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Metal speciation and attenuation in stream waters and sediments contaminated by landfill leachate

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Abstract The degree of metal contamination (Zn, Pb, Cu, Ni, Cd) has been investigated in the vicinity of an old unmonitored municipal landfill in Prague, Czech Republic, where the leachate is directly drained into a surface stream. The water chemistry was coupled with investigation of the stream sediment (*aqua regia* extract, sequential extraction, voltammetry of microparticles) and newly formed products (SEM/EDS, XRD). The MINTEQA2 speciation-solubility calculation showed that the metals (Zn, Pb, Cu, Ni) are mainly present as carbonate complexes in leachate-polluted surface waters. These waters were oversaturated with respect to Fe(III) oxyhydroxides, calcite ($CaCO_3$) and other carbonate phases. Three metal attenuation mechanisms were identified in leachate-polluted surface waters: (i) spontaneous precipitation of metal-bearing calcite exhibiting significant concentrations of trace elements (Fe, Mn, Mg, Sr, Ba, Pb, Zn, Ni); (ii) binding to Fe(III) oxyhydroxides (mainly goethite, FeO-OH) (Pb, Zn, Cu, Ni); and (iii) preferential bonding to sediment organic matter (Cu). These processes act as the key scavenging mechanisms and significantly decrease the metal concentrations in leachate-polluted water within 200 m from the direct leachate outflow into the stream. Under the near-neutral conditions governing the sediment/water interface in the landfill environment, metals are strongly bound in the stream sediment and remain relatively immobile.

Keywords Metals · Water · Sediment · Landfill leachate · Speciation · Attenuation · Prague · Czech Republic

Introduction

Uncontrolled municipal landfills may represent a potential risk for contamination of groundwater by landfill leachate. Although organic compounds are the principal contaminants in leachate-contaminated environments, inorganic compounds including metals (Zn, Pb, Cu, Ni, Cd) are also commonly leached from the landfills (Christensen et al. 2001). In municipal landfill leachates, the metal concentrations commonly vary from tens to hundreds of μg l^{-1} (Christensen et al. 2001; Jensen and Christensen 1999) and are only slightly higher than in unpolluted groundwater. However, long-term leakage of landfill leachate into the groundwater or leachate drainage into the surface water may locally represent a severe environmental risk. The behaviour of metals in such polluted environments is influenced by the following processes: (i) dilution by rain water during flushing events (Christensen et al. 2001; Johnson et al. 1999), (ii) adsorption on sediment/soil solid constituents, (iii) precipitation of newly formed phases incorporating these contaminants into their crystalline structure (Christensen et al. 2001).

This work was carried out to determine the degree of metal (Zn, Pb, Cu, Ni, Cd) contamination in the vicinity of an old uncontrolled municipal landfill at Dolní

Chabry on the northern periphery of Prague, the capital of the Czech Republic. In contrast to a large number of papers focused on leachate-induced groundwater contamination, this paper presents new data on the efficiency of metal scavenging processes at a landfill site, where the leachate is predominantly drained directly into a surface stream. A combination of analytical data on water chemistry, thermodynamic speciation-solubility modelling, and detailed investigation of the leachate-polluted sediments was used to determine possible mineralogical and geochemical controls of metal attenuation/mobility in such an environment. The influence of speciation of metals in water on their fractionation in contaminated stream sediments has also been emphasised.

Materials and methods

Sampling site

The approximately 30 ha large old municipal landfill at Dolní Chabry is located 5 km north of the centre of Prague, the capital of the Czech Republic (Fig. 1). Construction on the landfill began in 1983, practically without any engineering barriers to prevent leakage of the leachate, except for a soil layer at the bottom of the landfill body. The waste material filled two parallel valleys of a small stream (Draháňský potok), which has

its source directly in this area. Before construction of the landfill, the Draháňský stream was channelled into concrete pipes located at the bottom of the landfill. The leachate is drained directly below the soil layer at the bottom of the landfill and is connected by pipes into the Draháňský stream. It is necessary to note that the geological basement consists of rather permeable Cretaceous marl (hydraulic conductivity $k = 10^{-6}$ m s^{-1}) and Tertiary sandy gravel ($k = 10^{-4}$ m s^{-1}) with a minor portion of Quaternary loess ($k = 10^{-5}$ to 10^{-7} m s^{-1}) and small intrusions of Proterozoic basalt (Pacák 1975; Straka 1988). The groundwater flow is generally from E to W and the groundwater table varies from 0 to 4 m below the ground surface (Straka 1988). The landfill served as the principal disposal site for municipal waste for Prague between 1984 and 1993. In actual fact, no information is available on the amount and the nature of the waste deposited and the presence of some hazardous waste materials (hospital waste, industrial waste) at this site must be taken into consideration.

