of observations in other studies (Azimi et al., 2004; Khai et al., 2007). In the present study, quantitative monitoring of input and output was made through proper and close monitoring of farmers' management strategies and collection of natural atmospheric inputs (rainfall and dust). As previously alluded to, a time frame of two years seems to be too short for adequate quantification of changes in HM fluxes in heavily irrigated urban gardens. Similar research should be undertaken to assess HM balance in Kano urban soils under cereal production that are characterized by high mineral fertilizer and manure inputs. There also exist uncertainties related to analytical detection of Cd, which was present at very low concentrations in all the parameters involved in balance calculation. Graphite furnace atomic adsorption spectrophotometer should be used for Cd determination in soil and biological samples. This was however not within our reach during the field and laboratory phase of this research in Nigeria.

The main objective of sequential extraction of HMs is to convert metals bound in the solid phase into soluble and available forms using different extractants (Tokalioglu et al., 2000). Different exctraction procedures proposed over the years by researchers involve partitioning of HM into 3 to 8 fractions. These extraction procedures are based on different sequences of extracting reagents at different operational conditions like pH, temperature, agitation and time of extraction. The result of our metal fractionation and mobility using the fractionation scheme of Zeien and Brümmer (1989) corroborated several other fractionation studies (Kabala and Singh, 2001; Kashem et al., 2007) that used a different fractionation procedure. It seems however advisable to have a comparison of different extraction techniques in our garden soil for a better understanding of the extraction protocol that gives reliable concentrations of individual metal fractions in the soil. Also, water soluble and plant available fraction of HM should have been compared using different chemical extractants (1M NH_4NO_3, 0.1M $CaCl_2$, DTPA) commonly used in determining availability of HMs in soil and plant to know which one is the most suitable for the local urban garden soils with their likely high organic matter content in the surface layer.

Risk assessment followed reliable and accepted methodology by studying intake of HM through vegetable consumption and soil ingestion. However, in the present study risk associated with consumption of wastewater irrigated vegetables may have been underestimated. A critical assessment of health hazard emanating from HM pollution should include determination of HM in biological human samples like urine, blood serum etc. Moreover, the risks estimated in our study were all qualitative as no actual risk or hazard quotient determination. All the biometric data (body weight, exposure duration and frequency, etc) used were mainly USEPA based data from US. This information is officially not available for Nigerian farmers. Contamination with faecal coliforms, and mesophilic aerobic microorganisms, which is also an indication of health risk among vegetable producers and consumers, was not measured in our study. Microbial contamination of vegetables produced under wastewater irrigation has been reported for different West Africa cities (Drechsel et al., 2000; Amoah et al., 2005; Diogo et al., 2010).

6.5. Conclusions and recommendations

Despite the role that urban agriculture plays in combating food insecurity and its contribution to the household economy and livelihood strategies of urban farmers, its location-specific risks should be properly analysed and addressed. This study allows to conclude that:

- in Kano long-term wastewater irrigation has led to the accumulation of potentially toxic heavy metals in the soil and further uptake by crops. This is evident from the positive Zn and Cd budgets calculated

- Wastewater irrigation is the major source of heavy metal pollution in Kano's urban gardens
- Heavy metal accumulation in the soil is mainly of anthropogenic rather than natural origin
- Vegetable farmers as well as consumers in Kano are at a risk of heavy metal ingestion
- Urban agriculture in Kano (Nigeria) showed more contamination than Sikasso (Mali) and Bobo-Dioulasso (Burkina Faso). This is attributted to higher industrialization and urbanization in Kano that generates more solid and liquid wastes than in Bobo-Dioulasso and Sikasso
- There is a potential risk of contamination of the underground water reserve through leaching of heavy metals. Groundwater contamination study should be done to ascertain this

The following recommendations can be given to improve the safety of vegetable production in Kano, Nigeria:

- Treatment of municipal and industrial wastewater before dicharging to the city streams and rivers. Industrial wastewater can be treated using activation sludge system or trickling filter. HMs in particular can be precipitated from sludge or wastewater by changing the pH of the whole compound containing the waste
- Provision of alternative good quality irrigation water for the year round vegetable production. This involves capital investment on the side of the government through provision of irrigation scheme in the form of dam and acquifers. This may however, requires payment from the farmers
- Government legislation on discharge of untreated wastewater and sludge especially from industries. The local municipal authority should design a threshold toxic level of contaminants allowed to be discharged into city streams and rivers. A levy should be imposed on violators through frequent supervision
- Increasing awareness among farmers, consumers and all stakeholders involved on the risk of heavy metal pollution. This can

lead to pressure on the local authority to legislate against indiscriminate waste disposal and provision of alternative irrigation water sources

