ANALYSIS OF HEAVY METALS IN DIFFERENT REGIONS IN THE SULTANATE OF OMAN

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To my beloved father, mother, wife, children,
brothers, sisters, friends and all of my family

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ABSTRACT

Heavy metals can enter the food chain through water, soil and plant pollutions. It was therefore of interest to conduct a study to estimate the levels of these heavy metals in water, soil and plants of different regions of the Sultanate of Oman. This is the first comprehensive study for the analysis of heavy metals in soil, water and plant in the Sultanate of Oman. Samplings were conducted from four regions i.e. Batinah North (BN), Batinah South (BS), Dakhliyah (DH) and Sharqiyah (SH) between November 2009 and July 2010. For this purpose, five farms were selected from each region. Eleven heavy metals analyzed were cadmium (Cd), cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), lead (Pb), manganese (Mn), molybdenum (Mo), nickel (Ni), vanadium (V) and zinc (Zn) using inductively coupled-plasma emission spectroscopy (ICP-OES). For soil samples, high levels of Mn (3.406 μg/g) and Fe (2.494 μg/g) were detected, but not exceeding MPL, while Cd (0.006 μg/g) recorded the lowest concentration in all regions. For well water samples, only Ni (0.035 μg/mL) exceeded the Omani specifications standard for unbottled drink. Fe was detected at high concentration (170.554 μg/g) and Cd (0.058 μg/g) was the lowest detectable element for the animal grass plant samples. The proposed maximum permissible limit (MPL) of ten heavy metals (Cd, Co, Cu, Cr, Pb, Mn, Mo, Ni, V and Zn) in Omani soil was 0.8, 20, 10.0, 63.0, 100.0, 85.0, 500.0, 40.0, 50.0, 50.0 and 200.0 μg/g respectively. While for well water, MPL of most elements proposed followed the WHO guidelines except Cu and Mn that followed the lower Malaysian guideline of 1.0 and 0.1 μg/mL respectively. All heavy metals in soil and water samples analyzed were well below the limit of the proposed Omani MPL. There was no correlation found of the content of heavy metals in the soil, water and plant samples.

ABSTRAK

Logam berat boleh memasuki rantai makanan melalui pencemaran air, tanah dan tumbuh-tumbuhan. Oleh yang demikian adalah menjadi tujuan kajian ini untuk menganggarkan tahap kandungan logam berat ini di dalam air, tanah dan tumbuh-tumbuhan di beberapa wilayah di Kesultanan Oman. Ini adalah kajian pertama yang dijalankan untuk analisis terhadap kandungan logam berat dalam tanah, air dan tumbuh-tumbuhan di Oman. Pensampelan telah dijalankan di ladang-ladang terpilih tersebut yang terletak di empat wilayah iaitu Batinah Utara (BN), Batinah Selatan (BS), Dakhliah (DH) dan Sharqiah (SH) antara November 2009 dan Julai 2010. Untuk tujuan ini, lima ladang dipilih untuk setiap wilayah. Sebelas jenis logam berat telah dianalisis iaitu kadmium (Cd), kobalt (Co), kuprum (Cu), kromium (Cr), besi (Fe), plumbum (Pb), mangan (Mn), molibdenum (Mo), nikel (Ni), vanadium (V) dan zink (Zn) menggunakan Spektroskopi Pelepasan Plasma Berpasangan Teraruh (ICP-OES). Untuk sampel-sampel tanah, kandungan Mn(3.406 μg/g) dan Fe (2.494 μg/g) telah dikesan, tetapi tidak melebihi MPL, manakala Cd (0.006 μg/g) direkodkan pada kandungan terendah di semua wilayah. Untuk sampel air telaga, hanya Ni(0.035 μg/mL) melebihi spesifikasi piawaian Oman untuk minuman tidak dibotolkan. Fe dikesan pada kandungan tinggi (170.554 μg/g) dan Cd (0.058 μg/g) adalah elemen yang dikesan terendah untuk sampel rumput haiwan. Had maksimum yang dibenarkan yang dicadangkan (MPL) untuk sepuluh logam berat (Cd, Co, Cu, Cr, Pb, Mn, Mo, Ni, V and Zn) di tanah Oman adalah masing-masing 0.8, 20, 10.0, 63.0, 100.0, 85.0, 500.0, 40.0, 50.0, 50.0 dan 200.0 μg/g. Untuk air telaga, MPL untuk semua elemen yang dicadangkan mematuhi panduan WHO kecuali Cu dan Mn yang hanya mematuhi panduan Malaysia yang lebih longgar iaitu masing-masing 1.0 dan 0.1 μg/mL. Semua logam berat dalam sampel minyak dan air dianalisis adalah lebih rendah daripada MPL Oman. Tiada korelasi dijumpai antara kandungan logam berat dengan sampel tanah, air dan tumbuhan.

