



Association of trace elements with colloidal fractions in leachates from closed and active municipal solid waste landfills

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ABSTRACT

Leachates from two Czech municipal solid waste (MSW) landfills (closed site and active site) were size-fractionated using the cascade frontal filtration/ultrafiltration procedure with filter cut-offs of 3 μm , 0.8 μm , 0.45 μm , 0.1 μm , 10 kDa and 1 kDa. To evaluate the binding of trace elements to colloidal particles, the filtrates were analyzed for major compounds (FAAS, ICP-OES and HPLC) and trace elements (ICP-MS) and the obtained elemental patterns were statistically evaluated. Transmission electron microscopy (TEM) indicated that the colloids were mostly inorganic, mainly composed of carbonates and clays. Characteristic features of the behaviour of trace elements and the main compounds were more pronounced at the active landfill site. Amongst the main compounds, only Fe and Ca decrease significantly and have similar patterns to numerous trace elements, indicating their capture by colloidal particles (at least 25%). Arsenic, Se and Rb exhibit zero or negligible decrease in concentration in the leachate during the filtration procedure. This fact indicates their particularly high mobility, which should be considered in preventing the flux of harmful compounds from landfill systems.

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1. Introduction

Although the production of waste materials in the Czech Republic is decreasing in the long term, landfilling is still a predominant management scenario for municipal solid waste (MSW). According to the Ministry of Environment of the Czech Republic, only about 9% of MSW produced in 2007 was incinerated and about 80% was landfilled (the remainder was treated in different ways, mainly by recycling, chemical and biological processes) [1]. In the Czech Republic, there are 31 small and 3 large incinerators designed for treating MSW (mostly located in the vicinity of large cities), with a total annual capacity of 731 000 t. In contrast, there are 265 landfills with a total capacity of over 124 million m^3 of MSW. Of this amount, more than 250 landfills have been constructed during the last three decades. The EU “landfill” directive (Council Directive 99/31/EC [2]) was recently adopted in the Czech Republic, but a large number of older landfills are not equipped with appropriate technological barriers preventing leakage of harmful compounds into the envi-

ronment [1]. In Prague, the capital of the Czech Republic, 200 000 t of MSW were incinerated and 150 000 t were disposed in controlled landfill sites in 2008 [1].

Traditionally, environmental studies dealing with the risk related to landfill leachates are mostly focused on organic pollutants and metals (e.g. [3] and reference therein). In particular, metals (Pb, Cu, Zn, Cd and Ni) in landfill leachates have been found to be associated with colloidal particles of various sizes influencing their speciation, mobility and toxicity [4–6]. In our previous paper focused on long-term monitoring of landfill leachates [7], we showed that attention should also be devoted to other trace elements, and not only to metals. Binding of trace elements to colloids can have important implications for selection of the most efficient method for the landfill leachate treatment [8] and for evaluation of trace element mobility in the case of leakage from the landfill body into the surrounding environment [6]. In this perspective, the aim of the present article is to evaluate the binding of trace elements (including metals, metalloids, etc.) to colloidal particles in leachates from two MSW landfill sites with different histories (closed versus active) using filtration and ultrafiltration size-fractionation studies and accurate trace element analysis using ICP techniques.

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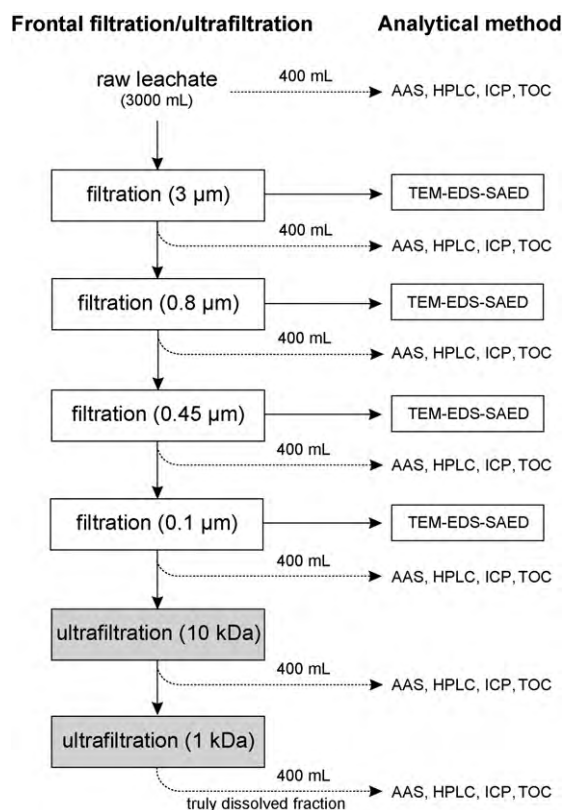


Fig. 1. Flow diagram of the frontal filtration and ultrafiltration process.

2. Materials and methods

2.1. Leachate sampling

A description of the two, closed and active MSW landfill sites located in the vicinity of Prague, the capital of the Czech Republic, is given in Table 1. Two sampling campaigns were carried out at these locations in November 2007 and November 2008. The samples from the closed landfill at Dolní Chabry (CH) were taken from tubes draining the leachate from the landfill body and conducting it directly to a small stream. More information on this landfill site is also given in our previous publications [7,9].

The samples from the active landfill at Ďáblice (D) were taken directly from the tube draining the leachate into the settling basin. Five liter HDPE containers were used for the sample collection.

