J Soils Sediments (2016) 16:1569–1583
DOI 10.1007/s11368-015-1327-8

SEDIMENTS, SEC 1 • SEDIMENT QUALITY AND IMPACT ASSESSMENT • RESEARCH ARTICLE

Effects of combined sewer overflows and storm water drains on metal bioavailability in small urban streams (Prague metropolitan area, Czech Republic)

Dana Komínková[1] · **Jana Nábělková**[2] · **Tomáš Vitvar**[1]

Received: 3 February 2015 / Accepted: 30 November 2015 / Published online: 16 December 2015

Abstract
Purpose The aims of the study were to evaluate the effect of combined sewer overflows (CSO) and storm water drains (SWD) on metal bioavailability in small urban streams in Prague and to evaluate levels of metals in water, sediment, and macroinvertebrates. The following working hypotheses were adopted: (a) sites dominantly affected by SWD are less polluted by metals, and (b) sites dominantly affected by SWD have higher bioavailability of metals.
Materials and methods Physical and chemical parameters (pH, conductivity, NO_3-N, NH_4-N, COD, alkalinity, and water hardness) and concentrations of the metals Cu, Zn, Pb, Ni, and Cr were determined in samples of water and sediment at five to six sites on four target streams—Zátišský Creek, Košíkovský Creek, Botič Creek, and Rokytka Creek—three to five times per year during the period 2002–2004. The sites from all studied creeks were categorized into five groups according to the prevailing type of urban drainage impact. Macroinvertebrates were sampled and analyzed for metals at each site for a period of 1 month. The concentration patterns of metals were interpreted by partition coefficient (Kd), hazard quotient (HQ), cumulative criterion unit (CCU), and biota sediment accumulation factor (BSAF).
Results and discussion Concentrations of metals in water as well as in sediment at sites receiving water from SWD were lower than at sites where creeks receive water from CSO, except for Pb. Concentrations of Cu, Zn, and Pb in sediment were higher at sites affected by CSO. Concentrations of metals in aquatic macroinvertebrates, expressed as BSAF, indicated higher values at sites affected by SWD. Frequencies of high BSAF (>1) were lower in CSO compared to SWD. This finding was explained by (a) a decrease of pH on SWD sites compared to the increase of pH on CSO sites during rain events, (b) a greater resuspension of sediment at SWD sites during rain events, and (c) an abundance of organic matter in CSO available for sorption of metals and a corresponding reduction of their bioavailability.
Conclusions In the study area, the type of urban drainage affects the bioavailability of metals—while SWD increase metal bioavailability, CSO cause its decrease. The sediments in SWD sites do not indicate risk to the benthic community according to the applied environmental quality standards. Water and sediment in creeks affected by SWD are less polluted by metals. Both working hypotheses were therefore supported.

Keywords Aquatic biota · Bioavailability · Sediment · Metals · Urban drainage · Urban streams

Responsible editor: Kimberly N. Irvine

Electronic supplementary material The online version of this article (doi:10.1007/s11368-015-1327-8) contains supplementary material, which is available to authorized users.

✉ Dana Komínková
kominkovad@fzp.czu.cz

[1] Faculty of Environmental Sciences, Czech University of Life Sciences Prague, Kamýcká 129, 165 21 Prague 6, Czech Republic

[2] Faculty of Civil Engineering, CTU in Prague, Thákurova 7, 166 29 Prague 6, Czech Republic

1 Introduction

The fate of metals in the aquatic environment depends on the origin of the metals and the level of other water quality parameters in the aquatic ecosystem (Komínková and Nábělková 2007; Miller and Miller 2007; Munksgaard and

Lottermoser 2010). Rainwater and streamwater contain metals predominantly from airborne sources such as automobiles, combustion of heating fuels as well as commercial and industrial discharge (Irvine et al. 2005; Gasperi et al. 2010). These substances accumulate on the catchment surface during dry periods and are washed off during rainstorms (Scholes et al. 2007). Under wet conditions, metals and other pollutants enter the aquatic environment mostly through storm water drains (SWD) and combined sewer overflows (CSO). While the SWD handle only the influx of water from surface runoff as the result of rainstorms or snowmelts, the combined sewerage systems carry both storm water and wastewater from residences, businesses, and some industries in one pipe (Drinan and Spellman 2013). It is not feasible to size the combined sewerage system pipe to carry the full combined flow at all times to treatment. At high flow rates, it is therefore necessary that a portion of the flow discharges to a stream through a CSO. CSO is an object on a combined sewerage system (Butler and Davis 2011). Other sources of metals and other pollutants are illegal discharges, which are in this case discharges of domestic wastewater connected directly to a SWD without legal permission of authorized water management authorities.

After discharge to aquatic ecosystems and prior to uptake by organisms, metals are partitioned between solid and liquid phases (John and Leventhal 1996) and affect not only streamwater but also adjacent aquifers (Roy and Bickerton 2012) and wetlands (Rouff et al. 2013).

The behavior of heavy metals in urban aquatic systems is often influenced by water quality indicators such as pH and redox potential. The pollution of receiving waters by biodegradable organic substances causes a decrease in dissolved oxygen concentration and decreases in redox potential of the aquatic ecosystem. Changes in the redox potential typically cause remobilization of metals from sediment and increased bioavailability (Revitt and Morrison 1987). In addition to pH and redox potential, other factors that regulate the partitioning behavior and spatial distribution of metals in the aquatic environment include hydrodynamics, biogeochemical processes, and other environmental conditions, including salinity, temperature and particle size distribution, and organic matter content of sediments (Cantwell et al. 2002).

Concentrations of metals in sediments usually exceed those in the overlying water by three to five orders of magnitude (Bryan and Langston 1992). With such a high concentration, the bioavailability of even a small fraction of the total metal concentration in sediment becomes critical (Mountouris et al. 2002). Metal concentrations in biota are governed by the bioconcentration process. These processes vary within species and depend on the season and the biota's development stage, behavior, sex, and its history of contaminant exposure (Luoma 1983; Eggleton and Thomas 2004; Stockdale et al. 2010). The elevated concentration of metals in aquatic biota may cause a decrease in biodiversity and potential toxicological risk to the human population, for people consuming organisms with a high metal content in their tissue.

Several previous studies have addressed the fate of metal species in waters receiving urban drainage. Carleton (1990) and Stead-Dexter and Ward (2004), among others, have reported that toxic pollutants exhibited an increase in the more readily available fractions at sites affected by SWD relative to sites not directly affected by urban drainage. On the other hand, some metals form organic complexes with organic matter transported in CSO during rainstorms (Morillo et al. 2002). These complexes presumably contain stable high molecular weight humic substances that slowly release small amounts of metals (Lors et al. 2004). A study of the ecotoxicological risks related to the discharge of CSO in the metropolitan area of Lyon (Angerville et al. 2013) also revealed risks to the associated aquatic ecosystems. A thorough study of metal behavior in water, sediments, and biota in receiving waters affected by various types of sewer systems, however, has not yet been carried out.

The aims of this study of four urban streams in Prague were to (1) evaluate the levels of metals in the aquatic environment as related to five types of urban drainage (CSO, SWD, combined CSO+SWD, SWD+illegal drainage, and reference sites) and (2) evaluate changes in the bioavailability of metals with respect to these types of urban drainage. This study focuses on a comprehensive investigation of the metals Cr, Cu, Ni, Pb, and Zn in water, sediment, and macroinvertebrates (*Erpobdella* sp. and *Asellus aquaticus*) from four urban streams affected by CSO and SWD and their combined types, respectively. The following working hypotheses were adopted with respect to the three examined components of the aquatic ecosystems:

a. Creeks affected by SWD are less polluted by metals than those affected by CSO.
b. Sites dominantly affected by SWD have higher bioavailability of metals than those affected by CSO.

2 Study area

The catchments of the four study creeks (Zátišský Creek, Košíkovský Creek, Botič Creek, and Rokytka Creek) are located in Prague, Czech Republic. All four creeks are right-bank tributaries of the Vltava River (Fig. 1). The Botič and Rokytka Creeks are both affected by CSO and SWD. Košíkovský Creek is affected by SWD and illegal discharge of domestic sanitary wastewater, and Zátišský Creek is affected by SWD only. Table 1 provides geographical and hydrological characteristics of the four streams.

Land use in the upstream parts of the Botič and Rokytka catchments includes agricultural and suburban settlements.

