

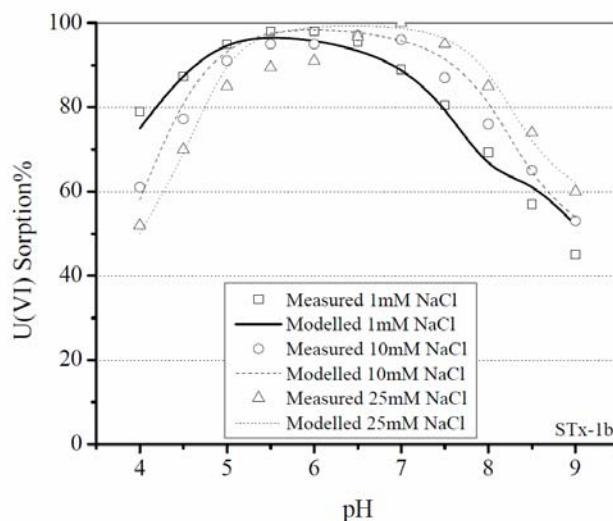
# FOG

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## Estimating Water Chemistry Parameters from Experimental Data Using PEST with PHREEQC

18 pages, 2 figure, 0 tables, 21 references

## Abstract

This note presents a method for estimating sorption constants from experimental data using the two computer programs PEST and PHREEQC. As geochemical case study, U(VI) sorption onto STx-1b montmorillonite as a function of pH (4 to 9) and ionic strength (0.001, 0.01, and 0.025 M NaCl) was investigated by conducting batch experiments for 24 hour under ambient atmosphere ( $P_{\text{CO}_2} = 10^{-3.5}$  bar). Advantages of this technique include estimation of uncertainties associated with estimated parameters, evaluation of information content of observations, statistical evaluation of the appropriateness of the conceptual model, and any number of parameters can be optimized (less, or equal to the number of observations).

## 1 Introduction

Chemical equilibrium constants can be calculated from laboratory data using different techniques, e.g., with graphical methods, by curve fitting, or with an optimization code such as FITEQL 4.0 (Herbelin&Westall 1999). These approaches, however, have certain drawbacks; for instance, comparison of different conceptual models is laborious and ultimately subjective and the uncertainties associated with the estimated parameters are difficult to quantify. In contrast, parameter estimation codes such as PEST (Doherty 2004) and UCODE\_2005 (Poeter et al. 2005) have the advantage that any number of parameters can be optimized (less, or equal to the number of observations) by using any numerical code in inverse mode. The only prerequisite for the numerical model is that it has the option to write calculated data in ASCII format. Using PEST or UCODE is very common with groundwater flow and transport modeling, but this approach can be employed as well for geochemical codes such as PHREEQC (Parkhurst&Appelo 1999), MINTEQA2 (Allison et al. 1991), and Geochemist's Workbench (Bethke 1996).

Only few attempts have been made so far by using PHREEQC and PEST. A modified version of PHREEQC was used by (Appelo et al. 1999) to estimate surface complexation constants. Similar approaches were used by the same author (Appelo&Postma 1999, Appelo et al. 2002, Appelo&Postma 2005). An example how to use PEST with PHREEQC to estimate surface complexation constants can be downloaded from [http://www.xs4all.nl/~appt/a&p/11/pest\\_lg.exe](http://www.xs4all.nl/~appt/a&p/11/pest_lg.exe). However, this example is related to an old version of PEST. PHREEQC and PEST was used as well to estimate cation exchange selectivity constants (Tournassat et al. 2009). Finally, the 1d transport option of PHREEQC was used for a reactive transport model of a landfill leachate plume using PEST to estimate concentrations of groundwater, kinetic rate constants for siderite and calcite precipitation, oxidation rates of DOC, cation exchange capacity, and total transport time (Van Breukelen et al. 2004). A similar complex 1d reactive transport model in the unsaturated was calibrated inversely with respect to mineral solubility,  $p\text{CO}_2$ , cation exchange coefficients and sorption parameters for Ni and Cd by using PEST and PHREEQC (Kerstin&Bernard 2005).