The physicochemical parameters were recorded in the field. The pH value was determined using a Schott Handylab 12 pH meter equipped with a Schott BlueLine 24 pH combined electrode. The Eh value was determined using a Schott Handylab 1 pH meter equipped with a Schott BlueLine 31 Rx redox electrode (Pt-Ag/AgCl). The specific conductivity was determined using a Schott Handylab LF1 conductometer equipped with a LF 513 T measuring cell. The leachate samples were immediately transported to the laboratory and treated within 1 h after sampling.

2.2. Leachate processing

The leachate samples were filtered through progressively decreasing filter pore size using the cascade frontal filtration technique as reported in Fig. 1. The first steps of the filtration were performed in Sartorius® polycarbonate holders through filters having a diameter of 47 mm and pore size of 3 µm, 0.8 µm, 0.45 µm and 0.1 µm (Millipore® nitrocellulose membranes, USA). Subsequently, ultrafiltration steps were carried out using the Amicon

(Millipore®, USA) 50 mL stirred ultrafiltration cell and Millipore® membranes with diameter 47 mm and pore size 10 kDa (~3 nm) and 1 kDa (~1 nm). The ultrafiltration was performed under a N₂ atmosphere. Before each filtration step, the filtration units were washed with acid and the filters were cleaned by flushing with 2% (v/v) HNO₃ and deionised water (MilliQ, Millipore® Academic purifying system, USA). For each filtration, the filter was replaced when the flow rate during the procedure decreased significantly (indicating clogging of the filter membrane). The subsamples resulting from each filtration or ultrafiltration step were collected, diluted and prepared for analysis. The samples were stored in clean 10-mL polyethylene (PE) vials for inorganic analysis and in clean 100-mL borosilicate glass bottles (Schott Duran®, Germany) for organic carbon analysis.

Colloidal particles were collected on a holey-carbon film supported by copper-mesh TEM grids in order to study their morphology, chemistry and structure using transmission electron microscopy (TEM). The Cu-grids were placed directly on the membrane filters during leachate filtration down to a filter pore size of 0.1 µm. When sufficient amounts of colloidal particles were collected, the grids were dried in air at ambient temperature for 15 min and immediately studied by TEM.

2.3. Analytical determinations

2.3.1. Leachates

The first aliquot of this sample was used to determine the alkalinity (microtitration to pH 4.5 using the Schott TitroLine Easy automatic titrator with 0.05 M HCl) and the major anions (Dionex ICS-2000 ion chromatography). The DOC content was determined using the Skalar Formacs^{HT} TOC analyzer. In addition, chemical oxygen demand (COD) was determined according to ISO 15705, Water quality—determination of the chemical oxygen demand index (ST-COD)—small-scale sealed-tube method [10]. The amount of dichromate used in the oxidation of the sample was determined by measuring the absorbance of the Cr(III) formed at a wavelength of 600 nm with a WTW MPM 3000 photometer.

The second aliquot was acidified by HNO₃ or HCl and analyzed for major cations (Varian SpectrAA 280 FS flame atomic absorption spectrophotometer, FAAS and ThermoScientific iCAP 6500 inductively coupled plasma optical emission spectrometry, ICP-OES) and trace elements (ThermoScientific X Series 2 inductively coupled plasma mass spectrometer, ICP-MS). In total, the following elements and compounds were determined in the leachates (without the charge for the sake of simplicity, in alphabetic order): Al, As, Ba, Ca, Cd, Cl, Co, COD, Cr, Cu, DOC, Fe, HCO₃, K, Mg, Mn, Na, NH₄, Ni, NO₃, Pb, Rb, Sb, Se, Si, SO₄, Sr, V and Zn. Cadmium was below the detection limit of ICP-MS for all the studied samples (0.003 µg L⁻¹). The reproducibility of the analytical determinations was always better than 15%. The following standard materials were used for quality control of the instrumental analyses: internal laboratory standards and Merck IV ICP multielement standard solution for AAS and ICP-OES determinations, Analytika CRM CZ9102 (MIX 022-IC) for HPLC determinations and NIST standard reference materials 1640 (Trace Elements in Natural Water) for trace element measurements by ICP-MS. The accuracy of all the determinations was better than 15% of the relative standard deviation (RSD).

2.3.2. Colloidal particles

For the TEM investigations, we used a JEOL JEM-3010 instrument (LaB₆ cathode; accelerating voltage of 300 kV, point-to-point resolution of 0.17 nm) permitting energy dispersive analysis (EDS) and selected area electron diffraction (SAED) of the individual particles.

Table 1

Description and geographical location of the two sampled landfill sites (CH, closed landfill; D, active landfill).

Code	Site name Location	Basic description	Built-up area	Volume of deposited wastes	Type of wastes
CH	Dolní Chabry 5 km N of Prague N 50°8'58.3" E 14°27'4.1"	Old landfill, closed in 1993 after 9 years of operation. The landfill was constructed without any leakage-preventing barriers and no records of deposited material were kept.	26.00 ha	3 000 000 m ³	No records—all types of waste are expected Unsorted municipal solid waste Construction waste Hazardous wastes (medical waste, batteries, etc.) Industrial waste of various types
D	Ďáblice 6 km NNE of Prague N 50°9'18.8" E 14°28'57.6"	The landfill, in operation since 1993, was equipped with leakage-preventing technical barriers and drainage system for the leachate. Leachate is collected and recycled back to the landfill body. No evidence of detectable leaching from the landfill to the groundwater has been reported.	22.31 ha ^a	3 500 000 m ^{3a} 190 000–340 000 t a ^{-1b}	Municipal solid waste Inert construction debris and waste

^a 2009.^b 2005–2009.

