Leaching, geochemical modelling and field verification of a municipal solid waste and a predominantly non-degradable waste landfill

H.A. van der Sloot **(Hans van der Sloot Consultancy)**
D.S. Kosson **(Vanderbilt University)**
A. van Zomeren **(ECN)**

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H.A. van der Sloot [a,*], D.S. Kosson [b], A. van Zomeren [c]

[a] Hans van der Sloot Consultancy, Dorpsstraat 216, 1721BV Langedijk, The Netherlands
[b] Vanderbilt University, Department of Civil and Environmental Engineering, Nashville, TN 37235, USA
[c] ECN, Environment & Energy Engineering, P.O. Box 1, 1755 ZG Petten, The Netherlands

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ABSTRACT

In spite of the known heterogeneity, wastes destined for landfilling can be characterised for their leaching behaviour by the same protocols as soil, contaminated soil, sediments, sludge, compost, wood, waste and construction products. Characterisation leaching tests used in conjunction with chemical speciation modelling results in much more detailed insights into release controlling processes and factors than single step batch leaching tests like TCLP (USEPA) and EN12457 (EU Landfill Directive). Characterisation testing also can provide the potential for mechanistic impact assessments by making use of a chemical speciation fingerprint (CSF) derived from pH dependence leaching test results. This CSF then forms the basis for subsequent chemical equilibrium and reactive transport modelling to assess environmental impact in a landfill scenario under relevant exposure conditions, including conditions not readily evaluated through direct laboratory testing. This approach has been applied to municipal solid waste (MSW) and predominantly non-degradable waste (PNW) that is representative of a significant part of waste currently being landfilled. This work has shown that a multi-element modelling approach provides a useful description of the release from each of these matrices because relevant release controlling properties and parameters (mineral dissolution/precipitation, sorption on Fe and Al oxides, clay interaction, interaction with dissolved and particulate organic carbon and incorporation in solid solutions) are taken into consideration. Inclusion of dissolved and particulate organic matter in the model is important to properly describe release of the low concentration trace constituents observed in the leachate. The CSF allows the prediction of release under different redox and degradation conditions in the landfill by modifying the redox status and level of dissolved and particulate organic matter in the model runs. The CSF for MSW provides a useful starting point for comparing leachate data from other MSW landfills.

1. Introduction

Recent characterisation of materials, such as soil, contaminated soil, sediments, sludge, compost, wood, coal combustion residues, waste and construction products by means of more extended leaching tests and associated chemical speciation modelling has led to much more detailed insights into release controlling processes (Kosson et al., 2002, 2009, 2014; Dijkstra et al., 2004; Carter et al., 2009; Schoknecht et al., 2005; van der Sloot et al., 1997, 2007a, 2007c; van der Sloot, 2002; van der Sloot and Dijkstra, 2004; van der Sloot and Eikelboom, 2003). Similarity in release controlling factors across this wide spectrum of materials provides the potential for full mechanistic impact assessments by making use of a chemical speciation fingerprint (CSF) derived from the pH dependence leaching test on each of the materials (van der Sloot et al., 2007a, 2007c; Kosson et al., 2014). In the case of landfilling, the potential prediction of constituent release from a landfill cell or site is complicated by the fact that the material to be evaluated is generally heterogeneous. This heterogeneity may be apparent macroscopically (visual) and in terms of content, but the behaviour of the material may very well be far more consistent in case of leaching (van der Sloot and Dijkstra, 2004) because of volumetric integration by the leaching process (local equilibrium)

Abbreviations: MSW, municipal solid waste; PNW, predominantly non-degradable waste; CSF, chemical speciation fingerprint; TCLP, toxicity characteristic leaching procedure; LEAF, leaching environmental assessment framework; HA, humic acid; FA, fulvic acid; DHA, dissolved humic acid; SHA, solid humic acid; DOC, dissolved organic carbon; TOC, total organic carbon; POM, particulate organic matter; HFO, hydrated iron oxide; SI, saturation index; L/S, liquid to solid ratio (L/kg); pH+pe, measure of redox state.

* Corresponding author.
E-mail address: hans@vanderslootconsultancy.nl (H.A. van der Sloot).

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and thermodynamically imposed consistency in liquid-solid partitioning at a macro-scale based on the dominant system chemistry.

Improved insights into the release controlling factors are needed to be able to better design and control release from landfills and, where possible, manage wastes in a manner that is more sustainable (Mathlener et al., 2006; Van Vossen et al., 2009; Heimovaara et al., 2013). In the framework of the Dutch Sustainability project (Mathlener et al., 2006) municipal solid waste and predominantly non-degradable waste (subsequently referred to as PNW) were studied in detail at laboratory-scale and using field lysimeters and large pilot-scale test landfill cells. The objectives of this paper are to (i) compare laboratory and field testing results for MSW and non-degradable waste matrices to identify to what extent similarities in leaching behaviour exist, and (ii) illustrate the usefulness of chemical speciation modelling through use of a CSF to evaluate factors controlling leaching. It is important to recognize that after degradation of organic rich waste, such as typical municipal solid waste (MSW), a residual material remains, that has similarities with the predominantly non-degradable waste studied already in detail (van der Sloot et al., 2001a,b; van Zomeren et al., 2005). In the review paper by Kjeldsen et al. (2002), the factors controlling metal release from MSW are discussed and studies by others are highlighted. The overall conclusion is that there are still many unknowns due to multiple interactions. This paper seeks to reduce a number of the uncertainties surrounding release of inorganic substances from MSW landfills. It focuses on calibration of a mechanistic leaching model based on pH static experiments; the application of the calibrated model to column leaching tests (with a further limited calibration step); the application of the calibrated model to assess data obtained from field sites; and finally the application of the calibrated model to assess effects of redox and variation in DOC levels resulting from organic matter degradation.

2. Experimental

The waste matrices selected are representative of a group of waste mixes covering a significant portion of wastes typically landfilled in practice and for which release behaviour is expected to have many common aspects.

2.1. Materials

Both wastes discussed here were evaluated using leaching characterisation tests and reported earlier (Luning et al., 2006; van Zomeren and van der Sloot, 2006a, 2006b) and are analogous to and directly comparable with the US EPA leaching environmental assessment (LEAF) tests (Garrabrants et al., 2011, 2012). Field test results have been reported in the framework of the Dutch Sustainable landfill project (Mathlener et al., 2006; Oonk et al., 2013). A comparison of laboratory, lysimeter and field scale testing on two waste types was reported in Kosson et al. (2014). The present work focuses on modelling the release behaviour from these different matrices based on characterisation leaching test results in comparison with leachate from MSW and PNW landfills and accounting for differences in conditions between laboratory and field.

2.1.1. MSW

A composite sample of MSW representing organic rich waste was prepared from separately collected samples of waste prior to landfilling for testing the release behaviour from the bioreactor (45,000 m^3) operated at the Landgraaf landfill (Luning et al., 2006). Test results for this waste have been reported in the context of the Dutch Sustainable Landfill Project (2006). In 2010 the 8 year old pilot cell was dismantled, which provided the opportunity to sample material from different spatially distributed locations within the cell subjected to leachate recirculation and aeration cycles (Oonk et al., 2013). Composite samples were subjected to laboratory characterisation leaching tests (EN 14429, 2015; PrEN 14405, 2015), while individual samples were tested using a single step batch leaching test (EN12457-2, 2002; extraction with deionized water at liquid/solid ratio of 10 mL/g).

2.1.2. Mixed waste

A waste mixture of predominantly non-degradable waste (PNW) was prepared from volumetrically representative portions of the waste delivered at the landfill test cell (Nauerna Landfill, NL). These waste samples were mixed to constitute a composite waste for testing at lysimeter and at lab scale (van Zomeren et al., 2005; van Zomeren and van der Sloot, 2006a). The main components in the waste mixture were soil cleaning residues, contaminated soil, sediments, small industrial waste streams, and construction and demolition waste. Only largely degraded organic matter was allowed in this pilot, hence the term predominantly non-degradable waste (PNW). Leachate from the pilot cell was collected.

2.2. Methods

2.2.1. Leaching tests

The upflow percolation test (PrEN 14405, 2015; continuous elution with deionized water and 7 eluate collection intervals ranging from L/S 0.2–10 mL/g and linear flow velocity of 15 cm/day) and pH dependence leaching test (EN 14429, 2015; parallel batch extraction at L/S 10 mL/g with various acid and base additions to attain specified endpoint pH values) were performed on the composite of collected waste samples. More detailed descriptions of the procedures are given in (van der Sloot et al., 1997). Similar methods and applicable method reproducibility statistics are described in Kosson et al. (2002), Lopez Meza et al. (2008) and Garrabrants et al. (2011, 2012).

2.2.2. Estimation of model parameters

The quantities of "reactive" organic carbon in the solid phase (i.e. HA and FA) were estimated by a batch procedure (van Zomeren and Comans, 2007), which is derived from the procedure recommended by the International Humic Substances Society (IHHS) for solid samples (Swift, 1996). In short, the procedure is based on the solubility behaviour of HA (flocculation at pH < 1) and the adsorption of FA to a polymer resin (DAX-8). The amounts of amorphous and crystalline iron (hydr)oxides in the waste mixture were estimated by a dithionite extraction (Kostka and Luther, 1994). The amount of amorphous aluminium (hydr)oxides were estimated by an oxalate extraction (Blakemore et al., 1987). The extracted amounts of Fe and Al were summed and used as a surrogate for hydrous ferric oxides (HFO) in the model. The methods now have been standardised in ISO/TS 12782 parts 1–5 (2011). The clay content of the samples was quantified by a sedimentation method (NEN 5753, 1994).

2.2.3. Chemical analysis

The leachates and extracts from laboratory tests were analysed for major, minor and trace elements by ICP-OES (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Tl, V, Zn). DOC (dissolved organic carbon) and TIC (total inorganic carbon) were analysed by a Shimadzu TOC 5000a analyser. Cl, F, ammonium and sulphate were analysed by ion-chromatography. Unless measurements are close to the detection limits of the analytical methods employed, the measurement error is generally small compared to the uncertainty involved in testing

(Garrabrants et al., 2011, 2012) and uncertainties associated with multi-element modelling.

2.3. Geochemical speciation and release modelling approach

Chemical speciation of the solutions was calculated with the ORCHESTRA modelling framework (Meeussen, 2003) embedded in LeachXS™. Aqueous speciation reactions and selected mineral precipitates were taken from the MINTEQA2 database. Ion adsorption onto organic matter was calculated with the NICA-Donnan model (Kinniburgh et al., 1999), with the generic adsorption reactions for all elements as published by Milne et al. (2001, 2003). Adsorption of ions onto iron and aluminium oxides was modelled according to the generalized two layer model of Dzombak and Morel (1990).

The database/expert system LeachXS™ (www.leachxs.net) was used for data management, e.g. pH dependent leaching data, percolation test data, lysimeter and field leachate data and for visualization of the calculated and measured results (van der Sloot et al., 2001b, 2003, 2007a,c, 2008a,b; Kosson et al., 2014). The use of ORCHESTRA coupled and embedded within LeachXS allowed for rapid data retrieval, automatic input generation for modelling, processing of calculated results and graphical and tabular data presentation.

2.3.1. Modelling laboratory test data – pH dependent leaching

The input to the model consists of fixed element available contents (i.e., the amount of each element present that can participate in liquid-solid equilibrium partitioning) derived from the pH dependent leaching test results, selected potential solubility controlling minerals (from ORCHESTRA thermodynamics database), active Fe-and Al-oxide sites, particulate organic matter (from HA and FA analyses) and a description of the DOC concentration as a function of pH (using polynomial curve fitting to pH dependent leaching test results). Fe- and Al-oxides were summed and used as input for HFO as described in Meima and Comans (1998).

As a starting point for the model calculations, the maximum value of release as obtained in the pH dependence leaching test (between pH 2 and 13) was used as the available solid phase concentration (i.e., available content, mg/kg dw). As the pH dependence test is carried out on separate sub-samples of the composite of the collected waste samples, the variability in subsampling can be assessed from the analysis of non-reacting elements (e.g. Cl, Na, K). Basically, the speciation of all elements is calculated in one problem definition within the model with a common parameter set and values. This substantially limits the degrees of freedom in selecting parameter values, because improvement of the model description for one element may deteriorate the outcome for other elements.

The DOC analysis of the extracts does not directly represent the reactive part of the dissolved organic matter. Based on experience with other similar samples, where the relationship between hydrophilic, fulvic and humic acid fractions in DOC was quantified (van Zomeren and Comans, 2007), reactive fractions of DOC (dissolved humic acid – DHA) are defined as a function of pH (lowest proportion of reactive forms are in solution at neutral pH with increasing proportions towards both low and high pH). A polynomial fit is created through the 8 data points to allow quantification of DHA at intermediate pH values in modelling. As Cu is the most sensitive element for particulate and dissolved organic matter interaction, the agreement between model and measurement of Cu is used to fix the DHA/DOC ratio at different pH values. All other elements interacting with DHA are thereby fixed.

It was found that the leachable carbonate concentration is too low to describe the important role of carbonate in the model calculations due to release of CO_2 from solution at pH < 5. This parameter was therefore adjusted until Ca as calcite showed a good match with the observed leaching data. As all of the calcium carbonate and magnesium carbonate is dissolved at pH < 4, it is assumed that solid phase measurement of total inorganic carbon content can be used to estimate solid phase carbonate.

The mineral phases that were allowed to precipitate were selected after calculation of their respective saturation indices (SI) in the original pH dependence leaching test eluates. Saturation indices were calculated for more than 650 minerals in the thermodynamic database, and a selection of the most likely and relevant phases was made based on the degree of fit over a wide pH range, the closeness of the SI value to 0 (ideal fit) and expert judgment on the suitability of possible minerals for the waste mixture (e.g., exclusion of minerals requiring high temperature for formation). Generally, minerals were selected if the SI was in the range of −0.2 to 0.2 for more than two pH data points. It must be realized that SI's are based on concentrations as measured without taking into account interactions between elements and other reactions (e.g., DOC complexation). This implies that a wider search may be needed to properly describe a complex multi-element, multi-phase system. In addition, phases may appear to be relevant based on SI calculation, but are not relevant due to the slow kinetics of dissolution (Nordstrom, 2009). This relates in particular to several clay minerals and rock phases. Furthermore, there often are significant differences between the primary minerals identified by XRD on bulk samples and the mineral and sorptive phases controlling leachability, which may be either trace phases or minor quantities present as coatings on particles. The selection of minerals and sorptive phases aims to describe the measured data well within one order of magnitude over as wide as possible pH range. Uncertainties in or lack of thermodynamic data for trace substances may limit this ambition. Finally, the authors acknowledge that the selected chemical speciation assemblage often will not be a unique solution but rather view the results in terms of its utility in representing the liquid-solid partitioning behaviour over a wide range of conditions (e.g., pH, L/S, batch and percolation column extractions, laboratory and field conditions) and therefore is useful in scenario and uncertainty analysis. The suitability of the resulting CSF is further evaluated based on the ability to independently predict results from percolation column testing.

