EFFECT OF pH AND PARTICLE SIZE ON THE SOLUBILITY OF COPPER AND ZINC IN RIVER SEDIMENTS

JONG HUI LAN

DISSERTATION SUBMITTED AS PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF BACHELOR OF SCIENCE WITH HONOURS

INDUSTRIAL CHEMISTRY PROGRAMME
SCHOOL OF SCIENCE AND TECHNOLOGY
UNIVERSITI MALAYSIA SABAH

MAY, 2008

PUMS99:1

UNIVERSITI MALAYSIA SABAH

BORANG PENGESAHAN STATUS TESIS@

JUDUL: KESAN pH DAN SAIZ PARTIKEL KE ATAS KELARUTAN LOGAM KUPRUM (Cu) DAN ZINK (Zn) DALAM SEDIMEN SUNGAI.

IJAZAH: SARJANA MUDA SAINS DENGAN KEPUJIAN (KIMIA INDUSTRI)

SAYA JONG HUI LAN (HURUF BESAR) SESI PENGAJIAN: 2005/2006

mengaku membenarkan tesis (LPSM/Sarjana/Doktor Falsafah) ini disimpan di Perpustakaan Universiti Malaysia Sabah dengan syarat-syarat kegunaan seperti berikut:-

1. Tesis adalah hakmilik Universiti Malaysia Sabah.
2. Perpustakaan Universiti Malaysia Sabah dibenarkan membuat salinan untuk tujuan pengajian sahaja.
3. Perpustakaan dibenarkan membuat salinan tesis ini sebagai bahan pertukaran antara institutsi pengajian tinggi.
4. Sila tandakan (/)

[ ]	SULIT	(Mengandungi maklumat yang berdarjah keselamatan atau Kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA RASMI 1972)
[ ]	TERHAD	(Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan)
[/]	TIDAK TERHAD	

Disahkan Oleh

Jong Hui Lan

(TANDATANGAN PENULIS)

(TANDATANGAN PUSTAKAWAN)

Alamat Tetap: 327F, LRG 6A5, TMN PEONY, MATANG JAYA, 93050 KUCHING, SARAWAK.

PROF. MADYA DR. MARCUS JOPONY
Nama Penyelia

Tarikh: 15.05.08

Tarikh: 15.05.08

CATATAN:- *Potong yang tidak berkenaan.
**Jika tesis ini SULIT atau TERHAD, sila lampirkan surat daripada pihak berkuasa /organisasi berkenaan dengan menyatakan sekali sebab dan tempoh tesis ini perlu dikelaskan sebagai SULIT dan TERHAD.
@Tesis dimaksudkan sebagai tesis bagi Ijazah Doktor Falsafah dan Sarjana secara penyelidikan atau disertai bagi pengajian secara kerja kursus dan Laporan Projek Sarjana Muda (LPSM).

DECLARATION

I hereby declare that this literary work was resulted from my own effort except for statements and summaries that each of it had been stated its source.

12 May 2008

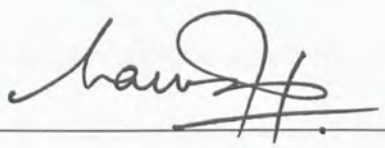
JONG HUI LAN

HS2005-4460

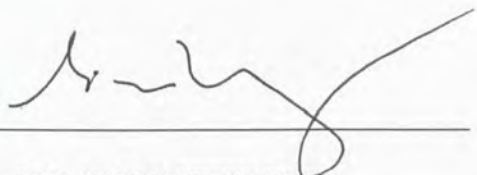
VERIFICATION

Name: Jong Hui Lan

Title: Effect of pH and Particle Size on the Solubility of Copper and Zinc in River Sediments

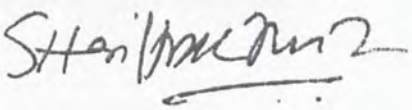


PROF. MADYA DR. MARCUS JOPONY



DR. HOW SIEW ENG

DR. NOUMIE SURUGAU



PROF. MADYA. DR SHARIFF A.K. OMANG

May, 2008

ACKNOWLEDGEMENT

First of all, I would like to take this opportunity to thank School of Science and Technology, University Malaysia Sabah for giving me chance and facilities to run this final year project. I would also like to express my sincere gratitude and appreciation towards my thesis supervisor Prof. Madya Dr. Marcus Jopony for his valuable advice, expert guidance, patience and continuous encouragement at various stages throughout the completion of dissertation. It has been an honour to have a supervisor who is willing to offer his constructive comments, experience and knowledge to the success of this desertation.