The direct drainage of leachate outflows into the settling basin (S1) and continues through a 20-m-long pipeline into the former bed of the stream about 250 m down the landfill (Fig. 1). The leachate-polluted surface waters were sampled in the settling basin (S1), at the outflow into the stream (S2) and in the stream after 100 and 200 m (S3 and S4) (Fig. 1). In addition, three piezometers located around the E–W transect were used for groundwater sampling: one piezometer upgradient

Fig. 1 Location of uncontrolled municipal landfill at Dolní Chabry with the positions of the sampling points
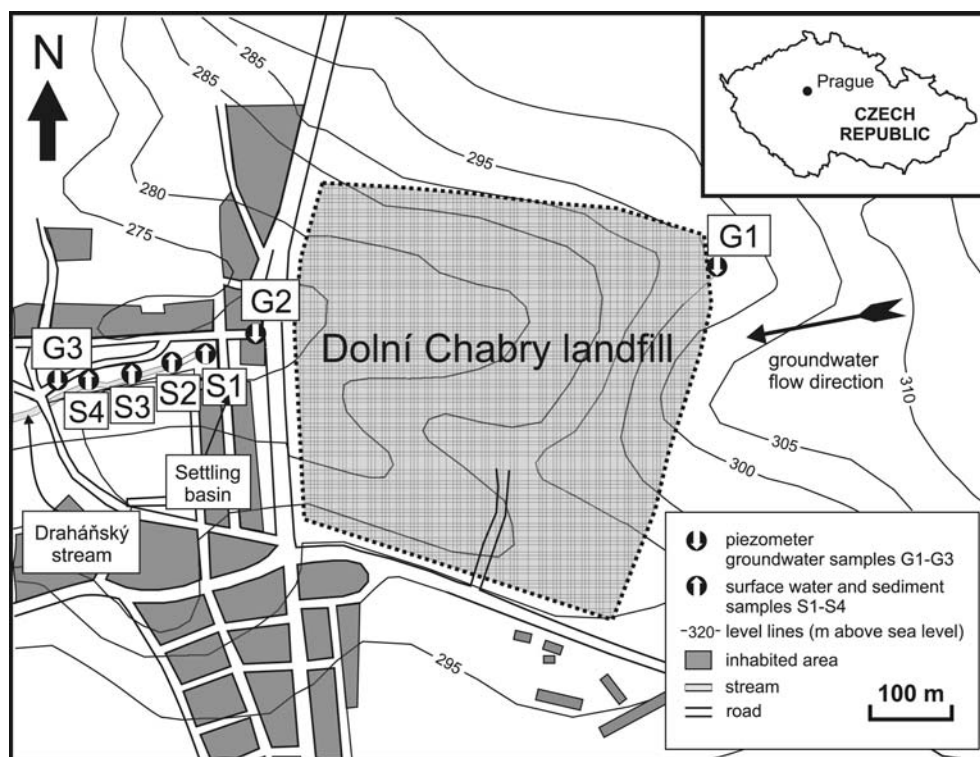
(G1) and two piezometers downgradient to the landfill (G2 and G3) (Fig. 1). Piezometer G2 is located in the vicinity of the road embankment serving as a barrier for the landfill body (Fig. 1). Each well consists of a protective metallic well top (15 cm in diameter) with a plastic pipe (10 cm in diameter), where the groundwater samples were collected.

Sample collection and preparation

Five sampling campaigns from November 2001 to December 2002 according to the seasons of the hydrological year were carried out to determine the role of precipitation and the annual seasons on bulk metal contamination and chemical speciation in the ground and the surface water. The average annual precipitation measured by the Czech Meteorological Station at Kbely, located about 5 km E from the landfill site, is about 580 mm. The sampling campaign of mid-April 2002 corresponded to the driest period, with total precipitation as low as 2.1 mm in 10 days prior to sampling. In contrast, the sample collection at the end of June 2002 corresponded to a very wet period with two significant rain events with a total of 40.3 mm of precipitation in 5 days prior to sampling.

The surface waters were sampled directly in the settling basin (S1) or in the stream (S2–S4) and the pH, Eh, conductivity and temperature were immediately measured. The pH value was determined using a Schott-Geräte Handylab 1 pH meter equipped with a Schott L 7137 A combined electrode (accuracy of ± 0.01 std pH unit). The Eh value was measured using a Schott-Geräte Handylab 1 pH meter equipped with a Schott PT 737 A (Pt-Ag/AgCl) redox electrode (accuracy of ± 0.5 mV) with automatic correction against a hydrogen redox electrode. Temperature and conductivity measurement were performed using a Schott-Geräte Handylab LF 1 conductometer equipped with a LF 513 T measuring cell and a temperature detector. The accuracy of the measurement was ± 0.001 mS cm^{-1} for the conductivity and 0.1°C for the temperature. The water samples for inorganic analysis were stored in 1 l acid-washed HDPE bottles (Azlon, UK) and, for DOC measurements, in clean 100 ml borosilicate glass bottles (Schott Duran®, Germany). Groundwaters were sampled using a HDPE bailer sampler following slow pumping (200 ml min^{-1}) in order to remove stagnant water. Purging was applied to constant conductivity; approximately 25 l of stagnant water was removed from each well before sample collection. The groundwater samples were submitted to the same procedure of measurement of the physico-chemical parameters.

Stream sediments (approximately 300 g samples) and newly formed products were collected at the same sampling points as that of surface waters and were stored in plastic bags. No storage in an inert atmosphere (N$_2$, Ar) was necessary for the stream sediment samples, due to oxidising conditions revealed by Eh measurements in the surface waters.