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LIST OF GLOSSARY

AAS	Atomic Absorption Spectrometry
FAAS	Flame Atomic Absorption Spectrophotometer
GPS	Global Positioning System.
GFAAS	Graphite Atomic Absorption Spectrophotometer
ICP-OES	Inductively Coupled Plasma- Optical Emission spectrometry.
PTWIs	Provisional Tolerable Weekly Intakes
PMTDIs	Provisional Maximum Tolerable Daily Intakes
JECFA	Joint Expert Committee on Food Additives
FAO	Food and Agriculture Organization
MPL	Maximum Permissible Level
TN	Total Nitrogen
USEPA	United State Environmental Protection Agency
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

1.1 Background

Environmental pollution by heavy metals can occur by many different ways, either directly or indirectly. Soils, water and plants are contaminated by material from the air or by direct deposition of pollutants. Heavy metals are introduced into the eco-system by the manufacturers and the use of materials containing heavy metals as well as the disposal of this waste. Heavy metals in air, soil, and water are global problems that are a growing threat to the environment. There are many sources of heavy metal pollution, including the coal, natural gas, paper, and industries (Alloway, 1990).

The main routes to transfer metals throughout the environment are the atmosphere and flowing waters. Under normal conditions, the end results of migration are sediments, soil and underground waters. Heavy metals may enter the food chain as a result of their uptake by edible plants, thus, the determination of heavy metals in environmental samples is very important. The importance of interactions between metals and solid phases of soils, soil water, and air within and above soil depends on a variety of chemical factors. Absorption of metals from soil water to soil particles is the most important chemical determinant that limits mobility in soils (Barałkiewicz and Siepak 1999).

The accumulation of these contaminants is aided by the capability of soil to bind them with clay minerals or organic substances. Heavy metals are natural components of soil. Most elements are only present in minimal, insignificant eco-toxicological concentrations in undisturbed locations. A few heavy metals are important as trace elements for physiological processes in plants and animals. Heavy metals contamination of soil is widespread due to metal processing industries, tannery, combustion of wood, coal and mineral oil, traffic, and plant protection (Margesin & Schinner 2005). Heavy metals may reach and contaminate plants, vegetables, fruits and canned foods through air, water, and soil during cultivation (Husain *et al*., 1995; Ozores *et al.*, 1997; Geert *et al*., 1989).

Inhalation and ingestion of heavy metals may cause various diseases such as anemia, neuropsychological effects, liver diseases, gastrointestinal pathologies, teratogenic implications (Needleman & Bellinger, 1991). Moreover, it is known that the DNA-damaging effects of certain metals in humans can lead to induction of cancer and a decrease of fertility (Snow, 1992). In addition, heavy metals in soils may adversely affect soil ecology, agricultural production or products and water quality (Wang *et al*., 2001).

Some metals are essential for life, but if an individual's intake exceeds a certain threshold, toxicity may develop. Metals and minerals in food and fodder are of great interest because of their potential effects on human and animal health. Some have no beneficial biological function but exposures in differs on deficiency may be harmful to health. For example, organic mercury compounds are neurotoxins, exposure to lead can be harmful to neurophysiological development; inorganic arsenic is a human carcinogen and cadmium can affect renal function. While some elements, such as cobalt, iron and copper are essential to health, they may be toxic at high levels of exposure. Exposure to metals can be in a number of ways, including at work in certain industries, from drinking water and eating contaminated foods (Ministry of Agriculture, Fisheries and Food, UK, 1998a,b).