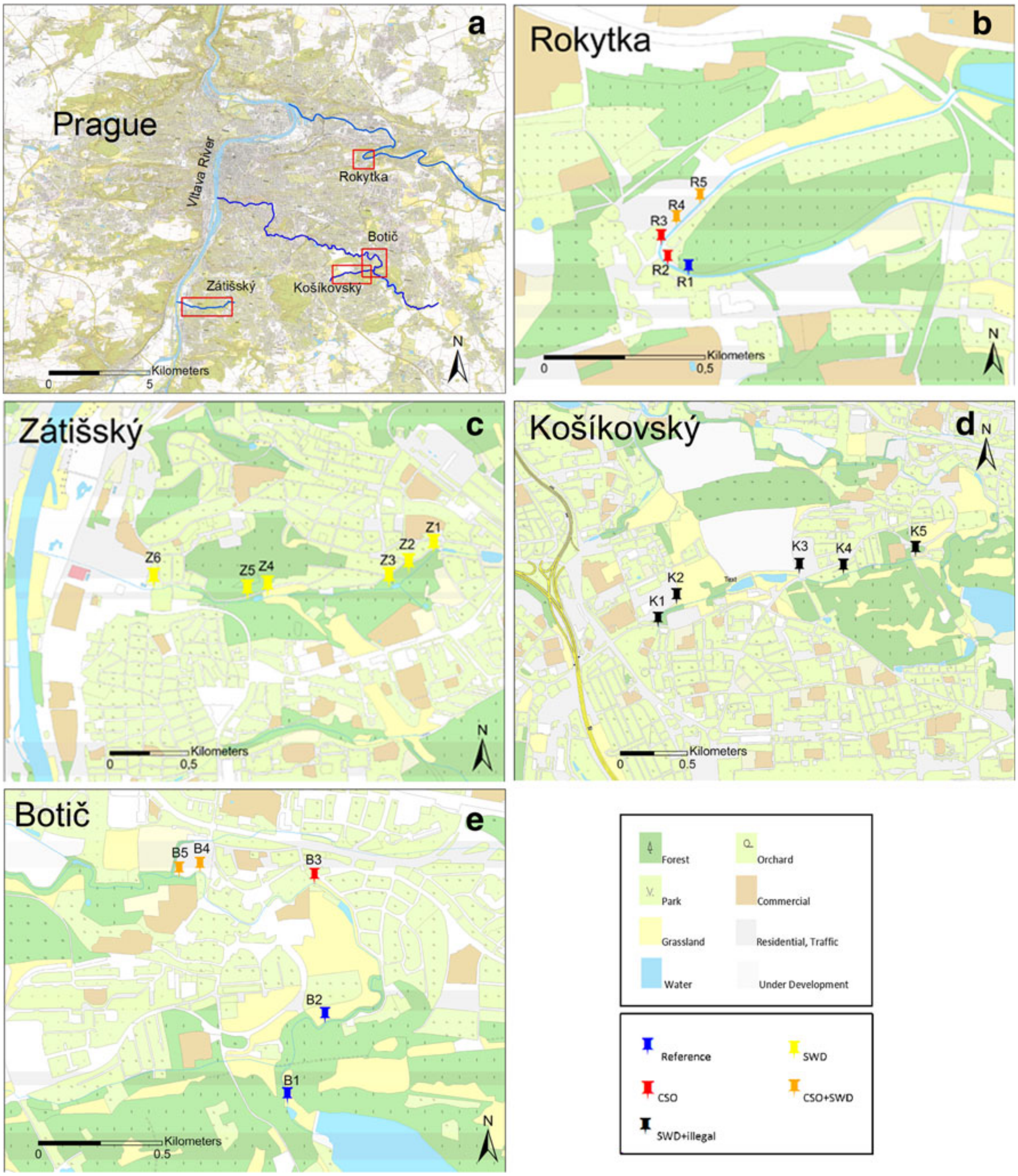

Fig. 1 Map of the study area with locations of the sampling sites. (**a** Map of Prague with indication of study creeks; **b** map of the study section of Rokytka Creek including sampling sites; **c** map of Zátišský Creek including sampling sites; **d** map of Košíkovský Creek including sampling sites; and **e** map of the study section of Botič Creek including sampling sites). Background map source: ZABAGED-Fundamental Base of Topographic Data of the Czech Land Survey Office, http://www.cuzk.cz/

Land use near the study sections is mainly characterized by residential area, roadways, and industry (Fig. 1b–e). Košíkovský and Zátišský Creeks flow through residential areas, with some areas of meadows (Košíkovský Creek) or forests (Zátišský Creek). There are two storm water management ponds on Košíkovský Creek and three on Zátišský Creek. According to the current geographic base data of the Czech Republic (*ZABAGED*®), about 50 % of the areas along the studied creeks are considered impervious.

3 Data and methods

3.1 Sampling

Samples of water, sediment, and biota at five sites on each of the target streams (six sites on Zátišský Creek) were collected during the period 2002–2004. Paired sampling sites upstream and downstream of sewer outfalls were chosen to assess the influence of the different sewer systems (CSO and SWD) on

Table 1 Hydrological and geographical characteristics of the study creeks (source of overflow volume was provided by Prague Water and Sewerage Company—PVK)

Creek	Length [km]	Catchment area [km^2]	Average discharge [m^3 s^{-1}]	Length of the study section [km]	Annual overflow volume [m^3 year^{-1}]
Botič (B)	34.5	135	0.4	2	47,500
Rokytka (R)	36.2	132	0.39	0.6	37,300
Košíkovský (K)	2.4	4.8	0.01	2.4	300,000
Zátišský (Z)	3.1	3.02	0.004	2.9	87,700

the quality of the aquatic ecosystems. The sampling sites were selected to study the impact of each type of sewer system. Sites below CSO or SWD outfalls were located a suitable distance downstream to allow thorough mixing with streamwater. Water samples were collected between three and five times per year, and sediment sampling and macroinvertebrate surveys were carried out two or three times per year. All sampling campaigns were carried out during baseflow periods. The distances between the sites downstream and upstream from outfalls depended on the size of the creek, from 250 m at Zátišský and Košíkovský Creeks, up to 400 m at Botič and Rokytka Creeks. The sampling regime was designed to identify differences in the fate of various metals in creeks affected by the two different types of sewer, with respect to chronic effects caused by differences in metal bioavailability.

Water samples were collected near the midpoint of the stream, immediately below the water surface, at a depth between 5 and 20 cm. The water samples were collected by hand in prewashed PE bottles. Samples were not filtered prior to analysis because it was important to obtain information about the total metal concentration (dissolved as well as bound to suspended matter) to which the aquatic organisms are exposed. Water samples were stored in polyethylene bottles; those used for metal samples were prewashed with acid (1 % HNO_3). After transport to the laboratory, the samples for metal analysis were acidified by HNO_3 (super grade) and stored at 4 °C for later analysis. Basic physical and chemical parameters (pH, electrical conductivity, NO_3-N, NH_4-N, chemical oxygen demand (COD), alkalinity, and water hardness) were determined on the day of sampling.

For sediment sampling, approximately 1 kg of sediment was collected down to 5-cm depth using a plastic scoop (at most sites, there was only a thin layer of sediment; hence, it was possible to sample sediment only to 5-cm depth). Five to eight subsamples were composited from each site to minimize differences in sediment composition resulting from different sedimentation conditions in particular sections of the creek. Samples were placed in clean polyethylene containers and freeze-dried, and the ≤609-μm fraction was separated by a nylon sieve. This fraction size was chosen based on previous studies conducted at the study creeks and also considering the grain size distribution of sediment in urban creeks (Pollert et al. 2000). The sediment of all sites was characterized by a larger coarse fraction relative to fine fraction.

Macroinvertebrates were collected by artificial substrate samplers (Taylor and Kovats 1995) deployed on the bottom of the streams for a period of 1 month (sufficient to obtain adequate sample for metal analyses; Komínková and Nábělková 2007). Sorted stone of grain size 0.5–2.5 cm was used as the artificial substrate. Organisms in the samplers and on their surface were collected and identified to the family or species level. The samples were frozen and then freeze-dried, with full content of their guts. The reason for applying this approach was to identify the amount of metals that can potentially be ingested by the predator, who consumes the entire prey. Hence, the predator can consume metals bound in biological tissue as well as metals present in sediment and water in the guts of the prey. To minimize differences in metal content related to different species and their position in the trophic chain, the two most common groups occurring on almost all sites were used (*Erpobdella* sp, *A. aquaticus*).

3.2 Chemical analyses

3.2.1 Water

Water samples were analyzed for the following parameters: pH, electrical conductivity, NO_3-N, NH_4-N, COD, alkalinity, hardness, Cu, Zn, Pb, Ni, and Cr.

The following analytical equipment was used: multiparameter probes (Hach, Loveland, CO, USA) for the measurement of conductivity and pH in the field (Mihu-Pintilie et al. 2014); colorimetric tests (Hach, Loveland, CO, USA) for NO_3-N, NH_4-N, and COD (dichromate reflux method, Czerniawski and Domagała 2010); and atomic absorption spectrometer (AAS) (Farkas et al. 2003) with flame and graphite furnace (type SolaarS by Thermo Fisher Scientific, Waltham, MA, USA) for metal analysis.

3.2.2 Sediment and biota

Samples of sediment were digested following the US EPA 3051 microwave (MW) digestion method (slightly modified by Nábělková 2005). A mass of 1–2 g of sediment was placed in 9 ml HNO_3 and 1 ml H_2O_2. Digestion was performed in a microwave oven (Milestone Ethos TC, Shelton, CT, USA) at 180 °C for 15 min. After cooling, the digests were filtered, adjusted to 50 ml with deionized Milli-Q water, and stored at 4 °C in polypropylene bottles until analysis. A procedure blank (reagents without any sample) was subjected to the same digestion procedure. This method provides information about the available fraction of the metal content (Bettiol et al. 2008) and is comparable to the pseudototal digestion method using aqua regia (Müller et al. 1994); the usual difference between the results obtained by both methods is less than 10 % (Florian et al. 1998; Nábělková 2011). The binding behavior of metals to different geochemical fractions and the biological availability of metals bound to sediment were assessed by a sequential extraction procedure (Tessier et al. 1979). The following five fractions were operationally identified in this procedure: (1) exchangeable—sediment was extracted at room temperature for 1 h with 8 ml of 1 M $MgCl_2$, pH 7 with continuous agitation; (2) bound to carbonates—the residue from step 1 was leached at room temperature with 8 ml of 1 M NaOAc adjusted to pH 5 with acetic acid (HOAc with continuous agitation; (3) bound to Fe and/or Mn oxides—the residue from step 2 was extracted with 20 ml 0.04 M $NH_2OH{\cdot}HCl$ in 25 % (*v*/*v*) HOAc, heated to 96±3 °C, with occasional agitation; (4) bound to organic matter—to the residue from step 3, 3 ml of 0.02 M HNO_3 and 5 ml of 30 % H_2O_2 were added, adjusted to pH 2 with HNO_3, heating the mixture to 85±2 °C for 2 h with occasional agitation. After that, 3 ml of 30 % H_2O_2 (pH 2 with HNO_3) was added and the mixture was heated again to 85±2 °C for 3 h, with intermittent agitation. After cooling, 5 ml of 3.2 M NH_4OAc in 20 % (*v*/*v*) HNO_3 was added and samples were diluted to 20 ml and agitated continuously for 30 min; and (5) residual—the residue from step 4 was digested on a hot plate with aqua regia (2 ml HCl+6 ml of HNO_3) and 3 ml of 30 % H_2O_2. After evaporation of the liquid phase, 10 ml HF (conc.), 3 ml of HNO_3 (conc.), and 3 ml of 30 % H_2O_2 were added, and microwave digestion with controlled pressure conditions was performed using EPA method 3052 (modified by Nábělková 2005), optimized to avoid manipulation with $HClO_4$. After each step, the supernatant was separated from the sample residue by centrifugation and diluted to 25 or 50 ml. Two replicates of each sample were digested and analyzed.