Water analysis

Waters were filtered using a Millipore® membrane filter 0.45 μm and Sartorius filtration device for dissolved organic carbon (DOC) and inorganic carbon (IC) analysis (SKALAR Formacs^{HT} TOC analyzer). The rest of the solution was filtered using a 0.1 μm Millipore® membrane filter and split into two parts: (i) for cation and trace element analysis and (ii) for anion analysis and alkalinity measurements. The first aliquot was acidified to pH < 2 with nitric acid (Merck, Germany) to prevent metal precipitation and adsorption on the container surface. The alkalinity, measured immediately by titration to pH 4.5 using 0.1 M HCl (reagent grade Lachema, Czech Republic), was recalculated to the HCO$_3$ content. The major cations (Na, K, Ca, Mg, Si, Mn, Fe) were analysed using a Varian SpectrAA 200 HT flame atomic absorption spectrophotometer (FAAS) under standard analytical conditions. The major anions (F, Cl, SO$_4$, NO$_3$) were analysed using a Dionex DX100 high-pressure liquid chromatograph. The concentrations of the trace metals and other elements (Zn, Pb, Cu, Ni, Cd, Cr, Ba, Sr, I, Br) were measured by a VG Elemental PlasmaQuad 3 quadrupole based mass spectrometer with inductively coupled plasma (ICP-MS). NIST standard reference materials 1640 (Trace Elements in Natural Water) and 1643d (Trace Elements in Water) were used for quality control of instrumental analyses. The relative standard deviation with respect to the certified values was less than 5% for all the analysed elements.

Sediment analysis

The sediment samples were wet-sieved through a 63-μm mesh nylon sieve, dried to constant weight at 35°C and ground in an agate mortar. The *aqua regia* extract (ISO 11466, ISO 1995) was used as an equivalent for the pseudo-total bulk metal concentration in the sediment. Three grams of the sample were placed in a 250 ml reaction tube and a mixture of 21 ml of HCl (12 mol l^{-1}) and 7 ml of HNO$_3$ (15.8 mol l^{-1}) was added carefully. The mixture was allowed to stand for 16 h at room temperature, and then refluxed for 2 h at 130°C. Following cooling, the solutions were filtered using a Whatman No. 40 paper filter and the volume was made up to 100 ml by the addition of 0.5 mol l^{-1} HNO$_3$. The bulk concentrations of the metals in the *aqua regia* extracts (Pb, Zn, Cu, Cd, Ni, Mn, Fe) were determined by a Varian SpectrAA 200 HT FAAS. The standard

deviation for the second replicate was lower than 5% for all elemental analyses. The accuracy of measurement was controlled by simultaneous dissolution and analysis of LGC 6139 River Clay Sediment Standard certified by the LGC analytical laboratory, UK (RSD < 5%). In order to determine the chemical fractionation of the principal metals (Zn, Pb, Cu, Ni, Mn), the four stream sediments were submitted to a sequential extraction (SE) procedure according to Tessier et al. (1979). The extractions were conducted in 50 ml PE centrifuge tubes with 1 g of sediment sample. Each chemical fraction was operationally defined as indicated in Table 1. Following the extraction, the solid was centrifuged off and the supernatant was transferred into a 25 ml flask. The solid phase was washed with 2 ml of deionised water before the next extraction step. The washes were added to the supernatant of the previous fraction before adding an acidifying agent (1 ml of concentrated double-distilled HNO_3) and filling the 25 ml volumetric flask to the mark with MilliQ + deionised water and analyses. The residual sediment sample was used for the subsequent extraction step.

All the chemicals used in the SE procedure were reagent grade (Merck or Lachema). The concentration of metals (Pb, Zn, Cu, Ni) in the individual fractions was determined using a Varian SpectrAA 200 HT FAAS by matrix-matched calibration. A procedural blank was run for every extraction fraction. The standard deviation for the duplicate analysis was less than 10% RSD for the individual SE steps. The pseudo-total digestion results were in good agreement with the sum of the recoveries in the individual extraction steps ($R^2 = 0.9926$).

Bulk sediment samples and macroscopically visible secondary precipitates were analysed by X-ray powder diffraction analysis (XRD) on a Siemens D5005 instrument, Cu Kα radiation at 40 kV and 45 mA, with a diffracted beam monochromator, scanning over the range 5–80° in 2Θ. Qualitative analysis was performed with the Diffrac-Plus software package, version 8.0 (Bruker AXS, Germany) and JCPDS PDF-2 database (ICDD 2001). The observations of newly formed phases were made with a Jeol 6400 scanning electron microscope and a Delta Kevex energy dispersion spectrometer (SEM/EDS). The contents of inorganic and organic C were determined by catalytic oxidation (1,250°C) using an Eltra Metalyt CS1000S elemental analyser (Neuss, Germany).

Voltammetry of microparticles (VMP) was employed for stream sediment samples in order to detect the presence of Fe and Mn oxides. VMP was performed according to Grygar and van Oorschot (2002) using a µAutolab potentiostat, a paraffin-impregnated graphite working electrode, 0.2 M sodium acetate–acetic acid buffer (1:1), and a scan rate of 3 mV/s. Goethite and hematite were distinguished after heating a small amount of sample at 320°C. Interpretation of the voltammetric peak potentials was carried out in accordance with Grygar et al. (2002). The voltammetric peaks were clearly discernible in the first scan without the need to subtract the second scan.

Speciation-solubility modelling

The element speciation and the degree of saturation of waters with respect to mineral phases were performed using the MINTEQA2 geochemical code (Allison et al. 1991). The thermodynamic calculations were carried out for all the water samples in order (i) to speciate the solutions and (ii) to determine the degree of supersaturation of the solutions with respect to the mineral phases. A temperature of 10°C, corresponding to the mean temperature for the sampled ground and surface waters, was used for all the model calculations. The dissolved organic matter (DOM) concentration was entered into the MINTEQA2 code in eq l^{-1} and was recalculated

Table 1 Sequential extraction scheme employed for a 1 g sample of leachate-polluted stream sediments (Tessier et al. 1979)

