

# A STUDY ON IDENTIFICATION AND GEOCHEMICAL PROPERTIES OF HEAVYMETALS IN SOIL

Shobha M S<sup>1</sup> and Mahadeva Murthy S<sup>2</sup>

<sup>1</sup>Department of Microbiology, Government College for Women, Chintamani, Chikkaballapura-563 125, Karnataka.

<sup>2</sup>Department of Microbiology, Yuvaraja's College, University of Mysore, Mysuru- 570 005, Karnataka.

## Abstract

In the recent Era, due to the rapid growth of Urbanization, Industrialization, Mining activity the pollution problem arises in tremendous way. The effects of the heavymetals in soil, water and sediments were the main focal theme of the all the current researchers. An environmental geochemical investigation was carried out in industrial area of the Mysuru city to assess the contamination of the heavymetals in the different fraction and the extent of chemical contamination in soil. The purpose of this study was to assess the chemical partitioning of selected heavy metal in soil and to assess the degree of pollution in the study area. A five-step sequential extraction technique was used to assess the environmental status of heavy metals. Most of metals were considered to be mobile due to the ionic movement. The seasonal variations of heavy metals was observed and found slightly higher in summer than in monsoon season due to the dilution factor. The result shown of heavy metal concentrations reveal that the industrial area soil is highly contaminated due to improper disposal of solid waste, hazardous waste and improper treatment of effluent.

**Key Words:** Heavymetals, Soil, Fraction, Sequential Extraction, Hazardous waste

## I. Introduction

Heavy Metals are considered very important and highly toxic pollutants in the various environmental aspects. Inputs of metals to the environment as a result of anthropogenic activities is difficult to measure due to the very large natural inputs from the erosion or rocks, wind-blowing dusts, volcanic activity and forest fires. Some metals that have received more attention are Hg, Cd, and Pb, because of their highly toxic properties and their effects on the environment and the living organisms. The inputs of metals to the environment from anthropogenic activities is complicated to distinguish as there are very large natural inputs from the erosion, wind-blown dust, volcanic activity and forest fires. Atmospheric and river inputs, dredging spoil, direct discharges, industrial dumping and sewage sludge are some of the important contributors to metal pollution, which lead to the release of metals to the marine environment. Some metals are deposited by gas exchange at the sea surface, by fallout of particles (dry deposition) or are scavenged from the air column by precipitation (rain) which is called wet deposition. Rivers make a major contribution of metals in the marine environment. The nature of metals depends on ore-bearing deposits in the catchment area

and the discharge of human waste and discharges when the river passes through urban areas. Dredging of shipping channels produces large quantities of metal pollution. Much smaller quantities of metals are being entered to the sea by direct discharges of industrial and other waste and the dumping of sewage sludge (Depledge MH *et al.*, 1998; Phillips DJH, 1995).

The extent of bioaccumulation of metals is depending on the total amount of the metal, the bioavailability of each metal in the environmental medium and the route of uptake, storage and excretion mechanisms. The requirements of different organisms for essential metals vary substantially but optimal concentration ranges are narrow and frequently under careful homeostatic control. Excess metal concentration in an organism must be actively excreted, compartmentalized in cells or tissues, or metabolically immobilized. Essential metals at high concentrations can have sub-lethal toxicity effects to some organisms or lethal consequences to others. Also, metals at deficient concentrations can have again adverse health effects. Thus essential metals can have a double “toxic” threshold (Rainbow PS, 2007). Living organisms exposed environmentally to high metal concentrations follow various mechanisms to counter potential toxicity.

#### *Speciation of Heavy Metals in Soil sample:*

Speciation analysis is the analytical activity of identifying and/or measuring the quantities of one or more individual chemical species in a sample. The chemical species are specific forms of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure. The speciation of an element is the distribution of an element amongst defined chemical species in a system. Speciation analysis provides the necessary information to describe the effects of active species which is not available from the results of total trace element determinations.

