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Modelling of trace metals leaching behaviour in sludge deposits with high organic contents.

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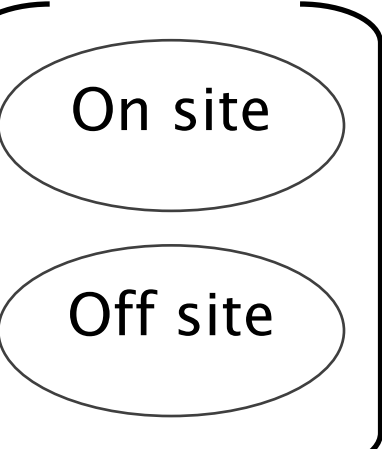
HAL Authorization

The matrix considered in this study comes from a small wastewater treatment plant called Vertical Flow Constructed Wetland. These are increasingly used in France with some 5000 plants already installed in 2018. Sludge deposits accumulated at the top of the filter are composed by organic matter but also by inorganic pollutants such as trace metals. Improving the understanding of the interactions between minerals and organic matter is necessary to predict the pollutant retention / release dynamics.

Context

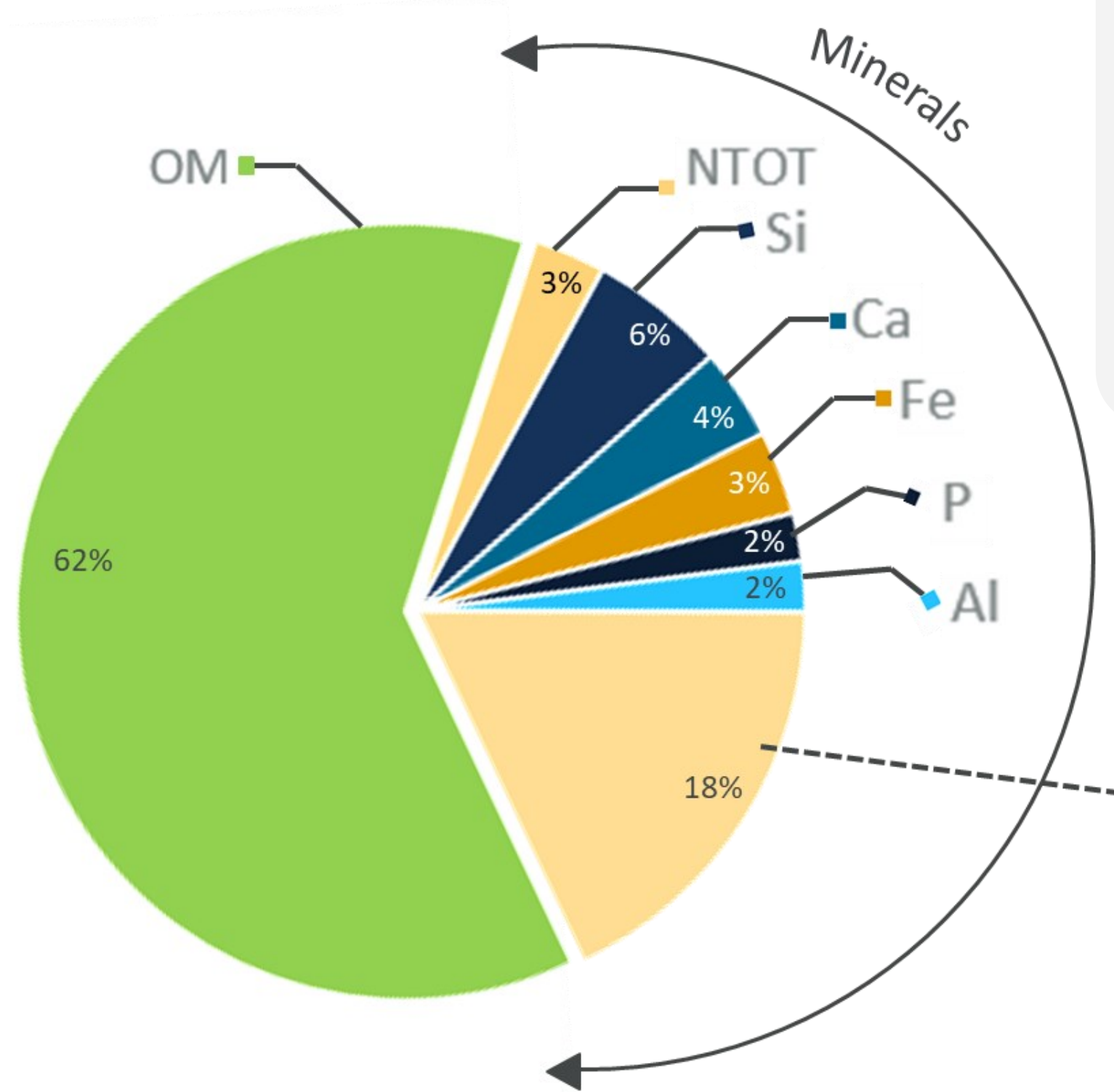
Purpose

- Definition of a solid organo-mineral assemblage representative of the matrix;
- Evaluate the impact of different scenarios on the release and speciation of pollutants into the matrix;
- Better predict the behavior of trace metals.