2.4. Data treatment

Data processing and statistical analysis was performed using Matlab and its Statistical Toolbox, with one-way ANOVA, Kruskal–Wallis one-way analysis of variance, multiple comparisons, regression and correlation (with both Pearson and Spearman coefficients). In all the tests, *p*-values < 0.05 were considered to be significant. Due to the large range of results, we present only those related directly to our reasoning in the discussion. A simple model of decrease of trace element/major compound concentration was designed and coded in Matlab providing quantification of the trace element binding to the colloidal fractions.

Speciation-solubility modelling was carried out using the PHREEQC-2 geochemical code, version 2.16 for Windows [11]. The Minteq.v4.dat thermodynamic database (derived from MINTQA2 code, version 4, released by U.S. EPA in 1999) was used for all the calculations. This database was amended with the thermodynamic data of Rb and binding constants for dissolved organic matter (DOM) from the T&H.dat database derived from the WHAM code and downloaded from the web site of Tony Appelo (<http://www.xs4all.nl/~appt>). The dissolved organic matter was entered into the code as fulvate, which is the predominant form in the landfill leachate [12].

3. Results and discussion

3.1. Physicochemical and chemical characteristics of the raw leachates

Table 2 gives a general chemical characterization of raw leachates from the two landfill sites reported as a range for the two sampling campaigns. The pH values for both leachates lie in the alkaline region (mean: 7.87 for CH and 8.43 for D). Slightly lower redox potential was observed in the leachate from D (ranging from 162 mV to 212 mV). The conductivity indicated that the amount of dissolved salts in the leachate was significantly higher for the D leachate (factor ~6, Table 2). Generally, the major and minor compounds were higher in the D leachate (factor 3–119) with the exception of Ca, SO₄, NO₃, Mn and Sr (Table 2). The mean concentrations of Mg were nearly identical for both types of leachate. For the majority of the analyzed compounds, the studied leachate samples were within the concentration ranges previously published for

Table 2

Ranges of the basic chemical properties of raw leachates from closed (CH) and active (D) landfills.

Parameter	Units	CH	D
<i>Physicochemical parameters</i>			
<i>T</i>	°C	11.6–13.4	19.3–19.5
<i>pH</i>	Standard units	7.84–7.90	8.40–8.46
<i>Eh</i>	mV	452–454	162–212
<i>Conductivity</i>	mS cm ⁻¹	3.40–3.89	19.1–21.9
<i>Major cations</i>			
<i>Na</i>	mg L ⁻¹	214–307	2321–2816
<i>K</i>	mg L ⁻¹	76.7–91.4	829–1010
<i>Ca</i>	mg L ⁻¹	218–223	54.2–69.4
<i>Mg</i>	mg L ⁻¹	49.5–68.6	54.4–69.0
<i>Si</i>	mg L ⁻¹	7.90–8.40	34.3–40.2
<i>Fe</i>	mg L ⁻¹	0.20–0.30	2.60–3.70
<i>Major anions</i>			
<i>F</i>	mg L ⁻¹	2.50–4.80	9.50–13.8
<i>Cl</i>	mg L ⁻¹	621–695	2837–3018
<i>HCO₃</i>	mg L ⁻¹	444–706	8951–11460
<i>SO₄</i>	mg L ⁻¹	103–226	10.0–167
<i>NO₃</i>	mg L ⁻¹	17.1–126	<dl ^a –11.8
<i>Other parameters</i>			
<i>DOC</i>	mg L ⁻¹	40.3–52.0	1450–1740
<i>COD</i>	mg L ⁻¹	93–125	4997 ^b
<i>Trace elements</i>			
<i>Al</i>	µg L ⁻¹	6.9–49.7	250–336
<i>As</i>	µg L ⁻¹	9.7–11.2	196–233
<i>Ba</i>	µg L ⁻¹	125–133	489–786
<i>Co</i>	µg L ⁻¹	5.6–11.1	40.7–56.9
<i>Cr</i>	µg L ⁻¹	5.22–8.22	594–1005
<i>Cu</i>	µg L ⁻¹	9.72–13.3	8.9–63.3
<i>Mn</i>	µg L ⁻¹	275–481	162–163
<i>Ni</i>	µg L ⁻¹	40.3–43.8	311–381
<i>Pb</i>	µg L ⁻¹	<dl ^a –0.46	3.0–7.3
<i>Rb</i>	µg L ⁻¹	59.3–66.3	930–1067
<i>Sb</i>	µg L ⁻¹	0.8–1.3	25.5–26.4
<i>Se</i>	µg L ⁻¹	7.56–7.64	26.6–35.0
<i>Sr</i>	µg L ⁻¹	1311–1555	358–595
<i>V</i>	µg L ⁻¹	20.0–24.8	261–358
<i>Zn</i>	µg L ⁻¹	24.1–42.1	104–122

^a dl = detection limit (1 mg L⁻¹ for NO₃ and 0.03 µg L⁻¹ for Pb).^b Only one sampling campaign measured.