Heavy metal pollution is a rising environmental problem, which requires immediate attention. With current commercial remediation reagents failing to provide the needed requirements as safe and effective metal chelators, the need for new technology is critical. The emissions of sulfur per day, together with dust loaded heavy metals, both discharged from smelter and industries cause many environmental pollution. The annual mean of the global emissions into the atmosphere reach about 150 ton of sulfur and 3.5 ton of dust loaded with heavy metals (Lacatusu *et al*., 1999).

The risk to health from certain elements in food can be assessed by comparing estimates of dietary exposures with the Provisional Tolerable Weekly Intakes (PTWIs) and Provisional Maximum Tolerable Daily Intakes (PMTDIs) recommended by the Joint Expert Committee on Food Additives (JECFA) of Food and Agriculture Organization (FAO) and World Health Organization (WHO) programmes on chemical safety (WHO, 1982a,b, 1989a,b, 1993a,b).

Extreme accumulation of heavy metals in agricultural soils through wastewater irrigation, may not only result in soil contamination, but also lead to elevated heavy metal uptake by crops, and thus affect food quality and safety. Heavy metal accumulation in soils and plants is of increasing concern because of the potential human health risks. This food chain contamination is one of the important pathways for the entry of these toxic pollutants into the body of the human. Heavy metal accumulation in plants depends on plant species, and the efficiency of different plants in absorbing metals is evaluated by either plant uptake or soil-to plant transfer factors of the metals. Vegetables cultivated in wastewater-irrigated soils take up heavy metals in large enough quantities to cause potential health risks to the consumers. In order to assess the health risks, it is necessary to identify the potential of a source to introduce risk agents into the environment, estimate the amount of risk agents that come into contact with the human-environment (Khan *et al*., 2008).

Anthropogenic activities (mining, ultimate disposal of treated and untreated waste) effluents containing toxic metals as well as metal chelates from different industries and also the indiscriminate use of heavy metal containing fertilizers and pesticides in agriculture resulted in deterioration of water quality rendering serious environmental problems posing threat on human beings. However some of the metals for example Cu, Fe, Mn, Ni and Zn are essential as micronutrients for life processes in plants and microorganisms, while many other metals like Cd, Cr and Pb have no known physiological activity, (*Kar et al*., 2007).

As a result, monitoring heavy metals is important for safety assessment of the environment and human health in particular. Regarding this background, it was therefore of necessity to determine heavy metals in water, soil and plant.

1.2 Statement of the Problem

During the past few years, many death causes of animal have been reported by the Veterinary Research Center in the Sultanate of Oman including infectious and non infectious diseases. In addition, some animal diseases which could be related to animal fodder or drinking water may be correlated to heavy metals. However, there were some animal fatalities for which the potential cause of death could not be agreed upon and affected animals showed no specific symptoms before death. An atmosphere, waters, soils and plants contaminated by heavy metals via increasing industrial areas and the use of fertilizers and insecticide in the farms. To date, no comprehensive study has been conducted to estimate the levels of these metals in the water, soil and plants in The Sultanate of Oman. It was therefore of interest to conduct a study to estimate the levels of these heavy metals in water, soil and plants of different regions of The Sultanate.

1.3 Objectives

This study embarks on the following objectives:

i. To determine the concentration of several heavy metals in soil, well water and animal grass samples in different regions in The Sultanate of Oman.
ii. To find a correlation between the concentrations of heavy metals in soil, well water and plant.
iii. To propose a maximum permissible level of heavy metals present in soil and water in The Sultanate of Oman.

