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The role of leaching and geochemical modelling in the assessment of coal fly ash and sewage sludge use in agriculture

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Overview of presentation

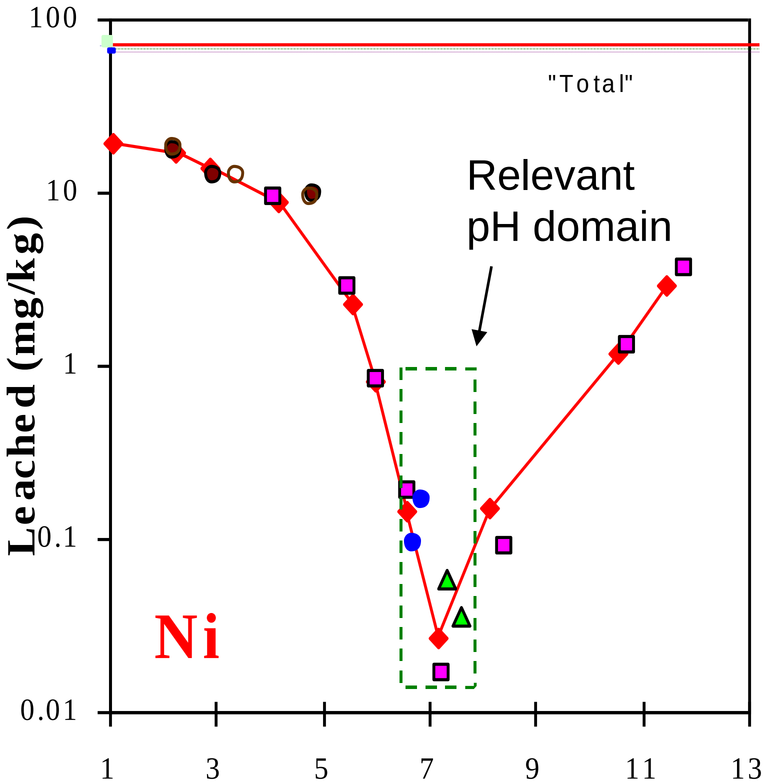
- Total content versus leachability
- Standardised leaching tests
- Soil leaching data
- Geochemical speciation modelling
- Mixture modelling
- Conclusions and Recommendations

- When of interest, ecotoxicity versus leaching

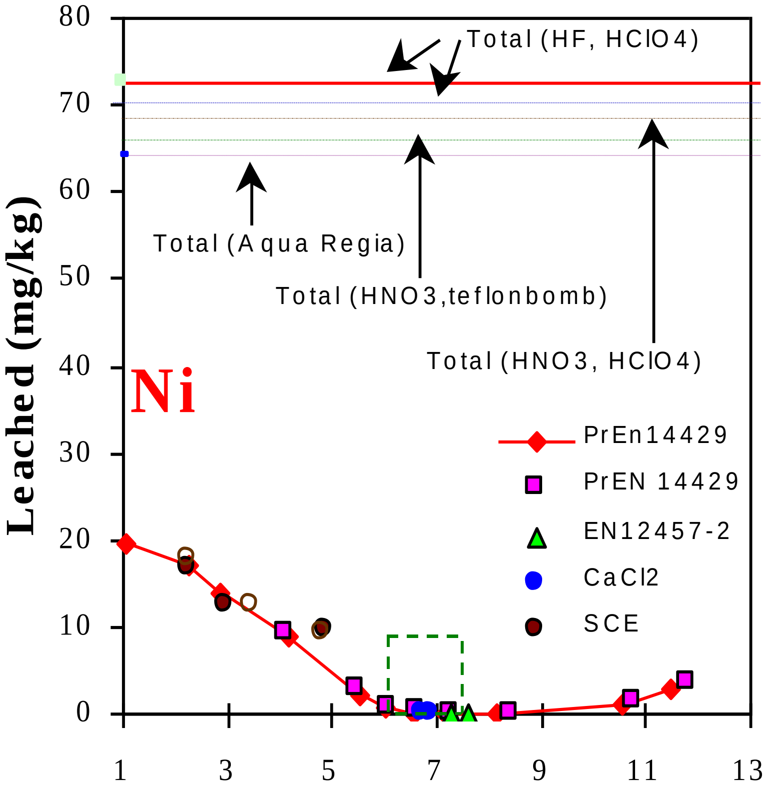
Questions to be answered in relation to contaminated soil and agricultural soil

- Does a given soil or agricultural soil show elevated concentration levels and, if yes, does it pose an health or an environmental risk?
- What treatment of an agricultural soil is suitable and how to judge that?
- When a treatment process has been selected, how can its preformance be verified in a practical manner?
- What are the consequences of prolonged fertilizer use or application of soil amendment on soil quality?
- How can a soil be judged beforehand on its capacity to sustain certain uses?
- To what extent are local circumstances relevant? What are key release controlling factors?

Judgment of environmental impact on total composition or on leaching?



Log-scale pH



Linear-scale pH

Contaminated harbour sediment (Rhine)

Relevance of different methods for total composition for environmental judgement questionable. Leaching by far more relevant for environmental impact assessment

Judgment on total composition or leaching

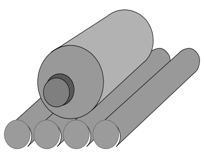
The answer is that none of the questions posed in relation to soil contamination or agricultural issues can be solved by a judgment on the basis of total composition!!

However, that is the regulatory approach today and the sooner it is complemented or replaced by a judgement based on leachability, the more realistic the decisions in terms of true environmental impact and health will become.

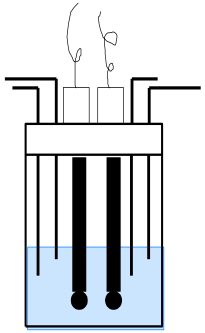
Characterisation leaching tests

Standardisation:
CEN/TC292,
ISO/TC190,
CEN/TC345,
CEN/TC351,
SW846 (US EPA)