landfill leachates [4–6,13–16]. According to the EU Drinking Water Directive (Council Directive 98/83/EC [17]), metals and metalloids were mostly below the limits for drinking water, with the exceptions of some chemical parameters in the leachate from landfill D

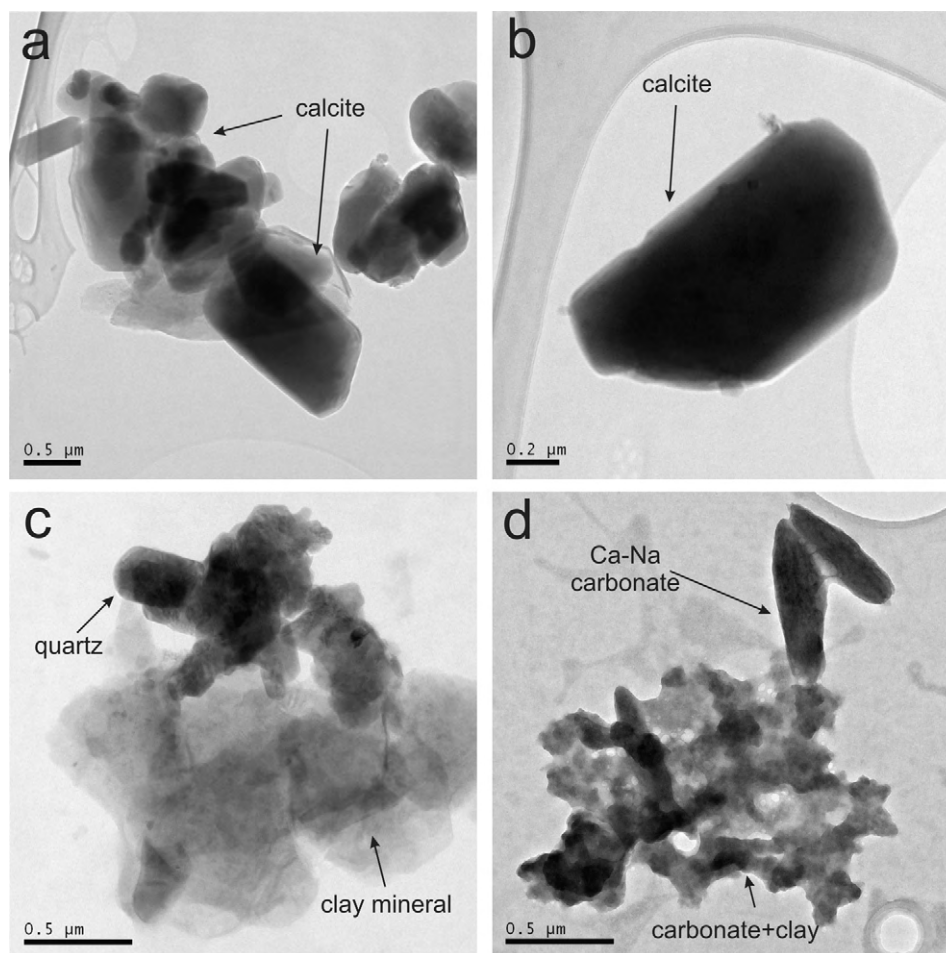


Fig. 2. Transmission electron micrographs of the colloid particle associations from landfill leachates: (a) calcite (CaCO_3) crystals 0.2–1.5 μm in size, closed landfill CH (EDS spot analysis indicated Ca and O as major components and trace levels of P and Si); (b) 1 μm large crystal of calcite, closed landfill CH (EDS analysis indicated predominant Ca and O, with minor amount of Si); (c) aggregate of clay minerals (EDS analysis indicated predominance of Si, Al, O and K) associated with quartz crystals (EDS indicated Si and O), closed landfill CH; (d) up to 0.7 μm large elongated crystals of Ca–Na carbonate (EDS analysis indicated predominant Ca, O with a minor amount of Na and trace levels of Mg, Mn and Si) associated with a mixture of carbonate and clay, active landfill D. *Note:* All the phases were confirmed by SAED.

(As, limit $10 \mu\text{g L}^{-1}$; Cr, $50 \mu\text{g L}^{-1}$; Ni, $20 \mu\text{g L}^{-1}$; Sb, $5 \mu\text{g L}^{-1}$; Se $10 \mu\text{g L}^{-1}$) (Table 2).

3.2. Mineralogy of colloidal particles and speciation-solubility modelling

The TEM investigation indicated that the majority of colloidal particles were inorganic phases. As we collected colloids larger than 100 nm during the frontal filtration procedure, smaller colloidal particles were not analyzed, unless they formed larger aggregates. Thus the chemical/mineralogical composition of colloids <100 nm can only be estimated from the elemental patterns in filtrates or can be assumed to be similar to the larger particles described below. It is important to note that EDS analysis did not reveal any trace elements bound to colloidal particles, due to their low concentrations, presumably below the detection limit of the method (see also bulk concentrations in the leachate in Table 2).

