Geosci. Model Dev. Discuss.,
https://doi.org/10.5194/gmd-2017-38-RC1, 2017

Geoscientific Model Development Discussions
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EGU

Interactive comment on "Particle Swarm Optimization for Surface complexation with the PHREEQC geochemical model" *by* Ramadan Abdelaziz et al.

Anonymous Referee #1

Received and published: 24 August 2017

This paper studies the applicability of coupling particle swarm optimization (PSO) to the geochemical PHREEQC code for estimating complexation constants, in this case the reaction of uranium compounds with quartz surfaces. The results are compared to previous estimations where the PEST algorithm was used. The manuscript is within the scope of this journal as this seems to be a new approach to the optimisation of surface complexation constants derived from experimental data. However, as various passages are not clearly written, it is only recommended for publication after major revision.

General comments include:

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The manuscript would greatly benefit from a short introduction to the principles of PSO in contrast to PEST, as one can assume that the average reader may not be familiar with these codes.

Much effort is put into the technical description of coupling hydroPSO to PHREEQC, e.g. what files are used and how they are formatted (if necessary at all, this could be described in an appendix) , but how the actual coupling (e.g. the fitting process itself) is done remains vague.

It is unclear what the fitting data are and under which assumptions (e.g. ES or NES model of complexation, presence or absence of alkaline earth elements in solution) the fits are done.

Be consistent with citing:

Text: Author (year)

In brackets: (Author 1, year 1; Author 2, year 2;. . .)

Specific comments:

l. 1: The title is misleading. Surface complexation itself cannot be optimised (only the model). Suggest something like “Particle swarm optimization for the estimation of surface complexation constants with the geochemical model PHREEQC<version>”

l. 18: Specify what the acronym PEST means.

l. 35: what does “multi-objective” mean in this context?

l. 53: Need to include that parameter estimations will be compared to PEST. This may also be the right place to give a short introduction to the principles of PEST vs. PSO.

l. 58: This is unclear. Do you mean “databases were modified by adding complexation constants for (. . .) species”? Are these species (and the corresponding alkaline earth ions) constituents of your aqueous model solution?

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l. 60: Define “SCM” here instead of line 62.

l. 65/66: Rephrase sentence with something like “A group of reactions of aqueous species from the bulk solution with the surface of the sorbent leads to the formation of surface complexes. The constants for these reactions (surface complexation constants, log K) are indispensable for SCM”.

l. 67: Unclear what “site-specific” and “transferable” means.

l. 75-77: This passage is not clearly written. Do you mean that the quartz surface is considered to have only one type of binding site? And certainly the database does not determine the reactions that take place (only the reactions and species you may consider in your model).

l. 78ff.: Please rewrite passage. It is not clearly described what the experimental conditions are (e.g. are alkaline metal ions present or not ?) and which assumptions (e.g. sorption model and PHREEQC parameters used for complexation modelling) are made for parameter estimation. Please state clearly whether the experimental conditions and the PHREEQC modelling assumptions were the same during the PEST optimisation. For instance, in Nair et al. (2014), ES and NES models are used; here you refer to the GTLM model generally, so what is compared to what?

l. 91: From the given reference it cannot be seen what the parameter ranges mean and how they come about. Do the minima and maxima constitute the parameter space for the particle swarm? Have they been chosen arbitrarily?

l. 92: The caption is a bit confusing. Suggest something like “Complexation reactions with their respective log K range values”. Change the table headings accordingly (the first column is not the name of the parameter but the corresponding reaction). The “calibrated parameters” are results and should be omitted here. They should be presented in the results section alongside the corresponding values from the PEST study. As to the ID, please use capital K throughout the text!

l. 98: Do you have references for the successful application of hydroPSO to hydrogeological and hydrological models?

l. 100 – 118: For my taste, this is too technical to be included in this place. Suggest to move this and Figure 1 to an appendix, if necessary at all. Instead, a more detailed description of the interaction of hydroPSO and PHREEQC would be appropriate here, especially how the individual "particles" are initially located in the parameter space and what the individual iterations are. A flow chart for this may be helpful. What is the difference in applying PEST, especially the required number of iterations?

