Urban drainage and its effect on bioavailability of heavy metals in recipient

L´assainissement pluvial urbain et ses conséquences sur la biodisponibilité des métaux lourds dans les milieux récepteurs

Dana Kominkova and Jana Nabelkova

Czech Technical University in Prague, Faculty of Civil Engineering, Department of sanitary and ecological engineering, Thakurova 7, Prague 6, Czech Republic

Kominkova@lermo.cz, nabelkova@lermo.cz

RESUME

En matière d´eaux, les métaux lourds demeurent les plus dangereux car leurs conséquences sur le plan toxicoécologique ne sont pas encore totalement cernées, surtout lorsqu´il s´agit de leur présence dans des solutions. Cet article met en exergue dans l´exemple de trois écoulements à Prague, les changements biologiquement accessibles par rapports aux différents paramètres environnementaux et selon les types d´égouts. Les métaux présents dans les sédiments issus de drainage d´ eaux pluviales sont biologiquement plus accessibles, s´accumulent dans des organismes en plus forte concentration que ce qui ont été relevés dans les écoulements provenant de chaque canalisation.On notera dans certains résultats, une concentration en plomb très élevée dans la masse biologique des poissons. Ces chiffres sont largement au-dessus du seuil recommandé (EC 466/2001) pour la consommation .Du point de vue technique, les résultats exortent à une amélioration des méthodes de séparations dans les sites urbains, principalement le processus de séparation des microparticules, car se sont en réalité, ceux là qui sont responsables de la pollution des structures d´eaux.

ABSTRACT

Heavy metals comprise one of the most hazardous groups of pollutants entering the aquatic environment. Their behaviour and ecotoxicological effects are not well understood especially if they are occur as a mix of metals. Drawing on data from three Prague creeks, the paper illustrates changes in heavy metals bioavailability resulting from different environmental conditions and related differences in urban drainage types. Heavy metals in sediment from creeks impacted by stormwater drain discharges are more bioavailable and accumulate in organisms to higher concentrations than in organisms from creeks affected by combined sewer overflows. The results also show that bioassay levels of lead in fish from the creeks exceed acceptable concentrations for human consumption (EC 466/2001) and therefore represent a potential health risk for humans. The results demonstrate the importance of providing improved interception efficiency in the drainage system structures. In particular, a higher level of interception of fine particles is critical, because of their higher metal adsorption capacity than for coarser particles.

KEYWORDS

Bioavailability, Heavy metals, Urban drainage, Urban stream.

1   INTRODUCTION

One of the most hazardous groups of chemicals impacting on urban waterways is heavy metals (HM). Their levels in the environment are significantly increasing as a result of human activities. The main anthropogenic sources of HM are urban areas, where HM originate not only from industry, but also from traffic, heating and number of other activities. The toxicological effect of HM has not been well understood, especially if they occur in mixture of metals or are present with other chemical components such as nutrients or sulfides.

The paper is focused on the assessment of chemical status of rivers and the importance of HM bioaccumulation in aquatic ecosystems as a part of the ecological status assessment. Currently, routine water quality monitoring is limited to chemical analysis of water and sediments only.   With increasing levels of anthropogenic substances entering the environment, including substances which are able to accumulate in the ecosystems over a long period of time, organisms living in such an environment may be impacted. This understanding necessitates the incorporation of long term monitoring of cumulative substances in the food chain, in addition to the routine monitoring of water and sediment quality.

The main goal of this paper is to show on HM bioaccumulation in aquatic food chain the necessity of introducing new approaches to monitoring and to environmental standards identification. Consequently, there is a need to incorporate ecological assessment into sewer system design and operation.

2   METHODS

2.1   Site description

The assessment of chemical status and HM bioaccumulation was undertaken on three small urban streams impacted by combined sewer overflows (CSO) or stormwater drain discharges (SWD) in the capital of the Czech Republic. Two streams, the Botic and the Rokytka creeks, are impacted by CSO and the last one, the Zatissky creek, is impacted by SWD. There are significant differences between the CSO and SWD creeks in terms of the characteristics of their catchment areas. The creeks impacted by CSO comprise industrial and residential areas, while the creek impacted by SWD comprises residential and natural or semi-natural areas.