Fraction	Description	Procedure
A	Exchangeable (salt-displaceable)	8 ml 1 M $MgCl_2$, 1 h at 25°C, continuous agitation
B	Acid extractable (bound to carbonates)	8 ml 1 M NaOAc, adjusted to pH 5 with HOAc, 5 h at 25°C, continuous agitation
C	Reducible (bound to Fe and Mn oxides)	20 ml 0.04 M $NH_2OH \cdot HCl$ in 25% HOAc, 6 h at 96°C, occasional agitation
D	Oxidisable (bound to organic matter and sulphides)	3 ml 0.02 M HNO_3 and 5 ml 30% H_2O_2, adjusted to pH 2 with HNO_3, 2 h at 85°C; additional 3 ml 30% H_2O_2 adjusted to pH 2 with HNO_3, 3 h at 85°C; 5 ml 3.2 M NH_4Ac in 20% HNO_3 added after cooling, dilution to 20 ml, continuous agitation for 30 min
E	Residual (silicates)	10 ml HF and 2 ml $HClO_4$ in Pt crucibles, evaporated to dryness, repeated with 1 ml $HClO_4$ and 10 ml HF, final addition of 1 ml $HClO_4$, evaporation and dissolution in 5 ml HCl

from the DOC concentrations assuming 50% carbon content and molar site concentrations of 6.92 and 7.44 meq l^{-1}, as reported by Christensen et al. (1999) for leachate-polluted groundwaters. These molar site concentration values differ from the Suwannee River DOM values originally present in the MINTEQA2 database and were successfully used for MINTEQA2 speciation calculations by Christensen et al. (1999). Default stability constants for the metal–DOM complexes supplied by MINTEQA2 database were used for all the calculations.

Results and discussion

Water chemistry

Chemical analyses of the water samples indicated significant differences in the concentrations of the macro-components and trace metals between the leachate-polluted ground and surface waters (Table 2). The pH varied from 6.85 to 7.5 in the groundwater and from 7.25 to 8.13 in the surface waters. The DOC concentrations in the groundwater increased up to five times in the E–W transect, varying from < 10 mg l^{-1} in sample G1 to 54.7 mg l^{-1} in sample G3 and confirming the influence of the landfill on groundwater quality. The DOC concentrations in the surface water were higher in the dry sampling periods (up to 212.9 mg l^{-1}) and remained relatively unchanged as a function of distance from the direct leachate outflow.

An increase in the conductivity was also typical in the groundwater downgradient to the landfill (Table 2). The highest conductivity (up to 6.2 mS cm^{-1}) and concentrations of major elements were observed in the surface water from the direct leachate output (S1) during the dry sampling periods (Table 2). The effect of dilution after the rain event was particularly significant in the surface

waters, exhibiting a sharp decrease in the specific conductivity (five times) and concentration of macro-components (e.g., DOC, alkalinity) (Table 2).

A strong variation in the trace elements (Zn, Pb, Cu, Cd, Ni) concentrations was observed in both ground and surface waters (Table 2). The cadmium concentrations were very low (up to 0.78 μg Cd l^{-1} in the groundwater) mostly exhibiting values close to the detection limit of ICP-MS (0.2 μg Cd l^{-1}). The contents of Zn, Pb, Cu and Ni in the groundwater generally increased around the E–W transect of the sampled piezometers. Compared to the surface waters, the trace element concentrations in the groundwaters were relatively more stable for both the dry and the wet sampling periods (Table 2). The effect of rain events on the bulk trace element concentrations was more pronounced in the surface waters. Significantly higher concentrations were observed in the dry sampling period, generally with the highest content in sample S1, corresponding to the water from the settling basin (up to 31 μg Zn l^{-1}, 8.3 μg Pb l^{-1}, 14.3 μg Cu l^{-1}, 88.9 μg Ni l^{-1}) (Table 2). A general decreasing trend with the distance from the leachate outflow was observed for the trace element concentrations (Table 2). This phenomenon is strictly related to existing geochemical/mineralogical attenuation mechanisms at the stream water/sediment interface (see below).

According to the U.S. EPA drinking water standards, the concentrations of all trace elements in the studied leachate-polluted waters were below the maximum contaminant level (MCL) values given by U.S. EPA (2002).

Speciation calculations by MINTEQA2

The results of MINTEQA2 speciation modelling for ground and surface water samples in the dry and wet

Table 2 Variations in selected physicochemical and chemical parameters in the most polluted groundwater (G3), surface water from the settling basin (S1) and stream surface water 200 m distant (S4)

Parameter		Dry sampling period				Wet sampling period		
		DL	G3	S1	S4	G3	S1	S4
PH	Std units		7.05–7.20	7.66–7.96	7.87–8.08	6.96–7.17	7.25–8.13	7.37–7.54
Eh	mV		145–234	123–166	121–163	217–287	195–220	188–192
Specific conductivity	mS cm^{-1}		3.50–4.44	5.03–6.18	4.41–5.50	3.15–4.92	1.41–2.90	1.09–2.51
DOC	mg l^{-1}	0.02	43.5–54.7	69.4–212.9	67.3–194.3	38.2–50.9	28.9–104.0	20.5–35.2
HCO_3^-[a]	mg l^{-1}	1.00	659–970	1,324–1,998	1,239–1,921	336–702	357–1,135	302–305
Zn	μg l^{-1}	0.10	20.7–29.0	8.7–31.0	8.9–21.0	8.9–38.2	11.2–19.1	7.7–13.2
Pb	μg l^{-1}	0.05	0.44–5.49	1.76–8.30	< 0.05–1.00	1.21–1.32	0.83–2.60	< 0.05–0.17
Cu	μg l^{-1}	0.10	8.3–12.8	1.6–14.3	2.4–5.0	5.6–10.1	4.7–11.9	1.5–3.0
Ni	μg l^{-1}	0.50	83.4–99.5	53.3–88.9	44.4–89.5	54.4–85.5	15.5–90.2	9.5–19.9
Cd	μg l^{-1}	0.20	0.30–0.55	< 0.20	< 0.20	< 0.20–0.78	0.22–0.73	< 0.20

