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Multi surface modeling of trace metals behavior in treated dredged sediments: experimental study and modeling of metals retention on artificial assemblage of natural sorbent phases.

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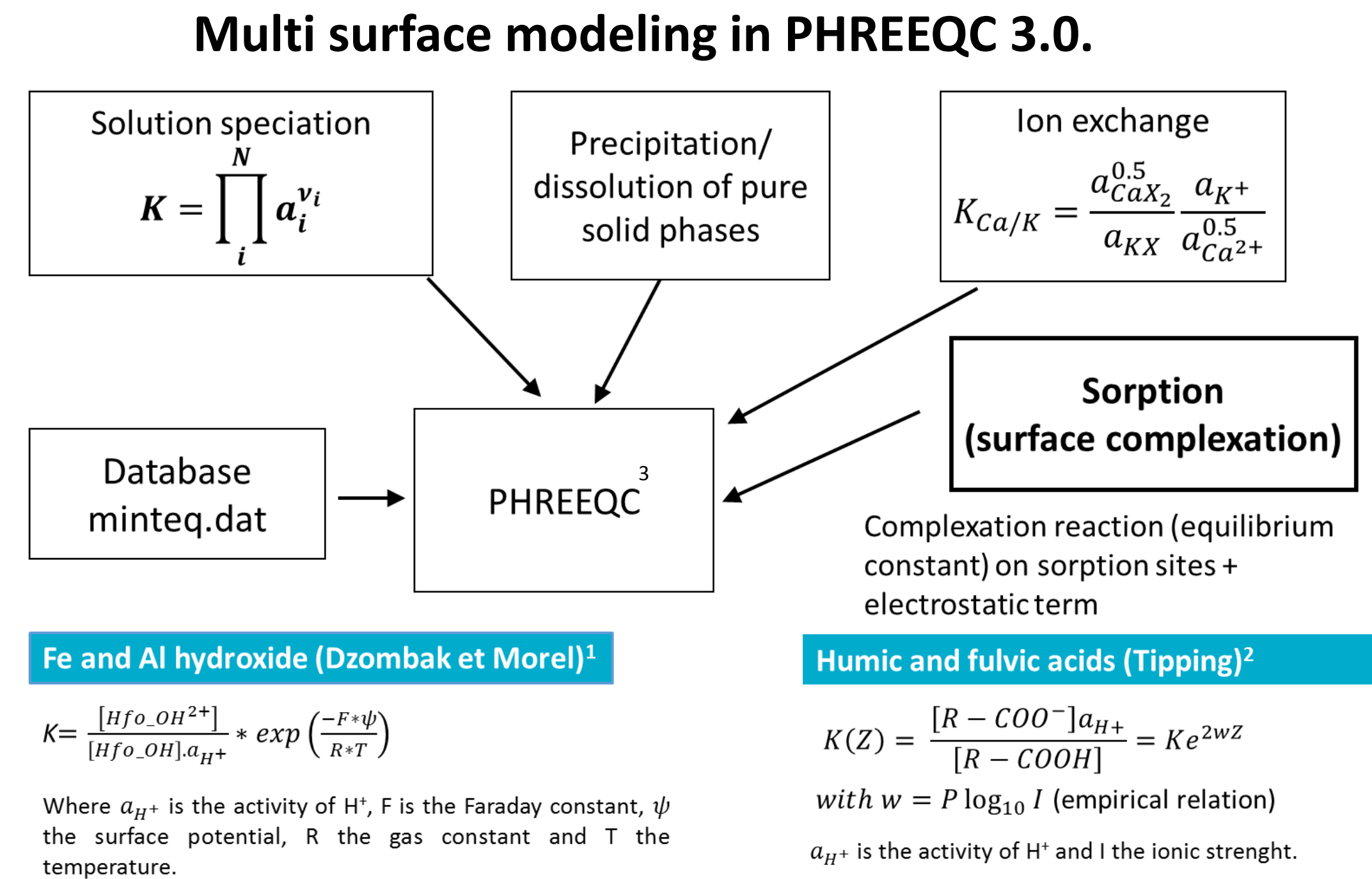Louise.Chenoy@umons.ac.be

INTRODUCTION-CONTEXT

-According to the Walloon legislation (AGW 30/11/1995), dredged sediments are classified as waste materials (A or B type in function of the contamination level) and must eventually be treated before valorization or disposal.