However, the above mentioned publications do not explain how PEST and PHREEQC works together. Therefore this note was written to describe how PEST (version 11.8) exchanges data with

PHREEQC (version 2.16.0) based on an example estimating chemical equilibrium constants for surface interactions between uranium(VI) species and surface sites of montmorillonite. Both PHREEQC (Windows Batch version) and PEST can be downloaded from [http://wwwbrr.cr.usgs.gov/projects/GWC\\_coupled/phreeqc/](http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/)

and <http://www.sspa.com/pest/downloads.shtml>, respectively. The goal of this note is to describe the method with sufficient details so that the reader can duplicate the procedure and adopt it for own problems. For further work a thorough reading of the PEST manual is recommended.

On contrary FITEQL 4.0 is a program to determine chemical equilibrium constants and in particular surface complexation constants from experimental data (titration experiments) according to the Diffuse Layer model, the Stern model, and the Triple Layer model. However, FITEQL 4.0 is not well suited for the requirements of the CD-MUSIC model of (Hiemstra&Van Riemsdijk 1996). Thus, the example given in this note dealing with a multisite surface complexation model can not be treated by FITEQL 4.0. This would, however, be possible by using a modified version of FITEQL which is available as download from <http://www.lwr.kth.se/forskningsprojekt/MoW/fiteql.htm>.

Another disadvantage of FITEQL is that the ionic strength correction is made in any case by using the DAVIES equation (the only option is to skip the ionic strength correction and thus calculate conditional constants) and an activity/ionic strength dummy component, while PHREEQC is based on a complete water analysis and offers more choices including Pitzer equation because the usage of a certain model in PHREEQC is controlled by the thermodynamic data set used. Finally, PEST delivers in contrast to FITEQL statistical information e.g. the sensitivity of observations and parameters while FITEQL uses the WSOS/DF (weighted sum of squares divides by degrees of freedom) as indicator of the goodness of the fit. But, it is beyond the scope of this note to compare the goodness of fit of PEST and FITEQL 4.0.

## 2 Geochemical Case Study

The expandable 2:1 clay mineral (montmorillonite) has been extensively used for removal of uranium(VI) from ground- and surface water (McKinley et al. 1995, Olguin et al. 1997, Chisholm-Brause et al. 2001, Bachmaf et al. 2008). We have previously examined the U(VI) sorption behavior onto STx-1b montmorillonite as a function of pH (4 to 9) and ionic strength (0.001, 0.01, and 0.025 M NaCl) by conducting batch experiments for 24 hour under ambient atmosphere ( $P_{CO_2} = 10^{-3.5}$  bar). After that the solution was separated from the solids by centrifugation and filtration and immediately analyzed for U(VI) concentration by inverse voltammetry or ICP-MS. Sorption of U(VI) species on montmorillonite was modeled by means of a multisite surface complexation model. In the following we are using a subset of our experimental data to describe how the non-linear optimization program PEST in combination with PHREEQC can estimate the intrinsic sorption constants.

### 3 Procedure

PHREEQC and PEST is executed stepwise in details in the following section, and all required files are included in the appendix.

#### 3.1 Installation of PEST and PHREEQC

First, the user has to create a new directory (e.g., C:\PEST), download PEST and unzip pest.zip to that directory. Second, the PEST directory has to be added to the PATH environmental variable (autoexec.bat) for old Windows versions. The equivalent of autoexec.bat in Windows NT is named autoexec.NT in the system folder Windows/system32. Using Windows 2000, XP, Vista, and Windows 7 the system environment variables has to be changed via My Computer / Properties Advanced / Environment Variables / Edit. Add the PEST path (e.g. c:/pest) separated with a semicolon.