2.3.2. Modelling laboratory test data – percolation test

For modelling the column test results, the following percolation test parameters are needed in addition to the geochemical properties derived from the pH dependence test data: the initial pH from low L/S fractions of the percolation test, the porosity of the packed column, the density of the material, the height of the packed column and the eluant flow rate and composition (assumed constant for the duration of the laboratory test and simulation). The available contents as derived from the pH dependence test are used in modelling the percolation test results. Some variability in comparisons between pH dependence test results, percolation test results and model results can be caused by sub-sampling from the composite of collected waste for laboratory testing. By applying a limited number of cells over the length of the column a certain level of dispersion is included in the model. A diffusion distance between stagnant and mobile zones is assumed, which is calibrated on the release of non-interacting elements (usually salts such as K, Na, Cl). Once this parameter is fixed, the initial pH is slightly adjusted to be able to predict the pH response as measured because the initial L/S from the column is substantially less than 10 (e.g., on the order of 0.2–0.6 mL/g dw). In the percolation model approach, local equilibrium dictated by the mineral and sorptive phases as determined from the modelling of the pH dependence test results is assumed. For the initial condition, concentrations throughout the column are assumed to be the same, which is in

agreement with the pre-equilibration period of the column test. It is assumed that biodegradation is not leading to significant changes in the amount and type of particulate and dissolved organic matter phases during the short duration (<10 days) of the percolation test. The redox condition also is assumed not to change over the duration of the percolation test. Normally, the eluant is demineralised water,[1] which has very low concentrations of all substances in the materials. A prediction of DOC release from the organic matter content of the solid is not (yet) possible, and therefore the DOC data as measured in the percolation test is used in the simulation as input data. These data have been corrected to obtain the reactive fraction of DOC (DHA) relevant for metal interaction. A power function fit is used based on the equation: $DHA_{L/S} = q_2 + q_0 * e(-q_1 * L/S)$, which gives at present the best possible description for DHA at intermediate L/S values necessary for modelling.

2.3.3. Comparison with field data

About 8 years after filling the MSW bioreactor landfill at Landgraaf in 2001 (Luning et al., 2006; Mathlener et al., 2006) the bioreactor was excavated which presented the opportunity to sample field exposed material at different locations in the cell (Oonk et al., 2013; Kosson et al., 2014). The individual samples were taken from the face of the excavated cell and subjected to leaching by the single step EN12457-2 (2002) batch test. A composite of the different samples was tested using the pH dependent leaching test EN14429. The batch test data collected at different locations from the face of the excavated cell and leachate samples collected over the time the bioreactor landfill was monitored (1999–2010; including leachate recirculation and some water supplementation) are placed in context with pH dependent leaching of fresh mixed MSW composite and a composite of the individual MSW samples excavated after 8 years of operation. A separate comparison is made between MSW characterisation based on pH dependence test data and MSW leachate data from other sources.

2.3.4. Modelling different redox conditions and consequences of organic matter degradation

Since maintaining the redox condition of sampled (reducing) material is very difficult in a lab atmosphere and testing degradation in a column test is not practical either, assessing the effect of changes in redox state and different degrees of organic matter degradation on release behaviour through modelling is applied with the model description for MSW release based on pH dependence as the starting point.

3. Results

3.1. Chemical speciation modelling of pH dependence test data

In Figs. 1–3 the model results for MSW and PNW are given in comparison with the original pH dependence test data. In all cases, the percolation test data are given for comparison with the modelling results at both L/S = 10 mL/g (dry weight basis) and L/S = 0.2 mL/g (all other parameters remaining the same) to assess the accuracy of the model with the given mineral and sorption parameter selection for both a wide pH range as well as a wide L/S range.

The starting point for the modelling is the L/S = 10 mL/g leach test data. The mineral selection is based on obtaining a simulation that provides the closest fit between model and actual test results. The low L/S modelling (around 0.2 mL/g), using the first fraction of the percolation test, is meant to test whether the same selection of minerals or a slight modification can simultaneously predict the release behaviour at low L/S under the assumption that local equilibrium prevails. The L/S of 0.2 mL/g is assumed to reflect initial pore water conditions in the column.

Based on the preliminary screening model run to determine SI values and expert knowledge (relevant mineral phases formed under ambient conditions), a preliminary set of minerals is identified for inclusion in the simulation of the pH dependence test data. Minerals estimated to represent less than 0.1‰ of the element present and available for leaching were excluded to narrow the set of relevant minerals (as marked with asterisks in Table 1).

The geochemical speciation modelling for the MSW and PNW includes 25 elements and additional constituents (e.g., inorganic and organic carbon). The partitioning of additional constituents for MSW and PNW is available as supplemental information. The input parameters for the modelling are given in Table 1 and is comprised of the element available contents, the mineral selection, the content of clay to the extent relevant, the quantity of reactive Fe- and Al-oxide surfaces (HFO) and the reactive part of particulate and dissolved organic matter. The material properties in terms of element available content, Fe- and Al-oxide quantity, clay content, relevant minerals and reactive particulate (designated as solid humic acid – SHA) and dissolved organic matter (designated as dissolved humic acid DHA) form the chemical speciation fingerprint (CSF) for the material of interest. This chemical speciation fingerprint is then used in subsequent chemical reaction transport modelling to describe local equilibrium.

The multi-element chemical speciation equilibrium modelling includes much complexity, but remains very feasible with runtimes typically less than 2 min (e.g., on a typical Intel i7 processor with 16 Mb RAM and a 256 Gb Hard disk). In the speciation modelling, the outcome of the simulation result is improved iteratively by applying changes in the mineral assemblage. Since simultaneous model runs at L/S = 10 and L/S around 0.2 or 0.3 are carried out with the same mineral set, sorption parameters and HA, FA and DOC complexation parameters, a good match for a large group of major, minor and trace elements across both L/S conditions and the full pH domain is an indication that a converging solution is approached.

3.1.1. Municipal solid waste

In spite of the limitations discussed earlier, simultaneous simulation of many elements can represent batch laboratory experimental results over a wide pH range (with an emphasis around the own pH of the material[2]) and laboratory percolation column results over a wide L/S range at the measured pH conditions. For many elements, the measured concentrations at L/S = 10 mL/g and L/S around 0.2 mL/g for MSW are very similar (e.g., Cd, Cu, Ni, Pb, Zn, Cr, Mo, Al, F) and correspond well with the model simulations. This result indicates the solubility control of solution concentrations as described by the assemblage of minerals and sorptive phases provides a reasonable description of MSW behaviour over a wide pH and L/S values under mildly reducing conditions, which is the condition for laboratory handled MSW. Conductivity, acid neutralisation capacity, pe (measured Eh recalculated to pe) and DHA match well with the measurements, which is indicative of a quite reasonable selection of minerals and sorptive phases. The pH response of pe is in indication of the suitability of expressing redox state with the sum of pH+pe as a constant value. Obviously, highly soluble salts present below aqueous saturation behave differently, with the aqueous concentration increased at the initial low L/S in percolation

[1] For percolation tests and simulations on soil systems, 1 mM $CaCl_2$ is used as the eluant to avoid deflocculation of soil agglomerates and clays.

[2] "own pH" or "natural pH" is defined here as the extract pH that results at L/S = 10 mL/g using deionized water without addition of acid or base as part of the pH dependence test.

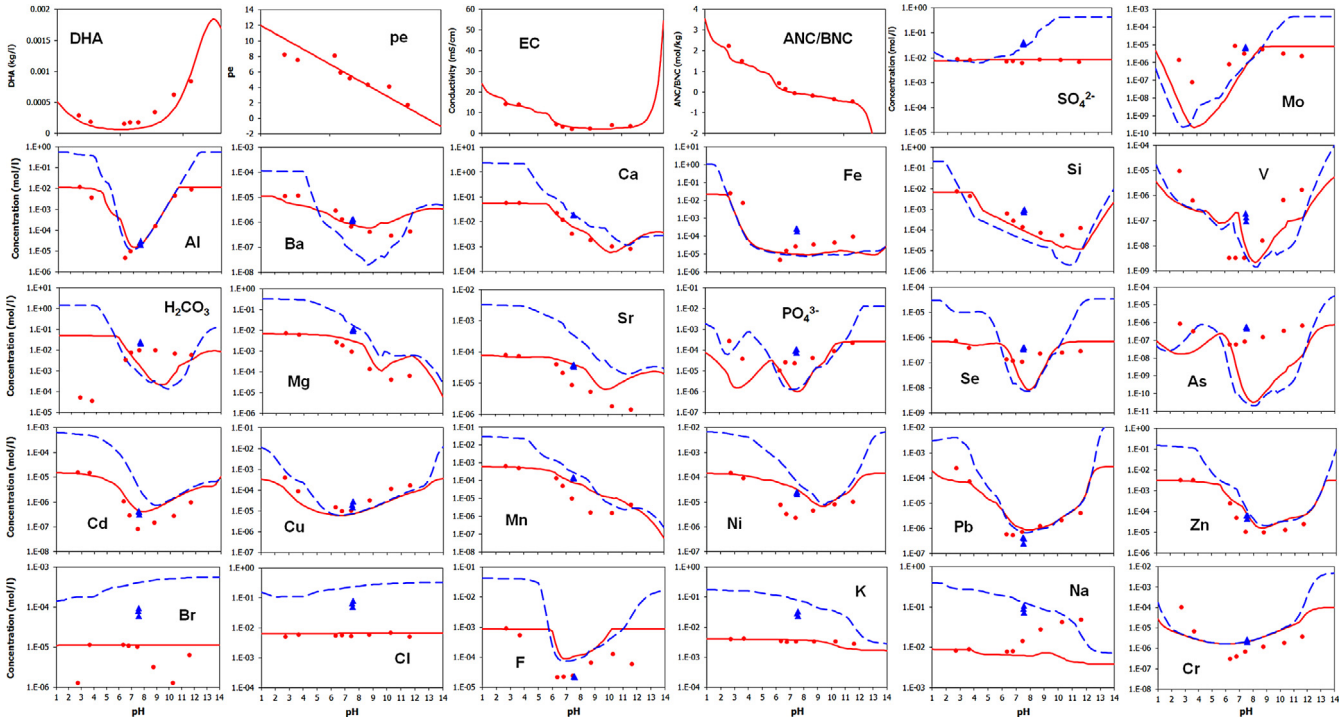

Fig. 1. Measured and predicted leaching behaviour of major, minor and trace elements as a function of pH in the MSW mixture. Solid circles: pH dependence test; triangles: percolation test data; line: prediction at L/S = 10 mL/g; dashed line: prediction at L/S = 0.2 mL/g.

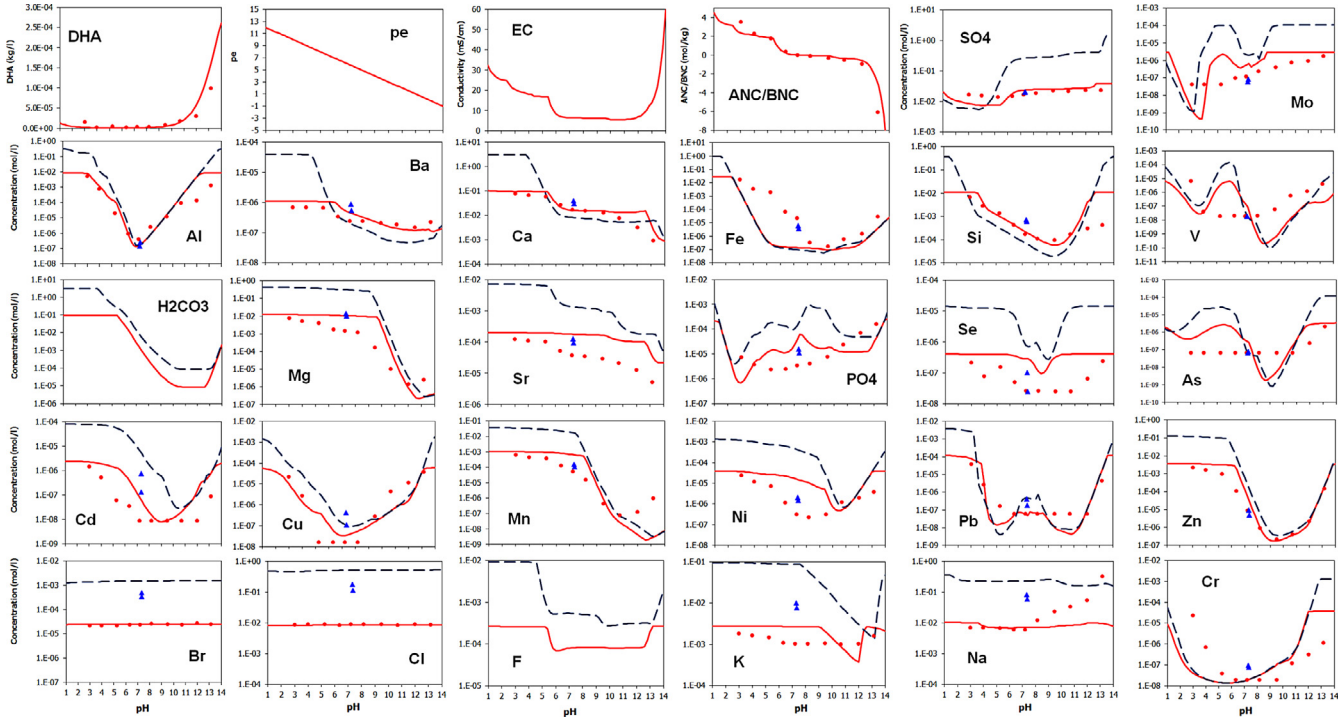

Fig. 2. Measured and predicted leaching behaviour of major, minor and trace elements as a function of pH in the PNW mixture. Solid circles: pH dependence test; triangles: percolation test data; line: prediction at L/S = 10 mL/g; dashed line: prediction at L/S = 0.2 mL/g.

column experiments relative to the concentration measured at L/S = 10 in batch pH dependence test measurements. This leaching behaviour is observed for Br, Cl, K and Na.[3] Oxyanions like As are more difficult to model because As partitioning is largely controlled by competitive sorption onto iron-oxide surfaces and the precise oxidation state of the system is not known, which affects the sorption substantially. For Ca and Mg it is clear that the low L/S simulation results in a systematic increase in the aqueous concentration, which is also reflected in the column test data.

[3] The increase in Na from pH 7 and higher in the pH dependence test is caused by the addition of NaOH to control pH.