1.4 Significance of Study

The study will provide the baseline data of the levels of cadmium (Cd), cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), lead (Pb), manganese (Mn), molybdenum (Mo), nickel (Ni), vanadium (V) and zinc (Zn) in well water, soil and plants of selected regions and will help to make a basis for further studies/ monitoring of their concentrations in soil, water and plants of The Sultanate of Oman. Moreover, it will help in forecasting the potential threats caused by their excess or deficiency to animal population of The Sultanate. The outcomes of this study will be of great interest to the environmental agency, veterinary agency and agricultural societies particularly in The Sultanate of Oman.

1.5 Scope of Study

The scope of the present study encompasses the analysis of eleven heavy metals, namely as cadmium (Cd), cobalt (Co), copper (Cu), chromium (Cr), iron

(Fe), lead (Pb), manganese (Mn), molybdenum (Mo), nickel (Ni), vanadium (V) and zinc (Zn). Environmental samples analyzed included water, soil and grass. Heavy metals are analyzed in four regions namely; Batinah North (BN), Batinah South (BS), Dakhiliyah (DH) and Sharqiyah (SH) by using inductively coupled plasma-optical emission spectrometry (ICP-OES) and FAAS

1.6 Outline of the Thesis

This thesis consists of five chapters. Chapter 1 presents the background of the research, statement, objectives, significance and scope of study. Chapter 2 compiles the literature review. Experimental of the research is presented in Chapter 3. In Chapter 4, the results of the study are illustrated and discussed. Finally, Chapter 5 concludes the results obtained and offers suggestions for future work.

REFERENCES

.

Abrol I.P., Yadav J.S.P., Massoud F.I. (1998). Salt-Affected Soils and their Management Food And Agriculture Organization Of The United Nations Rome, Italy.

Agricultural Census, (2005). Ministry of Agriculture and Fisheries. The Sultanate of Oman.

Aguilar F, Charrondiere U, Dusemund B (2008). Scientific opinion on 5'-deoxyadenosylcobalamin and Methylcobalamin as sources for Vitamin B12 added as a nutritional substance in food supplements. *J. EFSA.*

Al-Futaisi, A., Rajmohan, N., & Al-Touqi,S. (2007). Groundwater quality monitoring in and around Barka dumping site, Sultanate of Oman. In: Water Resources Management (WRM 2007), J Wilson(ED), ACTA Press, Canada, 578-099

Alloway, B.J.(1990). *Heavy Metals in Soils* . Blackie and Sons Ltd, Glasgow, UK.

Al Omron A.M., El-Maghraby S.E., Nadeem M.E.A., El-Eter A.M., Al-Mohani H., (2011). Long Term of Irrigation with the Treated Sewage Effluent on Some Soil Properties of Al-Hassa Governorate, Saudi Arabia. *J. Saudi Soci.Agric.Sci*. (11), 15-18.

Al-Oud S. S., Nadeem M. E. A. and Al-Shabel B. H., (2011). Distribution of heavy metals in soil and plants around a cement factory in Riyadh city, central of Saudi Arabia. *American-Euraian J. Agric & Environ. Sci*., 11 (2), 183-191

Appenroth KJ (2009). *The definition of heavy metals and their role in biological system.*, vol 19, Soil biologySpringer, Berlin.

Al Sabahi E, Abdul Rahim S,Wan Z., Al NozailyF., Alshaebi F. (2009) A Study of Surface Water and Groundwater Pollution in Ibb City, Yemen, EJGE (4) bund F.

Al-Zidjali, T. M. (1996). Oman- Country Report. FAO International Technical Conference on plant genetic resources, held at Leipzig, Germany.

American Public Health Association, (1989). *Standard methods for the examination of water and wastewater*, 17th ed. Washington.

Aslam B, I Javed, FH Khan and ZU Rahman, (2011). Uptake of heavy metal residues from sewerage sludge in the milk of goat and cattle during summer season. Pak Vet J, 31(1), 75-77.

Assadian N.W., Esparza L.C., Fenn L.B., Ali A.S., Miyamoto S., Figueroa U.V., Warrick A.W., (1998). Spatial Variability of Heavy Metals in Irrigated Alfalfa Fields in the Upper Rio Grande River Basin. *Agric. Water Management.* 36, 141-156.