GRANULAR MATERIALS



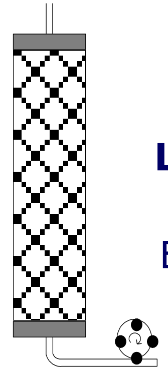
or



pH DEPENDENCE TEST

BATCH MODE - ANC, PrEN 14429, or EPA Method 1313

COMPUTER CONTROLLED - PrEN 14997

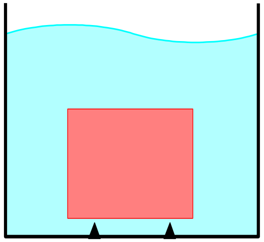


PERCOLATION LEACHING TEST

PrEN 14405 or EPA Method 1314

MONOLITHIC MATERIALS

Same as granular +



MASS TRANSPORT LEACH TEST

MONOLITH
PrEN 15863 or
EPA Method 1315

COMPACTED GRANULAR
NEN 7347 or
EPA Method 1315

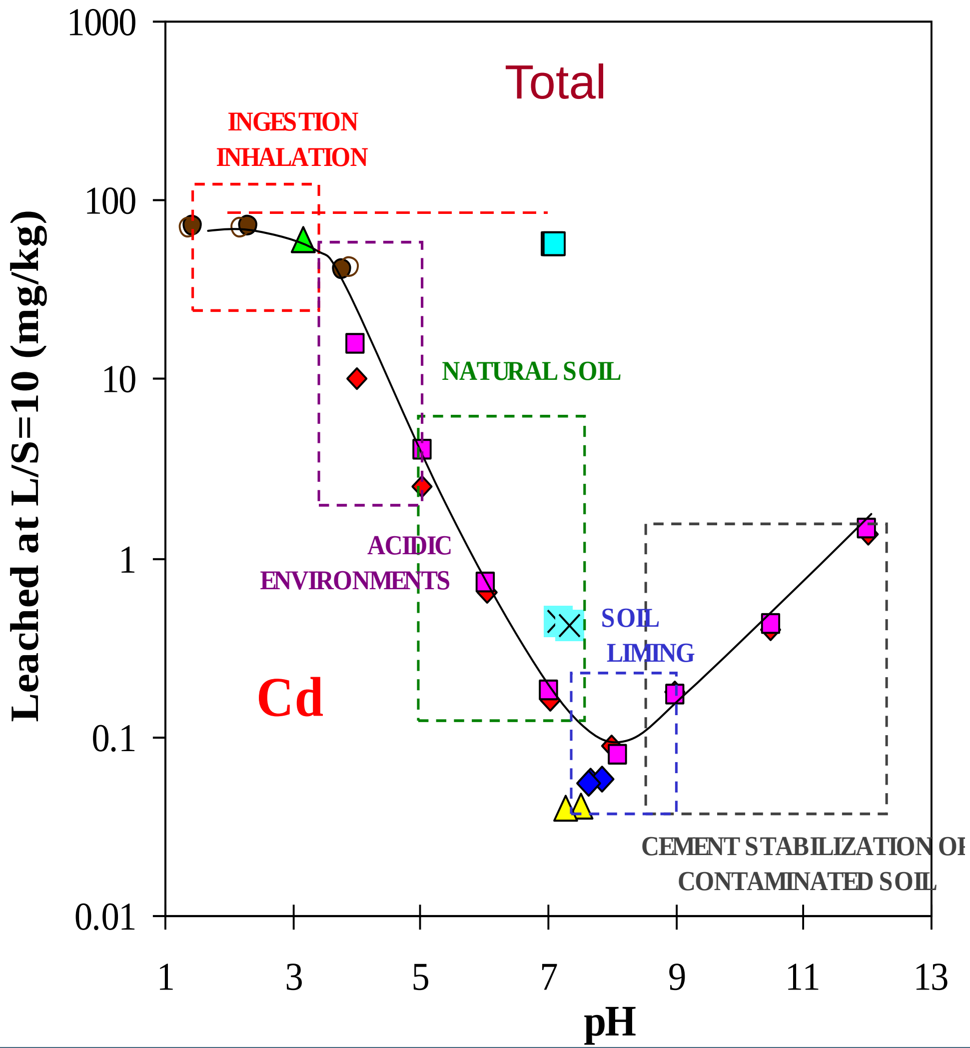
Chemical speciation aspects

Time dependent aspects of release

Test set covers most practical conditions for wide range of materials

Test conditions related to different exposure conditions

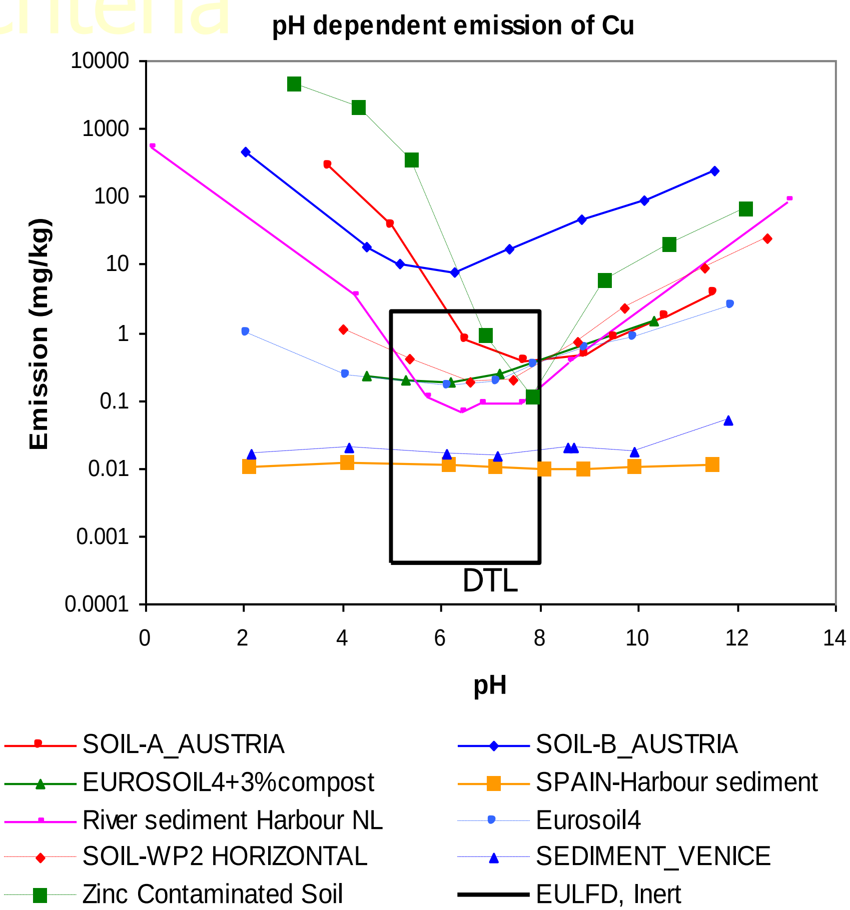
Relevant pH domains for assessing different questions in relation to different types of impact

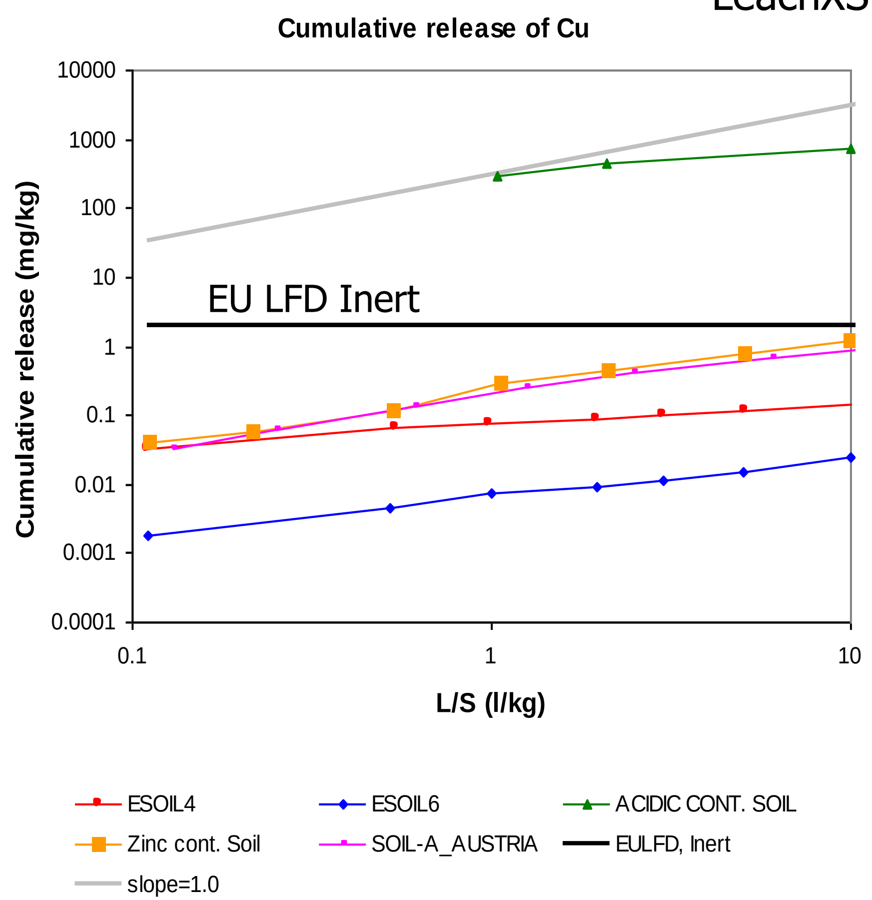


Heavily Sewage Sludge Amended Soil

Comparison of soil and sediment leaching data with regulatory criteria – Inert EU Landfill criteria