The amount of organic matter in sediment samples was determined gravimetrically by loss on ignition (LOI) at 550 °C (until constant weight) (CSN EN 15169 2007; 838026) of 3 g of the freeze- dried subsamples. The mineralogical composition of the sediment was identified by X-ray powder diffraction (XRPD), performed on selected samples using an XPertPro (PANalytical, Almelo, Netherlands) with a secondary graphite monochromator with CuKα radiation over the range from 3 to 60° 2Θ.

The biotic samples were microwave digested following the method described in Barwick (1999), Burt (2001), and Komínková (2006). A maximum 1 g of crushed organisms was placed in 9 ml HNO_3 and 1 ml H_2O_2. Digestion was performed in a microwave oven (Milestone Ethos TC) in four steps; the first step was at 250 W, 120 °C, and 15 bar for 6 min. The second step was at 0 W, 120 °C, and 15 bar for 2.5 min. This step was to prevent a blustering reaction. The third step was at 1000 W, 200 °C, and 25 bar for 30 min. The last step was a cooling step of duration approximately 30 min, until temperature decreased to room temperature (22 °C). After cooling, the digests were filtered, adjusted to 20–50 ml with deionized Milli-Q water, and stored at 4 °C in polypropylene bottles until analysis. A procedure blank (reagents without any sample) was subjected to the same digestion procedure.

The concentrations of metals in the extracts were determined using flame AAS (FAAS) and graphite furnace AAS (GFAAS) (Thermo Fisher Scientific, Waltham, MA, USA). The relative standard deviations for triplicate measurements were lower than 10 % for the FAAS and lower than 15 % for the GFAAS. The accuracy of the analytical procedure for pseudototal metal concentration in sediment was checked using certified reference material by Metranal (sediment reference material QCM06, fine sediment; and QCM01, river sediment). Replicate analyses of these reference materials showed good accuracy, with recovery rates for metals between 90 and 108 %. As an additional check on the analytical procedure, selected samples were digested and analyzed in duplicate or triplicate.

3.3 Data interpretation

The evaluation of metal concentrations in water was carried out by the hazard quotient (HQ) calculated after Barnthouse et al. (1982):

$$\mathrm{HQ} = \frac{C_M}{\mathrm{BC}}$$

where C_M is the measured concentration of a particular metal in water (μg ml^{-1}) and BC is the benchmark value or environmental quality standard (in our case ambient water quality limits specified in the Czech legislation).

The partitioning behavior of metals was expressed by the logarithmic partition coefficient (Kd) in milliliters per gram (Page 1999):

$$\mathrm{Kd} = \log\frac{C_s}{C_w}$$

where C_s is the metal concentration in sediment (μg g^{-1}) and C_w is the metal concentration in water (μg ml^{-1}) at equilibrium. Kd values of 3 or less identify metals occurring mostly in dissolved form, while Kd values above 4 identify metals preferably bound to sediment (Borovec et al. 1993).

The evaluation of metal concentrations in sediment was carried out by the cumulative criterion unit (CCU) calculated according to Clements et al. (2000) as the linear sum of the available metal concentrations of each metal (m_i) divided by the environmental quality standard (EQS—concentrations above which adverse biological effects are associated) of each metal (c_i):

$$\mathrm{CCU} = \sum \frac{m_i}{c_i}$$

Clements et al. (2000) defined m_i as the total recoverable metal concentration after aqua regia digestion of solid samples. Florian et al. (1998) and Nábělková (2011) have shown that the obtained concentration (m_i) is comparable to digestion by HNO_3 and H_2O_2 (differences up to 10 %), and the CCU was therefore also calculated for the digestion method presented above. The US EPA toxicological benchmark criterion threshold effect concentration (TEC) (Jones et al. 1997) was used as the criterion (c_i) above which the chronic effect can occur.

Clements et al. (2000) applied this equation to classify field sites according to four levels of metal pollution—background, low, medium, and high metal concentrations (Table 2).

Metal concentration in the tissue of aquatic organisms was evaluated by the biota sediment accumulation factor (BSAF) according to Rand (1995):

$$\mathrm{BSAF} = \frac{c_o}{c_s},$$

where C_o is the metal concentration in tissue and C_s is the metal concentration in sediment.

To assess the different effects of CSO and SWD on the bioavailability of metals, the study sites were divided into five groups according to the prevalent effect (Table 3). The groups are as follows:

a. Reference sites—this type of site was identified only at Botič and Rokytka Creeks, where only the lower section of creek was studied. The reference sites provide information about water, sediment, and biota contamination by metals above the studied CSO and SWD. Zátišský and Košíkovský Creeks were studied over their entire length. In these cases, the first SWD (or SWD and illegal discharge of waste water) was located immediately below artificial springs, typically in the form of a pipe.
b. CSO—sites affected mainly by CSO.
c. CSO+SWD—this category represents sites that are affected by CSO and SWD and it is not possible to distinguish their effects.
d. SWD+illegal discharge of sewage—this category was identified at Košíkovský Creek, where officially only SWD enters the creek, but chemical composition as well as visual observation showed that there is an illegal discharge of sewage from the watershed.
e. SWD—the sites at the Zátišský Creek are affected only by SWD.

Table 2 Cumulative criterion unit (Clements et al. 2000)

Level	CCU	Impact on biota
Background	<1	No effect
Low	1–2	No risk for biota, although adverse effect may occur
Medium	2–10	Higher mortality of sensitive species, changes in macroinvertebrate diversity
High	>10	Significant decrease of macroinvertebrate diversity

4 Results and discussion

4.1 Water

Water quality was evaluated with respect to total metal concentration and chemical parameters such as pH, conductivity, COD, NH_4-N, NO_3-N, water hardness, and alkalinity. Chemical parameters were observed as supplementary data to gain information about dominant hydrochemical conditions of the study sites. The values were evaluated in view of the EQS applicable to ambient water in receiving streams (Czech Government Order 61/2003 Sb amended by 23/2011 Sb.). Figure 2 shows that pH, alkalinity, and COD reflect the impact of urban drainage types. Water hardness, conductivity, NO_3-N, and NH_4-N (for the latter three parameters, graphs are presented in the Electronic supplementary material, Supplement 1, Figs. S1–S3) are more affected by geogenic factors or other anthropogenic activities. Creeks affected by CSO (Botič and Rokytka Creeks) primarily showed high COD (EQS—C_{90} (90 % of the measured values must comply with the standard 35 mg l^{-1})). Severe storm events accompanied by a complete overflowing of the sewer system increased the concentrations of suspended solids (to 30 mg l^{-1}; EQS=20 mg l^{-1}), NO_3-N (to 7 mg l^{-1}; EQS=5.4 mg l^{-1}), and NH_4-N (to 0.5 mg l^{-1}; EQS=0.23 mg l^{-1}) (Pollert et al. 2004). Exceeded levels of NH_4-N and NO_3-N in the Košíkovský Creek (sites affected by SWD+illegal discharge of domestic wastewater) suggest an illegal discharge of sewage into storm sewers; this assumption was also confirmed by visual observations. Water quality of Zátišský Creek (sites affected by SWD) mostly satisfies the ambient water quality limits, except for TOC (13 mg l^{-1}; EQS=10 mg l^{-1}), TP (0.2 mg l^{-1}; EQS=0.15 mg l^{-1}), and suspended solids (20 mg l^{-1}) (Pollert et al. 2004).

Figure 3a–c presents the concentrations of the three most ubiquitous metals in the urban aquatic ecosystems: Cu, Zn,

Table 3 Distribution of sites to groups according to prevailing impact of different urban drainage types

Impact	Reference	CSO	CSO+SWD	SWD+illegal discharge	SWD
Sites	B1, B2, R1	B3, R2, R3	B4, B5, R4, R5	K1, K2, K3, K4, K5	Z1, Z2, Z3, Z4, Z5, Z6

and Pb (Ni and Cr are provided in the Electronic supplementary material, Supplement 1, Fig. S4a, b). Differences in the concentration of total metals at sites affected by different types of urban drainage are shown: while Cu is the highest at sites affected by CSO and CSO+SWD, Pb is the highest at sites affected by SWD+illegal discharge of domestic wastewater (Košíkovský Creek), and Zn is the highest at sites affected by CSO+SWD. Sites affected only by SWD have the lowest concentration of total metals.

