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Metal speciation in landfill leachates with a focus on the influence of organic matter

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Abstract

This study characterises the heavy-metal content in leachates collected from eight landfills in France. In order to identify heavy metal occurrence in the different size fractions of leachates, a cascade filtration protocol was applied directly in the field, under a nitrogen gas atmosphere to avoid metal oxidation. The results of analyses performed on the leachates suggest that most of the metals are concentrated in the < 30 kD fraction, while lead, copper and cadmium show an association with larger particles. Initial speciation calculations, without considering metal association with organic matter, suggest that leachate concentrations in lead, copper, nickel and zinc are super-saturated with respect to sulphur phases. Speciation calculations that account for metal complexation with organic matter, considered as fulvic acids based on C1(s) NEXAFS spectroscopy, show that this mechanism is not sufficient to explain such deviation from equilibrium conditions. It is therefore hypothesized that the deviation results also from the influence of biological activity on the kinetics of mineral phase precipitation and dissolution, thus providing a dynamic system. The results of chemical analyses of sampled fluids are compared with speciation calculations and some implications for the
assessment of metal mobility and natural attenuation in a context of landfill risk assessment are discussed.
1. Introduction

Public concern regarding the impacts of landfills is often focused on the long term fate of heavy metals contained in the wastes. Several heavy metals or metalloids, that may be present in landfill leachates, are considered as priority pollutants for groundwater resources (for example lead, cadmium, nickel; (OJEC, 2001). However, in the subsurface, different processes such as precipitation or co-precipitation participate in the natural attenuation of landfill leachate and help explain why heavy metals are rarely detected in groundwater at significant distances from landfills (Christensen et al., 2000b; Christensen et al., 1994; Christensen et al., 2001). In a 15-year old sanitary landfill (Sarnia, Ontario) overlying a 30 m thick natural clay deposit, Cu, Zn and Pb migration was detected only up to 10 cm (Yanful et al., 1988a; Yanful et al., 1988b). Based on selective chemical dissolution analyses data and thermodynamic calculations, these authors suggest the occurrence of heavy-metal precipitation as carbonate minerals. In Horn, located in the Austrian part of the bohemian massif, the mineralogical and geochemical investigation of a 10-year old base sealing from a municipal waste deposit (Kugler et al., 2002) highlights a very efficient retention of heavy metals. Structural incorporation during iron (hydrated) oxides and probably carbonate precipitation were considered to be mainly responsible for the retention of heavy metals, in addition to retention on clay mineral surfaces. Other illustrations of the natural attenuation of heavy metals can be found in (Essington et al., 2004; Howari, 2004; Johnson et al., 1999).

Further to the documented occurrence of heavy metal natural attenuation mechanisms in the subsurface, monitored natural attenuation has been proposed as an eligible management strategy for landfills during their post-closure phase (Baun et al., 2003; Christensen et al., 2000b; Christensen et al., 1994; Hubé et al., 2011; Tuxen et al., 2006; Van Vossen et al., 2009). There still remains, however, a relative paucity of documented field data regarding to landfill leachate composition, that take into account the complexing behaviour of heavy metals. Such complexing behaviour has a major influence on the potential occurrence of attenuation mechanisms, since it directly influences mobility and saturation indices. A particular reason for this paucity is the sensitivity of heavy metals to oxidation conditions, which hampers sampling in the field. Detailed data regarding the speciation of heavy metals in landfill leachate are provided for example by Li et al. (2009), Ostman et al. (2008), Oygard et al. (2007), Ponthieu et al. (2007), Ward et al. (2005), Jensen et al. (1999), Jensen and Christensen (1999). Extensive reviews of the composition of landfill leachates are proposed by
Kjeldsen et al. (2002) and Christensen et al. (2001). Reliable data regarding heavy metal content of landfill leachate are particularly important in a context of landfill post-closure, in particular to define the so-called “source term” (CEN, 2006). If this term is known with some confidence, it can be fed as input to models that couple transport and chemical reactions in the subsurface (e.g. PHAST, Parkhurst, 2004), in order to assess the potential impacts of residual leakage from landfills on groundwater resources.