→ Increased costs → dredging operation slowed down→ accumulation of 6.10^6 m³ of sediments, whose about 65% are polluted by **heavy metals (Zn, Pb, Ni, Cr, Cu…) or organic compounds**.

- Over the past few years, ERDF funded project SOLINDUS aimed to assess the feasibility of a mineralurgical process to separate unpolluted coarse fractions (> 63 µm) from polluted fine fractions (silt fraction 15-63 µm and fine fraction <15µm) of dredged sediments. Study of purification of silt fraction by a flotation treatment has also been made with various success. Purified fraction could then be reused.

-**The comprehension of retention phenomena of heavy metals in these treated sediments is of importance to improve the treatment and to evaluate environmental risks linked to further sediment reuse.**
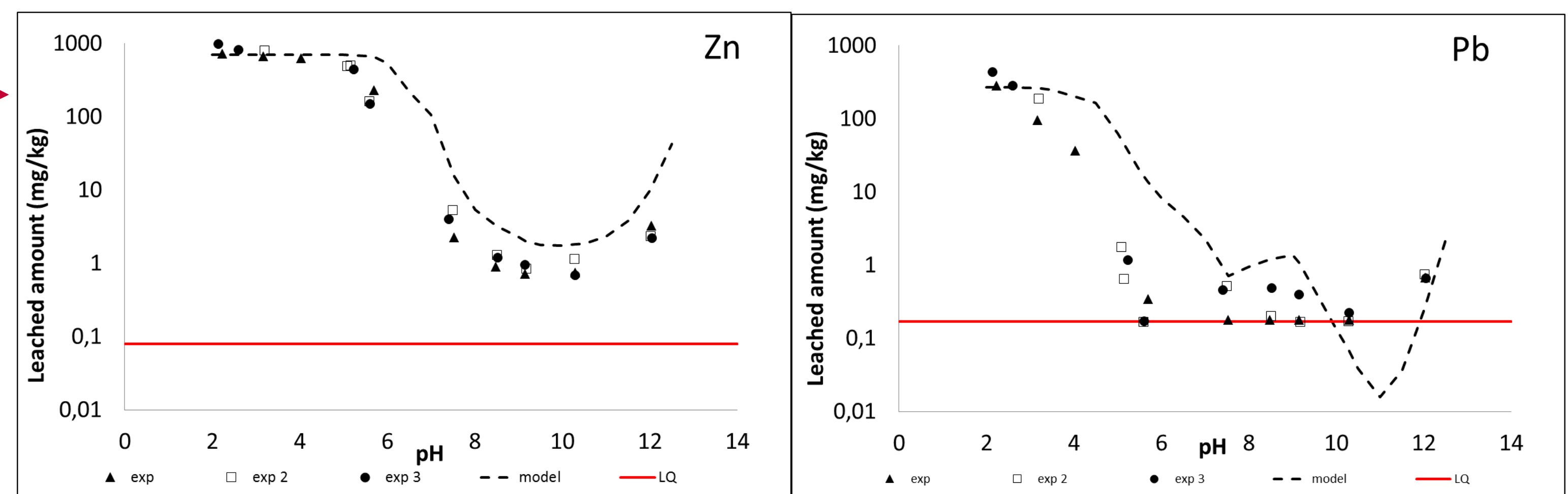**Study of the behavior of heavy metals in the silt fraction for three sediments samples has been conducted in a previous work by combining experimental characterization and multi surface modelling.**

Experimental results and modelling of batch leaching test in function of pH (EN 14429) for Zn and Pb for the silt fraction of a sediment dredged in the Nimy-Blaton channel.