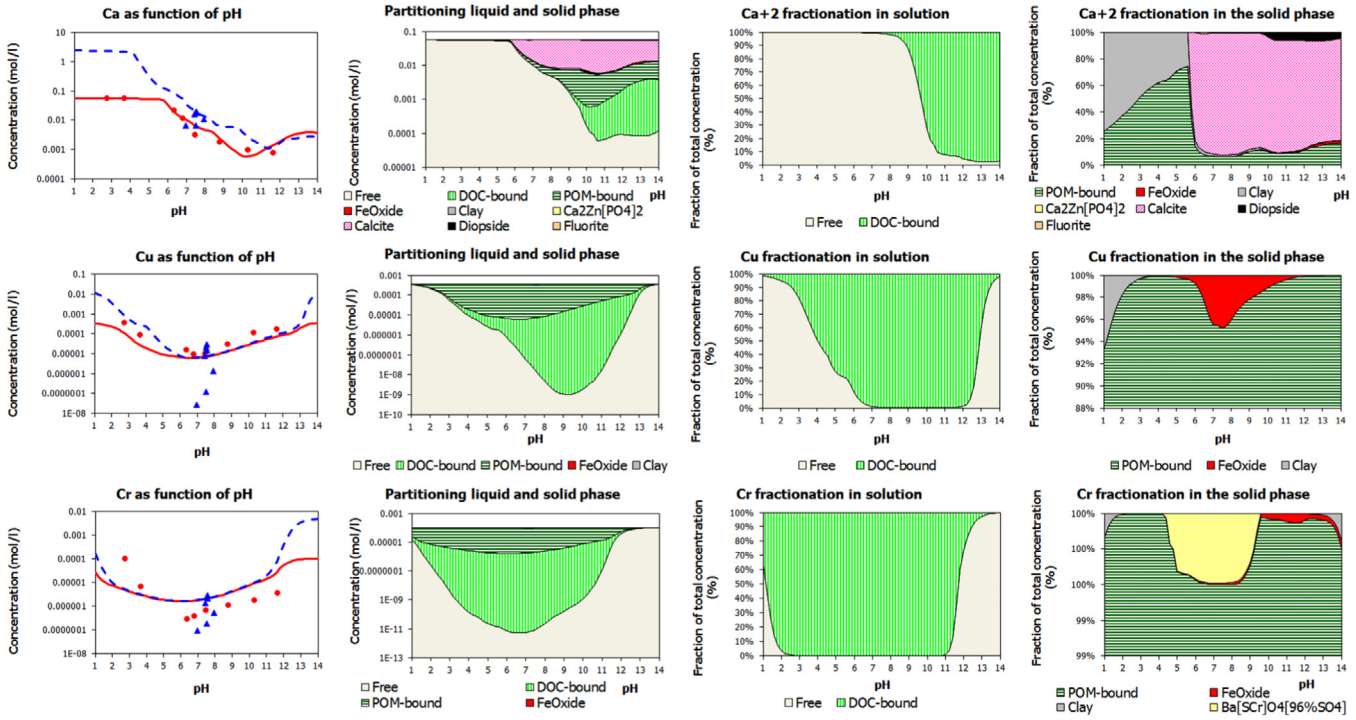

Fig. 3. Major (Ca) and trace element (Cu, Cr) partitioning from chemical speciation modelling of the MSW mixture using pH dependent test data (EN 14429; solid dots) and percolation column data (PrEN 14405 data; triangles). Solid line and dashed line: simulations at L/S = 10 mL/g and L/S = 0.3 mL/g respectively. Partitioning in the solution and in the solid are given on a total unit cell volume basis.

In Fig. 3 the comparison of measured and modelled data is complemented with the partitioning of a single element over different chemical phases as obtained from the modelling. The "free" (i.e., dissolved) and DOC associated elements belong to the solution; all other phases are in the solid phase. The percent distribution of both dissolved and particulate phases is given illustrating that the partitioning may change significantly with pH. It is also clear that for the case of an organic rich matrix like fresh MSW, a very significant portion of the metals and even of Ca is associated with DOC and POM (particulate organic matter). This affects their bioavailability as many organisms are not capable of taking up metals in DOC associated form (van der Sloot et al., 2008a). DOC complexation also may affect trace element mobility in soil, as complexed anionic forms are likely to be transported over greater distances than the free metal ions (McCarthy and Zachara, 1989).

3.1.2. Predominantly non-degradable waste mixture

For the predominantly non-degradable waste mixture, very similar behaviour as described above for MSW is noted. Solubility control (i.e., solution phase saturation) over a wide pH range and a wide L/S range is observed for several elements (e.g., Pb, Ca, Ba, Cr, Mo, Cu). In addition, the predicted acid/base titration behaviour from the simulations corresponds well with the measured acid/base behaviour, which indicates that the selected major minerals and sorptive phases provide a good description of pH response behaviour. Dissolved concentrations also range over several orders of magnitude and the correspondence between measured data and simulation is presented in Fig. 2. In spite of the largely non-degradable nature of this PNW, interaction with DOC and POM is still dominating the release behaviour of several constituents. SHA in PNW is only a factor of 2 smaller than the partially degraded MSW, while DHA is about a factor 100 lower.

3.2. Comparison between MSW (Landgraaf) and PNW (Nauerna)

In Fig. 4 the comparison between the leaching behaviour of sulphate, Cu, Pb, Zn, Cr and Cl from organic rich MSW and PNW is given as a function of pH together with modelling results for L/S = 10 mL/g and L/S = 0.2 mL/g. There is almost no difference between modelling and experimental results for Cl. For sulphate the PNW is just slightly higher in release, possibly due to a higher input of gypsum containing waste. For the metals, a substantial difference between the fresh organic rich MSW and the largely non-degradable organic matter containing PNW mix is noted, which in all cases points at much lower leaching levels from the PNW mixture, having a much lower DOC level and reactive fraction of DOC than the MSW. As can be seen in Fig. 3, Cu and Cr are fully dominated by binding to dissolved and particulate organic matter, hence this strong reduction in metal release for PNW vs. MSW.

3.3. Simulation of percolation test results using reactive transport modelling

Starting from the chemical speciation fingerprints (CSF) of the respective matrices (Table 1), simulations have been carried out using a dual porosity model coupled to chemical speciation calculations (Dijkstra, 2007; Grathwohl and van der Sloot, 2007) to describe the release from a percolation test carried out with the respective wastes. In Table 2 the model parameters for the two matrices are given.

3.3.1. MSW

Fig. 5 presents the results of reactive transport modelling of a percolation column test of MSW in comparison with the actually measured major, minor and trace elements of in the column effluent. As the modelling is based on available contents obtained from the pH dependence test, the error caused by sub-sampling from the composite of collected waste samples is embedded in these results.

Table 1
Chemical speciation fingerprint used for the speciation modelling of MSW and PNW (pH dependent leaching test and percolation column leaching test simulations; * Indicates minerals actually identified minerals over a threshold.).

Speciation session	MSW mix					Speciation session	Predominantly non-degradable waste mix			
Sum of pH+pe	13.0					Sum of pH+pe	13.0			
L/S	10.0					L/S	10.0			
Clay	1.0E−01	kg/kg				Clay	0.0E+00	kg/kg		
HFO	1.0E−02	kg/kg				HFO	1.5E−03	kg/kg		
SHA	4.0E−02	kg/kg				SHA	1.9E−02	kg/kg		
Porewater simulation	0.20	l/kg				Porewater simulation	0.20	l/kg		
DOC/DHA data						*DOC/DHA data*				
pH	[DOC] (kg/l)	DHA fraction	[DHA] (kg/l)	Polynomial coefficients		pH	[DOC] (kg/l)	DHA fraction	[DHA] (kg/l)	Polynomial coefficients
1.00	4.539E−04	0.55	2.496E−04	C0	−3.446E+00	1.00	2.914E−05	0.20	5.828E−06	C0 −4.684E+00
2.75	2.810E−04	0.40	1.124E−04	C1	−8.161E−02	3.02	1.500E−05	0.15	2.250E−06	C1 −5.010E−01
3.69	1.790E−04	0.30	5.370E−05	C2	−7.705E−02	4.00	1.840E−06	0.12	2.208E−07	C2 5.562E−04
6.37	1.470E−04	0.25	3.675E−05	C3	1.349E−02	5.27	3.800E−06	0.10	3.800E−07	C3 7.768E−03
6.81	1.730E−04	0.20	3.460E−05	C4	−5.311E−04	6.36	2.580E−06	0.15	3.870E−07	C4 −3.543E−04
7.48	1.740E−04	0.20	3.480E−05	C5	0.000E+00	7.23	2.700E−06	0.18	4.860E−07	C5 0.000E+00
8.78	3.330E−04	0.25	8.325E−05			8.18	3.560E−06	0.25	8.900E−07	
10.32	6.195E−04	0.35	2.168E−04			9.51	7.800E−06	0.35	2.730E−06	
11.66	8.380E−04	0.55	4.609E−04			10.70	1.756E−05	0.50	8.780E−06	
14.00	9.574E−04	0.90	8.617E−04			12.01	2.960E−05	0.70	2.072E−05	
						13.17	9.860E−05	0.90	8.874E−05	
						14.00	1.408E−04	0.95	1.338E−04	
Reactant concentrations						*Reactant concentrations*				
Reactant	mg/kg	Reactant	mg/kg	Reactant	mg/kg	Reactant	mg/kg	Reactant	mg/kg	Reactant mg/kg
Al	3080	F	168	Ni	85	Al	2276	Cu	40	Ni 23
As	0.61	Fe	13400	P	79	As	2.6	F	50	P 82
B	73	H2CO3	30100	Pb	588	B	18.6	Fe	16360	Pb 250
Ba	15.7	K	1580	S	2770	Ba	1.5	K	1060	S 12720
Br	9.0	Li	2.7	Sb	1.8	Br	34.5	Li	2.6	Sb 0.4
Ca	22700	Mg	1630	Se	0.55	Ca	50150	Mg	3002	Se 0.3
Cd	16.9	Mn	339	Si	1970	Cd	2.8	Mn	574	Si 3015
Cl	2330	Mo	7.7	Sr	68	Cl	5268	Mo	2.9	Sr 176
Cr	53	Na	2079	V	4.7	H2CO3	56000	Na	2360	V 5.2
Cu	234	NH4+	2030	Zn	2110	Cr	19	NH4+	610	Zn 2401
Selected minerals						*Selected minerals*				
Al[OH]3[a]*	Birnessite	CuCO3[s]	Huntite	Otavite	Wairakite	Albite[low]*	Bunsenite*	Cr[OH]3[A]*	Manganite*	PbMoO4[c]* Struvite
alpha-TCP	Brucite*	Diopside*	Hydrozincite*	Pb2V2O7*	Witherite	AlOHSO4*	Ca_Vanadate	Cu[OH]2[s]*	OCP*	Plgummite[1] Willemite*
Analbite*	Ca2Zn[PO4]2*	Dolomite	Magnesite	Pb3[VO4]2	Zn[OH]2[B]*	alpha-TCP*	Ca2V2O7	Ferrihydrite*	Otavite	Plgummite[2]* Zincite
Anglesite*	CaCu2[PO4]2	Fe_Vanadate	Manganite *	PbMoO4[c]*	ZnCO3:H2O*	Anhydrite*	Ca3[VO4]2	Fluorite*	Pb[OH]2[C]	Portlandite*
Anhydrite	Calcite*	Fe2[OH]4SeO3	NiCO3[s]	Rhodochrosite		Ba[SCr]O4[96%SO4]*	Calcite*	Gypsum	Pb2V2O7*	Sb[OH]3[s]
Ba[SCr]O4[96%SO4]*	CaMoO4[c]	Ferrihydrite*	Nsutite	Strontianite		Boehmite*	CaZincate*	Hydromagnesite	Pb3[VO4]2	Strengite*
BaSrSO4[50%Ba]*	Cerrusite	Fluorite*	OCP	Talc*		Brucite*	Cd[OH]2[C]*	Leucite*	PbCrO4	Strontianite

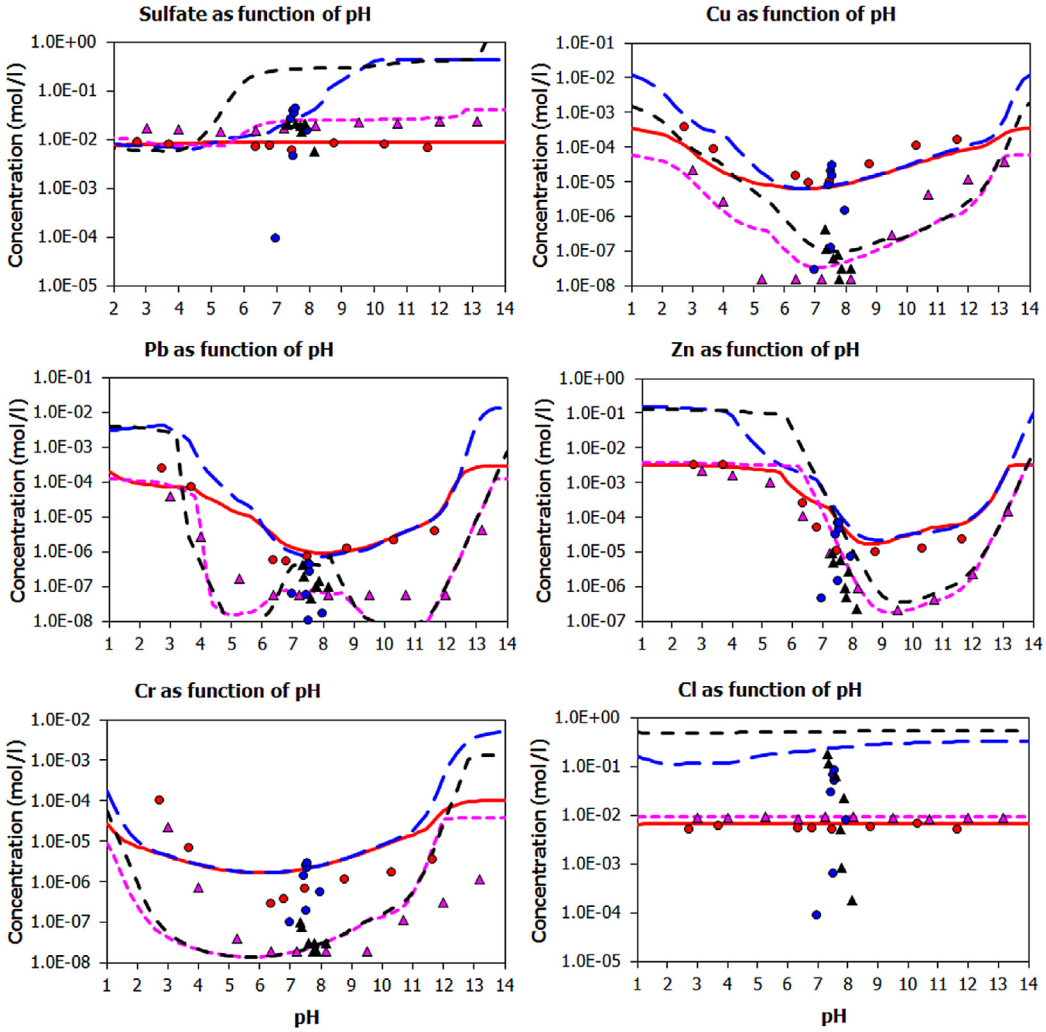

Fig. 4. Comparison of the leaching of sulphate, Cu, Pb, Zn, Cr and Cl as a function of pH (EN14429) for the organic rich MSW and the PNW mix. Legend: dots: MSW; triangles: PNW; solid line: L/S = 10 mL/g simulation MSW; dotted line: L/S = 10 mL/g simulation PNW; broken line: L/S = 0.2 mL/g prediction for MSW; dashed line: L/S = 0.2 mL/g prediction for PNW; data points around neutral pH: percolation test data ranging from L/S = 0.1–10 mL/g (PrEN14405) for MSW (dots) and PNW (triangles).