Third, download the PHREEQC (Batchversion for Windows) and install the software. During the installation you may change the default folder (e.g. C:/PHREEQC) and you will be asked if you like to modify the PATH environment variable so that PHREEQC can be operated from any directory. Here you have to check the “yes” button. If you use the default folder you have to change the path for LLNL.dat in the pst.file (see appendix 2)

Finally create a work-file for your test case (e.g. C:/CASE). This folder has to contain the four PEST input files, which will be explained in the following section.

##### 3.1.1 Create a PHREEQC model.

For convenience it is likely that one will create the PHREEQC input files by using the PHREEQC for Windows of the PHREEQCI Graphical User Interface. Surfaces species are site-specific and have to be defined by the user. However, PHREEQC databases offer an example for iron hydroxides according to data from Dzombak and Morel, (Dzombak&Moral 1990) which may be taken as an example. In our case, the edge surface sites of aluminol (Edg\_al) and silanol (Edg\_si) were defined as surface species within the SURFACE\_MASTER\_SPECIES data block in the PHREEQC input file. The surface site density and the surface area are defined under SURFACE block. The interactions between the U(VI) species and the available surfaces are defined in the SURFACE\_SPECIES data block. Each interaction is associated with an equilibrium constant (log\_k) that is either known or will be estimated by PEST. In order to test the PHREEQC input file in a stand-alone run any log\_k values can be used at this stage. To facilitate the extraction of simulated data with PEST the percentage of U(VI) sorption is written in a selected output file using SELECTED\_OUTPUT and USER\_PUNCH.

### 3.2 Create the four PEST input files.

To run PEST 11.8 with PHREEQC, four files are needed:

1. a template file (filename.tpl)
2. a PEST control file (filename.pst)
3. an instruction file (filename.ins); and
4. a batch file to run PEST and PHREEQC (filename.bat,) in the DOS environment.

Example files with the name “case” are given in the electronic appendix. All PEST input files can be written using a general purpose text editor following the specifications given in this section and the PEST manual.

#### Template File (\*.tpl)

The template file is a modified PHREEQC input file into which PEST inserts trial values of the parameters to be estimated (eight parameters in our example); the template file differs from the PHREEQC input file only by

- the extension: tpl instead of phrq
- by adding a first line: ptf @ (some other signs instead of @ are possible as well)
- replacing those values for parameters (e.g. log\_k) to be estimated by PEST through @K<sub>N</sub> @ (N is a index for K: 1,2,3 ....)

After a successful run, PEST removes the first line and insert the estimated parameters in between the markers @ @ and write a standard PHREEQC input file; in the example template file (appendix 1), the log\_k @k1 @, to the . log\_k @k8 @ will be replaced after running with log\_k 7, log\_k -6, log\_k -0.1, log\_k -6, log\_k 5, log\_k 6.7, log\_k -5.6, and log\_k -0.1, which represent the optimized sorption constants. The number of spaces between the @ @ markers has to be sufficient for inserting the estimated value of the parameter by PEST.

#### PEST Control File (\*.pst)

The PEST control file controls the iteration process: it tells PEST which model(s) to execute, what parameter(s) to optimize, how to extract PHREEQC-simulated values, and what observations to compare them to. Lines beginning with # are comments and can be added, but, the # sign must not be used as trailer of a normal line, since this will end with an error from the parser, (this was possible with older PEST versions only). In our example, we have three observation groups for three Na<sup>+</sup> concentrations (0.001, 0.01, and 0.025 M NaCl). Other explanations for the control file are given in appendix 2. Since the sorption experiments were performed for three ionic strengths, three groups of data have to be used. Note that for high optimization efficiency, one has to choose an initial parameter value which is close to what one thinks will be the parameter’s optimized value. The initial parameter value must lie between the lower and upper bounds.

