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Monitoring and flux determination of trace metals in rivers of the Seversky Donets basin (Ukraine) using DGT passive samplers

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Abstract

This paper reports the results of the *in situ* application of diffusive gradients in thin-films (DGT) passive samplers for trace metals (Cd, Co, Cr, Cu, Ni, Pb and Zn) monitoring in transboundary Udy and Lopan rivers of the Seversky Donets watershed in the Kharkiv region, Ukraine, which has a long history of industrial development. The research discusses potential sources of DGT-measured labile metals in water and seasonal variations. Also, our results demonstrate the performance of using DGT to identify and to measure labile metal concentrations in contrasted climate conditions (cold snowy winter and hot summer) and appropriateness of such a tool for continuous water monitoring with the presence of an ice cover. Results show that DGT-measured concentrations of most of trace metals were much higher downstream of the wastewater treatment plants discharges than upstream; thus wastewater treatment plants seem not able to reduce or to remove the trace metals contaminations and become major sources of studied pollutants in the studied rivers. The calculation of the average metal fluxes to base on the DGT-measured concentrations confirmed that urban wastewater discharges significantly contribute to the metal fluxes into the Udy and the Lopan rivers during both low-flow and high-flow periods. Compared to the wastewaters inputs in the rivers, the transboundary effect is limited, but should also be taken into account as the origin of some metals is from sources located on the adjacent Russian territory.

Keywords: Passive Samplers, DGT, Trace Metals, Transboundary Rivers, Water Treatment Plant, Seasonal Variation, Eastern Europe

1. Introduction

Ukraine is one of the post-soviet East European countries (46,08 million inhabitants by 2009) with a long history of large-scale industrial and agricultural activity. It borders Romania, Slovakia, Poland, Russia, Belarus and Moldova and shares transboundary watersheds with these countries. Earlier studies on the contamination of water bodies in the eastern part of Ukraine (Linnik, 2003; Vasenko et al, 2006) showed that concentrations of Cu, Zn, Cr, and Pb are not in the agreement with national water quality standards (GCPL, 1991; SNPL, 1991) (Table 1). These investigations concluded that the main sources of metals are transboundary effluents, discharges of treated wastewaters and run-off from urban and agricultural areas.

In spite of the importance of the evaluation of the metal contamination in natural waters, the monitoring of these elements in Ukraine is not regular and yet insufficient. Limiting factors for an adequate water monitoring are the lack of equipment and financing for research laboratories and environmental control authorities (e.g. the Ministry of Environmental Protection). The number of sampling sites is usually limited to just two or three per river and only rivers receiving effluents from wastewater treatment plants are monitored. The water monitoring laboratories in Ukraine use mostly grab methods of sampling, which do not take into account influences (e.g. changes in hydrologic conditions and/or pollutants inputs). Moreover only the total concentrations of metals are determined, no evaluation of other metals forms and metals bioavailability is conducted. Thus, there is a lack of data on the presence of labile metals in rivers of industrial areas of Ukraine, whereas it is well-known that they play a crucial role in the bioaccumulation and eco-toxicity in living organisms (Alfaro-De la Torre et al, 2000; Janssen et al, 2003).

In order to improve the knowledge on labile metals concentrations and fluxes of this metal form in rivers of industrial and urbanized areas of Ukraine, *in situ* water sampling was undertaken using the passive sampling technique as diffusive gradients in thin-films (DGT) technique. This passive sensor tool was developed about 20 years ago at Lancaster University for the integrative

sampling and measurement of dissolved labile metals. It bases on the diffusion of metals through a hydrogel layer of a certain thickness to a binding phase where they are concentrated (Buffle and Horvai, 2000; Zhang and Davison, 2000; Motelica-Heino et al, 2003). DGT samplers have been increasingly used for measuring labile metal concentrations in the aquatic environment, soils and sediments (Meylan et al, 2004; Buzier at al, 2006; Dunn et al, 2007; Roulier et al, 2008; Schintu, et al., 2008). The DGT technique demonstrates simplicity of deployment and retrieval during the field procedures, minimum sample handling between installation and analysis and easy storage (Denney et al, 1999). Compared to grab sampling and subsequent laboratory analysis of spot samples, DGT are used without additional reagents, energy sources and DGT-measurements are able to reduce the risk of uncontrolled changes that can occur during the sampling, storage or treatment (Alfaro-De la Torre et al, 2000). Because of the pre-concentration capability of DGT that integrates temporal variations in the sampled media; lower metal concentrations can be measured in water in contrast to grab sampling. This integrating property helps to take into account different pollution events (run-off, random wastewaters discharge and etc) even if the sampling frequency is not high enough.

Other important point is that DGT shows very positive results while used in various climate conditions. There are in fact evidences of successful application of the DGT technique from subtropics (Denney et al, 1999; Dunn et al, 2003) to the polar environments (Larner et al, 2006; Stark et al, 2006). This is an important issue for the utilisation of these sensors in very continental regions with hot dry summer and cold snowy winter, despite potential problems with highly diluted waters (ionic strength lower than 2×10^{-4} M) (Alfaro-De la Torre et al, 2000). With adequate detection limits and accuracy, the technique suites to the monitoring of labile metals in various aquatic environments such as coastal and seawaters (Australian seawaters: Munksgaard and Parry, 2003), rivers (Sava River, Croatia: Dragun et al, 2008) and lakes (5 lakes in England: Gimpel et al, 2003).

