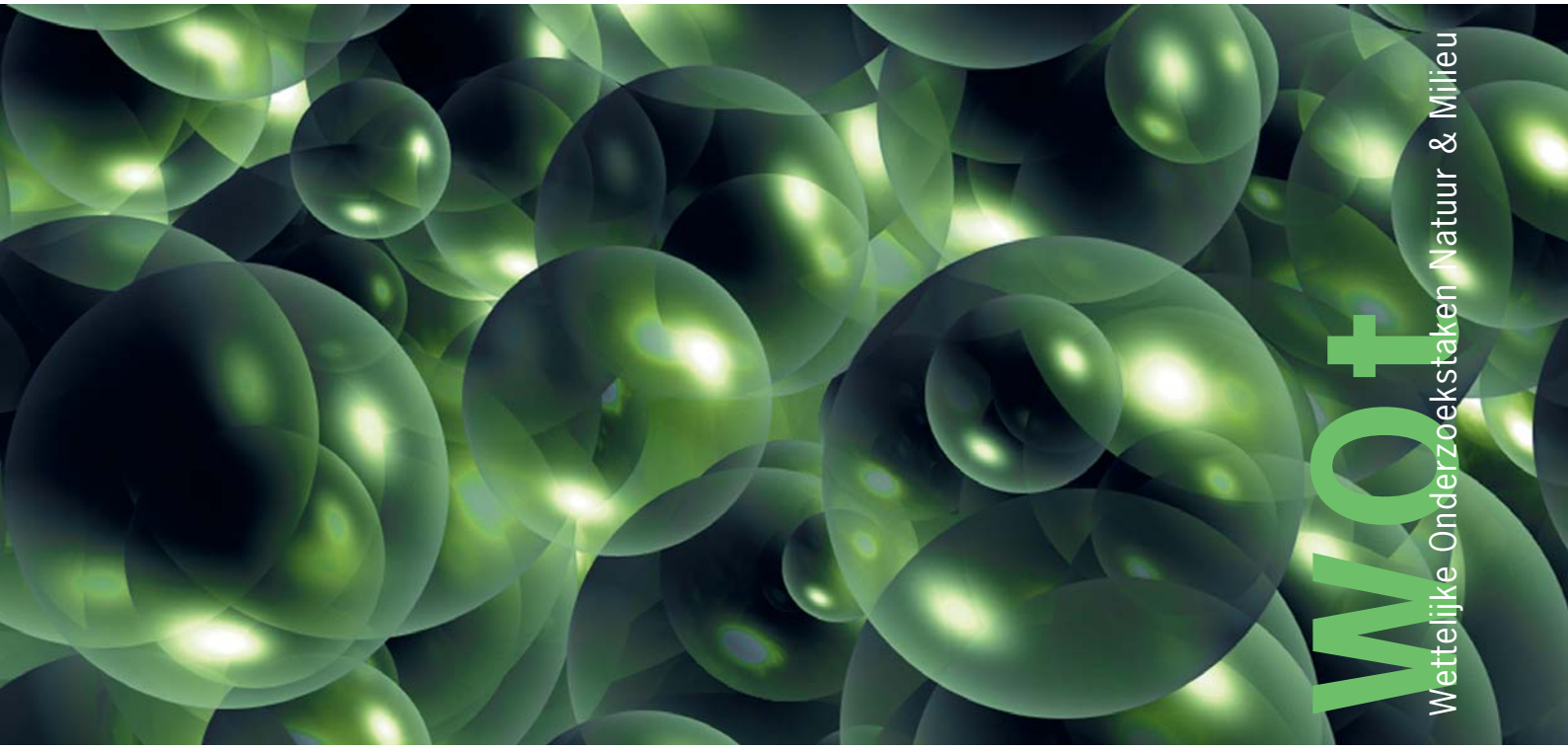
71

Manual of PEARLNEQ v4

J. J. T. I. Boesten
A. Tiktak
R. C. van Leerdam

werkdocumenten



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Manual of PEARLNEQ v4

J. J. T. I. Boesten

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Werkdocument 71

Wettelijke Onderzoekstaken Natuur & Milieu

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Contents

Summary 5

1 Introduction 7

2 Precautionary remark 8

3 Description of the incubation experiment 9

4 Theoretical background 10

5 Fitting procedure for parameters with PEST 13

6 Installation of PEARLNEQ 14

7 Running the example 15

8 Run PEARL_Neq with your own data 17

9 Concluding remark 19

Literature 20

Appendix 1 Example input file 21

Appendix 2 Results of the default example 23

Appendix 3 Comparison between an analytical solution and PearlNeq 25

Appendix 4 Listing of Fortran program PearlNeq 27

Summary

This manual describes the PEARLNEQ v4 sofware package . This package can estimate long-term sorption parameters using results of aged-sorption studies with soil. using a submodel for sorption and transformation that is identical to the submodel used for that purpose in the FOCUS_PEARL v3.3.3.

The submodel assumes two types of sorption sites: equilibrium sites and non-equilibrium sites. The sorption isotherms for bot sites are described with Freundlich equations. The content sorbed at the equilibrium site is assumed to be continuously at equilibrium and the content sorbed at the non-equilibrium site is described with a pseudo first-order sorption rate equation. The transformation rate in soil is assumed to be proportional to the amount in the liquid phase plus the amount sorbed at the equilibrium site. So the content sorbed at the non-equilibrium site is not subject to transformation.

The mathematical equations describing the submodel are solved via a FORTRAN programme. An additional FORTRAN programme generates the necessary input files for the PEST optimisation package. Instructions are given how to obtain optimized parameters using an example dataset and, subsequently instructions are given how to obtain parameters using your own data.

1 Introduction

This document describes a PEARLNEQ-PEST combination, which can be used to estimate the parameters for long-term sorption kinetics in the PEARL model on the basis of an incubation experiment for a certain soil and a certain pesticide. The combination provides also the transformation half-life at reference temperature (when long-term sorption kinetics are included in PEARL, the definition of this half-life changes so it has to be recalculated; see Boesten and van der Linden, 2001). If the incubation experiment has been carried out at multiple temperatures, the Arrhenius activation energy for the transformation rate in soil can be optimised simultaneously.

2 Precautionary remark

This PEARLNEQ-PEST software tool should be seen as an introduction to fitting results of experiments on long-term sorption kinetics to the sorption submodel used in the PEARL model. The tool shows you how PEST can be coupled to a fortran programme that contains this PEARL sorption submodel (i.e. PEARLNEQ.EXE) but it should not be seen as a ready-to-use tool. The tool provides you with example input files for the PEST optimisation package and shows you how to organise this optimisation. We had to make a number of assumptions for generating these PEST input files (e.g. upper and lower bounds of parameters, weighing factors for each measurement, etc. etc.). We do not claim that these assumptions are defensible for your problem; they are our best guesses but they may not be appropriate for your problem. It is your responsibility to check the appropriateness of the result obtained. We do not accept any responsibility for use of PEARLNEQ.