This paper presents the results of a study on leachates representative of landfills in France. The aim of the study was (i) to apply a sequential filtration protocol in order to identify the effect of filter pore size on dissolved metal concentrations, (ii) to perform speciation calculations based on analyses results, to explore potential equilibrium/disequilibrium with respect to the solid phase and (iii) to propose some implications regarding landfill risk assessments.

2. Materials and methods

2.1 Landfill sites and collection points

Seven non-hazardous waste landfills (primarily municipal solid waste) and one hazardous waste landfill were sampled. All landfill waste cells that contributed the collected leachates were less than ten years old and were in stabilized methanogenic conditions. The leachate samples were collected at various sampling points, depending on possibilities offered by the specific landfill designs. Some landfills were equipped with leachate collection systems that could be sampled directly at an outlet, before discharge into a leachate collection pond. This situation is the most favourable in terms of geochemical representativeness of the leachate samples. On other landfills, however, the outlet was not accessible and therefore samples were collected from the leachate collection pond. Table 1 summarizes sampling conditions. In accordance with the industrial partners of the project, the locations of the landfills are not provided for reasons of confidentiality.
2.2 Sample collection protocol

A leachate sampling protocol was adapted from Baun et al. (2004) and Beaucaire et al. (2000). For each sample, three levels of sequential filtration were performed directly in the field: 5.0 μm, 0.45 μm and 0.1 μm. Cascade filtration was performed using a polycarbonate Sartorius system to which was applied a pressure of nitrogen gas (1.5 bar). An additional level of ultrafiltration was performed under a slightly over-pressured azote atmosphere in the laboratory using 30 KDa membranes. Due to the high suspended particulate matter content, the filters had to be frequently replaced during filtration in the field. This was considered to be necessary both from the viewpoint of filtration duration (otherwise the flow of filtered leachate rapidly decreased to a few drops per minute), but also to avoid over-filtration related to the presence of the filter cake. All the filters were preserved for analysis in order to perform mass balances and quantify the proportions of heavy metals associated with particles of different sizes. Sub-samples of leachate were conditioned for the various analyses in the laboratory (cation sub-samples were acidified with nitric acid to pH 2, total organic carbon samples were acidified to pH 2 with sulfuric acid, etc.).

Parameters such as pH, electrical conductivity, dissolved oxygen, redox potential and temperature were analysed directly on site with, respectively, a MP 120 Mettler Toledo pH meter, a Jenway 9200 portable dissolved oxygen Meter, a WTW pH 320 voltmeter and a Jenway 4200 portable conductivity meter. Temperature was measured alongside pH and electrical conductivity. Redox-sensitive species such as ferrous iron, nitrite, sulphite and chromate, were also measured on site using field spectrophotometric kits (Spectroquant references) and a field spectrophotometer (Merck – Nova60).