Validation of the multi surface model is difficult due to the complexity of sediments matrix (Fe oxides, organic matter, mineral phases, clays…). The present study aims to test the modeling approach against experimental data of metals sorption to artificial assemblage of pure, well characterized phases. The first experiments will concern Zn retention.

Multi surface modeling in PHREEQC 3.0.

Solution speciation
$$K = \prod_i^N a_i^{\nu_i}$$

Precipitation/dissolution of pure solid phases

Ion exchange
$$K_{Ca/K} = \frac{a_{CaX_2}^{0.5}}{a_{KX}} \frac{a_{K^+}}{a_{Ca^{2+}}^{0.5}}$$

Database minteq.dat

PHREEQC [3]

Sorption (surface complexation)

Complexation reaction (equilibrium constant) on sorption sites + electrostatic term

Fe and Al hydroxide (Dzombak et Morel)[1]
$$K = \frac{[Hfo\_OH^{2+}]}{[Hfo\_OH]a_{H^+}} * exp\left(\frac{-F*\psi}{R*T}\right)$$
Where a_{H^+} is the activity of H⁺, F is the Faraday constant, ψ the surface potential, R the gas constant and T the temperature.

Humic and fulvic acids (Tipping)[2]
$$K(Z) = \frac{[R - COO^-]a_{H^+}}{[R - COOH]} = Ke^{2wZ}$$
with $w = P \log_{10} I$ (empirical relation)
a_{H^+} is the activity of H⁺ and I the ionic strenght.

→ Use of generic thermodynamic parameters, hypotheses (e.g. composition of dissolved organic matter) and experimental data (extraction of iron hydroxides and solid organic matter (ISO 12782), XRD analysis, total available concentration of trace and major elements…)

Zn / Pb leaching plots (Leached amount (mg/kg) vs pH): exp, exp 2, exp 3, model, LQ

EXPERIMENTAL PROCEDURE

Experimental conditions are selected to mimic batch leaching test EN14429 on real sediment samples either with [Zn] = 100 mg/l (exp (1)-(2)-(3)) or to test sorption model only (exp (4) – [Zn] = 1 mg/l)
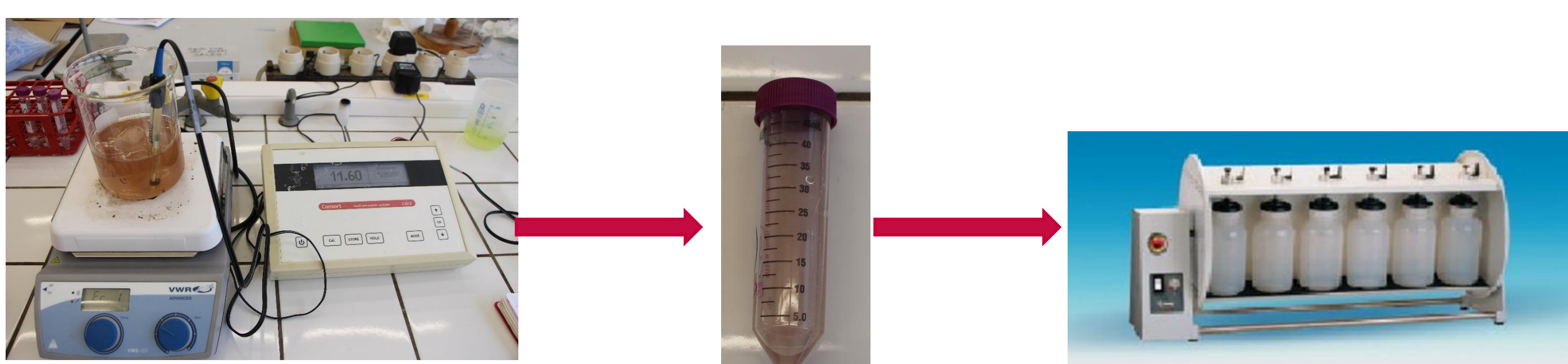
Main characteristics of studied (real) sediment samples				
	Dampremy	Nimy-B	Seneffe	unit
Quartz	70	37	54	%
CaCO₃	6	37	9	%
Clays (mainly illite)	12	17	17	%
Zn (aqua regia digestion)	585	1149	8707	mg/kg
available at pH=2	483	725	8157	
Pb (aqua regia digestion)	128	434	2629	mg/kg
available at pH=2	122	268	2288	
Amorphous iron oxides (ISO 12782)	406	439	577	mg/kg