The solid points are actual measurements. The line reflects the predicted concentration as a function of L/S for continuous elution, while the open circles reflect integration of elution segments consistent with the sampling intervals as followed in the column experiment. The first graph gives the measured and modelled pH, which shows that the model does not capture the pH decrease at L/S 1–2. Conductivity (largely controlled by Na, K, Cl, Ca, sulphate) is predicted adequately. The match between measured and predicted concentrations is reasonable given the complexity of the multi-element model approach (>25 elements simultaneously), but there is obviously room for improvement. The reactive dissolved humic acid fraction (DHA) is a small part of the total DOC. DHA has been taken from the DHA/DOC ratio as obtained from the modelling of the pH dependence test data at the average pH measured in the column eluate (0.2 for both MSW and PNW; see Table 1). The prediction of DHA in column experiments is still in its infancy. We have assumed an exponential decay curve based on a certain washout rate of DOC. These parameters are derived from the measured DOC concentrations in the effluent. At low L/S many elements are strongly interacting with DHA and SHA (reactive fraction of particulate organic matter POM; very abundant relative to DOC!) and therefore uncertainty in the description of DOC elution represents a definite uncertainty in the description of column test results as well as for lysimeter experiments and actual field measurements. This must be kept in mind when judging the correspondence between simulation and measured data.

Fig. 6 presents the results from the percolation test on MSW for a few major, minor and trace elements as cumulative release, which allows other conclusions to be drawn than based solely on eluate concentrations. In general, the agreement between measured and modelled cumulative release is rather good for several elements. From the data it is clear that Cl is completely washed out (cumulative release is not further increased after L/S ~ 1), while F is still solubility controlled up to at least L/S = 10 (slope of 1 in cumulative release curve). Several other elements show a tendency to reach a plateau at higher L/S. From infiltration measurements (Hjelmar et al., 2001) in landfills it was found that an L/S of 1 may correspond to 500–1000 years of percolation.

3.3.2. Predominantly non-degradable waste

The simulation of eluate concentrations for the PNW mix is fairly similar to that for the MSW (Fig. 7). In spite of the fact that the level of DOC in PNW is lower than in MSW, DOC and POM are also important to obtain a proper match between model and simulation for the trace constituents Pb and Zn. The prediction of pH and EC are quite reasonable. Prediction of Ca, Mg and sulphate is matching well with the measurements. Partitioning is provided as supplemental information.

Table 2
Chemical speciation fingerprint and additional parameters for reactive transport (dual porosity) modelling of MSW and PNW percolation column test simulations. Composition and mineral selection is the same as in Table 1.

Case	MSW mix		Case	Predominantly non-degradable waste mix	
Sum of pH+pe	13.0		Sum of pH+pe	13.0	
Clay	0.10	kg/kg	Clay	0.10	kg/kg
HFO	0.010	kg/kg	HFO	0.0043	kg/kg
SHA	0.04	kg/kg	SHA	0.0103	kg/kg
Porosity fraction	0.45		Porosity fraction	0.48	
Density	1.7	kg/l	Density	1.75	kg/l
Initial pH (solid)	7.0		Initial pH (solid)	7.25	
Column length	30	cm	Column length	30	cm
Rel. stagnant volume	10	%	Rel. stagnant volume	18	%
Eff. diffusion dist.	4	cm	Eff. diffusion dist.	2	cm

[DOC/DHA data]

L/S	[DOC] (kg/l)	DHA fraction	[DHA] (kg/l)
0.07	2.13E−03	0.20	4.25E−04
0.17	1.93E−03	0.20	3.87E−04
0.48	1.71E−03	0.20	3.41E−04
0.98	1.18E−03	0.20	2.36E−04
1.98	5.64E−04	0.20	1.13E−04
4.98	2.33E−04	0.20	4.66E−05
10.15	3.05E−04	0.20	6.10E−05

Curve fitting coefficients

q0	1.10E−04
q1	1.00E+00
q2	1.20E−05

[DOC/DHA data]

L/S	[DOC] (kg/l)	DHA fraction	[DHA] (kg/l)
0.19	2.20E−04	0.20	4.40E−05
0.37	1.63E−04	0.20	3.26E−05
0.83	1.07E−04	0.20	2.14E−05
1.57	6.04E−05	0.20	1.21E−05
3.09	3.15E−05	0.20	6.30E−06
7.72	1.51E−05	0.20	3.02E−06
15.63	8.90E−06	0.20	1.78E−06

Curve fitting coefficients

q0	5.52E−05
q1	1.00E+00
q2	2.00E−06

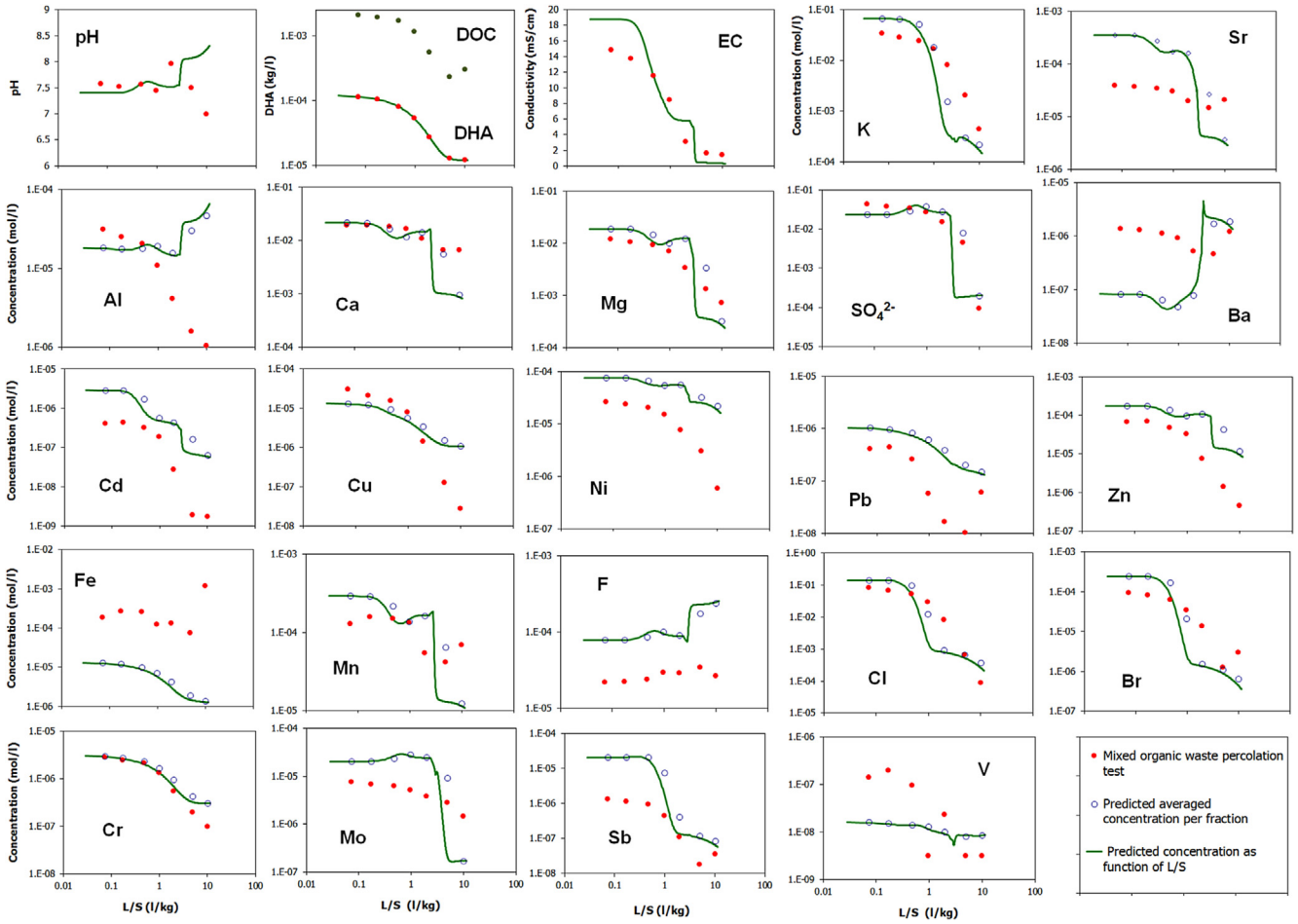

Fig. 5. Measured (solid dots) and predicted release (line: continuous concentration change; open circles: calculated concentrations corresponding with the measurement points) in a column test (PrEN 14405) on the MSW mixture. Solid dots in the DHA graph are measured DOC values uncorrected for DHA fraction.

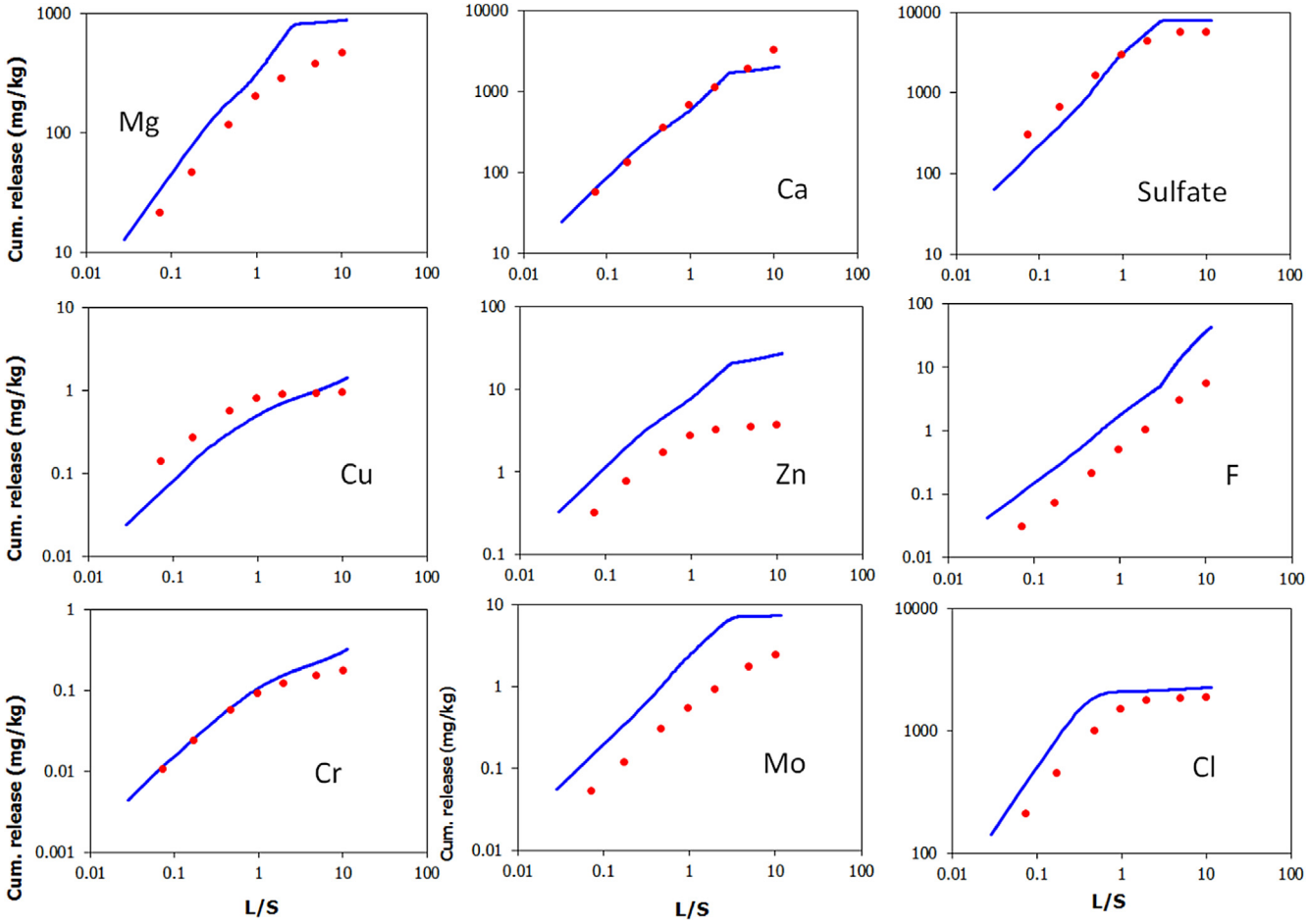

Fig. 6. Measured (solid dots) and predicted cumulative release (line) from the percolation test (PrEN14405) on the MSW mixture. Slope of 1 reflects solubility control; flattening curve depicts depletion of a soluble form or change in leaching controlling conditions, such as a significant pH change (example Zn).

