

kinfit -  
Routines for fitting kinetic models to chemical  
degradation data

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August 18, 2016

**Abstract**

In the regulatory evaluation of chemical substances like plant protection products (pesticides), biocides and other chemicals, degradation data play an important role. For the evaluation of pesticide degradation experiments, detailed guidance has been developed, based on nonlinear regression. The R add-on package **kinfit** implements fitting the models recommended in this guidance from within R and calculates the recommended statistical measures for data series within one compartment without metabolite data.

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**Key words:** Kinetics, FOCUS, nonlinear fitting

## 1 Introduction

Many approaches are possible regarding the evaluation of chemical degradation data. The **kinfit** package ([kinfit, 2013](#)) in R ([R Development Core Team, 2009](#)) implements the approach recommended in the kinetics report provided by the FORum for Co-ordination of pesticide fate models and their USE ([FOCUS Work Group on Degradation Kinetics, 2006](#)) for simple data series for one parent compound in one compartment.

## 2 Example

In the following, requirements for data formatting are explained. Then the procedure for fitting the four kinetic models recommended by the FOCUS group to an example dataset given in the FOCUS kinetics report is illustrated. The explanations are kept rather verbose in order to lower the barrier for R newcomers.

## 2.1 Data format

The following listing shows example dataset C from the FOCUS kinetics report as distributed with the **kinfit** package

```
R> library("kinfit")
R> data("FOCUS_2006_C", package = "kinfit")
R> print(FOCUS_2006_C)
```

```
      t parent
1     0  85.1
2     1  57.9
3     3  29.9
4     7  14.6
5    14   9.7
6    28   6.6
7    63   4.0
8    91   3.9
9   119   0.6
```

Note that the data needs to be in the format of a data frame containing a variable **t** containing sampling times and a variable **parent** containing the measured data. Replicate measurements are not recorded in extra columns but simply appended, leading to multiple occurrences of the sampling times **t**.

Small to medium size dataset can be conveniently entered directly as R code as shown in the following listing

```
R> kindata_example <- data.frame(
+   t = c(0, 1, 3, 7, 14, 28, 63, 91, 119),
+   parent = c(85.1, 57.9, 29.9, 14.6, 9.7, 6.6, 4, 3.9, 0.6)
+ )
```

## 2.2 Fitting the kinetic models

The user can choose for which kinetic models the **kinfit** function will try to find optimised parameters. This is achieved by the argument **kinmodels** to the function, as shown below. The models currently implemented are abbreviated **SFO** (Single First-Order), **FOMC** (First-Order Multi-Compartment), **DFOP** (Double First-Order in Parallel) and **HS** (Hockey-Stick) as defined by the [FOCUS Work Group on Degradation Kinetics \(2006\)](#). From the DFOP model, corresponding parameters in the notation of the SFORB model (Single First-Order Reversible Binding) are additionally calculated.

```
R> kinfits.C <- kinfit(FOCUS_2006_C, kinmodels = c("SFO", "FOMC", "DFOP", "HS"))
```