- Options to optimize resource use efficiency while reducing human and environmental risk should be designed. This can be achieved through provision of infrastructures in the rural areas to reduce the rate of rural-urban migration and hence reduced pressure on the limited urban resources
- The government should urgently enforce safe threshold limits for heavy metals in agricultural soils and irrigation waters through sound scientific research
- Extensive research is encouraged to link the prevalence of cardiovascular and cancer related diseases observed in the Aminu Kano Teaching Hospital, Kano, with heavy metal ingestion

6.6. References

Agbenin, J.O. and Atin, A.M. 2003. Copper sorption characteristics and activity in a savanna acid soil from Nigeria. Water, Air, and Soil Pollution 150: 43-58.

Agbenin, J.O., Danko, M and Welp, M. G. 2009. Soil and vegetable compositional relationships of eight potentially toxic metals in urban garden fields from northern Nigeria. Journal of the Science of Food and Agriculture 89: 49-54.

Amoah, P., Drechsel, P. and Abaidoo, R.C. 2005. Irrigated urban vegetable production in Ghana: sources of pathogen contamination and health risk examination. Irrigation and Drainage 54: 49 – 61.

Awode. U.A., Uzairu, A., Balarabe, M.L., Harrisson, G.F.S and Okunola, O.J. 2008. Assessment of peppers and soils for some heavy metals from irrigated farmlands on the Bank of river Challawa, Northern Nigeria. Pakistan Journal of Nutrition 2: 244-248

Azimi, S., Cambier, P., Lecuyer, I. and Thevenot, D. 2004. Heavy metal determination in atmospheric deposition and other fluxes in northern France agrosystems. Water Air and Soil Pollution 157: 295-313

Bassanino, M., Grignani, C., Sacco, D. and Allisiardi, E. 2007. Nitrogen balance at the crop and farm-gate scale in livestock farms in Italy. Agriculture Ecosystem Environment 122: 282-294

Binns, J.A., Maconachie, R.A. and Tanko, A.I. 2003. Water, land and health in urban and peri-urban food production: the case of Kano, Nigeria. Land Degradation and Development 14: 413-444.

Bradl, H.B. 2004. Adsorption of heavy metal ions on soils and soils constituents. Journal of Colloid Interface Science 277: 1–18.

Brummer, G. and Herms, U. 1983. Influence of soil reaction and organic matter on the solubility of heavy metals in soils. In: Ulrich, B. and Pankrath, J. (Eds), 1983. Effects of accumulation of air pollutants in forest ecosystems. Reidel Publishing Company. Dordrecht. pp. 233-243.

Cai, S., Yue, L., Hu, Z.N., Zhong, X.Z., Ye, Z.L., Xu, H.D., Liu Y.R., Ji, R., Zhang, W. and Zhang, F.G. 1990. Cadmium exposure and health effects among residents in an irrigation area with ore dressing wastewater. The Science of the Total Environment 90: 67-73

Christensen, T.H. 1984. Cadmium soil sorption at low concentrations: I. Effect of time, cadmium load, pH, and calcium. Water, Air, and Soil Pollution 21: 105-114.

Cui, Y., Zhu, Y. G., Zhai, R., Huang, Y., Qiu, Y. and Liang, J. 2005. Exposure to metal mixtures and human health impacts in a contaminated area in Nanning, China. Environment International 31: 784–790.

Dijkstra, J., Meeussen, J. and Comans, R. 2004. Leaching of heavy metals from contaminated soils: an experimental and modeling study. Environmental Science and Technology 38: 4390–4395.

Diogo, R.V.C., Buerkert, A. and Schlecht, E. 2010. Horizontal nutrient fluxes and food safety in urban and peri-urban vegetable and millet cultivation of Niamey, Niger. Nutrient Cycling Agroecosystems 87:81–102.

Drechsel, P., Abaidoo, R.C., Amoah, P. and Cofie, O.O. 2000. Increasing use of poultry manure in and around Kumasi, Ghana: is farmers' race consumers' fate? Urban Agricultural Magazine 2: 25 – 27.

Fest, E.P.M.J., Temminghoff, E.J.M. and Comans, R.N.J. 2008. Partitioning of organic matter and heavy metals in a sandy soil: Effect of extracting solution, solid to liquid ratio and pH. Geoderma 146: 66-74.

