Influence of Agriculture on Water Quality: Significance of Heavy Metals Monitoring

Nusreta ĐONLAGIĆ (✉)
Amra ODOBAŠIĆ
Amra BRATOVČIĆ

Summary

Agricultural activities directly influence the quality of water systems. Investigations showed that application of various agro-technical measures results with the pollution of water streams with heavy metals and other polluters. Increased concentrations of heavy metals result with intake of heavy metals and their transfer to food chains, and for that reason it is necessary to monitor the content of heavy metals regularly. Broad investigations of bio-geochemical cycling of heavy metals in the region of Lake Modrac were performed with combined methodology of determination of heavy metal traces with the estimation of bioavailability, based on the determination of complexing constants for Pb, Cu, Cd and Zn. Monitoring was performed at the locations in the vicinity of agricultural soil. The results achieved showed that the content of organic matter in water streams presents the key factor that determines the extent of bioavailability of heavy metal traces in water systems.

Key words

agriculture, monitoring, heavy metals, bioavailability

Universty of Tuzla, Faculty of Technology,
Univerzitetska 8, 35000 Tuzla, Bosnia and Herzegovina
✉ e-mail: nusreta.djonlagic@untz.ba

Received: November 24, 2006 | Accepted: April 16, 2007

Introduction

Conventional agriculture is the major polluter of an environment, especially if the chemicals are used without control. The development of fertilisation is closely related to the agriculture development. Due to its chemical composition and raw materials, fertilisers can be polluters of water and soil. Uncontrolled application of fertilisers without the knowledge of soil characteristics increases the risks of pollution. In the areas of intensified agriculture water streams are endangered, and pollution with heavy metals, nitrates, phosphates, pesticides and polycyclic aromatic hydrocarbons is the reality.

Nitrogen from mineral and organic fertilizers is present in soil, and with flooding of arable land it is transferred into water streams. Especially nitrates present great danger and are intensive polluters of underground water streams. With the adsorption of NH_4^+ in complexes with the soil constituents, part of nitrogen intake is bound and unavailable.

As a consequence of nitrogen accumulation in Lake Modrac process of eutrophication is very intensive, and flora and fauna of the aquatic systems are endangered. (HEIS, 2006)

Seasonal stagnation of water streams, as well as an increase of nutrient content results in trophic status of the hydro accumulation of Modrac, as well as seasonal blooming of phytoplankton. The main cause for the intensive eutrophication is the increase of nutrient content.

Phosphorus fertilizers are also used in conventional agriculture and they contain heavy metals (Cd, Ni, Cr, Hg and Zn). Their content depends on the origin of fossil raw materials. The pollution with cadmium is usual consequence of application of these fertilizers. The addition of phosphate fertilizers could help in immobilisation of lead with the formation of lead-phosphate compounds.

The cadmium content in soil is very low (below three ppm), and cadmium pollution is largely caused by mineral fertilizers, organic fertilizers and fertilizers produced from sludge. Addition of NPK (Nitrogen, Phosphorous and Potassium) fertilizers could cause the increase of heavy metal content in agricultural soil, i.e. lead, zinc, iron and cadmium (Keran, 2006).

From the ecological aspect, it is important to monitor the content of all heavy metals, because of their toxicity and the fact that they can not be biodegraded in soil, but they can accumulate in soil for very long period (Kabata-Pendias and Dudka, 1991).

Heavy metals could be present in soil in the form of hydrates, hydroxiderivates, as inorganic cations; metal complexes with organic compounds or organometallic compounds with chemical bonds of C-M type. Depending on the form in which metal exists, the bioavailability of metals and their biological effect and motion in the water layers are defined (Filipović and Lipanović, 1998).

Metals that present toxic polluters are transition metals and they are characterised by closed structure. Cu, Cd, Pb and Hg present Lewis acids with tendency to bind with Lewis bases, such as sulfids (Odobašić, 2005). Toxicity of these metals is primary due to their tendency to exchange with other metals with biological function, in enzymes, and form very strong bonds. Critical concentrations of some heavy metals in natural waters are given in Table 1.

Forms and amounts of a given metal that can be adsorbed by an organism can be defined as bioavailable. Therefore, bioavailability is one of keys to understanding of chemistry of heavy metals in soil (Grzbisz et al., 1997; Kabata-Pendias and Pendias, 1992).

Taking into the consideration the environment of Modrac Lake as well as water streams coming from agricultural land and from nearby coal separation, it is important to monitoring the content of heavy metals, such as lead, copper, zinc and cadmium and their speciation and availability. Also, water from Modrac Lake is used for agricultural purposes in down streams, where big Spreca valley is under agricultural crops used in nearby fruit and vegetable processing factory.

