

**Trace Metals Mobility in Soils and Availability to Plants from a Long-Term
Biosolids Amended Soil**

By

Beshr F. Sukkariyah

Dissertation submitted to the faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY
IN
CROP AND SOIL ENVIRONMENTAL SCIENCES

Gregory K. Evanylo, Co-Chair

Lucian W. Zelazny, Co-Chair

Rufus L. Chaney

Matthew J. Eick

Raymond B. Reneau, Jr.

December, 2003
Blacksburg, Virginia

Keywords: Biosolids, Trace metals, Availability, Mobility,
Cadmium, Copper, Nickel, Zinc, Uptake, Recovery.

Copyright © 2003, Beshr F. Sukkariyah

Trace Metals Mobility in Soils and Availability to Plants from a Long-Term Biosolids Amended Soil

Beshr F. Sukkariyah

ABSTRACT

The long-term mobility and availability of trace metals has been cited as a potential hazard by critics of EPA 503 rule governing the land application of biosolids. The purpose of this research was to investigate the long-term effects of biosolids application on trace metals distribution and mobility. A single application of aerobically digested biosolids was applied to 1.5 x 2.3 m confined plots of a Davidson clay loam (clayey, kaolinitic, thermic, Rhodic Paleudult) in 1984 at 0, 42, 84, 126, 168, and 210 Mg/ha. The highest biosolids application supplied 4.5, 760, 43, and 620 kg ha⁻¹ of Cd, Cu, Ni, and Zn, respectively. Radish (*Raphanus sativus* L.), lettuce (*Lactuca sativa* Var longifolia) and barley (*Hordeum vulgare*) were planted at the site. Soils were sampled to a depth of 0.9 m and sectioned into 5 cm increments after separating the Ap horizon. Total (EPA 3050B), available (Mehlich-I), sequential extraction, and dispersible clay analyses were performed on samples from the control, 126 Mg/ha and 210 Mg/ha treatments. Extractable (0.005 DTPA, 0.01 M CaCl₂, and Mehlich-1) Cd, Cu, Ni, and Zn were measured on 15 cm-depth samples from each plot. Simple linear regression between plant metal concentration and biosolids-added trace metals were computed to determine uptake coefficients (UC) of crops for each metal as outlined by USEPA Part 503 Rule. Results indicated that more than 80% of the applied Cu and Zn are still found in the topsoil where biosolids were incorporated with slight enrichment down to 0.3 m. Biosolids application increased the concentration of trace metals in all the extracted fractions, with a large proportion of Zn and Cd present in the available forms. The major portion of Cu, Zn and Ni was associated with the metal-oxides fraction. Biosolids treatments had no significant effect on the yield of the crops. Plant uptake of trace metals differed among crops. Plant tissue metal concentrations increased with biosolids rate but were within the normal range for these crops. Trace metals concentration in plants generally correlated well with their concentrations extracted with 0.005 M DTPA, 0.01 M CaCl₂ and Mehlich-1. Mehlich-1 gave the highest correlation coefficients for Cu and Zn and, therefore, was the most reliable in predicting their availability and uptake by the crops grown. Availability of trace metals as measured by Mehlich-I, DTPA, and CaCl₂ extraction were higher in amended plots as compared to the control and increased linearly in response to biosolids addition. Metal concentration in the plants exhibited a plateau response in most cases. Several linear increases were observed in some cases in 2003 when the soil pH decreased below 5.5. The uptake coefficients values generated for the different crops were in agreement with the values set by the Part 503 Rule.

Dedication

I dedicate this work to my family for their continuous support, love, and understanding.

Acknowledgements

I would like to extend my sincere appreciation to my co-advisors Dr. Lucian Zelazny and Dr. Gregory Evanylo for their supervision, assistance, patience and encouragement throughout my graduate study. They have been great mentors and good friends.

I would like to thank my committee members Dr. Matthew Eick, Dr. Raymond Reneau Jr., and Dr. Rufus Chaney for their scientific inputs and positive attitude. Their advice and patience are greatly appreciated. It has been a pleasure working with them.

My deepest appreciation goes out to Hubert Walker, Caroline Sherony, John Spargho, Chandra Bowden, and Justin Evanylo for their assistance with lab and field works.

I extend my gratitude for the staff of the NPAREC, Dave Starner, Steve Gulick, Alvin Hood, Denton Dixon, Wes Atkinson for their tremendous help with work.

Special thanks to Dr Ozzie Abaye, Dr Gaber Hassan , Meriem El hadj, and Jarrod Miller for their support and positive encouragement throughout this process. I will always cherish their friendship.

I am grateful to the faculty, staff, and graduate students of the Department of Crop and Soil Environmental Sciences for their support at all times. I especially want to recognize, Todd Luxton, Jafar Mamadov, Mindy Waltham, Pat Donovan, W.T. Price, and Kelly Smith. I have truly enjoyed working with you. Thanks for your help and support.