Fuller, W.H. 1977. Movement of selected metals, asbestos, and cyanide in soil: Applications to waste disposal problems. EPA-600/2-77-020. Prepared for Municipal Environmental Research Lab, Cincinnati, OH.

Graefe, S., Schlecht, E. and Buerkert, A. 2008. Opportunities and challenges of urban and peri-urban agriculture in Niamey. Outlook on Agriculture 37: 47–56.

Gray, C.W., McLaren, R.G., Roberts, A.H.C., and Condron, L.M. 1999. The effect of long-time phosphatic fertilizer applications on the amounts and forms of cadmium in soils under pasture in New Zealand. Nutrient Cycling Agroecosystems 54: 267-277.

Hayes, K.F. and Traina, S.J. 1998. Metal ion speciation and its significance in ecosystem health. In: Huang, P.M., Adriano, D.C., Logan, T.J. and Checkai, R.T. (Eds), 1998. Soil chemistry and ecosystem health. Soil Science Society of America special publication No. 52. SSSA, Madison, WI, USA.

Icopini, G.A., and Long, D.T. 2002. Speciation of aqueous chromium by use of solid phase extractions in the field: Environmental Science and Technology 36: 2994-2999.

Intawongse, M. and Dean, J.R. 2006. Uptake of heavy metals by vegetable plants grown on contaminated soil and their bioavailability in the human gastrointestinal tract. Food Additives and Contaminants 23: 36-48.

Kabata-Pendias, A. and Pendias, H. 1992. Trace Elements in Soils and Plants, 2nd ed. CRC Press, Boca Raton. 365 p.

Kabala, C. and Singh, B.R. 2001. Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter. Journal of Environmental Quality 30: 485–492.

Karpukhin, M. M. and Ladonin, D. V. 2008. Effect of Soil Components on the Adsorption of Heavy Metals under Technogenic Contamination. Eurasian Soil Science 41: 1228–1237.

Kashem, M. A., Singh, B.R. and Kawai, S. 2007. Mobility and distribution of cadmium, nickel and zinc in contaminated soil profiles from Bangladesh. Nutrient Cycling Agroecosystems 77: 187-198.

Khai, N.M., Ha, P.Q., and Öborn, I. 2007. Nutrient flows in small-scale peri-urban vegetable farming systems in South Asia-A case study in Hanoi. Agriculture Ecosystem Environment 122: 192-202.

Kumar, N., Soni, H., Kumar, R.N. and Bhatt, I. 2009. Hyperaccumulation and mobility of heavy metals in vegetable crops in India. The Journal of Agriculture and Environment 10:29–38.

Li, Z. and Shuman, L.M. 1996. Heavy Metals movement in metal contaminated soil profiles. Soil Science 161: 656 – 666.

Mashi, S.A. and Alhassan, M.M. 2007. Effects of wastewater discharge on heavy metals pollution in Fadama soils in Kano city, Nigeria. Biomedical and Environmental Science 20: 70-77.

McBride, M.B., Nibarger, E.A., Richards, B.K. and Steenhuis, T. 2003 Trace metal accumulation by red clover grown on sewage sludge-amended soils and correlation to Mehlich 3 and calcium chloride-extractable metals. Soil Science 168: 29-38.

McBride, M.B. 1994. Environmental chemistry of soils. Oxford University Press, New York.

Mercuri, A.M., Duggin, J.A., Daniel, H., Lockwood, P.V. and Grant, C.D. 2006. Estimating the unknown components of nutrient mass balances for forestry plantations in mine rehabilitation, upper Hunter valley, New South Wales, Australia. Environmental Management 34: 496-512.

Naidu, R., Kookana, R.S., Sumner, M.E., Harter, R.D. and Tiller, K.G. 1997. Cadmium sorption and transport in variable charged soils: A review. Journal of Environmental Quality 26: 602- 617.

Predotova, M., Schlecht, E. and Buerkert, A. 2010. Nitrogen and carbon losses from dung storage in urban gardens of Niamey, Niger. Nutrient Cycling Agroecosystems 87:103–114.

Ryan, J.A., Pahren, H.R. and Lucas, J.B. 1982. Controlling cadmium in the human food chain a review and rationale based on health effects. Environmental Research 28: 251-302

Sipos, P., Németh, T., Kis, V. and Mohai, I. 2008. Sorption of copper, zinc and lead on soil mineral phases. Geoderma 73: 461–469.

Tokalioglu, S., Kartal, S. and Elci, L. 2000. Determination of heavy metals and their speciation in lake sediments by flame atomic absorption spectrometry after a four stage sequential extraction procedure. Analytica Chimica Acta 413: 33-40.

