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ESTIMATION OF METALS BIOAVAILABILITY IN RIVER WATERS BY IN SITU SPECIATION USING THE TECHNIQUE OF DIFFUSION GRADIENTS IN THIN FILMS (DGT)

MARIN ŞENILĂ[a], ERIKA-ANDREA LEVEI[a], CECILIA ROMAN[a], LĂCRIMIOARA ŞENILĂ[b], BELA ABRAHAM[a], CORDOŞ EMIL[a,b]

ABSTRACT. Trace metals such as Cu, Zn, Mn and Ni play an important role as essential elements in aquatic systems. Elevated concentrations of these elements and of non-essential elements such as Cd, however, may be toxic. Investigation of the speciation of trace metals is a prerequisite to evaluating their bioavailability and mobility. Biological responses of organisms often have been shown to be related to the free-ion activity of a metal ion or to the concentration of labile metal species in solution. We evaluated the application of DGT as a tool to determine Cu, Zn, Ni, Cd and Mn concentrations and speciation in Crisul Alb River. Total metals, dissolved metals and labile-DGT metals concentration were determined. The DGT-labile species of Cu and Zn amounted to 15–30% of the total dissolved concentrations, Cd and Ni to 40-50% and Mn to 70-80%.

Keywords: *DGT, metals bioavailability, speciation, ICP-MS*

INTRODUCTION

The developed technique of Diffusive Gradients in Thin-films (DGT) is used to measure in situ concentrations and fluxes of trace substances in sediments and natural waters. It operates by introducing a localized sink which induces a diffusional flux to the DGT device [1].

DGT can be used for many different purposes, including: in situ measurements, monitoring (time averaged concentrations), speciation (labile inorganic and/or organic species), bioavailability (effective concentration), fluxes in sediments and soils, kinetic and thermodynamic constants, high spatial resolution measurements (sub-mm), 2D concentration images.

Reliable measurements of trace metal speciation in the aquatic environment are essential for studies of trace metal cycling and metal bioavailability [2].

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[a] *INCDO-INOE Institutul de Cercetări pentru Instrumentație Analitică, Str. Donath Nr. 67, RO-400293 Cluj-Napoca, Romania, icia@icia.ro*

[b] *Universitatea Babeş-Bolyai, Facultatea de Chimie şi Inginerie Chimică, Str. Kogălniceanu, Nr.1, RO-400084 Cluj-Napoca, România*

DGT - diffusive gradients in thin-film technique comprises a layer of hydrogel overlying a layer of immobilised binding agent (ion-exchange resin) [3-6]. The DGT technique is based on Fick's first law of diffusion. By ensuring that transport of metal ions to an exchange resin is solely by free diffusion through a gel layer of known thickness, the concentration in the bulk solution can be calculated from the metal mass measured in the resin. If a sufficiently thick diffusion layer is selected, the flux of metal to the resin is independent of the hydrodynamics in solution above a threshold level of convection [7-9].

The response of DGT devices depends on a variety of factors, including reaction and transport parameters, DGT assembly design, and sediment characteristics. In an effort to quantify the influence of some of these on DGT response, Harper et al. developed the DIFS (DGT Induced Fluxes in Sediments and Soils) model, which they used principally to investigate the effect of different resupply regimes on DGT measurements. As a result they were able to derive in situ estimates for solute resupply kinetics and capacities of solid phase reservoirs [10].

We evaluated the application of DGT as a tool to determine Cu, Zn, Fe, Co and Mn concentrations and speciation in Crisul Alb and Certej River. Total metals, dissolved metals and labile metal species concentration were determined.

EXPERIMENTAL SECTION

The *in situ* measurements were performed in June 2007, by placing the DGT devices for two days in Certej and Crişul Alb river water. The locations of the two selected catchments are presented in figure 1.

Unfiltered, filtered and DGT water samples were collected from five sampling points in Crişul Alb and three sampling points in Certej. Sampling points description are presented in table 1.