The main purpose of this work is to implement the new methodology in monitoring of heavy metals in combined approach of monitoring the physical and chemical characteristics of water, heavy metal trace analyses and determination of complexing capacity with respect to the bioavailability of heavy metals.

Material and methods

Monitoring of heavy metals content in Lake Modrac was performed in four year's seasons, as well as physical and chemical characteristics and the complexing capacity of copper.

Electroanalytical Differential Pulse Anodic Stripping Voltammetry (DPASV) technique was used in metal trace analyses. This method has advantages with respect to other classical methods because of the simplicity, higher sensitiv-

Table 1. Critical concentrations of some heavy metals in natural waters (EPA)

Metal	Maximal allowed concentration (μg ml^{-1})
Mercury	0.002
Arsenic	0.5
Lead	0.5
Copper	0.6
Cadmium	0.04
Zinc	5

Table 2. Half-wave potentials

Metal	Initial potential (mV)	Final potential (mV)
Pb	-0.65	-0.25
Cu	-0.45; -0.35	0; 0.05
Cd	-0.9	-0.6
Zn	-1.2	-0.9

Table 3. Chemical composition of Lake Modrac water

Chemical composition	Concentration [mg l^{-1}]
carbonate	15
bicarbonate	125
nitrogen	0.21
nitrate	0.12
chloride	8.5
sulphate	82.2
calcium	38.1
magnesium	26.7
Ionic strength, I (mol l^{-1})	$7.400 \cdot 10^{-3}$

Table 4. Heavy metals content in Lake Modrac in four year's seasons

Metal	Summer (mg l^{-1})	Autumn (mg l^{-1})	Winter (mg l^{-1})	Spring (mg l^{-1})
Pb	0.157	0.026	0.01	0.028
Cu	$9.36 \cdot 10^{-4}$	$6.43 \cdot 10^{-4}$	$4.43 \cdot 10^{-4}$	$7.96 \cdot 10^{-4}$
Cd	$1.65 \cdot 10^{-4}$	$2.56 \cdot 10^{-4}$	-	$8.85 \cdot 10^{-5}$
Zn	0.0023	0.0065	0.0098	0.003

ity and due to the fact that it is possible to determine the chemical form in which metal exists, stability constants and complexing capacity.

Electrochemical cell, Princeton Applied Research model 303 A, with 10 ml volume and with working, reference and counter electrode, was used. Voltammetric measurements were supported by software programme Model 270/250 Research Electrochemistry Software, vers.4.3.

As working electrode, HMDE electrode was used, Ag/AgCl reference electrode and platinum wire counter electrode.

High purity chemicals from Merck were used (HNO_3, $HClO_4$, HCl and KNO_3).

All samples were treated with redistilled ultrapure water. Standard solutions of heavy metals (Pb, Cd, Cu and Zn) were prepared in range 10^{-4} – 10^{-8} mol l^{-1} from supra pure nitrate standard solutions in supra pure HNO_3.

Water samples were taken from the same depth of 2.5 m and treated in accordance with AOAC standard (Odobašić, 2005).

Instrumental parameters in DPASV measurements:

— working electrode HMDE

— reference electrode Ag/AgCl (E = 0.222V)

— deaeration time with N_2 120 sec

— stabilisation time 15 s

— scanning rate 2 mV/s

— deposition time 300 s

Half-wave potentials for each metal are given in Table 2.

Results and discussion

The results of monitoring of chemical characteristics of Lake Modrac are given in Table 3. The results of voltammetric investigations with DPASV method are presented for Cd, Pb, Zn and Cu in figures 1-4. The results of monitoring of heavy metals content in Lake Modrac in four year's seasons are given in table 4.

Complexing capacity, CC, was determined for copper, since complexing of copper is considered as representative for the complexation of heavy metals and as a measure of their bioavailabilty. CC value for Lake Modrac water was $1.06 \cdot 10^{-8}$ mol l^{-1}, and stability constant was $2.5 \cdot 10^{9}$, what corresponds to very stable complex, even compared to CuEDTA which is considered as very stabile.

Toxicity of dissolved metal species is related to the ability to react with biological membrane, depending on the lipid solubility of metal, as well as on the reaction rate of metal species with membrane proteins.