I would like to extend my heartiest appreciation to a great number of people who has contributed in my conquest of completing this dissertation. First, I would like to thank Miss Amelia Mavis Lee for her aids during my laboratory works. I am also greatly in debt for Mr. Yusri (lab assistant) and Mr. Rashidi (lab assistant) for their cooperation in operating the instrument. Their helps had simplified my lab work.

I would also like to thank all the SST's staffs and my fellow course mates for helping me throughout my work. Lastly, a grateful thanks to my parents for giving me full moral and financial supports throughout the completion of this dissertation.

ABSTRACT

This study was conducted to determine the effect of pH and particle size on the solubility of copper (Cu) and zinc (Zn) in river sediments. The sediment samples were collected from Bambangan River and Mentaki River in Ranau and divided into three fractions according to particle size: $X \leq 0.25$ mm, $0.5 \leq X \leq 0.25$ mm and $1.0 \leq X \leq 0.5$ mm. Each fraction was extracted using aqueous solutions with pH ranging from 2.0 to 6.0, and also digested in concentrated nitric acid. The concentrations of Cu and Zn extracts and digests were analyzed using atomic adsorption spectrophotometer (AAS). The results showed that the solubility of Cu was the highest compared to that of Zn, which was 34.45 μg/g obtained at pH 2 and particle size of ≤ 0.25 mm. The solubility of Cu and Zn increased as the pH and particle size decreased. The amount of soluble Cu and Zn were very low compared to the total concentration. The observed solubility of Cu and Zn in the sediment were under saturated with respect to the solid phases of CuO, $Cu(OH)_2$ and $CuCO_3$ and ZnO, $Zn(OH)_2$ and $ZnCO_3$.

KESAN pH DAN SAIZ PATIKEL KE ATAS KELARUTAN LOGAM KUPRUM (Cu) DAN ZINK (Zn) DALAM SEDIMEN SUNGAI

ABSTRAK

Kajian ini dijalankan untuk menentukan kesan pH dan saiz partikel ke atas keterlarutan logam kuprum (Cu)dan zink (Zn) dalam sedimen sungai. Sampel-sampel sedimen diperolehi dari sungai Bambangan dan sungai Mentaki dari Ranau dan dibahagikan kepada tiga fraksi mengikut saiz partikel, iaitu ≤ 0.25 *mm,* $0.5 \leq X \leq 0.25$ *mm and* $1.0 \leq X \leq 0.5$ *mm. Setiap fraksi diekstrak dengan larutan akueus dari pH 2 hingga pH 6 dan juga dihadam dengan asid nitrik pekat. Kepekatan logam Cu dan Zn dalam larutan ekstrak dan hasil penghadaman ditentukan dengan menggunakan spektrofotometer serapan atom (AAS). Hasil kajian ini menunjukkan bahawa kelarutan logam Cu adalah tertinggi berbanding dengan logam Zn iaitu 34.45 µg/g yang diperolehi pada keadaan pH 2 dan saiz partikel* ≤ 0.25 *mm. Keterlarutan logam Cu dan Zn meningkat dengan penurunan pH dan saiz partikel. Amaun logam Cu dan Zn yang terlarut adalah rendah dengan kepekatan jumlah. Nilai terlarut Cu dan Zn dalam sampel sediment didapati kurang tepu jika dirujuk kepada fasa pepejal mineral* CuO, $Cu(OH)_2$ *dan* $CuCO_3$ *serta* ZnO, $Zn(OH)_2$ *and* $ZnCO_3$.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDIXES

LIST OF SYMBOLS

%	Percentage
°C	Degree Celsius
g	Gram
mg	Milligram
mm	Millimetre
L	Litre
mL	Mllilitres
mg/L	Milligram per litre
mol/L	Mol per litre
µg/g	Microgram per gram
µg/mL	Microgram per millilitre
>	More than
<	Less than
Ksp	Solubility product constant
K_d	Distribution coefficients
Eh	Redox potential
LogK°	Equilibrium constants
AMD	Acid Mine Drainage
AAS	Atomic Absorption Spectrophotometer

CHAPTER 1

INTRODUCTION

1.1 Relevance of Study

Sediments comprise of several components, including different mineral species as well as organic debris. Sediments represent one of the ultimate sinks for heavy metals discharged into the environment. More than 90% of the heavy metal load in aquatic systems is bound to suspended particulate matter and sediments. Therefore, sediments serve as a pool of metals that could be released to the overlying water and potentially cause adverse effects (Figueroa *et al.*, 2006).