The chemical composition of soil influences to a great extent the speciation of heavy metals. In river water large proportion of metals is bound to organic and inorganic particulate matter. Other factors which influence speciation are: pH, hardness, and organic matter (Elbay-Poulichet F *et al.*, 1987 ; Salomons W, *et al.*, 1984) Large amounts of dissolved organic complexes and particulate matter with heavy metals are transported great distances to end up in the sediments of the estuaries. Some metals, such as Cd, can be released from their organic complexes by increasing Cl (chlorine) concentrations, which form chloride complexes (Zamuda CD, *et al.*, 1982) Some metals are available for uptake into organisms from solution only as free ions, whereas others are transported over biological membranes as inorganic complexes. In experiments with Cu and Cd their toxicity and their bioavailability is correlated with the concentration of free metal concentration (Sunda WG, *et al.*, 1978; Bienvenue E. 1984). Inorganic Hg in the other hand is transported over lipid membranes principally as uncharged chloride complexes (Luoma SM, 1989). Sediments are more complex chemical environment than water and there are not reliable methods for assessing bioavailability of metals in such media (Alloway BJ. 1990) It has been shown that heavy metal in soils are associated with several distinct geochemical phases, such as clay minerals, organic matter, carbonates and sulphates.<sup>48</sup> The types of reactions that are likely to control the partitioning of metals in soils are: adsorption and desorption, precipitation and

solubilisation, surface complex formation, ion exchange and biological mobilization or immobilization (Chao TT,1984).

## II. MATERIALS & METHODS

### *Study Area:*

The study area Mysore is having more than 10 lakh populations and was capital of former state and 11o61 latitude and 77o71 longitude and general elevation is little more than 1800 feet above sea level. The climate of the city is moderated throughout the year with temperature during summer ranging from 30oC to 34oC. The rainy season is from June to October. The winter season starts from November to February. The source of water for domestic purpose is mainly from the Cauvery River and ground water. Mysore is one of the growing cities of Karnataka and it is largely due to presence of industrial resources and a well-developed communication network. Mysore has a rich and vibrant history and heritage and hence attracts a huge number of tourists. Also Mysore is now active centre for production and industrialization. The city has been growing as a country parallel to Bangalore, with a large presume of software companies and the population is growing at a faster rate due to the influx of many industrial and commercial activities.

### *Sampling and pre-treatment of the sample*

In the present study, sampling locations are included in all the 3 major industrial areas of Mysore city. The soil samples were collected at different points of the industrial zone of Mysore city, India. The samples were collected in polythene covers and immediately brought to the laboratory for analysis. Soil samples were dried with the help of oven in the laboratory and then ground in an agate mortar and pestle to pass through a 0.5mm stainless steel sieve. Then they were stored in polythene covers at room temperature. The soil samples were analyzed for basic physico-chemical properties using standard analytical methods and finally we digested the soil sample to quantify the total metal concentration by using di-acid mixture.

### *Determination of Total Heavy Metals:*

1g of soil sample was taken in to the test tube and mixed well with the concentrated H<sub>2</sub>SO<sub>4</sub>, Perchloric acid and Nitric acid. Heat the test tube content till the solution become whitish color. If white color appears it indicates that the soil sample is digested completely. Cool the solution to room temperature and filter using whatman filter paper. Make up the filtered solution to 100ml using distil water and take the readings after injecting the solution to AAS.

### *Multi-step sequential extraction .*

The sequential extraction procedure used in this study is Tessier *et al.* 1979 method. According to Tessier *et al.* heavy metals are associated with the fractions as described as follows:

- 1) *The exchangeable fraction*, which is likely to be affected by changes in water ionic composition as well as sorption–desorption processes;
- (2) *The carbonate fraction*, that is susceptible to changes in pH;
- (3) *The reducible fraction*, that consists of iron and manganese oxides which are unstable under anoxic conditions;

(4) *The organic fraction*, that can be degraded leading to a release of soluble metals under oxidizing conditions and