This paper discusses the presence of priority trace metals as Cd, Cu, Cr, Pb, Ni and Pb, but also the potentially toxic metal as Co in labile forms in the Udy and Lopan rivers of industrial and urbanised the Kharkiv region, Ukraine, the origin and fluxes of labile trace metal forms in the studied water bodies, seasonal variations in metal concentrations and whether these metals are problematic for the long-term exploitation of transboundary water resources according to the water regulation standards.

2. Methods

2.1. Sampling area

Deployment of DGT samplers was conducted in the Lopan and Udy rivers of the Kharkiv region (Eastern part of Ukraine) during August 2008 and January 2009. These alluvial transboundary rivers are extensively used for recreation activities, drinking water supply, irrigation and fishing in the Belgorod region of Russia and the Kharkiv region of Ukraine (about 4,500,000 inhabitants totally in both regions). Major anthropogenic factors able to impact on these water bodies are associated with the long-term industrial and municipal water supply, as well as discharges of wastewaters (Vasenko et al, 2006).

The Kharkiv region is one of the largest industrial regions in Ukraine, with a population of ca. 3 million (2009). During the soviet times (1919-1990), an extensive industrial development took place in the region featuring military production, machinery, mechanical, electrical, chemical and radio-electronic engineering. This region is characterized by a relative scarcity and an uneven distribution of available resources of freshwater. Regional water supply for the household and industries is mostly coming from surface water sources (85% of the total consumption). The Udy and Lopan rivers, with a total catchment area in Ukraine of about 3460 km², along which the city of Kharkiv is located (Figure 1) have their sources in the Forest-Steppe natural zone of the southern slopes of the Mid-Russian rolling plane. Soils of the region are represented by grassland *chernozems* and grey forest types. The duration of winter is about 125 to 130 days, and the warm

period is about 118 to 200 days per year. The coldest month is January (average temperature of -7.1°C), and the warmest is July (average temperature of +20.5°C). The mean annual temperature is around 7.6 °C and rainfall amount varies between 470 and 540 mm per year (Jakovlev et al, 2002).

The total length of the Udy River is 164 km and its tributary, the Lopan River, is about 98 km long. The river depth ranges from 0.4 to 2.3 m and their flows are regulated by several dams constructed along the watercourses. The mean annual discharge of the Lopan River is 1.4 m³ s⁻¹ in winter and 0.9 m³ s⁻¹ in summer whereas the discharge of the Udy River is 6.8 m³ s⁻¹ and 2.5 m³ s⁻¹, respectively. Rivers are partly covered by ice from the end of November to the end of March. The subsurface geological structures of the catchment area are dated from Palaeogene and consist mainly of sedimentary rocks like sandstone, marl and chalk. The major land use categories on the watershed are agriculture (40 %), urban lands (50%) and water reservoirs (10%).

Both rivers are still impacted by metal inputs from urban and agricultural origin despite the significant decrease of production activities after the collapse of the Soviet Union; in fact the water quality has not improved since (NRDW, 2006). These rivers receive the most of the municipal and industrial wastewaters (about 1,000,000 m³ per day). Wastewaters are discharged into the same river basins, which are used for water supply, thus the aquatic pollution has a strong impact on the sanitary conditions and on the health of the population (NRDW, 2006).

2.2. River water sampling

Four sites on the Udy River and four sites on the Lopan River were selected with special attention to the potential pressure points on the watercourses, like sewage treatment plants, landfill sites or inputs from industries and the urban areas themselves (Figure 1). DGT samplers with a 0.4 mm resin gel layer, a 0.8 mm diffusive gel layer and a 0.45 µm pore-size filter were purchased from DGT Research Ltd. (Lancaster, UK). In August 2008 and January 2009, DGT

probes were deployed at selected sampling sites for a period from 15 to 30 days. The duration of DGT-samplers exposure was chosen based on the low flow (July-August) and the high flow (January-February) data in order to compare two extreme periods of the hydrological cycle.

Probes were exposed using a fishing line and attached at a depth of 0.20 – 0.25 m to avoid turbulent flow zones. During the winter campaign, samplers were installed at a depth of 0.15 m below the ice-layer, the thickness of which varied from 0.05 to 0.20 m. For stations all stations duplicate DGT probes were installed to allow the estimation of the reproducibility of the measurements and intra-site variation. In order to prevent the contamination of DGT by trace elements from the air, the probes were open from the plastic protection at sampling sites and installed immediately in the water. After the retrieval the DGT were therewith packed in the plastic protection. The DGT probes were stored before the analysis at a temperature of 4 °C in plastic bags and in humid conditions (a few drops of distilled water were added to allow some moisture).

Two DGT probes were used as blanks i.e. were only exposed to air in the laboratory but not set in the water. Water temperature, pH and conductivity were measured *in situ* with a WTW[®] Multiline P4 meter. The water temperature at sampling points ranged between 19.0 and 25.0 °C during the summer and between 2.0 and 7.0 °C during the winter sampling campaigns. Conductivity varied from 1010 to 1360 μScm^{-1} and pH from 6.8 to 7.9. Total organic carbon (TOC) was determined from spot unfiltered samples during the summer campaign only and measured by TOC-5000, Shimadzu[®] automated analyzer following ISO 10694. Physico-chemical parameters of the Udy and Lopan rivers for both campaigns are reported in Table 2.