Generally, heavy metals in solid phase (sediment) are in equilibrium with the metals in the solution phase. This equilibrium is dependent on several processes, namely adsorption, precipitation, desorption and dissolution. The significance of each process is dependent on several factors such as pH, redox potential (Eh) and temperature (Karshem and Singh, 2001).

The release of metals from the solid phase to solution phase is generally termed as mobilization. Mobilization of heavy metal in the solution is governed by two processes, namely desorption and dissolution. A change in pH will alters the

interaction between sediment components and subsequently affects metal distribution among sediment components (Yin *et al.*, 2001).

Heavy metals in sediments can be present in primary and/or secondary minerals (Wen *et al.*, 1998). The solubility of these metal-containing minerals is dependent on several factors including pH (Yin *et al.*, 2001) and Eh (Mansfeldt, 2004). For example, metal solubility decreased with increased pH and decreased Eh in the soil solution (Karshem and Singh, 2001). However, the actual solubility is dependent on the type of metal and type of mineral (Cappuyns *et al.*, 2007). In other words, the mobility of heavy metal can be dependent on the geochemical make-up of the sediment. Heavy metals can be distributed in various geochemical forms and particle sizes. The geochemical forms or fractions have varying solubility while the concentrations of heavy metals tend to increase as the grain sizes get finer (Singh *et al.*, 1999).

1.2 Objectives of Study

The objectives of this study were:

a) To determine the effect of pH on the solubility of Cu and Zn from river sediments.

b) To determine the effect of particle size on the solubility of Cu and Zn in river sediments.

c) To compare the solubility of Cu and Zn in river sediments.

d) To compare the observed solubility of Cu and Zn in the sediments with theoretical solubility of selected Cu and Zn minerals.

1.3 Scope of Study

This study focused on the solubility of two heavy metals, namely Cu and Zn, in sediments collected from 2 different river at Ranau, Sabah, namely Bambangan River, Lohan River and Mentaki River. The main factors investigated were pH and sediment grain sizes. The concentration of Cu and Zn in solutions filtrates were analysed using Atomic Absorption Spectrophotometer (AAS). Subsequently, the observed Cu and Zn concentrations in the solutions were compared with the calculated solubility of selected Cu and Zn minerals to determine whether the selected mineral control the solubility of Cu and Zn in the sediments.

REFERENCES

Adriano, D.C., 1986. *Trace Element in the Terrestrial Environmental: Biogeochemistry, Bioavailability, and Risks of Metals.* Springer-Verlag, New York, p. 22-24

Alloway, B.J., 1990. *Heavy metals in soils.* Blackie & Son Ltd, Glasgo, p. 367.

Andersen, V., Maage, A. and Johannessen, P.J., 1996. *Heavy Metal in Bleu Mussels (Mytilus edulis) in the Bergen Area.* New York, p. 589.

Ankley, G.T., Lodge, K., Call, D.J., Balcer, M.D., Brooke, L.T, Cook, P.M, Kresis Jr., Baptista Neto, J.A., Smith, B.J. and Mc Allister, J.J., 1992. Heavy metal contaminations in surface sediments in a nearshore environment, Jurujuba Sound. *Sountheast Brazil Environ. Pollut.* **109**, 1-9.

Audry, S., Schäfer, J., Blanc, G., Bossy, C. and Lavaux, G., 2003. Anthropogenic components of heavy metal (Cd, Zn, Cu, Pb) budgets in the Lot-Garonne fluvial system (France). *Applied Geochemistry* **18**, 1-18.

Banum, S.J., 1982. *Introduction to Organic and Biological Chemistry*, 3rd edition, Macmillan, New York.

Brummer, G.W., Tiller, H.G., Herms and Clayton, P.M., 1983. Adsorption-desorption and/or precipitation-dissolution processes of zinc in soils. *Geoderma* **31**, 337-354.