The maximum concentrations (data provided in the Electronic supplementary material, Supplement 1, Table S1) identify the highest acute risk for aquatic biota, and the mean concentrations indicate long-term risks. The overall concentrations of total metals meet the required ambient water quality standards. Only Pb concentrations (EQS=14.4 μg l^{-1}) in Košíkovský Creek present acute risks for aquatic biota and can be related to storm water runoff from a busy road and a parking lot in the proximity of sites K1, K3, and K4. Domestic wastewater is generally not expected to be an important source of lead and metals. The toxicity of such sources depends on traffic intensity, according to Marsalek et al. (1999) and Kayhanian et al. (2008). Figure 3d shows the sum of hazard quotients for all analyzed metals. It reveals lower risk at sites affected only by SWD, while on the sites in the remaining categories, the risk is more than two times higher. The small differences among the other categories show that one or two particular metals in each category have a major effect on the potential hazard (data provided in the Electronic supplementary material, Supplement 1, Table S1).

4.2 Sediment

The XRPD analysis suggested that the mineralogical composition of all sediments in the target creeks was very similar, characterized by the presence of quartz, albite, microcline, muscovite, kaolinite, magnesium hornblende, chlorite, and

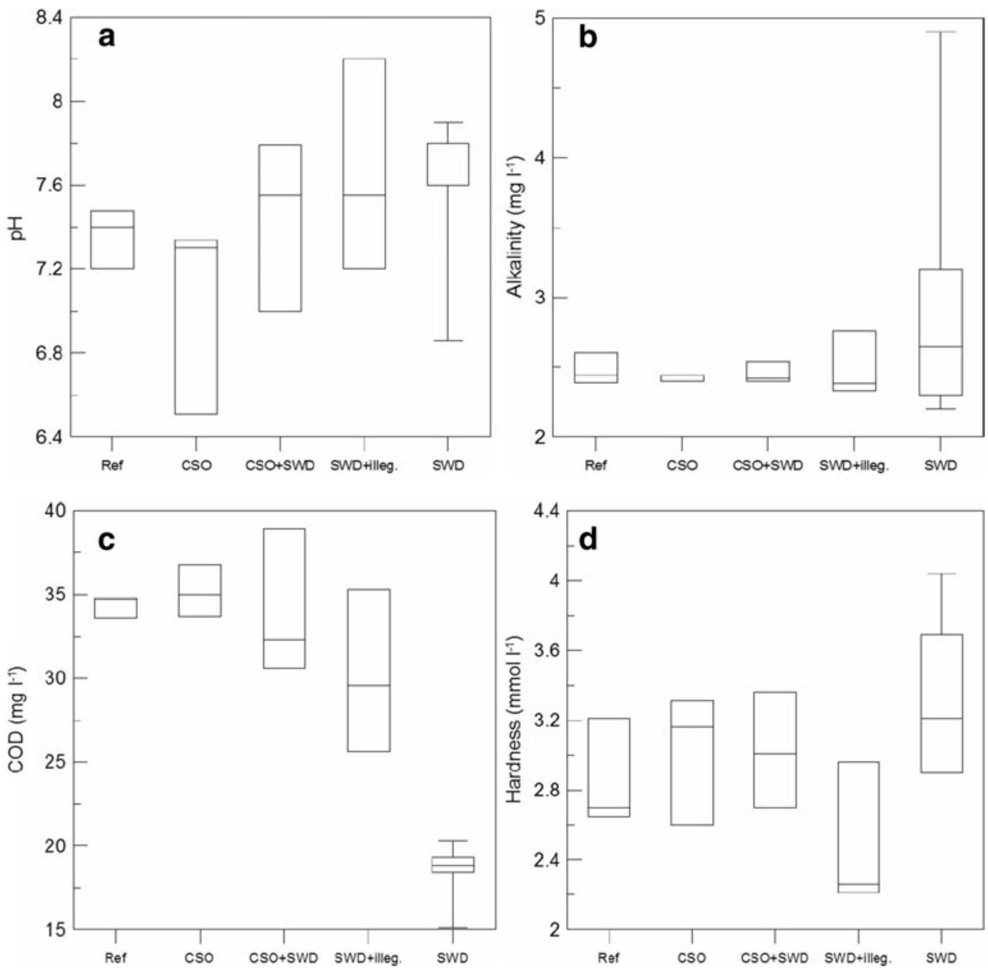

Fig. 2 Box and whisker plot of mean values of water quality parameters at sites grouped according to prevailing impact of different urban drainage types (**a** pH, EQS=6–9; **b** alkalinity, EQS=not applicable (N/A); **c** COD, EQS=35 mg l^{-1}; **d** water hardness, EQS=NA)

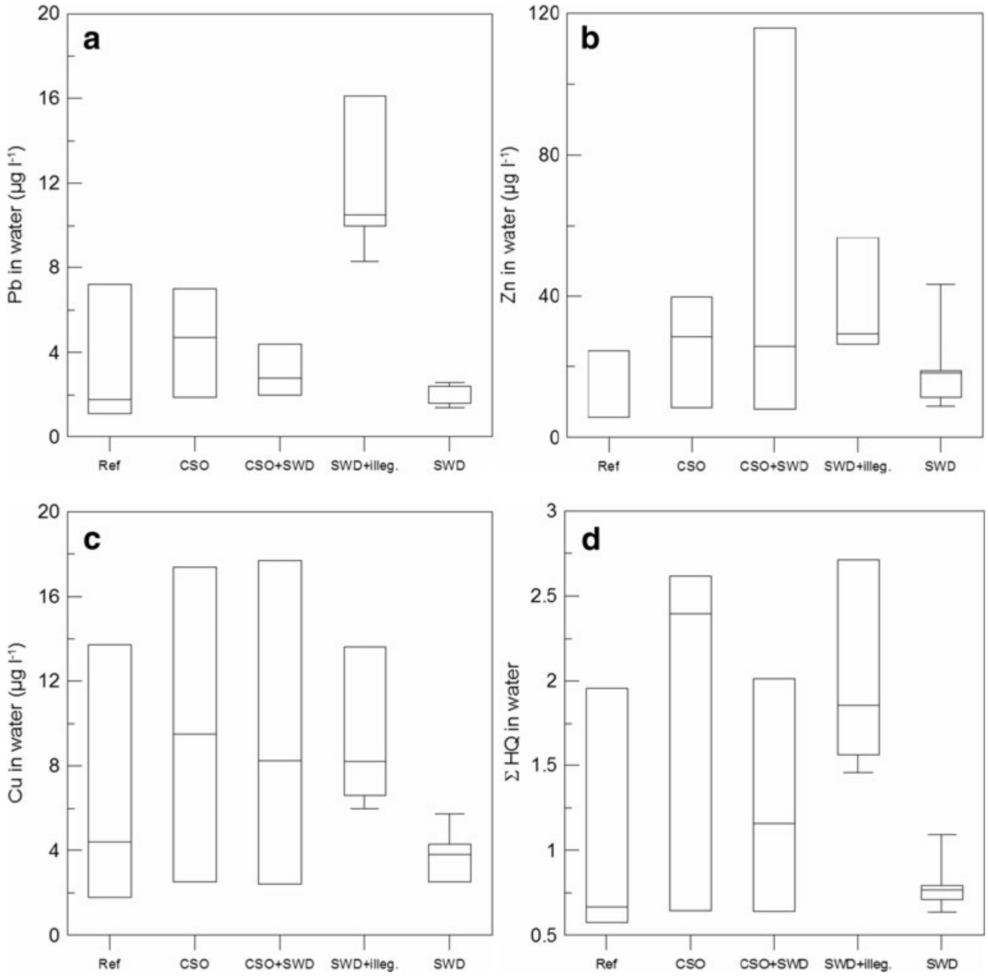

Fig. 3 Box and whisker plot of mean values of total metals and total hazard quotient (HQ) in water at sites grouped according to prevailing impact of different urban drainage types (**a** lead, EQS=14.4 µg l^{-1}; **b** zinc, EQS= 160 µg l^{-1}; **c** copper, EQS= 25 µg l^{-1}; **d** total hazard quotient HQ)

calcite. The similar mineralogical composition precluded possible differences in binding behavior of metals in sediment caused by different minerals.

Figure 4 presents the concentrations of selected metals (Cu, Pb, and Zn) in sediment. Figures showing Ni and Cr are provided in the Electronic supplementary material, Supplement 2, Figs. S1 and S2. The concentrations of metals differ according to the type of urban drainage system. Sites receiving water from CSO exhibited the highest concentrations of the three most ubiquitous metals in the urban environment: Cu, Zn, and Pb. The CSO in the study areas combined a variety of sources of metal pollution, including drainage of domestic wastewater, industrial wastewater, parking areas, and other impervious area of the watershed. The maximum and mean values of these metals exceeded the toxicological benchmark TEC, indicating a possible negative effect on biota (data provided in the Electronic supplementary material, Supplement 2, Table S1). Sites affected by CSO also have the highest concentrations of Cr. The highest concentration of Ni was observed at sites affected by SWD+illegal discharge of sewage. Sites affected by SWD+illegal discharge of sewage, mainly K1, had concentrations of Cu, Zn, and Pb exceeding TEC levels; the origin of those metals can be linked to runoff from a parking lot and a busy road near the sampling site. Beasley and Kneale (2004) observed high levels of Zn (present in automobile tires) in urban sediment and identified runoff from heavily trafficked roads as the primary source of Zn. Sansalone and Buchberger (1997) and Göbel et al (2007) reported elevated concentrations of Cu, Cd, Zn, and Pb in runoff from highways. Our results from the Botič, Rokytka, and Košíkovský Creeks also support their findings concerning the critical role of road transportation in the balance of metals. These creeks are strongly affected by major city roads. On the other hand, no major highways are in the catchment of Zátišský Creek. The metal levels in sediment of Zátišský Creek were therefore lower, posing a lower risk for macroinvertebrates.