All reagent used were of analytical grade (suprapure nitric acid). Ultrapure water was used obtained using a Millipore system. DGT deployment units from DGT Research Ltd Lanchester, UK were used for deployment on the domain. An OI Analytical Microwave digestion unit was used for samples digestion. All instrumental determinations were done using an ICP-MS ELAN DRC II, Perkin-Elmer with reaction cell for reducing interferences.

Clean bottles (washed with nitric acid 0.2 M) were used to collect water samples. For total metals determinations, unfiltered water was sampled and acidulated immediately on the field (pH<2) using 2-3 drops of concentrate nitric acid suprapure. The collected samples were then digested in laboratory using the digestion unit.

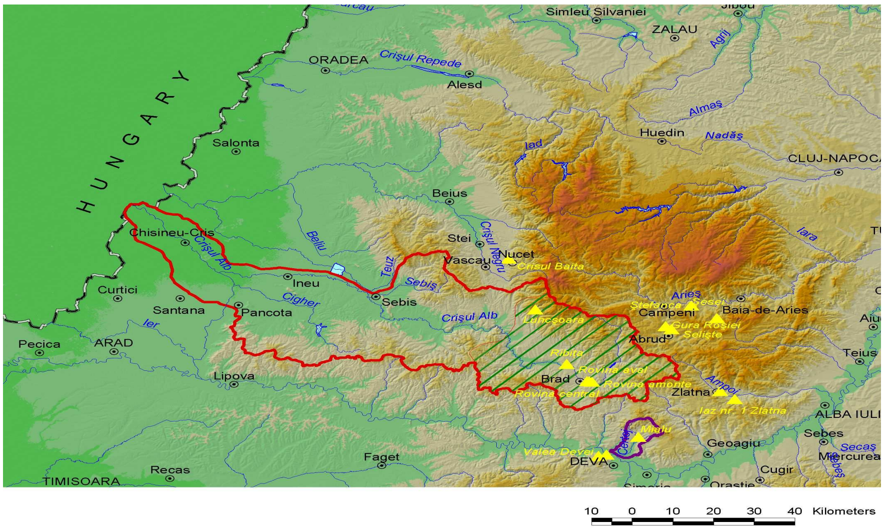

Figure 1. Crişul Alb and Certej catchments.

Table 1.

Sampling points in Crişul Alb and Certej.

Sampling Points	Locations	Comments	Water pH values (measured on the field)
CA1	Crişul Alb, Varsand, near to Hungarian boundary	Slightly polluted	7.47
CA2	Crişul Alb, Ineu	Slightly polluted	7.90
CA3	Crişul Alb, Gurahont	Slightly polluted	8.30
CA4	Crişul Alb, Brad, downstream Rovina dam	Slightly polluted	7.82
CA5	Crişul Alb, Criscior, backgroud	Natural background for Crisul Alb	8.17
C1	Certej, Harau	Polluted	4.92
C2	Certej, near Mialu dam	Polluted	2.54
C3	Certej, near acid mine stream	Polluted	2.98

For total dissolved metals determinations, the water samples were filtered on the field using syringes with filter holder (0.45 micron) and acidulated to pH<2.

DGT labile metal species were measured by deploying the DGT devices in the river water for metals accumulation. After two days, the devices were retrieved and the resins containing the retained metals were placed into plastic tubs and 10 ml nitric acid 1 M was added for metals elution.

RESULTS AND DISCUSSIONS

Total, total dissolved and labile DGT concentrations of Cu, Zn, Fe, Co and Mn were measured simultaneously by ICP-MS. The total and total dissolved concentrations were measured directly by ICP-MS. Calculations of the DGT measured concentration are based on the Fick's first law of diffusion:

$$F = D\,dC/dx \qquad (1)$$

where,

F - steady state flux of an ion
D - diffusion coefficient
dC/dx - concentration gradient

Each metal has a specific diffusion coefficient trough the diffusive gel. After measurement of metals in elution solution, we calculated the mass of metal accumulated in the resin gel layer (M) using equation (2):

$$M = Ce\,(V_{HNO3} + Vgel)/fe \qquad (2)$$

where,

Ce is the concentration of metals in the 1M HNO_3 elution solution (in µg/l)
V_{HNO3} is the volume of HNO3 added to the resin gel
V_{gel} is the volume of the resin gel, typically 0.15 ml
fe is the elution factor for each metal, typically 0.8