Buccolieri, A., Buccolieri, G., Cardellicchio, N., Atti, A. D., Leo, A. D. and Maci, A., 2006. Heavy metals in marine sediments of Taranto Gulf (Ionian Sea, Southern Italy). *Marine Chemistry* **99**, 227-235.

Cappuyns, V., Swennen, R. and Niclaes, M., 2007. Application of the BCR sequential extraction scheme to dredged pond sediments contaminated by Pb-Zn mining: A combined geochemical and mineralogical approach. *Journal of Geochemical Exploration* **93**, 78-90.

Carroll, S.A., O'Day, P.A. and Piechowski, M., 1998. Rock-water interactions controllingzinc, cadmium, and lead concentrations in surface waters and sediments, U.S. Tri-state Minind District 2. *Environ. Sci. Technol.* **32(7)**, 956-965.

Chakrabarti, C.L., Lu, Y.J., Cheng, J.G. and Back, M.H., 1993. Studies on metal speciation in the natural environment. *Anal. Chim. Acta.* **276**, 47-64.

Cheng, J.G., Chakrabarti, C.L., Back, M.H. and Schroeder, W.H., 1994. Chemical speciation of Cu, Zn, Pb and Cd in rain water. *Anal. Chim. Acta.* **288**, 141-156.

Chuan, M.C., Shu, G.Y. and Liu, J.C., 1996. Solubility of heavy metals in a contaminated soil: Effect of redox potential and pH. *Earth and Environmental Science* **90**, 543-556.

Cresser, M. S. and Morr, L., 1991. Optical spectrometry in the analysis of pollutants. In: Hewitt, C. N., *Instrumental analysis of pullutants.* Elsevier Applied Science, London, p. 103-110.

De Groot, A.J., Zschuppe, K.H. and Salomons, W., 1982. Standardization of methods of analysis for heavy metals in sediments. *Hydrobiologia* **92**, 689-695.

De Groot, A.J., 1995. Metals and sediments: A global prospective. In: Allen, H.E., *Metal Contaminated Aquatic Sediments.* Ann Arbor Press, New York, p. 6-7.

Dold, B. and Fontbote, L., 2001. Element cycling and secondary mineralogy in porphyry copper tailings as a function of climate, primary mineralogy, and mineral processing. *Journal of Geochemical Exploration* **74**, 3-55.

Eriksen, R.S., Mackey, D.J., Van Dam, R. and Nowak, B., 2001. Copper speciation and toxicity in Macquarie Harbour, Tasmania: an investigation using a copper ion selective electrode. *Marine Chemistry* **74**, 99-113.

Figueroa, D.A., Jiménez, B.D. and Sierra, C.J.R., 2006. Trace metals in sediments of two estuarine lagoons from Puerto Rico. *Environmental Pollution* **141**, 336-342.

Finney, B.P. and Huh, C.A, 1989. History of metal pollution in the Southern California Bight: an update. *Environmental Science and Technology* **23**, 294-303.

Förstner and Wittmann, 1983. *Metal Pollution in Aquatic Environment*, 2nd Edition. Springer-verlag, Berlin, p. 567.

Forstner, U., 1989. Contaminated Sediments. In: Bhattacharji, S., Friedman, G.S., Neugebauer, H.J. and Seilacher, A. (Eds). *Lecture Notes in Earth Sciences 2.* Springer-verlag, New York, p. 138

Francois, M., Dubourguier, H.C., Li, D. and Douay, F., 2004. Prediction of heavy metal solubility in agricultural topsoils around two smelters by the physico-chemical parameters of the soils. *Aquatic Sciences* **66**, 78-85(8).

Fukushima, M., Nogawa, K., Sakamoto, M. and Kobayashi, E., 1974. Epidemiological studies on renal failure of inhabitants in "Itai-itai" disease endemic district. Part 1. Some abnormal urinary findings of inhabitants living in and around the endemic district of the Jinzu River bank. *Japan Journal Public Health* **21**, 65-73.

Galán, E., Gómez-Ariza, J.L., González, I., Fernández-Caliani, J.C and Giráldez, I., 2003. Heavy metal partitioning in river sediments severely polluted by acid mine drainage in the Iberian Pyrite Belt. Applied Geochemistry 18(3), 409-421.