The assessment of sediment contamination on the basis of the CCU shows that biota in sites affected by CSO are exposed to a medium to high risk (according to CCU calculated from maximal values—data in the Electronic supplementary material, Supplement 1, Table S1) due to concentrations of metals in sediment. Even the CCU at sites affected by CSO+SWD and SWD+illegal discharge of sewage are lower (both mean and maximal value) than at sites affected by CSO only, but they also belong to the medium to high risk level. The medium level is presumably characterized by higher mortality of sensitive species and changes in macroinvertebrate diversity. The high level is characterized by a decrease of macroinvertebrate diversity (Clements et al. 2000). The low diversity of macroinvertebrates and missing sensitive species were observed previously at the study sites (Nábělková et al. 2004; Pollert et al. 2004). The sites affected by SWD fall in the low to medium risk level. The sites in the "reference" category include sites not affected by close proximity to urban drainage. The results show a comparable level of pollution by metals at reference sites as well as at sites affected by CSO+SWD and SWD+illegal discharges of domestic wastewater. This may indicate possible transport of metals down the creeks over greater distance.

Figure 5 summarizes the results of the sequential extraction analysis of sediment samples. Among the three metals analyzed, Zn was the most available (potentially mobile) with the highest proportion bound to the most readily available exchangeable fraction. On the other hand, Pb was the least available, mostly bound to the residual and OM fractions. Availability of metals in the study creeks can therefore be generalized to Zn>Cu>Pb.

Although the results of sequential extraction are presented only for a selected set of samples, similar binding trends were observed also in samples collected from the same sites later (Race 2012). However, other studies (Klavinš et al. 2000; Xiangdong et al. 2001) present different binding tendencies in geochemical fractions of sediment. Klavinš et al. (2000) conclude that bioavailability (i.e., binding into more available geochemical fractions) increases with pollution. A higher amount of metals is typically bound onto Fe/Mn oxides and organic matter in more polluted sampling sites of a watercourse. In turn, metals at sites with background levels bind into organic matter and residual fractions. The binding behavior of metals is also affected by the amount of a particular geochemical fraction. For example, Cu predominates in sediment fractions with a high amount of organic matter. Because Pb forms complex compounds with Fe/Mn oxides, it can predominate in Fe/Mn oxides and be more available in comparison to the residual fraction (Xiangdong et al. 2001).

Cu and Zn were the most potentially bioavailable at sampling site Z2 (Zátišský Creek) affected by SWD. The patterns

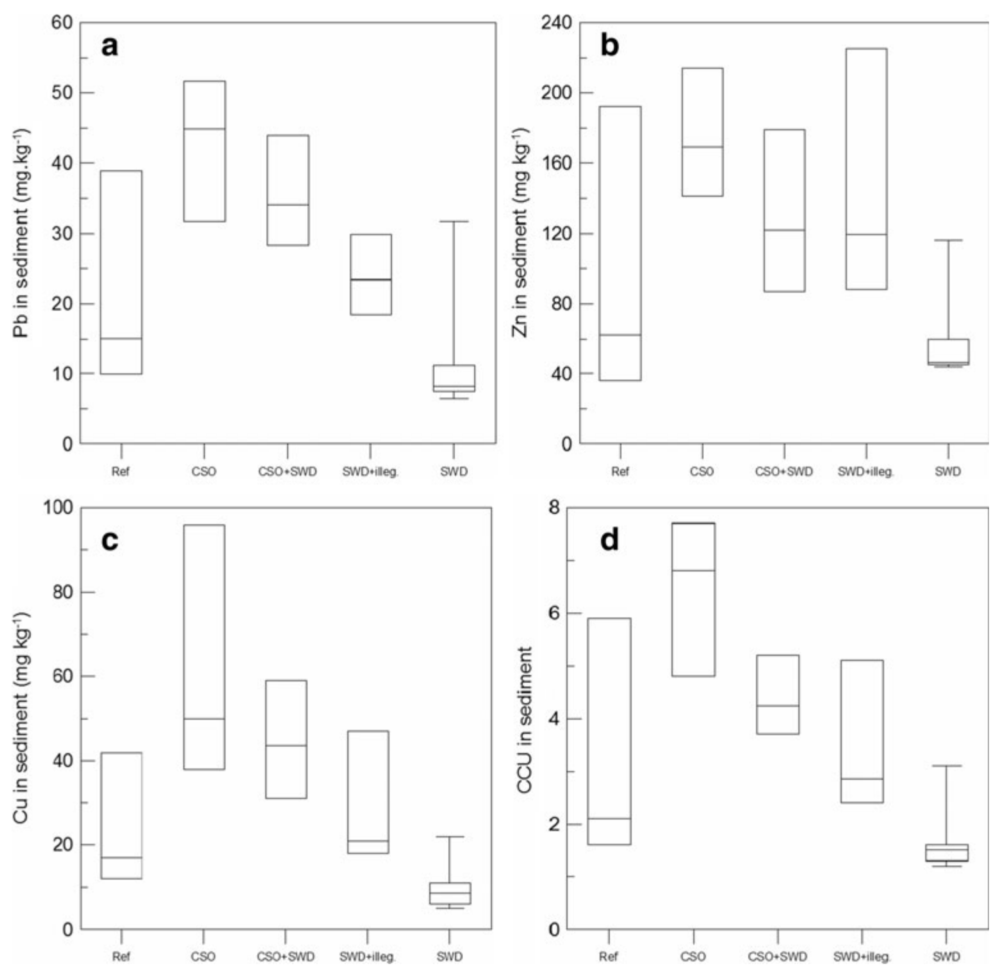

Fig. 4 Box and whisker plot of mean values of metals in sediment and cumulative criterion unit (CCU) at sites grouped according to prevailing impact of different urban drainage types (**a** lead, TEC=34.2 mg kg^{-1}; **b** zinc, TEC=159 mg kg^{-1}; **c** copper, TEC=28 mg kg^{-1}; **d** cumulative criterion unit)

of Pb were less evident, consistent with Pb binding predominantly to the residual fraction. Previous studies of urban Prague streams by Hnaťuková et al. (2009) revealed a substantial increase of the less available oxidizable fraction of Cu (from 60–70 to 80–90 %) in sediment samples at sites below CSO discharges in Botič Creek in the Prague metropolitan area. Hence, concentrations of Cu in other geochemical fractions were lower. Anderson et al. (1999) showed that bioavailability of some metals, in particular Cu, can be related to the amount of organic matter in sediment, which could be smaller in a creek impacted by SWD. In turn, increased potential bioavailability of other metals such as Zn can be caused by a lower pH during rain (Nábělková 2005). While pH typically increased during rain events in CSO-impacted waters due to higher concentrations of ammonia from the sewer system, pH in waters impacted by SWD often decreased. The decrease of pH is typically reported in small creeks where the runoff contribution of the SWD often exceeds the flow rate in the creek above the runoff gauge (Karlavičiene et al. 2009). The decrease of pH to below 6 affects the mobility of pollutants, particularly metals, which in turn become more mobile and bioavailable to aquatic organisms (Calmano et al. 1993).

While the sediment affected most by SWD (Zátišský Creek) showed the highest bioavailability of metals, sediment at SWD-affected sampling sites in other study creeks (B4—CSO+SWD or K2—SWD+illegal discharge) did not confirm higher potential bioavailability compared to sampling sites impacted by SWD only. It is an interesting observation that the combination of more pollution sources (SWD, CSO, illegal outlets, and overall higher level of water pollution) in Botič, Rokytka, and Košíkovský Creeks can decrease the bioavailability of metals in sediments. The binding behavior and bioavailability of pollutants in sediment is affected not only by the type of main impact (CSO, SWD) but also by the characteristics of the sediment material (organic matter and particle size distribution), the frequency of critical events (rain, discharge from reservoirs), and the level of contamination by other pollutants (Calmano et al. 1993; Eggleton and Thomas 2004). Longitudinal assessment of metal concentrations along the course of streams affected by CSO showed that sites affected directly by CSO exhibited a higher portion of metals bound to less available fractions than sites above CSO outfalls or at a greater distance downstream of outfalls (Hnaťuková et al. 2009). Various studies focusing on speciation of metals (Revitt and Morrison 1987; Stead-Dexter and Ward 2004) revealed that metals in drainage systems conveying storm water had a high available fraction compared to other geochemical fractions.

Differences in the partitioning coefficient of selected metals among different impacts are presented in Fig. 6 and Supplement 2, Electronic supplementary material (Table S2 and Figs. S3 and S4). It reveals that Cu, Pb, and Zn at sites affected by CSO bond preferentially to sediment. Other sites show binding to sediment in decreasing order CSO>CSO+SWD>SWD+illegal discharges>SWD. Metals on sites affected by SWD are presumably easily released from sediment or suspended matter. Metals with low Kd present a higher risk for aquatic biota than metals with higher Kd.