Observed pH values of Lake Modrac are in critical range for the adsorption of heavy metals on particles, so that very small change of pH could cause the disruption of

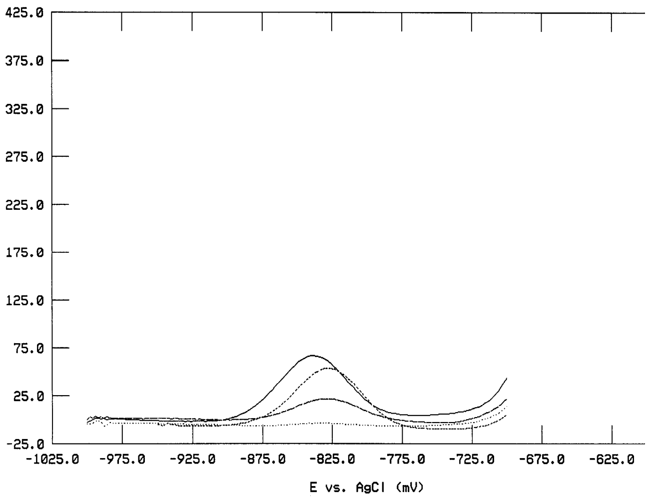

Figure 1.
Cadmium in Lake Modrac water in summer period

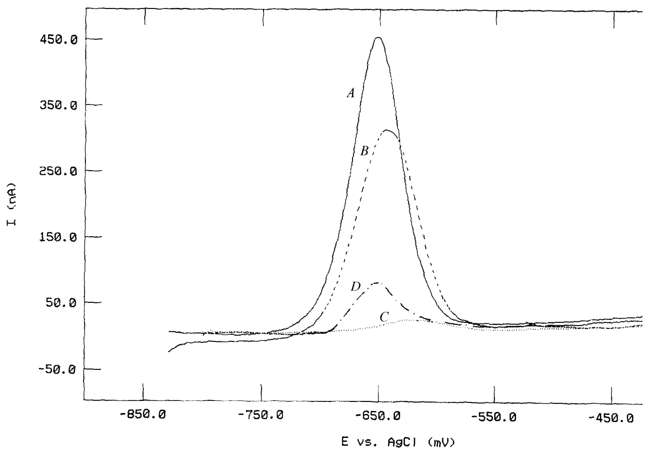

Figure 2.
Lead in Lake Modrac water in summer period

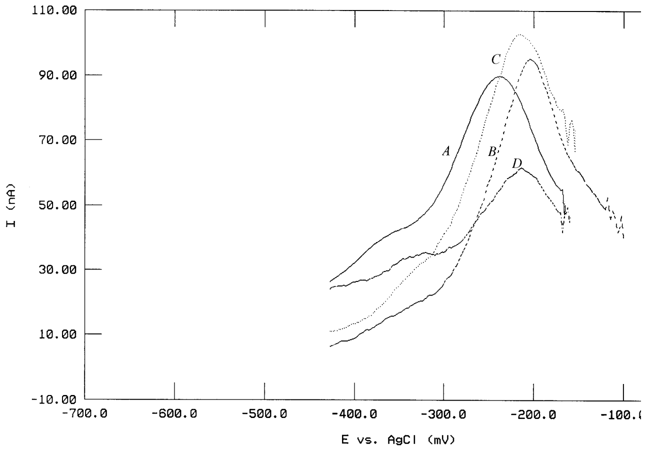

Figure 4.
Copper in Lake Modrac

equilibrium between adsorption and desorption process, which are vital in regulation of solubility and availability of heavy metals. pH value of lake water was from 6.5 in summer period until pH 8 in winter period.

The results of investigations showed that concentrations of labile fractions of heavy metals traces (Pb, Cu, Cd, Zn) were below maximally allowed limits in all four year's seasons in accordance with EPA.

The content of lead in Lake Modrac water was in the range of maximally allowed concentration, The content of copper was ten times lower, on average 10^{-8} mol l^{-1}.

The content of zinc was relatively high and could be attributed to soil characteristics and sediment characteristics of Lake Modrac.