l. 123: Here and in eq. (1) it is not defined what the model output and the observed values are. Presumably the C_iˆO are the observed U-carbonate concentrations at 6 different pH-values and the C_iˆS are the respective simulated concentrations. This should be stated somewhere.

l. 124: "iteration step", not "time step". If the presumption in comment l. 123 is correct, the index i in eq. (1) cannot be equal to the iteration step index, so please use a different index, e.g. j.

l. 129 f.: I downloaded the supplementary material and tried to run the batch file but obviously the input file is missing.

l. 134 f.: Remove sentence "It is clear. . .". Change next sentence into something like "The coefficient of determination (R2) for the relation between calculated and observed values is 0.89, indicating a high linear correlation and thus high model quality".

l. 138: It is unclear how the remaining iterations were performed. What does "placed" mean in this context?

l. 146f.: I do not agree that the figure shows the global optimum, because this is the place in parameter space the algorithm wants to approximate. What you probably mean is the RSS.

l. 148f.: Please explain the criteria for convergence. What is the "optimum value" and

at which iteration was it reached? Is there any stop criterion for δ_norm (or rather $\Delta\delta$_norm ?) and/or RSS (ΔRSS)?

l. 153: Quartiles of the distribution densities of log Kj?

l. 156: Do you mean “total number of iterations”?

l. 158: The vertical axes of the box plots should be denoted by log K1 . . . log K6 and not by RSS.

l. 158: What do these plots show in addition to Figure 7 and how relevant is this?

l. 163: Not sure whether equifinality is the suitable concept here. As far as I know, the term is used if fundamentally different sets of parameters lead to comparable results. In this case, the identification of parameter ranges is a kind of uncertainty estimation. By the way, a correct citation would be Beven (2006), as the term “equifinality” does not appear in the cited paper.

l. 171 (Legend of Figure 5): SSR ranges. Check brackets (round or angular). Suggest using scientific notation and two significant digits throughout .

l. 175: Do you mean “showing a small uncertainty range”? The standard deviation can only be defined if the underlying distribution is known (which is obviously not the case).

l. 176 f.: This sentence is unclear. The small uncertainty range has been mentioned before.

l. 183: What do you mean by “near-normal”? Did you perform a normality (e.g. KS or Lilliefors) test?

l. 187: The red line is not discernible in my printout. Please check. Also, the axes should be denoted by log Kj and not Kj .

l. 188: What are the widths of the bars? It is not quite clear what “frequency” means. Is the integral the total number of iterations? If so, normalizing the frequency to this

number may be more appropriate.

l. 190 ff.: Not sure whether this kind of representation is necessary. The plots in the lower left half are basically the same as in Figure 5. The diagonal elements do not provide new information, either. What are the red lines? Why do the numbers have different font sizes? - Suggest simply showing the formal correlation (or covariance) matrix ("formal" because the underlying distributions are in most cases non-normal, see e.g. Press et al. "Numerical Recipes in C", 1992, Sect. 15. 6, p. 695). Also change the caption of Figure 8 as well as the corresponding text accordingly and discuss the correlations between parameters qualitatively.

l. 198: Not sure whether p values are meaningful here, remembering this is only a formal correlation matrix.

l. 201: (Figure 9) Please give uncertainties for the experimental values. The connecting lines between the simulation results do not add any information and should be omitted.

l. 203: Do you mean the reactions in Tab. 1? There is only one equation in this paper.

l. 204: I am not sure what the meaning of "important in optimizing" is. Do you mean some weighting function should be applied in the optimisation process?

l. 205: I do not quite agree what the most dominant sorbed species are. As this is clear for parameters K1 and K2 as their log K is very high, one can see from Figure 7, that log K5 is substantially higher than log K4 , thus sorption of (UO2)2CO3(OH)32- is preferred to sorption of UO2OH+.