DL detection limit, *DOC* dissolved organic carbon
[a]Calculated from alkalinity titration

Table 3 Variations of speciation of Zn, Pb, Cu, and Ni in leachate-polluted groundwater and surface waters as calculated by MINT-EQA2 (in % of total speciation)

Metal	Complex	Dry sampling period		Wet sampling period	
		Groundwater	Surface waters	Groundwater	Surface waters
Zn	Zn^{2+}	55–66	2–3	60–68	46–52
	Zn–DOM	5–8	3–4	3–5	11–14
	Zn–carb[a]	23–38	93–95	29–32	32–43
	$ZnSO_4$	< 2	–	< 2	< 1
	$ZnCl^+$	< 1	–	< 1	–
Pb	Pb^{2+}	3–5	–	4–5	2
	Pb–DOM	14–30	5–9	12–17	18–31
	Pb–carb	63–83	91–95	77–83	67–81
	$PbCl^+$	< 2	–	< 2	–
Cu	Cu^{2+}	7–11	–	10	3–5
	Cu–DOM	16–33	7–12	13–20	15–32
	Cu–carb	47–63	63–66	61–62	42–45
	$Cu(OH)_2$	9–14	23–29	7–15	18–40
Ni	Ni^{2+}	8–16	–	12–21	4–7
	Ni–DOM	< 1	–	–	< 1
	Ni–carb	83–92	100	77–88	91–96

[a]Metal–carbonate complexes: $MeHCO_3^+$, $MeCO_3$ (aq), $Me(CO_3)_2^{2-}$

sampling periods are given in Table 3. The calculations indicated that a significant part of the metals (Zn, Pb, Cu, Ni) is bound in carbonate complexes, such as $MeHCO_3^+$, $MeCO_3$(aq) and $Me(CO_3)_2^{2-}$, especially in the surface waters. This is in agreement with the calculations of Jensen et al. (1999), who studied the metal speciation in landfill-leachate-polluted groundwater.

Zinc speciation in groundwaters did not change in the dry and wet sampling periods, predominantly with the free ionic form, and with a minor percentage of carbonate and bicarbonate complexes (up to 38% in sample G3) and Zn–DOM complexes (up to 8% of total speciation) (Table 3). Zn speciation in the surface waters sampled in the dry period was predominated by carbonate and bicarbonate complexes (up to 95% of the total speciation). In contrast, the Zn speciation in the surface waters sampled in the wet period after a significant rain event showed a marked shift towards the free ionic forms (up to 52%), due to a dramatic decrease in the alkalinity (Table 3). Lead is mainly present in carbonate and bicarbonate complexes in both ground and surface waters (Table 3). During the dry sampling season, the presence of carbonate complexes is more pronounced, especially for stream waters (90–95%) while, during the wet sampling season, these complexes account for 62–83% in both surface and groundwaters. Up to 31% of total Pb speciation can be attributed to Pb–DOM complexes (Table 3). The speciation of Cu is very complex, and also involves the presence of $Cu(OH)_2$(aq), which became important especially in the surface waters (up to 40% of the total speciation) (Table 3). The prevailing carbonate and bicarbonate complexes accounted for 66% in the surface waters sampled in the dry period,

while their percentage dropped to 42–45% after the rain event. The Cu–DOM complexes (up to 33%) are important, especially in water samples with highest DOC concentrations (G3, S1) (Table 3). Nickel is mainly present in carbonate and bicarbonate complexes in both types of sampled water, with a minor percentage of the free ionic form (8–12%) in groundwater G3 (Table 3). The occurrence of the free ionic form (up to 7%) was observed in the Ni speciation after the rain event (Table 3).

The MINTEQA2 calculations showed a strong supersaturation of ground and surface water samples with respect to hydrous ferric oxides, such as ferrihydrite ($Fe(OH)_3$) or goethite (α-FeOOH). The saturation indices (SI) of ferrihydrite in the groundwater were quite stable, varying from 1.2 to 1.6, while surface waters showed stronger supersaturation in the dry sampling period (SI = 3), in contrast to the wet sampling period (SI = 1.8–1.9). During the dry period, leachate-polluted ground and surface waters are highly supersaturated with respect to calcite ($CaCO_3$; SI = 0.6–1.5), dolomite ($CaMg(CO_3)_2$, SI = 0.6–2.8) and rhodochrosite ($MnCO_3$; SI = 0.2–0.3). Magnesite ($MgCO_3$) is supersaturated only in the surface waters. Supersaturation of landfill leachates with respect to carbonate species is quite common (Jensen and Christensen 1999; Manning 2001). In contrast, during the wet sampling period, the SI values of these carbonate phases decreased in the most contaminated groundwater G3 (0.1–0.5). In surface water after the rain event, the SI values of these carbonates were < 0 and only calcite was close to saturation ($SI_{calcite}$ = −0.03–0.16). All the other carbonate species (strontianite $SrCO_3$, witherite $BaCO_3$, smithsonite $ZnCO_3$, otavite $CdCO_3$, cerussite $PbCO_3$, $CuCO_3$,