ASTDR (Agency for Toxic Substances and Disease Registry), (2000). Toxicological Profiles for Arsenic. US Department of Health and Human Service, Public Health Service, USA.

Bala, M., Shehu R. A. and Lawal, M. (2008). Determination of the level of some heavy metals in water collected from two pollution – prone irrigation areas around kano metropolis. *Bayero J. Ppure Applied Sci*, 1, 36 – 38

Baralkiewicz D. and Siepak J., (1999). Chromium, Nickel and Cobalt in Environmental Samples and Existing Leegal Norms. *Polish J. Environ. Studies.* 4, 201-208.

Bard, A.J . and Faulkner L.R. (2001). Electrochemical Methods- Fundamental and Application. 2nd Ed., John Wiley and Sons , New York, 458-464.

Bradl H.B. (2005). *Heavy Metals in the Environment*, Elsevier Ltd.

Dampare, S. B., Ameyaw, Y., Adotey, D. K., Osae, S., Serfor-Armah, Y., Nyarko, B. J. B. and Adomako, D. (2006). Seasonal trend of potentially toxic trace elements in soils supporting medicinal plants in the eastern region of Ghana. *Water, Air, and Soil Pollution*; 169, 185-206.

Doggett, H. (1988). Sorghum, 2nd Ed, Longman Scientific & Technical, Harlow, UK.

Duffus, J. H. (2002) , “Heavy metals”—a meaningless term? (IUPAC Technical Report), *Pure Appl. Chem.*, 74(5), 793–807.

Duruibe, J. O., Ogwuegbu, M. O. C. and Egwurugwu, J. N., (2007). Heavy metal pollution and human biotoxic effects, *Int. J. Phys. Sci.* 25, 112-118.

Fergusson J. E. (1989). *The Heavy Elements: Chemistry, Environment Impact and Health Effects*, Pergamon Press, Oxford.

Frame, J. & Laidlaw, A.S. (2005) Prospects for Temperate Forage Legumes. *In* Eds S.G. Reynolds and J. Frame. FAO (2005) *Grasslands: Developments,*Opportunities, Perspectives Science Publishers, Inc Plymouth UK.

Geert, E., W. van Loon Johannes, and T. Kars. (1989). Heavy metals in vegetables grown in the Netherlands and in domestic and imported fruits. Z Lebensm Unters Forsch. 190,34-39.

Geo-Environmental Engineering (2008). Management for Soil and Ground water Contamination. Kyoto University, Japan.

Gillian, F. J. (2007). *Principles of Instrumental Analysis*, Thompson, Brooks, Cole, 6th Edition.

Golub M. S. (2006). *Metals, Fertility, and Reproductive Toxicity*, Taylor & Francis Group. LLC, USA.

Gulab S. N. (2009). Studies in Environmental Pollution: Absorption of Heavy Metal by Some Vegetable Plant Parts from Polluted Irrigation Canal Water and River Water at Yamuna Nagar, proceedings of international conference on energy and environment march 19-21.

Hanaa, M., S., Eweida, A., Eweida and Azza F. (2000), Heavy Metals in Drinking Water and their Environmental Impact on Human Health. ICEHM2000, Cairo University, Egypt, 542- 556.

Harris D. C. (2007). Quantitative Chemical Analysis, Seventh Edition, W. H. Freeman and Company, New York.

Hashem A. R. (1993). Heavy Metals Analysis of Water and Soils from Saudi Arabia, *J. King Saud Univ.* Science 5(1), 39-46.

Haapala H., Goltsova N. and Lodenius M. (2001). Heavy Metal Solubility in Podzolic Soils Exposed to the Alkalizing Effect of Air Pollutants. *Environmental Pollution* 115, 33-41

Husain, A., Baroon Z., Al-Khalafawi S., Al-Ati T. and Sawaya W. (1995). Heavy Metals in Fruits and Vegetables grown in Kuwait during the Oil Well Fires. *Arab Gulf J. Sci. Research.* 535-542.