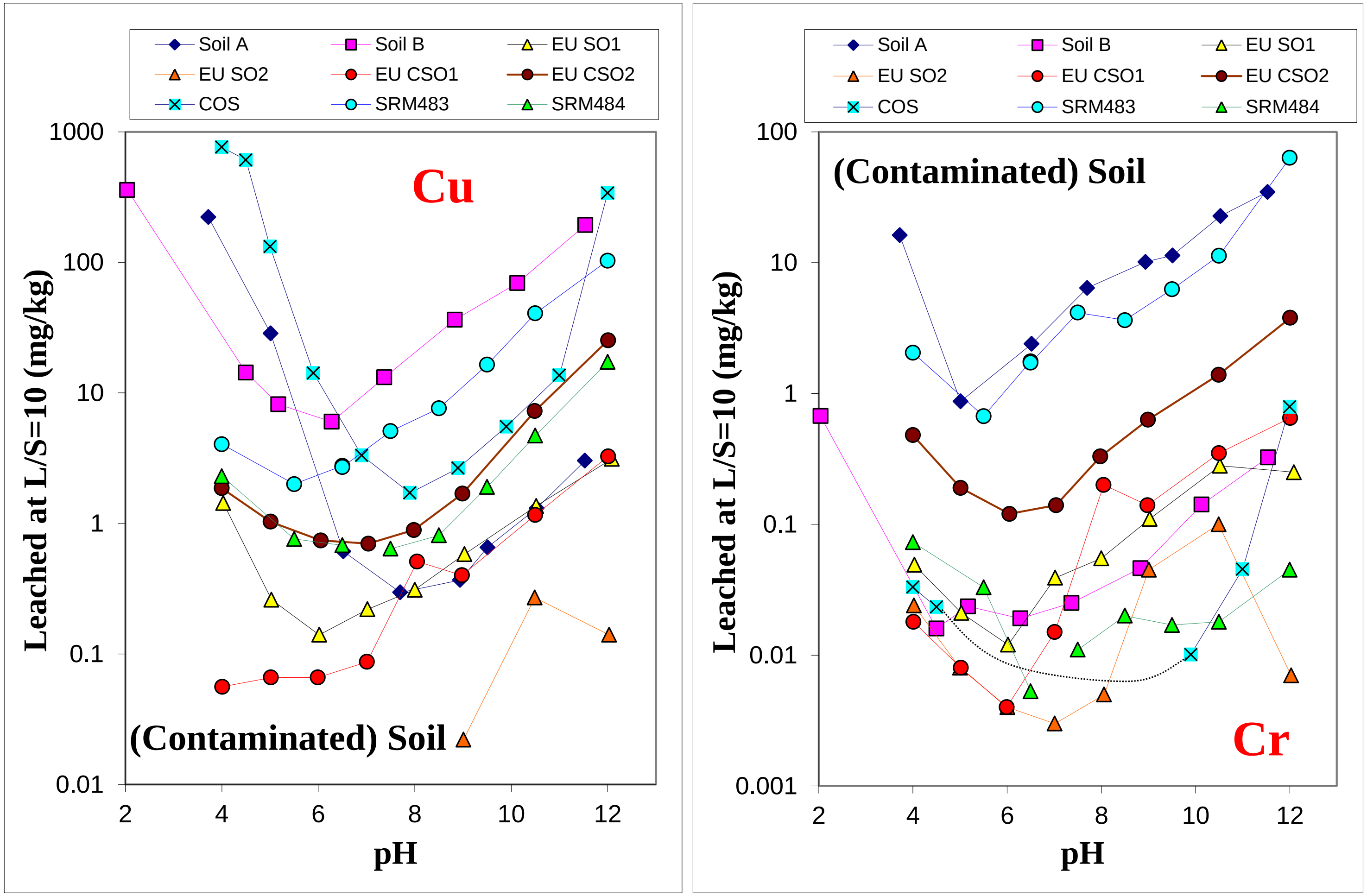
LeachXS





Data from pH dependence and percolation is complementary. In this case, Cu proves not to be critical in most cases (percolation), except for a very acidic, highly contaminated soil. Based on pH dependence two more soils could be problematic.

Comparison of soil leaching for Cu and Cr



SOIL A, SOIL B & CSO: INDUSTRIALLY CONTAMINATED SOILS

SO 1 & SO 2: NATURAL SOILS (Uncontaminated Euro Soils)

CSO 1 & CSO 2: SEWAGE SLUDGE AMENDED SOILS (Moderate, Heavy; ISPRA)

Why Use Geochemical Speciation Modeling?

Geochemical Speciation modeling can:

- Provide insights into distribution of constituents within and between solid and liquid phases that controls leachability and bioavailability/toxicity.
- Explore liquid-solid partitioning at conditions beyond laboratory test conditions
  - Liquid-solid ratio, redox conditions
  - Composition changes (increased clay, iron, DOC, carbonation, constituents of concern, etc.)
- Provide scenario-based evaluation of management options
  - Effects of physical form (monolith, granular), preferential flow, infiltration patterns & chemistry, material interfaces, etc.
- Guide testing and evaluation of material mixtures, treatment and use

Input (Chemical Speciation Fingerprint)

- Element availabilities (major minor and trace elements from pH dependence test, maximum release from 2<pH<13)
- Liquid to Solid ratio (L/S=10 mL/g)
- Redox status of material/product pH+pe = 15 (oxidised)
- Clay content (kg/kg)
- Reactive Hydrated Iron oxide surface (HFO in kg/kg)
- Reactive Solid Humic Acid (SHA in kg/kg)
- Dissolved Organic Carbon (DOC in mg/L from pH dependence test)
- Selection of potentially relevant minerals controlling solubility (Partly taken from a model run to determine saturation indices (SI) for all available minerals in the thermodynamic database)

Example Input (Chemical Speciation Fingerprint) for a Zn contaminated soil

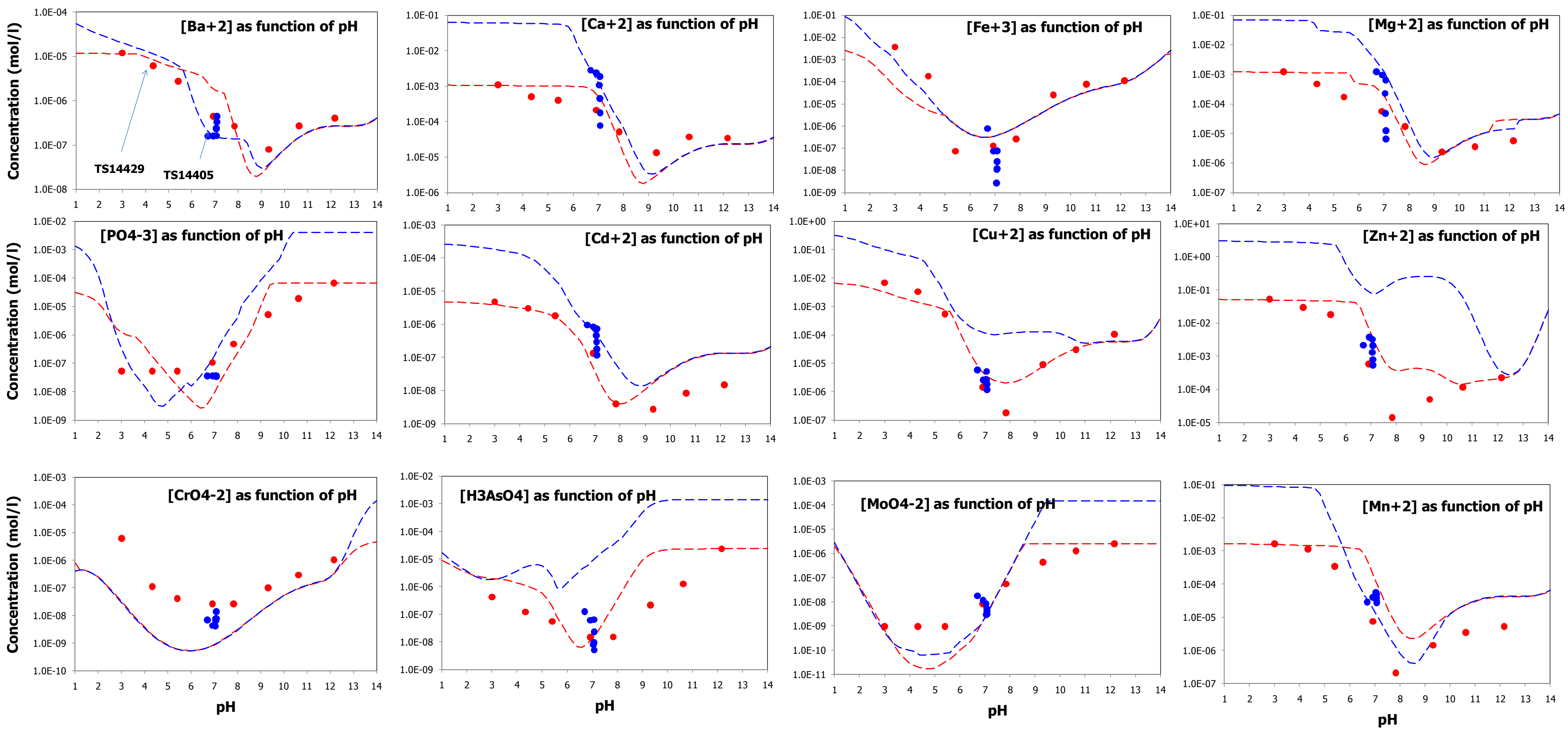
Prediction case	SOC DOC Zn soil + kolom2		**DOC/DHA data**				**Polynomial coeficients**	
Speciation session	Zn soil + kolom		**pH**	**[DOC] (kg/l)**	**DHA fraction**	**DHA] (kg/l**	**C0**	-4.991E+00
Material	Zinc_Soil (P,1,2)		1.00	7.770E-04	0.30	2.331E-04	**C1**	2.526E+00
			3.00	2.060E-04	0.07	1.442E-05	**C2**	-1.406E+00
Solved fraction DOC	0.2		4.33	3.340E-05	0.06	2.004E-06	**C3**	2.446E-01
Sum of pH and pe	15.00		5.41	4.000E-06	0.06	2.400E-07	**C4**	-1.712E-02
L/S	10.0230	**l/kg**	6.92	7.000E-06	0.08	5.600E-07	**C5**	4.234E-04
Clay	1.000E-01	**kg/kg**	7.84	1.400E-05	0.09	1.260E-06		
HFO	1.500E-03	**kg/kg**	9.32	1.400E-04	0.10	1.400E-05		
SHA	7.000E-02	**kg/kg**	10.63	4.300E-04	0.12	5.160E-05		
Percolation material	Zinc_Soil (C,1,1)		12.16	6.260E-04	0.15	9.390E-05		
Avg L/S first perc. fra	0.1650	**l/kg**	14.00	7.300E-04	0.20	1.460E-04		
Reactant concentrations								
Reactant	**mg/kg**	**Reactant**	**mg/kg**	**Reactant**	**mg/kg**	**Reactant**	**mg/kg**	
Ag+	not measured	CrO4-2	3.180E+00	Mg+2	3.019E+02	SO4-2	1.083E+03	
Al+3	6.348E+02	Cu+2	4.398E+03	Mn+2	9.120E+02	Sb[OH]6-	3.485E+00	
H3AsO4	1.751E+01	F-	8.359E+00	MoO4-2	2.400E+00	SeO4-2	6.299E+00	
H3BO3	2.204E+00	Fe+3	2.110E+03	Na+	7.416E+01	H4SiO4	3.040E+03	
Ba+2	1.657E+01	H2CO3	1.000E+04	NH4+	1.000E+00	Sr+2	2.734E+00	
Br-	not measured	Hg+2	not measured	Ni+2	1.888E+02	Th+4	not measured	
Ca+2	4.383E+02	I-	not measured	NO3-	5.000E+01	UO2+	not measured	
Cd+2	5.399E+00	K+	5.373E+01	PO4-3	2.066E+01	VO2+	6.170E-01	
Cl-	2.132E+01	Li+	1.198E+00	Pb+2	1.934E+03	Zn+2	3.450E+04	
Selected Minerals								
Albite[low]	Ca2Cd[PO4]2	FCO3Apatite	Kaolinite	Ni[OH]2[s]	PbMoO4[c]	Zn-Rockbridgite		
AlOHSO4	Ca2Zn3[PO4]3OH	Ferrihydrite	Laumontite	Ni2SiO4	Pyrophyllite			
Anglesite	Ca4Cd[PO4]3OH	Fluorite	LDH_Zn	NiCO3[s]	Rhodochrosite			
Ba[SCr]O4[96%SO4]	Calcite	Forsterite	Magnesite	Otavite	Sb[OH]3[s]			
BaSrSO4[50%Ba]	CaZincate	Huntite	Microcline	Pb[OH]2[C]	Strontianite			
Boehmite	Cd[OH]2[C]	Hydromagnes	MnHPO4[C]	Pb3[VO4]2	Tenorite			
Brucite	CuCO3[s]	Illite[1]	Monticellite	Pb4[OH]6SO4	Zincite			
Bunsenite	Dioptase	Illite[2]	Montmorillonite	PbCrO4	Zn[OH]2[A]			