#### Instruction File (\*.ins)

The instruction file (appendix 3) informs PEST which values have to be extracted from the PHREEQC-selected output file, which is defined in the PHREEQC input file. Every observation for which data are supplied in the PEST control file must be listed in the instruction file. Conversely, every observation listed in the PEST instruction file has to be one line of data in the “observation data” section of the PEST control file.

#### Batch File (\*.bat)

Finally the batch file (appendix 4) runs PEST and tells PEST the common name of the 4 PEST files. The statements *@echo on* and *pause* are not mandatory but useful in case errors occur.

It is recommended to run the PHREEQC input file stand alone first to check for correctness as already mentioned above and to check the output file because PHREEQC generates output for each SOLUTION statement and not only the USE SOLUTION statement. One can take care for this by the first two signs in the instruction files: I1 means read line 1; I2 means read line 2 (the second line) and thus skip one line (see appendix 3). Note that PEST instruction file must not contain any comment lines.

### **3.3 Checking PEST’s Input Data.**

Before running PEST for a parameter estimation one should check for syntactical correctness and consistency using the utility programs PESTCHECK.exe and TEMPCHECK.exe.

### **3.4 Running PEST and PHREEQC.**

Once the PEST input files are created and checked for correctness, PEST and PHREEQC can be run via the batch file (case.bat, appendix 4).

New files will be created in the data folder with the extension \*.REC, \*.RES, \*.MTT, \*.SEN, \*.SEO (appendix 5). The outputfile \*.REC contains all information of the run, while \*.MTT provides statistic information (covariance matrix, correlation coefficient matrix, normalized Eigenvectors, and Eigenvalues). The file \*.RES provides measured and modeled data and the residuals. The files \*.SEN and \*.SEO contain parameter and observation sensitivity which are calculated from the Jacobian matrix (for details see PEST manual). Because parameters with low sensitivity are likely to cause problems during a parameter estimation run the sensitivity files are useful to eventually skip those critical parameters from further runs.

After a run is completed it is recommended to compare the PHREEQC values (selected PHREEQC output file) with the values that PEST extracts (main PEST output file). If the values are different, it is obvious that errors exist in the PEST input files. Measured and modeled data versus pH and ionic strength for the case study are plotted in Figure 1.