3 Description of the incubation experiment

The PEARLNEQ-PEST tool can be used to fit the results of the following experiment. A number of jars is filled with soil. Each jar contains the same mass of moist soil. At the start of the experiment the same initial mass of pesticide is added to the moist soil in all jars. The jars are incubated at a fixed temperature (or at a few temperatures). At certain time points the remaining total amount of pesticide is measured via an extraction with organic solvent. At the same time the concentration in the liquid phase of the moist soil is measured. The liquid phase can be collected by centrifuging the moist soil over a filter. As an alternative for centrifuging, a desorption experiment can be carried out by adding a certain volume of water and subsequent shaking for about 24 h.

It is assumed that additionally an adsorption isotherm with an equilibration time of about 24 h has been measured for the same soil and pesticide.

4 Theoretical background

PEARLNEQ assumes a Freundlich two-site sorption submodel: one site for equilibrium sorption and the second site for long-term sorption kinetics. The operational definition for the equilibrium sorption sites is that they have reached equilibrium after about 24 h shaking of a well-stirred suspension of the soil in water. The long-term sorption sites do not reach equilibrium within 24 h. PEARLNEQ assumes first order degradation kinetics for the molecules present in liquid phase and sorbed to the equilibrium site; however, molecules sorbed on the kinetic site are assumed not to degrade. This conceptual model is presented in Figure 1. The submodel for sorption and degradation kinetics used in PEARLNEQ can be described as follows (Leistra et al., 2001):

$$M_p = V\, c_L + M_s\,(X_{EQ} + X_{NE}) \qquad (1)$$

$$X_{EQ} = K_{F,EQ}\, c_{L,R} \left(\frac{c_L}{c_{L,R}} \right)^N \qquad (2)$$

$$\frac{dX_{NE}}{dt} = k_d \left(K_{F,NE}\, c_{L,R} \left(\frac{c_L}{c_{L,R}} \right)^N - X_{NE} \right) \qquad (3)$$

$$K_{F,NE} = f_{NE}\, K_{F,EQ} \qquad (4)$$

$$\frac{dM_p}{dt} = -k_t\,(V\, c_L + M_s\, X_{EQ}) \qquad (5)$$

$$K_{F,EQ} = m_{OM}\, K_{OM,EQ} \qquad (6)$$

where:
M_p = initial total mass of pesticide in each jar (μg), acronym MasIni
V = the volume of water in the soil incubated in each jar (mL), acronym VolLiq
M_s = the mass of dry soil incubated in each jar (g), acronym MasSol
c_L = concentration in the liquid phase (μg/L), acronym ConLiq
$c_{L,R}$ = reference concentration in the liquid phase (μg/L), acronym ConLiqRef
X_{EQ} = content sorbed at equilibrium sites (μg/g)
X_{NE} = content sorbed at non-equilibrium sites (μg/g)
$K_{F,EQ}$ = equilibrium Freundlich sorption coefficient (mL/g), acronym CofFreEql
$K_{F,NE}$ = non-equilibrium Freundlich sorption coefficient (mL/g), acronym CofFreNeq
N = Freundlich exponent (-),acronym ExpFre
k_d = desorption rate coefficient (d^{-1}), acronym CofRatDes
f_{NE} = a factor for describing the ratio between the equilibrium and non-equilibrium Freundlich coefficients (-), acronym FacSorNeqEql
k_t = degradation rate coefficient (d^{-1})
m_{OM} = mass fraction of organic matter in the soil (kg/kg), acronym CntOm
$K_{OM,EQ}$ = coefficient of equilibrium sorption on organic matter (mL/g), acronym KomEql

PEARLNEQ does not use the transformation rate coefficient (k_t) as input parameter, but the half-life at reference temperature (acronym DT50Ref, *dt50*). They are related as follows (assuming first order kinetics):

$$dt50 = \ln(2) / k_t \qquad (7)$$

The effect of soil temperature on the transformation rate coefficient in soil is described by the Arrhenius equation:

$$f_T = \exp\left(\frac{-E}{R}\left[\frac{1}{T} - \frac{1}{T_{REF}}\right]\right) \qquad (8)$$

where
f_T = the multiplication factor for the rate coefficient (-)
E = Arrhenius activation energy (kJ/mol)
T = temperature of the soil (K)
T_{REF} = the reference temperature for the specified *DT50* (K)
R = the gas constant (kJ mol^{-1} K^{-1}).

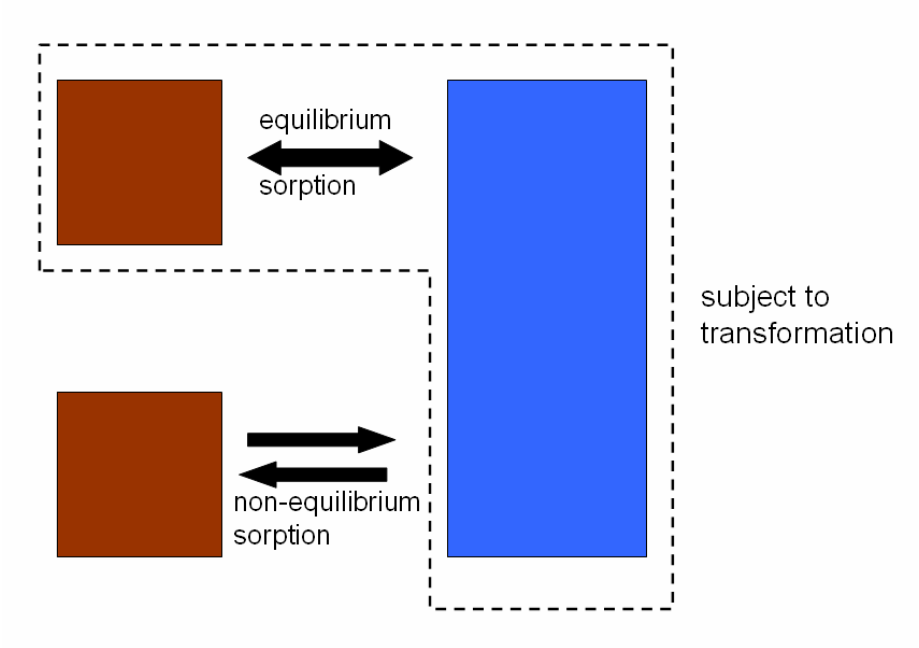


Figure 1. Conceptual representation of the PEARLNEQ model.

Often no concentration measurements in the soil pore water are available but instead at each sampling point in time a certain volume of water (usually a $CaCl_2$ solution) is added to soil and the suspension is shaken for about 24 h after which the concentration in the supernatant is measured. In such a case the fit has to be based on these concentration measurements in the supernatant of the soil-water suspension.