(5) *The residual fraction* that contains mainly primary and secondary minerals, which may hold metals within their structure. These metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature. The extraction was carried out progressively on an initial mass of 1.00 g of sample of soil samples. The samples for sequential extraction were dried in an oven at 60°C for 24 h in order to avoid, as far as possible, the transformation of some chemical forms (exchangeable and carbonate). This fraction was calculated as the difference between the total metals and the sum of extracted metals. The selective extractions were conducted in 50 ml capacity centrifuge tubes. After each extraction step, the sample was subjected to 30 min of centrifugation at 4,000 rpm, the supernatant was separated from the residue with a pipette and transferred into a 25-ml calibrated flask. The residue was centrifugation and later washed thoroughly, the obtained second supernatant was added to the flask, which was diluted to the desired volume. The extracts obtained were acidified using aquaregia and stored in stopper polyethylene vessels until their analysis by using inductively coupled plasma atomic emission spectroscopy techniques (ICP-AES). The total content of metals was determined after digesting 1 g of sample with aquaregia. The concentration of particular heavy metals was expressed per 1 kg of air dry sample. The content of heavy metals in the obtained solution was determined by using ICP-AES.

### **III. Results and Discussion**

The physico-chemical properties have been determined by standard methods to understand the quality of the industrial area soil. From the physico-chemical characteristics clearly indicated that the soil organic carbon and organic matter is very low with the range of 0.12% to 0.41%. In the present study the speciation of heavy metals was carried out according to Tessier method as described earlier. Table 4 shows the results of different fractions of the heavy metals in soil of the industrial area of Mysore city. The exchangeable fraction (F1) contains metal elements in the ionic form, which have a high mobility and can be drained by water. The fraction related to the carbonates (F2) is extractable and can be accumulated in the plants. The fraction related to the oxides of iron and manganese (F3) and that related to organic matter (F4) contain metals enclosed in the matrix. The fraction (F5) contains the inert metals.

In the fractionation studies, the iron occurred mainly in residual fraction and which is varied from 48.7% and 67.94% at sampling station no.7 and 1 respectively and also 19.42% to 42.02% of iron is bound to organic matter. It is bound in much smaller amounts in the form of oxides, which is ranged from 8.72%–19.45% in different samples.

Table. 1: Physico-chemical properties of Industrial area soil of Mysore city

Station code	pH	EC ( $\mu$ s/)	Lime content (mg/kg)	OC (%)	OM (%)	Na (ppm)	K (ppm)	Ca (mg/kg)	Mg (mg/kg)
S1	6.78	82.6	2.16	0.402	0.6930	4.0	6.8	148.2	56
S2	7.3	84.1	1.12	0.12	0.206	4.3	9.3	120.4	46
S3	7.1	80.6	1.98	0.16	0.2758	4.4	7.5	148.2	68
S4	7.4	83.9	7.24	0.5	0.862	3.7	5.7	112.0	56
S5	7.1	81.6	5.94	0.16	0.2758	3.8	13.2	142.3	72
S6	7.5	78.6	3.02	0.32	0.5516	4.9	10.3	176.7	112
S7	7.1	85.9	3.14	0.296	0.5103	4.5	10.9	136.1	86
S8	7.2	84.3	5.88	0.316	0.5447	5.2	12.7	132.4	72
S9	7.3	81.7	5.18	0.298	0.5137	6.0	12.2	322.7	236
S10	7.2	82.5	4.24	0.416	0.7171	4.7	10.6	166.6	122

Table.2:Heavy metal concentration in Industrial area soil of Mysore city

Station code	Fe	Cu	Cr	Zn	Ni
S1	3926.9	19.0	17.5	118.9	16.1
S2	4062.4	13.6	8.9	86.1	22.0
S3	6350.4	15.1	13.8	68.6	12.9
S4	5902.2	14.8	12.6	89.8	15.2
S5	6405.7	18.8	17.7	96.0	15.1
S6	4447.5	15.8	14.6	110.8	13.6
S7	4311.8	17.5	10.8	84.1	13.4
S8	2862.6	15.7	19.2	94.6	10.3
S9	3650.2	16.5	14.0	126.8	10.7
S10	3812.2	16.5	18.7	110.9	16.5