The results of the fitting procedure are returned by the function, and can then be inspected by the function `kinresults`.

```
R> kinresults(kinfits.C)
```

```
$parms
```

```
$parms$SFO
```

```
$parms$SFO$parent.0
```

```
[1] 82.49211
```

```
$parms$SFO$k
```

```
[1] 0.3060624
```

```
$parms$FOMC
```

```
$parms$FOMC$parent.0
```

```
[1] 85.87489
```

```
$parms$FOMC$alpha
```

```
[1] 1.053292
```

```
$parms$FOMC$beta
```

```
[1] 1.91739
```

```
$parms$DFOP
```

```
$parms$DFOP$parent.0
```

```
[1] 85.00274
```

```
$parms$DFOP$k1
```

```
[1] 0.4595574
```

```
$parms$DFOP$k2
```

```
[1] 0.01784879
```

```
$parms$DFOP$g
```

```
[1] 0.8539455
```

```
$parms$SFORB
```

```
$parms$SFORB$parent.0
```

```
[1] 85.00274
```

```
$parms$SFORB$k1out
```

```
[1] 0.3950438
```

```
$parms$SFORB$k21
```

```
[1] 0.02076363
```

```
$parms$SFORB$k12
[1] 0.0615987
```

```
$parms$HS
$parms$HS$parent.0
[1] 84.50157
```

```
$parms$HS$k1
[1] 0.3561582
```

```
$parms$HS$k2
[1] 0.02266097
```

```
$parms$HS$tb
[1] 5.152758
```

```
$stats
      n.times df mean.means      RSS      err.min      R2
SFO      9  7  23.58889 196.533408 0.15843954 0.9713629
FOMC     9  6  23.58889  31.050882 0.06656760 0.9954755
DFOP     9  5  23.58889   4.362714 0.02662111 0.9993643
HS       9  5  23.58889  13.585774 0.04695151 0.9980204
```

```
$results
      DT50      DT90
SFO  2.264725  7.523253
FOMC  1.785233 15.147927
DFOP  1.886911 21.250733
HS    1.946195 25.778024
```

The higher level functions `kinplot` and `kinreport` work on lists called `kinobject`. They contain the fitted models, optionally the data used for fitting the models, and the name of the parent compound as well as the test system type used for generating the data, as well as some more optional entries. The construction of such an object is shown below.

```
R> kinobject.C <- kinobject <- list(
+   parent = "Compound XY",
+   type = "Degradation in the environment",
+   system = "System 1",
+   source = "Synthetic example data from FOCUS kinetics",
+   data = FOCUS_2006_C,
+   fits = kinfits.C,
+   results = kinresults(kinfits.C))
```

The plotting and reporting functions then work on this object. The example below outputs the report to the console, because no `file` argument is specified. If a filename is specified, the report will be written to a text file.

```
R> kinreport(kinobject.C)
```

```
Parent compound: Compound XY
Study type:      Degradation in the environment
System:         System 1
Source:         Synthetic example data from FOCUS kinetics
kinfit version: 1.1.14
R version:      3.3.1
Report generated: Thu Aug 18 13:15:45 2016
```

```
Data:
```

```
      t parent
1     0   85.1
2     1   57.9
3     3   29.9
4     7   14.6
5    14    9.7
6    28    6.6
7    63    4.0
8    91    3.9
9   119    0.6
```

```
---
```

```
Nonlinear least squares fit of the SFO model
```

```
Parameter estimation:
```

|          | Estimate | Std. Error | t value | Pr(>t)   |
|----------|----------|------------|---------|----------|
| parent.0 | 82.492   | 4.7402     | 17.40   | 2.54e-07 |
| k        | 0.306    | 0.0459     | 6.67    | 1.43e-04 |

```
Chi2 error estimation: 15.84 %
```

```
---
```

```
Nonlinear least squares fit of the FOMC model
```

```
Parameter estimation:
```

|          | Estimate | Std. Error | t value | Pr(>t)   |
|----------|----------|------------|---------|----------|
| parent.0 | 85.87    | 2.246      | 38.23   | 1.07e-08 |
| alpha    | 1.05     | 0.169      | 6.23    | 3.95e-04 |
| beta     | 1.92     | 0.537      | 3.57    | 5.89e-03 |

Chi2 error estimation: 6.66 %

---

Nonlinear least squares fit of the DFOP model

Parameter estimation:

|          | Estimate | Std. Error | t value | Pr(>t)   |
|----------|----------|------------|---------|----------|
| parent.0 | 85.0027  | 0.89067    | 95.44   | 1.20e-09 |
| k1       | 0.4596   | 0.02036    | 22.57   | 1.59e-06 |
| k2       | 0.0178   | 0.00304    | 5.87    | 1.02e-03 |
| g        | 0.8539   | 0.01344    | 63.54   | 9.14e-09 |