Jordan, W.R. and Sullivan, C.Y. (1982). Reaction and Resistance of Grain Sorghum to Heat and Drought. In ‘Sorghum in the Eighties, Vol 1,’ (J.V. Mertin, ed), ICRISAT, Patancheru, India, pp 131-142.

Kabata-Pendias A. (2000). *Trace Elements in Soils and Plants*, CRC Press LLC, USA.

Kar D., Sur P., Mandal S. K., Saha T. and Kole R. K. (2007). Assessment of Heavy Metal Pollution in Surface Water. *Int. J. Environ. Sci. Tech*., 5 (1), 119-124,

Kennish M. J., (1992). *Ecology of Estuaries. Anthropogenic effects*. CRC. Press, Inc., Boca Raton, F1.

Khan S., Cao Q.,. Zheng Y.M , Huang Y.Z., Zhu Y.G. (2008). Health Risks of Heavy Metals in Contaminated Soils and Food Crops Irrigated with Wastewater in Beijing, China. *Environ. Pollution,* 152 686-692

Kim J. H., Gibb H. J., Howe P. D. (2006). Cobalt and Inorganic Cobalt Compounds. Concise international chemical assessment document ; 69, *World Health Organization (WHO)* press.

Kimber, C.T. (2000). Origins of domesticated sorghum and its early diffusion into India and China. In 'Sorghum: Origin, History, Technology, and Production', (C. Wayne Smith and R.A. Frederiksen, eds), John Wiley & Sons, New York 3-98.

Kumar N. R. & Nagendran R. (2007). Influence of Initial pH on Bioleaching of Heavy Metals from Contaminated Soil Employing Indigenous Acidithiobacillus thiooxidans, Kluwer Academic Publishers, Netherlands.Science Direct, Chemosphere (66) 1775–1781

Lacatusu R., Dumitru M., Risnoveanu I., Ciobanu C., Mihaela Lungu, Carstea S., Beatrice Kovacsovics and Carmen Baciu (1999). Soil Pollution by Acid Rains and Heavy Metals in Zlatna Region, Romania 10th International Soil Conservation Organization Meeting held May, 24-29

Landner L. and Reuther R. (2004). *Metals in Society and in the Environmet*, Kluwer Academic Publishers, Netherlands.

Liang J., Chen C, Song X. , HanY., Liang Z,. (2011). Assessment of Heavy Metal Pollution in Soil and Plants from Dunhua Sewage Irrigation Area. *Int. J. Electrochem. Sci.*, 6; 5314 - 5324

MAF. (2005a). Agriculture Census 2004/2005. Department of Statistics and Information. Ministry of Agriculture and Fisheries. Sultanate of Oman.

MAF, (2003). Guidelines to the soil, water, plant And manure analysis. Ministry of Agriculture. Sultanate of Oman.

Manahan S. E. (1993), *Fundamentals of Environmental Chemistry,* Lewis publishers, (USA).

Margesin R. & Schinner F. (2005). Manual of Soil Analysis – Monitoring and Assessing Soil Bioremediation, *Soil Biology,* Volume 5. page 155 Springer-Verlag Berlin Heidelberg.

Marx, E.S., Hart J. and Stevens R.G. (1999). Soil Test Interpretation Guide, Oregon State University Extension Service, USA.

Mengel, K. & Kirkby. E.. (1982). Principles of plant nutrition. Internatl. Potach Inst. Worblaufen-Bern/Switzerland, p. 655.

Milićević D. R. , Jovanović M., Jurić V. B., Petrović Z. I. and Stefanović S. M. (2009). Toxicological Assessment of Toxic Element Residues in Swine Kidney and Its Role in Public Health Risk Assessment, *Int. J. Environ. Res. Public Health, 6*, 3127-3142

Ministry of Agriculture, Fisheries and Food (1998a). Lead, Arsenic and Other Metals in Food. Food Surveillance Paper No. 52 (London: The Stationary Office).

Ministry of Agriculture, Fisheries and Food (1998b). Cadmium, mercury and other metals in food. Food Surveillance Paper No. 53 (London: The Stationary Office).