The concentration of metal measured by DGT (C_{DGT}) can be calculated using equation (3).

$$C_{DGT} = M\Delta g/(DtA) \qquad (3)$$

where,

Δg is the thickness of the diffusive gel (0.8mm) plus the thickness of the filter membrane (typically 0.14 mm)
D is the diffusion coefficient of metal in the gel
t is deployment time
A is exposure area (A=3.14 cm^2)

The obtained results for measured concentrations of Cu, Zn, Fe, Co and Mn are presented in figure 2.

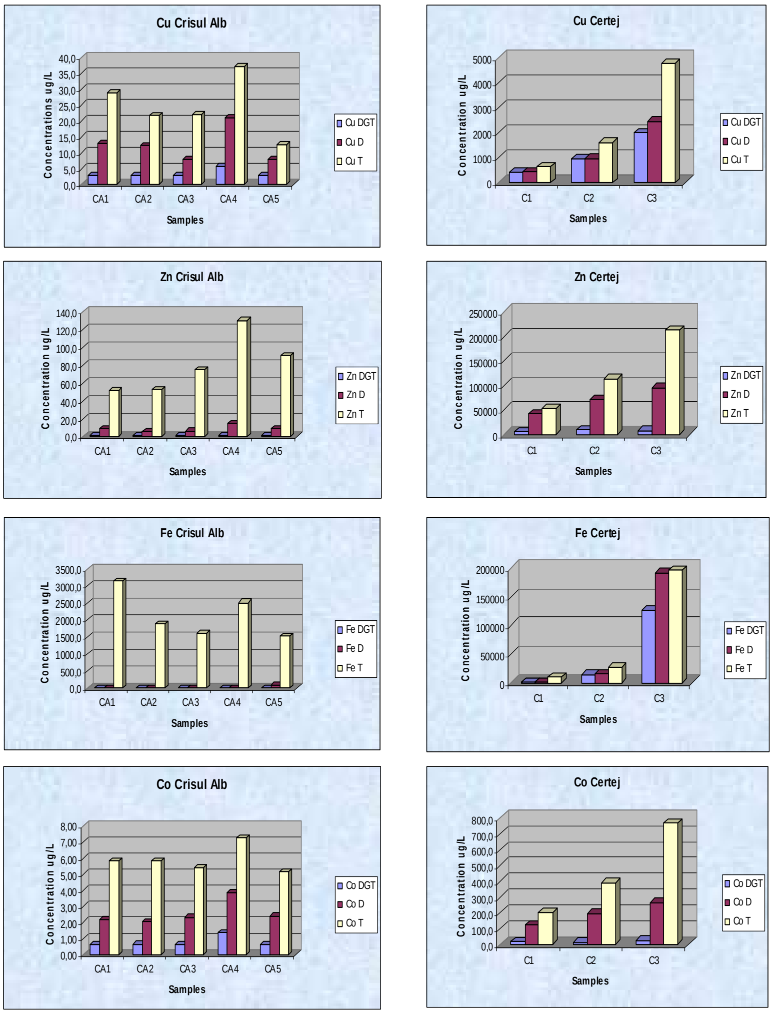

Figure 2. Total, total dissolved and DGT labile metals in Crişul Alb and Certej.

CONCLUSIONS

The DGT-labile species of Cu and Zn amounted to 15–30% of the total dissolved concentrations, Cd and Ni to 40-50% and Mn to 70-80%.

A slight pollution of Crisul Alb River with heavy metals can be observed. The pH values ranged between 7.47 – 8.30 and the higher concentrations of heavy metals were founded in particulate matter. Also, from total dissolved concentration only a low part is in labile forms.

In the sampling stations from Certej the pH values ranged between 2.54 and 4.92 indicating a strong impact of acid mining drainages. High concentrations of heavy metals were founded, a high proportion in dissolved form and most then that, bioavailable.

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