Chi2 error estimation: 2.66 %

---

Nonlinear least squares fit of the HS model

Parameter estimation:

|          | Estimate | Std. Error | t value | Pr(>t)   |
|----------|----------|------------|---------|----------|
| parent.0 | 84.5016  | 1.53770    | 55.0    | 1.89e-08 |
| k1       | 0.3562   | 0.01852    | 19.2    | 3.51e-06 |
| k2       | 0.0227   | 0.00567    | 4.0     | 5.18e-03 |
| tb       | 5.1528   | 0.41051    | 12.6    | 2.85e-05 |

Chi2 error estimation: 4.7 %

---

Endpoint estimates

|      | DT50 | DT90 |
|------|------|------|
| SFO  | 2.3  | 7.5  |
| FOMC | 1.8  | 15.1 |
| DFOP | 1.9  | 21.3 |
| HS   | 1.9  | 25.8 |

Plotting is done on an on-screen device. Graphics files in vector based formats can be obtained using the R devices `pdf`, `eps`, or, subject to platform restrictions, `windows.metafile`.

A residual plot can be obtained with the function `kinresplot` as shown in Figure 2.

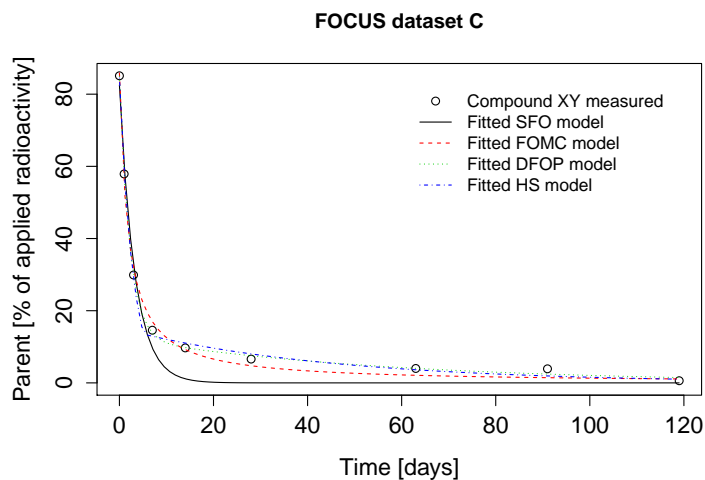


Figure 1: Fits of standard models to FOCUS dataset C.

### 3 Validation

In the following comparisons, the results for fitting the four recommended kinetic models to FOCUS datasets A to F with **kinfit** were obtained.

#### 3.1 Single First Order Model

In Tables 1 to 6, the results from fitting the SFO model to FOCUS example datasets with various software packages as given in the report by the [FOCUS Work Group on Degradation Kinetics \(2006\)](#) are compared with the results obtained with **kinfit**.

The comparisons show that all packages evaluated in the FOCUS report give very similar results for the SFO model. The results obtained with **kinfit** are very close to the median of the results reported for the other packages.

#### 3.2 First Order Multi Compartment Model

The comparison of the results obtained for the FOMC model show much more variability between software packages. For dataset A, results for the **alpha** and **beta** parameters differ over several orders of magnitude between the different packages. The method used by the **kinfit** routine does not converge for this dataset. The same applies to the total system and water phase only data for example dataset F and the FOMC model.

For datasets B and C, the **kinfit** function produces results which are very close to the median of the results obtained by the other packages.



Table 1: Results of fitting the SFO model to the example dataset A ([FOCUS Work Group on Degradation Kinetics, 2006](#)), as given in the report, in comparison to the results obtained by **kinfit**.