2.2   Methods of chemical analyses

The creeks are regularly sampled for their water and sediment quality. The water quality is assessed in terms of a number of physical and chemical parameters (NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}, pH, conductivity, Cl^-, COD, BOD, DO,) and concentration of HM (Cd, Pb, Cu, Zn).The concentration of HM was measured using FAAS and GF AAS (Solaar S). Sediment samples were microwave extracted (ETHOS TOUCH CONTROL) prior to analyses by HNO_3 and H_2O_2 (Nabelkova, 2005).

The biological availability of metals bound into sediment has been assessed by sequential extraction procedure proposed by Tessier (1979). The amount of organic matter in sediment samples was analyzed as a loss of ignition (LI).

During the monitoring period, benthic organisms, attached algae and fish were collected to identify HM concentration in their biomass. Benthic organisms were collected using samplers, to obtain sufficient amounts of biomass for trace analyses (Kominkova and Nabelkova, 2006). The benthic organisms were separated according to species and size and analysed separately. Sampling of fish was limited to capture during Kick net sampling. All biological samples were microwave digested by HNO_3 and H_2O_2 prior to analyses (Kominkova, 2006).

2.3   Heavy metals hazard identification

The results from chemical analyses were used as an indicator of the potential for a HM hazard in the aquatic ecosystems. The hazard was assessed by two types of indexes and coefficients. The first group contains indexes, which evaluate the HM concentration in the sediments relative to a 'natural system' reference condition. The most commonly used index in this group is the distribution coefficient (Page et al., 1999). The distribution coefficient provides information about distribution of an element between water and sediment components and gives information about potential availability for organisms (elements bounded to sediment are less available than elements dissolved in water).

Index		Formula	Explanation
Distribution Coefficient	Kd	$Kd = \dfrac{Cs}{Cw}$	Cs-concentration in sediment Cw-concentration in water
Hazard Quotient	HQ	$HQ = \dfrac{C_M}{BC}$	C_M- measured concentration BC-benchmarker value or environmental quality standard
Cumulative Criterion Unit	CCU	$CCU = \dfrac{Cm}{c}$	Cm-bioavailable amount C – environmental quality standard
Biota Sediment Accumulation Factor	BSAF	$BSAF = \dfrac{C_{or}}{Cs}$	Cor – concentration in organism Cs-concentration in sediment

Table 1: Mathematical formulas for calculation of used indexes

The second group contains indexes and coefficients, which assess HM from the perspective of their ecotoxicological hazard for the environment. There are three main indexes, which are used; the hazard quotient (Barnthouse et al., 1982), cumulative criterion unit (Clements et al, 2000) and biota sediment accumulation factor (Rand, 1995). The hazard quotient (HQ) and the cumulative criterion unit (CCU) are based on comparison with environmental quality standards or benchmarkers. While the HQ takes in account total concentration, the CCU is calculated based on biologically available part only. Because there is a substantial gap in environmental quality standards or benchmarkers in Europe, the US EPA benchmarkers are used for calculation of these indexes (TEC -Threshold effect concentration, PEC –Probable effect concentration). The last index, biota sediment accumulation factor (BSAF) is the only one giving information about possible hazard cause by HM accumulation in the organisms.

3   RESULTS AND DISSCUSION

3.1   Basic physical and chemical parameters of water quality

For the physical and chemical water quality data, N-NH$_4$, N-NO$_3$, DO and COD are the most impacted parameters, failing to meet the environmental quality standards (Czech regulation 61/2003) in all monitored creeks. In terms of the European legislation, this means that all study creeks fail in achieving good chemical status. With the exception of rainfall events, the concentrations of dissolved HM are usually within acceptable standards. During rainfall events, standards may be exceeded when the first flush is highly contaminated by HM or during accidental spill of industrial waste waters to creeks. The concentrations of HM can cause acute risk for

aquatic organisms during these types of events, but otherwise there is not a hazard present in respect to the HM concentration.

3.2 Identification of heavy metals hazard in sediment

3.2.1 Sequential extraction

Biological availability of HM from sediments varies among creeks impacted by different types of urban drainage (Figure 1). There are differences in binding of metals into particular geochemical fractions of sediment (exchangeable, carbonates, Fe/Mn oxides, organic matter and residual fraction) both among metals and among different sampling sites. From four assessed metals (Cu, Pb, Zn and Cd) Pb has been identified as the least available, because it is bound in highest amount into the least available fraction – residual. On the other hand, Cd is the most bioavailable, it is bound into the most available fraction – exchangeable – in the highest amount. Biological availability of these four metals is in order: Cd>Zn>Cu>Pb.