ISO/TS 12782 series

From pH dependence test data

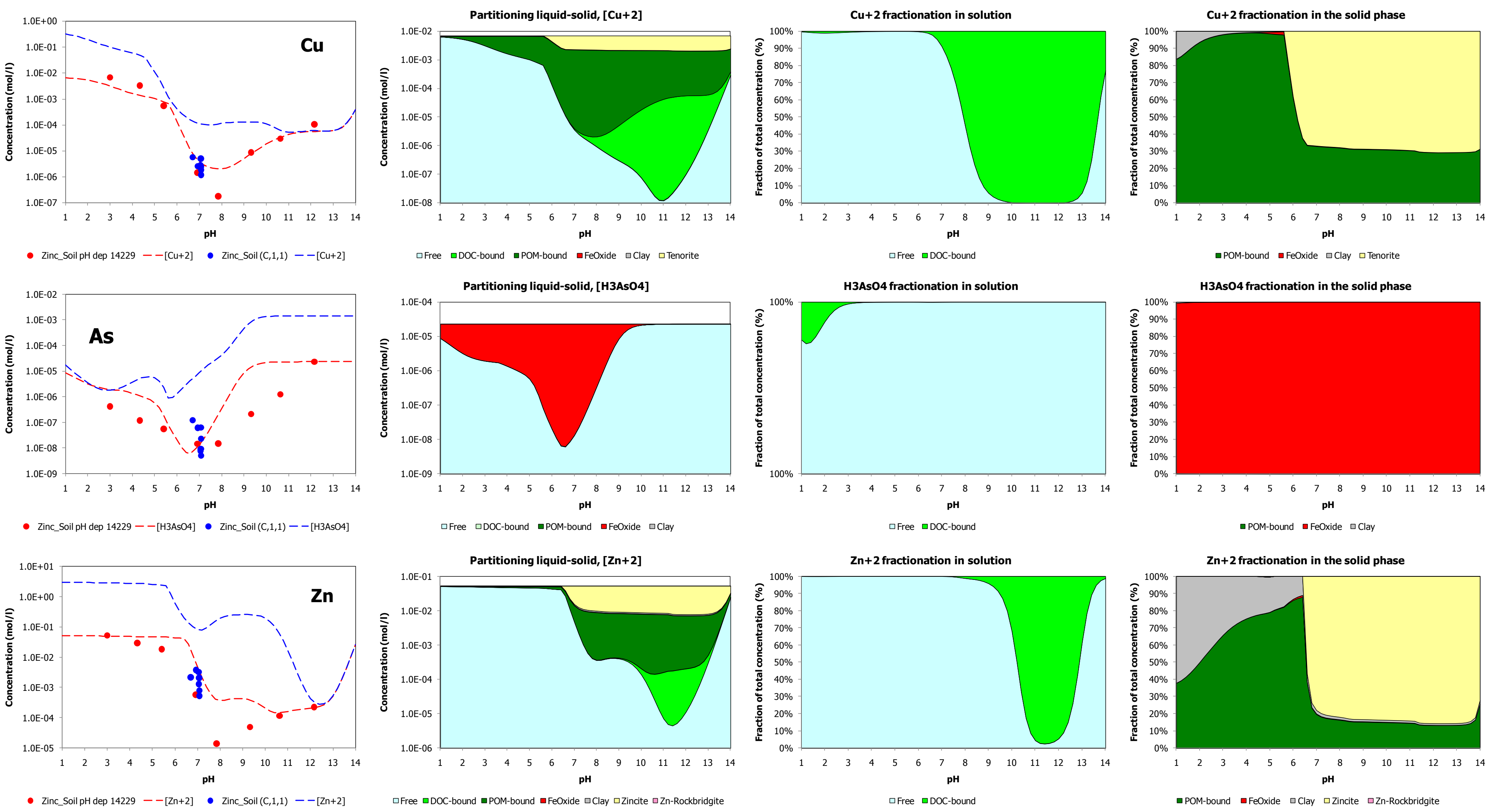
Expert judgement

Model simulation L/S=10 and model prediction at L/S=0.2 for a Zn contaminated soil

