PEST-ORCHESTRA: A tool for optimizing NICA-Donnan model parameters for humic substances reactivity

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PEST-ORCHESTRA: A tool for optimizing NICA-Donnan model parameters for humic substances reactivity

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Introduction

The chemical speciation and solid-solution partitioning of trace metals are of key importance to their bioavailability and environmental fate. Mechanistic assemblage or multisurface models, which combine separate models for metal binding to reactive soil or sediment constituents, have been successfully applied to describe trace metal partitioning in soils and surface waters. These models are implemented in various model platforms, i.e., ECOSAT, Visual MINTEQ, PHREEQC, WHAM 7.0 or ORCHESTRA. Among these, ORCHESTRA has certain advantages. It is free and independent of the operating system (Microsoft-Windows, OS-X (Mac) or LINUX), but most importantly, its model definitions are in text format and thereby accessible by users for extensions and modifications. However, up to date, no parameters fitting abilities are available with ORCHESTRA .

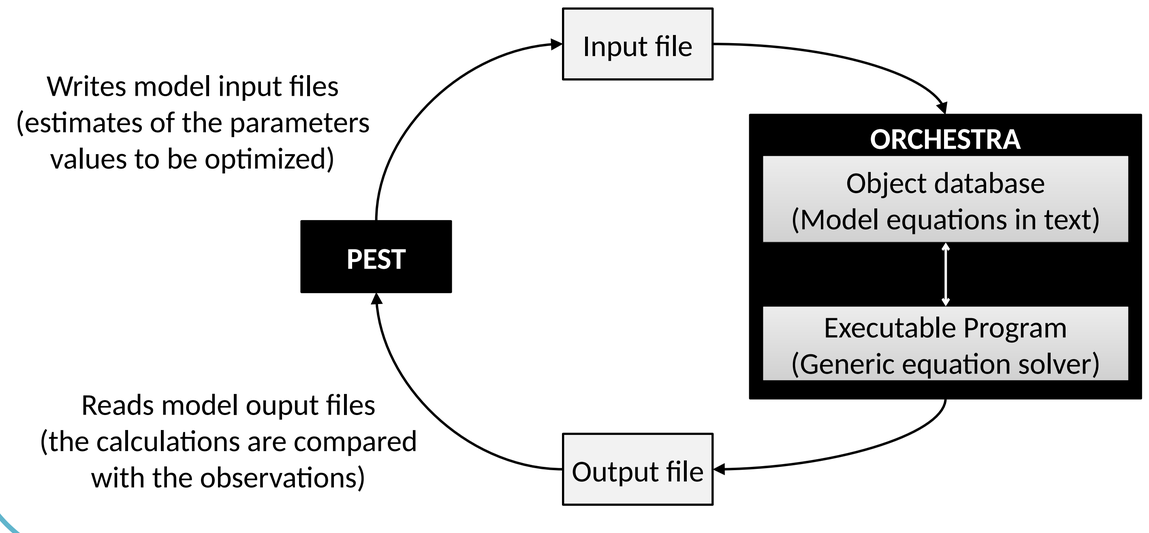
Here, we describe the combination of ORCHESTRA with the parameter estimation software PEST (www.pesthomepage.org) to derive optimized model parameters for proton- and metal-binding to a fulvic acid.

Objectives

1. Validate PEST-ORCHESTRA as a reliable tool to optimize model parameters to describe proton- and metal- binding to humic substances.
2. Determine a more constrained procedure to derive coherent NICA-Donnan parameters.
3. Use this procedure to determine metal-binding parameters for Laurentian Fulvic Acid (LFA).

PEST-ORCHESTRA framework

- Communication organized via the input and output files of ORCHESTRA(1).
- Several iteration cycles, repeated until the difference between the parameter values of successive iterations is smaller than a user-defined criterion.
- Goodness of fit quantified by the sum of the squared residuals, which is to be minimized.



The NICA-Donnan model(2)

- Non-Ideal Competitive Adsorption (NICA): competitive binding of protons and metal cations to humic substances
- Donnan equilibrium model: non-specific electrostatic interactions.
- For a component *i* with solution concentration c_i (mol/L), its amount bound Q_i (mol/L) is given by:

Carboxylic sites (sites 1) | Phenolic sites (sites 2)

$$Q_i = \frac{n_{i,1}}{n_{H,1}} Q_{\max,1} \frac{(\tilde{K}_{i,1}\, c_{i,D})^{n_{i,1}}}{\sum_i (\tilde{K}_{i,1}\, c_{i,D})^{n_{i,1}}} \times \frac{\left[\sum_i (\tilde{K}_{i,1} c_{i,D})^{n_{1i}}\right]^{p1}}{1+\left[\sum_i (\tilde{K}_{i,1} c_{i,D})^{n_{i,1}}\right]^{p1}} + \frac{n_{i,2}}{n_{H,2}} Q_{\max,2} \frac{(\tilde{K}_{i,2}\, c_{i,D})^{n_{i,2}}}{\sum_i (\tilde{K}_{i,2}\, c_{i,D})^{n_{i,2}}} \times \frac{\left[\sum_i (\tilde{K}_{i,2} c_{i,D})^{n_{i,2}}\right]^{p2}}{1+\left[\sum_i (\tilde{K}_{i,2} c_{i,D})^{n_{i,2}}\right]^{p2}}$$

Site density | Median affinity | Stoichiometry factor | Ligand heterogeneity | HS-specific | ion-specific

- Charge of the particle Q is balanced by ions concentrations in the Donnan gel $c_{D,i}$: $Q + V_D\left(\sum z_i * c_{D,i}\right) = 0$
- Donnan volume V_D depends on ionic strength *I* following an empirical relation:

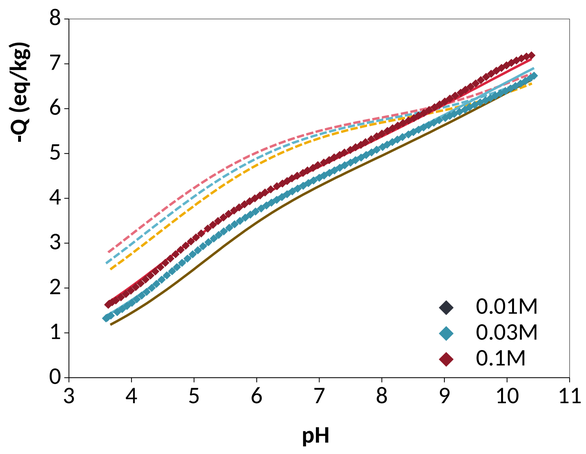
$$\log V_D = \alpha + \beta \log I \quad (3) \qquad \text{later simplified as} \qquad \log V_D = b(1 - (2)\log I) - 1 \quad (2)$$

- *7 or 8 parameters to optimize, depending on the electrostatic equation used*

Determination of proton-binding parameters

Dataset

- Potentiometric titrations of LFA at three ionic strengths(4)
- Part of database used to determine generic proton-binding parameters to fulvic acids(5)
- Milne et al.(5): unconstrained optimization using ECOSAT-FIT software.



***LFA titration results**. Symbols are experimental data, and lines are fits, using generic parameters (dashed) and optimized ones (plain).*

Procedure	Milne et al.(5)	Un-constrained	Un-constrained	2-step
b	0.32	0.35±0.02	-	-
α	-	-	0.88±0.19	0.93±0.20
β	-	-	-0.28±0.04	-0.27±0.05
$Q_{max,1}$	2.64	2.82±1.23	3.01±1.61	5.05±0.02
$logK_{H,1}$	2.43	2.47±0.17	3.82±0.19	4.11±0.11
m_1	0.65	0.62±0.17	0.57±0.18	0.41±0.01
$Q_{max,2}$	7.77	7.43±2.47	7.06±3.37	2.81±0.04
$logK_{H,2}$	7.30	7.38±0.68	8.83±0.62	8.64±0.13
m_2	0.17	0.18±0.06	0.19±0.09	0.46±0.02
RMSE	*0.069*	*0.067*	*0.064*	*0.070*
r^2	*0.9983*	*0.9983*	*0.9985*	*0.9982*

- Goodness of fit similar with all procedure used

✓ Good agreement:
Validation of PEST-ORCHESTRA tool

Influence of the electrostatic model

- No influence on Q_{max} or m values
- Considerable influence on $logK_H$
- $logK_{H,1}$ values obtained with the original equation in better agreement with other models (Model VI, Stockholm Humic Model) and more realistic for carboxylic groups

***LFA Donnan volumes (L/kg)**, depending on I and electrostatic equation.*

Procedure	I (M)		
	0.01	0.03	0.1
Unconstrained (b)	1.1	0.8	0.5
Unconstrained (α, β)	27.5	20.2	14.5
Viscometric data	6.0	-	6.0

- Donnan model poorly represents physical phenomena observed for fulvic acids

Influence of the optimization procedure

- Unconstrained procedure: fit 8 parameters together
- 2-step procedure:
  1. Optimization of Q_{max} values, using apparent $logK_H$
  2. Optimization of 6 other parameters together

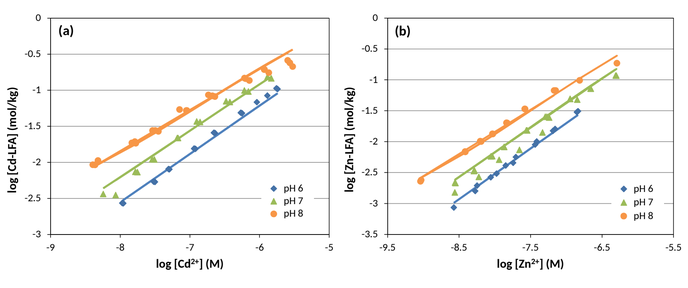
- Different amount of binding sites ($Q_{max,1}$ + $Q_{max,2}$)
- Different proportion of sites 1 vs. sites 2
- Illustrate the high correlation between parameters

Determination of metal-binding parameters

Experimental details

- Cd(II) and Zn(II) titrations of LFA.
- Free metal ion determination using electro-analytical AGNES technique(6).
- Optimization of the amount of metal bound to LFA.
- Fix $Q_{max,i}$, $logK_{H,i}$, α and β parameters from the 2-step optimization procedure.

Results



	Site 1	Site 2
p	0.77 ± 0.09	0.46 ± 0.86
n_H	0.53 ± 0.07	0.97 ± 1.61
$logK_{Cd}$	0.88 ± 0.23	4.56 ± 29.7
n_{Cd}	0.67 ± 0.06	0.14 ± 0.83
$logK_{Zn}$	1.73 ± 0.22	2.30 ± 18.5
n_{Zn}	0.82 ± 0.06	0.20 ± 1.10

Conclusions

✓ Validation of PEST-ORCHESTRA as a tool to determine NICA-Donnan model parameters for proton and metal binding to humic substances

- Extend the evaluation of the optimization procedure to a larger set of data
- Need a more physically realistic approach for description of electrostatic effects in fulvic acids
- Develop multisurface models including mineral surfaces

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