This is simulated in PEARLNEQ as follows:
(A) it is assumed that full equilibrium is reached for the equilibrium sorption site during the desorption experiment (i.e., shaking for 24 h)
(B) it is assumed that desorption from the non-equilibrium sorption site can be ignored during the desorption experiment.

Assumption A is justifiable because this is exactly the operational definition of the equilibrium sorption site. Assumption B is justifiable because desorption coefficients for long-term kinetics are usually in the order of 0.01 d^{-1}, which implies that amounts desorbed within 1 day are negligibly small.

Using these assumptions, the concentration in the liquid phase of the supernatant after desorption can be estimated by stating that (i) the total content of substance in the moist soil and the soil-water suspension have to be equal, and (ii) the content sorbed at the non-equilibrium sites in the moist soil and in the soil-water suspension are equal. Using Equation 1 then results in the following equation

$$V\, c_{L,MS} + M_s \left(X_{EQ,MS} + X_{NE} \right) = \left(V + V_{ADD} \right) c_{L,SUS} + M_s \left(X_{EQ,SUS} + X_{NE} \right) \qquad (9)$$

where:
the subscript MS indicates the moist-soil system
the subscript SUS indicates the soil-water suspension system and
V_{ADD} = volume of liquid (usually $CaCl_2$ solution) added to the soil at each sampling point just before starting the 24 h desorption experiment (mL), acronym VolLiqAdd.

At each sampling point in time, Equation 9 can be rewritten (using Eqn 2) into an equation that contains only one unknown variable, i.e. the concentration in the liquid phase of the soil suspension ($c_{L,SUS}$). PEARLNEQ provides as output always the concentration in the soil-water suspension as a function of time. If V_{ADD} = 0, then this implies that the concentration in the moist soil is given.

PEARLNEQ solves the set of Eqn 1 to Eqn 9 numerically using Euler's method for integration of the state variables M_p and X_{NE}. The time step for integration can be set as an input parameter (we recommend 0.01 d). The concentration in the liquid phase is calculated via an iteration procedure as described in Appendix 4 of FOCUS (2006). Appendix 3 shows a test of the PEARLNEQ results against an analytical solution for the case of a linear isotherm (N=1), indicating good correspondence between numerical and analytical results.

5 Fitting procedure for parameters with PEST

The provided package assumes that the following variables need to be optimized:
- the initial mass of the pesticide (MasIni)
- the ratio between the equilibrium and non-equilibrium Freundlich coefficients (FacSorNeqEql)
- the desorption rate coefficient (CofRatDes)
- the half-life at reference temperature (DT50Ref)
- the molar activation energy (MolEntTra); this can only be optimized if the experiment has been carried out at multiple temperatures.

It is assumed that all other variables are known.

The provided package assumes that the measurements that are fitted, consist for each point in time of
- a mass of pesticide in μg
- a concentration in liquid phase in μg/mL.

PEST needs a number of input parameters for the fitting procedure (e.g. upper and lower bounds of parameters, weighing factor for each measurement, etc. etc.). Our experience is that the weighing factor for each measurement is the most important input parameter.

Therefore we offer two options for weighing:
'equal' which gives a weight of 1.0 to all observations (so equal weights)
'inverse' which gives a weight that is proportional to the inverse of the observed value.
If the observed value is zero, the weight is set equal to 1.0 in any case.

The option 'equal' implies that high observed values get more weight than low observed values. As described above, the fitting procedure considers two quantities: mass of pesticide and the concentration in the liquid phase. This may lead to completely different weights for these two types of quantities.
E.g. if the mass is initially 50 μg and the concentration in the liquid phase is in the order of 1 μg/mL, then the fitting procedure will be completely dominated by the decline of the mass of pesticide. So if the option 'equal' is used, the user should choose a mass of solid phase such that the values of the mass of pesticide in μg should be in the same order of magnitude as the concentration in liquid phase in μg/mL.

The option 'inverse' implies that each measurement gets more or less equal weight for the parameter estimation. This 'inverse' option gave the best results in a few tests. However, we do not claim that this is the best choice for your dataset nor do we claim that the other PEST input parameters are the best choice for your dataset.

The provided package cannot handle duplicate or triplicate observations for each point in time. Within PEST there are procedures available to do so but these have not yet been implemented in PEARLNEQ. So the user has to average first all measurements for each point in time.

6 Installation of PEARLNEQ

PEARLNEQ is distributed in a zip file. Unzip the file and specify a path (e.g. c:\pearlneq). Be sure there is no space within the specified path, because this will cause of failure. The package contains four directories, i.e. Neq_Bin, Pest, Neq_fortran_source_files and Neq_Example.

- The Neq_Bin directory contains the PEARLNEQ executables, PEARLNEQ.EXE and PEARLMK.EXE.
- The PEST optimisation software is available in the Pest directory. As PEST is now available freeware (http://www.sspa.com/pest), we included the latest version as of 29-10-2003 (version 7.0.1.). Separate installation of PEST is not necessary.
- The Neq_fortran_source_files directory contains the fortran source files used to generated the PEST input files and the programme that calculates the sorption kinetics
- The Neq_Example directory contains results from an example study, as described in the FOCUS PEARL user manual, version 1.1.1 § 3.2.10 (page 51-54).

7 Running the example

The following steps must be followed.

1 Run the example, to check if everything works and get experience with the system. Go to the Neq_Example directory, and run the example, example.bat.
- The batch file will first call PEARLMK. This pre-processing program generates the input files for PEST, i.e. example.pst, example.tpl and example.ins (see Figure 2, RunId = "example")
- Then, the optimisation starts. PEST calls PEARLNEQ several times (see Figure 2; in the example 39 times).
- If you get an error message after the first step (PEARLMK), type control-break to stop the process and check the error messages available in the example.err file.

2 After successful optimisation, read the results from the file example.rec. Choose "select the program from the list" and open with Notepad. The relevant results, including parameter values, 95% confidence intervals and correlation matrices can be found at the end of this file (Section OPTIMISATION RESULTS, see Appendix 2). The meaning of the short acronyms in this rec-file is as follows:
fsne = FacSorNeqEql
crd = CofRatDes
dt50 = DT50Ref
masini = MasIni
met = MolEntTra.
PEST also generates parameter sensitivity files etc. Details can be found in the PEST manual, which is available in the PEST subdirectory of the package.

3 If you encounter errors during the second step, you can try running PEARLNEQ directly. PEARLMK has created a file example.neq (in …\Neq_Example) which is the input file for pearlneq. You can run PEARLNEQ by typing "..\Neq_Bin\pearlneq example" in a DOS-box.

4 PEARLNEQ will create an output file (example.out) and a log file (example.log). The output files are self-explaining. The output file contains the result of the last run which is in PEST by definition the run with the optimised parameters.