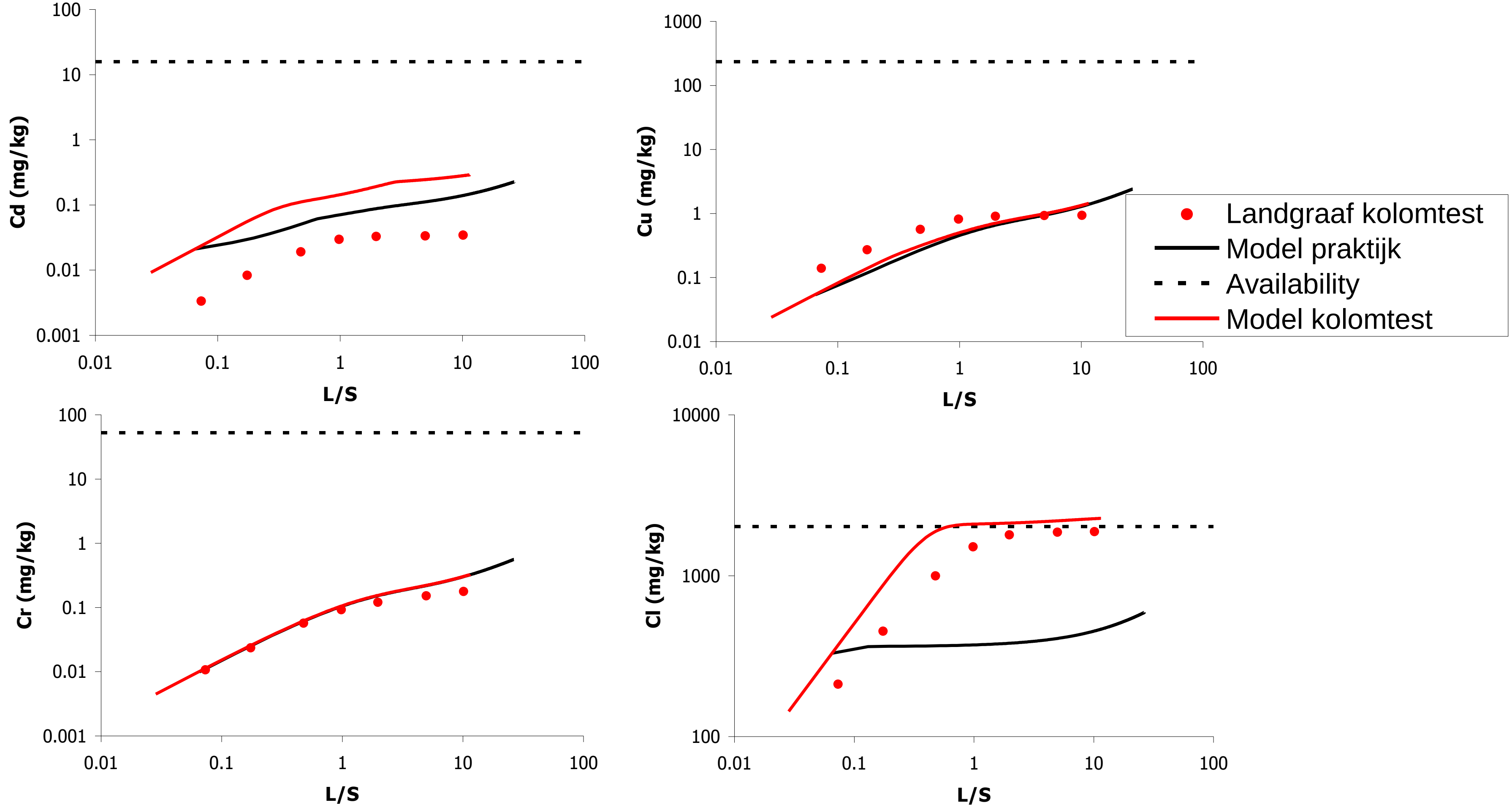


Simulation of release behaviour at L/S=10 (red lines) and at L/S=0.2 (blue lines)
red dots: pH dependence test data (red dots); percolation test data (blue dots).

Partitioning of particulate and dissolved phases for a Zn contaminated soil



Prediction leachate quality taking preferential flow into account (80% stagnant- dual porosity model)



Cd affected by substantially reduced Cl release, other metals not influenced (solubility controlled). Cl substantially reduced by preferential flow.

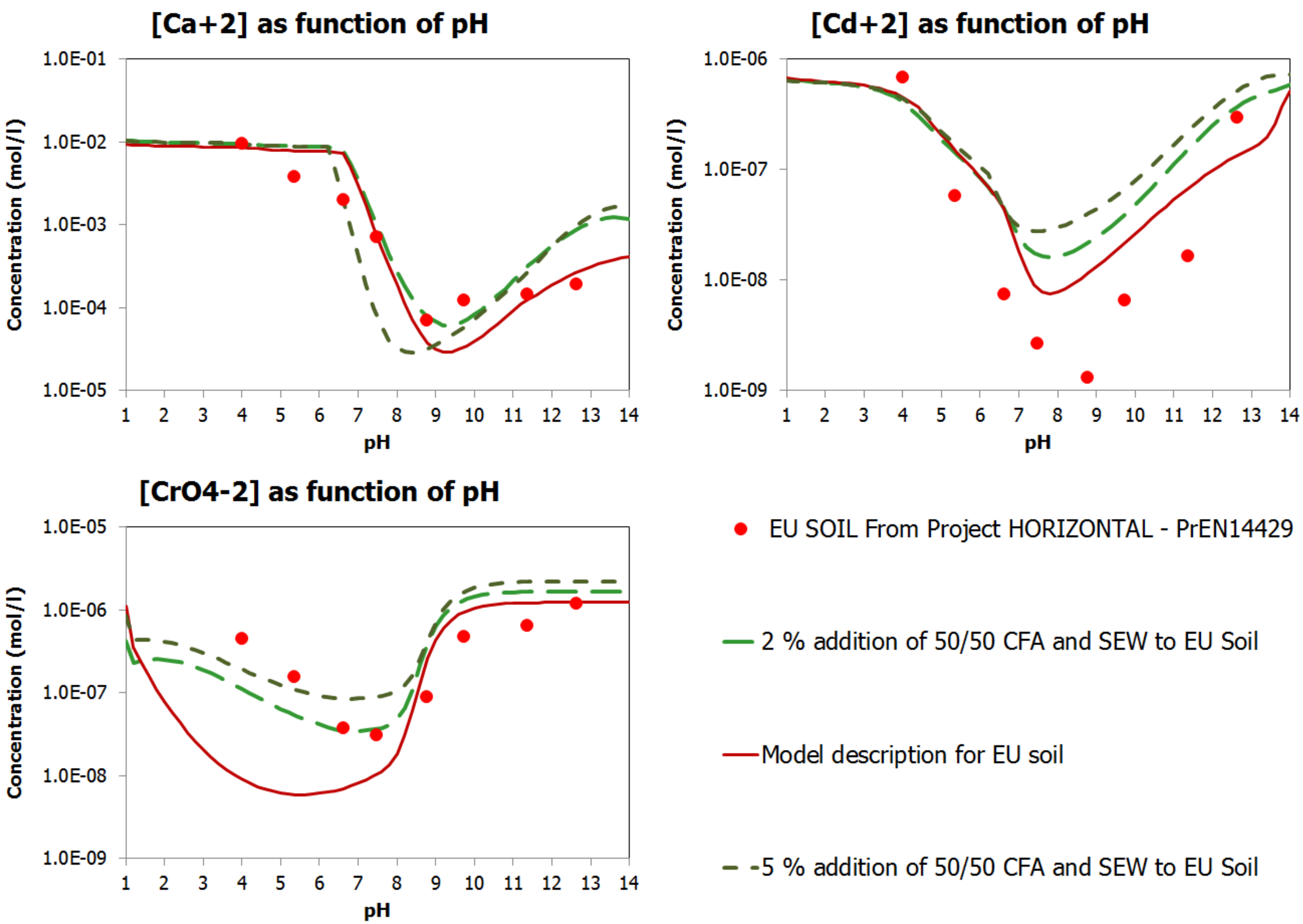
Modelling of Soil – Admixtures

In the case of soil amendment or in contaminated sites with a specific input of contaminants, modelling of material mixtures is feasible using existing Chemical Speciation Fingerprint (CSF) data on soil and on the admixture.

This can be realized in different mixing ratios with verification of suitability of prediction at selected conditions. This forms an economic way of assessing a wide range of possible conditions in a contaminated site.

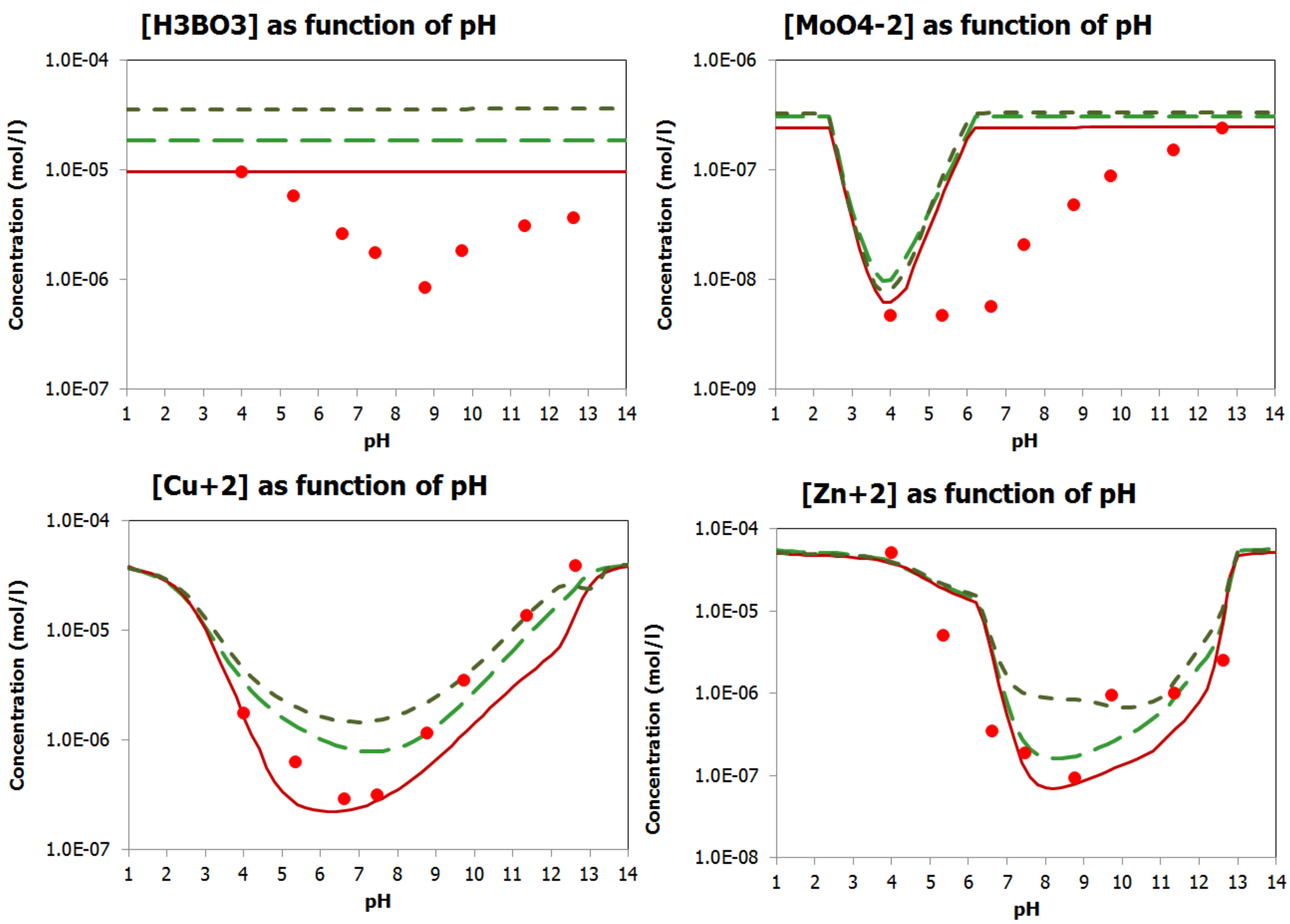
Geochemical modelling of material mixtures (e.g. soil with industrial residues in varying proportions) and verification by experimental leaching work is a new means to assess contaminated sites