2.3 Laboratory Measurements

One implication of investigating the effects of speciation on metal attenuation is that sample analyses must necessarily include all the chemical elements that might influence speciation, including in particular major ions. Major cations and anions were analysed in the laboratory using a Dionex DX600 ion chromatographer. A control on cation analyses was performed using an inductively-coupled plasma atomic emission spectrometer (ICP-AES, Jobin Yvon Ultima2), following the standard NF EN ISO 11885-T90-136 of the international organization for standardization. For K, Na, Ca and Mg, detection limits were 0.5 mg kg⁻¹. Total organic carbon
(TOC) in the raw leachate was analysed following acid oxidation with sodium persulfate (standard NF EN 1484). The organic carbon, converted into CO₂(g), was detected and measured by an infrared cell (OI Analytical 1010 Bioritech). The estimated quantification limit based on the XPT90-210 standard is 0.5 mg kg⁻¹ of carbon. Dissolved organic and inorganic carbon (DOC and DIC) were measured on a Shimadzu 5000 TOC analyser. Total dissolved carbon (TDC) is measured first, followed by DIC, while DOC is obtained as the difference between TDC and DIC. Detection limits are also around 0.5 mg kg⁻¹ C. Trace elements were analysed by inductively-coupled plasma mass spectrometry with a PQ3 Thermoelectron apparatus. The aqueous samples were digested with nitric acid (70%) in a closed vessel using pressure and temperature controlled microwave heating (SW 846 Method 3015 from CEM). Indium was used as an internal standard. Detection limits are in the µg kg⁻¹ range. The measurement accuracy was checked by comparison with certified reference materials (TMDA62 and NIST1643) following the laboratory’s COFRAC accreditation rules.

Carbon K-edge NEXAFS spectra were measured at the Scanning Transmission X-ray Microscopy (STXM) beamline X1A1 (NSLS), operated by the State University of New York at Stony Brook. The principle of the method is described in detail elsewhere (Jacobsen et al., 1991). The absorption by different carbon structures follows the Beer-Lambert Law; i.e., the absorption is directly proportional to the mass absorption coefficients of different carbon functional groups, depending on the X-ray wavelength. The optical density (OD) is equal to the product of sample thickness \(d\), the sample density \(\rho\) and the mass absorption coefficient \(\mu(E)\), which is related to the ratio between the incident flux on the sample \(I_0(E)\) and the flux detected behind the sample \(I(E)\) via the following equation:

\[
\text{OD} = -\ln \left[ \frac{I(E)}{I_0(E)} \right] = \mu(E) \cdot \rho \cdot d
\]

STXM sample preparation was performed by drying a 1 µL droplet of resuspended lyophilised fraction on a Si₃N₄ window (100 nm thick). The spectra were extracted from images taken at different energies across the absorption edge and were aligned using cross-correlation to acquire image stacks (Jacobsen et al., 2000). Energy calibration of the spherical grating monochromator was achieved using the photon energy of the CO₂ gas adsorption band at 290.74 eV (Hitchcock and Mancini, 1994).
3. Numerical methods

Speciation calculations were performed to provide information about possible controls on heavy metal concentrations in the leachates, based on concentrations of heavy metal and major dissolved species, pH and temperature values. These speciation calculations rely on the equilibrium constants for solute complexes, with an underlying hypothesis of thermodynamic equilibrium. Therefore a shortcoming of these calculations is the fact that the various redox couples in the system may be in disequilibrium (e.g. sulphate/sulphide vs. nitrate/ammonium; cf. Christensen et al., 2000a). Most of the investigated heavy metals exist in a single (or primary) redox state in low temperature solutions (e.g., Pb(+2), Zn(+2), Ni(+2) and to a lesser extent Cu(+2) and Co(+2)). For these elements, knowledge of the redox potential is not mandatory to compute their solute speciation, provided that concentrations of their solute complexing ions are known (e.g. carbonates, sulphides, sulfates).

For As and Cr, on the other hand, experimental determination of their speciation (As(3+) vs. As(+5) and Cr(+3) vs. Cr(+6)) should allow the calculation of their solute speciation, for each redox state. However, the analysis of solution speciation of As and Cr after leachate collection is not trivial as it is very sensitive to changes occurring during sample handling. For this reason, such calculations were not performed for As and Cr.