Experimental

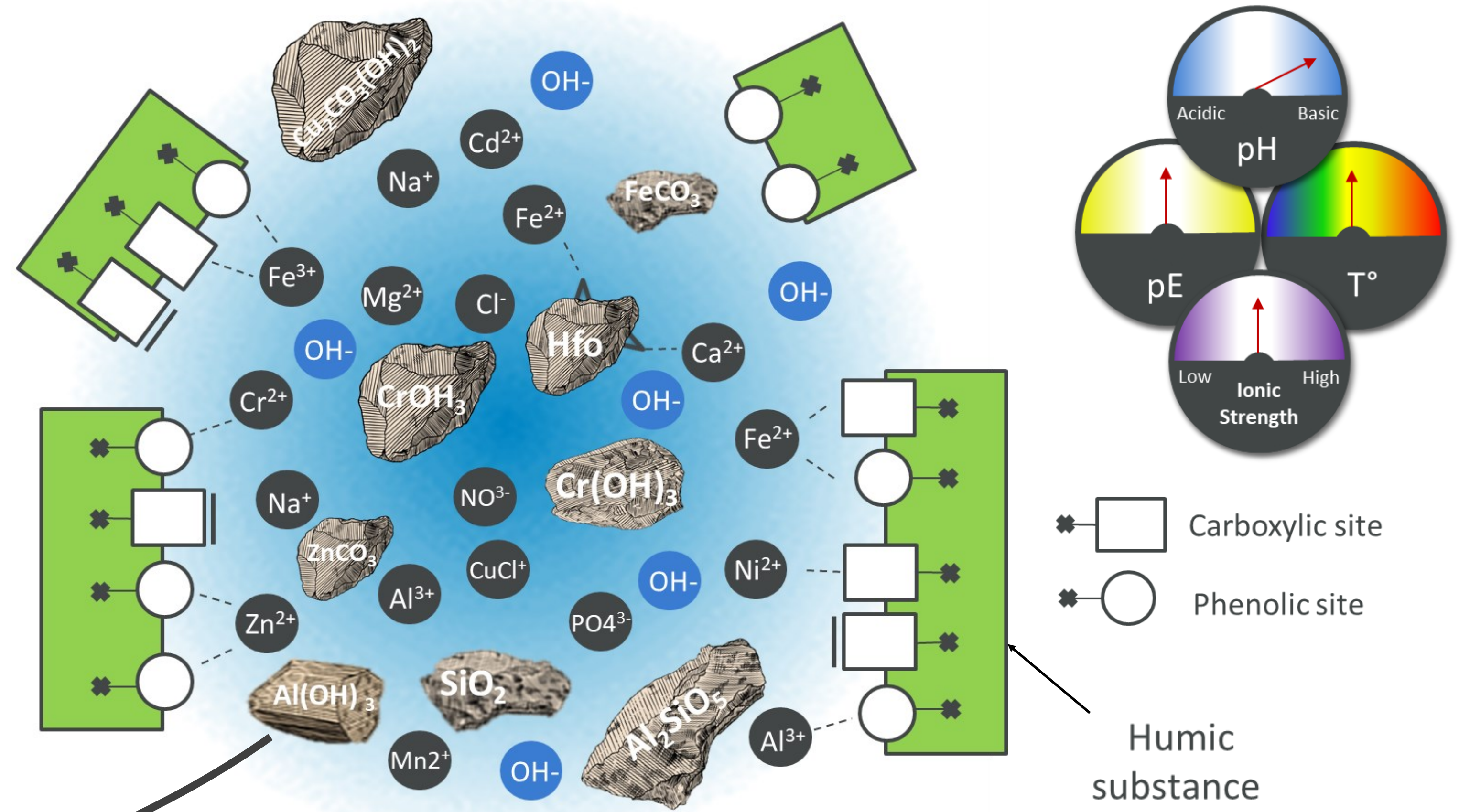
Results of elemental analysis



Others analysis :
 . Acid and Base neutralisation (CENTS/TS 14429)
 . Sequential extraction (method from Tessier et al., 1979)
 . X-Ray diffraction

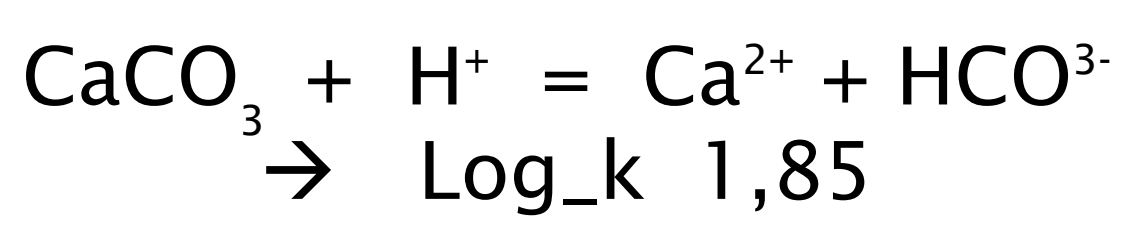
| Trace elements | Concentrations (mg/kgDM) | Thresholds limits (mg/kgDM) |
|----------------|--------------------------|-----------------------------|
| Zn | 1219 | 3000 |
| Cu | 623 | 1000 |
| Pb | 64.2 | 800 |
| Cr | 57.4 | 1000 |
| Ni | 30.5 | 200 |
| Cd | 1.7 | 20 |
| ... | | |

Conceptual model



Pure mineral phases

By their dissolution / precipitation properties, these phases will influence the concentration available in major elements but also in pollutant. The following example shows the CaCO₃ dissolution reaction :