Modelling of
Soil – Coal fly ash – Sewage sludge mixtures



For Cd and Cr the effect is DOC related (originating from sewage sludge)

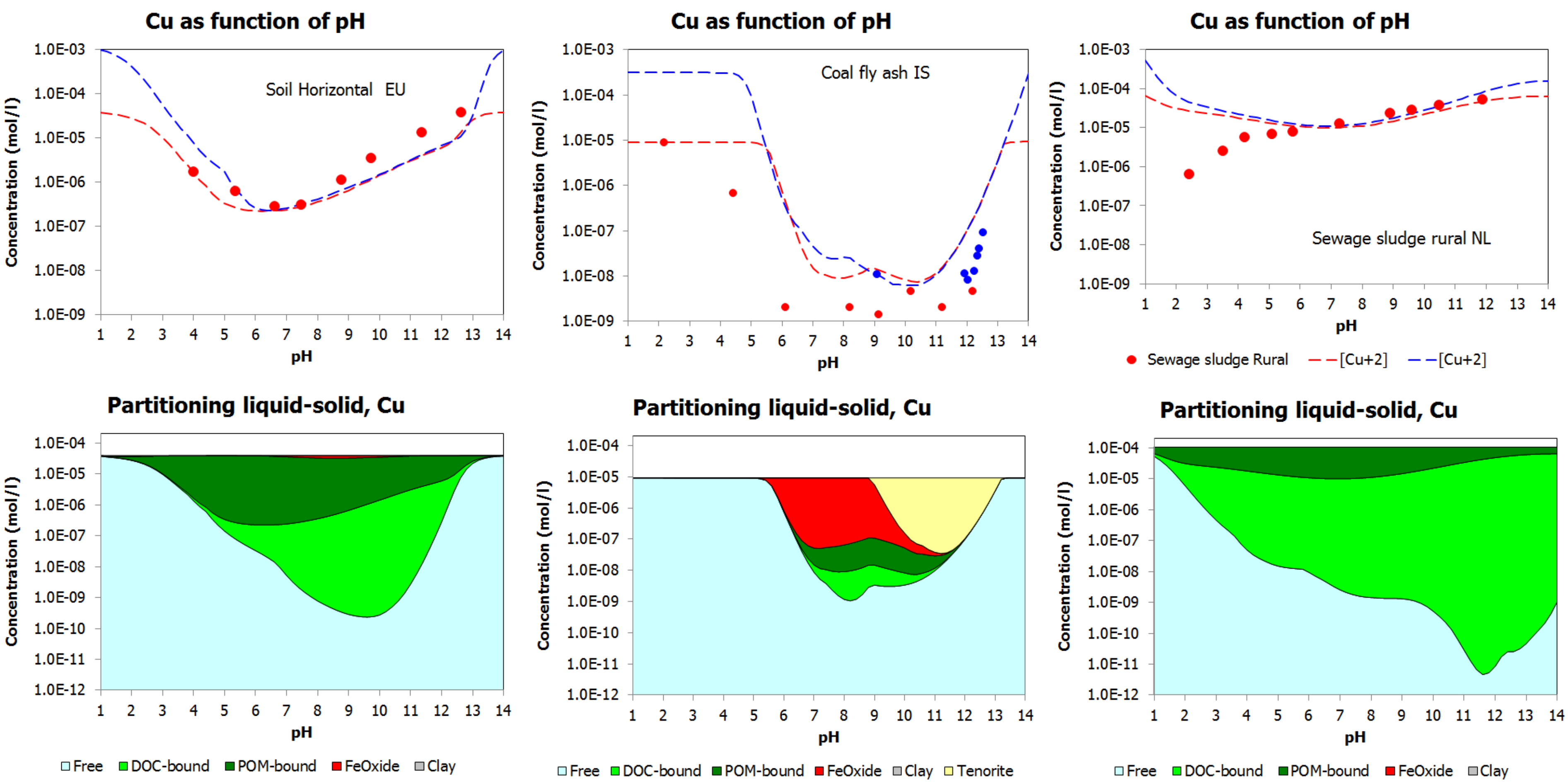
Modelling of
Soil – Coal fly ash – Sewage sludge mixtures (2)



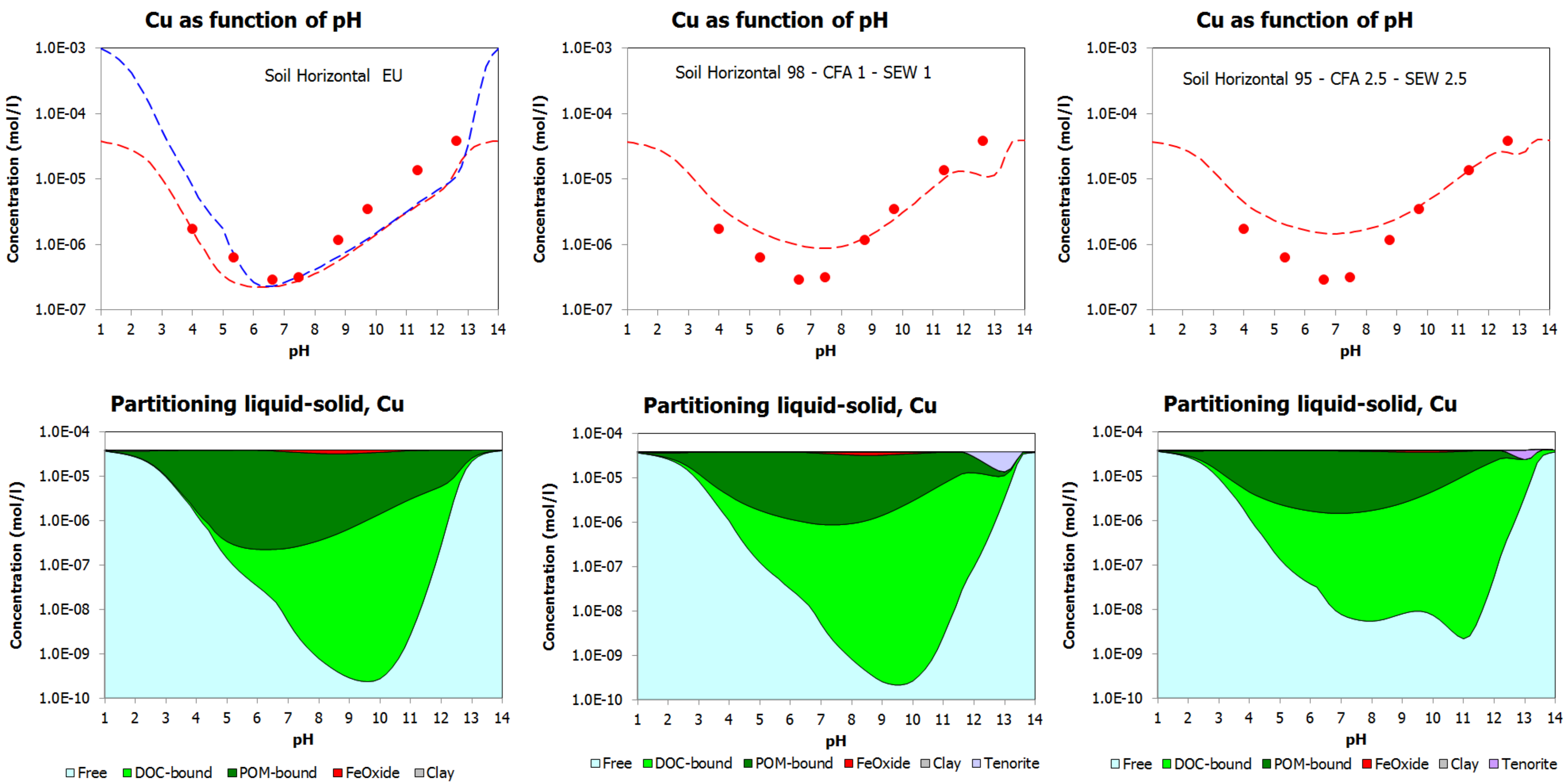
The effect for B (from CFA) seems proportional to the addition. However, the observed B behaviour in soil is not captured - thermodynamic data for possible controlling phases missing.