Garrels, R.M. and Christ, C.L., 1965. *Solution, Minerals and Equilibria.* Harper and Row, New York, p. 450.

Gleyzes, C., Tellier, S. and Astruc, M., 2002. Fractionation studies of trace elements in contaminated soils and sediments: A review of sequential extraction procedures. *TrAC Trends Anal. Chem.* **21**, 451-467.

Gómez Ariza, J.L., Giráldez-Ridaz, D. and Morales, E., 2000b. Selectivity assessment of a sequential extraction procedure for metal mobility characterization using model phases. *Talanta* **52**, 545-554.

Gray, N.F., 1997. Environmental impact and remediation of acid mine drainage: A management problem. *Environmental Geology* **30**, 62-71.

Han, Fengxiang X., 2007. *Biochemistry of Trace Elements in Arid Environments*. 1st Edition. Springer, Netherlands.

Hall, G.E.M., Gauthier, G., Pelchet, P. And Vaive, J.E., 1996. Application of a sequential extraction scheme to ten geological certified reference materials for the determination of 20 elements. *Journal of Analysis Atomic Spectrom* **11**, 787-796.

Harrington, J.M.,Fendorf, S. and Rosenzweig, R.G., 1998. Biotic generation of As(III) in metal(loid) contaminated freshwater lake sediments. *Environ. Sci. Technol.* **32(16)**, 2425-30.

Hermann, R. and Neumanann-Mahlakau, P., 1985. The mobility of zinc, cadmium, copper, lead, iron and arsenic in ground water as a function of redox potential and pH. *Sci. Tot. Eviron.* **43**, 1-12.

Hodgson, J.F., Lindsay, W.L. and Trierweiler, J.F., 1979. Micronutrients cation complexing in soil solution II. In: Complexing of Zn and Cu in displaced solution from calcareous soils. *Soil Science Society of America Proceedings* **30**, 723-726.

Huang, Q., Chen, W. and Guo, X., 2004. Chemical Fractionation of Copper, Zinc, and Cadmium in Two Chinese Soils as Influenced by Rhizobia. *Communications in Soil Science and Plant Analysis* **35**, 947-960.

Inaba, S. and Takenaka, C., 2005. Changes in chemical species of copper added to Brown Forest Soil in Japan. *Earth and Environmental Science* **162**, 285-293.

Jenne, E.A., 1995. Metal adsorption onto and desertion from sediment: I. Rates. In: Allen, H.E., *Metal Contaminated Aquatic Sediments*. Ann Arbor Press, New York, p. 82.

Jennet, J.C., Ettler, S.W. and Wixson, B.G., 1980. Mobilization and toxicological aspect of sedimentary contaminations. In: Baker, R.A. (Ed*). Contaminatns and Sediments, 1: Fate and Transport Case Studies, Modelling, Toxicity,* Pub. Inc. Orichigan **23**, 429-444.

Jones, B. and Turki, A., 1997. Distribution and speciation of heavy metals in surficial sediments from the Tees Estuary, Northeast England. *Mar. Pollut. Bull.* **34**, 768-779.

Karathanasis, A. D., 1999. Subsurface migration of copper and zinc mediated by soil colloids. *Soil Sci. Soc. Am. J.* **63**, 830-838.

Karius, V. and Hamer, K., 2001. pH and grain-size variation in leaching tests with bricks made of harbour sediments compared to commercial bricks. *The Science of the Total Environment* **278**, 73-85.

Karshem, M.A. and Singh, S.B., 2001. Metal availability in contaminated soils: I. Effects of flooding and organic matter on changes in Eh, pH and solubility of Cd, Ni and Zn. *Earth and Environmental Science* **61(3)**, 247-255.

Kinniburgh, D.G. and Jackson, M.L., 1981. Cation adsorption by hydrous metal oxides and clay. In: Anderson, M.A. and Rubin, A.J. (Eds) *Adsorption of Inorganic at Solid-Liquid Interface*. Ann Arbor Science, Ann Arbor, p. 91-160.

Kittrick, J.A., 1976. Control of Zn^{2+} in the soil solution by Sphalerite. *Soil Sci. Soc. Am. J.* **40**, 314-315.

Lindsay, W.L, 1979. *Chemical Equilibria In Soils*. John Wiley & Sons, New York.