5 You can use the XyWin program to make a graph. (After running the example this will be done automatically.) XyWin is available in the neq_bin\xypearl directory of PEARLNEQ: you can also get the graph via typing in a DOS box: "..\Neq_Bin\xypearl\xywin –j example.job –W l". However, XyWin is not userfriendly so we recommend to use the results from the output file (example.out) as the source for the best fit and create graphs with software of your own choice.

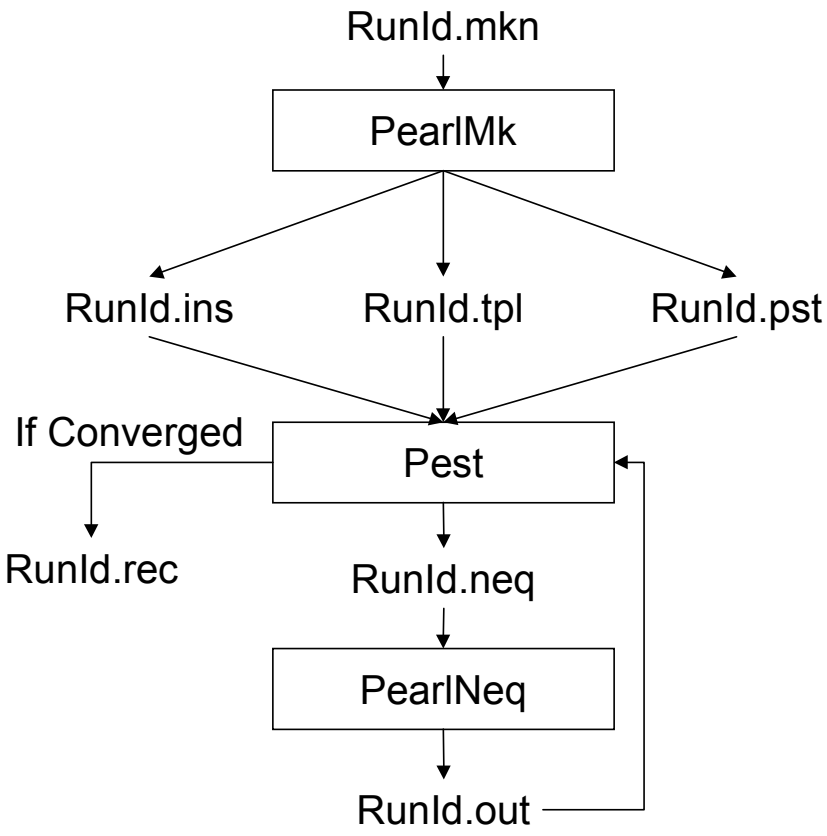


Figure 2. Dataflow diagram for the PEARLNEQ-PEST combination. The acronym RunId is "example" for the example provided.

8 Run PEARL_Neq with your own data

1 We assume that you have carried out an appropriate incubation experiment as described before. The first step of optimising your own data consists of **editing the file example.mkn**, which can be found in the example subdirectory of the **PEARLNEQ directory**. Open the file with Notepad. *Please make a copy of this file before editing.* Make sure there is no space in the new name. This will give an error. An example of this input file is listed in Appendix 1. The following parameters must be provided:

- TimEnd (d): The duration of the incubation experiment.
- MasSol (g): The mass of dry soil incubated in each jar.
- VolLiqSol (mL): Volume of liquid in the moist soil *during* incubation.
- VolLiqAdd (mL): Volume of liquid added to the soil *after* incubation (i.e. the amount of liquid added to perform a conventional desorption equilibrium experiment).
- CntOm (kg.kg^{-1}): Mass fraction of organic matter in the soil.
- ConLiqRef (mg L^{-1}): Reference concentration in the liquid phase.
- ExpFre (-): Freundlich exponent; use value taken from adsorption isotherm measured for this pesticide-soil combination
- KomEql (L kg^{-1}): coefficient of equilibrium sorption on organic matter; use value taken from adsorption isotherm measured for this pesticide-soil combination; in case you have no organic matter content of the soil, set the organic matter to 1.0 and specify the measured Freundlich equilibrium coefficient (see Eqn 6)
- MasIni (µg): The initial total mass of pesticide in each jar. *In contrast to initial versions of PEARLNEQ, this parameter will be optimised. There is no default value for this parameter.*
- FacSorNeqEql (-): factor describing the ratio $f_{NE} = K_{F,NE}/K_{F,EQ}$ as defined by Eqn 4. *This parameter will be optimised*, but you have to specify an initial guess here. The default value is 0.5.
- CofRatDes (d^{-1}): the desorption rate coefficient. *This parameter will be optimised*, but you have to specify an initial guess here. The default value is 0.01 d^{-1}.
- DT50Ref (d): the transformation half-life under reference conditions, applying to the equilibrium domain. *This parameter will be optimised*, but you have to specify an initial guess here. As a default value, you can use the 'classical' half-life, which applies to the total soil system (i.e. the equilibrium domain + the non-equilibrium domain).
- TemRefTra (C): The reference temperature, for which the half-life will be provided (set to incubation temperature if data for only one temperature are available and set to 20^{o} C if you have data for multiple temperatures).
- MolEntTra (kJ mol^{-1}): the molar enthalpy of transformation. *This parameter will be optimised if you have carried out the experiment at multiple temperatures; otherwise it is a model-input*. In any case you have to specify a value (e.g. 60 kJ mol^{-1}) which will be used as an initial guess in case of data for more than one temperature.
- table Tem (C): List of temperatures at which the incubation experiment has been carried out. One temperature is OK if only data for one temperature are available.
- table Observations: List of observations. The first column contains the time (d), the second column the temperature, column 3 contains the total mass of pesticide in the system (µg), column 4 contains the concentration of pesticide (µg mL^{-1}) measured in the pore water of moist soil (then VolLiqAdd = 0) or in the water phase after a desorption experiment (in which case VolLiqAdd is not zero) and column 5 contains the characters 'OBS'.

- option Opt_weights: options for weights. Two options for weighing are offered: 'equal' which gives a weight of 1.0 to all observations (so equal weights) and 'inverse' which gives a weight that is proportional to the inverse of the observed value; if the observed value is zero, the weight is set equal to 1.0 in any case; you can inspect the weigths in the 'pst' file.

2. Modify the contents of the example.bat file (with right mouse button): **replace "example" everywhere it occurs by the name of the copied input file and delete last line of the file (which would generate the graph).** Repeat step 1-5 of chapter 7.

3. If the optimization is not succesfull, you can try re-running PEARLNEQ with different initial guesses of MasIni, DT50Ref, FacSorNeqEqI and CofRatDes.

9 Concluding remark

While using PEARLNEQ, we noticed that very regularly the results depend on the initial guesses of the parameters. Therefore we advise you to perform always a number of runs with different initial guesses. We advise you also to analyse the results very carefully, especially the 95% confidence intervals of your parameters. If the interval is wide for a certain parameter, this indicates that the estimated variable is very uncertain. As a consequence it is usually not meaningful to use it any further in the risk assessment.