In a first approach, solute speciation and saturation index calculations were performed using total concentrations of heavy metals in the soluble fraction. While dissolved organic matter is well known to be a strong complexing agent for metals, the distribution between “free” metal in solution and metal complexed with organic matter was not determined experimentally. Considering the high concentrations of organic matter in the dissolved fraction, speciation calculation results using this first approach are therefore potentially erroneous. As a consequence, in a second approach, speciation calculations were performed while considering generic organic matter complexation models, according to the methods described in Appelo and Postma (1996). Speciation calculations were performed using the code PHREEQC2 v2.12 (Parkhurst and Appelo, 1999) and the LLNL thermodynamic data base (lnl.dat 85 2005-02-02 Lawrence Livermore National Laboratory).
4. Results

4.1 Physico-chemical parameters measured on-site on untreated leachate samples

Results of analyses performed on site are presented in Tables 2 and 3. As seen in Table 2, the values of pH are neutral to basic. Redox potentials measured in the field with the platinum electrode vary from negative to positive values and dissolved oxygen measurements suggest anoxic conditions in most samples but these both measurements are not in agreement from a thermodynamic point of view: redox potentials calculated on the basis of oxygen measurement are always higher than the potential given by the electrode. Based both on in situ spectrophotometric measurements and laboratory analyses for redox sensitive species, speciation calculations show that the other redox couples potential values are not in mutual agreement (see Table 2). Redox sensitive species are not in thermodynamic equilibrium in the leachate samples, as can be expected for such dynamic systems (Christensen et al., 2000a).

Tabulated values of major ion analyses are given in Table 4. The primary anions in these leachates are chloride and bicarbonate. Bicarbonate concentrations were computed based on dissolved inorganic carbon, pH and ionic strength (a method considered to be more reliable than alkalinity measurements due to the possible presence of organic acids such as acetate or inorganic sulphur ions that would have contributed to the measured alkalinity values). Cation concentrations are dominated by the presence of sodium, potassium and ammonium. Ionic balances are good (< 8%) suggesting that no major anion or cation was omitted or measured erroneously.

4.2 Trace elements analysis and size distribution

Results of trace element analyses are shown in Table 5 while Figure 1 compares trace element concentrations measured in samples filtered at 0.1 µm with those measured in ultrafiltered samples (< 30 kDa). The same comparison is given in Table 6 for organic carbon. Results generally show little difference between the two collected fractions, suggesting that elements in the < 0.1 µm fraction are either truly dissolved, or else associated with very small organic colloids/particles (e.g. fulvic or humic acids). It is worth noticing that significant fractions of heavy metals have been found in colloidal fractions with a cut off 100 times lower than the smallest one used in this study (Jensen and Christensen, 1999; Jensen et al., 1999). In the following, the <0.1 µm fraction is termed “colloidal fraction”. The metal complexation by small organic colloids/molecules in this fraction is taken into account below in the speciation calculations.
4.3 Association of heavy metal with solid particles.

Particles collected on the various filters were analysed and mass balances performed (Figure 1). Four different fractions were determined: (i) larger than 5 µm, (ii) between 0.45 and 5 µm, (iii) between 0.45 and 0.1 µm and (iv) below 0.1 µm. Arsenic, cadmium, chromium, nickel and zinc are found mainly in solution and thus, do not appear to be associated with particles (except in rare occasions). Cadmium, copper and lead, behave differently, displaying the associations with the largest particle fraction.

4.4 Organic matter characterisation

Carbon edge XANES spectroscopy measurements were performed on the fraction below 0.1 µm for samples S6, S8 and S9 as well on a raw (without filtration) sample S8 in order to identify the organic compounds in the leachates. The XANES spectra are shown on Figure 2. The spectrum of the Suwannee river, United States, fulvic acids (FA), recorded during the same run, is also reported for the purpose of comparison. Indeed, several studies have shown that leachate organic matter is composed mainly of humic and fulvic acids (Artiolafortuny and Fuller, 1982; Christensen et al., 1998a; Christensen et al., 2001; Frimmel and Weis, 1991; Weis et al., 1989). The spectra were normalized with the peak at 295 eV. For all spectra, three main peaks located respectively at 285.2, 286.6 and 288.6 eV (corresponding to the C(1s)→π* transitions) can be identified (Figure 2). The 285.2 eV band corresponds to aromatic C-C or C-H bonds (Cody et al., 1995). The 286.6 eV transition can be assigned to aromatic C-O (phenols) or C-X (halogen) bonds (Cody et al., 1995). The most intense band around 288.6 eV is related to the oscillation strength of the C=O bonds of carboxylic groups (Hitchcock and Brion, 1980; Urquhart and Ade, 2002). This latter peak is clearly asymmetric, suggesting that both the 289.5 eV transition (assigned to the O-alkyl group of alcohols/carbohydrates), and the mixed Rydberg valence band around 287.4 eV (generally assigned to aliphatic groups), are masked (Ade et al., 1992).