Fig. 2 *Aqua regia* extract values and chemical fractionation of Zn, Pb, Cu, and Ni in leachate-polluted stream sediments sampled as a function of the distance from the direct leachate outflow into the settling basin (S1). The maximum background values are compiled from litogeochemical databases (Čadková 1984; Čadková and Mrázek 1987; Gürtlerová et al. 1997)
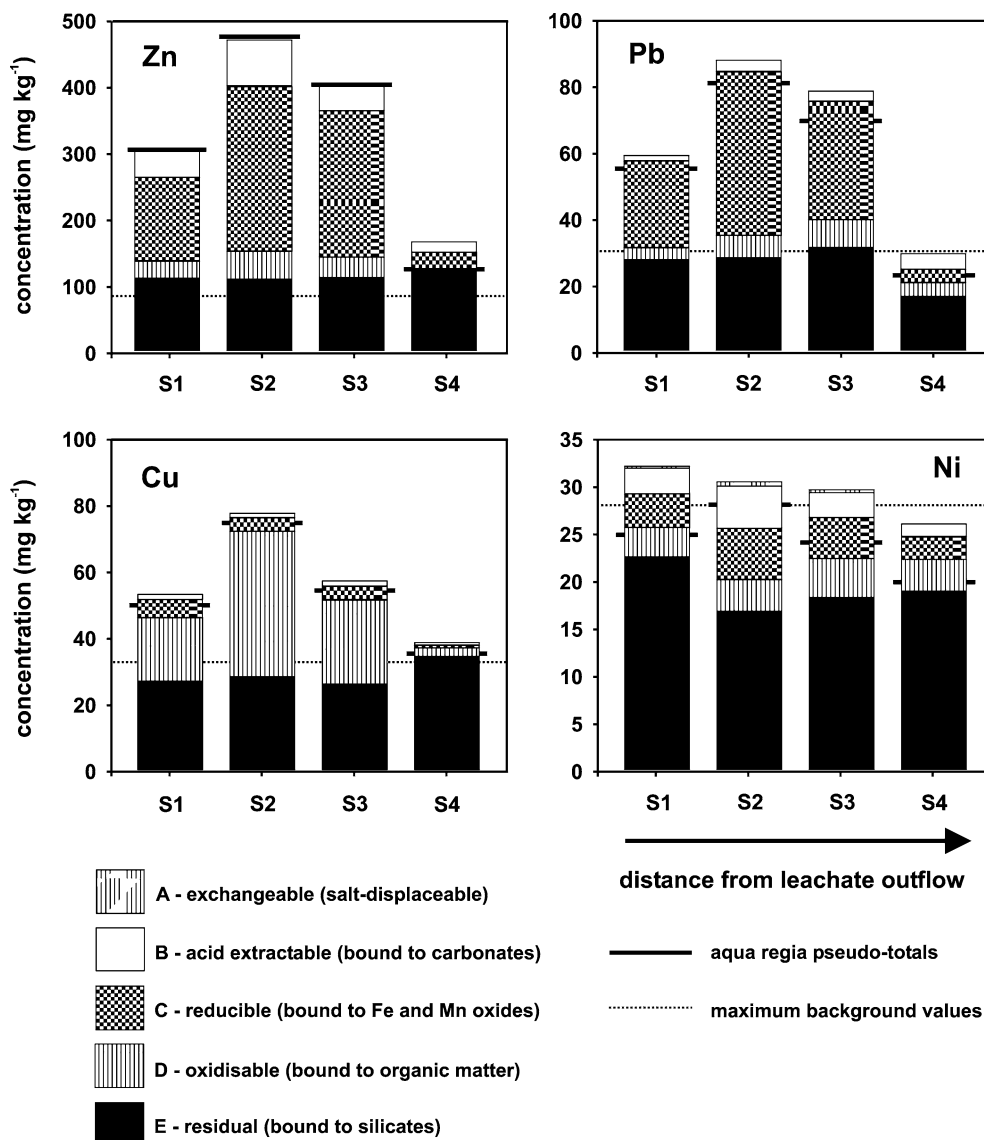
and NiCO₃) were undersaturated in both ground and surface waters and their SI values were not significantly affected by rain events.

Metal speciation in stream sediment

The results of pseudo-total *aqua regia* extracts yielded the highest contents in sediment S2 (Zn, Pb, Cu) or in sediment S1 from the settling basin (Ni) (Fig. 2). The concentrations of Cd in the *aqua regia* extracts were below the detection limit of FAAS (0.003 mg Cd l^{-1}). In spite of the relatively good agreement with the sums of SEs ($R^2 = 0.9926$), some pseudo-totals were underestimated due to inefficiency of silicate mineral dissolution by the *aqua regia* procedure. The bulk concentrations of

all elements significantly decreased with distance from the direct leachate outflow (Fig. 2). The bulk concentrations of Zn and Cu in all stream sediments exceeded the geochemical background values (Čadková 1984; Čadková and Mrázek 1987; Gürtlerová et al. 1997), while Pb and Ni decreased below the background values in the most distant sample S4 (Fig. 2). According to the Czech legislation defined by the Regulation of the Ministry of Environment of the Czech Republic (Regulation No. 13/1994), samples S1-S3 with concentrations of 312–476 mg Zn kg^{-1} exceeded the defined limit of 200 mg Zn kg^{-1} (Fig. 2). The contents of the other studied metals were below the limits defined by this regulation.