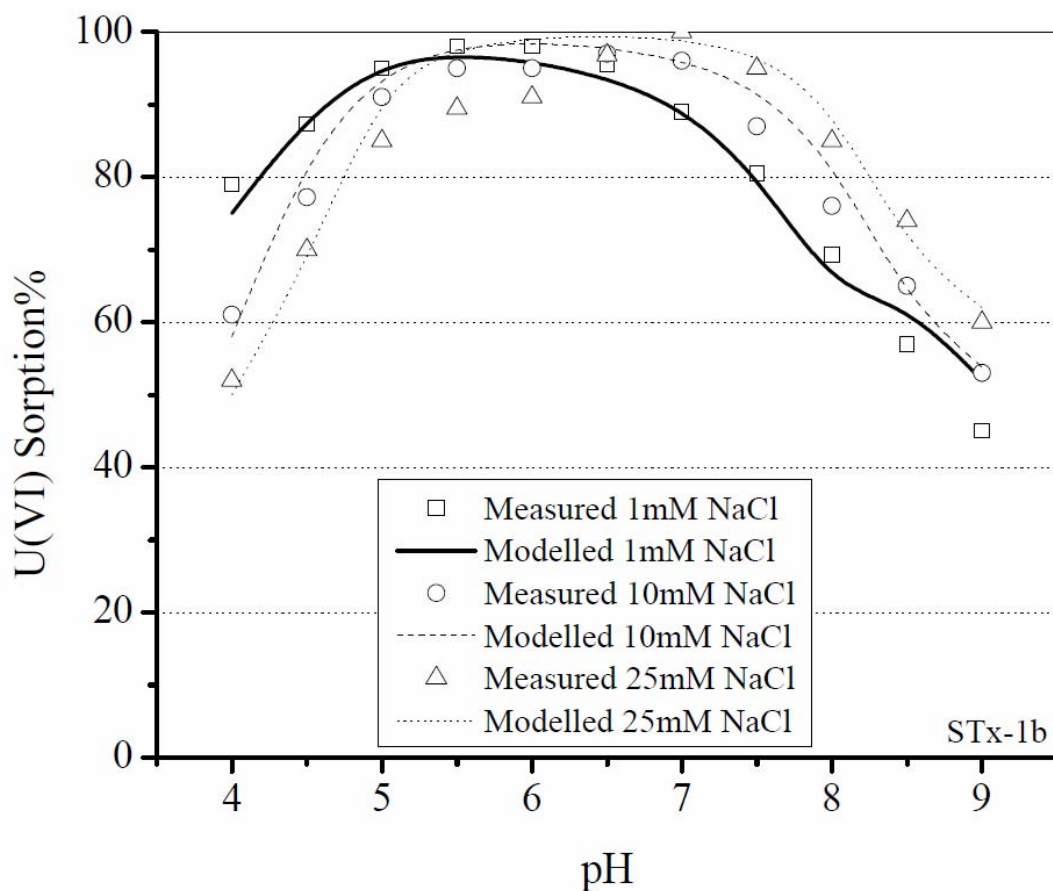


Figure 1. Model prediction of U(VI) adsorption on montmorillonite (STx-1b), using surface complexation model (SCM). Experimental conditions:  $\Sigma U=100 \mu g L^{-1}$ , suspension density =  $1.66 g L^{-1}$ ,  $P_{CO_2}=10^{-3.5}$  bar,  $25 \text{ }^\circ C$ ,  $I = 0.001, 0.01, \text{ and } 0.025 M$ , reaction time = 24 h. The lines present the sum of individual U(VI) surface species, whereas scatters present the measured data.

### 3.5 Conclusion

In comparison to FITEQL 4.0 which is mainly focused on estimating sorption constants the combination of PEST and PHREEQC is an extremely powerful tool to estimate any thermodynamic and kinetic parameters such as equilibrium constants for surface reactions, complex stability constants, solubility products of minerals, cation exchange capacity, and decay rates from experimental data. Simultaneously, as well hydraulic parameters like dispersivity and diffusion coefficients may be calibrated in PHREEQC's 1d reactive transport model. A major advantage of combining PHREEQC with PEST (or UCODE) is the option to determine the uncertainties of estimated parameters and a statistical analysis to assess the appropriateness of the conceptual model. Furthermore PHREEQC offers in contrast to FITEQL the choice of different methods for ionic strengths correction including the PITZER equation. A further drawback of FITEQL is that the Pre-Processor of Fiteql (screen II)

does not accept species names having more than 10 characters (e.g.,  $\text{Edg\_alO(UO}_2)_2\text{CO}_3(\text{OH})_3^{2-}$ ). Using PEST in combination with PHREEQC to determine uncertainties of any parameters used in PHREEQC (not shown in this note) overcomes some restrictions of LJUNGSKILE (Ödegaard-Jensen et al. 2002) which can only calculate uncertainties of complex stability coefficients, but not e.g. solubility products, surface complexation constants, and kinetic rates. Last but not least PEST and PHREEQC in contrary to FITEQL are public domain programs which can be downloaded for free.

#### 4 Reference

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## APPENDIX (1), Template file