| Package       | $M_0$  | $k$    | DT <sub>50</sub> | DT <sub>90</sub> |
|---------------|--------|--------|------------------|------------------|
| ACSL          | 109.20 | 0.0372 | 18.63            | 61.90            |
| Excel         | 109.15 | 0.0372 | 18.62            | 61.87            |
| Kinetica      | 109.11 | 0.0371 | 18.66            | 62.00            |
| Madonna       | 109.20 | 0.0372 | 18.63            | 61.90            |
| Mathematica   | 109.15 | 0.0372 | 18.62            | 61.87            |
| MatLab        | 109.15 | 0.0372 | 18.63            | 61.87            |
| ModelMaker    | 109.10 | 0.0371 | 18.68            | 62.06            |
| ModelManager  | 109.15 | 0.0372 | 18.62            | 61.86            |
| PRISM         | 109.20 | 0.0372 | 18.63            | 61.90            |
| Statistica    | 109.15 | 0.0372 | 18.63            | 61.90            |
| Tablecurve    | 109.15 | 0.0372 | 18.62            | 61.87            |
| Median        | 109.15 | 0.0372 | 18.63            | 61.90            |
| <b>kinfit</b> | 109.15 | 0.0372 | 18.62            | 61.87            |

Table 2: Results of fitting the SFO model to the example dataset B ([FOCUS Work Group on Degradation Kinetics, 2006](#)), as given in the report, in comparison to the results obtained by **kinfit**.

| Package       | $M_0$ | $k$    | DT <sub>50</sub> | DT <sub>90</sub> |
|---------------|-------|--------|------------------|------------------|
| ACSL          | 99.20 | 0.0782 | 8.86             | 29.44            |
| Excel         | 99.17 | 0.0782 | 8.87             | 29.46            |
| Kinetica      | 99.17 | 0.0781 | 8.87             | 29.47            |
| Madonna       | 99.18 | 0.0782 | 8.87             | 29.46            |
| Mathematica   | 99.17 | 0.0782 | 8.87             | 29.46            |
| MatLab        | 99.17 | 0.0782 | 8.89             | 29.46            |
| ModelMaker    | 99.20 | 0.0780 | 8.89             | 29.52            |
| ModelManager  | 99.17 | 0.0782 | 8.87             | 29.46            |
| PRISM         | 99.17 | 0.0782 | 8.87             | 29.46            |
| Statistica    | 99.17 | 0.0782 | 8.87             | 29.46            |
| Tablecurve 2D | 99.17 | 0.0782 | 8.87             | 29.46            |
| Median        | 99.17 | 0.0782 | 8.87             | 29.46            |
| <b>kinfit</b> | 99.17 | 0.0782 | 8.87             | 29.46            |

Table 3: Results of fitting the SFO model to the example dataset C ([FOCUS Work Group on Degradation Kinetics, 2006](#)), as given in the report, in comparison to the results obtained by **kinfit**.

| Package       | $M_0$ | $k$    | DT <sub>50</sub> | DT <sub>90</sub> |
|---------------|-------|--------|------------------|------------------|
| ACSL          | 82.50 | 0.3062 | 2.26             | 7.52             |
| Kinetica      | 82.40 | 0.3043 | 2.28             | 7.57             |
| Madonna       | 82.49 | 0.3060 | 2.27             | 7.52             |
| Mathematica   | 82.49 | 0.3060 | 2.26             | 7.52             |
| MatLab        | 82.49 | 0.3060 | 2.27             | 7.52             |
| ModelMaker    | 82.49 | 0.3054 | 2.27             | 7.54             |
| PRISM         | 82.49 | 0.3061 | 2.26             | 7.52             |
| Tablecurve 2D | 82.49 | 0.3061 | 2.26             | 7.52             |
| Median        | 82.49 | 0.3060 | 2.265            | 7.52             |
| <b>kinfit</b> | 82.49 | 0.3061 | 2.26             | 7.52             |

Table 4: Results of fitting the SFO model to the example dataset D ([FOCUS Work Group on Degradation Kinetics, 2006](#)), as given in the report, in comparison to the results obtained by **kinfit**.

| Package       | $M_0$ | $k$    | DT <sub>50</sub> | DT <sub>90</sub> |
|---------------|-------|--------|------------------|------------------|
| ACSL          | 99.64 | 0.0989 | 7.01             | 23.29            |
| Madonna       | 99.45 | 0.0979 | 7.08             | 23.52            |
| MatLab        | 98.31 | 0.0989 | 7.00             | 23.28            |
| PRISM         | 99.44 | 0.0979 | 7.08             | 23.51            |
| Tablecurve 2D | 99.44 | 0.0979 | 7.08             | 23.51            |
| Median        | 99.44 | 0.0979 | 7.08             | 23.51            |
| <b>kinfit</b> | 99.44 | 0.0979 | 7.08             | 23.51            |