Table. 3: Speciation of Heavy metals in Industrial area soil of Mysore city

	Fractions I	Fractions II	Fractions III	Fractions IV	Fractions V
<b>S1</b>					
<b>Fe</b>	2.9	23	467	817	2617
<b>Cu</b>	ND	ND	ND	4.8	14.2
<b>Cr</b>	ND	ND	2.9	5.2	9.4
<b>Zn</b>	ND	4.7	78	18.6	17.6
<b>Ni</b>	ND	ND	3.6	5.6	6.9
<b>S2</b>					
<b>Fe</b>	3.4	19	491	789	2760
<b>Cu</b>	ND	ND	ND	3.7	9.9
<b>Cr</b>	ND	ND	2	3.4	3.5
<b>Zn</b>	ND	3.9	48	27	7.2
<b>Ni</b>	ND	ND	3	2.9	16.1
<b>S3</b>					
<b>Fe</b>	7.1	16.3	791	1918	3618
<b>Cu</b>	ND	ND	ND	2.1	13
<b>Cr</b>	ND	ND	2	4.6	7.2
<b>Zn</b>	3.1	6.7	26	16.9	15.9
<b>Ni</b>	ND	ND	3	4.8	5.1
<b>S4</b>					
<b>Fe</b>	3.2	18	681	1410	3790
<b>Cu</b>	ND	ND	ND	3.6	11.2
<b>Cr</b>	ND	ND	ND	4.5	8.1
<b>Zn</b>	3.2	5.6	39	35	7
<b>Ni</b>	ND	ND	4.7	3.4	7.1
<b>S5</b>					
<b>Fe</b>	48	15.9	670	2515	3200
<b>Cu</b>	ND	ND	1.8	2.9	14.1
<b>Cr</b>	ND	ND	2.8	6.7	8.2
<b>Zn</b>	4.1	6.9	61	10.2	13.8
<b>Ni</b>	ND	ND	3.4	5.6	6.1
<b>S6</b>					
<b>Fe</b>	3.4	14.1	437	1177	2816
<b>Cu</b>	ND	ND	1.9	2.8	11.1

<b>Cr</b>	ND	ND	ND	3.8	10.8
<b>Zn</b>	3.6	7.2	51	27	22
<b>Ni</b>	ND	ND	2.8	3.6	7.2
<b>S7</b>					
<b>Fe</b>	3.8	20	376	1812	2100
<b>Cu</b>	ND	ND	ND	3.8	13.7
<b>Cr</b>	ND	ND	2.7	4.2	3.9
<b>Zn</b>	3.1	5.6	48	22.2	5.2
<b>Ni</b>	ND	ND	2.2	5.8	5.4
<b>S8</b>					
<b>Fe</b>	5.6	31	487	789	1550
<b>Cu</b>	ND	ND	ND	5.2	10.5
<b>Cr</b>	ND	ND	3.1	5.9	10.2
<b>Zn</b>	2.9	3.8	28	56.1	3.8
<b>Ni</b>	ND	ND	2	3.6	4.7
<b>S9</b>					
<b>Fe</b>	4.2	30	710	815	2091
<b>Cu</b>	ND	ND	ND	2.9	13.6
<b>Cr</b>	ND	ND	ND	6.8	7.2
<b>Zn</b>	2.8	36.6	48.2	35.2	4
<b>Ni</b>	ND	ND	4.3	3.6	2.8
<b>S10</b>					
<b>Fe</b>	4.2	41	383	417	2967
<b>Cu</b>	ND	ND	2.8	6.1	7.6
<b>Cr</b>	ND	ND	2.6	7.2	8.9
<b>Zn</b>	3.1	6.7	39	48	14.1
<b>Ni</b>	ND	ND	3.2	4.7	8.6