Mineral assemblage

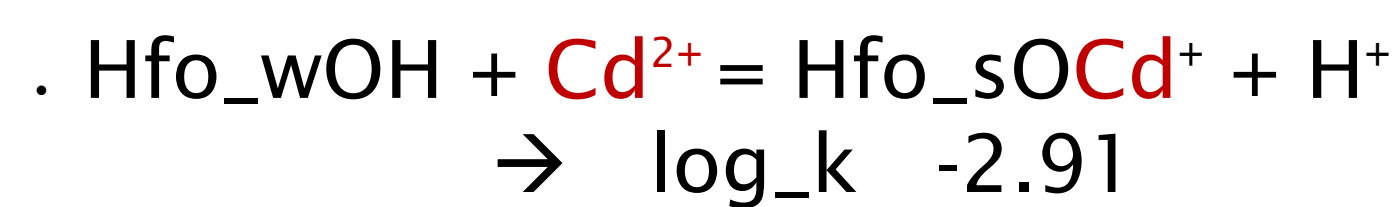
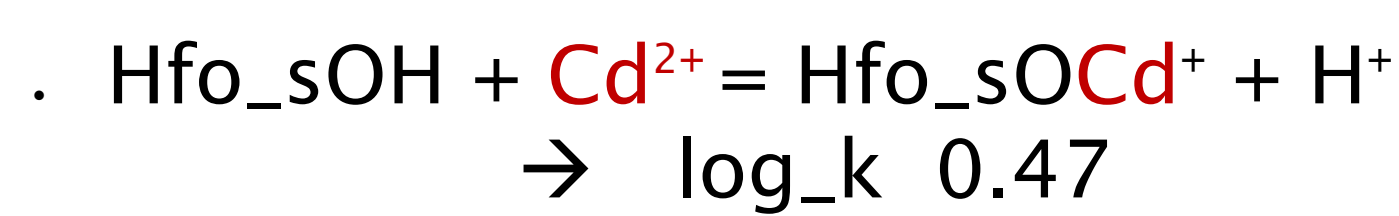
PhreeQc software (Parkhurst and Appelo, 1999) allows to simulate the dissolution of the different mineral phases implemented. For this, the software uses the thermodynamic data available in the database that has been specified. In our case, pure and mineral-bearing phases were implemented.

Electrostatic part

Depends on coulombic interactions that results from the **negative charge density** present on the molecule. Model VII considers that the charges of humic substances are located **only on the surface**.

Mineral-bearing phases

These matrices are also composed of mineral surfaces that can adsorb / release some pollutants through their binding sites. Example of Iron oxyhydroxides :