3.4. Comparison of lab test data with samples from excavation and landfill leachate

In Fig. 8a (major, minor elements and DOC) and Fig. 8b (trace substances) the results of single step EN12457-2 (2002) data of the individual MSW samples collected at different depth from the excavated face of the MSW bioreactor landfill at Landgraaf (Oonk et al., 2013) and leachate samples (collected over the time the bioreactor landfill was monitored, which included leachate recirculation and some water supplementation) are placed in context with pH dependent leaching of fresh mixed MSW composite and a composite of the MSW samples excavated after 8 years of operation. The relationship between fresh and aged material has been described before (Kosson et al., 2014). Here the leaching data of the multiple MSW samples from the Landgraaf landfill after operation and collected leachate relative to the corresponding pH dependent behaviour of the composite is discussed. The main difference between the batch tests and pH dependence test on the one hand and the landfill leachate data on the other hand is the difference in L/S, which is 10 mL/g in the laboratory tests and variable in the pilot as some parts of the cell are flushed more than others. This is illustrated for Na and Cl where the batch data plot right on top of the pH dependent curve (both carried out at L/S of 10 mL/g), whereas the leachate data collected at low L/S values are a factor 10–20 higher in concentration. This is explained by the fact that both Na and Cl are fully soluble in the porewater and hence the concentration in the low L/S leachate should be higher, and the results suggest an effective field L/S of 0.5 to 1 mL/g. Since the Na and Cl are still a factor 10–20 higher than the L/S = 10 values, the loss of Na and Cl from the discharge or bleed stream from leachate recirculation and possible loss through the bottom liner is very limited. For the elements Al, Ca, Si, Sr, Mn, Ni, Pb and Zn, the results of batch testing and field leachate are plotting along with the pH dependent leaching curve for the composite sample, which indicates that the same solubility controlling phases control leachability during the entire bioreactor experiment and also at different depths in the excavated MSW bioreactor pilot. In case of solubility control variation in L/S does not change the concentration; only pH variation does, which is consistent with the observations. DOC, Cr and Co show a good agreement with the individual batch samples, but the leachate concentrations are higher. DOC is in solution and a lower L/S in leachate should lead to a higher concentration. In the case of Cr and Co the association with DOC explains the elevated concentration in leachate. For Fe, As and V the lower redox state in field leachate leads to a higher mobility of Fe (as Fe^{2+}) and mobilisation of HFO associated As and V (both As and V are identified as HFO associated elements in modelling). Sulphate, Ba and Mg also fit well with the pH dependent curve, but the sulphate concentration is lower and leachate concentrations for Ba and Mg are higher. In case of sulphate this is most likely linked to part of the sulphate concentration decreased due to reduction under field leachate conditions with associated higher Ba levels. In case of Mg, the higher concentration in field leachate (low L/S) is expected based on the location of the solubility curve of brucite and magnesite. In case of Mo, Sb and W, the batch data match well with the batch composite data. The Mo leachate data

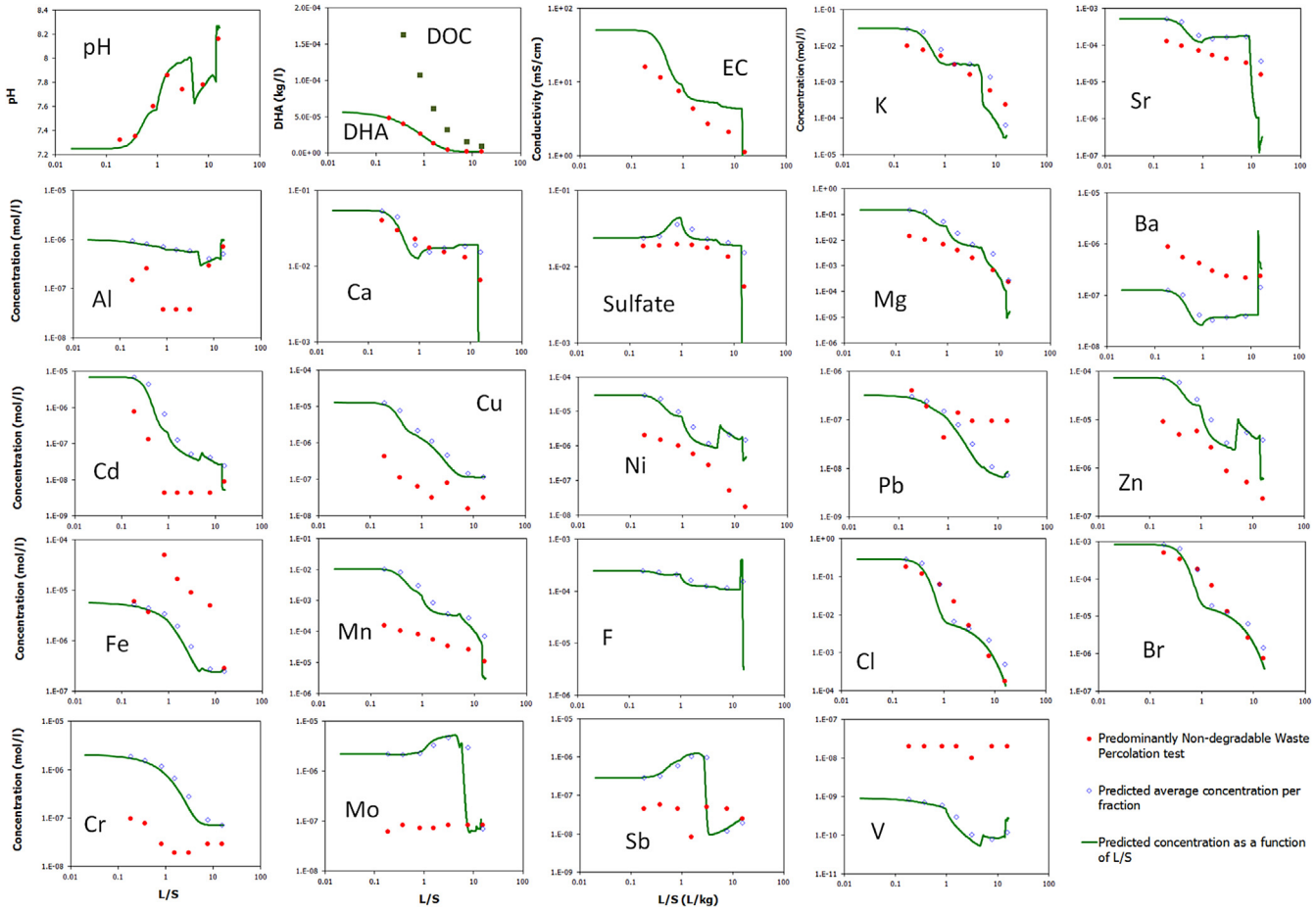

Fig. 7. Measured (solid dots) and predicted concentrations as a function of L/S (line: continuous concentration change; open circles: calculated concentrations corresponding with the measurement points) in a column test (PrEN 14405) on the PNW mixture. Solid dots in the DHA graph are measured DOC values uncorrected for DHA fraction.

are lower in leachate. This may be related to the sharp precipitation edge at pH 5–8. For both Sb and W the leachate data are limited, thus giving only a trend. Cu is a special case as both the batch data and the leachate data show lower concentrations. This seems linked to the Cu+ and Cu sulphide precipitation as discussed in the next section.

In Fig. 9 the model description for organic rich waste and predominantly non-degradable waste are placed in context with a wide range of landfill leachate data under the assumption that the organic rich waste will degrade in time to approach the PNW mix (this mix is not strictly inorganic, but the organic matter present is of a stable and largely non-reactive nature). The data from landfills includes relatively new as well as old landfills (Flyhammar, 1995; Genon et al., 1995; Gomez-Martin et al., 1995a, 1995b; Hjelmar, 1991; Robinson, 1995; Rowe, 1995; van der Sloot et al., 2000). It also contains data from mechanically separated organic waste and from bioreactors (Blakey et al., 1996; Collins et al., 1998; Doedens et al., 1998; Eschkötter and Morscheck, 1998; Ham, 1990; Reinhardt and Ham, 1974; Reynolds and Blakey, 1992). In addition, there is a set of data from an old municipal solid waste incinerator ash landfill (Hjelmar, 1991). MSWI bottom ash can be considered as the almost completely inorganic residue from MSW. As can be seen from the figure, the model results for MSW correspond reasonably with the MSW leachate data. The Ca is largely explained by the calcite controlling solubility in the carbonate rich environment in a degrading organic landfill and partly by association with particulate organic matter. The Mg appears to be controlled by mineral phases (talc, diopside and brucite; only brucite in the PNW). DOC is very high in the mechanically separated organic waste landfills, where the low L/S condition (upper line of solid and dotted line in of each graph) matches closer with the actual leachate composition as one would expect. The Na levels in landfills fall within the envelope defined by the low and high L/S condition. The Zn in leachate corresponds well with both the organic rich and the predominantly inorganic waste mix. The incinerator ashes (burnt MSW) agree with the curve for the PNW mix. For Pb the behaviour in the organic rich matrix is controlled by iron phases and organic matter interaction, while in the PNW mix specific Pb minerals – $Pb(OH)_2$ and plgummite a lead aluminophosphate – are potential solubility controlling phases. An issue to be considered in the comparison is uncertainty associated with reported field pH measurements because experience has shown that the sampling technique is crucial for pH measurement and the time at which pH measurement takes place after sampling is crucial (degassing). Additional factors that may affect concentration levels in leachate are dilution with run-off water, lower redox conditions and variation in the level of organic matter degradation. For Pb, in particular, the lower concentrations are around or close to the detection limit of the analytical methods commonly employed in leachate analysis. Overall, the observed consistency in the data implies that the processes controlling leachate concentrations under field conditions in an MSW matrix are more uniform than would be inferred based on the heterogeneous nature of MSW. The relatively consistent

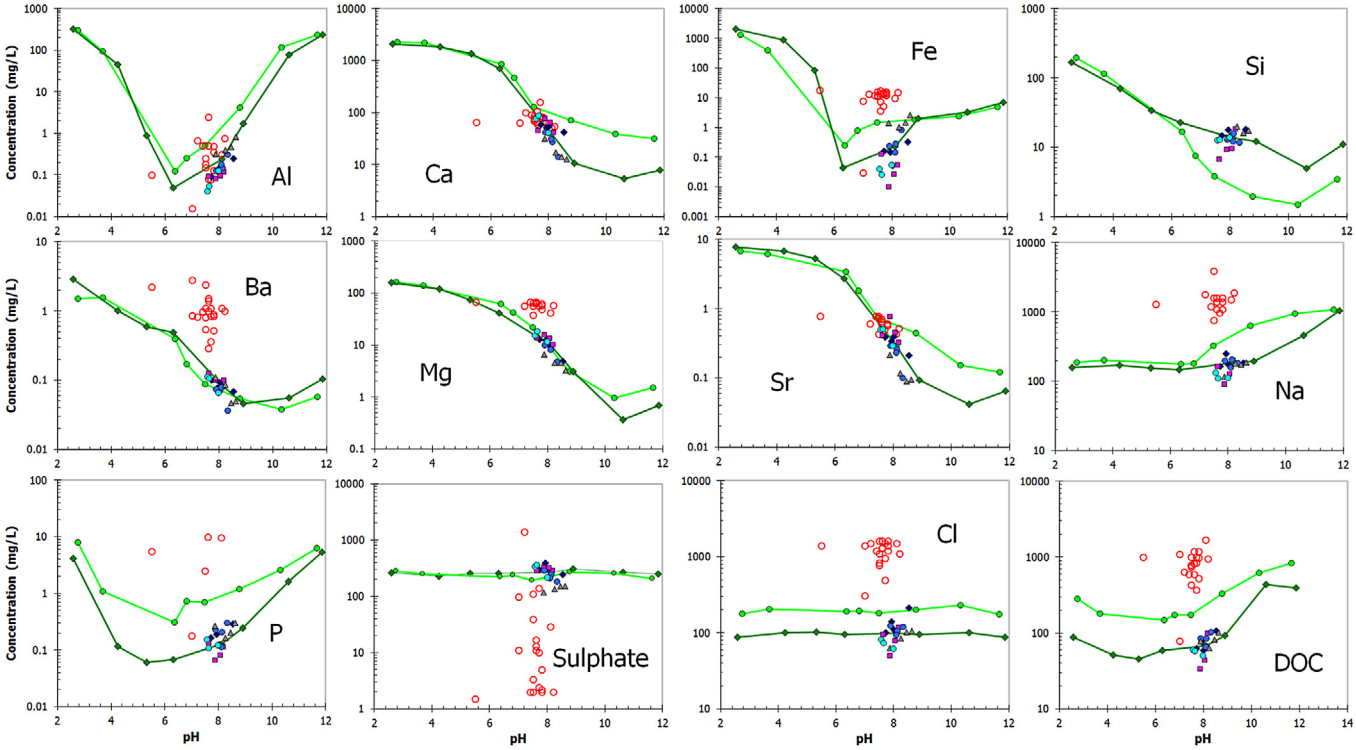

Fig. 8a. Comparison of pH dependent leaching of the fresh MSW composite (dots) and MSW composite from pilot excavation (diamonds) with leachate collected over the duration of the bioreactor experiment (open circles) and the individual samples taken during excavation (various symbols; batch at L/S = 10) – major, minor elements and DOC.

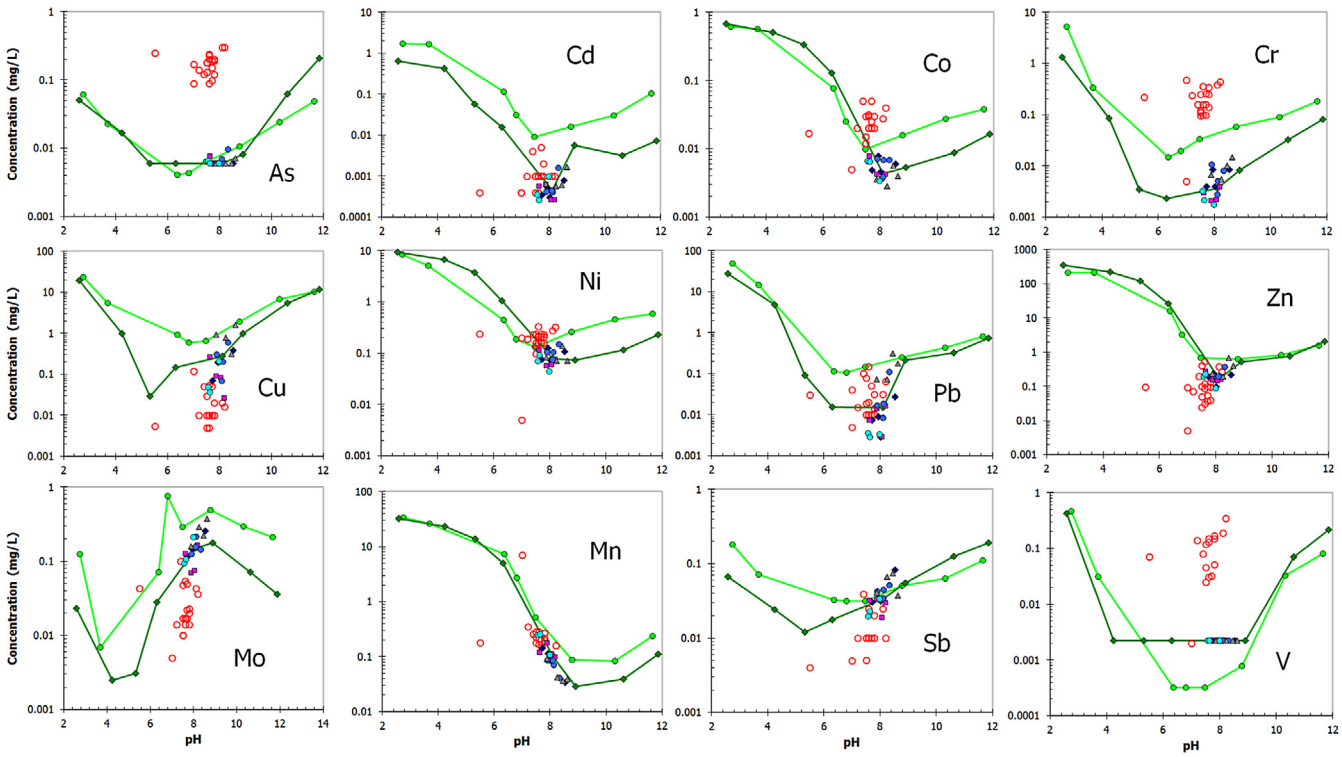

Fig. 8b. Comparison of pH dependent leaching of fresh MSW composite (dots) and MSW composite from pilot excavation (diamonds) with leachate collected over the duration of the bioreactor experiment (open circles) and the individual samples taken during excavation (various symbols; batch at L/S = 10) – trace substances.