case.tpl

```

ptf @ # PEST fills parameters in between @ @
Title sorption of U(VI) on STx-1b
SURFACE_MASTER_SPECIES
  Edg_al Edg_alOH # aluminol edge sites
  Edg_si Edg_siOH # silanol edge sites
SURFACE_SPECIES
  Edg_alOH = Edg_alOH
  log_k 0.0
  Edg_alOH + H+ = Edg_alOH2+
  log_k 12.3 # Zachara and Mckinley, 1993,
  Edg_alOH = Edg_alO- + H+
  log_k -13.16 #Zachara and Mckinley, 1993
  Edg_alOH + UO2+2 = Edg_alOUO2+ + H+
  log_k @k1 @ # to be optimized by PEST
  Edg_alOH + Na+ = Edg_alONa + H+
  log_k @k2 @ # to be optimized by PEST
  Edg_siOH = Edg_siOH
  log_k 0.0
  Edg_siOH + H+ = Edg_siOH2+
  log_k -0.95 # # Mckinley et al, 1993
  Edg_siOH = Edg_siO- + H+
  log_k -6.65 # # Mckinley et al, 1993
  Edg_siOH + UO2+2 = Edg_siOUO2+ + H+
  log_k @k3 @ # to be optimized by PEST
  Edg_siOH + UO2OH+ = Edg_siOUO2OH + H+
  log_k @k4 @ # to be optimized by PEST
  Edg_siOH + UO2(CO3)3-4 = Edg_siOHUO2(CO3)3-4
  log_k @k5 @ # to be optimized by PEST
  Edg_siOH + UO2(OH)3- = Edg_siOHUO2(OH)3-
  log_k @k6 @ # to be optimized by PEST
  Edg_siOH + Na+ = Edg_siONa + H+
  log_k @k7 @ # to be optimized by PEST
  Edg_alOH + 2UO2+2 + CO3-2 + 3H2O = Edg_alO(UO2)2CO3(OH)3-2 + 4H+
  log_k @k8 @ # to be optimized by PEST
SURFACE 1 edge sites on STx-1b
Edg_alOH 9.213e-5 83.8 1.66
Edg_siOH 9.99e-5
Phases; fix_pH; H+ = H+; log_k 0
fix_pe; e- = e- ; log_k 0
Solution 1; units mmol/l; temp 23; pH 3; U 100 ug/l; Na 1; Cl 1
END
SELECTED_OUTPUT; -file case.prn; -reset false; -high_p true
USER_PUNCH
-start
10 q_sorb = mol("Edg_alOUO2+") + mol("Edg_siOUO2+") + mol("Edg_siOUO2OH")
15 q_sorb = q_sorb + mol("Edg_siOHUO2(CO3)3-4") + mol("Edg_siOHUO2(OH)3-") +
mol("Edg_alO(UO2)2CO3(OH)3-2")
20 punch q_sorb / 0.42e-6*100
-end
use solution 1; use surface 1; EQUILIBRIUM_PHASES 1; CO2(g) -3.5; fix_pH -4.0 NaOH 10; end
use solution 1; use surface 1; EQUILIBRIUM_PHASES 1; CO2(g) -3.5; fix_pH -4.5 NaOH 10; end