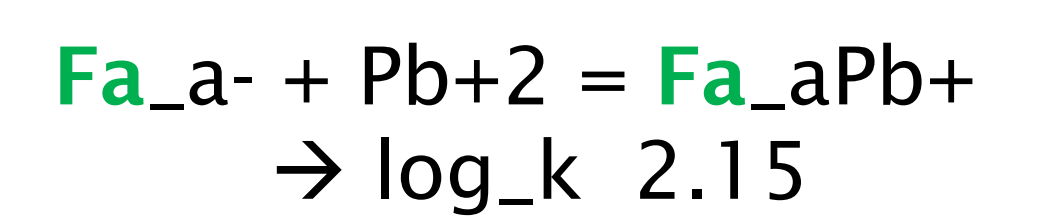


Organic assemblage

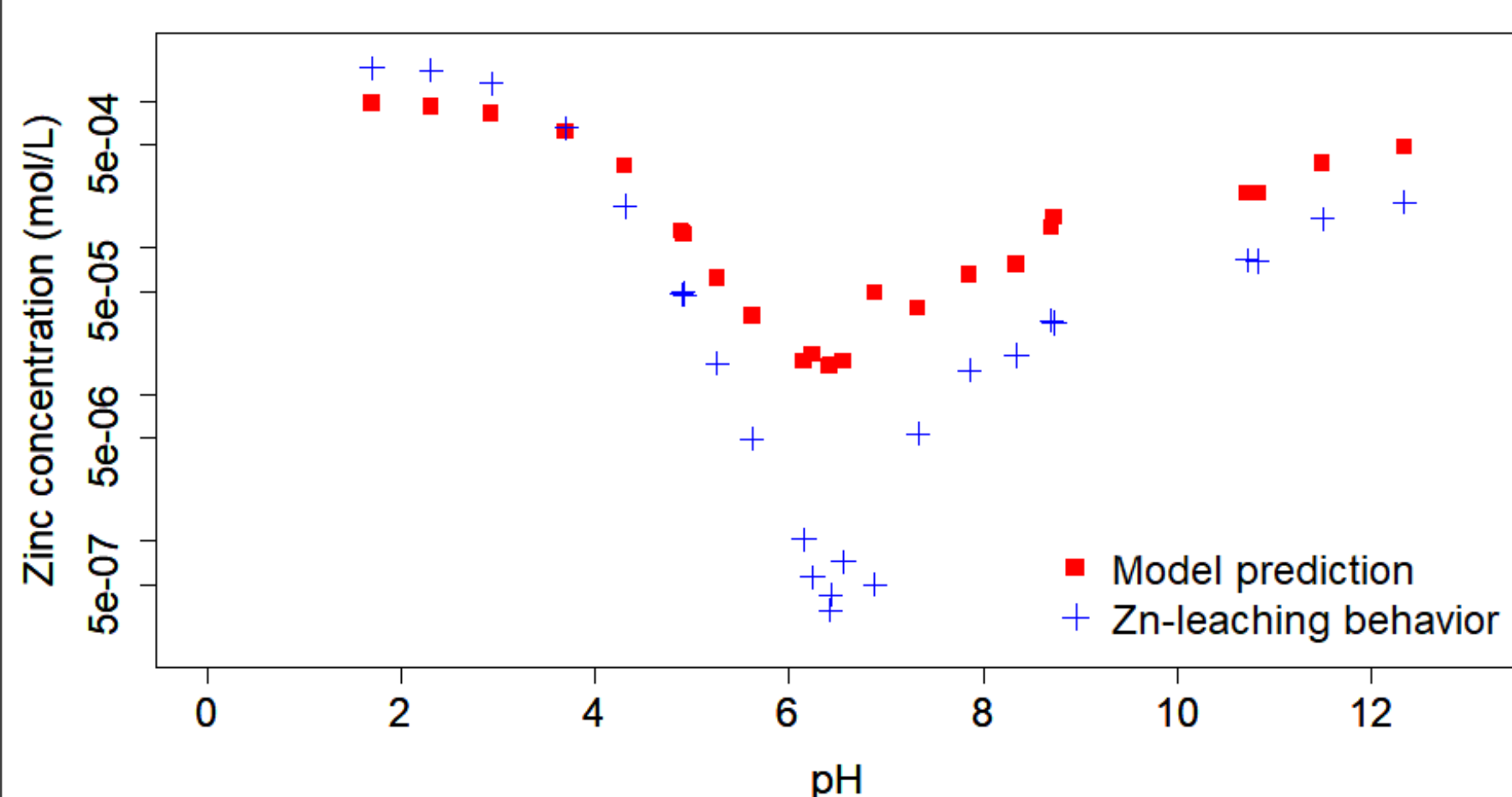
Model VII, developed by Tipping and its teams in 2011, is a database for simulating the adsorption capacity of humic substances (HS) via carboxylic and phenolic sites. The HS affinity for cations has two components: the **intrinsic part** and the **electrostatic part**.