2.3. DGT retrieval and data interpretation

Elution of metals from the binding phase of the DGT probes (3.14 cm²) was carried out by immersion in 1 mL of 1 M HNO₃ (Supra-pure, Merck, Darmstadt, Germany) for 48 hours (Zhang and Davidson, 2000) in the laboratory and then diluted to 10 ml with HNO₃ 2%. Milli-Q water (Millipore, UK) was used to prepare all samples. Analyses of trace metals (Cd, Co, Cr, Cu, Ni,

Pb and Zn) in the eluted samples were performed with the use of a PQ3 (VG, Manchester, UK) ICP-MS at the French Geological Survey (BRGM) in Orléans according to the European standard NF EN ISO 5667-3. The limits of detections are presented in Table 3.

The concentrations of each metal determined by DGT (C_{DGT}) were then calculated using the temperature dependent diffusion coefficient (1):

$$C_{DGT} = M \cdot \Delta g / (D \cdot t \cdot A) \quad (1)$$

where Δg is the thickness of the diffusive gel (0.8 mm) plus the thickness of the filter membrane (0.13 mm), D the diffusion coefficient of metal in the gel, t deployment time and A the exposure area ($A=3.14 \text{ cm}^2$) (Zhang and Davison, 1995; DGT Research, 2002).

The mass of metal in the resin gel (M) was obtained using the following equation (2):

$$M = C_e (V_{HNO_3} + V_{gel}) / f_e \quad (2)$$

where C_e is the concentration of metals in the 1M HNO₃ eluting solvent ($\mu\text{g L}^{-1}$), V_{HNO_3} the volume of HNO₃ added to the resin gel, V_{gel} the volume of the resin gel, equal to 0.16 mL, and f_e the elution factor is equal to 0.8 for all metals as given by the manufacturer. C_{DGT} corresponds to the interpreted concentration of the water sample and is a time-averaged concentration over the time of the probe deployment. Similarly analytical detection limits in terms of C_{DGT} were calculated from the ICP-MS detection limits and blank values were determined from the DGT blank probes. Additionally field detection limits used in this study were calculated as 3 times the standard deviation of the field blank concentrations. Blank values and detection limits are reported in Table 3.

2.4. Trace metal fluxes determination

In order to determine the influence of potential metal sources, labile metal fluxes were calculated using the following equation (Warnken and Santschi, 2009) based on the flow corresponding to the period for which the samples were deployed:

$$F_{Me} = Q \cdot C \cdot 8.64 \cdot 10^{-2}, \quad (3)$$

where F_{Me} is daily flux of trace metal, kg d^{-1} , Q the mean water flow rate, $\text{m}^3 \text{s}^{-1}$, C is the mean concentration of trace metal, $\mu\text{g L}^{-1}$, measured by DGT (blank subtracted) and the coefficient $8.64 \cdot 10^{-2}$ is for the transformation of data in kg d^{-1} .

3. Results and discussion

3.1. Performance of the DGT use

The results obtained after the deployment of DGT in contrasting climate conditions confirmed the possibility of using these passive techniques for sampling under the river ice cover during winter. Taking into account the difficulties of grab water sampling on icy river sites as present approach needs to make numerous holes for the time and space integrative water sampling, the DGT can be proposed to simplify the sampling procedure, save energy and man power. Concerning the accuracy of the analysis, the detection limits are identified as lower during the summer period than during the winter, as shown in Table 3 and Table 4. In this case, the interpretation of the data depends on the diffusion coefficient values of which vary with the water temperature and possibly impact on the data determination. As regards to other contrasted influences, earlier reported results showed minor impact of the water flow on the DGT measurements (Gimpel et al, 2003). The determination of the total dissolved concentration of highly complexed metals (*e.g.* Cu) by DGT could be underestimated as metal speciation directly affects the DGT measurements and hereby DGT measures the labile metal species only (Warnken et al, 2007).

3.2. Trace metals and potential sources

The DGT-measured concentrations (blank subtracted) are presented in Table 5 and show significant spatial variability along both watercourses. Trace metal composition patterns and concentrations appeared different in the two rivers, however, in both cases average concentrations decreased in the following order $\text{Zn} > \text{Ni} > \text{Cu} > \text{Cr} > \text{Co} > \text{Cd} > \text{Pb}$.

In the Lopan River, maximum concentrations of Co, Cr, Ni, Zn, and Pb were found downstream of the wastewater discharges (site L09), both in summer and winter. During winter sampling the maximum concentrations of Cd and Cu were found downstream of the wastewater discharges, and in summer the maximum of Cd was measured at the sampling site located next to the border with Russia (site L01), and the maximum of Cu was obtained from the sampling site at the very centre of the city (site L06).

In the Udy River, the highest concentrations of Cd, Cu, Ni, and Pb were measured downstream of the wastewater discharge (site U07) for both seasons. The maximum concentrations of Co, Cr, and Zn in winter period were found in U07, as well, and the maximum level of Cr and Zn in August 2008 was observed in sites located close to the border with Russia (U01 and U02). Only the DGT-measured concentrations of Zn during summer in sampling sites U01 and U02 were even higher than the total metal concentrations permitted by the Ukrainian water quality standards for the fishery water use category (GCPL, 1991). In comparison with previous study on trace metals in the Udy and Lopan River (Vasenko et al, 2006), the value of DGT-measured concentrations of Cu, Cr, Zn and Pb were two orders of magnitude lower than the total metal concentrations (Table 1).