Table 5: Results of fitting the SFO model to the total system data from example dataset F (FOCUS Work Group on Degradation Kinetics, 2006), as given in the report, in comparison to the results obtained by **kinfit**.

| Package       | $M_0$  | $k$    | DT <sub>50</sub> | DT <sub>90</sub> |
|---------------|--------|--------|------------------|------------------|
| Kinetica      | 104.42 | 0.0398 | 17.40            | 57.80            |
| Madonna       | 104.49 | 0.0399 | 17.35            | 57.64            |
| Mathematica   | 104.48 | 0.0399 | 17.35            | 57.64            |
| MatLab        | 104.48 | 0.0400 | 17.35            | 57.63            |
| ModelMaker    | 104.50 | 0.0398 | 17.42            | 57.85            |
| ModelManager  | 104.47 | 0.0399 | 17.35            | 57.64            |
| PRISM         | 104.50 | 0.0400 | 17.35            | 57.64            |
| Median        | 104.48 | 0.0399 | 17.35            | 57.64            |
| <b>kinfit</b> | 104.47 | 0.0399 | 17.35            | 57.64            |

Table 6: Results of fitting the SFO model to the water phase data from example dataset F (FOCUS Work Group on Degradation Kinetics, 2006), as given in the report, in comparison to the results obtained by **kinfit**.

| Package       | $M_0$   | $k$    | DT <sub>50</sub> | DT <sub>90</sub> |
|---------------|---------|--------|------------------|------------------|
| ACSL          | 100.54  | 0.0551 | 12.58            | 41.80            |
| Kinetica      | 100.88  | 0.0554 | 12.51            | 41.57            |
| Madonna       | 100.54  | 0.0550 | 12.59            | 41.83            |
| Mathematica   | 100.55  | 0.0551 | 12.58            | 41.80            |
| MatLab        | 100.55  | 0.0551 | 12.58            | 41.80            |
| ModelMaker    | 100.50  | 0.0549 | 12.63            | 41.94            |
| ModelManager  | 100.55  | 0.0551 | 12.58            | 41.80            |
| PRISM         | 100.50  | 0.0551 | 12.58            | 41.80            |
| Median        | 100.545 | 0.0551 | 12.58            | 41.80            |
| <b>kinfit</b> | 100.55  | 0.0551 | 12.58            | 41.80            |

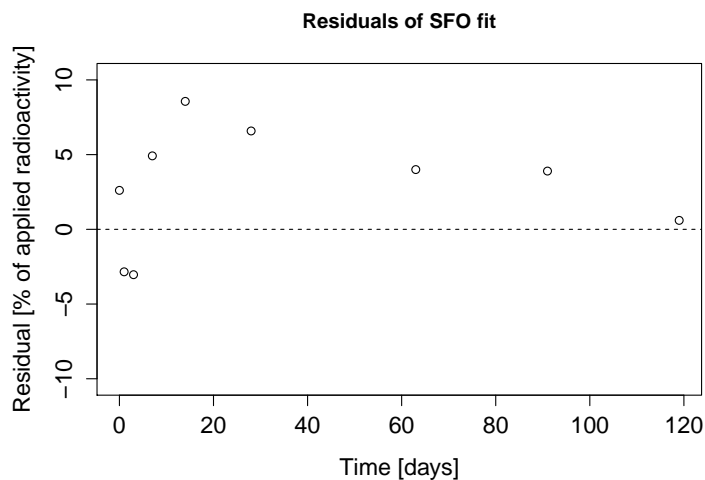


Figure 2: Residual plot for fitting the SFO model to FOCUS dataset C.