The amount of both organic matter and metals bound in sediment was highly variable. The content of organic matter in sediment was not affected by the type of urban drainage but by local conditions such as morphology and hydrology (mainly velocity and discharge) of the stream. A very low organic matter content from 0 to 2 % was found at all sites on Botič Creek, while Rokytka Creek sediment had between 6 and 14 % organic matter. Zátišský and Košíkovský Creeks had organic matter concentrations of 2–5 and 1.5–8.7 %, respectively. No correlation was found between metals and organic

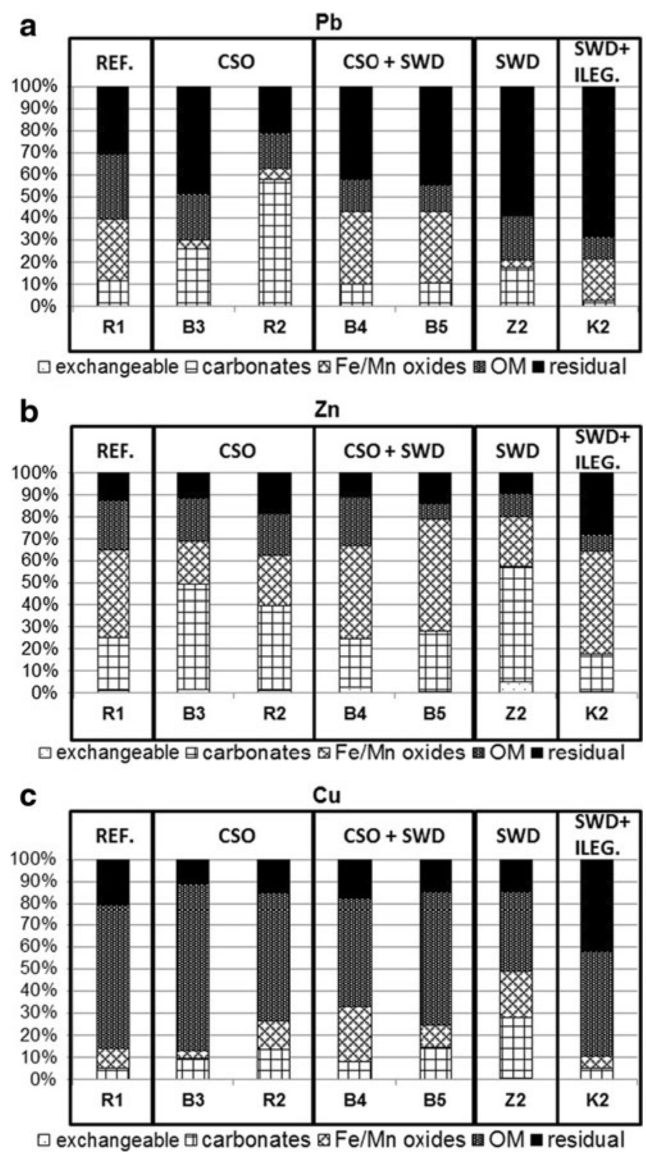

Fig. 5 Proportions of selected metals bound in particular geochemical fractions in the study creeks (**a** lead; **b** zinc; **c** copper)

matter at Botič Creek. A good correlation with organic matter was found at Rokytka Creek for copper (0.85), nickel (0.91), zinc (0.9), and chromium (0.87). A good correlation of metals with organic matter was found at Zátišský Creek for chromium (0.83), copper (0.87), and nickel (0.84). In the case of Košíkovský Creek, a good correlation with organic matter was found only for Cr (0.83) and Ni (0.93). The remaining metals showed correlations lower than 0.75.

4.3 Biota

Figure 7 displays results of the box and whisker plot of BSAF for two groups of organisms, *A. aquaticus* and *Erpobdella* sp. While *A. aquaticus* is a member of the collector-filter feeding group, *Erpobdella* sp. belongs to the predator feeding group. These two groups were the most abundant at the study sites and provided sufficient sample amount for metal analysis. The BSAF for *A. aquaticus* shows increasing trends for Cu, Pb, and Zn according to the impact (Fig. 7a–d). Whereas the highest value was associated with SWD, the lowest value was associated with CSO. *A. aquaticus* had the lowest BSAF at sites affected by CSO and the highest BSAF at sites affected by SWD.

The sum of BSAF (for all monitored metals) for *A. aquaticus* confirms the trend observed for single metals. Compared to *A. aquaticus*, which feeds mainly by collecting debris from sediment or filtering it from water, *Erpobdella* sp. is a predator and gets metals not only from the environment but also from its prey. Figure 8a–d therefore shows different results compared to *A. aquaticus*. The highest values of BSAF for Pb were recorded at sites affected by SWD+illegal discharge of sewage. It is assumed that they are caused by high concentrations of Pb in the environment due to close proximity to a busy road and parking lot. Only a minor contribution of illegal discharges of domestic wastewater to metal pollution is expected. High variability of Zn was observed at sites affected by CSO with the lowest and the highest values. BSAF for Cu shows the lowest values on sites affected by CSO+SWD and the highest at sites affected by SWD only. The total BSAF for *Erpobdella* sp. shows similar trends as the BSAF for Cu. Complementary data are provided in the Electronic supplementary material, Supplement 3, Table S1 and S2 and Figs. S3 and S4.

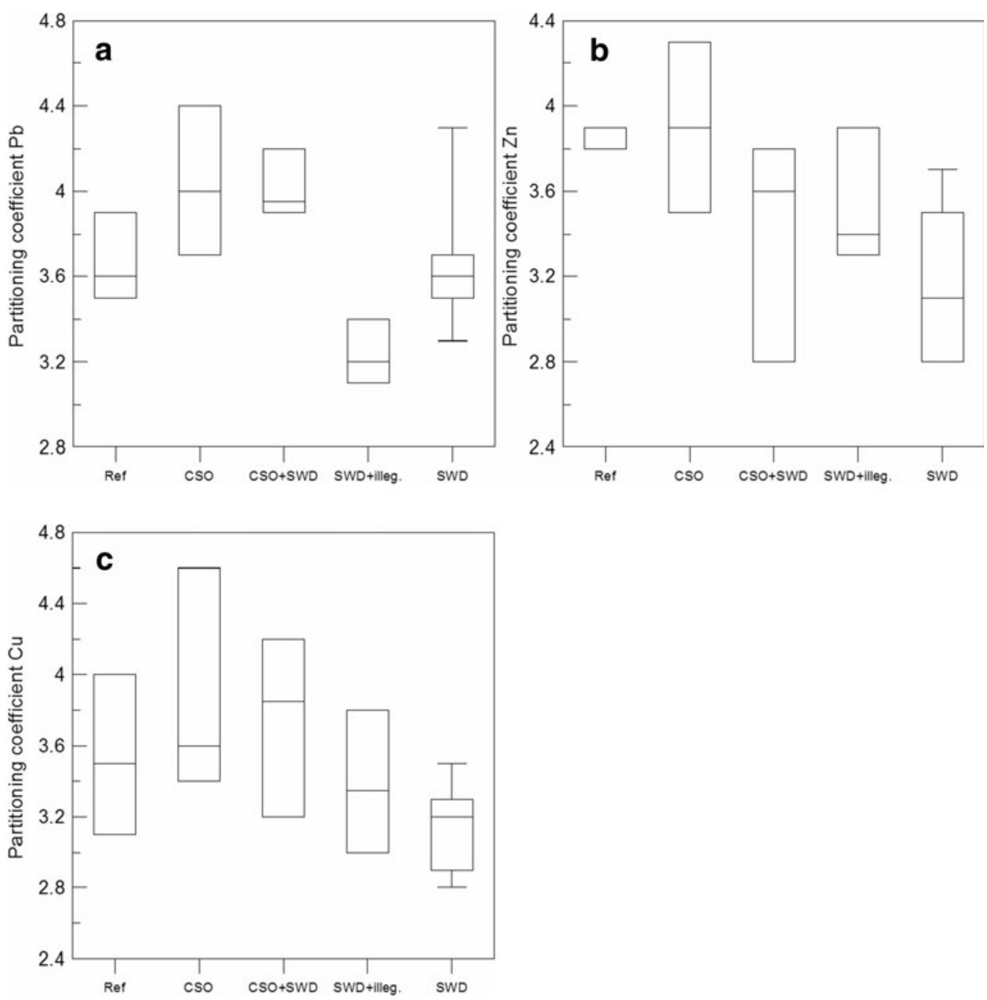

Fig. 6 Box and whisker plot of mean values of partitioning coefficient at sites grouped according to prevailing impact of different urban drainage types (**a** lead; **b** zinc; **c** copper)