The most common phase was calcite (CaCO_3) and other chemically more complex carbonates forming individual crystals or aggregates (often associated with clays) ranging from 200 nm to 2 μm in size (Fig. 2a, b and d). The presence of carbonate minerals in landfill systems was reported in numerous papers dealing with landfill leachates [4,6,18]. Carbonates were suggested to be key phases for binding trace metals and metalloids either by adsorption or by incorporation into their mineral structure [9,19,20]. Quartz

(SiO_2) was also observed within the colloidal particles forming individual grains below 500 nm in size (Fig. 2c). Clay minerals generally formed flocks or aggregates up to 2 μm in size (Fig. 2c and d). Both these silicates were also observed in landfill leachates in previous papers, probably reflecting the composition of the surrounding geological environment but without very clear importance with respect to metal contaminant binding [4,6,13]. According to previous investigations, the presence of organic colloids reflects the waste composition and degradation in the landfill body [4]. In spite of this fact, the TEM observations did not indicate any organic colloidal particles. The DOC trends in Figs. 3 and 4 show that only in campaign 1 for landfill D was a decrease in DOC concentration observed in cut-offs below 0.45 μm , whereas the DOC patterns for other leachates were significantly more stable during the filtration procedure, indicating that organic matter remained in the “truly dissolved” fraction, which is in agreement with previously published data (e.g., [21]). The DOC patterns also indicate that fulvic acids with significantly lower molecular mass (less than 10 kDa) will probably be the most important fraction of the organic matter in the leachate [12,21]. The role of organic colloids in effective trace element binding (suggested by Baun and Christensen [4] and references therein) is probably minor for our landfill leachates.

In agreement with the TEM observation, the PHREEQC-2 calculation indicated that a number of phases were susceptible to precipitation from the leachates, mainly carbonates (calcite, CaCO_3 ;

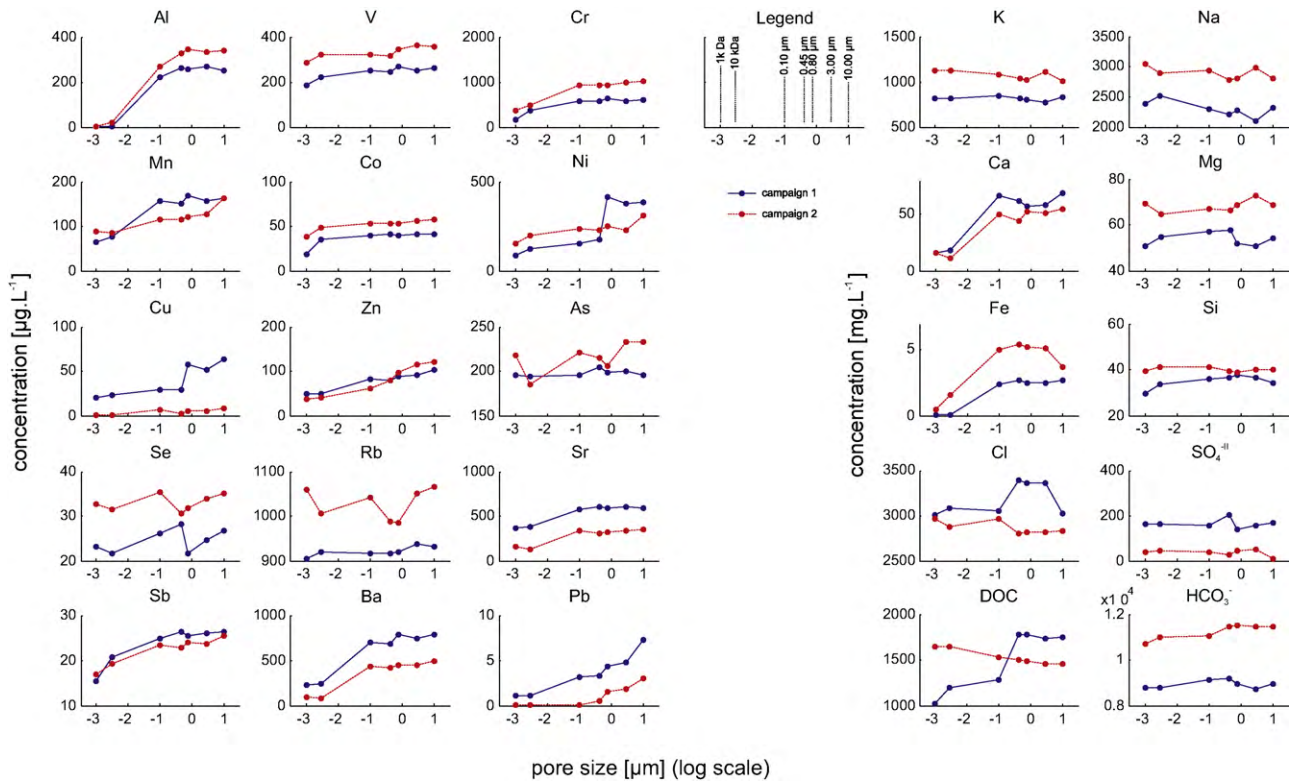


Fig. 3. Concentration patterns for selected trace elements and major compounds obtained during the filtration and ultrafiltration of leachate from active landfill D.