The differences are evident also between binding of particular metals into fractions of sediment impacted by CSO and SWD. Below SWD (the Zatissky creek) Cd, Zn and Cu are more available than below CSO (the Botic and the Rokyta creeks), and higher amount of these metals are bound into the first two most available fractions – exchangeable and carbonates. Lower availability of Cu and Zn in sites impacted by CSO can be associated with higher amount of organic matter in sediment and the potential for Cu and Zn to be bound into this less bioavailable fraction of sediment.

3.2.2 Hazard assessment by different indexes

The distribution coefficient gives valuable information about the availability of each metal for organisms and their distribution between water and sediment components. **Erreur ! Source du renvoi introuvable.** shows differences among monitored creeks in distribution coefficient for all observed metals. The minimal and maximal values for each creek are presented and they show that differences among different sites on one creek are higher than for differences among creeks. The most hazardous element is cadmium, which is present mostly in dissolved form (log Kd<3) on all study creeks. The other metals are present mostly in sediment (log Kd>4) or in suspended matter (3<log Kd<4) and they are not easily accessible for aquatic organisms. Therefore they are less hazardous. The availability of metals by their distribution coefficients is in agreement with results of sequential extraction.

The results show that most of monitored HMs have high values of distribution coefficients, reflecting the high ratio of pollutants bound to insoluble particles. Handová (1994) showed that the critical fraction of sediment for HM sorption is the fraction 6-60 μm. This fraction is not intercepted in drainage structures and is discharged to the receiving water body. Problems with maintenance and cleaning of drainage structures occur elsewhere. Due to insufficient maintenance, the fine sediment is very often washed out by the next rainfall discharge. A biological transformation of HM within the sedimentation basins may result in the formation of even more toxic forms of the contaminants and their mobilisation and washout to the river.

Creek	Type of drainage	Cd		Cu		Pb		Zn	
		Min	Max	Min	Max	Min	Max	Min	Max
Botic ck.	CSO	1.6	2.0	3.6	4.3	3.3	4.1	2.2	3.5
Rokytka ck.	CSO	2.3	3.0	3.1	3.6	3.5	4.3	3.3	3.6
Zatissky ck.	SWD	2.2	2.9	3.0	3.6	3.5	4.1	2.9	3.9

Table 2: Distribution coefficient for all study creeks (coefficient is presented as log Kd value)

	CSO impact		SWD impact
	The Botic creek	The Rokytka creek	The Zatissky creek
LI	7,7%	5,7%	2,2%