Liu, W.X., Coveney, R.M and Chen, J.L., 2003. Environmental quality assessment on a river system polluted by mining activities. *Applied Geochemistry* **18**, 749-764.

Lo, C.K. and Fung, Y.S., 1992. Heavy Metal pollution profiles of dated sediment cores from Hebe Haven, Hong Kong. *Water Reseach* **26**, 1605-1619.

Luo, X.S., Zhou, D.M., Liu, X.H and Wang, Y.J., 2006. Solid/Solution partitioning and speciation of heavy metals in the contaminated agricultural soils around a copper mine in eastern Nanjing city, China. *Journal of Hazardous Materials* **A131**, 19-27.

Moriarty, F. and Hanson, H.M., 1988. Heavy Metals in Sediments of the River Ecclesbourne, Derbyshire. *Water Research* **22(4)**, 475-480.

Mansfeldt, T., 2004. Redox potential of bulk soil and soil solution concentration of nitrate, manganese, iron, and sulphate in two Gleysols. *Journal of Plant Nutrition Soil Science* **167**, 7-16.

Marcus, J., 1987. Particle size and distribution of copper mine tailings from Lohan Ranau Sabah and its relationship with heavy metal content. *Pertanika* **10 (1),** 37-40.

McBride, M.B. and Blasiak, J.J., 1979. Zinc and copper solubility as a function of pH in an acid soil. *Soil Sci Soc Am J* **43**, 866-870.

McBride, M.B., 1981. Forms and distribution of copper in solid and solution phases of soil. In: Loneragan, J.F., Robson, A.D. and Graham, R.D. *Copper in Soil and Plants*. Academic Press, Sydney, Australia. p. 25-45.

Meena, A.K., Mishra, G.K., Rai, P.K., Rajagopal, C. and Nagar, P.N., 2005. Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent. *Journal of Hazardous Material B* **122**, 161-170.

Merian, E., 1991. *Metals and Their Compounds in the Environment: Occurrence, Analysis and Biological Relevance.* Verlahsgesellschaft, p. 311-315.

Meyer, R. A., 2000. Encyclopedia of Analytical Chemistry. John Wiley & Sons, Ltd, New York.

Miao, S., DeLaune, R.D. and Jugsujinda, A., 2006. Influence of sediment redox conditions on reverse/solubility of metals and nutrients in a Louisiana Mississippi River deltaic plain freshwater lake. *Science of the Total Environment* **371**, 334-343.

Mitchell, R.L, 1964. Trace elements in soils. In: Bear, F.E, *Chemistry of the Soil, AACS Monograph Series*, Ed. Reinhold, New York, p. 320-368.

Moore, J.N. and Luoma, S.N., 1990. Hazardous waste from large-scale metal extraction. *Environmetal Science Technology* **24**, 1278-1285.

Nirel, P.M.V. and Morel, F.M.M., 1990. Pitfalls of sequential extractions. *Water Res.* **24**. 1055-1056.

Nriagu, J.O., 1979. Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. *Nature* **279**, 409-411.

Nriagu, J.O. and Pacyna, J.M., 1988. Quantitative assessment of world-wide contamination of air, water and soils by trace-metals. *Nature* **333**, 134-139.

Papadopoulos, P. and Rowell, D.L., 1989. The reactions of copper and zinc with calcium carbonate surfaces. *European Journal of Soil Science* **40(1)**, 39-48.

Pickering, W.F., 1980. Zinc interaction with soil and sediment components. In: Nriagu, J.O. (Ed) *Zinc in Environment Part 1: Ecological Cycling*. John Wiley & Sons, New York, p. 71-112.

Pierzynski, G.M. and Schwab, A.P., 1993. Bioavailability of zinc, cadmium, and lead in metal-contaminated alluvial soil. *Journal of Environment Quality* **22**, 247-254.

Prokop, Z., Curp, P., Zlevorova-Zlamalikova, V., Komarek, J., Dusek, L. and Holoubek, I., 2003. Mobility, bioavailability, and toxic effects of cadmium in soil samples. *Environ. Res.* **91**, 119-126.

Purchase, N.G. and Fergusson, J.E., 1986. Distribution and geochemistry of lead in river sediments, Christchurch, New Zealand. *Environmental Pollution* **12(3)**, 203-216.