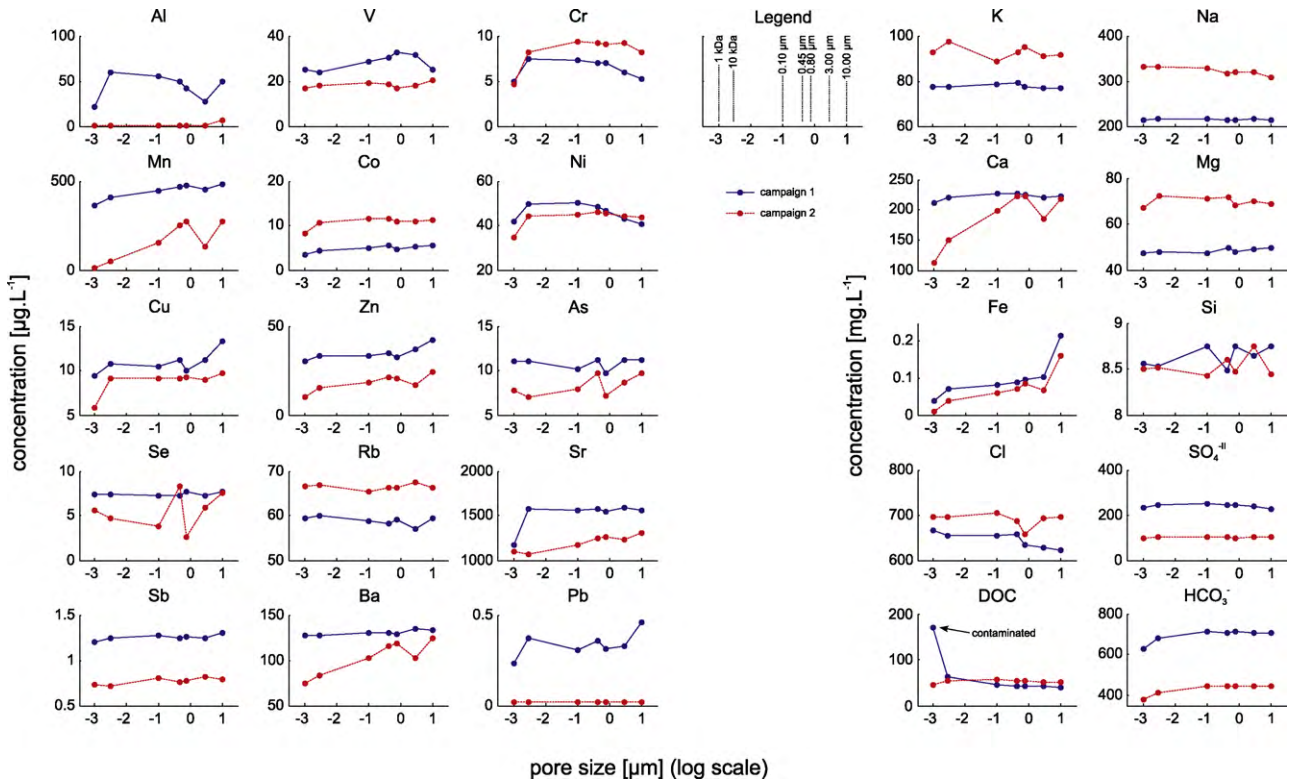


Fig. 4. Concentration patterns for selected trace elements and major compounds obtained during the filtration and ultrafiltration of leachate from closed landfill CH.

rhodochrosite, $MnCO_3$; strontianite, $SrCO_3$; witherite, $BaCO_3$), chalcidony (SiO_2) and clays (kaolinite, $Al_2Si_2O_5(OH)_4$). The calculation also predicted the precipitation of Al-, Mn- and Fe-oxides and hydroxides, which numerous authors suggest as the key phases in

the colloidal fractions from landfill leachates [4,6,22,23]; the presence/absence of HFO within the colloidal matter cannot be verified by TEM. It is also possible that Fe is partly bound to clay-type colloidal particles (such as illite), which were documented by TEM.

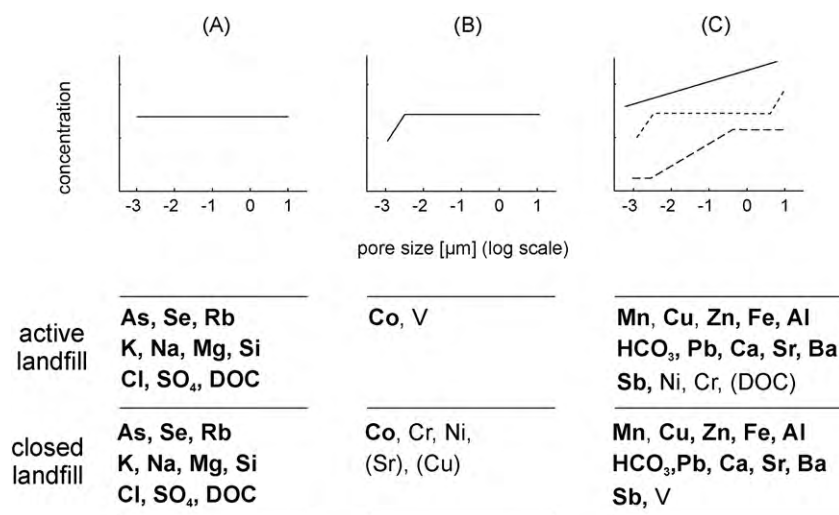


Fig. 5. Conceptual patterns indicating the binding of trace elements and major compounds to colloids of various sizes in leachates from closed and active landfills. The bold letters indicate similar trends for both landfills.