This research was funded by the Metropolitan Washington Council of Governance. Their financial support is greatly appreciated.

My thanks go out to my friends Amer Fayad, Zahi Nakad, Munir and Nada Melki, Eid and Katia Rustum, Serah and Tim Selmon and my housemates Barbar Akle, Clarissa Dominguez, Ibrahim Geha and Samer Katisha that I have been very fortunate to share these past three years with them. They helped make my stay a very enjoyable experience. Thank you for all the good times.

TABLE OF CONTENTS

| | |
|---|-----|
| Title..... | i |
| DISSERTATION ABSTRACT..... | ii |
| AUTHOR S ACKNOWLEDGEMENTS..... | iv |
| TABLE OF CONTENTS..... | v |
| LIST OF TABLES..... | vii |
| LIST OF FIGURES..... | ix |
| CHAPTER ONE..... | 1 |
| INTRODUCTION..... | 1 |
| OBJECTIVES..... | 6 |
| REFERENCES..... | 7 |
| CHAPTER 2 LITTERARTURE REVIEW..... | 8 |
| Introduction..... | 8 |
| Soil factors affecting metal availability..... | 8 |
| Trace metal binding capacity of biosolids..... | 9 |
| Trace element immobilization..... | 11 |
| Potential for colloids to facilitate metal leaching..... | 12 |
| Long-term availability of biosolids-added trace metals..... | 15 |
| Plant uptake..... | 16 |
| Plateau vs. linear uptake response..... | 17 |
| Use of chemical extractants to assess metal availability..... | 19 |
| Sequential extraction..... | 22 |
| LITERATURE CITED..... | 24 |
| CHAPTER THREE. Recovery and Distribution of Biosolids-Derived Trace metals in a Davidson Clay Loam Soil..... | 37 |
| ABSTRACT..... | 37 |
| INTRODUCTION..... | 37 |
| MATERIALS AND METHODS..... | 40 |
| Background..... | 40 |
| Plot Management..... | 42 |
| Soil Sampling and Processing..... | 42 |
| Metal Analysis..... | 42 |
| Fractionation..... | 43 |
| Dispersible Clay..... | 43 |

| | |
|---|-----|
| Mass Balance..... | 44 |
| Statistical Analysis..... | 45 |
| RESULTS AND DISCUSSION..... | 45 |
| Vertical translocation of trace metals..... | 45 |
| Mehlich-I..... | 45 |
| EPA-3050B..... | 48 |
| Dispersible Clay..... | 52 |
| Fractionation..... | 53 |
| Metal Recovery..... | 57 |
| CONCLUSIONS..... | 58 |
| REFERENCES..... | 60 |
| CHAPTER FOUR. Trace Metals Availability in a Biosolids-Amended Piedmont Soil 19 Years after Application..... | 66 |
| ABSTRACT..... | 66 |
| INTRODUCTION..... | 66 |
| MATERIALS AND METHODS..... | 69 |
| Field Plots and Treatments..... | 69 |
| Cropping System..... | 71 |
| Sampling and Sample Preparation..... | 72 |
| Plant Analysis..... | 72 |
| Soil Analysis..... | 73 |
| Statistical Analysis..... | 73 |
| RESULTS AND DISCUSSION..... | 74 |
| Crop Yield..... | 76 |
| Metal Uptake..... | 76 |
| Soil Test..... | 80 |
| Plant Uptake Coefficients..... | 86 |
| Uptake Curve..... | 87 |
| CONCLUSIONS..... | 95 |
| REFERENCES..... | 97 |
| CHAPTER FIVE..... | 102 |
| DISSERTATION CONCLUSIONS..... | 102 |
| REFERENCES..... | 104 |