Filtration of sample S8 led to a slight decrease of aromatic and phenolic functional groups, whereas carboxylic groups content remained constant (Figure 2). Chemical analyses show that both sulfur and acetate concentrations in S9 are higher in comparison to other leachates (Tables 3 and 4). NEXAFS spectroscopy indicates that carboxylic functional group content is slightly lower than the ones measured in S6 and S8, while aromatic and phenolic functional group contents are higher. In
comparison to the Suwannee river sample, the leachates seem to have a lower aromatic and phenolic functional group content and a higher carboxylic group content. These differences could either be related to true chemical differences or to extraction procedures. Indeed, it is worth reminding that Suwannee river fulvic acid is purified following a standardized procedure on a column, whereas the leachates were only filtered.

5. Discussion

5.1 Scope of speciation calculations

Speciation calculations allow the computation of saturation indices for many mineral phases that could potentially control heavy metal maximum concentration levels. For instance, metal sulphide phases such as PbS or ZnS could form as a consequence of the increase of the leachate sulphide concentration, consecutive to bacterial sulphate reduction. Intense bacterial activity is suggested by the measured sulphide concentration as well as the high calculated partial pressure of CO$_2$ in the leachate. Calcite is strongly oversaturated for all samples, due to this continuous bacterial activity and bicarbonate production (Figure 3). In the context of municipal waste storage, scavenging of heavy metals by carbonate phases has been described by several authors (Ettler et al., 2006a; Ettler et al., 2008; Ettler et al., 2006b; Kugler et al., 2002; Manning, 2001; Strnad et al., 2009; Yanful et al., 1988b). Curti (1999) has shown that metals are incorporated into calcite following well-defined and predictable geochemical rules.

5.2 Calculations without consideration of organic matter complexation

As a first approach, saturation index were computed on the basis of total metal concentrations in the <0.1 µm fraction. Redox potential was considered to be at the value of the redox couple S(-2)/S(+6), because of the potential effect of sulphide phase precipitation on metal solubility (Weber et al., 2009). For lead, speciation calculations (Figure 4) suggest leachate super-saturation with respect to galena (PbS). In addition to lead, for all our speciation calculations (figures not shown) similar conclusions ensue for other heavy metals (Zn, Cu, Cd, Co, Ni) where sulphide phases (sphalerite ZnS, covellite CuS, greenockite CoS, millerite NiS, …) are above saturation in all
leachate samples. The question then arises as to the reason of such a deviation from equilibrium conditions; i.e. why do the sulphide phases not precipitate?

The predominance of sulphate reducing bacteria in landfill leachate has been shown by several authors. Yunes et al. (2009) identified sulphate-reducing bacteria (SRB) as one of the main microbial populations in leachate from landfills in Argentina. Zhou et al. (2008) investigated biogeochemical processes occurring in a column filled with sandy soil and fed with leachate and observed a predominance of sulphate-reducing bacteria. Formation of metal sulphides as a result of SRB activity was investigated also by Ehrlich (1999). Galena precipitation has been observed in a bioreactor where sulphate reduction occurred (Schroder-Wolthoorn et al., 2008). Gallegos-Garcia et al. (2009) recovered metal sulphides (pyrite FeS₂, sphalerite ZnS and greenockite CdS), separated from the biomass in a one-stage sulphate-reducing process. Labrenz et al. (2000) have also reported low-temperature, biologically mediated sphalerite precipitation from dilute natural solutions. Moller et al. (2004) studied the impact of sulphate-reducing bacteria for the removal of heavy metals As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn from four leachates at two landfills in Sweden. The experiments showed that Cd and Cu were most efficiently removed, while Cr was the most difficult to precipitate. In the batch experiments, precipitation of the metals was found to be a relatively fast process.