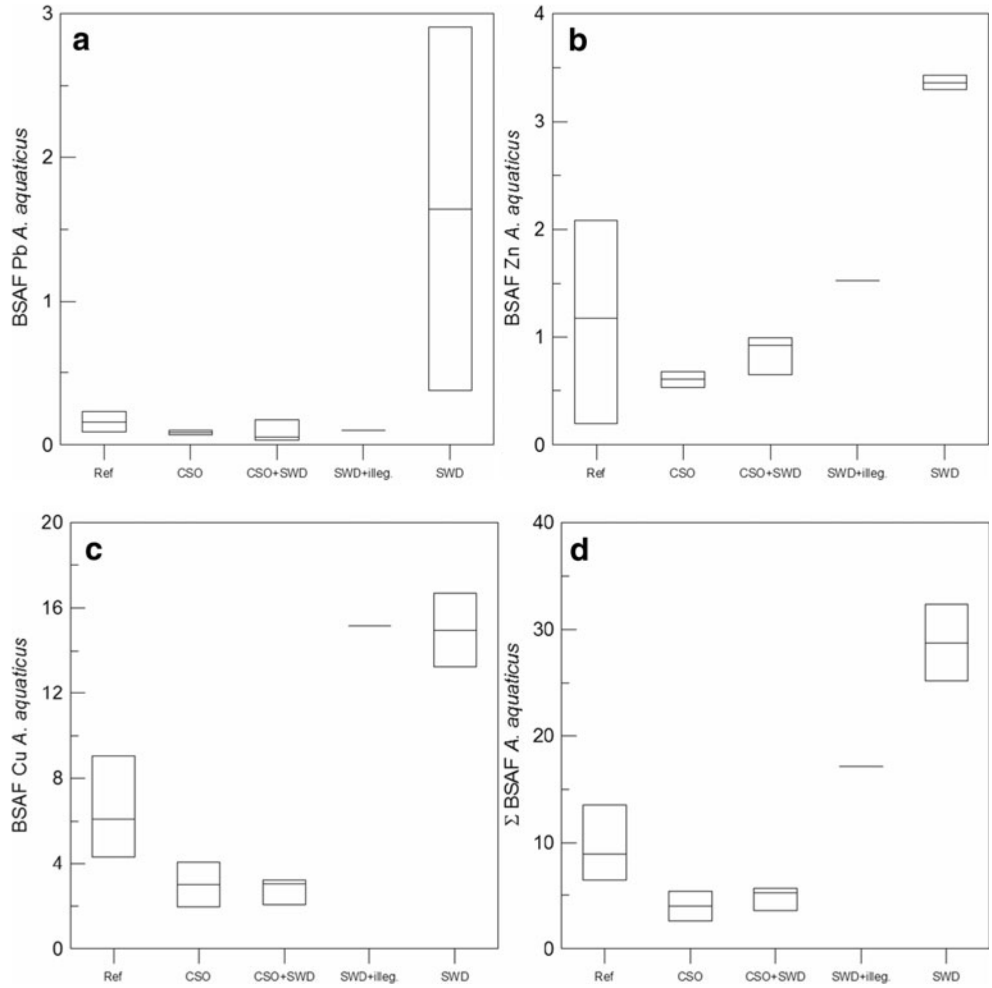

Fig. 7 Box and Whisker plot of mean values of BSAF for *A. aquaticus* at sites grouped according to prevailing impact of different urban drainage types (**a** lead; **b** zinc; **c** copper; **d** total BSAF)

It appears that *A. aquaticus* accumulates more Cu and *Erpobdella* sp. accumulates more Zn. Metal accumulation in benthos of streams affected by CSO differs from that in Zátišský Creek, which receives water only from SWD. These findings support the speciation study of Stead-Dexter and Ward (2004), which reported that all metals studied (with the exception of Pb) exhibited an increase in the more available fractions through storm water sewers. Both the absence of CSO and the low organic pollution at Zátišský Creek indicate higher bioavailability of metals in its sediments affected only by discharge of SWD. On the other hand, some metals can form complexes with organic matter discharged from CSO during rainstorms (Morillo et al. 2002). These complexes contain stable high molecular weight humic substances that slowly release small amounts of metals (Lors et al. 2004). This finding is also supported by the toxicity data for CSO and SWD reported by Marsalek et al. (1999) for various urban sources. Frequencies of toxicity detection were lower in CSO compared to SWD, and this finding was explained by an abundance of organic matter in CSO available for sorption of metals and a corresponding reduction of their bioavailability (Marsalek et al. 1999).

In accordance with other studies (Cantwell et al. 2002), the results have confirmed that the bioavailability of metals was also affected by hydrodynamics. Table 1 shows that the amount of overflowing water in creeks affected by SWD and SWD+illegal discharge of waste water is greater than for creeks affected by CSO, suggesting that the disturbance of the sediment is greater and more frequent than at sites affected by CSO. In line with Eggleton and Thomas (2004), these results suggest that the exposure to different chemical conditions results in desorption and transformation of contaminants into more bioavailable or toxic chemical forms.

5 Conclusions

This study has shown that urban drainage discharges impair the quality of aquatic ecosystems in small urban creeks in the Prague metropolitan area. It has been shown in this study area that the type of discharge plays an important role in the fate of metals in the aquatic environment of small urban creeks. In our study, sites affected by CSO had the highest concentration of metals in water and sediment but the lowest BSAF. While sites affected only by SWD had low concentration of metals in the environment (water and sediment), they showed a high value of BSAF, indicating higher bioavailability of metals at sites affected by SWD.

Metal contamination at all water sampling sites complied with the requirements of Czech legislation for the concentration of total metals in water, with the exception of a high concentration of Pb in Košíkovský Creek at a site affected by SWD+illegal discharge of sewage in close proximity to a busy road and parking lot. It can therefore be assumed that the present concentrations of metals in water do not cause acute risk for aquatic biota in the target ecosystems.

The sediment at sites affected by CSO was typically characterized by both individual higher concentrations of Cu, Zn, and Pb and the cumulative criterion. This may cause negative effects on the benthic community. In turn, the sediments in creeks affected by SWD do not indicate risk to the benthic community according to the applied environmental quality standards for individual metals, but the cumulative criterion unit indicates a possible risk. The hypothesis that water and sediment in creeks affected by SWD are less polluted by metals was supported.

The assessment of metal concentrations by two approaches showed that the evaluation based on the EQS only was not sufficient and did not capture potential synergistic effects of multimetal mixtures in sediment as well as water. The evaluation of metal concentrations in biota showed differences in the uptake of benthic organisms. Organisms from Zátišský Creek, affected by SWD only, exhibit a higher BSAF, which suggests that the metals in the sediment from this creek are more bioavailable than from sites affected by CSO or from sites affected by CSO+SWD and sites affected by SWD+illegal discharge of sewage. The hypothesis on higher availability of metals in biota of creeks affected by SWD was therefore supported.

The type of urban drainage plays an important role in the fate of metals in the receiving aquatic environment. The results also demonstrate a high necessity to develop individual EQS for individual types of urban drainage and to identify different requirements to protect the biota. As the SWD cause increased bioavailability of metals, the adjusted EQS has to particularly address the protection of aquatic biota from bioaccumulation of metals to hazardous levels.

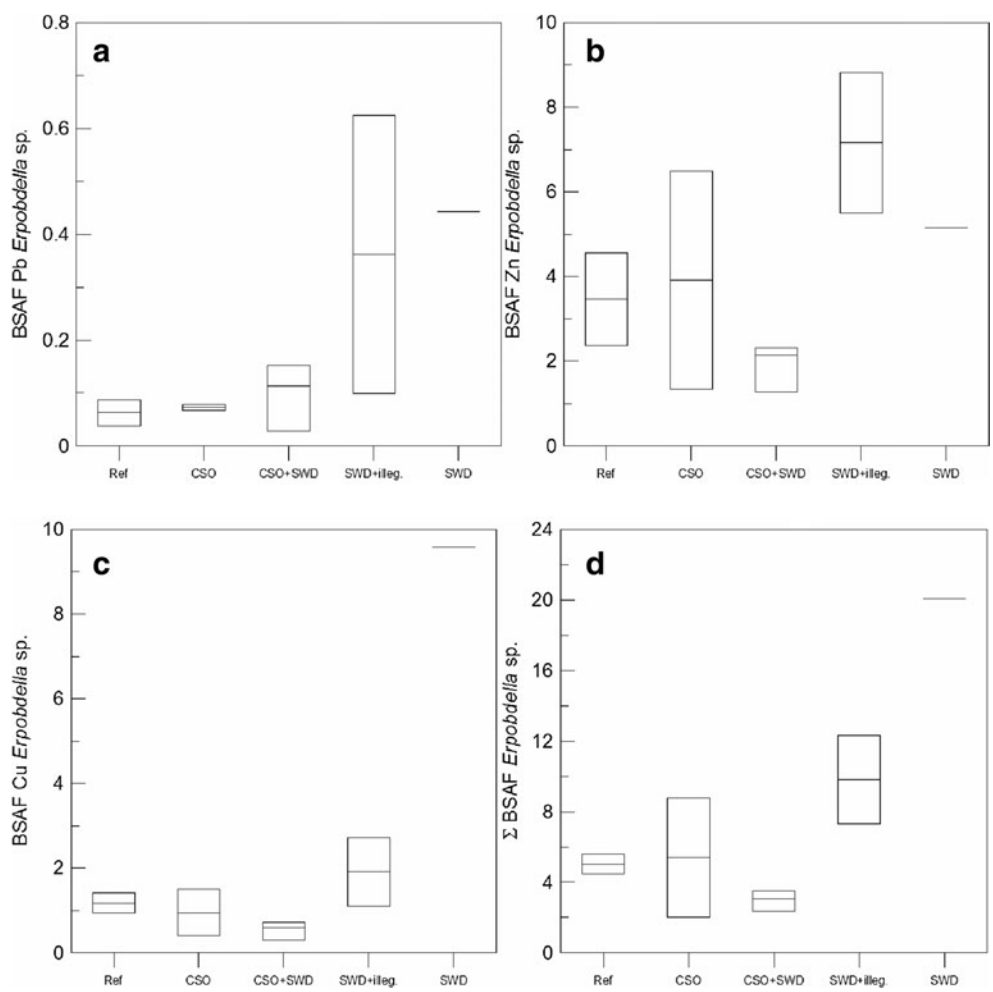

Fig. 8 Box and whisker plot of mean values of BSAF for *Erpobdella* sp. at sites grouped according to prevailing impact of different urban drainage types (**a** lead; **b** zinc; **c** copper; **d** total BSAF)

Acknowledgments This work was supported by the project of Ministry of Education of CR No. MSM 6840770002, projects of CULS, Faculty of Environmental Science 42220/1322/3243 and 4200/1312/3166. The authors wish to thank James B. Shanley for linguistic correction. We also appreciate the careful work of our reviewers who substantially helped to improve data presentation and organization of the paper.