Literature

Boesten JJTI & AMA van der Linden (2001) Effect of long-term sorption kinetics on leaching as calculated with the PEARL model for FOCUS scenarios. BCPC Symposium Proceedings No. 78: Pesticide behaviour in soils and water, p. 27-32.

FOCUS (2006). Guidance document on estimating persistence and degradation kinetics from environmental fate studies on pesticides in EU registration. EC Document Sanco/10058/2005 version 2.0, European Commission, Brussels, 434 pp. (Available at http://viso.ei.jrc.it/focus.)

Leistra, M, AMA van der Linden, JJTI Boesten, A Tiktak & F van den Berg (2001). PEARL model for pesticide behaviour and emissions in soil-plant systems: description of the processes in FOCUS PEARL version 1.1.1. Alterra Report 013, Alterra, Wageningen. RIVM Report 711401009; RIVM Bilthoven. (Available at PEARL website to be found via Help-button in main screen of PEARL.)

Tiktak A, F. van den Berg, JJTI Boesten, D van Kraalingen, M Leistra & AMA van der Linden, 2000. Manual of FOCUS PEARL version 1.1.1. RIVM report 711401008, RIVM Bilthoven, the Netherlands. (Available at PEARL website to be found via Help-button in main screen of PEARL.)

Appendix 1 Example input file

```
Example input file "example.mkn"
*-----------------------------------------------------------------------------------------
* STANDARD FILE for pearlmk version 4
* Program to fit the half-life, activation energy and parameters for long-term sorption
* kinetics of pesticides in soil
*
* This file is intented for use with the PEST program (Doherty et al., 1991).
* Please see manual of PEARLNEQ
*
* (c) RIVM/MNP/Alterra 2003, 2005, 2006, 2007
*-----------------------------------------------------------------------------------------

* Model control
Yes               ScreenOutput
0.0               TimStart          (d)          Start time of experiment
500.0             TimEnd            (d)          End time of experiment
0.01              DelTim            (d)          Time step of Euler's integration procedure

* System characterization
54.64             MasIni            (ug)             Initial guess of initial mass
45.36             MasSol            (g)              Mass of soil in incubation jar
6.64              VolLiqSol         (mL)             Volume of liquid in the moist soil
0.0               VolLiqAdd         (mL)             Volume of liquid ADDED
0.047             CntOm             (kg.kg-1)        Organic matter content

* Sorption parameter
1.0               ConLiqRef         (mg.L-1)       Reference liquid concentration
0.87              ExpFre            (-)            Freundlich exponent
2.1               KomEql            (L.kg-1)       Coefficient for equilibrium sorption
0.5               FacSorNeqEql      (-)            Initial guess of ration KfNeq/KfEql
0.01              CofRatDes         (d-1)          Initial guess of desorption rate constant

* Transformation parameters
14.00             DT50Ref           (d)       Initial guess of half-life at ref. temperature
20.0              TemRefTra         (C)             Reference temperature
110.0             MolEntTra         (kJ.mol-1)      Initial guess of molar activation energy

* Temperature at which the incubation experiments have been carried out
table Tem (C)
1  5.0
2  15.0
```

```
end_table

* Provide the results of the measurements
* Tim  Tem  Mas       ConLiq
* (d)  (C)  (ug)      (ug/mL)
table Observations
2      5    51.6300   5.7285       OBS
10     5    50.5900   5.0560       OBS
42     5    46.0200   3.6635       OBS
87     5    38.6100   2.9320       OBS
157    5    32.8150   1.9280       OBS
244    5    25.8700   1.4650       OBS
358    5    20.3150   0.8820       OBS
451    5     9.4250   0.6015       OBS
2     15    51.3300   5.8955       OBS
6     15    47.3950   4.4425       OBS
10    15    45.0650   3.9510       OBS
42    15    23.1400   1.6470       OBS
87    15    10.8950   0.6710       OBS
157   15     3.1350   0.1525       OBS
244   15     1.4400   0.0305       OBS
358   15     0.4500   0.0000       OBS
451   15     0.1500   0.0000       OBS
end_table

* Option for weights of observations:
*'equal' gives equal weights to all measurements
*'inverse' gives weigth equal to inverse value of each measurement (if measurement is zero
then weight is 1.0)
inverse    Opt_weights
```

Appendix 2 Results of the default example

Results (taken from last section of REC-file)

These are the results of the defaultexample, provided with the package.

OPTIMISATION RESULTS

Parameters ----->

Parameter	Estimated value	95% percent confidence limits lower limit	upper limit
fsne	0.600286	0.408681	0.791892
crd	1.226317E-02	9.886449E-03	1.463989E-02
dt50	13.0062	11.5100	14.5024
masini	56.0664	52.1243	60.0084
met	108.755	102.806	114.705

Note: confidence limits provide only an indication of parameter uncertainty.
They rely on a linearity assumption which may not extend as far in parameter space as the confidence limits themselves - see PEST manual.

See file EXAMPLE.SEN for parameter sensitivities.

Observations ----->

Observation	Measured value	Calculated value	Residual	Weight	Group
o1	51.6300	55.5316	-3.90156	1.9000E-02	no_name
o2	5.72850	5.39742	0.331082	0.1750	no_name
o3	50.5900	53.4684	-2.87844	2.0000E-02	no_name
o4	5.05600	5.08081	-2.480823E-02	0.1980	no_name
o5	46.0200	46.2635	-0.243511	2.2000E-02	no_name
o6	3.66350	4.06320	-0.399703	0.2730	no_name
o7	38.6100	38.2669	0.343149	2.6000E-02	no_name
o8	2.93200	3.09390	-0.161897	0.3410	no_name
o9	32.8150	29.0458	3.76922	3.0000E-02	no_name
o10	1.92800	2.16483	-0.236828	0.5190	no_name
o11	25.8700	20.9646	4.90536	3.9000E-02	no_name
o12	1.46500	1.47675	-1.175005E-02	0.6830	no_name
o13	20.3150	13.8380	6.47702	4.9000E-02	no_name
o14	0.882000	0.932184	-5.018437E-02	1.134	no_name
o15	9.42500	9.90684	-0.481840	0.1060	no_name
o16	0.601500	0.648450	-4.694962E-02	1.663	no_name
o17	51.3300	53.3843	-2.05426	1.9000E-02	no_name
o18	5.89550	5.17830	0.717199	0.1700	no_name
o19	47.3950	48.4369	-1.04190	2.1000E-02	no_name
o20	4.44250	4.62304	-0.180537	0.2250	no_name
o21	45.0650	43.9959	1.06909	2.2000E-02	no_name
o22	3.95100	4.12910	-0.178099	0.2530	no_name
o23	23.1400	21.3140	1.82600	4.3000E-02	no_name
o24	1.64700	1.70735	-6.034768E-02	0.6070	no_name
o25	10.8950	8.98367	1.91133	9.2000E-02	no_name
o26	0.671000	0.544736	0.126264	1.490	no_name
o27	3.13500	3.26320	-0.128203	0.3190	no_name
o28	0.152500	0.131795	2.070505E-02	6.557	no_name
o29	1.44000	1.24259	0.197406	0.6940	no_name
o30	3.050000E-02	3.866613E-02	-8.166130E-03	32.79	no_name
o31	0.450000	0.399623	5.037676E-02	2.222	no_name
o32	0.00000	1.077987E-02	-1.077987E-02	1.000	no_name
o33	0.150000	0.162574	-1.257429E-02	6.667	no_name
o34	0.00000	4.019330E-03	-4.019330E-03	1.000	no_name

See file EXAMPLE.RES for more details of residuals in graph-ready format.