Given the fact that our leachates exhibited relatively high Eh values (Table 1), the precipitation of Fe(II) phases such as siderite (FeCO₃) or pyrite (FeS₂) observed in highly reducing leachates from other landfills (e.g., [13]) is not probable.

3.3. Binding of trace elements to colloidal fractions

The changes in concentration of trace elements and selected major compounds in filtrates obtained by cascade filtration/ultrafiltration for samples D and CH are given in Figs. 3 and 4, respectively. The slope of the curve between individual filters indicates the efficiency of the element capture by colloids corresponding to the given cut-off. For example, the substantial decrease in the Al concentration (Fig. 3) indicates that Al is mainly bound to colloidal particles with size between 10 kDa (~3 nm) and 100 nm. A detailed investigation of Figs. 3 and 4 shows that the concentration patterns for individual filter cut-offs observed for trace element and major compounds can be grouped in a small number of basic patterns, which are summarized in a conceptual plot in Fig. 5: (i) no concentration decrease (group A; examples: As or Na), (ii) significant concentration decrease takes place during the last filtration step corresponding to the binding to the smallest colloids between 1 nm and 3 nm (group B; example: Co) and (iii) continuous quasi-linear decrease or more complicated pattern indicating the binding to colloidal particles of various size (group C; examples: Zn, Ca and Fe). A detailed description of elemental patterns obtained by filtration/ultrafiltration of leachates is first given for the active landfill D, where the observed phenomena are more pronounced.

3.3.1. Elemental patterns in leachate from an active landfill (site D)

No change in concentration occurred during the (ultra)filtration procedure for Se, As and Rb. Regression analysis and analysis of variance indicated that these three elements, as well as numerous major compounds (Na, K, Mg, Si, Cl and SO₄), exhibited no statistically significant decrease in concentration during the filtration (Fig. 3), as also reported by Jensen and Christensen [13]. Of the set of major compounds, a significant decrease was observed only for Ca and Fe for both sampling campaigns, DOC for the first campaign and HCO₃ for the second campaign. Some trace elements, particularly Sr, Ba and Al, were characterized by similar trends as Ca and Fe, suggesting binding to and/or direct formation of carbonate or clay-like colloidal particles, both occurring in this type of leachate (Fig. 2d). Other trace elements could also be bound to the surfaces of

carbonate colloidal particles, whose occurrence is also manifested by the decrease in Ca and HCO₃ in filtrates during the filtration procedure (Fig. 3). Clay-like colloids yielding the chemical composition of Si–Al–K–O may also play a role in the trace element binding (Fig. 2d), although no significant decrease of Si and K related to the capture of clay particles during the filtration was observed due to the relatively high concentrations of these elements in the leachate (in contrast to Al, Fig. 3). The decrease in DOC in the filtrates in one sampling campaign indicates the possible presence of organic colloids, which were nevertheless only rarely observed by TEM.

Whereas V and Co were mainly bound to the smallest colloidal fraction (between 1 kDa and 10 kDa), the remaining trace elements (Cr, Mn, Ni, Cu, Zn, Sb and Pb) were characterized by a continuously decreasing concentration trend during the filtration (Fig. 3) indicating that these elements were more homogeneously distributed between the individual colloidal fractions. A comparison of trace element concentrations between the raw leachate and fraction below 1 kDa (“truly dissolved” fraction) indicated the % efficiency of trace element binding to colloidal particles. The highest capture by colloids was observed for Ca, Fe, Pb, Ba and Al (>70%). Relatively high capture efficiency by colloids (between 25% and 70%) was observed for trace elements such as V, Cr, Mn, Co, Ni, Cu, Zn, Sr and Sb. Similarly high level of binding of metallic elements (Fe, Cu, Zn, Cd and Pb) to colloidal particles was also observed at other landfill sites [4,5,23]. Øygaard and Opedal [23] also tested how aeration of the landfill leachate (as a pre-treatment step before sedimentation) affects the binding of metals to particulate material and colloids. The aeration method was based on the oxidation of dissolved Fe(II) to Fe(III) followed by the formation of new colloidal particles such as Fe(III)-oxides with high adsorption potential [5,22,23]. Although the massive precipitation of Fe-oxides occurred during the aeration of leachates with initial Fe concentrations between 8.4 mg L⁻¹ and 120 mg L⁻¹, levels of metallic elements in leachates were not significantly lowered [23]. The main reason for this observation was that metals have already been bound to existing colloidal particles (>70%) [23]. This finding also supports our results, showing that partly due to low Fe totals in leachates, colloidal Fe-oxides have probably minor role in trace element binding compared to clays, carbonates and other phases observed by TEM (see Fig. 2). The Fe-oxide formation could only be enhanced by the artificial addition of Fe(III) in the leachate system [8] (see also implications below).

In contrast to the above mentioned elements, As, Rb and Se were present only in the “truly dissolved” fraction, as was also documented by the PHREEQC-2 speciation calculation, where these

elements form mobile complexes or free ions and thus are not bound to colloids at all (Fig. 3).