References

Anderson BC, Vanloon G, Watt WE, Marsalek J (1999) Ecotoxicity of sediments in stormwater quality control facilities. Proceedings of the CSCS ASCE Environmental Engineering Conference, American Societa of Civil Engineers, Reston, VA, pp 121–130

Angerville R, Perrodin Y, Bazin C, Emmanuel E (2013) Evaluation of ecotoxicological risks related to the discharge of combined sewer overflows (CSOs) in a periurban river. Int J Environ Res Public Health 10:2670–2687

Barnthouse LW, DeAngelis DL, Gardner RH, ÓNeill RV, Suter GW II, Vaughan DS (1982) Methodology for risk environmental risk analysis. ORNL/TM/8167. Oak Ridge National Laboratory, Oak Ridge, pp 82–96

Barwick M (1999) Assessment of copper, cadmium, zinc, arsenic, lead and selenium biomagnification within a temperate eastern Australian seagrass food web. Dissertation, University of Canberra

Beasley G, Kneale P (2004) Assessment of heavy metals and PAH contamination of urban streambed sediments on macroinvertebrates. Water Air Soil Pollut 4:563–78

Bettiol C, Stievano L, Bertelle M, Delfino F, Argese E (2008) Evaluation of microwave-assisted acid extraction procedures for the determination of metal content and potential bioavailability in sediments. Appl Geochem 23:1140–1151

Borovec Z, Tolar V, Mraz L (1993) Distribution of some metals in sediments of the central part of the Labe (Elbe) River: Czech Republic. Ambio 22:200–205

Bryan GW, Langston WJ (1992) Bioavailability, accumulation and effects of heavy metals in sediment with special references to United Kingdom estuaries: a review. Environ Pollut 76:89–131

Burt A (2001) The accumulation of Zn, Se, Cd, and Pb and physical conditions of Anadara trapezia transplanted to a contamination gradient in Lake Macquarie, New South Wales. Dissertation, University of Canberra

Butler D, Davis JW (2011) Urban drainage, 3rd edn. CRC, Boca Raton, 619 pp

Calmano W, Hong J, Förstner U (1993) Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential. Water Sci Technol 8–9:223–235

Cantwell MG, Burgess RM, Kester DR (2002) Release and phase partitioning of metals from anoxic estuarine sediments during period of simulated resuspension. Environ Sci Technol 36:5328–5334

Carleton MG (1990) Comparison of overflows from separate and combined sewers—quantity and quality. Water Sci Technol 22:31–38

Clements WH, Carlisle DM, Lazorchak JM, Johnson PH (2000) Heavy metals structure of benthic communities in Colorado mountain streams. Ecol Appl 10:626–38

Czerniawski R, Domagała J (2010) Zooplankton communities of two lake outlets in relation to abiotic factors. Cent Eur J Biol 5:240–255

Drinan JE, Spellman FR (2013) Water and wastewater treatment. A guide for the nonengineering professionals. 2nd edn. CRC, Boca Raton, 278pp

EN 15169 (2007) Characterization of waste. Determination of loss on ignition in waste, sludge and sediments. BSI, London, 16 pp

Eggleton J, Thomas KV (2004) A review of factors affecting release and bioavailability of contaminants during sediment disturbance events. Environ Int 30:973–980

Farkas A, Salánki J, Varanka I (2003) Crustaceans as biological indicators of heavy metal pollution in Lake Balaton (Hungary). Hydrobiologia 506–509:359–364

Florian D, Barnes RM, Knapp G (1998) Comparison of microwave-assisted acid leaching techniques for the determination of heavy metals in sediments, soils, and sludges. Fresen J Anal Chem 362: 558–565

Gasperi J, Gromaire MC, Kafi M, Moilleron R, Chebbo G (2010) Contribution of wastewater runoff and sewer deposit erosion to wet weather pollutants loads in combined sewer systems. Water Res 44:5875–5886

Göbel P, Dierkes C, Coldewey WG (2007) Storm water runoff concentration matrix for urban areas. J Contam Hydrol 91:26–42

Hnaťuková P, Benešová L, Komínková D (2009) Impact of urban drainage on metal distribution in sediments of urban streams. Water Sci Technol 59:1237–1246

Irvine KN, Caruso J, McCorkhill G (2005) Consideration of metals levels in identifying CSO abatement options. Urban Water J 2:193–200

John DA, Leventhal JS (1996) Bioavailability of metals. In: du Bray EA. Preliminary compilation of descriptive geoenvironmental mineral deposit model. U.S. Geology Survey Open File report 95-831. http://pubs.usgs.gov/of/1995/ofr-95-0831/CHAP2.pdf. Accessed 18 February 2011

Jones DS, Hull RN, Suter GW (1997) Toxicological benchmarks for screening contaminants of potential concern for effects on sediment-associated biota: revision 1997. Oak Ridge National Laboratory, Oak Ridge, 34 pp

Kayhanian M, Stransky C, Bay S, Lau SL, Stenstrom MK (2008) Toxicity of urban highway runoff with respect to storm duration. Sci Total Environ 389:386–406

Karlavičiene V, Švediene S, Marčiulionine DE, Randerson P, Rimeika M, Hogland W (2009) The impact of storm water runoff on a small urban stream. J Soils Sediments 9:6–12

Klavinš M, Briede A, Rodinov V, Kokorite I, Parele E, Klavina I (2000) Heavy metals in rivers of Latvia. Sci Total Environ 262:175–183

Komínková D, Nábělková J (2007) Effect of urban drainage on bioavailability of heavy metals in recipient. Water Sci Technol 56:43–50

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

Lors C, Tiffreau C, Laboudigue A (2004) Effects of bacterial activities on the release of heavy metals from contaminated dredged sediments. Chemosphere 56:619–630

Luoma SN (1983) Bioavailability of trace metals to aquatic organisms. Sci Total Environ 28:1–22

Marsalek J, Rochfort Q, Mayer T, Servos M, Dutka B, Brownlee B (1999) Toxicity testing for controlling urban wet-weather pollution: advantages and limitations. Urban Water 1:91–103

Mihu-Pintilie A, Romanescu G, Stoleriu C (2014) The seasonal changes of the temperature, pH and dissolved oxygen in the Cuejdel Lake, Romania. Carpath J Earth Environ 9:113–123

Miller JR, Miller SM (2007) Contaminated rivers. Springer, Dordrecht, 413 pp

Morillo J, Usero J, Garcia I (2002) Partitioning of metals in sediments from the Odiel River (Spain). Environ Int 28:263–271

Mountouris A, Voutsas E, Tassios D (2002) Bioconcentration of heavy metals in aquatic environments: the importance of bioavailability. Mar Pollut Bull 44:1136–1141

Müller HW, Schwaighofer B, Kalman W (1994) Heavy-metal contents in river sediments. Water Air Soil Pollut 72:191–203

Munksgaard NC, Lottermoser BG (2010) Mobility and potential bioavailability of traffic-derived trace metals in a 'wet-dry' tropical region. Northern Australia. Environ Earth Sci 60:1447–1458

Nábělková J (2005) Mobility of heavy metals in the environment of small urban streams. Dissertation, Czech Technical University in Prague (in Czech)
Nábělková J (2011) Heavy metals in sediments of small urban streams. Habilitation, Czech Technical University in Prague (in Czech)
Nábělková J, Komínková D, Šťastná G (2004) Assessment of ecological status in small urban streams of Prague agglomeration. Water Sci Technol 50:285–291
Page SD (1999) Understanding variation in partition coefficient Kd values. US EPA Office of Air and Radiation, EPA 402-R-99-004A, Washington, USA
Pollert J, Jančárková I, Koudelák P, Stránský D (2000) Laboratory of ecological risks of urban drainage. Final report of the project VS 97038. Prague (in Czech)
Pollert J, Komínková D, Handová Z (2004) Impact of floods on technical and ecological stability of small urban streams. Final report of the project GAČR 103/03/Z017. Prague (in Czech)
Rand GM (1995) Fundamentals of aquatic toxicology. Effects. Environmental fate and risk assessment, 2nd edn. CRC, Boca Raton, 1148 pp
Race M (2012) Assessment of heavy metals in sediments of Prague creeks. Diploma thesis, University of Naples Federico II
Revitt DM, Morrison GMP (1987) Metal speciation variations within separate stormwater systems. Environ Technol Lett 8:361–372
Roy JW, Bickerton G (2012) Toxic groundwater contaminants: an overlooked contributor to urban stream syndrome? Environ Sci Technol 46:729–736
Rouff AA, Eaton TT, Lanzirotti A (2013) Heavy metal distribution in an urban wetland impacted by combined sewer overflow. Chemosphere 93:2159–2164
Sansalone J, Buchberger S (1997) Partitioning and first flush of metals in urban roadway storm water. J Environ Eng 123:134–143
Scholes L, Mensah R, Revitt DM, Jones RH (2007) An investigation of urban water and sediment ecotoxicity in relation to metal concentrations. Highway and urban environment. Alliance for global sustainability bookseries 12:359–370
Stead-Dexter K, Ward NI (2004) Mobility of heavy metals within freshwater sediments affected by motorway stormwater. Sci Total Environ 334–335:271–277
Stockdale A, Tipping E, Lofts S (2010) Toxicity of proton-metal mixtures in the field: linking stream macroinvertebrate species diversity to chemical speciation and bioavailability. Aquat Toxicol 100:112–119
Taylor B, Kovats Z (1995) Review of artificial substrates for benthos sample collection, for Canada centre for mineral and energy technology http://www.nrcan.gc.ca/mms/canmet-mtb/mmsl-lmsm/enviro/reports/3_2_1.pdf. Accessed 18 February 2011
Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of trace metals. Anal Chem 51:844–851
Xiangdong L, Shenguo S, Onyx WHW, Yok-Sheong L (2001) Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River estuary. Mar Pollut Bull 42:215–223