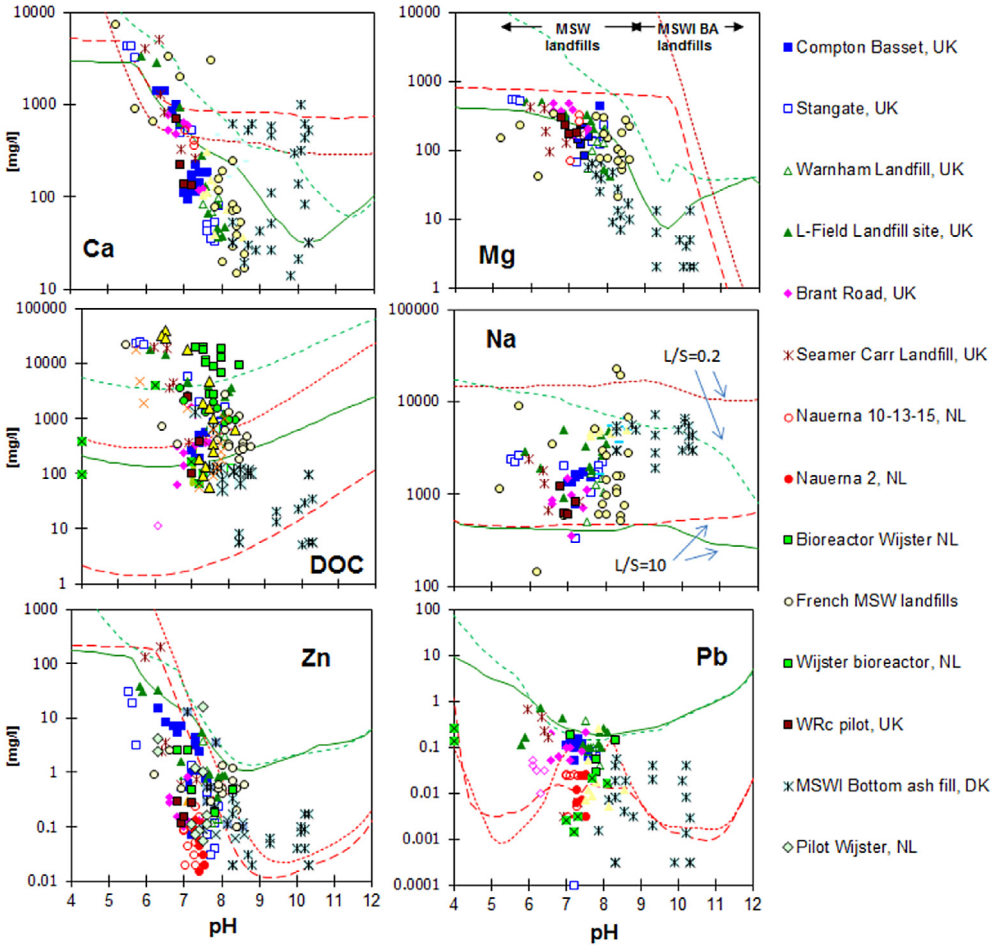

Fig. 9. Concentrations as modelled for MSW (line: L/S = 10; dashed line: L/S = 0.2) and PNW (broken line: L/S = 10; dotted line: L/S = 0.2) in comparison with a wide range of landfill leachate data (MSW landfills at pH < 8; data at pH > 8 MSW incinerator bottom ash landfill DK).

processes present in MSW landfills around the world suggests that the work presented here can be a good starting point for evaluation of MSW in other locations.

3.5. Modelling of other exposure conditions

3.5.1. Redox conditions

Based on the chemical speciation fingerprint (CSF) for MSW as described in Table 1, other scenario conditions can be assessed such as other redox conditions than the one used in modelling laboratory data and different stages of degradation of organic matter. Obviously, when MSW is sampled and handled for testing in the laboratory, the redox status of the material is affected by the exposure to the atmosphere. In the landfill, the redox potential is lower than in the laboratory resulting from biological activity, although more reducing conditions may occur as the laboratory column tests progress. Therefore, a full range of pH+pe conditions has been modelled to assess what the likely pH+pe condition in the landfill is based on comparison with leachate quality data from different landfills. When the redox status is modified additional minerals need to be included in the model, such as pyrite, Cd, Pb, Ni, Cu and Zn sulphides. The Fe concentration in leachate provides a good indicator for the redox state. In Fig. 10, the Fe concentrations measured in pH dependence test (clearly oxidised conditions) and in the column test (somewhat reduced) are compared with modelling Fe concentrations at pH+pe values ranging from 13 (mildly reduced; reflecting laboratory processed MSW) to 3 (strongly reducing) at L/S = 10 and at L/S = 0.3 (simulated pore water conditions). Besides the dissolved concentrations, the partitioning in dissolved and particulate phases is given, which shows that only at pH+pe $\leqslant$ 4 pyrite formation starts to occur. In Fig. 11 the Fe concentrations in leachate from many different MSW landfills are placed in perspective to the modelled Fe concentrations as function of pH and redox state expressed as pH+pe. On average a pH+pe of 5.5 matches well with the observed field concentrations of Fe. Both the fresh and the 8-year old composite MSW sample, when tested in the pH dependence test at L/S = 10, are only mildly reducing (see Figs. 8a and 8b).

The influence of redox variation and changes in the state of organic matter degradation are illustrated for Cu. Firstly, because Cu is the first element to precipitate as sulphide and undergoes an additional reduction step from Cu^{2+} to Cu^{+} and secondly, because Cu is one of the most sensitive elements for interaction with particulate or dissolved organic matter. In Fig. 12 the Cu concentrations measured in pH dependence test (clearly more oxidised conditions) and in the column test (more reduced) are compared with modelling Cu concentrations at pH+pe values ranging from 13 to 3 (strongly reducing) at L/S = 10 and at L/S = 0.3 (simulation of pore water conditions). One of the mineral phases, that was identified as crucial in the modelling of Cu was cuprite (Cu_2O; formed by reduction of CuO) at pH+pe values below 11. In addition to the concentrations as a function of pH, the partitioning of Cu in dissolved and particulate phases is given, which shows that from pH+pe $\leqslant$ 6 Blaublei (Cu_2S-CuS mixed mineral)

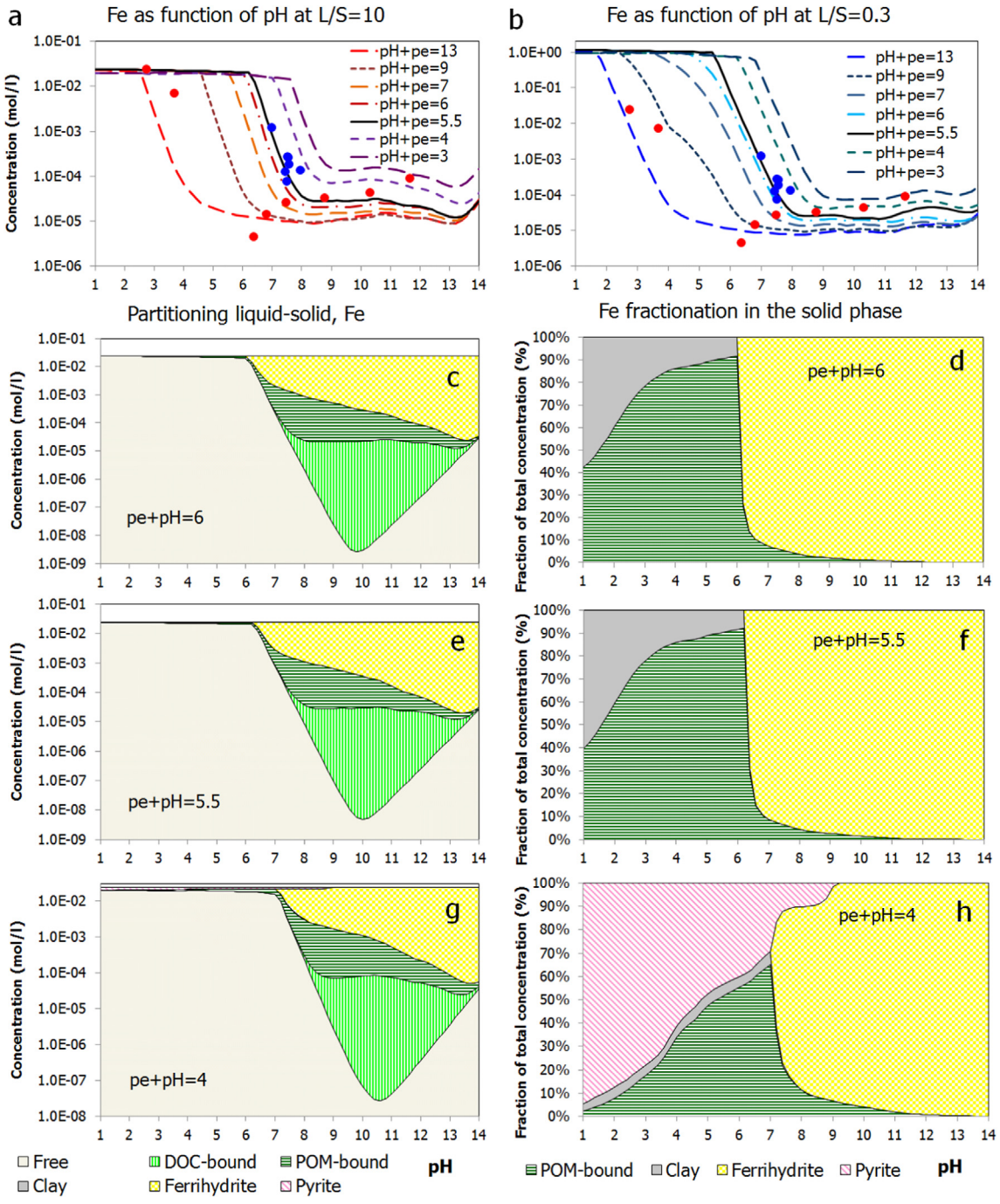

Fig. 10. Modelling the Fe concentration in MSW leachate as a function of pH, redox state (pH+pe ranging from 13 to 3) and L/S = 10 (a) and L/S = 0.3 mL/g (b) with partitioning between dissolved and particulate phases for 3 pH+pe conditions (c, e and g) and percent distribution of phases in the solid (d, f and h). Dots: pH dependence test data at L/S = 10; dark dots; column test data fresh MSW composite.

formation starts to occur. In Fig. 13 the Cu concentrations in leachate from many different MSW landfills are placed in perspective to the modelled Cu concentrations for MSW as function of pH and redox state expressed as pH+pe. In Fig. 13 the Cu concentrations in leachate from the PNW pilot (PNW) are placed in perspective to the modelled Cu concentrations for PNW in comparison with modelled Cu concentrations as a function of pH for pH+pe = 5.5 at L/S = 10 and L/S = 0.3. The leachate from the lysimeters is more oxidised than that from the pilot, which has consequences for the interpretation of the lysimeter data for long term behaviour of landfill leachate. On the other hand, it does provide valuable insight in release behaviour from atmosphere exposed waste and waste aeration (Heyer et al., 2013). From the comparison of Figs. 12 and 13, a redox state of pH+pe < 4 (reduction level needed for iron sulphide precipitation and several other metals, except Cu) is not consistent with the observations in the field as all leachate data fall within the domain depicted by pH+pe = 5.5 ± 0.5.

3.5.2. Degree of degradation of organic matter

In fresh MSW very high DOC levels are common. Upon degradation the DOC level decreases. As indicated before, a reactive fraction of DOC (DHA) affects metal (and organic contaminant)

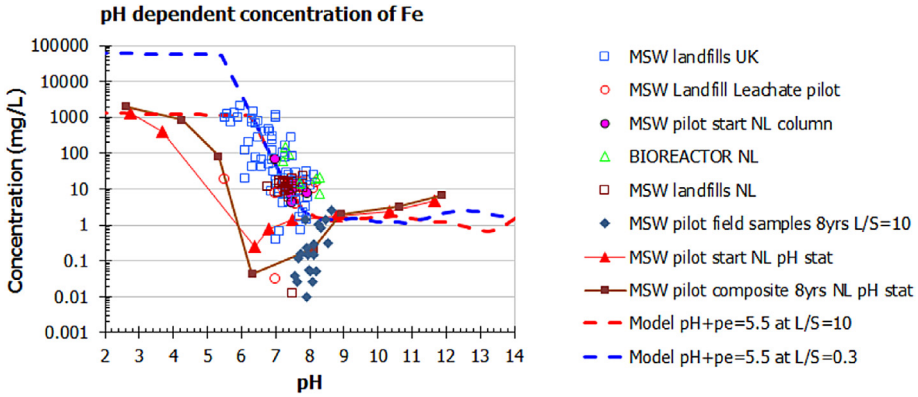

Fig. 11. Fe concentration in leachate from different MSW landfills, fresh and 8 year old MSW tested in the pH dependence test in comparison with modelled Fe concentrations in leachate for pH+pe = 5.5 at L/S = 10 and 0.3 mL/g.

release through mobilisation as DHA – complex, hence understanding the effect of the degree of degradation of organic matter is important for evaluating long term release of hazardous substances. To model the effect of changes in particulate and dissolved organic matter on release of substances, the following assumptions have been adopted. Not all organic matter will fully degrade, not even after a very long time, as part of the particulate organic matter (POM) degrades only extremely slowly. The degradable fraction is assumed to be 50% of the measured particulate TOC. From measurements of DOC in fresh MSW and very far degraded MSW in a laboratory bioreactor, the DOC concentration is found to be less than 1% of the initial concentration (van der Sloot et al., 2001a). Obviously, in a regular MSW landfill without recirculation or other measure to increase the rate of degradation, it may take very long to reach this condition (Brandstätter et al., 2015). Based on these considerations the following conditions for modelling have been selected, while the same ratio between DHA and DOC has been applied as in the previous modelling:

Initial condition – TOC solid: 100% and DOC: 100% (as measured).
Partial degradation – TOC solid: 75% and DOC: 10% of initial condition.
Full degradation – TOC solid: 50% and DOC: 1% of initial condition.