Such evidence of metal sulphide precipitation via biogeochemical processes raises the question as to why calculations presented here show saturation indices above zero. This discrepancy can be explained either by the validity of the available thermodynamic data or to kinetic effects induced by the microbiological activity. But the fact that metal complexation by organic matter is not taken into account in the latter calculations could also explain the positive saturation indices. This latter hypothesis is tested in the following section. With respect to thermodynamic data, solubility data need to be carefully evaluated. For example, in the case of millerite (NiS), the most likely Ni sulphide mineral to form, widely used solubility product constants turn out to be based only on crude estimates and accurate solubility data are missing (Thoenen, 1999). In the case of greenockite, Clever et al. (1992) have suggested a solubility constant of -15.89 log units, emphasizing that the uncertainty on this value is high but without quantifying it. Wang and Tessier (1999) have experimentally determined a value of 14.82 log units. Nevertheless, even assuming an error of 1 or 2 log unit for the solubility constant of these sulphide minerals, calculations will still show them as
over-saturated. Kinetic effects are likely to play a major role in this apparent supersaturation (Moller et al., 2004).

5.4 Calculations with consideration of organic matter complexation

As most of the measured pollutants are divalent metals (Cd, Zn, Ni, Co, Cu and Pb), which tend to form complexes with organic matter, calcium measured in high concentrations in the leachates can compete with divalent cations for complexation with organic matter. The different pH values, between 7.25 and 8.65, as well as measured sulphate (< 65 mg L\(^{-1}\)) or calcium (< 152 mg L\(^{-1}\)) concentrations, suggest that these leachates are characteristic of methanogenic conditions, implying that fatty acids produced during the acidic stage are not representative of the organic matter in these leachates. XANES results confirm this hypothesis and shows that fulvic acid (FA) is representative of the leachate organic matter. Organic matter complexation was taken into account using the WHAM model (Tipping, 1994, 1998) that can be implemented in the speciation code PHREEQC (Appelo and Postma, 1996). As shown previously with NEXAFS spectroscopy, the organic matter can be considered, in a first approximation, as humic substances (fulvic and humic acids).

Inputs for the quantity of the four carboxylic sites, the four phenolic sites and the twelve bidentate sites are provided in Table 7. The latter sites were calculated by multiplying the charge in meq g\(^{-1}\) of the different sites by the DOC mass content. The different charges were calculated using the algorithm and the formalism defined in Tipping and Hurley (1992). The pK used in the WHAM model for the metal dissociation was taken from Christensen et al. (1999; 1998b) and Lofts and Tipping (2000). According to the speciation calculations, Pb, Cd, Ni, Cu and Zn are strongly complexed with OM, except for cadmium in the case of S1 and S2 (Figure 5). This is related both to a lower affinity of cadmium for OM and to a lower concentration of OM in these two samples. Association of these metals with colloidal OM is not sufficient to decrease metal concentrations below the metal sulphide solubility limit (Figure 6). As an example, this leads to a two log units decrease of galena saturation index, in agreement with a hundred-fold reduction of lead concentration in the solution (Figure 4).
5.5 Implications for landfill risk assessments