LIST OF TABLES

| | | |
|------------|--|----|
| Table 1.1 | Exposure pathways used in USEPA Part 503..... | 3 |
| Table 1.2 | The limiting pathways according to the USEPA Part 503 risk assessment..... | 4 |
| Table 1.3 | Pollutant limits in USEPA Part 503 Regulations..... | 5 |
| Table 3.1 | Chemical and physical properties of the Ap horizon of the Davidson clay loam used for the biosolids study in 1984 at the NPAREC..... | 40 |
| Table 3.2 | Properties of the aerobically digested sewage sludge (ADSS) and Part 503 Ceiling Concentration Limit (CCL) and Pollutant Concentration Limit (PCL) standards for land applied Biosolids... | 41 |
| Table 3.3 | Quantity of biosolids, trace metals and total N and P applied at the NPAREC study site..... | 41 |
| Table 3.4 | Distribution of dispersible clay content by depth (g kg^{-1})..... | 52 |
| Table 3.5 | Total metal concentration of dispersible clay fraction in mg kg^{-1} as determined by EPA-3050B..... | 52 |
| Table 3.6 | Water-soluble concentrations (mg kg^{-1}) of Cu and Zn in the top 30 cm of the soil profile as influenced by biosolids application..... | 53 |
| Table 3.7a | Distribution of Cu and Zn among exchangeable, specifically adsorbed, metal oxide, and organic fractions as determined by sequential extraction..... | 54 |
| Table 3.7b | Distribution of Cd and Ni among exchangeable, specifically adsorbed, metal oxide, and organic fractions as determined by sequential extraction..... | 56 |
| Table 3.8a | Net plant metal removal for the 1985-2003 time period..... | 57 |
| Table 3.8b | Mass balance of Cu and Zn detectable at selected soil depth 17 years after biosolids application..... | 58 |
| Table 4.1 | Chemical and physical properties of the Ap horizon of the Davidson clay Loam used for the biosolids study at the NPAREC..... | 69 |
| Table 4.2 | Properties of the aerobically digested sewage sludge (ADSS) and Part 503 Ceiling Concentration Limit (CCL) and pollutant Concentration Limit (PCL) standards for land applied Biosolids... | 71 |
| Table 4.3 | Quantity of biosolids, trace metals and total N and P applied at the NPAREC study site..... | 71 |
| Table 4.4 | Soil pH (averages of 4 replicates) in the biosolids-amended soil experiment from 2001 to 2003..... | 72 |
| Table 4.5 | Long-Term effect of biosolids application on DTPA extractable Cu and Zn from soil..... | 74 |
| Table 4.6 | Effect of biosolids treatment on dry weight of romaine lettuce and radish..... | 76 |

| | | |
|------------|--|----|
| Table 4.7 | Trace metals concentrations in the dry matters of lettuce..... | 77 |
| Table 4.8 | Trace metals concentrations in the dry matters of radish globes.... | 78 |
| Table 4.9 | Trace metals concentrations in the dry matters of radish tops..... | 79 |
| Table 4.10 | Critical concentrations of trace metals in plant tissues..... | 79 |
| Table 4.11 | Pearson correlation coefficients for Cu and Zn uptake by all crops examined and 0.01 M CaCl ₂ , DTPA and Mehlich-1 extractable soil trace metals..... | 85 |
| Table 4.12 | Uptake coefficients of the different trace metals in lettuce and radish tops and globes..... | 86 |

LIST OF FIGURES

| | | |
|-----------|--|----|
| Fig.3.1a. | Distribution of Mehlich-1 extractable Cu with soil depth 17 years after biosolids application..... | 46 |
| Fig.3.1b. | Distribution of Mehlich-1 extractable Zn with soil depth 17 years after biosolids application..... | 47 |
| Fig 3.2a. | Distribution of EPA-3050 extractable Cu with soil depth 17 years after biosolids application..... | 49 |
| Fig 3.2b. | Distribution of EPA-3050 extractable Zn with soil depth 17 years after biosolids application..... | 50 |
| Fig 3.2c. | Distribution of EPA-3050 extractable Ni with soil depth 17 years after biosolids application..... | 51 |
| Fig 3.3. | Percent Distribution of Cu and Zn among exchangeable, specifically adsorbed, metal oxides, and organic fractions as determined by sequential extraction..... | 55 |
| Fig. 4.1. | Long-term effect of biosolids application on soil organic matter... | 75 |
| Fig 4.2a. | Effects of biosolids application on the levels of Mehlich1-extractable Cu and Zn..... | 81 |
| Fig 4.2b. | Effects of biosolids application on the levels of DTPA and CaCl ₂ extractable Cu 17 years after application..... | 82 |
| Fig 4.2c. | Effects of biosolids application on the levels of DTPA and CaCl ₂ extractable Cd and Zn 17 years after application..... | 83 |
| Fig 4.2d. | Effects of biosolids application on the levels of DTPA extractable Ni 17 years after application..... | 84 |
| Fig 4.3a. | Zinc accumulation in lettuce as a function of biosolids applied Zn | 88 |
| Fig 3b. | Cadmium accumulation in lettuce as a function of biosolids applied Cd..... | 89 |
| Fig 4.3c. | Zinc accumulation in radish globes as a function of biosolids applied Zn..... | 89 |
| Fig 4.3d. | Zinc accumulation in radish tops as a function of biosolids applied Zn..... | 90 |
| Fig 4.3e. | Zinc accumulation in Barley as a function of biosolids applied Zn. | 90 |
| Fig 4.3f. | Copper accumulation in radish tops as a function of biosolids applied Cu..... | 91 |
| Fig 4.3g. | Copper accumulation in Barley as a function of biosolids applied Cu..... | 91 |
| Fig 4.3h. | Copper accumulation in radish globes as a function of biosolids applied Cu..... | 92 |
| Fig 4.3i. | Nickel accumulation in radish tops as a function of biosolids applied Ni..... | 92 |
| Fig 4.3j. | Nickel accumulation in lettuce as a function of biosolids applied Ni..... | 93 |
| Fig 4.3k. | Nickel accumulation in radish globes as a function of biosolids applied Ni..... | 93 |