Although the redox state varies with the degradation stage, it is not well known how this property varies with time. Inside the landfill the conditions will likely stay strongly reducing, however, oxidation may take place on external boundaries of the waste. Aeration practiced to enhance degradation (Ritzkowski et al., 2009; Heimovaara et al., 2013) also may lead to partial oxidation. Therefore, two redox conditions (pH+pe = 5.5 and pH+pe = 13) have been modelled, each with the above mentioned organic matter degradation stages. Although all 25 major, minor and trace elements have been taken along, only the effect of these conditions on Cu concentrations is highlighted here. In Figs. 14 and 15 the modelled Cu concentrations and partitioning at the different organic matter degradation stages is given for pH+pe = 5.5 and pH+pe = 13, respectively. At low L/S, neutral pH and pH+pe = 5.5 the difference is not large, while at high L/S, the Cu concentration decreases by about an order of magnitude. The leachate concentrations from the pilot cell and the laboratory testing at L/S = 10 of landfill core samples tested both fall within the modelled domain ranging between L/S = 0.3 and L/S = 10.

At low L/S, neutral pH and pH+pe = 13, the difference between high and low L/S is rather small. Upon full degradation the difference in Cu concentration amounts to about a factor of 10. The Cu concentration in solution decreases by almost 2 orders of magnitude upon full degradation. This implies that retention of Cu is likely to occur over very long time frames under conditions present in PNW landfills.

4. Discussion and conclusions

4.1. Generation of a CSF from pH dependence

The pH dependence test data form the basis for developing a chemical speciation fingerprint (CSF) consisting of element available content, a mineral selection, reactive iron, dissolved and particulate organic matter quantities. This implies that seemingly there are many degrees of freedom, however, as it turns out the interrelations between elements, the competition between sorption sites and typical element behaviour such as Fe sensitivity to redox change and Cu sensitivity to DHA interaction provide guidance on selection of appropriate parameters leading to substantially less possibilities to vary properties without affecting other elements. As evidenced by the good match of measured conductivity, acid neutralisation capacity and Eh (recalculated to pe) illustrates that the mineral assemblage and sorptive properties for the main elements are not far from the truth. Uncertainties do exist in the estimation of the reactive part of DOC, although values of around 20% have been found for other matrices from measurement (van Zomeren and Comans, 2007). When Cu is used to calibrate the DHA fraction many other elements fall into place. The same situation is important for the redox state of the material. Dissolved Fe is very responsive to redox variation and hence pH+pe is calibrated to the Fe release. This appears to work well for other redox sensitive substances (e.g. Cr). As leachable carbonate is not a good measure for available carbonate, the use of total carbonate needs to be verified further to enhance model predictions.

4.2. Stepwise modelling approach

The modelling approach, in which a chemical speciation fingerprint (CSF) is developed from pH dependent leaching data and which is then used as basis for subsequent coupled reactive transport modelling of laboratory tests, lysimeter and field measurements, has proven potential benefits for understanding observed leaching behaviour (Kosson et al., 2014). The CSF describes the material behaviour under specified conditions of L/S, redox state and physical form (size reduced material). All other parameters in the CSF, are either directly derived from testing or adjusted to

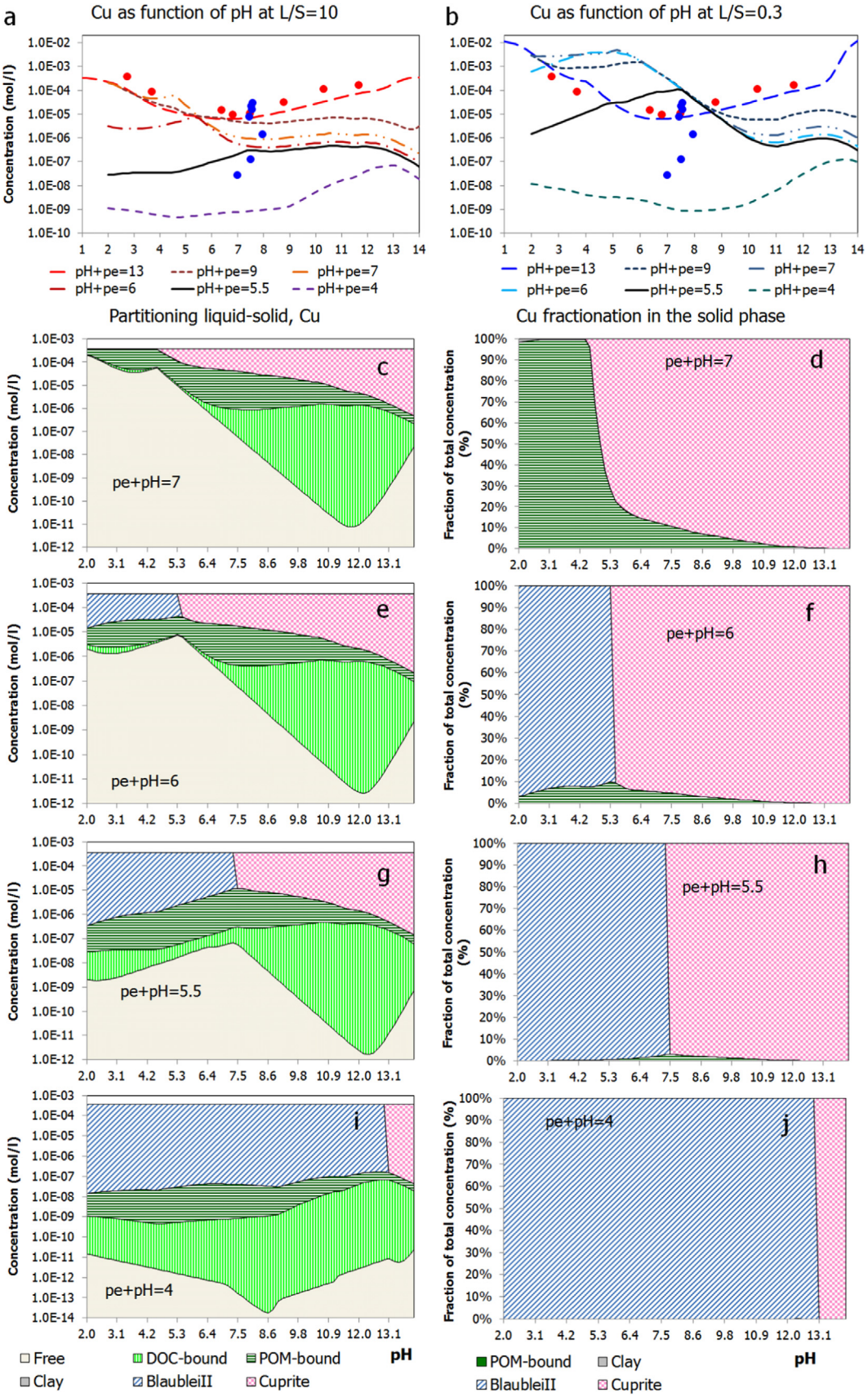

Fig. 12. Modelling the Cu concentration in MSW leachate as a function of pH, redox state (pH+pe ranging from 13 to 3) and L/S = 10 (a) and 0.3 (b) with partitioning between dissolved and particulate phases for 4 redox conditions (c, e, g, i) and percent distribution in the solid (d, f, h, j). Dots: pH dependence test; dark dots; column test MSW.

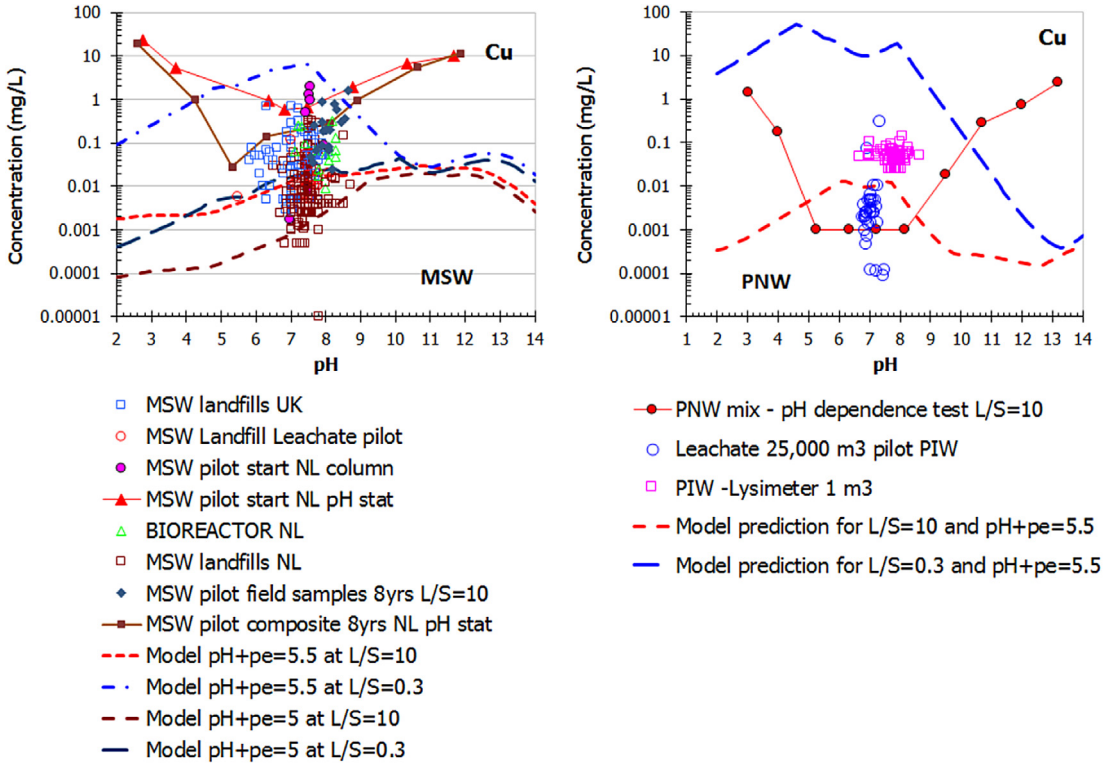

Fig. 13. Cu concentrations in leachate from many different MSW landfills in perspective to the modelled Cu concentrations for MSW as function of pH and redox (left) and comparison of Cu in leachate from lysimeters and a 25,000 m^3 pilot cell with predominantly non-degradable waste in comparison with modelled Cu concentrations as a function of pH for pH+pe = 5.5 at L/S = 10 and L/S = 0.3.

provide an optimized representation of leaching from the material against measurements. When transferring a CSF (or virtual material) to a percolation case additional information is needed (e.g., flow-rate, column dimensions, eluant composition) and the parameter settings (mobile fraction and diffusion distance for the stagnant zone) for release of very mobile substances (Na, K, Cl) are calibrated using one of the mobile substances (e.g. Na). Then the sum of pH+pe is chosen such that the release of iron and manganese are described well. The release behaviour of DOC is taken from the percolation test using the formula provided earlier, in which the reactive fraction is corresponding to the reactive fraction observed in the pH dependence test at the pH range covered in the percolation test. A comparison between Cu release (strong DHA association) and model parameters will reflect the extent to which the reactive fraction of DOC as derived from the pH dependence test agrees with the partitioning in the percolation test. It will be worthwhile to proceed in this direction because modelling of conditions beyond the scope of the laboratory conditions is crucial for understanding release behaviour over the range of anticipated field conditions as they evolve over time.

The multiple interactions taking place imply that poor choices for inclusion in the mineral reaction set or sorption parameters will result in a significant deviation (e.g., greater than an order of magnitude) from the actual measurement. However, as stated earlier, it is recognized that a unique solution is probably not achieved. In addition, since the modelling assumes equilibrium and equilibrium is not fully reached during laboratory testing, some differences between simulation results and laboratory measurements cannot be resolved. Non-equilibrium discrepancies can only be recognized by running laboratory tests using different contact times. In the work by Dijkstra et al. (2006) the influence of kinetics has been clearly demonstrated. In other cases, the stability constants or specific mineral phase assemblages may not be well defined or have inherent uncertainty, particularly for some less well studied trace elements like Sb, V and Mo in complex mixtures. However, these deviations also provide a useful starting point for defining further research needs.

Overall, the dual porosity model describes the leaching of highly soluble constituents well. Since the test is run in upflow mode, the stagnant zone is not very large. In predicting the release from a lysimeter experiment in down flow mode, a much larger proportion of stagnant conditions (e.g., up to 80% of the cell volume) must be assumed (van Zomeren and van der Sloot, 2006a). The difference in model parameterization between the simulation of release from a laboratory column test and a prediction for a lysimeter or a field scenario is not very large because saturation at solubility controls release for many constituents and hence concentrations are about the same over a wide range of conditions, including variation in the fraction of the stagnant zone. The highly soluble substances are affected by factors such as preferential flow and definition of the fraction of the stagnant zone (by approximately a factor of 5). All chemistry and transport is already present in the laboratory percolation test simulation, which constitutes the main complexity of the field simulations. A future improvement would be to reflect interaction between the stagnant and flow zones by diffusion from particles of specified dimensions. However, the main differences between simulation and experimental results for several trace elements cannot be explained by this factor. Thus, the primary focus will need to be on the role of organic matter interaction and improved mineral definitions including associated K_{sp} values. Major elements like Ca, sulphate, Mg are predicted rather well. When the pH at high L/S is predicted better, the Al description will most likely be improved as well. Given the relatively low concentration levels and the role of DOC in metal mobility, the predicted concentrations for Cd, Cu, Mn and Cr (as Cr3+) are rather good, while Pb, Ni, Mo, F and Zn are reasonable. For Sb and V insufficient mineral data and reliable sorption data are available.