l. 206 ff.: Again this is confusing (see comment l. 78 ff.). Do you refer to Nair et al. (2014)? If so, did you run the PHREEQC model with and without the –noedl option in the SURFACE definition? How was SURFACE defined in the present model (the input file is missing in the supplementary material)? So this section is not informative if it is not specified what is compared.

l. 211 f.: See last comment.

l. 212: change to: “. . .are better estimations than those obtained by PEST, except for pH=7.” Can you give a reason why this is different for pH=7 ? Is it possible that PSO did not find the global optimum but the Levenberg-Marquardt algorithm did?

l. 213: change to: “the parameter space as defined by the ranges given in Table 1”.

l. 223: One should be more cautious here. As is stated in l.36, PSO has never been used for estimating surface complexation constants before. So this is a first indication (not a confirmation) that this method could be a “robust tool” for this purpose. The discrepancy at pH=7 adds some doubts concerning robustness.

l. 227f.: If you compare the coefficients of determination, you also should also show the value for the PEST optimization and include the PEST results in Figure 2. But one should be cautious here, because a higher R2 does not necessarily show the model’s superiority because it does not tell you anything about statistical significance! For the comparison of models, tests (e.g. F-Test) are appropriate.

l. 233: what do you mean by “best fit”?

Technical comments:

l. 4: Country is missing.

l.19: Remove citation.

l. 24: The particle swarm. . ..

l. 27: . . .shares a few. . .. GA have. . .

l. 35: . . .derive rainfall runoff. . .

l. 36: Notwithstanding recent popularity, PSO has never been. . .

l. 48: . . .are available. . .

l. 52: Suggest “suitability” instead of “versatility”.

l. 55: In l. 53, the version number is 3.1.2 !

l. 55: Delete “is used the sorption by and”. Insert comma.

l. 57: . . .are used for sorption modelling.

l. 59: Delete “model”.

l. 62: . . .simulate the sorption of metal species. . ..

l. 75: . . .which take the charge. . .

l. 79: . . .with respect to these species.

l. 80: The sorption (. . .) was investigated. . .. See also general comment 4.

l. 81: . . .complexes shows a significant impact on the sorption. . ..

l. 82: Use “absence” and “presence” instead of “existence” and “non-existence”, respectively.

l. 83: Check number of U concentration.

l. 90: Delete “however”.

l. 109-114: Be consistent in using past or present tense.

l. 122: . . .residual sum of squares (RSS). . . Please be consistent using RSS throughout the text

l. 128: Remove “finally”.

l. 134: . . .are compared in Figure 2.

l. 137: . . .reach the region of the global optimum.

l. 148: . . .population in the range. . .

l. 150: . . .a small region in parameter space.

l. 152: The boxplots in Figure 4 are graphical representations. . .

l. 154: Change the end of the sentence to ". . .within the box denotes the median of the distribution."

l. 155: Remove "finally"; replace "notches" by "whiskers".

l. 159: Caption: "Boxplots for the optimised parameters. The. . ."

l. 161: Suggest removing the first sentence as this has already been explained in l. 122f.

l. 162: Suggest something like: "They are suitable for identifying ranges where different sets of parameters lead to the same goodness of fit."

l. 167: Replace the contents of the brackets by "RSS".

l. 168/169: point density

l. 178: Suggest replacing "calibrated" by "optimised" throughout text.

l. 180: . . .the median. . .

l. 181: . . .depict the corresponding parameter value, displayed at the top. . .

l. 182: The vertical red line in Figure 7 points out. . . (delete "Figure 7" at end)

l. 215: . . .parameters that minimize . . . and . . .via the Gauss-. . ..

l. 226: sorption rates

l. 232 f.: remove hyphens

l. 249: Reference does not appear in text.

l. 251: Check title of article.

l.298: Should be listed before Huber et al. (2009).

l. 323: Reference does not appear in text.

l. 330: Reference does not appear in text.

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