As shown in our study and by other researchers, there are strong solubility controls on the fate of heavy metals in the vicinity of landfills. However, the quantitative assessment of these controls is hampered by the occurrence of at least two mechanisms discussed in this paper: (i) kinetic effects related to microbial activity leading to a deviation from equilibrium conditions and (ii) the association between heavy metals and organic matter in the form of very small colloids associated with the < 30 kD fraction. However, in the area of landfill risk assessment, the assessment of heavy metal potential impact still often relies on the concept of equilibrium partitioning between the dissolved and solid (adsorbed) phases (i.e., the “K_d” approach; e.g., Slack et al., 2006). While limitations of this approach have been well documented (e.g., Reardon, 1981), its relative simplicity makes it attractive, particularly in a context of consulting studies. The K_d is expressed as:

\[ K_d = \frac{C_s}{C_{eq}} \times R_{LS} \]  

Where \( C_s \) is concentration on the solid surface (mol L\(^{-1}\)), \( C_{eq} \) is dissolved concentration at equilibrium (mol L\(^{-1}\)) and \( R_{LS} \) is the liquid to solid ratio (L kg\(^{-1}\)). The strict domain of validity of the K_d modelling approach is underlain by three strong hypotheses:

(i) The reactions that lead to the partition between the liquid and the solid phases are fast and reversible (which excludes for example mineral precipitation),

(ii) The isotherm representing the sorbed pollutant quantity on the solid as a function of its concentration in solution is linear,

(iii) The K_d value should be independent of physico-chemical conditions of the media (pH, ionic strength, alkalinity). This last point can be neglected if the solution containing the pollutant does not disturb the chemical conditions of the medium and if the K_d is measured in the same conditions.

In the advection-dispersion transport equation (Freeze and Cherry, 1979), the K_d enters the calculation of the retardation factor R, provided that the three conditions mentioned above are fulfilled and that a solid phase (e.g. colloidal transport) does not participate in the transport of the element of interest:

\[ R = 1 + \frac{\rho}{\varepsilon} K_d \]  

Where \( \rho \) is the dry density of the solid media (kg dm\(^{-3}\)) and \( \varepsilon \) is the porosity of the media (unitless).
Drawbacks of this approach in a context of landfill risk assessment are, on the one hand, that the underlying hypotheses are rarely, if ever, met and, on the other hand, that it usually leads to an overly conservative estimation of landfill potential impact. Regarding the first drawback, among the three criteria presented above that underlie the concept of $K_d$, the third one is particularly questionable in a context of leachate migration in the vicinity of a landfill, as shown by several authors (e.g., Rolle et al. 2008; van Breukelen and Griffioen, 2004; van Breukelen et al. 2004)). Regarding the second drawback, the $K_d$ approach accounts for retardation of pollutant migration, but does not yield an effective attenuation of long-term groundwater concentrations, compared to the situation without retardation, because attenuation mechanisms such as pollutant co-precipitation with mineral phases are not taken into account.

Process-oriented modelling approaches (e.g., Dijkstra et al., 2008) are required in order to account for the mechanisms involved in a true attenuation of emissions from landfills.

### 6. Conclusions

The results of analyses performed on leachates collected from eight landfills in France suggest that most of the metals (or metalloids) are concentrated in the $< 30$ kD fraction. For lead, copper and cadmium data show their association with larger particles. Initial speciation calculations suggest that the leachate concentrations of lead, copper, nickel and zinc are super-saturated with respect to sulphur mineral phases. Additional speciation calculations taking into account complexation of these metals with organic matter considered as fulvic acids, based on C1(s) NEXAFS spectroscopy, shows that this mechanism is not sufficient to explain this deviation from equilibrium conditions. It is therefore hypothesized that such deviation results from the influence of biological activity on mineral phase precipitation and dissolution kinetics, the controlling parameters of which are largely unknown.

Future work will be aimed at, on the one hand, sampling solid phase precipitated at the base of the landfill cells from which the sampled leachates originate and, on the other hand, investigating, in the laboratory precipitation and dissolution kinetics of sulphur phases in the presence of organic matter and sulphate reducing bacteria representative of the sampled leachates.
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