### 3.3 Double First Order in Parallel Model

Regarding fitting the DFOP model to FOCUS example dataset A, it is already indicated in the report that it is not a good example dataset for fitting this particular model, as the two kinetic constants postulated by the DFOP model are hardly distinguishable. As a consequence, the software packages strongly disagree especially on the model parameter  $f$  specifying the distribution between the kinetic domains that are characterised by the two kinetic constants. Again, the **kinfit** routine does not show convergence for this model and this dataset (Table 12).

Fitting the DFOP model with **kinfit** to dataset B yields results that are very close to the median of the results obtained by other packages, as illustrated in Table 13.

### 3.4 Hockey Stick Model

Analysis of dataset A shows basically two different parameter sets generated by the 8 packages reported in the FOCUS report ([FOCUS Work Group on Degradation Kinetics, 2006](#)). The **kinfit** package does not show conversion with the standard parameter defaults, but can reproduce the two parameter sets when given the respective parameter values as starting values, as shown in the last two lines in Table 14.

The HS fit did not converge for dataset B with **kinfit**. Again, this should be viewed in the light of the vastly differing results produced by the other software packages as listed in Table 15.

The results from fitting the HS model to dataset C with **kinfit** agree nicely with the median

Table 7: Results of fitting the FOMC model to the example dataset A ([FOCUS Work Group on Degradation Kinetics, 2006](#)), as given in the report, in comparison to the results obtained by **kinfit**.

| Package                 | $M_0$  | $\alpha$  | $\beta$  | DT <sub>50</sub> | DT <sub>90</sub> |
|-------------------------|--------|-----------|----------|------------------|------------------|
| ACSL                    | 109.34 | 2.93e+03  | 780000   | 18.43            | 61.32            |
| Excel                   | 109.20 | 2.36e+06  | 63300000 | 18.62            | 61.87            |
| Kinetica                | 107.29 | 4.26e+05  | 9640000  | 15.68            | 52.09            |
| Madonna                 | 109.18 | 2.08e+06  | 55900000 | 18.60            | 61.79            |
| Mathematica             | 109.15 | 1.07e+06  | 28700000 | 18.62            | 61.87            |
| MatLab                  | 109.45 | 2.74e+01  | 718      | 18.39            | 62.93            |
| ModelMaker              | 109.20 | 2.54e+04  | 682000   | 18.62            | 61.87            |
| Modelmaker <sup>a</sup> | 109.16 | 2.99e+02  | 8040     | 18.66            | 62.15            |
| ModelManager            | 109.17 | 5.15e+02  | 13800    | 18.61            | 61.93            |
| PRISM                   | 109.20 | 5.50e+05  | 14800000 | 18.62            | 61.86            |
| Statistica              | 109.20 | 1.25e+04  | 337000   | 18.62            | 61.87            |
| Tablecurve 2D           | 109.14 | -3.43e-04 | -922     | 18.62            | 61.90            |
| Median                  | 109.19 | 1.895e+04 | 731000   | 18.62            | 61.87            |
| <b>kinfit</b>           | no fit |           |          |                  |                  |

of the results obtained with the other packages, as shown in Table 16.

### 3.5 $\chi^2$ statistics

As no values for the minimum error rate that has to be assumed for the model to agree with the data ( $\chi^2$  statistics) are reported for the FOCUS datasets A to F, the respective values calculated by **kinfit** are compared to the  $\chi^2$  values calculated by the KinGUI package ([Schäfer et al., 2007](#)) as shown in Table 17.

For this, the possibility to write KinGUI input files using the function `kinwrite.KinGUI` from **kinfit** was used.

The comparison shows that whenever a minimum error level  $\chi^2$  was calculated using the **kinfit** package, it was very close to the value generated by KinGUI.