```



APPENDIX (2), Control file  
case.pst

```
pcf
* control data
restart estimation
8 33 1 0 3
# no of parameters, observations, group parameters, prior infos , groups
1 1 single point 1 0 0
# no of template files, no of instruction files, ...
10.0 2.0 0.3 0.03 10
3.0 3.0 0.001
0.1
30 0.001 3 3 0.01 3
1 1 1
* parameter groups
k1 relative 1e-2 0.000001 switch 2 parabolic
* parameter data
k1 none relative 7 3.0 12.0 k1 1.0 0.0 1
#param_name,type, initial, min, max, .....
k2 none relative -6.0 -15. 15.0 k1 1.0 0.0 1
k3 none relative -0.1 -10 5.0 k1 1.0 0.0 1
k4 none relative -6 -10.0 1.0 k1 1.0 0.0 1
k5 none relative 5 1.0 20.0 k1 1.0 0.0 1
k6 none relative 6.7 0.0 10.0 k1 1.0 0.0 1
k7 none relative -5.6 -10.0 0.0 k1 1.0 0.0 1
k8 none relative -0.1 -2.0 1.0 k1 1.0 0.0 1
* observation groups
group_1
group_2
group_3
* observation data
c1 79.0 1 group_1
# obs_name, value, weight, group no
c2 87.3 1 group_1
c3 95.0 1 group_1
c4 98.0 1 group_1
c5 98.0 1 group_1
c6 95.5 1 group_1
c7 89.0 1 group_1
c8 80.5 1 group_1
c9 69.3 1 group_1
c10 57.0 1 group_1
c11 45.0 1 group_1
c12 61.0 1 group_2
c13 77.2 1 group_2
c14 91.0 1 group_2
c15 95.0 1 group_2
c16 95.0 1 group_2
c17 97.0 1 group_2
c18 96.0 1 group_2
c19 87.0 1 group_2
c20 75.5 1 group_2
c21 65.0 1 group_2
c22 53.0 1 group_2
c23 52.0 1 group_3
```

```
c24 70.0 1 group_3
c25 85.0 1 group_3
c26 89.5 1 group_3
c27 91.0 1 group_3
c28 96.8 1 group_3
c29 100.0 1 group_3
c30 95.0 1 group_3
c31 85.0 1 group_3
c32 74.0 1 group_3
c33 60.0 1 group_3
* model command line
phreeqc.exe case.phrq case.out c:/phreeqc/llnl.dat scr.out
* model input/output
case.tpl case.phrq
case.ins case.prn
* prior information
```

APPENDIX (3), Instruction file  
case.ins

```
pif @          # read line 1 or 2 (l1 or l2); data to be read between position 1 and 25 i
l2 [c1]1:25
l1 [c2]1:25
l1 [c3]1:25
l1 [c4]1:25
l1 [c5]1:25
l1 [c6]1:25
l1 [c7]1:25
l1 [c8]1:25
l1 [c9]1:25
l1 [c10]1:25
l1 [c11]1:25
l2 [c12]1:25
l1 [c13]1:25
l1 [c14]1:25
l1 [c15]1:25
l1 [c16]1:25
l1 [c17]1:25
l1 [c18]1:25
l1 [c19]1:25
l1 [c20]1:25
l1 [c21]1:25
l1 [c22]1:25
l2 [c23]1:25
l1 [c24]1:25
l1 [c25]1:25
l1 [c26]1:25
l1 [c27]1:25
l1 [c28]1:25
l1 [c29]1:25
l1 [c30]1:25
l1 [c31]1:25
l1 [c32]1:25
l1 [c33]1:25
```

APPENDIX (4), Batch file  
case.BAT

@echo on

pest case

pause

APPENDIX (5), Residual and Observation files

case.REC (estimated results from PEST)

Current parameter values

k1	5.18431
k2	-15.0000
k3	3.04906
k4	-1.37520
k5	6.61135
k6	6.78168
k7	-5.22070
k8	1.00000

## Results

Observation	Measured	Calculated	Residual	Weight	Group
c1	79	66.3125	12.6875	1	group_1
c2	87.3	88.3356	-1.03564	1	group_1
c3	95	95.6469	-0.646884	1	group_1
c4	98	96.8813	1.11868	1	group_1
c5	98	95.9634	2.03664	1	group_1
c6	95.5	93.7147	1.78531	1	group_1
c7	89	89.6254	-0.625412	1	group_1
c8	80.5	80.4114	8.86E-02	1	group_1
c9	69.3	64.596	4.70395	1	group_1
c10	57	62.412	-5.41204	1	group_1
c11	45	54.985	-9.98502	1	group_1
c12	61	1.43E-90	61	1	group_2
c13	77.2	83.0883	-5.88829	1	group_2
c14	91	94.5525	-3.55248	1	group_2
c15	95	97.9539	-2.95392	1	group_2
c16	95	98.4949	-3.49487	1	group_2
c17	97	97.8718	-0.871821	1	group_2
c18	96	96.1586	-0.158592	1	group_2
c19	87	92.3998	-5.39983	1	group_2
c20	75.5	82.5418	-7.04176	1	group_2
c21	65	62.9273	2.07273	1	group_2
c22	53	53.7386	-0.738608	1	group_2
c23	52	22.9744	29.0256	1	group_3
c24	70	1.43E-90	70	1	group_3
c25	85	92.7887	-7.78868	1	group_3
c26	89.5	97.7014	-8.2014	1	group_3
c27	91	99.1709	-8.17095	1	group_3
c28	96.8	99.4038	-2.60382	1	group_3
c29	100	98.954	1.04598	1	group_3
c30	95	97.1112	-2.11123	1	group_3
c31	85	89.9981	-4.99806	1	group_3
c32	74	70.1543	3.84573	1	group_3
c33	60	72.8507	-12.8507	1	group_3