The calculation of labile metals fluxes (Figure 2) from the blank subtracted DGT metal concentrations showed that the urban wastewater discharge is a significant source of Cd, Co, Cu, Cr, Ni, Pb and Zn for both Lopan and Udy rivers. The presence of metals in the municipal wastewaters can be attributed to the galvanic industry wastewaters discharged into the municipal sewage system from local enterprises. The Kharkiv Wastewater Treatment Plant ‘Dykanivskiy’ (WWTP ‘D’ with a capacity of $700,000 \text{ m}^3 \text{ d}^{-1}$) and ‘Bezludivskiy’ (WWTP ‘B’ with a capacity of $250,000 \text{ m}^3 \text{ d}^{-1}$) both apply combined biological treatment for run-off and sewage consisting of mixed household (85% of total volume) and industrial (15% of total volume) wastewaters. Before entering the municipal WWTP, galvanic wastewaters are only pre-treated by very basic industrial WWTP owned and managed by the industrials. In that case the insufficiently treated

industrial wastewaters can enter the WWTP 'D' and WWTP 'B', what are not designed to cope with the reduction of the trace metals contamination in the water.

Organic matter can also influence on the mitigation of the bioavailability of metals resulting in the complexation of labile forms with organic particles (Tusseau-Vuillemin et al, 2007). The results show that the TOC contamination is decreasing in sites located downstream of wastewater discharges (Table 2), but further study should be done to evaluate the origin of the organic substances as it has an impact on the speciation of the metallic contaminants (Buzier et al, 2006b; Tusseau-Vuillemin et al, 2007).

3.3. Seasonal variations of trace metals contamination

Natural seasonal changes can influence the mobility of trace metals (Beck and Sanudo-Wilhelmy, 2007; Arain et al, 2008). The dilution, complexation with ligands (Sangi et al, 2002; Tusseau – Vuillemin et al, 2007; Balistrieri and Blank, 2008), sorption by particles (Linnik, 2003; Baalousha et al, 2005, 2006a and 2006b; Buzier et al, 2006a), bioaccumulation (Alfaro-De la Torre et al, 2000; Meylan et al, 2004) depend on temperature (Beck and Sanudo-Wilhelmy, 2007), precipitation (Aung et al, 2008) water chemistry (Dahlqvist et al, 2007; Pernet-Coudrier et al, 2008) and ionic strength of the solution (Baalousha et al, 2006a; Baalousha et al, 2006b). Additionally, labile forms of metals can be released from sediments which can also contain a significant amount of absorbed elements (Vystavna et al, 2008). These factors have seasonal patterns too.

Our results showed that the summer contents of all metals at the sampling point U07 (located on the Udy River downstream of the Lopan River influence and municipal wastewaters discharge) are increasing comparing to site L09 (where the Lopan River receives wastewaters from WWTP 'D'). The variation of DGT averaged metal fluxes can attributed to temporal changes of metals discharge with wastewaters, effluents from other sources (run-off etc.), remobilization of additional labile forms from the river sediments that can be caused by high water temperature

and low dissolved oxygen (Beck and Sanudo-Wilhelmy, 2007). Further research on the sediments quality of the Lopan and Udy rivers is foreseen to evaluate the contamination of metals in this media and processes of the water-sediments interaction.

In contrast to the summer season, winter DGT-measured concentrations of metals in U07 are decreasing compared to L09 as a likely combined effect of better dilution with a high water flow (due to increased precipitation inputs) and a lower water temperature. For comparison, the rate of the wastewater effluent to the river flow in summer is 22:1, whilst in winter such a ratio is 5:1. In contrast, results of metals fluxes calculation show that the amounts of all measured metals in the Lopan River during the winter were higher than in the summer in the site L09 (Figures 2). This is connected with seasonal variations in the economic activity of companies and municipal water users.

Additionally, correlations in spatial and seasonal patterns were found for almost all pairs of DGT-measured concentrations of metals for the winter season (Table 6). In contrast, for the summer season a good agreement was observed only for the Cr - Pb (Pearson's criterion, $r = 0.9023$, $\alpha < 0.05$, $n = 20$). The differences can be explained with changes in metals behaviour in cold high-flow and hot low-flow periods (Beck and Sanudo-Wilhelmy, 2007). Also these strong correlations between elements indicate that they have similar sources, maybe related to a few dominant inputs during the winter. The relationship between winter and summer seasons shows, that a strongest positive correlation was recorded in the Udy River for Cd ($r = 0.92$), Ni ($r = 0.99$) and Pb ($r = 0.70$) and in the Lopan River for Cr ($r = 0.87$), Ni ($r = 0.96$), Pb ($r = 0.95$) and Zn ($r = 0.83$). Such seasonal behaviour can be explained by the continuous release of these metals which only slightly depends on seasons; the pedogenic origin of these elements can also be called for especially for Ni and Pb. Some negative correlations were found for Zn in the Udy River ($r = -0.50$) and Cd in the Lopan River ($r = -0.35$), indicating the influences of different sources on the water chemistry during summer and winter. In summer, Zn can enter the river through run-off contaminated by agricultural activities using Zn-rich pesticides. Additionally, the

comparison of the two rivers pointed out, that the correlation of Zn in August was estimated as negative ($r = -0.35$), which demonstrates a different origin of pollution sources, while correlations in January have a very high level ($r = 0.99$).