- Zn containing solution ($Zn(NO_3)_2.6H_2O$) and solid phases ($HFO/HFO+SiO_2/HFO+SiO_2+CaCO_3$) are placed in appropriate amounts in a open beaker with magnetic agitation.

- HFO = hydrous ferric oxide (ferrihydrite 2-line), synthesized by precipitation from $Fe(NO3)_3$[4]
- SiO_2 : Powdered quartz (Millisil® M6, SIBELCO)
- $CaCO_3$: analytical grade

- HNO_3 (1M) or NaOH (1M) is added to achieve different pH values.
- Between each addition, a 30 ml subsample is removed and agitated during 48h to reach equilibrium

- After 48h, samples are centrifuged, filtered (0,2µm) and analyzed by ICP-AES

MODELING AND RESULTS

Experiences are simulated with PHREEQC using parts of the model presented above:
- Surface complexation on HFO
- Mineral dissolution/precipitation
- Solution speciation

[Zn] liquid phase (mg/l) vs pH:
(1) Zn 100 mg/l - HFO 500 mg/l; (2) Zn 100 mg/l - HFO 500 mg/l - SiO2 35 g/l; (3) Zn 100 mg/l - HFO 500 mg/l - SiO2 35g/l - CaCO3 30 g/l; model (1) sorption only; model (3) sorption only; model (1) with ZnO precipitation+sorption; model (3) precipitation + sorption

[Zn] liquid phase (mg/l) vs pH: model sorption only; Zn 1 mg/l - HFO 500 mg/l; LOQ

- Model fit well with experimental result, except for pH 10-11 (overestimation)

- Sorption to HFO represent maximum 25% of Zn retention

- ZnO precipitation for pH > 7

-The addition of quartz in the system don't have a significant impact on Zn retention → the assumption of neglect sorption on SiO_2 in the model is plausible

-The best model for exp (3) predict ZnO precipitation and sorption to HFO, without $ZnCO_3$ formation

Sorption model evaluation
- No Zn precipitation in pure mineral phases
- Simulated values are shifted in comparison to experimental results (pH 5-7)

PERSPECTIVES

- Further experiments will include sorption of Zn on a natural clay (illite) alone or mixed to HFO and SiO_2.

- Pb sorption, alone and mixed with Zn, will also be assessed

- These experiments will confirm which components play major role in Zn and Pb retention and will help to identify discrepancies between model and experimental results.
- Incorporation of organic matter (e.g. with a commercial humic acid) will be also possible.