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COMPLETION OF OPTIMISATION PROCESS

Composite sensitivities for observation group "group\_1" ----->

Parameter name	Group	Current value	Sensitivity
k1	k1	5.18431	0.147111
k2	k1	-15.0000	5.284803E-10
k3	k1	3.04906	5.71726
k4	k1	-1.37520	5.002027E-02
k5	k1	6.61135	6.51195
k6	k1	6.78168	2.60678
k7	k1	-5.22070	9.93890
k8	k1	1.00000	0.932026

Composite sensitivities for observation group "group\_2" ----->

Parameter name	Group	Current value	Sensitivity
k1	k1	5.18431	0.137870
k2	k1	-15.0000	1.024351E-10
k3	k1	3.04906	3.84559
k4	k1	-1.37520	4.479850E-02
k5	k1	6.61135	4.52265
k6	k1	6.78168	2.43845
k7	k1	-5.22070	5.54688
k8	k1	1.00000	0.719605

Composite sensitivities for observation group "group\_3" ----->

Parameter name	Group	Current value	Sensitivity
k1	k1	5.18431	0.147288
k2	k1	-15.0000	6.246567E-09
k3	k1	3.04906	2.37862
k4	k1	-1.37520	3.945916E-02
k5	k1	6.61135	4.93196
k6	k1	6.78168	2.25305
k7	k1	-5.22070	5.87319
k8	k1	1.00000	1.50617

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Observation	Group	Measured	Modelled	Sensitivity
c1	group_1	79.00000	66.31252	6.347751
c2	group_1	87.30000	88.33564	2.896950
c3	group_1	95.00000	95.64688	1.134142
c4	group_1	98.00000	96.88132	0.7920526
c5	group_1	98.00000	95.96336	0.9762608
c6	group_1	95.50000	93.71469	1.393486
c7	group_1	89.00000	89.62541	2.050889
c8	group_1	80.50000	80.41138	3.388537
c9	group_1	69.30000	64.59605	3.583756
c10	group_1	57.00000	62.41204	10.08098
c11	group_1	45.00000	54.98502	12.63383
c12	group_2	61.00000	1.4285714E-90	2.6612249-110
c13	group_2	77.20000	83.08829	4.013520
c14	group_2	91.00000	94.55248	1.455748
c15	group_2	95.00000	97.95392	0.5499647
c16	group_2	95.00000	98.49487	0.3970055
c17	group_2	97.00000	97.87182	0.5515890
c18	group_2	96.00000	96.15859	0.9391126
c19	group_2	87.00000	92.39983	1.639685
c20	group_2	75.50000	82.54176	3.130746
c21	group_2	65.00000	62.92727	3.560912
c22	group_2	53.00000	53.73861	9.592612
c23	group_3	52.00000	22.97441	8.408822
c24	group_3	70.00000	1.42857144285714E-90	2.6612249-110
c25	group_3	85.00000	92.78868	1.939100
c26	group_3	89.50000	97.70140	0.6614666
c27	group_3	91.00000	99.17095	0.2524648
c28	group_3	96.80000	99.40382	0.1863248
c29	group_3	100.0000	98.95402	0.3094536