Seasonal significant differences (Standard deviation, S.D. > 5) were observed in concentrations of Cu, Ni and Zn in both rivers. The higher mean concentrations of Cu, Ni and Zn in the Udy River were found in August, then Cu and Ni correlate positively with water conductivity ($r = 0.89$ and $r = 0.80$), Zn correlates positively with pH ($r = 0.65$). In the Lopan River, Cu, Ni and Zn show a negative correlation with the water conductivity ($r = -0.61$, $r = -0.31$ and $r = -0.4$ respectively), but a positive correlation exists for Cu and Zn with the pH ($r = 0.62$ and $r = 0.45$) in January. These results indicate that other factors such as pH and conductivity can be responsible for the remobilization of the bioavailable forms of metals in the water and cause secondary water pollution (Caruso and Bishop, 2009) depending on seasonal variations.

3.4. Transboundary issues

It was also found that the concentrations of Cd and Co in the upper Lopan River (L01) and Cd, Cr and Zn in the upper Udy River (U01) are significantly higher than downstream-located sampling sites (Table 5). Since both sampling sites are located near the border with Russia, we can assume that certain transboundary upstream influences on the water quality are taking place. It is difficult yet to identify and to evaluate the sources of metals in the neighbouring Belgorod region, Russia. There are no visible and reported industrial activities upstream of U01 and L01 on the Ukrainian part and no any referent data on the background of rivers sources were found. Downstream from the border with Russia and before entering the Kharkiv urban area (L03) contents of Cd in the Lopan River are much lower because of dilution processes. Similar patterns were also observed for Pb in the Udy River and Co in the Lopan River.

The Belgorod region (Russia), where the Lopan and the Udy Rivers have their sources, is a district of the territory of the Kursk Magnetic Anomaly (KMA) with very well developed mining

activities and iron ore-processing industry, metallurgical plants and at the same time with an important agricultural activity (Samarina, 2008). The results of researches carried out by Samarina (2003, 2007, 2008) show that the rivers of the Belgorod region are directly affected by the mining and smelting works and confirm the anthropogenic origin of Cr, Cu, Ni, Pb and Zn in the Oskol River (main tributary of the Seversky Donets River). Unfortunately, Samarina (2003, 2007, 2008) did not study Cd and Co, but other works have already demonstrated that high concentration of Cd and Co are connected with mining activities (Jordao et al, 1999; Kim et al, 2007) but it should be kept in mind that the transboundary pollution is limited compared to urban or wastewater derived pollution.

4. Conclusions

Our results demonstrate that the DGT technique can be applied to measure the water contamination by labile trace metals both in hot summer low-flow and cold snowy winter high-flow periods. This method appeared more convenient than the grab method of sampling, as it does not demand the collection of numerous samples for the estimation of time-weighted average concentrations of trace elements, especially in cold weather conditions (it does not require the drilling of many holes through the ice cover) and can be recommended for the continuous water monitoring of bioavailable forms of priority trace metals.

This first application of the DGT technique in Ukraine improved the knowledge on the labile trace metals contamination in one of the most industrialised region of the country and helped to point out the principal sources of metals in the rivers. Elements such as Cd, Co, Cr, Cu, Ni, Pb and Zn were found in most of the samples. The concentrations and fluxes of DGT-measured trace metals were much higher downstream of the wastewater treatment plant discharges compared to upstream. However, in locations close to the border with Russia, the concentration of Zn in the Udy River in summer exceeded the Water Quality Standards of Ukraine. Remarkably high contents of Cr and Cd were observed in the sampling sites next to the border

with Russia that probably reflects the transboundary upstream influences on the water quality and needs further research focus.

The concentration in trace metals in the water displayed a seasonal variation pattern. The anthropogenic inputs (wastewater discharges) affect the trace metal concentrations in a strong manner during the low flow summer period while increased flow conditions during the cold season provide a better dilution of pollutants.

Fluxes of metals during the hot low-flow summer period were lower compared to the cold high-flow winter period. This indicates that the metal release is continuous and at the same time seasonally variable depending on both natural and socio-economic conditions in the studied region.

Thus, this passive sampling technique can be used for the long-term water monitoring during various climatic conditions conducted by regional environmental and water authorities of Ukraine. In a further step the data gathered during this study will be used to model the water pollution processes considering many socio-economic indicators (demography, employment structure, economic structure, infrastructure, ...) and changes in the hydrological conditions (Chichurin and Vystavna, 2009). Such a tool (Vystavna, 2005) is now necessary to be developed in order to be able to forecast the water quality evolution in relation with the socio-economic dynamic of the region.