Wang, G., Su, M.Y., Chen, Y.H., Lin, F.F., Luo, D. and Gao, S.F. 2006 Transfer characteristics of cadmium and lead from soil to the edible parts of six vegetable species in southeastern China. Environmental Pollution 144:127-135.

Watanabe, T, Zhang, Z.W., Qu, J.B., Gao, W.P., Jian, Z.K., Shimbo, S. Nakatsuka, H, Matsuda-Inoguchi, N., Higashikawa, K. and Ikeda, M. 2000. Background lead and cadmium exposure of adult women in Xian City and two farming villages in Shaanxi Province, China. The Science of the Total Environment 247: 1-13.

Wild, A. 1988. Russell's soil condition and plant growth.11th edition. Longman, U. K.

You, S.J., Yin, Y.J. and Allen, H.E. 1999. Partitioning of organic matter in soils: effects of pH and water/soil ratio. Science of the Total Environment 227: 155-160.

Young, R.A. 1997. Toxicity profiles: Summary for Cadmium, Risk Assessment Information System. University of Tennessee. (http://rais.ornl.gov/tox/profiles/cadmium.html). Assessed: 28 May, 2010

Zeien, H. and Brümmer, G.W. 1989. Chemische Extraktion zur Bestimmung von Schwermetallbindungsformen in Böden. (in German) Mitteilgn. Dtsch. Bodenkundl. Gesellsch 59:505-510.

Curriculum vitae

Name:	Nafiu Abdu
Date and Place of Birth:	17th November, 1974; Zaria, Nigeria
Nationality:	Nigerian

Education and Degrees:

1986-1991	Kufena College, Zaria, Nigeria: Senior Secondary School Certificate
1992-1993	School of General and Remedial Studies, ABU, Zaria, Nigeria
1994-2000	Ahmadu Bello University, Zaria, Nigeria: Bachelor of Agriculture
2003-2006	Ahmadu Bello University, Zaria, Nigeria: Master of Science (MSc Soil Science)
2007-2010	PhD candidate, Department of Organic Plant Production and Agroecosystems Research in the Tropics and Subtropics, University of Kassel, Germany

Awards:

1986	Best Year Group student in Fine Arts, Kufena College, Zaria, Nigeria
1995-2000	Kaduna State of Nigeria Scholarship for Bachelor Degree
2003	Federal Government of Nigeria Postgraduate Scholarship

List of publications

Peer reveiwed journals:

N. Abdu, A. Abdulkadir and J.B. Jibril. 2009. Challenges and opportunities for solid waste management in urban interface of Kano, Nigeria. Waste Management 29:2603-2605.

Abdu Nafiu. 2009. Effects of soil properties on the kinetics of desorption of phosphate from Alfisols by anion exchange resins. Journal of Plant Nutrition and Soil Science 172:101-107

Abdu Nafiu, John O. Agbenin and Bashiru A. Raji. 2008. Kinetic desorption of native phosphorus from soils of varying lithogenic origins in the Nigerian savanna. Soil Science 173:837-844.

N. Abdu, A.A. Yusuf, A. Abdulkadir, U.L. Arunah, V.O. Chude and S.G. Pam. 2007. Zinc Soil Test Calibration based on 0.1N HCl Extractable Zinc and Cation Exchange Capacity from Upland Soils of Northern Nigeria. Journal of Agronomy 6:179-182.

Yusuf, A.A., **Abdu N**., Abdullahi, A.A. and Yusuf, A.A. 2007. Relationship between availability indices and plant uptake of zinc from upland soils of northern Nigeria. Biological and Environmental Science Journal for the Tropics 4:152-157.

N. Abdu. 2006. Soil-phosphorus extraction methodologies: A review. African Journal of Agricultural Research 1:159-161.

Yusuf, A.A., **N. Abdu**, V.O. Chude, H. A. Yusuf and S.G. Pam. 2005. Response of maize (*Zea mays*) to zinc fertilization in relation to Mehlich I extractable zinc. Nigerian Journal of Soil Research 6:32–41.

Papers submitted for publication in peer-reviewed journals

Abdu, N., Abdulkadir, A., Agbenin, J.O. and Buerkert, A. 2010a. Vertical distribution of heavy metals in wastewater-irrigated vegetables garden soils of three West African cities. Nutrient Cycling in Agroecosystems.