Table. 4: Correlation matrix of physico-chemical properties

	<b>pH</b>	<b>EC</b>	<b>L.C</b>	<b>O.C</b>	<b>O.M</b>	<b>Na</b>	<b>K</b>	<b>Ca</b>	<b>Mg</b>
<b>pH</b>	1								
<b>EC</b>	-0.24254	1							
<b>L.C</b>	0.290489	0.136031	1						
<b>O.C</b>	0.06055	0.143958	0.460441	1					
<b>O.M</b>	0.060271	0.143614	0.460782	0.999999	1				

<b>Na</b>	0.306186	-0.16862	0.039197	-0.02991	-0.0298	1			
<b>K</b>	0.122615	-0.01109	0.257142	-0.36989	-0.36961	0.54071	1		
<b>Ca</b>	0.167285	-0.37008	0.105757	0.013353	0.0136	0.792584	0.372069	1	
<b>Mg</b>	0.286856	-0.29771	0.213373	0.110997	0.111252	0.823741	0.449958	0.966178	1

Only minor amounts of iron were detected in the carbonate and bound to exchangeable fractions and they were in the range of 0.25% to 1.08%. and 0.07% to 0.19% respectively. The amount of zinc found in the residual fractions was varies from 3.15%- 23.17%. The analysis shows that zinc has been bound to hydrated oxides of iron and manganese fraction in the range of 42.2– 68.9% and also was bound to organic matter fraction in range of 10.6%– 59.3%. In exchangeable fraction the metal concentration was below the detection limit. The carbonate fraction was found that 3.95% to 28.86%.

In the present study, nickel concentration was found in the fraction bound to organic that is varies from 13.18% to 43.28%, whereas 26.16%-73.18% in residual fraction. It was bounded to oxide metal fraction for nickel is 13.63% to 40.18% and in carbonate bound fraction it is lower than the detection limit.. The concentration of nickel found in exchangeable metal fraction is once again lower than the detection limit. Toxicity of nickel is not important because of its low concentration in the mobile and bio-available fractions.

Copper concentration in the soil samples have been found in organic matter fraction ranged from 13.9%-33.12% and varied in the range of 66.87%-86.09% in residual form. In the exchangeable, carbonate fraction it was lower than the detection limit. The fractions bound to hydrated oxides of iron and manganese was estimated that 9.57% to 12.02%. Copper is bound in residual fraction than Ni and is much less likely to be displaced by the hydroxylamine hydrochloride reagent.

The analysis of fractionation of heavy metal shows in smaller amounts of chromium bound to hydrated iron and manganese oxides fractions ranges from 14.49% - 22.47%. The chromium in the soil sample is mainly found in the residual fraction in the range of 36.11%– 73.97% and lesser in the range of 26.02%–48.57% bound to the organic matter.

In exchangeable fraction, except iron and zinc, the concentration of all metals in this fraction is lower than the detection limit. The amounts of metals released in the carbonate fraction represent a low proportion of the total metal concentration. Copper, chromium and zinc are below the detection range and iron has low concentrations in this fraction due to this fraction is susceptible to acid rain. In the fractions bound to hydrated iron and manganese oxides, the amounts of nickel, iron and zinc associated are relatively high. These amounts of metals would be released under reducing conditions. The metal levels in fraction associated with organic matter are relatively high and they represent a large fraction of the total metal concentrations. These amounts of metals are released in soil under strong oxidizing conditions and consequently this fraction constitutes an important source of potentially



available trace metals. It can be observed that the greatest part of the metals studies, especially iron was associated with the residual fraction. This fraction, named as 'inert phase', corresponds to the part of the metals which cannot be mobilised. When the metal concentration is more in the residual fraction, the mobility is very less and even it cannot move. From this concentration there is no such metals cannot be available in natural cycle.