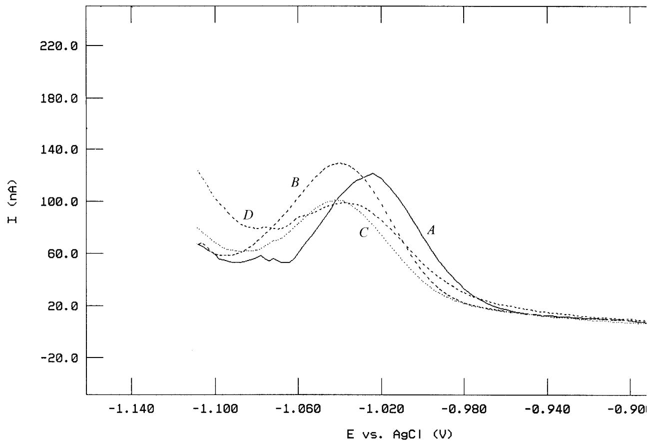

Figure 3.
Zinc in Lake Modrac water in summer period water

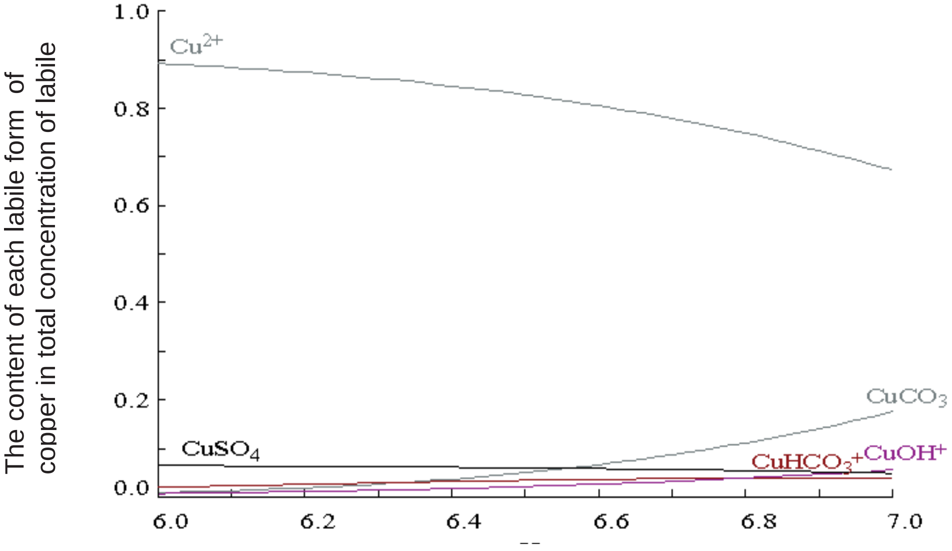

Figure 5.
Inorganic speciation of copper

Cadmium content is very low, and relatively sensitive DPASV technique allows accuracy of order 10^{-10} mol l^{-1}.

Results of investigations showed that concentrations of heavy metals were the highest in the summer period. Beside total concentrations of metals bound in labile and inert chemical forms, very important is the effective total concentration of ligand, C_L and apparent stability constant, K, of metal-ligand complex in water matrix. Ligand concentration presents the capacity of forming the complex with heavy metals.

Complexes of heavy metals with high K values are not biodegradable, and thus they are less toxic.

With pH of water in range 6.5-8, what is the characteristic for most seasons, metal ions of Pb, Cu, Cd and Zn easily dissociate into free metal ions which can enter the adsorption processes, which are fast and could be considered as equilibrium processes.

Conclusion

Total concentrations of heavy metals, Pb, Cd, Cu and Zn, were below maximally allowed concentrations in accordance with EPA and WHO[7], with concentrations of lead in the upper maximally allowed limit.

Higher concentrations in summer period can be attributed to lower pH values (6.5) where desorption of labile metal complexes take place. In summer period eutrphicity of lake takes place accompanied by the change of oxido-reduction conditions. Higher temperature and higher oxygen content play significant role in the increase of availability of heavy metal ions.

The value of complexing capacity shows that significant amount of organic active matter was present, which tend to bind heavy metals (copper) into inert complexes that decrease availability of toxic metals.

Due to the fact that about 45% of land around Lake Modrac is agricultural soil where different fertilizers and pesticides are used in regular agricultural practice, it is important to monitor the content and availability of heavy metals with combined methodology of determination of total content of heavy metals and speciation of metals for the purpose of defining the metal active species and their labile and inert complexes, as well as complexing capacity, as the measure of complexation with organic matter and bioavailability of metals.

References

HEIS (2006): Okvir za primjenu najboljih poljoprivrednih praksi usmjerenih na kontrolu difuznog zagađenja u Federaciji Bosne i Hercegovine, Hydroengineering Instutute Sarajevo.

Kabata-Pendias, A.; Dudka, S. (1991): Trace metal contents of Taraxacum officinale (dandelion) as a convenient anvironmental indicator. Environ. Geochem. Health. 13: 108-113

Grzebisz, W.; Kociałkowski, W.Z.; Chudziński B. (1997): Copper geochemistry and availability in cultivated soils contaminated by a copper smelter, Jour. of Geochemical Exploration 58, 301-307

Kabata-Pendias, A.; Pendias H. (1992): Trace elements in soils and plants, CRC Press Inc, Boca Raton, Florida, USA. (2nd Edition), 365.

Filipović; J.; Lipanović, S. (1998): Opšta i anorganska kemija, II dio, Zagreb.

Keran, H. (2006):: Faktori unosa teških metala u povrće i ocjena rizika unosa primjenom HACCP koncepta, Doktorska disertacija, Univerzitet u Tuzli, BiH.

Odobašić, A. (2005): Specijacija teških metala polarografskim tehnikama u prirodnim vodama, Doktorska disertacija, Univerzitet u Tuzli, BiH.

---

acs72_62