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Figure 1

Location of sampling sites

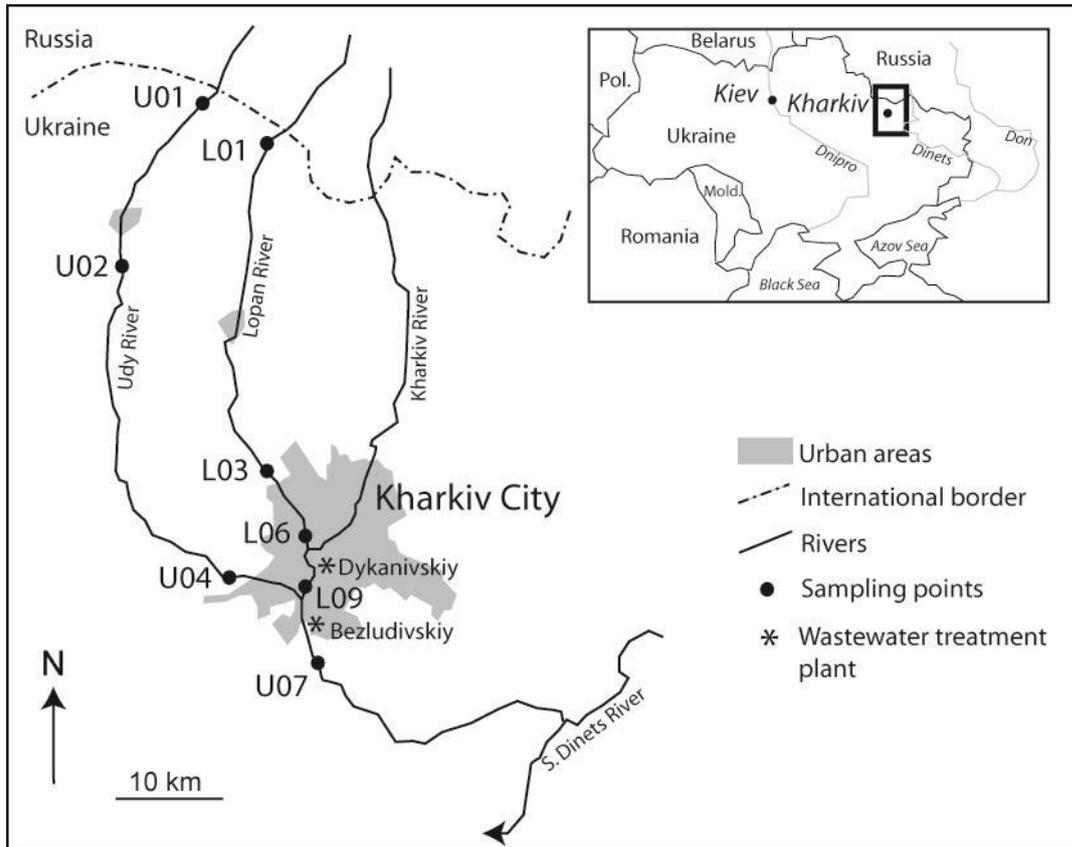


Table list:

Table 1. Total metals concentrations in the Udy and Lopan Rivers in the Kharkiv region, Ukraine in August 2005 determined by earlier study of Vasenko et al (2006), $\mu\text{g L}^{-1}$

Table 2. Physico-chemical parameters of the Udy and Lopan Rivers in August 2008 and January 2009

Table 3. Precision of the analytical technique

Table 4. Calculated mean values ($\mu\text{g L}^{-1}$), standard deviations (S.D. in $\mu\text{g L}^{-1}$) and the relative standard deviations (rsd) of DGT-measured concentrations of metals in sites with replicated deployment

Table 5. Blank subtracted DGT-measured concentrations of trace metals, $\mu\text{g L}^{-1}$

Table 6. Correlations between spatial patterns of paired DGT-measured metal concentrations (Pearson's coefficient)

Figure list:

Figure 1. Location of sampling sites

Figure 2. Average fluxes of trace metals in the Lopan River (L01-L09) and Udy River (U01-U07) in August 2008 (white bar) and January 2009 (grey bar)

Table 1

Total metals concentrations in the Udy and Lopan Rivers in the Kharkiv region, Ukraine in August 2005 determined by earlier study of Vasenko et al (2006), μgL^{-1}

Sampling site	Cu	Zn	Cr	Pb
Udy River - border with Russia (close to U01)	21±5	59±15	22±7	<1
Udy River - downstream the Zolochiv (close to U02)	17±4	58±15	200±7	2±1
Udy River, downstream the man-made water reservoir (close to U03)	34±1	43±10	13±4	2±1
Udy River - upstream the Kharkiv city (close to U04)	10±3	86±22	28±9	6±2
Udy River – upstream the wastewater discharge	13±4	66±16	34±11	4±2
Udy River, downstream the wastewaters discharge (close to U07)	147±37	111±28	59±20	41±14
Lopan River, downstream the wastewater discharge (close to L09)	92±23	118±30	17±6	1±1
GCPL ¹ , μgL^{-1}	5	10	1	0.2
SNPL ² , μgL^{-1}	1000	1000	50	30

¹- GCPL 1991: General code of the permitted limits and presumable save levels of impacts of hazardous substances in the waters used for fishery (in Russian)

²- SNPL 1991: Sanitary norms of the permitted limits of hazardous substances contents in the waters used for drinking and municipal water use (in Russian)

Table 2

Physico-chemical parameters of the Udy and Lopan Rivers in August 2008 and January 2009

	Temperature, °C		Velocity, ms ⁻¹		pH		Conductivity, μScm ⁻¹		HCO ₃ ⁻ , mgL ⁻¹		TOC, mgL ⁻¹	
	Aug	Jan	Aug	Jan	Aug	Jan	Aug	Jan	Aug	Jan	Aug	Jan
L01	18	2	0.3	0.3	7.6	6.9	1030	1360	390	292	172.5	nd*
L03	18	2	0.07	0.07	7.5	7.3	1010	1250	451	296	69.79	nd
L06	22	2	0.1	0.1	6.9	7.6	1060	1130	414	385	133.4	nd
L09	20	7	0.3	0.3	7.1	7.5	1110	1200	390	364	50.79	nd
U01	19	2	0.05	0.05	7.3	6.8	844	1010	506	362	84.05	nd
U02	23	2.5	0.07	0.07	7.6	7.2	953	1160	445	301	nd	nd
U04	20	4	0.07	0.07	7.2	7.4	960	1240	427	331	63.81	nd
U07	20	8	0.17	0.17	7.4	7.3	1120	1280	451	339	51.57	nd