Abdu, N., Agbenin, J.O. and Buerkert, A. 2010b. Phytoavailability, human risk assessment and transfer characteristics of cadmium and zinc contamination from urban gardens in Kano, Nigeria. Journal of the Science of Food and Agriculture.

Abdu, N., Agbenin, J.O. and Buerkert, A. 2010c. Fractionation and mobility of Cd and Zn in urban gardens of Kano, Northern Nigeria. Environmental Monitoring and Assessment.

Abdu, N., Agbenin, J.O. and Buerkert, A. 2010d. Geochemical assessment, distribution and dynamics of trace elements in contaminated urban soil under long-term wastewater irrigation in Kano, northern Nigeria. Journal of African Earth Science.

Abdulkadir Aisha, **Abdu Nafiu** and Ismail Jibril. 2010. Application of Kozeny-Carman equation to estimate saturated hydraulic conductivity of savanna soils of northern Nigeria. Arid Land Research and Management.

Official Conference Proceedings:

N. Abdu and M. Muazu 2007. Trace metals accumulation in urban soil: Effects of municipal waste fertilization. In: Olufajo et al. (eds) 2007. Reviving Agriculture for Sustainable National Growth and Stable Democracy. Proceedings of the 41st Annual Conference of the Agricultural Society of Nigeria held at the Institute for Agricultural Research, Samaru, at Ahmadu Bello University, Zaria, Nigeria. 22th–26th October, 2007.

N. Abdu and E.O. Uyovbisere 2007. Application of mechanistic rate equations to the description of ion desorption in soils. In: Uyovbisere et al. (eds) 2007. Soil and Water Management for Poverty Alleviation and Sustainable Environment. Proceedings of the 31st Annual Conference of the Soil Science Society of Nigeria held at Ahmadu Bello University, Zaria, Nigeria. 13th-17th November, 2006.

N. Abdu, I. Ibrahim and A.A. Abdullahi 2006. Effects of soil properties on boron sorption in a savanna soil. In: Idoga et al. (eds) 2006. Management of Fadama soils for environmental quality, food security and poverty alleviation in Nigeria. Proceedings of the 30th Annual Conference of the Soil Science

Society of Nigeria held at University of Agriculture, Makurdi, Nigeria. 5th-9th December, 2005.

Abstracts

Abdu N., Agbenin, J.O and Buerkert, A. 2009. Heavy metals deposit, transfer and balances in urban gardens in Kano, Nigeria. Paper presented at the Grantees meeting of the Volkswagen Foundation (Resources, their Dynamics, and Sustainability-Capacity-Development in Comparative and Integrated Approaches) Dar Es Salaam, 5th-8th January 2009.

N. Abdu and J.O. Agbenin. 2006. Formulation of a first order kinetic equation for describing desorption of added phosphorus in some savanna soils. Paper presentation at the 31st Annual Conference of the Soil Science Society of Nigeria held at Ahmadu Bello University, Zaria, Nigeria. 13th-17th November, 2006.

N. Abdu. 2006. On the Applicability of mechanistic rate equations in describing ion desorption from soils and related environment. Paper presentation at the 31st Annual Conference of the Soil Science Society of Nigeria held at Ahmadu Bello University, Zaria, Nigeria. 13th-17th November, 2006.

Odion, E.C., U.L. Arunah, **N. Abdu,** and U.U. Emeghara. 2006. Soil Degradation, Better Soil Management in Maintaining Food Production and Sustainability. Paper presented at 2nd National Conference on Organic Agriculture, University of Ibadan. 27th November–1st December, 2006.

N. Abdu and J.O. Agbenin. 2004. Charge properties of Clays from the savanna. 29th Annual Conference of Soil Science Society of Nigeria, University of Agriculture, Abeokuta, 6th–10th December, 2004.

Urban agriculture (UA) is often associated with industrial and municipal wastewater reuse, intensive use of pesticide, organic and inorganic fertilizers leading to the accumulation of potentially toxic heavy metals and pathogens in soil. This research was carried out in three West African cities of Kano (Nigeria), Bobo-Dioulasso (Burkina Faso) and Sikasso (Mali). It investigated the geochemical distribution, dynamics, movement and budget of heavy metals in urban garden soils of Kano. It also assessed the extent of the food chain contamination by determining the forms of heavy metals in soils and edible portions of vegetables and establishing a relationship between soil concentration and plant uptake. The potential health risk to producers and consumers of UA produced vegetables was also evaluated. Results from Kano were compared with comparable datasets from the two West African cities of Bobo-Dioulasso (Burkina Faso) and Sikasso (Mali).

ISBN 978-3-89958-956-6