For Cu and Zn the effect is DOC related (originating from sewage sludge)

Modelling of Soil - Coal fly ash - Sewage sludge
Cu behaviour of individual components



Modelling of Cu behaviour in Soil – CFA -Sewage sludge mixtures



Effect on Cu release entirely DOC related. Cu mobilised as Cu-DOC complex

Conclusions

- A limited set of proper characterisation leaching tests allows to describe release behaviour from soil and soil amendments to improve evaluation of management options and assess possible impacts
- Significant progress in understanding release controlling processes has been made (see papers *)
- Many substances are solubility controlled, thus providing a good understanding of effects at longer term.
- Dissolved organic carbon proves to be a major factor in ecotox response of organisms and plants.
- The multi-element multi-phase chemical reaction transport modelling is a challenge, but a highly rewarding one, when the behaviour of contaminated sites can be modelled at lab and field scale.

* Dijkstra et al, Environ. Sci. Technol. (2009) 43, 6196-6201; Dijkstra et al, Applied Geochemistry 23 (2008) 1544–1562; Dijkstra et al, Appl. Geochem. (2006) 21, 335 – 351; Centioli et al, Ann Ist Super Sanità (2008) Vol. 44, No. 3: 252-257.

Recommendations

- Emphasize leaching based judgment as opposed to content based judgment for management choices and environmental impact from soil amendments
- Soil amendments are different depending on the nature of the material, but similar types can be compared and bringing together information pertaining to specific mixtures makes sense
- For several types of admixtures already available full characterisation leaching data should be used, including data for various coal fly ashes and different types of sewage sludges
- Geochemical modelling of soil with admixtures should be used in conjunction with actual testing and analysis to provide economic efficiency
- Carry out leaching characterisation on composite samples from an agricultural site and some spatially distributed samples by a single step test to assess the nature of release controlling factors for the key contaminants
- Develop benchmark characterisation data for amended soils with specific admixtures - LeachXS Lite (free) can provided such option as the database structure is designed to handle content and leachability data.

References

Andrew C. Garrabrants, David S. Kosson, Leonard Stefanski, Rossane DeLapp, Paul F.A.B. Seignette, Hans A. van der Sloot, Peter Kariher, and Mark Baldwin. Interlaboratory Validation of the Leaching Environmental Assessment Framework (LEAF) Method 1313 and Method 1316. EPA-600/R-12/623 (2012).

Andrew C. Garrabrants, David S. Kosson, Leonard Stefanski, Rossane DeLapp, Paul F.A.B. Seignette, Hans A. van der Sloot, Peter Kariher, and Mark Baldwin. Interlaboratory Validation of the Leaching Environmental Assessment Framework (LEAF) Method 1314 and Method 1315. EPA-600/R-12/624 (2012).

Carter, C.M., van der Sloot, H.A. and Cooling D. pH dependent extraction of soils and soil amendments to understand the factors controlling element mobility - New approach to assess soil and soil amendments. European Journal of Soil Science. European Journal of Soil Science, August 2009, 60, 622–637.

Postma J.F., van der Sloot, H.A. and van Zomeren A. Ecotoxicological response of three waste samples in relation to chemical speciation modelling of leachates. In : Ecotoxicological characterization of waste – Results and experiences from a European ring test. Eds: J. Römbke, R. Becker & H. Moser, Springer Science+Business Media, Inc. Norwell (MA), 2009.

H.A. van der Sloot Harmonisation of leaching/extraction procedures for sludge, compost, soil and sediment analyses. In: Methodologies for Soil and sediment fractionation studies. Ed. P. Quevauviller. Royal Society of Chemistry, 2002, pp. 142-170.

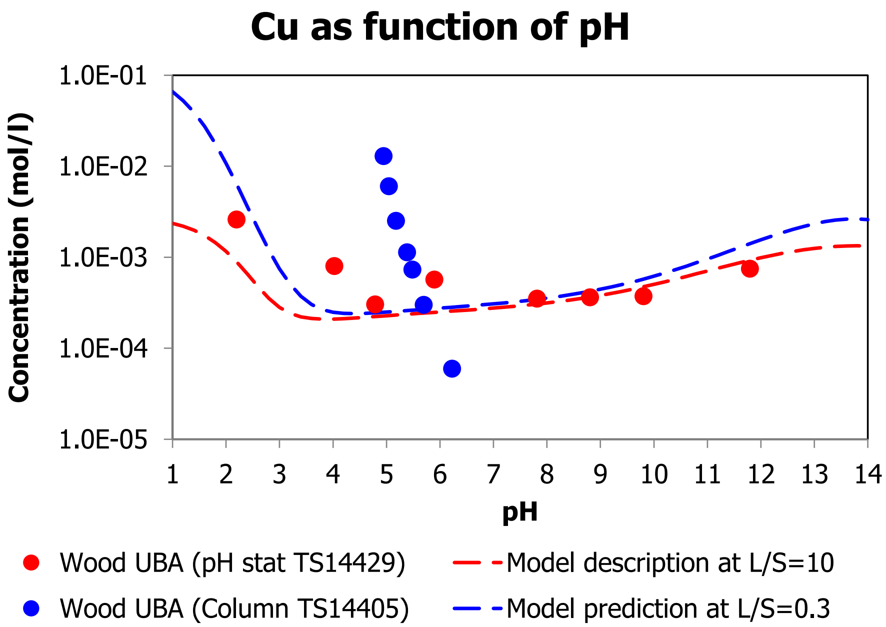
Unique Set of Leaching Experiments and Ecotox Measurements

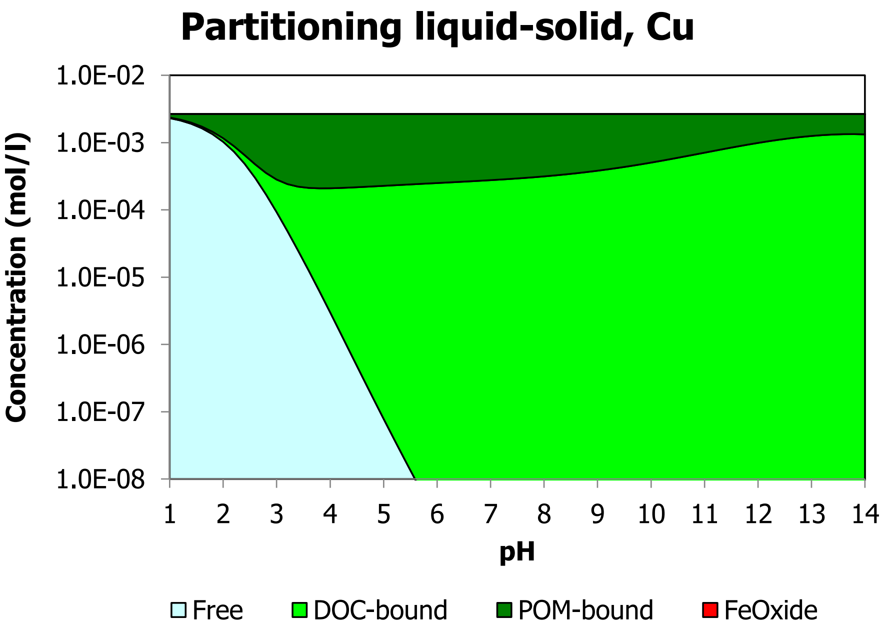
For three waste samples besides ecotox testing with aquatic and terrestrial organisms, a combination of a pH dependence (TS 14429) and a percolation test (TS14405) was carried out

With chemical speciation modelling (LeachXS-Orchestra), partitioning between dissolved (free and DOC associated) and solid phases (solid organic matter, clay surfaces, iron oxides and minerals) was calculated and the outcome compared with ecotox data.