Ministry of Health, Malaysia (2004). National Drinking Water Quality Standard Guidelines. Kuala Lumpur: Engineering Services Division, Ministry of Health, Malaysia

Montinaro S., Alessandro C., Massimo P., Giacomo C. (2008). Immobilization of Heavy Metals in Contaminated Soils Through Ball Milling with and without Additives. *Chem. Engin. J.*, 142, 271–284

MOOPAM, (2006). Manual of Oceanographic Observations and Pollutant Analysis Methods (MOOPAM), Kuwait.

National Research Council.(1996). Lost Crops of Africa, Vol 1, Grains, National Academy Press, Washington, D.C.

Needleman H.L., Bellinger D.D (1991). The Health Effects of Low Level Exposure to Lead, Annu. Rev. Public Health.12, 111–140.

Neuhoff J. (2008). Speciation of Cr (II) and Cr (III) complexes by IC-ICP-OES and HPLC, Department of Chemistry, University of Johannesburg.

Nguyen, H.T., Xu, W., Rosenow, D.T, Mullet J.E. and McIntyre (1997). Use of Biotechnology in Sorghum Drought Resistant Breeding, part A. In 'Proceedings of the International Conference on the Genetic Improvement of Sorghum and Pearl Millet,' Lubbock, USA, INTSORMIL and ICRISAT pp 412-424.

Ozores-Hampton M., E. Hanlon, H. Bryan and B. Schaffer. (1997). Cadmium, copper, lead, nickel and zinc concentrations in tomato and squash grown in MSW compost-amended calcareous soil. *Compost Sci & Utilization*. 5 (4), 40-45.

Qishlaqi A. and Moore F. (2007). Statistical Analysis of Accumulation and Sources of Heavy Metals Occurrence in Agricultural Soils of Khoshk River Banks, Shiraz, Iran. *American-Eurasian J. Agric. & Environ. Sci.*, 2(5), 565-573.

Papafilippaki A. K., M. E. Kotti and G. G. Stavroulakis, (2008). “Seasonal Variations In Dissolved Heavy Metals in the Keritis River, Chania”. Greece. *Global NEST Journal*, 10: 320-325.

Radostits, O. M., Gay C. C., Done S. H. and Hinchcliff K. W., (2007). Veterinary Medicine: A Text Book of Diseases of Cattle, Horses, Sheep, Pigs and Goats. Elsevier Saunders Co., USA.

Rahman M. M, L Haoliang , Y Chongling and Sirajul Hoque, (2007). Heavy Metal Hyper-accumulation in Plants and Metal Distribution in Soil on Tannery and Dying Industries Polluted Area in Bangladesh, Academic Open Internet Journal, Volume 21.

Raikwar, M. K., P. Kumar, M. Singh and A. Singh, (2008). Toxic effects of heavy metals in livestock health. Veterinary World, 1(1): 28-30

Rashed M. N. (2010). Monitoring of Contaminated Toxic and Heavy Metals, from Mine Tailings Through Age Accumulation In Soil And Some Wild Plants at Southeast Egypt *J. of Hazardous Material* (1978) 739-746

Rhoades J.D., Kandiah A. and Mashali A.M. (1992) The Use of Saline Waters for Crop Production. FAO irrigation and drainage paper Food And Agriculture Organization Of The United Nations Rome, Italy

Rui Yu-kui, Zhang Fu-suo, Shen Jian-bo, (2009). Effects of nitrogen fertilization on heavy metal content of corn grains. *Phyton (B. Aires)*, 78, 101-104

Sarkae Bibudhendra (2002). *Heavy Metals in the Environment*,; MarcelDekker, Inc., New York.

Selena M., Alessandro C., Massimo P., Giacomo C. (2008). Immobilization of Heavy Metals in Contaminated Soils Through Ball Milling With and Without Additives *Che. Engi. J.* 271–284.

Selim M. H & Kingery W. L. (2003). *Geochemical and hydrological reactivity of heavy metals in soils*, Lewis publishers, USA).

Selim M. H. & Sparks D. L. (2001). *Heavy Metals Release in Soils*, Lewis Publication, USA.