Reeder, R.J. and Schoonen, M.A.A., 2006. Metal speciation and its role in bioaccessibility and bioavailability. *Mineralogy and Geochemistry* **64(1)**, 59-113.

Sabri, A.W., Rasheed, K.A. and Kassim, T.I., 1993. Heavy metal in the water, suspended solids and Sediments of the River Tigris Impoundment at Samarra. *Water Research* **27(6)**, 1099-1103.

Sadiq, M., 1999. Solubility and speciation of zinc in calcareous soils. *Water, Air, and Soil Pollution* **57-58**, 411-421.

Sager, M., 1992. *Chemical Speciation and Environmental Mobility of Heavy Metal in sediments and soils*. Springer-verlag, New York, 324-326.

Sanders, J.R. and McGrath, S.P., 1988. Experimental measurements and computer predictions of copper complex formation by soluble soil organic matter. *Environmetal Pollution* **49**, 63-79.

Sauvé, S., McBride, M. and Hendershot, W., 1998. Soil solution speciation of lead(II): Effects of organic matter and pH. *Soil Sci. Soc. Am. J.* **62**, 618-621.

Schroeder, H.A., Nason, A.P., Tipton, I.H. and Balassa, J.J., 1967. Essential trace metals in man: Zinc. *Journal of Chronic Diseases* **20(4)**, 179-210.

Shang, A.A., Dang, Z., Liu, Y.R. and Liang, Z.S., 2000. Progress in study of the bioavailability of heavy metal in soils. *Soil (in Chinese)* **32(6)**, 294-300.

Shella, M.R., 1994. Toxic Metals In Soil-Plant Systems. *Journal of Department of Geography University of Bristol*, UK.

Silberberg, M.S., 2006. *Chemistry: The Molecular Nature of Matter and Change*. 4th Edition. McGraw-Hill, New York, p. 838-839.

Singh, A.K., Hasnain, S.I. and Banerjee, D.K., 1999. Grain size and geochemical partioning of heavy metals in sediments of the Damodar River – a tributary of the lower Ganga, India. *Environmental Geology* **39 (1),** 90-98.

Smith, S.R., 1994. Effect of soil pH on availability to crops of metals in sewage sludge-treated soils. I. Nickel, copper and zinc uptake and toxicity to ryegrass. *Environmental Pollution* **85**, 321-327.

Stead-Dexter, K. and Ward, N.I, 2004. Mobility of heavy metals within freshwater sediments affected by motorway stormwater. *Science of the Total Environment* **334-335**, 271-277.

Stumm, W. and Morgan, J., 1981. *Aquatic Chemistry: An Introduction Emphasizing chemical equilibria in natural waters*, 2nd Edition, John Wiley & Sons, New York, p. 236-238.

Tack, F.M., Callewaert, O.W.J.J. and erloo, M.G., 1996. Metal Solubility as a Functioon of pH in a Contiminated, Dredged Sediment affected by oxidation. *Environmental Pollution* **91**, 199-208.

Tessier, A., Campbell, P.G.C. and Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* **51(7)**, 844-850.

Uygur, V. and Rimmer, D.L., 2000. Reactions of zinc with iron-oxide coated calcite surfaces at alkaline pH. *European Journal of Soil Science* **51(3),** 511-516.

Wenzel, W.W. and Jockwer, F., 1999. Accumulation of heavy metals in plants grown on mineralized soils of Austrian Alps. *Environmental Pollution* **104**, 145-155.

Wen, Xianghua and Allen, Herbert E., 1999. Mobilization of heavy metals from Le An River Sediment. *The Science of the Total Environment* **227**, 101-108.

Whitten, M.G. and Ritchie, G.S.P., 1991. Calcium chloride extractable cadmium as an estimate of cadmium uptake by subterranean clover. *Australian Journal of Soil Residual* **29**, 215-221.

Yin, Y., Impellitteri, C. A., You, S. J. and Allen, H. E., 2002. The importance of organic matter distribution and extract soil:solution ratio on the desorption of heavy metals from soils. *The Science of the Total Environment* **287**, 107-119.

Yu, B., Zhang, Y., Shukla, A. and Dorris, K.L., 2000. The removal of heavy metal from aqueous solutions by sawdust adsorption-removal of copper. *Journal of Hazardous Material B* **122**, 33-42.