LI - organic matter content in sediment samples analyzed as a loss of ignition

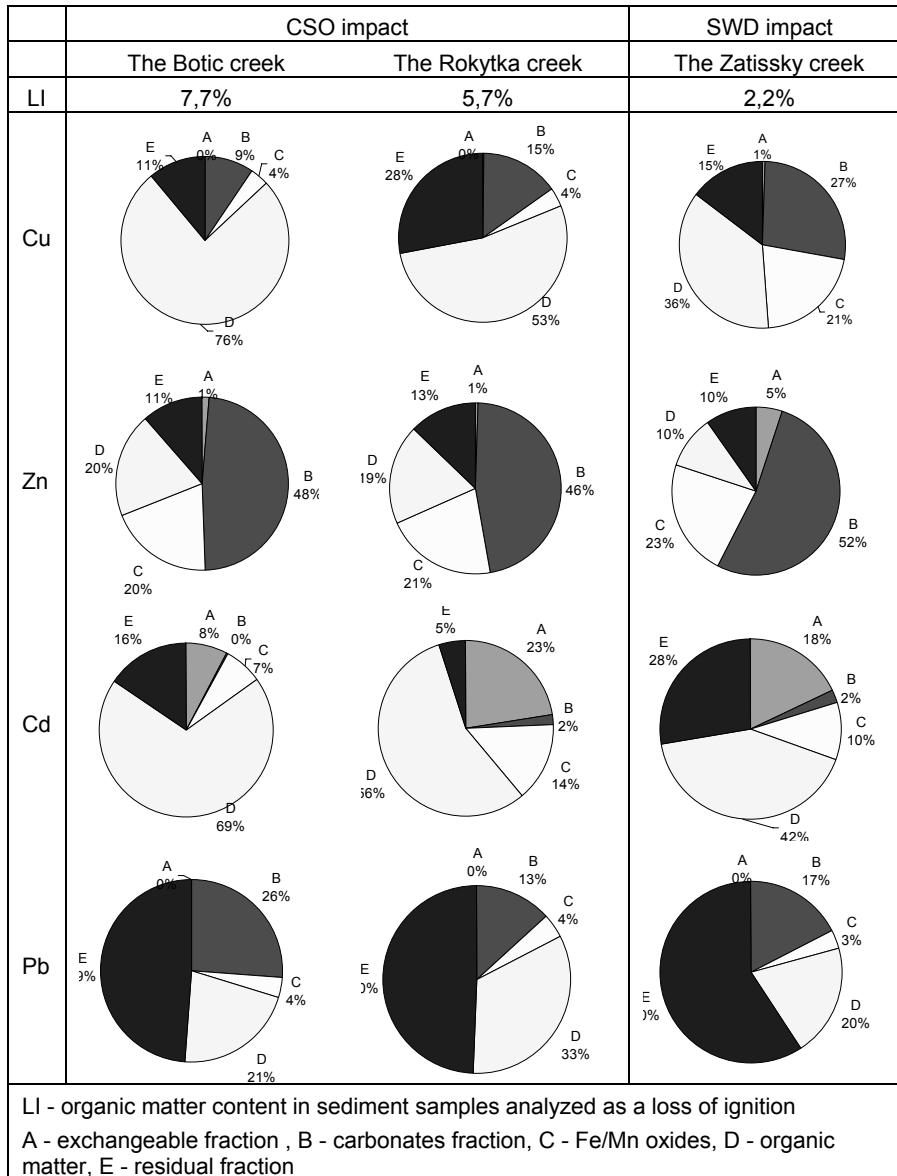A - exchangeable fraction , B - carbonates fraction, C - Fe/Mn oxides, D - organic matter, E - residual fraction

Figure 1: Binding of metals in particular geochemical fractions of different sediment samples: impacted by CSO (the Botic and the Rokytka creeks) and SWD (the Zatissky creek)

The results demonstrate the importance of achieving improved interception efficiency of structures in the sewer system. Improved interception of the finer particles is critical, in view of their significantly higher levels of metal adsorption than for the coarser particles. The development of more innovative maintenance and operational guidelines and incorporation of a regular cleaning of sedimentation areas are

important management measures. The provision of more efficient interception structures in the drainage system is required to minimize the entrance of cumulative pollutants (especially HM) into the aquatic environments and to minimize a potential health risk. The future development of sewer structures needs to not only re-evaluate the method of cleaning, but should also examine the opportunities for automation of cleaning and incorporation of coagulation processes. There is still much development work to be undertaken before a more efficient sewer structure can be put into practice. The other option for reducing the loading of HMs on aquatic ecosystems is the disconnection of SWD from streams and the installation of 'at-source' based biofiltration systems.

The second group of indexes, assessing sediment with respect to their potential ecotoxicological effect, show that there are differences among creeks. Table 3 compares HQ and CCU indexes calculated according to the more rigorous TEC benchmarker. It is evident, that if we use HQ, for evaluation, concentrations of Cu and Pb are hazardous in streams impacted by CSO. If the CCU index is used, the potential ecotoxicological effect could be characterized as having a low probability, even though in this case, the amount of metals bound into the three most available fractions of sediment (exchangeable, carbonates and Fe/Mn oxides) is considered as a bioavailable amount. In case PEC benchmarkers are used, then a toxicological hazard is not indicated.

Creek	Drainage type	Cd		Cu		Zn		Pb	
		HQ	CCU	HQ	CCU	HQ	CCU	HQ	CCU
Botic ck.	CSO	0.2	0.03	3.6	0.47	0.7	0.83	1.6	0.48
Rokytka ck.	CSO	0.1	0.04	1.6	0.30	1.0	0.71	2.0	0.34
Zatissky ck.	SSO	0.1	0.03	0.6	0.29	0.7	0.59	0.8	0.17

Table 3: Hazard Quotient and the Cumulative Criterion Unit of Cd, Cu, Zn and Pb for selected sediment samples. Criterion TEC as a quality standard was used for calculation

3.3 Heavy metals in aquatic organisms

The results of HM bioassays are presented in Figure 2. They are presented by feeding groups to indicate the occurrence of HMs in the food chain. Due to the extent of modification of the urban water bodies, not all feeding groups are present in all study streams.