Shaker Ibrahim M. and Saeed Samir M. (2008). Assessment of Heavy Metals Pollution in Water and Sediments and their Effect on Oreochromis Niloticus in the Northern Delta Lakes, Egypt. *8th international symposium on tilapia in aquaculture*. 475-490.

Skoog, Holler and Crouch 2007, *Principles of Instrumental Analysis*, 6^{th} edition, Thomson Higher Education, USA.

Snow, E.T. (1992). Metal Carcinogenesis: Mechanistic Implications, *Pharmacol.Ther*. 53, 31–65.

Soil Survey Staff. (1998). Keys to Soil Taxonomy. Eighth Edition. US Department of Agriculture Natural Resource Conservation Service, Washington DC.

Stamatis G., Lambrakis N., Alexakis D., Zagana E., (2006), Groundwater quality in Mesogia basin in eastern Attica (Greece), *Hydrol. Process.*, **20,** 2803-2818.

Tong C., Xiao H., Tang G., Wang H., Huang T., Xia H., Keith S. J., Li Y.a, Liu S., Wu J. (2009). Long-term fertilizer effects on organic carbon and total Nitrogen and coupling relationships of C and N in paddy soils in subtropical China. Soil & Tillage Research (106) 8–14.

U.S. Environmental Protection Agency (EPA), (2008). EPA's 2008 Report on the Environment. National Center for Environmental Assessment, Washington, DC; EPA/600/R-07/045F. Available from the National Technical Information Service, Springfield, VA, and online at http://www.epa.gov/roe.

Vernet, J,P. (1992). *Impact of Heavy Metals on the Environment*, Elsevier Science Publishers B.V., Netherlands.

Wang Y.M., Chen T.C., Yeh K.J., Shue M.F. (2001). Stabilization of an elevated heavy metal contaminated site, *J. Hazard. Mater* B88, 63–74.

Wang Y.M., How-Ran C, Lin-Chi W., Guo-Ping C. C., Tsui-Chun T. (2010). Characteristics of Heavy Metals Emitted from a Heavy Oil-Fueled Power Plant in Northern Taiwan. *Aerosol & Air Quality Res.*, 10: 111–118.

World Health Organization (2008). Guidelines for Drinking Water Quality, World Health Organization, (Geneva: WHO).

World Health Organization (1982a). Toxicological Evaluation of Certain Food Additives. Joint FAO/WHO Expert Committee on Food Additives. WHO Food Additives Series, Number 17 (Geneva: WHO).

World Health Organization (1982b). Evaluation of Certain Food Additives and Contaminants. Technical Report Series, Number 683 (Geneva: WHO).

World Health Organization (1989a). Toxicological Evaluation of Certain Food Additives and Contaminants. Thirty-third meeting of the Joint FAO/WHO Expert Committee on Food Additives. WHO Food Additives Series, Number 24 (Cambridge: Cambridge University Press).

World Health Organization (1989b). Toxicological evaluation of certain food additives. Joint FAO/WHO Expert Committee on Food Additives and Contaminants. Technical Report Series, Number 683 (Geneva: WHO).

World Health Organization (1993a). Evaluation of certain food additives and Contaminants. WHO Technical Report Series, Number 837 (Geneva: WHO).

World Health Organization (1993b). Inorganic Lead. Environmental Health Criteria Number 165 (Geneva: WHO).

Zeng F., Ali S., Zhang H., Ouyang Y, Qiu B., Wu F. & Zhang G.(2011). The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. *Environ. Pollut. (159) 84e91*.

Zeng F., Tiyip T., Jian-li D., Taff G. N., Qi-sheng HE. (2009). The Effects of the Chemical Components of Soil Salinity on Electrical Conductivity in the Region of the Delta Oasis of Weigan and Kuqa Rivers, *China. Agric. Sci. China*, 8(8): 985-993.

Zhang Hui. (2004).“Heavy Metal Pollution and Aseniasis in Hetao Region, China. AMBIO:” A *J. Human Environ.*, 33, 138-140.