[1] E. Tipping, Aquat. Geochemistry, vol. 4, no. 1976, pp. 3–48, 1998.
[2] D. A. Dzombak and F. M. M. Morel, Surface Complexation Modeling: Hydrous Ferric Oxide. New York, 1990.
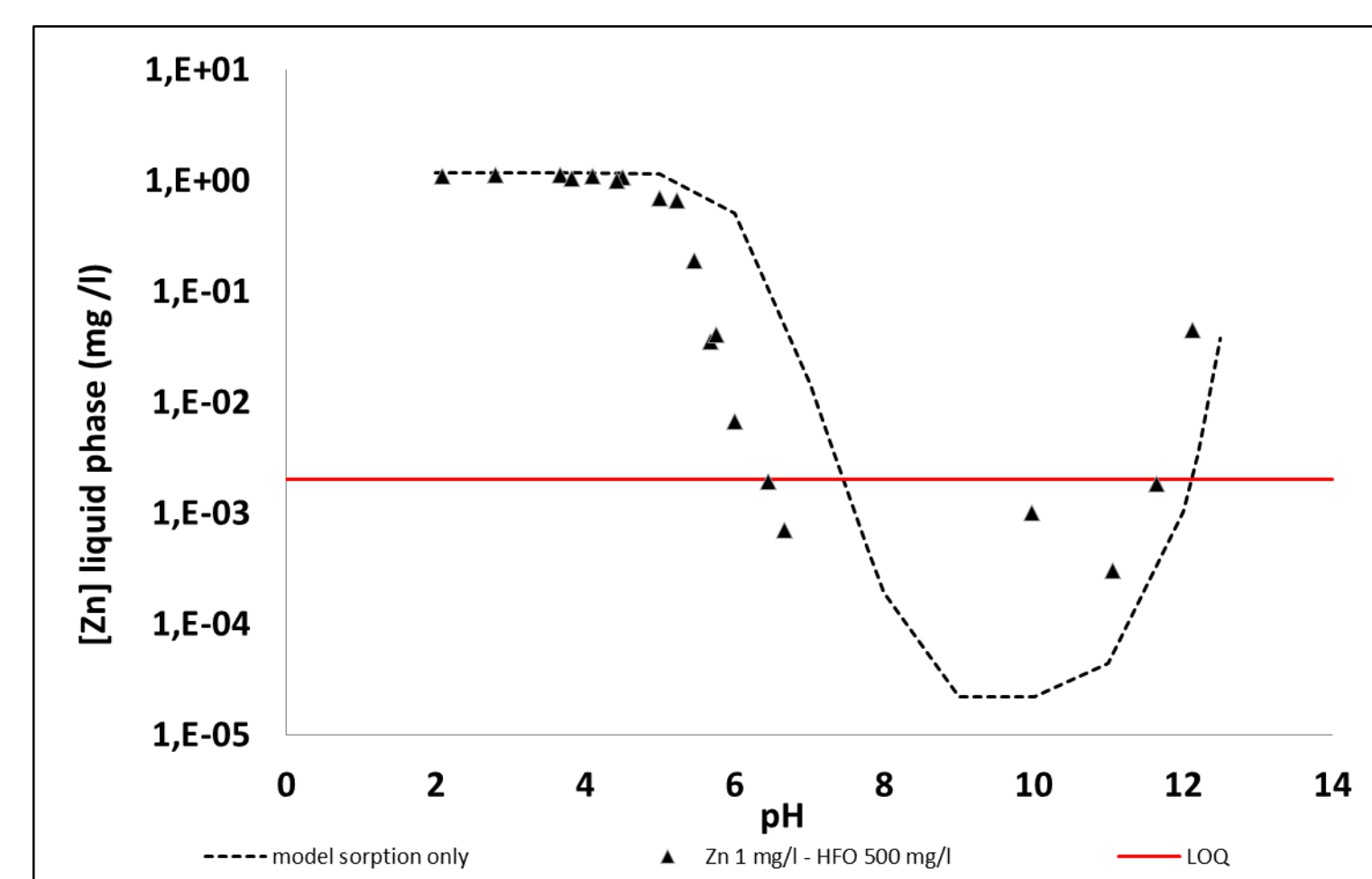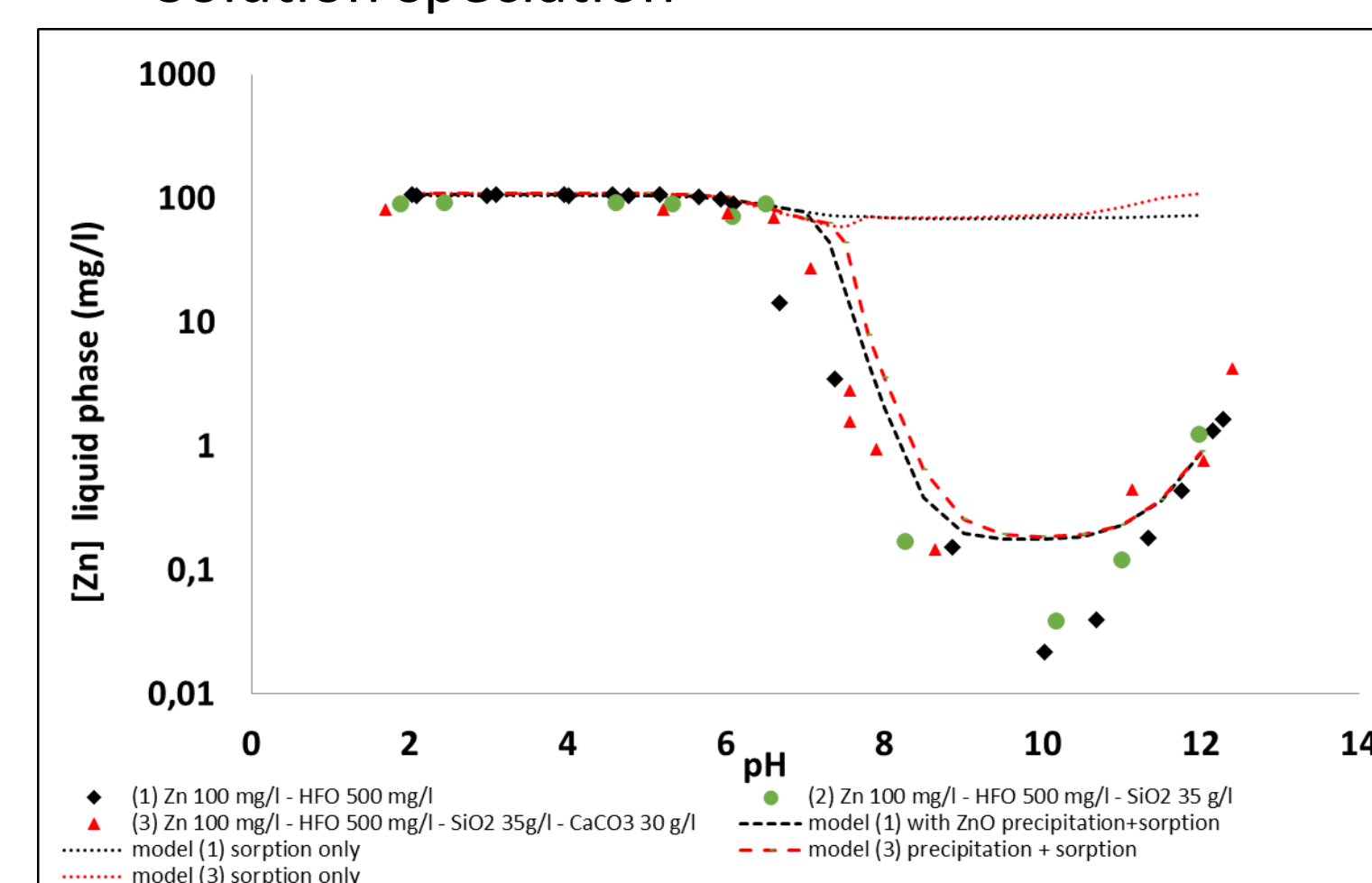[3] D. L. Parkhurst and C. A. J. Appelo, "Description of Input and Examples for PHREEQC Version - A Computer Program for Speciation , Batch-Reaction , One-Dimensional Transport , and Inverse Geochemical Calculations," 2013.
[4] U. Schwertmann and R. M. Cornell, Iron oxides in the laboratory: preparation and characterization, 2nd editio. Wiley-VCH, 2000.