Intrinsic part

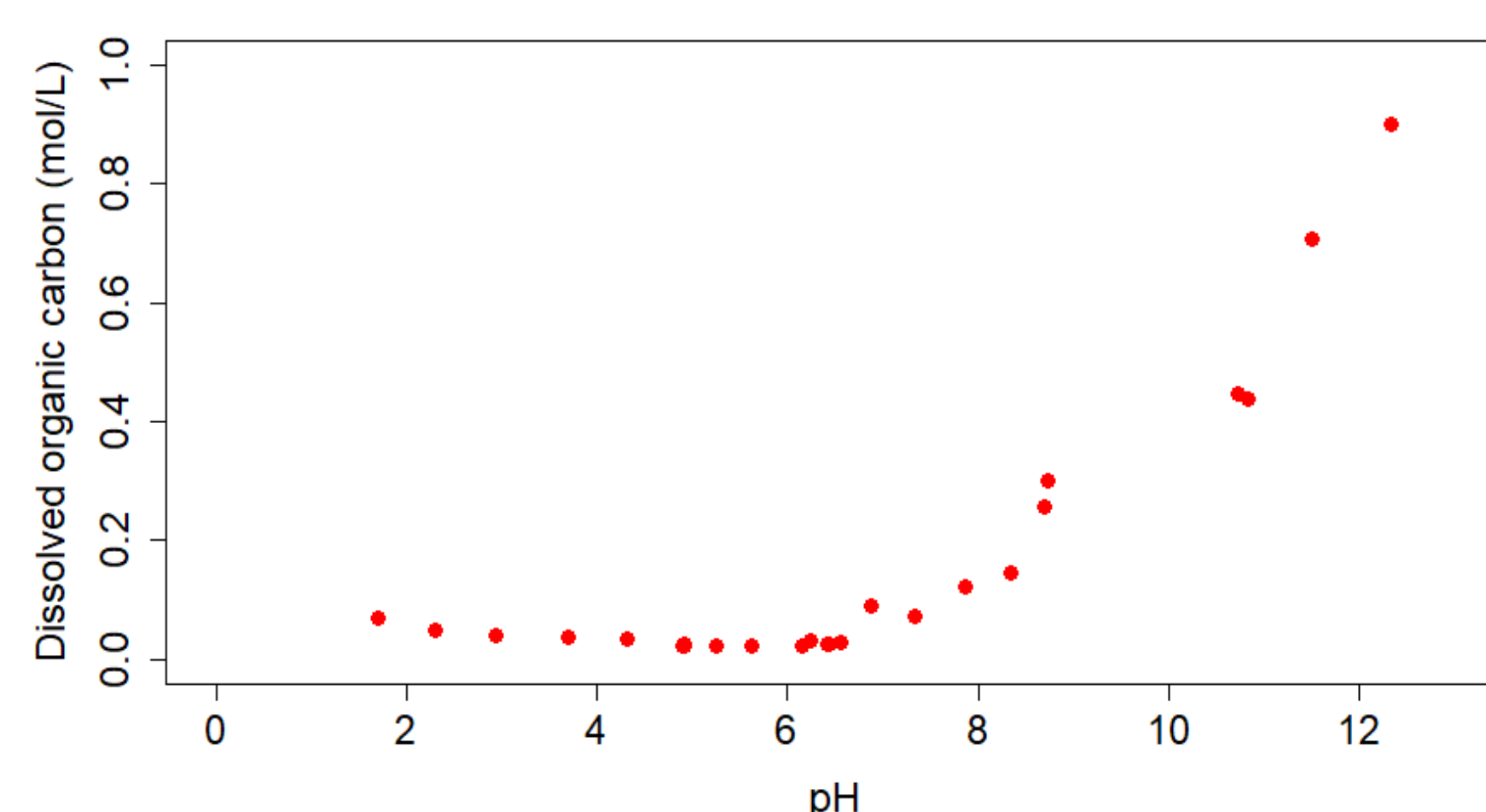
It takes into account the specific binding properties of humic substances. 50 different sites are specified including **mono, bi and tridentate** site. Example of binding of Lead with a **Fulvic acid** site :