*nd not determined

Table 3

Precision of the analytical technique

Sampling period	Cd	Co	Cr	Cu	Ni	Pb	Zn
Analytical detection limit, ngL⁻¹							
August 2008	0.92	0.95	1.11	0.90	0.97	0.70	0.92
January 2009	1.68	1.80	2.11	1.75	1.84	1.35	1.75
Blank value, ngL⁻¹							
August 2008	24.0	24.0	21.7	261	43.8	31.8	633
January 2009	38.9	4.47	1.31	721	23.0	24.0	622
Operational detection limit*, ngL⁻¹							
Both seasons	30	40	40	970	40	20	20

* determined as three times standard deviation multiple measurements of blank solutions

Table 4

Calculated mean values ($\mu\text{g L}^{-1}$), standard deviations (S.D. in $\mu\text{g L}^{-1}$) and the relative standard deviations (rsd) of DGT-measured concentrations of metals in sites with replicated deployment

site	Cd			Co			Cr			Cu			Ni			Pb			Zn		
	mean	S.D	rsd. %	mean	S.D	rsd. %	mean	S.D	rsd. %	mean	S.D	rsd. %	mean	S.D	rsd. %	mean	S.D.	rsd. %	mean	S.D	rsd. %
August 2008																					
L01	0.09	0.02	22	0.04	0.01	18	0.07	0.004	6	0.18	0.03	20	0.31	0.08	27	0.03	0.004	13	0.50	0.13	25
L03	0.02	0.01	64	0.02	0.004	17	0.03	0.01	29	0.95	0.11	12	0.61	0.09	15	0.02	0.002	10	0.64	0.12	19
L06	0.03	0.01	17	0.03	0.004	13	0.06	0.01	10	1.24	0.16	13	0.93	0.10	11	0.03	0.003	11	2.13	0.17	8
L09	0.07	0.04	60	0.05	0.003	5	0.32	0.25	76	0.64	0.06	10	4.32	1.07	25	0.04	0.01	17	5.45	2.50	46
U01	0.04	0.001	12	0.04	0.003	7	0.42	0.04	10	0.33	0.06	16	0.61	0.09	15	0.10	0.01	8	25.2	3.30	13
U02	0.03	0.01	49	0.60	0.10	16	0.28	0.09	30	0.60	0.04	13	0.69	0.15	21	0.07	0.01	12	7.21	3.13	12
U04	0.06	0.01	17	0.02	0.004	21	0.05	0.01	18	1.83	0.02	4	0.80	0.15	19	0.04	0.01	19	1.29	0.34	26
U07	0.20	0.14	70	0.16	0.10	60	0.39	0.13	34	1.83	0.13	7	4.85	1.91	39	0.11	0.01	11	13.6	9.10	67
January 2009																					
L01	0.03	0.03	11	0.09	0.01	8	0.05	0.01	21	0.79	0.18	22	0.80	0.08	9	0.04	0.01	26	1.11	0.13	12
L03	0.02	0.004	18	0.06	0.01	11	0.04	0.01	23	0.87	0.08	9	0.69	0.07	10	0.04	0.01	15	1.27	0.10	8
L06	0.06	0.06	11	0.03	0.003	9	0.17	0.05	32	2.31	0.26	11	0.65	0.13	20	0.06	0.01	21	2.86	0.16	5
L09	0.13	0.01	8	0.12	0.01	9	0.60	0.29	49	3.03	1.11	37	4.02	0.40	10	0.17	0.02	13	9.54	1.44	15
U01	0.02	0.003	18	0.04	0.01	19	0.05	0.01	20	0.69	0.51	7	0.23	0.03	12	0.07	0.01	9	0.76	0.07	9
U02	0.03	0.02	66	0.08	0.001	2	0.05	0.01	18	1.59	0.59	37	0.43	0.08	18	0.04	0.01	16	1.36	0.21	16
U04	0.04	0.01	21	0.09	0.01	8	0.06	0.01	14	2.20	0.22	10	0.58	0.03	5	0.05	0.02	18	3.23	0.41	13
U07	0.12	0.02	15	0.07	0.001	2	0.23	0.01	3	1.94	0.22	11	2.22	0.22	10	0.10	0.02	19	5.99	0.68	11

Table 5Blank subtracted DGT-measured concentrations of trace metals, $\mu\text{g L}^{-1}$

	Cd		Co		Cr		Cu		Ni		Pb		Zn	
	Aug	Jan	Au	Jan	Aug	Jan								
L01	0.09	<	0.01	0.09	0.06	0.04	0.13	<	0.33	0.73	<	0.02	0.15	0.30
L03	<	<	<	0.06	0.02	0.03	0.85	0.12	0.51	0.62	0.02	0.02	0.47	0.47
L06	0.01	0.02	0.003	0.03	0.04	0.13	1.10	1.80	0.82	0.54	0.03	0.05	1.99	2.03
L09	0.05	0.09	0.02	0.12	0.30	0.59	0.62	2.33	4.28	4.01	0.04	0.15	5.19	8.82
U01	0.01	<	0.01	0.04	0.36	0.04	0.33	0.03	0.63	0.23	0.10	0.05	27.3	<
U02	0.08	<	0.02	0.07	0.48	0.03	0.66	0.20	5.03	0.37	0.04	<	6.95	0.19
U04	0.04	<	<	0.08	0.02	0.05	0.59	0.89	0.65	0.41	0.05	0.02	0.78	0.64
U07	0.18	0.08	0.13	0.07	0.37	0.23	1.81	1.24	4.81	2.20	0.11	0.08	13.3	5.27