See file EXAMPLE.SEO for composite observation sensitivities.

Objective function ----->

Sum of squared weighted residuals (ie phi) = 0.4297

Correlation Coefficient ----->

Correlation coefficient = 0.8997

Analysis of residuals ----->

All residuals:-

Number of residuals with non-zero weight	= 34
Mean value of non-zero weighted residuals	= 1.3161E-02
Maximum weighted residual [observation "o13"]	= 0.3174
Minimum weighted residual [observation "o30"]	= -0.2677
Standard variance of weighted residuals	= 1.4816E-02
Standard error of weighted residuals	= 0.1217

Note: the above variance was obtained by dividing the objective function by the number of system degrees of freedom (ie. number of observations with non-zero weight plus number of prior information articles with non-zero weight minus the number of adjustable parameters.) If the degrees of freedom is negative the divisor becomes the number of observations with non-zero weight plus the number of prior information items with non-zero weight.

Parameter covariance matrix ----->

	fsne	crd	dt50	masini	met
fsne	8.7787E-03	8.4444E-05	-5.6502E-02	6.4073E-02	0.1016
crd	8.4444E-05	1.3507E-06	-4.5078E-04	6.0200E-04	6.0023E-04
dt50	-5.6502E-02	-4.5078E-04	0.5353	-0.5756	-1.463
masini	6.4073E-02	6.0200E-04	-0.5756	3.716	-0.8663
met	0.1016	6.0023E-04	-1.463	-0.8663	8.463

Parameter correlation coefficient matrix ----->

	fsne	crd	dt50	masini	met
fsne	1.000	0.7755	-0.8242	0.3548	0.3727
crd	0.7755	1.000	-0.5301	0.2687	0.1775
dt50	-0.8242	-0.5301	1.000	-0.4081	-0.6872
masini	0.3548	0.2687	-0.4081	1.000	-0.1545
met	0.3727	0.1775	-0.6872	-0.1545	1.000

Normalized eigenvectors of parameter covariance matrix ----->

	Vector_1	Vector_2	Vector_3	Vector_4	Vector_5
fsne	1.4335E-02	-0.9842	0.1744	-2.2879E-02	1.1198E-02
crd	-0.9999	-1.4279E-02	1.5744E-03	-1.9999E-04	6.4642E-05
dt50	9.4905E-04	-0.1745	-0.9453	0.2229	-0.1618
masini	7.8350E-05	-1.4702E-02	-0.2006	-0.9685	-0.1467
met	7.0894E-05	-1.9859E-02	-0.1889	-0.1084	0.9758

Eigenvalues ----->

4.7821E-07	1.7663E-03	0.1313	3.753	8.837

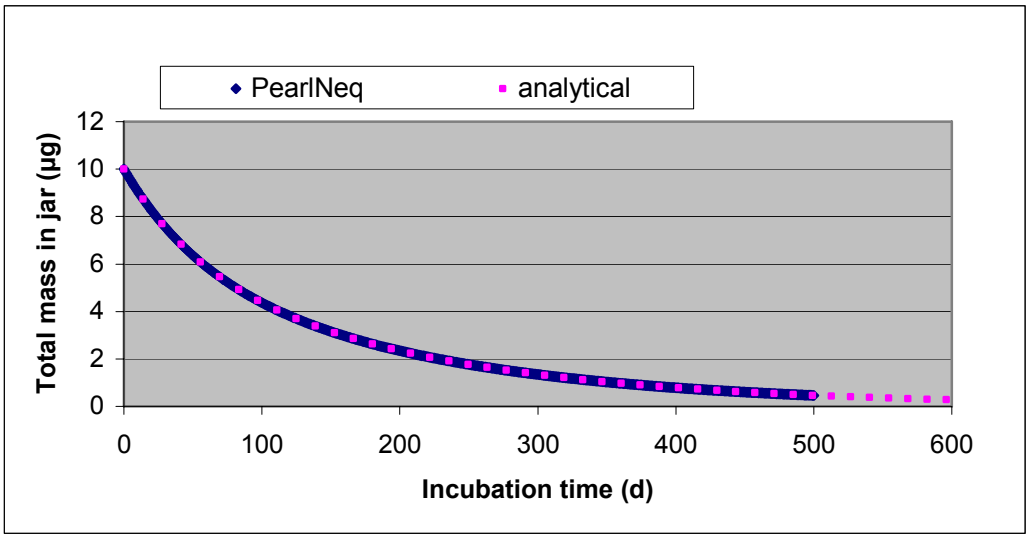
Appendix 3 Comparison between an analytical solution and PearlNeq

In this appendix an analytical solution for the remaining mass of pesticide is compared with the PearlNeq solution (appendix 4). The system properties were:

* Mass of dry soil (MasSol) (g)	1.0000
* Volume of water in moist soil (VolLiqsol) (mL)	0.2000
* Volume of water added (VolLiqAdd (mL)	0.0000
* Initial mass of pesticide (MasIni) (ug)	10.0000
* Reference concentration (ConLiqRef) (ug.mL-1)	1.0000
* Equilibrium sorption coefficient (CofFreEql) (mL.g-1)	1.0000
* Non-equili. sorption coefficient (CofFreNeq) (mL.g-1)	0.5000
* Freundlich exponent (ExFre) (-)	1.0000
* Desorption rate coefficient (CofRatDes) (d-1)	0.0100
* Half-life transformation (DT50Ref) (d)	69.3000
* Reference temperature (TemRefTra) (K)	293.1500

The analytical solution was taken from Appendix 4 of FOCUS (2006).

The figure shows that the PearlNeq solution coincides very well with the analytical solution.