There are significant differences between bioaccumulation of HM by organisms from creek impacted by SWDs and CSOs. Organisms within creeks affected by CSOs, accumulate HM to lower levels than organisms (of same size and species) from creeks impacted by SWD, even though the CSO creeks are a more polluted environment. The biological availability of metals in creeks affected by CSO is lower than in creeks impacted by SWD. The bioavailability of HM is dependent on environmental conditions and their modification. In case of creeks impacted by CSO the occurrence of acid volatile sulfides (AVS) (Allen et al, 1993, Hansen et al.1996) in waste water plays an important role in decreasing bioavailability of HM. The lower biological availability is also indicated by higher values of distribution coefficients and results of sequential analyses. In creeks affected by CSO it was observed that bioavailability increase with distance from CSO, as amount of AVS decrease. In case of creeks affected by SWD, HM bioavailability can increase due to decrease of pH, during first minutes of rain events when the highest levels of polluting substances are washed out from the atmosphere and from the drainage system.

The water entering streams at the beginning of the rainfall event, cause in the short term, a decrease of pH (especially in the case of small urban creeks, where the amount of water entering the creek from the drainage system is greater than the

amount flowing into the water body). The decrease of pH can cause a remobilization of HM from sediment (Nabelkova, 2005) and increase their bioavailability.
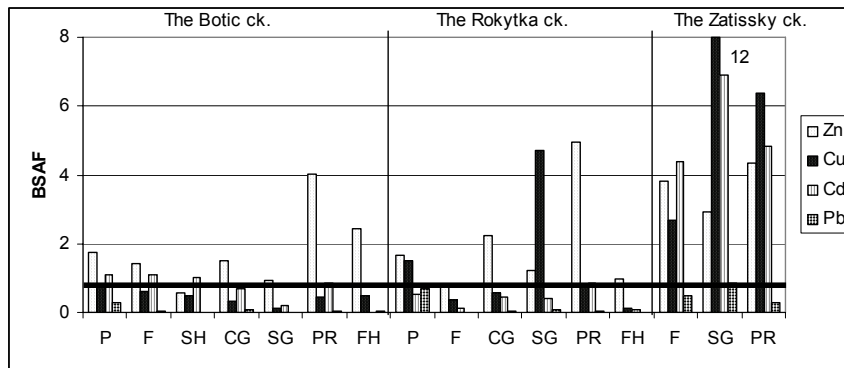

Figure 2: Biota sediment accumulation factor (BSAF) for feeding groups (BSAF>1 indicates accumulation to concentration higher than sediment concentration) (P-producent, F-filterer,SH-shredder, CG-collector-gatherer, SG-Scaper-grazer, PR-benthic predator, FH-fish)

The results also show that the concentration of HM in biomass is changing with the size of organisms as well as with the type of organisms. The dependence on size and species varies among the whole aquatic community. Kiffney a Clements (1993) showed that most of the present environmental quality standards for HM cause 100% mortality of juvenile benthic organisms. It means that the ecotoxicological test while identifying environmental quality standards has to include all age categories of organisms.

The results show, that the ability of aquatic organisms to accumulate HM is dependent on the environmental conditions, size of river, locality, order of river and number of other factors. Consequently, the identification of environmental quality standards for aquatic organisms is a very complicated process, which needs to consider all of these factors. All these factors should be also considered with respect to identification of urban drainage emission limits. The results clearly show that it is not possible to use similar environmental limits for combined sewer system and storm water system, because different conditions are affecting a fate of HM in aquatic environment. Presence of acid volatile substances (AVS) in waste water from combined sewers is one of the most important modification factors.

The concentration of Cd and Pb in fish biomass was compared with the European Commission regulation n. 466/2001. The fish biomass from the observed creeks (especially the Botic creek, 3.8 mg/kg wet weight) contains high values of Pb, which exceed concentrations acceptable for human consumption (0.2mg/kg wet weight) and their consumption may cause a health risk for human population.