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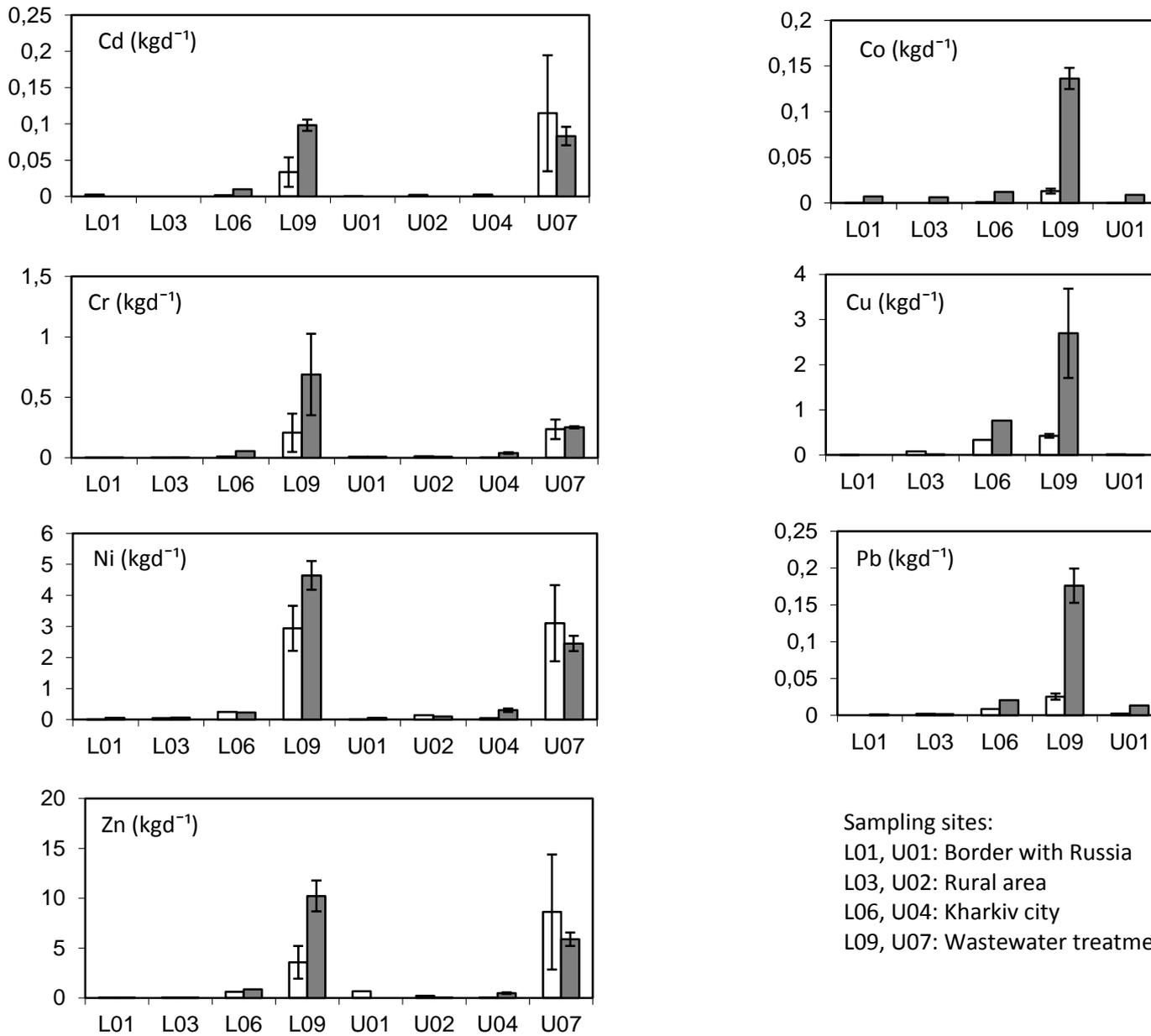
Table 6

Correlations between spatial patterns of paired DGT-measured metal concentrations (Pearson's coefficient)

summer winter	Cd	Co	Cr	Cu	Ni	Pb	Zn
Cd	1	- 0.25	0.06	0.21	0.29	0.13	- 0.34
Co	0.67	1	0.26	- 0.21	- 0.13	0.42	0.65
Cr	0.96	0.65	1	0.05	0.31	0.90	0.77
Cu	0.87	0.49	0.94	1	0.56	0.26	- 0.34
Ni	0.99	0.70	0.96	0.87	1	0.23	- 0.17
Pb	0.93	0.45	0.89	0.77	0.91	1	0.74
Zn	0.99	0.60	0.96	0.91	0.99	0.91	1

Figure 2

Average fluxes of trace metals in the Lopan River (L01-L09) and Udy River (U01-U07) in August 2008 (white bar) and January 2009 (grey bar)



Sampling sites:
L01, U01: Border with Russia
L03, U02: Rural area
L06, U04: Kharkiv city
L09, U07: Wastewater treatment