Postma J.F., van der Sloot, H.A. and van Zomeren A. Ecotoxicological response of three waste samples in relation to chemical speciation modelling of leachates. In : Ecotoxicological characterization of waste – Results and experiences from a European ring test. Eds: J. Römbke, R. Becker & H. Moser, Springer Science+Business Media, Inc. Norwell (MA), 2009.

Cu leaching from treated wood





Release of Cu from wood is controlled completely by particulate and dissolved organic matter

Copper as primary toxicity in undiluted eluates from CCA treated wood

Leaching at L/S=10 mL/g in DI water

	EC_{50} copper (mg/l)	TU-values for copper
Microtox	0,13	170
D. magna	0,024	919
P. subcapitata	0,15	147

Toxic Unit TU_i (Species) = $C_i/EC_{50,i}$

Dafnia magna, copper and wood

	Test solutions (vol%)		
	100	0.50	0.20
Total Cu (mg/l)	22.1		
Free Cu	0.5		
Total Cu, test solution		0.110	0.044
"Expected" free-Cu		0.002	0.001
"Modelled" free-Cu		0.015	0.006
% Free Cu	2.1	13.6	13.6

Conclusion: Toxicity is likely caused by copper, interaction with DOC varies with dilution

Comparison of PAH content, "availability" and actual leachability for gasworks soil SOI

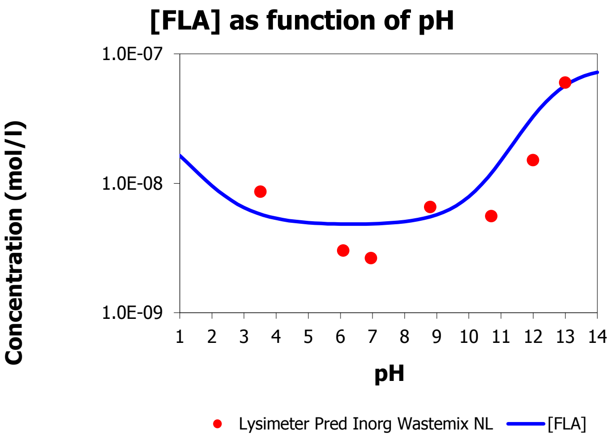
Table 4.1 Total PAH in relation to " available" and leachable PAH at own pH of SOI sample.

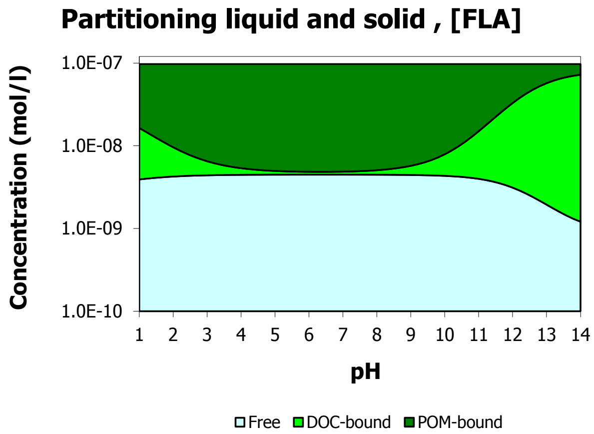
Parameter	Total	Concentration ug/l at L/S=10		Leached in mg/kg		% Available	% Leachable
	mg/kg	pH12	Own pH	pH12#	Own pH	for leaching	at own pH
Anthracene	23.4	5.180	1.521	0.0518	0.0152	0.2214	0.0650
Benzo(a) anthracene	87.2	17.585	1.659	0.1759	0.0166	0.2017	0.0190
Benzo(a)pyrene	59	9.946	0.656	0.0995	0.0066	0.1686	0.0111
Benzo(b) fluoranthene	78.6	15.114	1.045	0.1511	0.0104	0.1923	0.0133
Benzo(ghi) perylene	34.7	1.783	0.434	0.0178	0.0043	0.0514	0.0125
Chrysene	69.4	17.480	1.701	0.1748	0.0170	0.2519	0.0245
Dibenz(ah) anthracene	9.37	0.671	0.858	0.0067	0.0086	0.0716	0.0916
Fluoranthene	181.6	36.616	10.006	0.3662	0.1001	0.2016	0.0551
Fluorene	4.16	2.637	0.990	0.0264	0.0099	0.6338	0.2381
Phenanthrene	69.1	25.317	0.469	0.2532	0.0047	0.3664	0.0068
Pyrene	146	27.814	6.889	0.2781	0.0689	0.1905	0.0472

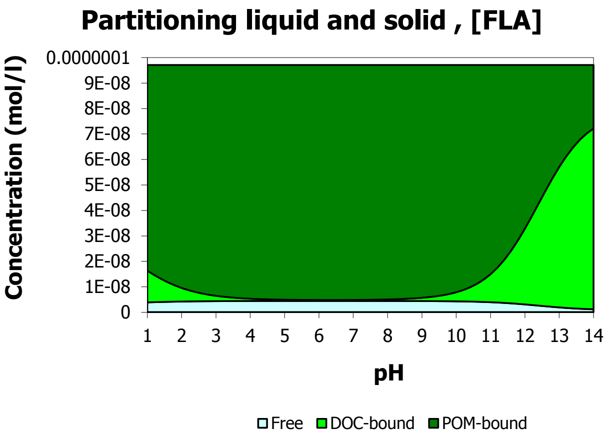
Considered to represent the "available" fraction for leaching

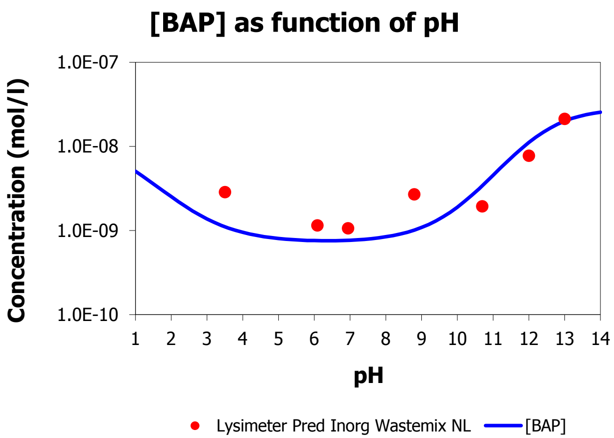
Postma J.F., van der Sloot, H.A. and van Zomeren A. Ecotoxicological response of three waste samples in relation to chemical speciation modelling of leachates. In : Ecotoxicological characterization of waste – Results and experiences from a European ring test. Eds: J. Römbke, R. Becker & H. Moser, Springer Science+Business Media, Inc. Norwell (MA), 2009.

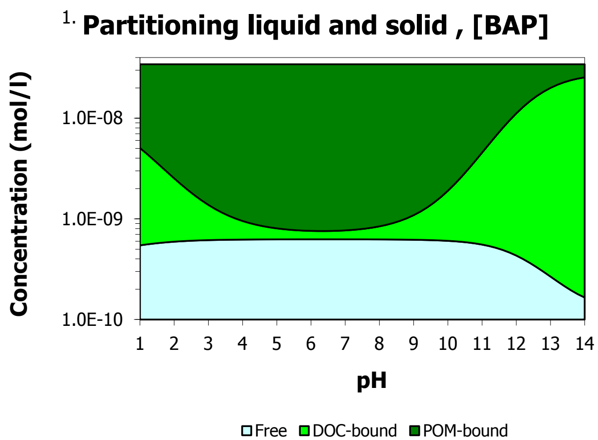
Partitioning of organic contaminants in contaminated soil relevant for ecotox effect

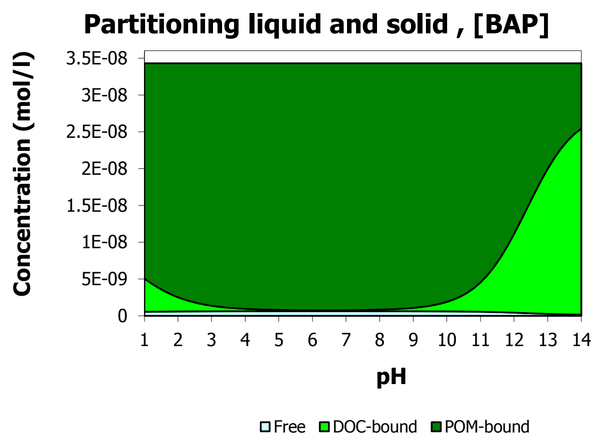












Rather low proportion of organic PAHs/PCBs, etc. free in solution, when natural organic matter is present. Koc values used to describe partitioning.