The results of chemical fractionation of selected metals (Zn, Pb, Cu, Ni) in stream sediments are given in

Fig. 3 SEM microphotographs of calcite ($CaCO_3$) newly formed in sediment from the settling basin S1 (in secondary electrons): **a** aggregates of calcite with trace element content; **b** zoom of the calcite surface
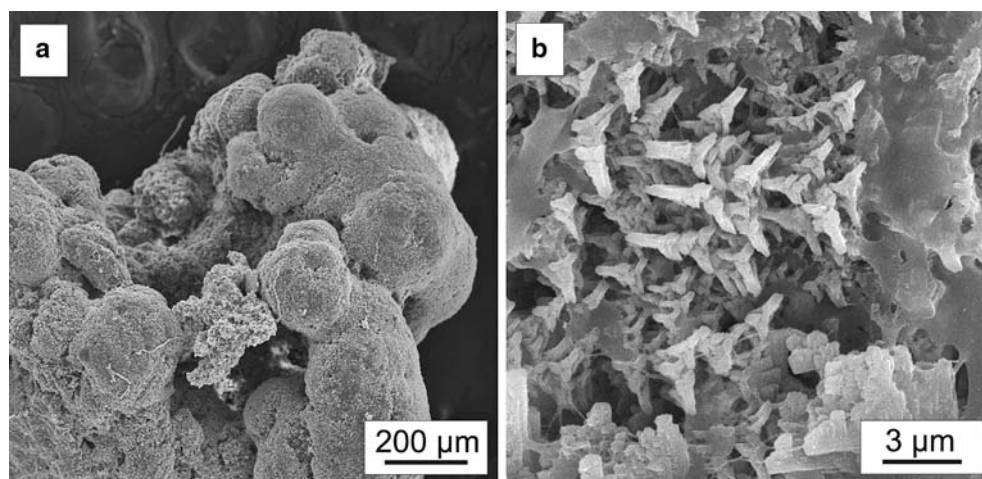

Fig. 2. Zn and Pb exhibit similar chemical fractionation with predominant reducible fraction (bound to Fe and Mn oxides and hydroxides). Lower amounts of Pb and Zn are bound in the acid-extractable fraction (carbonates) and in the oxidisable fraction (organic matter) (Fig. 2). These observations are in agreement with the MINTEQA2 modelling in surface waters, which confirmed the predominance of carbonate and bicarbonate species of Pb and Zn, precursors for the solid carbonate precipitation. Copper showed a strong tendency to be bound to organic matter (oxidisable fraction, up to 56%) with a minor percentage of reducible (Fe and Mn oxides) and acid extractable (carbonate) fractions (Fig. 3). The analytically confirmed concentrations of total organic carbon in sediment varied from 3.41 to 5.79 wt.%. Preferential binding of Cu to organic matter is not surprising because of the strong tendency towards complexation of Cu^{2+} ions with humic substances even at low concentrations (Stumm and Morgan 1981; Iglesias et al. 2003). Binding of Cu to ferric oxides can be attributed to their coprecipitation with $Cu(OH)_2$ complexes (Karthikeyan et al. 1997), predicted in the studied water samples by MINTEQA2 speciation calculations. Except for the predominant residual fraction (up to 73%), Ni exhibits uniform fractionation among the oxidisable, reducible and acid soluble fractions (5–18%) (Fig. 2). The exchangeable fraction of Ni was negligible, accounting only for 1.6% maximum.

Voltammetric analysis of the stream sediment samples revealed the presence of approximately 1% of medium-crystalline goethite (α-FeOOH, peak potential −0.63 to −0.74 V vs. SCE). The samples did not contain detectable amounts of hematite, ferrihydrite, or Mn(III,IV) oxides. The detection limit of voltammetry for hematite and Mn(III,IV) oxides is about 0.1 wt.% (Grygar and van Oorschot 2002) and about 1 wt.% to ferrihydrite.

Mineralogy of sediments and newly formed phases

The XRD analysis of the bulk stream sediment samples indicated the presence of quartz (SiO_2) and calcite ($CaCO_3$), with trace amounts of albite ($NaAlSi_3O_8$) and illite ($(Na,K)Al_2(Si_3AlO_{10})(OH)_2$). The concentrations of total inorganic carbon in the sediment decreased from 3.42 to 0.33 wt.% with increasing distance from the settling basin. Spontaneous precipitation of calcite was observed directly in the stream water. The SEM/EDS observations indicated the presence of calcite aggregates (Fig. 3) with the distinct peaks of Fe, Mn, Mg, and Sr in the EDS spectra. The chemical compositions of these calcites have been studied by Ettler et al. (2003) using acid dissolution and subsequent analysis by ICP-MS and FAAS. This investigation indicated the presence of the following elements associated with calcite: Ni (up to 8 mg kg^{-1}), Cu (4 mg kg^{-1}), Zn (41 mg kg^{-1}), Cd (0.2 mg kg^{-1}), Pb (4.8 mg kg^{-1}), Ba (220 mg kg^{-1}), Sr (1,990 mg kg^{-1}), Fe (620 mg kg^{-1}), Mn (870 mg kg^{-1}), Mg (5,670 mg kg^{-1}) (Speer 1990). The carbonates of Zn, Mg, Fe, Mn, Ni, Cd, and Cu are isostructural with calcite, having a rhombohedral structure (Speer 1990). As a result, the divalent ions of these elements can easily replace Ca^{2+} in the calcite structure. In contrast, other elements (Pb, Sr, Ba) are isostructural with orthorhombic $CaCO_3$ (aragonite), which has not been detected by XRD in our samples. However, a strong interaction of Pb with calcite has been observed experimentally, taking into account the sorption of Pb^{2+} ions on the calcite (Godelitsas et al. 2003). Even low miscibility in the systems calcite-strontianite ($SrCO_3$) and calcite-witherite ($BaCO_3$), observed by Tesoriero and Pankow (1996), could be sufficient for the Ba and Sr contents in our newly precipitated calcite samples. Because of these numerous elemental substitutions in the calcite structure, the cell dimensions of the newly formed