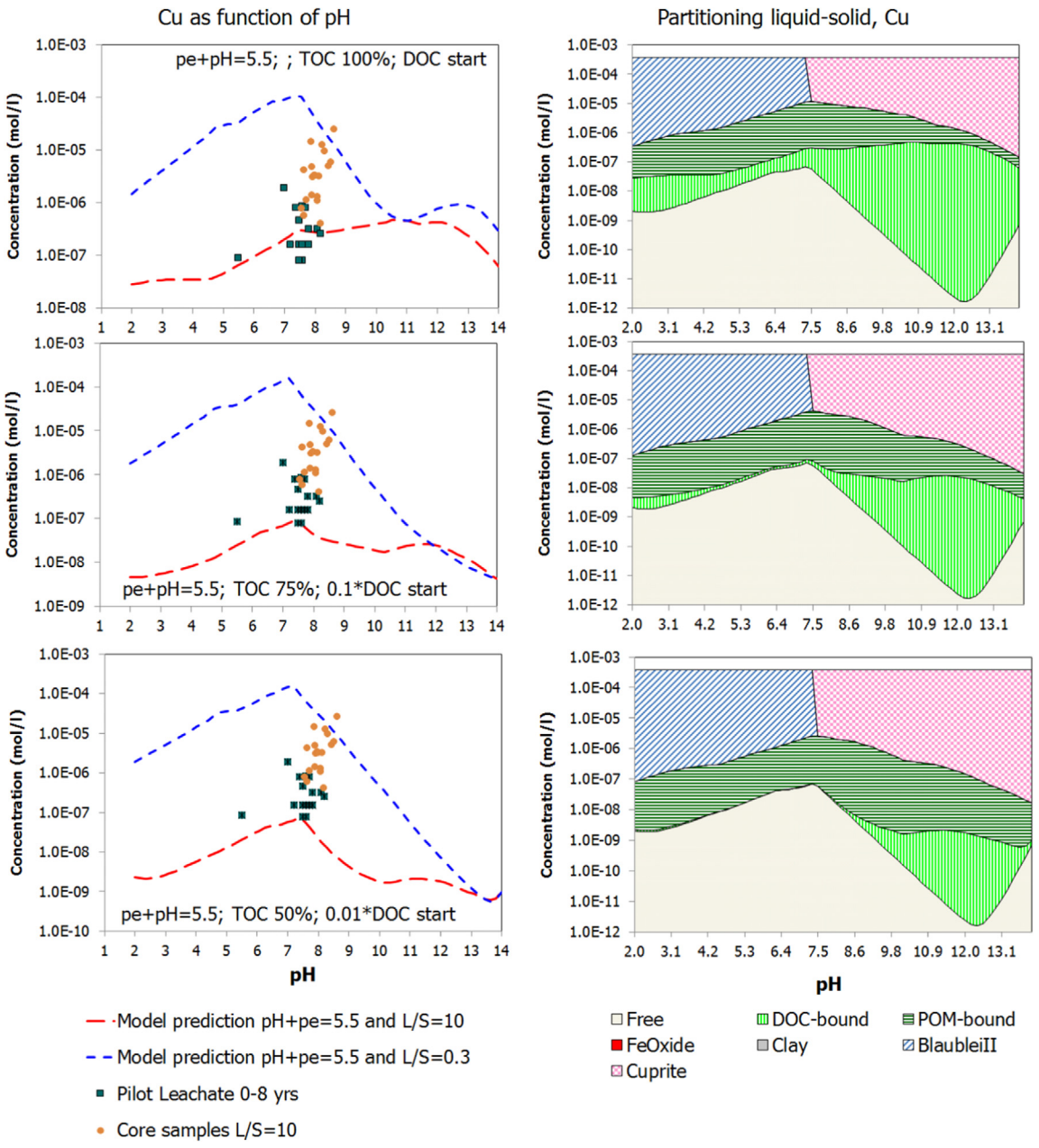

Fig. 14. Modelled Cu concentrations and partitioning at the different organic matter degradation stages at L/S = 10 (broken line) and L/S = 0.3 mL/g (dashed line) for pH+pe = 5.5. Blaublei is a mixed Cu_2S-CuS mineral. For reference the leachate data from the pilot and the batch test results on core samples after 8 years are included in all graphs.

In modelling release of some substances, the role of mineral precipitation and sorption reactions at low L/S are not yet covered in sufficient detail to allow proper descriptions at this time. This is important because other mineral phases may be relevant at low L/S than the ones found at higher L/S conditions (more practical from an experimental perspective). Examples are Ba-Ca sulphates which are relevant at low L/S, but not of importance at high L/S (completely dissolved). For this situation a better solution may be to develop a solid solution description for Ba, Ca, Sr, sulphate and chromate that can cover a large range of pH conditions. Independent verification of the presence of minerals identified through modelling is very complex in matrices like MSW or PNW, because of the highly amorphous, heterogeneous nature with organic matter potentially covering mineral surfaces. In addition, the mineral phases identified in leaching can be present in rather limited amounts relative to the sensitivity of some techniques (XRD and SEM). At present it is unclear if more sophisticated techniques like EXAFS can provide sufficient identification and quantification of controlling phases to be widely useful. Interactions with dissolved and particulate organic matter and sorption onto Fe and Al oxide surfaces affects many elements simultaneously. With the proper interaction parameters for major, minor and trace elements, the inter-element competition for binding sites can potentially be balanced to provide a good description of observed release.

If the percolation test up to L/S = 10 is considered to be indicative of long term release behaviour, predictions of release for several constituents seem possible within a factor of 2–3 and for some within a factor 10. From a regulatory perspective that may be sufficient for several purposes if the uncertainties about the modelling

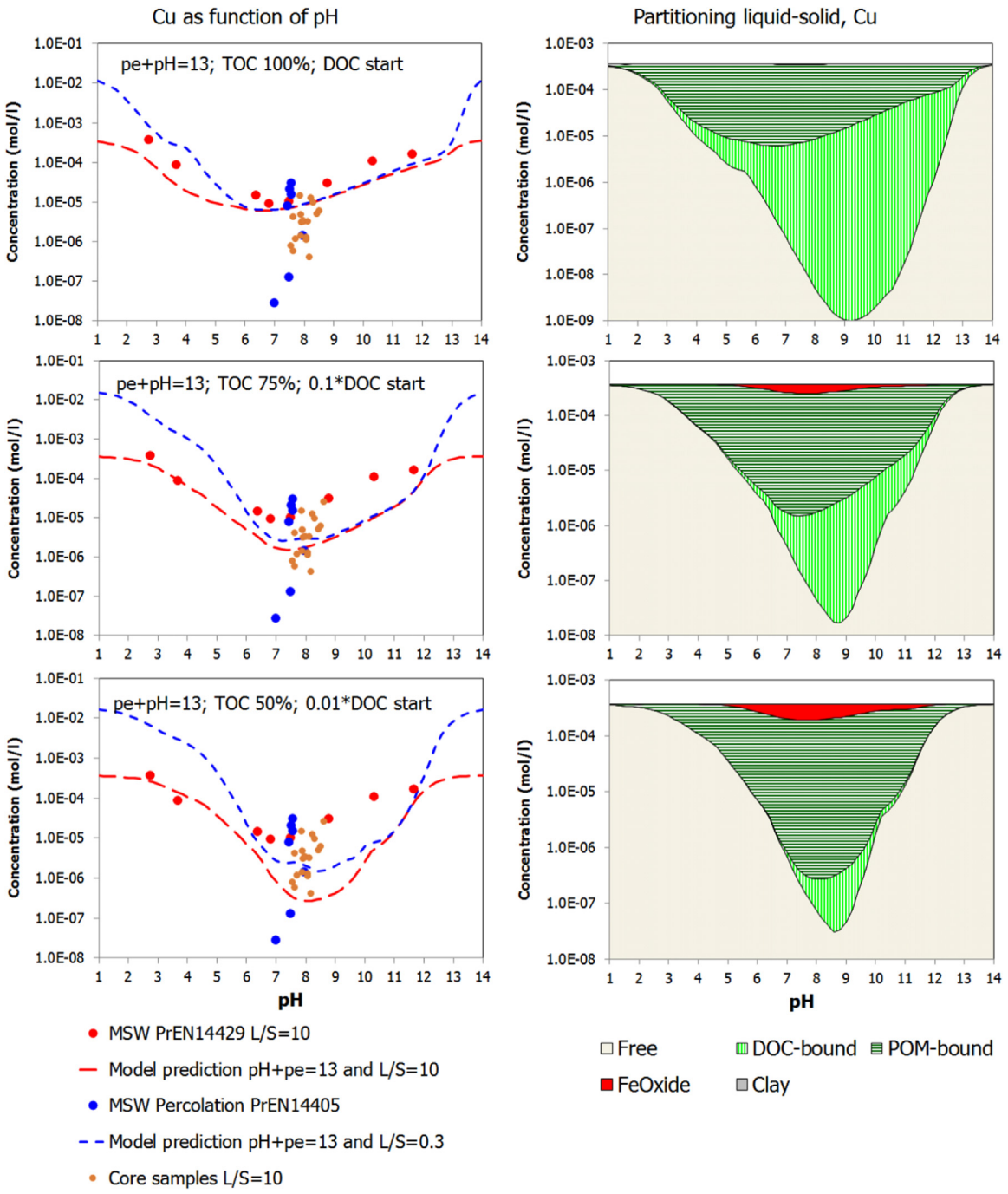

Fig. 15. Modelled Cu concentrations and partitioning at different organic matter degradation stages at L/S = 10 mL/g (broken line) and L/S = 0.3 mL/g (dashed line) for pH+pe = 13. For reference the pH dependence test data and percolation test data on fresh MSW are included in all graphs.

results are well defined and considering inherent variability and uncertainty in materials and field conditions.

The modelling of chemical speciation allows deriving conclusions on release behaviour that cannot be assessed from measuring the effluent from a column test when a leaching front has not progressed far enough to be observed in the effluent. Speciation modelling provides information that allows visualizing significant changes in concentration within a column before actual observation in the eluate occurs.

The CSF derived here seems a good starting point for MSW from diverse origins, since most minerals identified here will be relevant for unknown MSW samples, and the parameter settings for reactive surfaces are useful initial estimates.

4.3. Broad coverage in testing and modelling

The materials studied in this paper cover a broad spectrum of materials found in landfill practice. Chemical speciation modelling is both practical and useful for these heterogeneous matrices using a sophisticated multi-element chemical speciation tool such as LeachXS™ – Orchestra, which can handle the relevant chemical interactions using advanced descriptions for a large number of major, minor and trace elements simultaneously. This poses new possibilities to identify which properties of the waste are the key factors causing undesirable release and how such factors can be influenced. For developing sustainable landfill concepts, this type of understanding of both chemical and physical factors controlling

leaching is crucial. The mineral selection and parameter settings provided here will be relevant for modelling samples from other MSW and PNW sources.

Although this work is focused on inorganic elements, work is in progress on modelling organic contaminants as well (ISO/TS 21268-3, 2007; ISO/TS 21268-4, 2007; Comans and Roskam, 2002; Grathwohl et al., 2003; Grathwohl and van der Sloot, 2007). For both inorganic and organic substances the role of particulate organic matter (POM), DOC and sub-fractions of DOC is of great importance as it determines the degree of mobilisation to pore water and thus ultimately the concentration in leachate. The type of organic matter is of importance in this context. For example, both humic and fulvic acid are carriers of both inorganic and organic contaminants and POM serves as a reservoir for adsorbed constituents of interest. Tools have been developed (van Zomeren and Comans, 2007) and standardised (ISO/TS 12782 parts 1–5, 2011) to assess the distribution of organic matter form relevant for transport and bioavailability.

4.4. Relation between laboratory and field data

Bringing data from various laboratory leaching tests, lysimeter, field data together provides a substantially more complete picture of the release controlling factors in landfills than any single one of these data sources can supply. Analysing just a limited set of elements based on regulatory concern (e.g. excluding major elements) does not help to achieve a more complete understanding of the system behaviour. In view of the heterogeneous nature of MSW, it is striking to note to what extent the individual samples taken from an excavated bioreactor landfill match with the pH dependence test data of the composite sample (Figs. 8a and 8b). This must imply that the same solubility controlling (mineral or sorptive) phases are active throughout the landfill cell.

When MSW degrades, residual organic matter remains, which is less reactive with respect to DOC formation, but still has a high binding capacity. This is illustrated by the modelling of Cu, as the decrease in Cu leaching is mainly caused the increased proportion of binding to solid organic matter (SHA).

Sampling reducing materials like MSW is complicated as contact with the atmosphere in sample handling is very difficult. Modelling a perceived redox state under field conditions through modelling provides better possibilities to get detailed insight in relevant solubility controlling processes.

4.5. Common solubility controlling phases

Several elements are controlled by the same mineral phases and sorptive phases in the two waste types studied. This provides new possibilities in modelling waste leaching behaviour because modelling new samples of the same type can largely build upon this prior modelling work. This also extends to adding new substances with their relevant mineral and sorptive properties to the chemical speciation fingerprint.

The integrated characterisation testing and modelling approach presented here shows which factors, and under what circumstances, cause a change in leaching behaviour such as sensitivity to change in DOC and DOC-sub fractions due to degradation of organic matter, changes in pH due to sulphide oxidation, or addition of more alkaline or acidic wastes to a mixture of waste. In general, the assumption of local equilibrium is useful considering the time frame of release under landfill conditions, as well as the observation that even a waste mixture behaves rather consistently in spite of local variations in composition. Considering the various factors affecting release of elements from MSW, a significant step has been made to clarify the uncertainties surrounding release of metals from MSW as highlighted by Kjeldsen et al. (2002). What has been noted as remarkable before (van der Sloot et al., 2007b) and needs to be elaborated further is the fact that the leaching behaviour of a waste mix is not easily altered. This is related to a range of inherent buffer capacities (i.e. pH buffering, redox buffering, sorptive capacity buffering, controlling major mineral phases). This also holds a threat as a system may not show it is on the verge of major changes in constituent leaching and a minor additional input may create a significant change. The type of modelling presented here will help to understand such sensitivities.

4.6. General conclusions

Any material can become a waste, so when all materials can be assessed by a limited set of characterisation leaching test methods and associated modelling tools instead of the more than 60 procedures used worldwide (Environment Canada, 1990; van der Sloot et al., 1997), the comparability of material behaviour across different fields will be greatly improved. Recent standardization and interlaboratory validation of characterisation leaching test methods (Garrabrants et al., 2011, 2012) further the broad adoption of this approach in regulatory contexts.

Proper characterisation of waste and associated modelling is of importance to develop sustainable landfill concepts, because without more detailed insight, landfill management will not be able to cope with the challenging questions to reach that goal.

Mechanistic modelling requires a multi-element evaluation of a material, which is now possible due to the availability of sufficiently fast computers and programs that can handle the complexity of multi-element interaction in minerals and sorption reactions.

Analysis of a limited number of constituents in characterising waste is counterproductive, as it limits strongly the modelling capabilities. Major elements, of limited concern to regulators are of major relevance to speciation modelling as the major elements drive the main chemistry, which in turn affects trace element mobility.

In the waste mixes studied, the role of organic matter in dissolved (DOC) and in particulate form (POM) proved to be important to properly describe release of trace elements from these matrices.

Although there is room for improvement, in particular with respect to definition of mineral phases potentially relevant for less common elements, the results are quite promising and provide a means to distinguish between free metal-ion and complexed forms in solution. Interaction with gases was not yet considered in the present modelling, although the model descriptions to take these aspects into account are now becoming available.

The advantage of a full mechanistic modelling approach as opposed to correlation-based or sequential extraction based solutions, is that the results can be taken to other exposure conditions, whereas that is absolutely impossible in case of operationally defined procedures (e.g., sequential chemical extraction) or laboratory test methods designed to simulate specific disposal conditions (e.g., toxicity characteristic leaching procedure, TCLP) (van der Sloot et al., 1997; Kosson et al., 2002). This advantage is reflected in the fact that once the laboratory test can be modelled adequately, the step to useful field predictions is now practical, as the chemical parameters are largely fixed at this stage. Another advantage is that the chemical speciation fingerprint for a given material may require only limited adjustment for a new sample of a similar type. A major challenge remaining is to improve modelling release of DOC and DOC-associated metals (and organic contaminants) directly from the organic matter content and its degradation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.wasman.2016.07.032.

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ECN
Westerduinweg 3
1755 LE Petten
The Netherlands

P.O. Box 1
1755 ZG Petten
The Netherlands

T +31 88 515 4949
F +31 88 515 8338
info@ ecn.nl
www.ecn.nl