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Modelling protocols for derivation of Fe(III) NICA constants and calculations of ambient Fe speciation and apparent Fe(III) solubility in seawater

Kechen Zhu[1], Jan E. Groenenberg[2], Eric P. Achterberg[1], Martha Gledhill[1]

[1]GEOMAR Helmholtz Center for Ocean Research Kiel, Wischhofstr. 1-3, 24148 Kiel, Germany; [2]Wageningen University, Department of Environmental Sciences, PO Box 47, 6700 AA Wageningen, The Netherlands

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Kechen Zhu
GEOMAR, Helmholtz Centre for Ocean Research Kiel

ABSTRACT

Calculations of iron (Fe) speciation using the NICA-Donnan model can be useful for development of an understanding of the physico-chemical parameters (e.g. temperature, pH) that can influence Fe speciation in seawater (Hiemstra and van Riemsdjik. 2006; Gledhill et al. 2015; Avendano et al. 2016). Here we archive a protocol that can be used to calculate Fe speciation in seawater and derive new NICA constants for Fe binding to marine DOM, in combination with appropriately designed titration experiments. Importantly, for derivation of NICA constants, a pH dimension of sufficient resolution and breadth must be included in the experimental design. The protocol combines the chemical software ORCHESTRA with parameter estimation program PEST and was first described by (Janot et al. 2017) to successfully derive NICA constants for Cd and Zn binding to standard Laurentian Fulvic acid.

ATTACHMENTS

PEST-ORCHESTRA.zip

DOI

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PROTOCOL CITATION

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KEYWORDS

Trace metal, humic substance, PEST, ORCHESTRA, biogeochemical cycling

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LAST MODIFIED

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PROTOCOL INTEGER ID

46204

GUIDELINES

All necessary information written in the Manual and the original source code for this protocol are provided in the attachment.

References:

1. Janot, N., Pinheiro, J.P., Botero, W.G., Meeussen, J.C.L., Groenenberg, J.E., 2017. PEST-ORCHESTRA, a tool for optimising advanced ion-binding model parameters: Derivation of NICA-Donnan model parameters for humic substances reactivity. Environ. Chem. 14, 31–38. https://doi.org/10.1071/EN16039

2. Meeussen, J.C.L., 2003. Orchestra: An object-oriented framework for implementing chemical equilibrium models. Environ. Sci. Technol. 37, 1175–1182. https://doi.org/10.1021/es025597s

3. Doherty, J., 2019. PEST, Model-Independent Parameter Estimation, User Manual Part I.

SAFETY WARNINGS

Always check the constants in the Minteq4 data base for your chemical reactions of interest.

An important caveat with respect to the calculations in ORCHESTRA is that the applied ion pairing model uses the extended Davies equation to correct for ionic strength. The Davies equation is only valid up to an ionic strength of ca. 0.5 and is therefore not

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really appropriate for seawater. Seawater ionic strength corrections are best performed using Pitzer equations but at the time of writing (Jan 2021) there is no user-friendly way to interface Pitzer models with binding by organic matter.
The results are therefore biased in terms of absolute concentrations of metal species and results should be interpreted with this in mind.

BEFORE STARTING

1. The Java program must be installed on your computer.

2. Calculations via chemical speciation software ORCHESTRA can be performed on Windows, Linux and Apple OSX, but the combination of PEST-ORCHESTRA can only be performed using Windows. We have only applied the software in Windows and the manual we have written is thus relevant to Windows and may not be applicable to use on Apple OSX or Linux.

The application of PEST-ORCHESTRA to the estimation of NICA-Donnan parameters in seawater

1 Install chemical speciation software ORCHESTRA and parameter estimation program PEST

ORCHESTRA 2020
by Hans Meeussen

PEST: Model-Independent Parameter Estimation and Uncertainty Ana version 17.1 of
by John Doherty

2 Set up the calculation in ORCHESTRA

Please check the manual in the attachment.

3 Test the calculation in ORCHESTRA

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4 Set up the combination of PEST-ORCHESTRA

Please check the Manual in the attachment.

5 Derive NICA constants for Fe binding to marine dissolved organic matter

Please check example files in the attachment.

6 Check the results for optimization of Fe(III) NICA constants

Please check the manual in the attachment.

Calculations of ambient Fe speciation and apparent Fe(III) solubility using the NICA-Donnan model in seawater

7 Calculations of ambient Fe speciation via ORCHESTRA

An example calculation with original source code is provided in the attachment.

8 Calculations of apparent Fe(III) solubility via ORCHESTRA

An example calculation within original source code is provided in the attachment.

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