Table 4 Mobility factors (MF) and corresponding mobile concentrations for Zn, Pb, Cu, and Ni in leachate-polluted stream sediments

Element		Sample			
		S1	S2	S3	S4
Zn	MF (%)	14.5	15.0	10.7	10.4
	mg kg^{-1}	44.7	70.9	43.5	17.5
Pb	MF (%)	2.6	3.8	3.9	16.0
	mg kg^{-1}	1.6	3.3	3.0	4.7
Cu	MF (%)	2.7	1.6	2.6	2.0
	mg kg^{-1}	1.5	1.3	1.5	0.8
Ni	MF (%)	9.1	16.1	9.8	5.0
	mg kg^{-1}	2.9	4.9	2.9	1.3

calcite studied showed a significant contraction of the cell dimensions to $a_0 = 4.9809$ Å and $c_0 = 17.05$ Å (Ettler et al. 2003). The reference cell parameters of pure calcite (JCPDS file 5−0586) are $a_0 = 4.989$ Å, $c_0 = 17.062$ Å (ICDD 2001).

Environmental issues

The uncontrolled municipal landfill at Dolní Chabry (Czech Republic) has been found to have a distinct influence on the chemistry of waters and stream sediments. The concentrations of macrocomponents, DOC and trace metals (Pb, Zn, Cu, Ni) increased in waters downgradient to the landfill. The highest metal concentrations were observed in the leachate-polluted stream water. MINTEQA2 thermodynamic modelling demonstrated the predominance of free ionic metal species in polluted groundwaters and of carbonate and bicarbonate species in polluted surface waters. A significant decrease in the metal concentrations in leachate-polluted surface waters has been observed after and during precipitation events, exhibiting a significant shift to free ionic species in metal speciation due to a decrease in the alkalinity through water dilution.

Some recent works (e.g., Jensen et al. 1999) showed that, in some leachate-polluted waters, an important portion of some metals is associated with colloids in fraction < 0.01 μm. Such a small-size colloidal fraction may also be significant for our samples despite membrane filtration to only 0.1 μm. Inorganic precipitates (nanocrystals of calcite or ferric oxyhydroxides) or organic matter could probably form these colloids, as revealed by the strong supersaturation of solutions with respect to these phases (MINTEQA2 calculation) and high DOC concentrations, respectively. In contrast, the results of Jensen and Christensen (1999) suggest that, when the heavy metal content in the leachate is low (10 μg l^{-1}), it is probably not of major environmental concern that part of the metals is associated with colloids.

The concentrations of metals in surface stream water greatly decreased with increasing distance from the direct leachate outflow. This observation is related to efficient metal-scavenging processes occurring at the water/sediment interface directly in the settling basin and in the stream. In the stream sediment, the concentrations of the metals decreased below (Pb, Ni) or close (Cu) to the background concentration levels within 200 m from the direct leachate outflow. The newly formed ferric oxyhydroxides, mainly goethite FeOOH, and calcite, have been found to play an important role in the attenuation of metals. The SE procedure performed on stream sediments showed that Pb and Zn are mainly bound in acid-extractable (carbonate) and reducible (Fe and Mn oxides) fractions, while Cu is bound more to the oxidisable (organic matter) fraction. Spontaneous precipitation of calcite occurred in leachate-polluted surface waters and had a strong metal 'decontamination' effect. Trace concentrations of Fe, Mn, Mg, Pb, Zn, Cu, Ni, Cd, Sr, and Ba have been analytically confirmed within these secondary calcite precipitates. It has been observed that the maximum concentrations of Pb, Zn, Cu, and Ni in landfill calcites (Ettler et al. 2003) greatly agree with their concentrations extracted in the carbonate-bound fraction in SEs ($R^2 = 0.9938$).

In order to determine the 'mobilisable' fraction of metals bound in the stream sediments, the mobility factors (MF) were calculated from the SE results on the basis of the equation modified from Salbu et al. (1998) and Kabala and Singh (2001):

$$MF = [(\text{fraction A} + \text{fraction B})/\text{sum of SE fractions}] \times 100(\%)$$

Since some metal forms are relatively less mobile if bound in fractions C, D, and E, MF describes the potential mobility of metals in the system (Salbu et al. 1998). The results of MF calculations are given in Table 4. The highest mobility of Zn (15%), Pb (16%), and Ni (16.1%) corresponded to sediments with higher amounts of acid-extractable (carbonate) fraction. In contrast, the MF for Cu yielded relatively low values (< 2.7%), which is an indication of the high stability of Cu in the sediments (Table 4). The dissolution of the carbonate-bound fraction of metals in the sediments is highly improbable in the pH range (values 7–8) observed in surface waters. As a result, even the carbonate fraction will be relatively stable and the mobility of the metals in the stream sediments will

be extremely low. This is also true for goethite: its total dissolution would be required for the mobilisation of heavy metals chemisorbed in FeOOH.

The results of this study indicated that efficient immobilisation mechanisms of metals take place in an oxidising environment in systems where the landfill leachate is drained into the surface water. Thus, the environmental impact of even a long-term leakage of landfill leachate (with low metal content of up to $10 \ \mu g \ l^{-1}$) may be strongly attenuated by high metal fixation on sediment constituents.

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