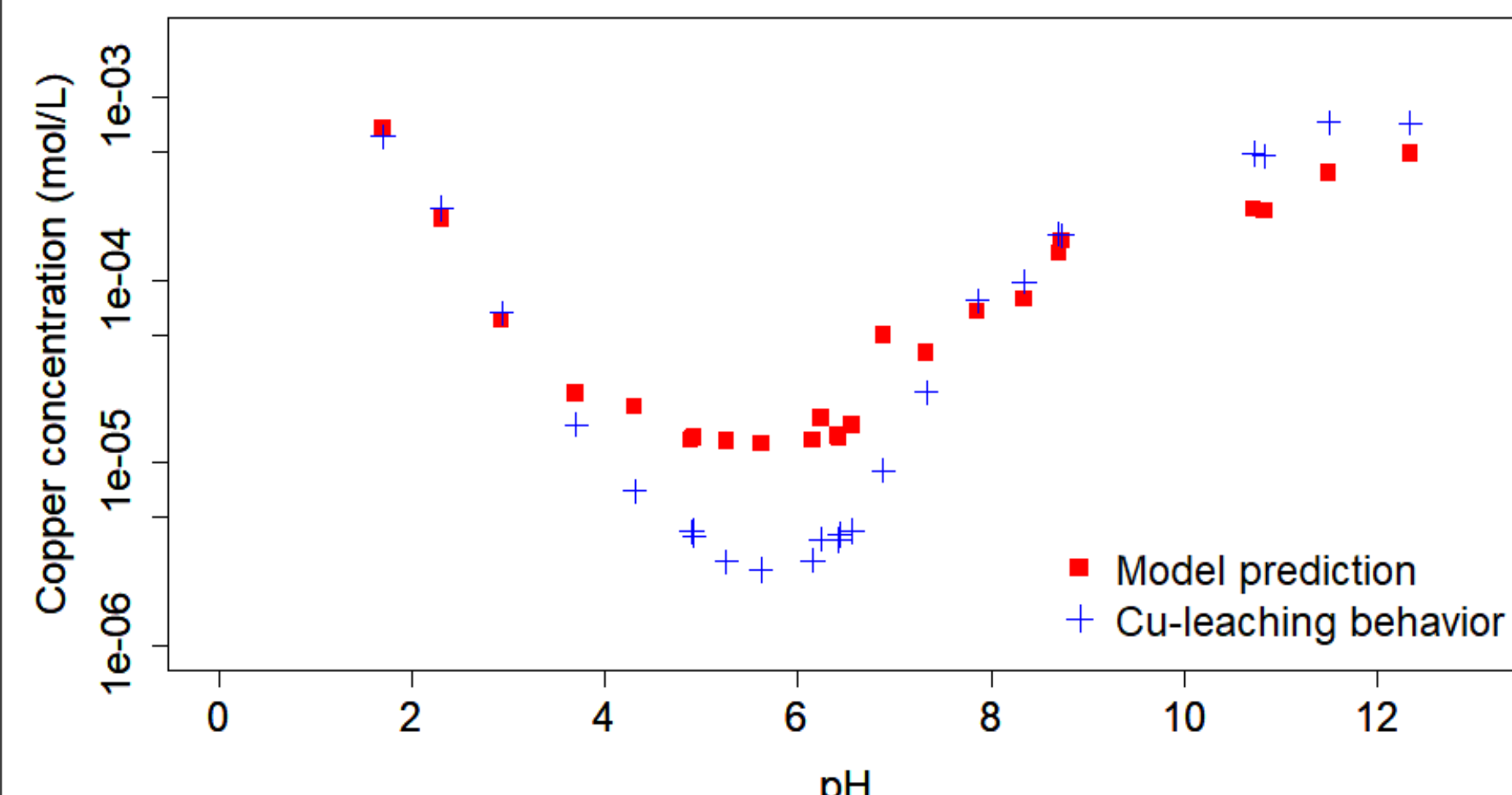
Evolution of Zn-leaching as a function of pH



Evolution dissolved organic carbon leaching concentration as a function of pH



Evolution of Cu-leaching as a function of pH



- . Importance of the sorption capacity of HS in basic solutions;
- . Copper is mainly related to HS;
- . Zinc is only partly bound to HS.

Results

Conclusions

- Combining PhreeQc and Model VII allows to reconstruct a complex organo mineral assemblage;
- The implementation of humic substances to the model provides good predictions of trace metals behavior ;
- Test on other type of matrices such as sediment from stormwater management pond.

References

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Kim, B., Gautier, M., Michel, P., & Gourdon, R. (2013). Physical-chemical characterization of sludge and granular materials from a vertical flow constructed wetland for municipal wastewater treatment. *Water Science and Technology*, 68(10), 2257-2263.

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