3.3.2. Elemental patterns in leachate from a closed landfill (site CH)

Although a number of similarities were observed between the leachates from the two landfills, the patterns for trace elements and major compounds in the leachate from landfill CH were less pronounced, probably due to the significantly lower bulk concentrations reported for the majority of components (Table 2, Fig. 4). No significant differences in concentration were observed during the (ultra)filtration procedure for As, Se and Rb. For the major compounds, regression analysis indicated no significant trend for K, Na, Mg, Si, Cl and SO_4 , whereas Fe and HCO_3 showed systematic decreases for both sampled leachates and for Ca in the second sampling campaign (Fig. 4). Organic matter will play a minor role in trace element binding, as no significant correlations were observed, perhaps also due to the fact that no organic colloids were formed according to TEM observations. The patterns of DOC were obscured by possible contamination during the filtration through the 1 kDa filters (Fig. 3); nevertheless organic matter mainly remained in the “truly dissolved” fraction. As no massive binding of trace elements to dissolved organic matter (fulvate) was predicted by the PHREEQC-2 calculations, we suggest that mobile inorganic species of metals and metalloids will be predominant in the dissolved fraction (carbonate, hydroxide and chloride complexes and free ionic forms).

With the exception of Fe, Al, Ca and Mn, other trace elements were bound to colloids to a lesser extent in comparison with the active landfill leachate, indicating the capture efficiency generally below 50% (see also Fig. 4).

3.4. Implications for mobility of trace elements in landfill systems

According to Baumann et al. [6], colloidal particles of larger size (larger than $1\ \mu\text{m}$) are generally less mobile and the attention must be paid to contaminants bound to colloids with size class between 10 nm and $1\ \mu\text{m}$, which are considered most mobile in porous systems. Our TEM observations indicated that the size of the colloidal particles was generally between 100 nm and $2\ \mu\text{m}$; the latter generally formed aggregates composed of smaller, particles several hundreds of nm in size and crystals (Fig. 2). Although colloids <100 nm were not directly studied by TEM, the investigation of elemental patterns obtained by the filtration/ultrafiltration procedure indicates a high level of retention by all colloidal fractions (between 1 nm and $>3\ \mu\text{m}$) for Al, Mn, Fe and Pb (generally between 70% and 100%). Other trace elements (Co, Cr, Ni, Cu, Zn, Sr and Ba for both landfill leachates, V and Sb for the leachate from landfill D) were associated with colloids to a lesser extent (20–50%) and thus they were also exhibited substantial presence in the “truly dissolved” fraction as free ionic forms or mobile chloride and carbonate complexes (according to the PHREEQC-2 calculations). These observations are in agreement with previously published key studies on size fractionation of metals in Danish and Norwegian landfill leachates [5,13].

For both types of landfill leachates, As and Se were found to be very mobile, without any systematic binding to colloids. This is in agreement with previously published results on speciation of As in landfill leachates, which indicated that As is mainly present as methylated forms and arsenate [24,25]. The latter was also predicted by PHREEQC-2 as the prevalent and thermodynamically stable form of As in our leachates. In addition, it is important to note that the binding of arsenate to surfaces is less effective in the alkaline region typical for landfill leachates (Table 2; see also [4]). Although the methylated forms of As and arsenates are less toxic species than the As(III) compounds found in the original

MSW [25], arsenic seems to be the most critical contaminant in landfill leachates, which should necessitate further leachate treatment. The first step of the “decontamination” procedure could be based on the decantation of larger colloidal particles in a settling pond, which could be efficient for partial elimination of trace elements bound to colloids (Al, Zn, Ni, etc.). The second step could be based on the application of conventional techniques, such as coagulation/flocculation with addition of ferric chloride as coagulant to eliminate the “truly dissolved” trace elements, such as As or Se [8,26]. In addition, the addition of Fe(III) salt to our Fe-poor leachates would accelerate the precipitation of newly formed colloidal Fe(III) oxides, which could provide additional sorption surfaces for truly dissolved metalloids and the remainder of metals not bound to other colloids [23].

4. Conclusions

We investigated the binding of a large set of trace elements to colloidal particles in leachates from closed and active MSW landfills, located in the vicinity of Prague, the capital of the Czech Republic. The cascade frontal filtration and ultrafiltration procedures with decreasing filter pore size from $3\ \mu\text{m}$ to 1 kDa ($\sim 1\ \text{nm}$) were employed and coupled with the ICP-MS analysis of trace elements and TEM investigation of colloidal particles. For both landfill sites, As, Se and Rb were found to be present in the “truly dissolved” phase, thus being very mobile with no indication of binding to colloids. In contrast, other trace elements (Fe, Al, Cr, Ni, Cu, Zn, Pb, Sr and Ba at both sites and V and Sb at the active landfill site) were partly bound to colloidal particles which, according to TEM observations, were mostly composed of inorganic phases, such as calcite and clays. Colloids in the leachate from an active landfill were responsible for the capture of a larger amount of trace elements ranging from $\sim 20\%$ (V, Co and Sb) to nearly 100% (Al, Fe and Pb). In addition, some of these trace elements (Fe and Al) directly form colloidal particles (e.g. clays) and are not present in truly dissolved forms. At the closed landfill, the concentration decrease of these trace elements during the filtration, i.e. capture by colloids, was generally lower than for the leachate from the active landfill. No systematic decrease was observed in the DOC concentration during the filtration procedure and relatively few organic colloids were detected by TEM, indicating their minor role in binding of trace elements. The fact that As in leachates from both landfills does not exhibit any binding to colloidal particles and occurs only in the dissolved fraction indicates its particularly high mobility, which should be considered in preventing the flux of harmful compounds from landfill systems.

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