#### IV. Conclusion

Pollution will occur from different sources in many ways either from natural or human made. When the pollution was caused by the nature, the effect of pollution is very low and pollution does not persist for a longer duration. When the pollution caused by the human beings the persistence capacity is more and it would cause very dangerous effects on the environment for the further more years. The present study of physico-chemical analysis of soil samples of Mysore city industrial area has shown optimum pH in all the soil samples. The organic matter and organic carbon (%) recorded showed minimum quantities during the study period. Increasing soil carbon can reduce the 25% of greenhouse gases created by agriculture and assist in ameliorating climate change. Increasing soil carbon will ensure good production outcomes and farm profitability. Soil carbon, particularly the stable forms such as humus increases farm profitability by increasing yields, soil fertility, soil moisture retention, aeration, nitrogen fixation, mineral availability, disease suppression, soil health and general structure. In this research work, results reveal that the soil has very low concentration of organic carbon and organic matter content. From the geochemical behavioral study the metals mobility is little low in the Exchangeable metal fraction and Carbonate bound metal fractions. But in the Fe– Mn oxide metal fraction and Organic and sulfide metal fractions mobility of the metals is comparatively little higher than the other fraction. If the mobility of the metals is higher in initial two stages of speciation, the toxicity will be more in nature and it can be bio available. In addition to that the heavy metals are at risky levels in the study area. After reaching the maximum level of contamination, it would percolate in to ground water and it result in bioaccumulation in the natural cycle. From the different processes going in industries releases toxic chemicals, discharging of untreated waste water, dumping of untreated solid waste to the surrounding environment leads to release of heavy metals, acids etc. When pollutants get contaminate with soil, it will lose their fertility by the loss of its microbes present in the soil. Here, the organic carbon (%) showed a value of 0.12 % to maximum of 0.41%, which clearly indicates that, soil fertility has reduced. All these above said pollution problems are arises from the increased industrial process. For the future years the proper environmental management aspect should be taken care in the industrial areas by industries itself by making proper treatment and disposal of waste materials to the environment.

**REFERENCES**

1. Alloway BJ (Ed.) 1990. Heavy Metals in Soils. John Wiley & Sons, New York.
2. Bal W, Kasprzak KS, 2002. Induction of oxidative DNA damage by carcinogenic metals. *Toxicology* 127:55-62.
3. Barak NAE, Mason CF, 1989. Heavy metals in water, sediment and invertebrates from rivers in eastern England. *Chemosphere* 19:1709-1714.
4. Bienvenue E, Boudou A, Desmazes JP, Gavach C, Sandeaux P, Seta P, 1984. Transport of mercury compounds across bimolecular lipid membranes: effect of lipid composition, pH and chloride concentration. *Chem Biol Interact* 48:91-101.
5. Burrows IG, Whitton BA, 1983. Heavy metals in water, sediment and invertebrates from a metal-contaminated river free of organic pollution. *Hydrobiologia* 106:263-273.
6. Chao TT, 1984. Use of partial dissolution techniques in geochemical exploration. *J Geochem Explor* 20:101-135.
7. Chapman PM, Allen HE, Z'Graggen MN, 1996. Evaluation of bioaccumulation factors in regulating metals. *Environ Sci Technol* 30(10) : 448A-452A.
8. Depledge MH, Weeks JM, Bierregaard P, 1998. Heavy metals. In: Callow P (Ed.). *Handbook of Ecotoxicology*. Blackwell Science, Oxford, pp. 543-569.
9. Elbay-Poulichet F, Martin JM, Huang WW, Zhu IX, 1987. Dissolved Cd behaviour in some selected French and Chinese estuaries. Consequences on Cd supply to the ocean. *Mar Chem* 322:125-136.
10. Forster U, Whittmann GTW, 1983. *Metal Pollution in the Aquatic Environment*. Springer-Verlag, Berlin.
11. GESAMP, 1990. *The State of the Marine Environment*. Blackwell Scientific Publications, Oxford.
12. Goyer RA. Toxic effects of metals. In: Amdur MO, Doull J, Klaasen CD (Eds.) 1991. *Casarett and Doull's Toxicology*, 4th edition. Pergamon Press, New York, pp.623-680.
13. Kullenberg G, 1986. The IOC programme on marine pollution. *Mar Pollut Bull* 17:341-352.
14. Kwapulinski, J., & Wiechula, D, 1993. Forms of selected heavy metals in the bottom sediments of Goczalkowice Reservoir. *Chemistry and environmental protection*, Ed. Polytechnical University of Lublin, 142.

