SEP 21, 2023

Protocol status: Working
We use this protocol and it's working

Created: Sep 07, 2023

Last Modified: Sep 21, 2023

🌐 Estimation uncertainty in calculations of apparent iron solubility in seawater

Kechen Zhu[1,2], Mark James Hopwood[1], Martha Gledhill[2]

[1]Southern university of Science and Technology;
[2]GEOMAR Helmholtz Centre for Ocean Research Kiel

Kechen Zhu
GEOMAR

ABSTRACT

The apparent iron (Fe) solubility ($SFe(III)_{app}$) was calculated via an ion paring-organic matter (NICA-Donnan) model at ambient pH, temperature and dissolved organic carbon (DOC). It suggests vertical distributions of dissolved Fe (DFe) were likely a function of $SFe(III)_{app}$ with changes driven by pH, temperature and DOC, in addition to non-equilibrium processes such as scavenging and redox cycling. It is necessary to constrain the uncertainty in the calculations that result from uncertainties in model parameters, since few sets of model parameters describing the acid-base properties of marine dissolved organic matter (DOM). Here we proposed an efficient methodology by ORCHESTRA-PEST++ to conduct both uncertainty and sensitivity analysis.

ATTACHMENTS

Zhu et al., submitted to Marine Chemistry.zip

Work flow of ORCHESTRA-PEST++ to conduct uncertainty and sensitivity analysis.pptx

GUIDELINES

All necessary information shown in attached ppt and the original source code for this protocol are provided in the attachment. Before any test, please carefully read the attached ppt document, as well as manual of PEST, PEST++ and ORCHESTRA.

SAFETY WARNINGS

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

Run the speciation code ORCHESTRA in parallel with code PES...

1   Set up *calculations of iron speciation and solubility* in seawater via the speciation code *ORCHESTRA*.

1.1   Please see details in our earlier protocol, 'Modelling protocols for derivation of Fe(III) NICA constants and calculations of ambient Fe speciation and apparent Fe(III) solubility in seawater' (DOI: dx.doi.org/10.17504/protocols.io.brc4m2yw).

2   In the *same sub-folder* of ORCHESTRA, write the code for *combining PEST++ to ORCHESTRA* and run the loop.

2.1   Please see details in earlier protocol (DOI: dx.doi.org/10.17504/protocols.io.brc4m2yw), or the manual of PEST++ and PEST.

Uncertainty analysis of apparent iron solubility via ORCHESTR...

3   *The uncertainty for this work* is considered as the results of *uncertainties in derivations of NICA Fe(III) constants* via comapring experimental data and modelling results, since few sets of model parameters describing the acid-base properties of marine dissolved organic matter. *Using a Monte Carlo-based uncertainty analysis method* to generate post-calibrated random sets of Fe(III) NICA constants to assess such uncertainties in calculated apparent iron solubility.

3.1   Both *PESTPP-IES and ORCHESTRA run in parallel*, to generate the post-calibrated random sets of Fe(III) NICA constants.
To date, the code *PESTPP-IES within PEST++*, based on the iterative ensemble smoother methodology, provides oppotunities to assess uncertainties in highly nonlinear model. Please

see details in the manual of PEST++, as well as the full script attached.

3.2   Both ***PESTPP-SWP with ORCHESTRA run in parallel***, to incorporate the post-calibrated random sets within ORCHESTRA and calculate apparent iron solubility.
To date, the results will be automatically summarized in one .csv file after the run finished.
Please see details in the manual of PEST++ and PEST, as well as the full script attached.

Sensitivity analysis of apparent iron solubility via ORCHESTRA...

4   ***The sensitivity for this work*** is mainly focused on ***the formation of ferrihydrite*** changing with temperature function. Therefore, ***using a Monte Carlo method*** to generate 1000 random sets of the solubility products, logks, as well as Fe(III) NICA constants to assess how seawater chemistry would affect iron speciation and solubility.

4.1   Both ***PESTPP-SEN and ORCHESTRA run in parallel***, to firstly generate 1000 random sets of the solubility products, logks, as well as Fe(III) NICA constants via a Monte Carlo method and then incorporate these random sets within ORCHESTRA to calculate the total sensitivity indices via a Sobol method.
Please see details in the manual of PEST++, as well as the full script attached.