Comparison between the analytical solution and the PearlNeq solution

Appendix 4 Listing of Fortran program PearlNeq

```
program PearlNeq
!=============================================================================================
!
! PEARLNEQ program - simulates pesticide behaviour in a closed incubation system assuming
!                    a two-site Freundlich sorption submodel and first-order transformation
!                    kinetics
!
! History
! -------
! 1.0.1 Initial version for Pearl 1.1
! 1.1.1 Version compatible with FOCUS Pearl 1.1.1
! 2.2.2 Version compatible with FOCUS Pearl 2.2.2
! 3.3.3 Version compatible with FOCUS Pearl 3.3.3
! Version 4 of 10 May 2007
!=============================================================================================

   use Sishell                ! General routines
   use CompilerSpecific       ! Compiler specific statements

   implicit none

   character (len=LineLength) :: Path

   integer :: T,Steps,StepsToPrint

   double precision, parameter :: RGas=8.31432d0   ! Molar gas constant
   double precision, parameter :: TimeStart=0.d0   ! Start time
   double precision, parameter :: DelTimPrint=1.d0 ! Print time step

   double precision :: CntOm,CofFreEql,CofFreNeq,CofRatDes,CofRatTra,DelTim, &
   DT50Ref,ExpFre,Mas,MasEql,MasIni,MasSol,VolLiqAdd,MolEntTra,TimeEnd,&

VolLiqSol,VolLiqSus,XNeq,ConLiqRef,Tim,Tem,FacTem,TemRefTra,KomEql,FacSorNeqEql,ConPor,ConS
us

   type (TableType) :: TemTab

   save

   IOMode = IOMode_Full
   ShowScreen = .false.

   ! Initial part of program
   !------------------------

   ! Set the model stamp (version numbers etc)
   Call SetModelStamp ()

   ! Open the input file
   call InitCh (Path)
   Call OpenPearlNeqFiles(Path)

   ! System properties
   !------------------

   ! Initial mass of pesticide
   call GetInput (MasIni,'MasIni','(ug)',Valmin=0.d0)

   ! Mass of dry soil
   call GetInput (MasSol,'MasSol','(g)',Valmin=0.d0)

   ! Volume of liquid in moist soil and volume of liquid added
   call GetInput (VolLiqSol,'VolLiqSol','(mL)',Valmin=0.d0)
   call GetInput (VolLiqAdd,'VolLiqAdd','(mL)',Valmin=0.d0)
```

```
! Calculate the volume of the suspension
VolLiqSus = VolLiqSol + VolLiqAdd

! Organic matter content
call GetInput (CntOm,'CntOm','(kg.kg-1)',ValMin=0.d0)

! End time
call GetInput (TimeEnd,'TimEnd','(d)',ValMin=0.d0)

! Time step
call GetInput (DelTim,'DelTim','(d)',ValMin=0.d0)

StepsToPrint = max(1,int((DelTimPrint+1.d-10)/DelTim))

! Sorption parameters
!--------------------

! Reference concentration
call GetInput (ConLiqRef,'ConLiqRef','(mg.L-1)',ValMin=0.1d0)

! Freundlich N
call GetInput (ExpFre,'ExpFre','(-)',ValMin=0.01d0,ValMax=1.3d0)

! Equilibrium Kom
call GetInput (KomEql,'KomEql','(L.kg-1)',ValMin=0.d0)
CofFreEql = KomEql * CntOm

! Ratio Kf,neq/Kf,eq
call GetInput (FacSorNeqEql,'FacSorNeqEql','(-)',Valmin=0.d0)
CofFreNeq = FacSorNeqEql * CofFreEql

! Desorption rate coefficient
call GetInput (CofRatDes,'CofRatDes','(d-1)',ValMin=0.d0,ValMax=0.5d0)

! Transformation parameters
!--------------------------

! Molar activation energy
call GetInput &
(MolEntTra,'MolEntTra','(kJ.mol-1)',ValMin=0.d0,ValMax=200.d0)
MolEntTra = 1.d3*MolEntTra

! Pesticide half-life
call GetInput (DT50Ref,'DT50Ref','(d)',ValMin=1.d-1,ValMax=1.d6)

! Reference temperature
call GetInput (TemRefTra,'TemRefTra','(C)')
TemRefTra = TemRefTra + 273.15d0

! Experimental temperatures
!--------------------------
call GetInput (TemTab,'Tem','(C)',Col=1)


! Main part of programme
!-----------------------

write (FilOut,'(a)') ' '
write (FilOut,'(a)') '-----------------------------------------------------------------'
write (FilOut,'(a)') '* System properties'
write (FilOut,'(a,f10.4)') '* Mass of dry soil (g)                  :',MasSol
write (FilOut,'(a,f10.4)') '* Volume of water in moist soil (mL)    :',VolLiqSol
write (FilOut,'(a,f10.4)') '* Volume of water added (mL)            :',VolLiqAdd
write (FilOut,'(a,f10.4)') '* Initial mass of pesticide (ug)        :',MasIni
write (FilOut,'(a,f10.4)') '* Reference concentration (ug.mL-1)     :',ConLiqRef
write (FilOut,'(a,f10.4)') '* Equilibrium sorption coeff (mL.g-1)   :',CofFreEql
write (FilOut,'(a,f10.4)') '* Non-equili. sorption coeff (mL.g-1)   :',CofFreNeq
write (FilOut,'(a,f10.4)') '* Freundlich exponent (-)               :',ExpFre
write (FilOut,'(a,f10.4)') '* Desorption rate coefficient (d-1)     :',CofRatDes
write (FilOut,'(a,f10.4)') '* Half-life transformation (d)          :',DT50Ref
```

```
   write (FilOut,'(a,f10.4)') '* Reference temperature (K)             :',TemRefTra
   write (FilOut,'(a)') '-------------------------------------------------------------'
   write (FilOut,'(a)') ' '

   write (FilOut,'("*",a6,1x,a6,3(1x,a20))') 'Temp','Time','Mas','ConLiq','XNeq'
   write (FilOut,'("*",a6,1x,a6,3(1x,a20))') '(C)','(d)','(ug)','(ug.mL-1)','(ug.g-1)'

   Temperatures: do T = 1,TemTab%NumRow

      ! Calculate the coefficient at ambient temperature
      Tem = TemTab%Y(1,T) + 273.15d0
      FacTem = exp((-MolEntTra/RGas)*((1.d0/Tem)-(1.d0/TemRefTra)))

      CofRatTra = FacTem*log(2.d0)/DT50Ref

      ! Initialize the time loop
      Mas = MasIni
      XNeq = 0.d0

      Tim = TimeStart
      Steps = 0
      TimeLoop: do

         MasEql = Mas - MasSol*XNeq
         ConPor = Freundlich (MasEql,MasSol,VolLiqSol,CofFreEql,ConLiqRef,ExpFre)
         ConSus = Freundlich (MasEql,MasSol,VolLiqSus,CofFreEql,ConLiqRef,ExpFre)

         if ((mod(Steps,StepsToPrint)) == 0) then
            ! ConSus is always the only output concentration allowing direct fits of
desorption
                     ! measurements
                     write             (FilOut,'(2(1x,f6.1),3(1x,f20.8))')             Tem-
273.15d0,Tim,Mas,ConSus,XNeq
         end if

         ! Integration of total mass
         Mas = Mas + DelTim * (-1.d0*CofRatTra*(Mas-MasSol*XNeq))

         ! Integration of non-equilibrium domain
         XNeq = XNeq + DelTim * &
         (CofRatDes*(CofFreNeq*ConLiqRef*(ConPor/ConLiqRef)**ExpFre-XNeq))

         ! Increase time
         Tim = Tim + DelTim
         Steps = Steps + 1

         if (Tim .dge. TimeEnd) exit

      end do TimeLoop

      write (FilOut,'(2(1x,f6.1),3(1x,f20.8))') Tem-273.15d0,Tim,Mas,ConSus,XNeq