4   CONCLUSION

Pollution of rivers by HMs is one of the most serious global issues. A good understanding of ecological effects of HM on aquatic ecosystems is an important pre-requisite to decisions on sustainable use and management of water resources in urban and industrial areas, and in the identification of environmental quality standards

The results demonstrate the importance of implementing improved fine particle interception efficiency in urban drainage structures, to minimize the entry of pollutants bound onto fine sediment and suspended matter and consequently to avoid their accumulation in the aquatic environment. Improved interception efficiency of

urban drainage structures decrease a potential health risk for human population caused by bioaccumulation of HM in the food chain.

The paper demonstrates the necessity of incorporating monitoring of aquatic organisms (different species and size) into routine monitoring programs. While concentrations of HM in water do not present hazard for the aquatic environment, concentration in sediment signal possible hazards caused by Cu and Pb according to the TEC benchmarker in study creeks. The concentration of Pb in fish from the study creeks exceeds acceptable level for human consumption.

The results show that bioavailability of HM is affected by the type of urban drainage and environmental conditions. Consequently, the emissions standard identified for creeks impacted by CSO are not applicable to creeks affected by SWD. There is a necessity to accept an individual approach to the identification of emission limits.

The results also show that there are significant differences among age stages of organisms in their ability to cumulate HM and to resist stress connected to occurrence of HM in their environment. These differences, together with the adoption of the most sensitive life stages of the organisms, need to be taken into account when identifying environmental quality standards.

LIST OF REFERENCES

Allen, H.E., Fu, G., Deng, B., (1993). Analysis of Acid- Volatile Sulphide (AVS) and Simultaneously Extracted Metals (SEM) for the Estimation of Potential Toxicity in Aquatic Sediments. *Env. Tox. & Chem.*, 12 (8): 1441- 1453

Barnthouse, L.W. et al., (1982): Methodology for Risk Environmental Risk Analysis. ORNL/TM/8167. Oak Ridge, TN: Oak Ridge National Laboratory

Clements, W.H., Carlisle, D.M., Lazorchak, J.M., Johnon, P.H. (2000). Heavy metals structure benthic communities in Colorado mountain streams. *Ecol. Appl*. 10 (2), 626-638

Commission regulation No.466/2001 setting maximum levels of certain contaminants in foodstuffs.

Handová, Z. (1994). The Storm Water Pollution in the Integrated Urban Drainage System, Proceeding of the Conference New Requirements for Structure and their Reliability, Prague.

Hansen, D. J, Berry, W. J., Mahony, J. D. et al. (1996). Predicting the Toxicity of Metal-Contaminated Field Sediments Using Interstitial Concentration of Metals and Acid-Volatile Sulfide Normalizations. *Env.Tox. & Chem.* 15(12): 2080 -2094

Kiffney, P.M., Clements, W.H. (1993). Bioaccumulation of heavy metals by benthic invertebrates at the Arkansas River, CO. *Env. Tox. & Chem*. 12, 1507-1517.

Komínková, D. (2006). Impact of urban drainage on heavy metals bioaccumulation. Habilitation thesis. Czech Technical University in Prague,

Komínková, D. and Nábělková, J. (2006). The Risk Assessment of Heavy Metals in the Ecosystem of Urban Creeks. *Wat.Sci & Tech*,53(10)

Nábělková, J. (2005):Heavy metals mobility in small urban creeks environment. Ph.D thesis CTU, Prague.

Page, S.D. et al., (1999): Understanding Variation in Partition Coefficient, Kd, Values. US EPA, Office of Air and Radiation. EPA 402-R-99-004A. Washington DC, USA

Rand, G.M. (1995): *Fundamentals of Aquatic Toxicology. Effects, Environmental Fate and Risk Assessment*. Second Edition. Taylors & Francis. North Palm Brach.

Tessier, A., Campbell, P.G.C., Bisson, M. (1979): Sequential Extraction Procedure for the Speciation of Trace Metals. *Analytical Chemistry* 51, 844-851

The Czech Government Regulation N° 61/2003, about indicators and values of acceptable pollution of surface waters and wastewaters, about requirements of permissions for drainage of wastewaters into surface waters and into sewer systems, and about sensitive areas.