15. Luoma SM, 1989. Can we determine the biological availability of sediment-bound trace metals? *Hydrobiologia* 176/177:379-396.
16. Malins DC, Ostrander GK (Eds.)1993. *Aquatic Toxicology-Molecular, Biochemical and Cellular Perspectives*. Lewis, Boca Raton, FL, pp. 387-420.
17. Market B, Friese K (Eds),2000. *Trace Elements. Their Distribution and Effects in the Environment*. Elsevier, Amsterdam.
18. McLaren,R.G. & Clucas, L. M.,2001. Fractionation of copper, nickel, and zinc in metal-spiked sewage biosolid. *Journal of Environmental Quality*, 30, 1968–1975.
19. Meria E, (Ed),1991. *Metals and Their Compounds in the Environment. Occurrence, Analysis and Biological Relevance*. Verlag Chemie, New York.
20. Newman MC, McIntosh AW (Eds)1990. *Metal Ecotoxicology, Concepts and Applications*. Lewis, Boca Raton, FL.
21. Nriagu JO (Ed.),1978. *The Biogeochemistry of Lead in the Environment. Part A. Ecological Cycles, Part B. Biological Effects*. Elsevier/North Holland Biomedical Press, Amsterdam.
22. Nriagu JO (Ed.)1979. *Copper in the Environment. Parts 1 and 2*. Wiley Interscience, Chichester, UK.
23. Nriagu JO (Ed.)1980. *Zinc in the Environment, Parts 1 and 2*. Wiley Interscience, Chichester, UK.
24. Nriagu JO (Ed.)1980. *Cadmium in the Environment Part 1*. Wiley Interscience, Chichester, UK.
25. Nriagu JO, Nieber E (Eds.)1987. *Chromium in the Natural and Human Environment*.Wiley & Sons, New York.
26. Nriagu JO, Pacyna JM,1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* 333:134-139.
27. Pennelas J, Filella I, 2002. Metal pollution in Spanish terrestrial ecosystems during the twentieth century. *Chemosphere* 46: 501-505.
28. Phillips DJH,1995. The chemistries and environmental fates of trace metals and organochlorines in aquatic ecosystems. *Mar Pollut Bull* 31:193-200.
29. Rainbow PS,2007. Trace metal bioaccumulation: Models, metabolic availability and toxicity. Review. *Environ Int* 33: 576-582.
30. Rand GM, Petrocelli SR (Eds)1985. *Fundamentals of Aquatic Toxicology. Methods and Applications*. Hemisphere, New York, pp. 374-415.

31. Salomons W, Forstner U, 1984. Metals in the Hydrocycle. Springer-Verlag, Berlin.
32. Schindler PW, 1991. The regulation of heavy metals in natural aquatic systems. In: Vernet JP (Ed.) Heavy Metals in the Environment. Elsevier, Amsterdam, pp. 95-123.
33. Sprenger M, McIntosh A, 1989. Relationship between concentrations of aluminium, cadmium, lead and zinc in water, sediments and aquatic macrophytes in six acidic lakes. Arch Environ Contam Toxicol 18:225-232.
34. Sunda WG, Engel DW, Thuotte RM, 1978. Effect of chemical speciation on toxicity of cadmium to grass shrimp *Palaemonetes pugio*: importance of free cadmium ion. Environ Sci Technol 12:409-413.
35. Zamuda CD, Sunda WG, 1982. Bioavailability of dissolved copper to the American oyster *Crassostrea virginica*. I. Importance of chemical speciation. Mar Biol 66:77-82.
36. Zufiaurrea, R., Olivara, A., Chamorroa, P., Nerín, C., & Callizoa, A., 1998. Speciation of metals in sewage biosolid for agricultural uses. Analyst 123, 255– 259.