   end do Temperatures

!=============================================================================================
!=============================================================================================

contains

   double precision function Freundlich (Mas,MasSol,VolLiq,CofFreEql,ConLiqRef,ExpFre)
   ! This function calculates the equilibrium concentration in a system
   !---------------------------------------------------------------------------------------

      implicit none

      double precision, parameter :: Err=1.d-4

      double precision :: ConLiqOld,ConLiq,CofFre
      double precision, intent(in) :: Mas,MasSol,VolLiq,CofFreEql,ConLiqRef,ExpFre
```

```
      ConLiq=ConLiqRef
      do
         ConLiqOld = ConLiq
         CofFre = &
         CofFreEql * ConLiqRef**(1.d0-ExpFre) * (max(ConLiq,1.d-30) )**(ExpFre-1.d0)
         ConLiq=Mas/(VolLiq+MasSol*CofFre)
         if (abs(ConLiq-ConLiqOld) < Err*abs(ConLiq)) exit
      end do

      Freundlich = ConLiq

   end function Freundlich

!=======================================================================================
!=======================================================================================

   subroutine SetModelStamp ()
   ! Set the model stamp
   !=====================================================================================

      implicit none

      Model%ExtInp = '.neq'
      Model%ExtOut = '.out'
      Model%ExtLog = '.log'
      Model%ExtErr = '.err'
      Call InitCh (Model%Date)
      Call InitCh (Model%PearlVersion)
      Call InitCh (Model%GeoVersion)
      Call InitCh (Model%FocusVersion)
      Model%PearlVersion = '3.3.3'
      Model%Date = '10-May-2007'

   end subroutine SetModelStamp

!=======================================================================================
!=======================================================================================

   subroutine OpenPearlNeqFiles (ProgramPath)
   ! Performs the following tasks:
   ! (1) Opens the input and output files
   ! (2) Prints the date-and-time and the Run Id to all opened output files.
   ! (3) Reads the start-time and end-time, gets the print interval
   ! (5) Sets the begin CPU time in seconds
   !
   ! The following input and output files are used by the model:
   ! Unit FilInp:   The input file (extension prl)
   ! Unit FilOut:   The output file (extension out)
   ! Unit FilLog:   The log file (extension log)
   !=====================================================================================

      implicit none

      ! Declaration of local variables
      !-------------------------------
      character (len=LineLength) :: InFile,OutFile,LogFile,SumFile,ErrFile,RunName
      integer :: IOS
      character (len=WordLength) :: DateVal,TimeVal,ZoneVal
      character (len=LineLength) :: ProgramName,ProgramPath
      integer :: F
      integer, dimension(8) :: TimArray

      ! Main part of procedure
      !-----------------------

      ! Create Memory Space for the Words variable
      Words%Allocated = .false.
      Call Create (Words,NumWords)

      ! Date and time
      Call Date_And_Time (Date=DateVal,Time=TimeVal,Zone=ZoneVal,Values=TimArray)
```

```
      ! Get the run ID
      Call InitCh (RunName)
      RunName = GetRun()

      ! Get the path for the program
      Call GetProgramName (ProgramName)
      Call GetPath (ProgramName,ProgramPath)

      ! Construct the file names (add the extensions)
      call InitCh (InFile)
      call InitCh (OutFile)
      call InitCh (LogFile)
      call InitCh (SumFile)
      call InitCh (ErrFile)
      InFile  = trim(RunName)//Model%ExtInp
      OutFile = trim(RunName)//Model%ExtOut
      LogFile = trim(RunName)//Model%ExtLog
      ErrFile = trim(RunName)//Model%ExtErr

      ! Open the input file
      Open (FilInp,file=trim(InFile),status='old',IOStat=IOS)
      if (IOS /= 0) then
         ! Error condition - abort program execution
         Error%Code = -1
         write ( Error%m1,'("Cannot find file ",a," with status old")') trim(InFile)
         stop 'Illegal run id - no error file generated'
      end if
      rewind (FilInp)

      ! Open the error file
      Call OpenAfterDelete (FilErr,trim(ErrFile))

      ! Open the output file
      Call OpenAfterDelete (FilOut,trim(OutFile))

      ! Open the log file
      Call OpenAfterDelete (FilLog,trim(LogFile))

      write (*,'("* ")')
      write (*,'("* ------------------------------------------------------------")')
      write (*,'("* PEARLNEQ (c) MNP/RIVM/Alterra")')
      write (*,'("* ------------------------------------------------------------")')
      write (*,'("*")')
      write (*,'("* PEARLNEQ version 4")')
      write (*,'("* PEARLNEQ created on ",a)') trim (Model%Date)
      write (*,'("* ")')
      write (*,'("* ------------------------------------------------------------")')
      write (*,'("* ")')

      ! Write the Run ID, file-names and date-and-time to the output file
      do F = 21,22
         write (F,'("* ------------------------------------------------------------&
         &------------------")')
         write (F,'("* Results from PEARLNEQ (c) MNP/RIVM/Alterra")')
         write (F,'("* PEARLNEQ version 4")')
         write (F,'("* PEARLNEQ created on ",a)') trim (Model%Date)
         write (F,'("* ")')
         write (F,'("* Run ID                                                  : ",a)') trim
(GetRun())
         write (F,'("* Input file generated on                       : ",a2,"-",a2,"-",a4)')
&
         DateVal(7:8),DateVal(5:6),DateVal(1:4)
         write (F,'("* ------------------------------------------------------------&
         &------------------")')
         write (F,'("* ")')

      end do
   end subroutine OpenPearlNEQFiles
end program PearlNeq
```

WOt-onderzoek

Verschenen documenten in de reeks Werkdocumenten van de Wettelijke Onderzoekstaken Natuur & Milieu – vanaf mei 2005

Werkdocumenten zijn verkrijgbaar bij het secretariaat van Unit Wettelijke Onderzoekstaken Natuur & Milieu, te Wageningen. T 0317 – 47 78 44; F 0317 – 41 90 00; E info.wnm@wur.nl

De werkdocumenten zijn ook te downloaden via de WOt-website www.wotnatuurenmilieu.wur.nl

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