### 3.6 $R^2$ value

In a similar manner, the coefficient of determination calculated by **kinfit** according to the formula

Table 8: Results of fitting the FOMC model to the example dataset B ([FOCUS Work Group on Degradation Kinetics, 2006](#)), as given in the report, in comparison to the results obtained by **kinfit**.

| Package                 | $M_0$ | $\alpha$ | $\beta$  | DT <sub>50</sub> | DT <sub>90</sub> |
|-------------------------|-------|----------|----------|------------------|------------------|
| ACSL                    | 99.60 | 1.32e-03 | 161      | 8.69             | 30.71            |
| Excel                   | 99.20 | 4.94e+06 | 63200000 | 8.87             | 29.46            |
| Kinetica                | 99.66 | 1.27e+01 | 155      | 8.67             | 30.72            |
| Madonna                 | 99.66 | 1.28e+01 | 13.8     | 8.69             | 30.76            |
| Mathematica             | 99.67 | 1.28e+01 | 156      | 8.68             | 30.75            |
| MatLab                  | 99.75 | 1.10e+01 | 133      | 8.65             | 30.98            |
| ModelMaker              | 99.70 | 1.28e+01 | 156      | 8.69             | 30.76            |
| ModelMaker <sup>a</sup> | 99.67 | 1.25e+01 | 153      | 8.72             | 30.95            |
| ModelManager            | 99.67 | 1.28e+01 | 156      | 8.68             | 30.75            |
| PRISM                   | 99.67 | 1.28e+01 | 156      | 8.68             | 30.74            |
| Statistica              | 99.66 | 1.28e+01 | 156      | 8.68             | 30.76            |
| Tablecurve              | 99.66 | 1.28e+01 | 156      | 8.68             | 30.76            |
| Median                  | 99.66 | 1.28e+01 | 156      | 8.68             | 30.76            |
| <b>kinfit</b>           | 99.67 | 12.8053  | 156.1158 | 8.68             | 30.75            |

Table 9: Results of fitting the FOMC model to the example dataset C ([FOCUS Work Group on Degradation Kinetics, 2006](#)), as given in the report, in comparison to the results obtained by **kinfit**.

| Package       | $M_0$ | $\alpha$ | $\beta$ | DT <sub>50</sub> | DT <sub>90</sub> |
|---------------|-------|----------|---------|------------------|------------------|
| Kinetica      | 85.87 | 1.06     | 1.92    | 1.79             | 15.12            |
| Madonna       | 85.88 | 1.05     | 1.92    | 1.79             | 15.14            |
| Mathematica   | 85.87 | 1.05     | 1.92    | 1.79             | 15.15            |
| MatLab        | 85.88 | 1.05     | 1.92    | 1.79             | 15.15            |
| ModelMaker    | 85.88 | 1.04     | 1.89    | 1.79             | 15.39            |
| PRISM         | 85.88 | 1.05     | 1.92    | 1.79             | 15.16            |
| Tablecurve 2D | 85.87 | 1.05     | 1.92    | 1.79             | 15.15            |
| Median        | 85.88 | 1.05     | 1.92    | 1.79             | 15.15            |
| <b>kinfit</b> | 85.87 | 1.0533   | 1.9174  | 1.79             | 15.15            |

Table 10: Results of fitting the FOMC model to the total system data from example dataset F ([FOCUS Work Group on Degradation Kinetics, 2006](#)), as given in the report, in comparison to the results obtained by **kinfit**.

| Package       | $M_0$  | $\alpha$  | $\beta$  | DT <sub>50</sub> | DT <sub>90</sub> |
|---------------|--------|-----------|----------|------------------|------------------|
| Kinetica      | 103.94 | 2.21e+03  | 52200    | 16.41            | 54.55            |
| Madonna       | 104.49 | 2.51e+06  | 62700000 | 17.34            | 57.59            |
| Mathematica   | 104.47 | 1.28e+06  | 31900000 | 17.35            | 57.64            |
| MatLab        | 104.68 | 3.84e+01  | 942      | 17.17            | 58.26            |
| ModelMaker    | 104.50 | 1.05e+02  | 2630     | 17.39            | 58.21            |
| ModelManager  | 104.48 | 2.13e+03  | 53200    | 17.35            | 57.65            |
| PRISM         | 104.50 | 8.38e+04  | 2.1e+07  | 17.35            | 57.65            |
| Median        | 104.49 | 2210.0000 | 52200    | 17.35            | 57.65            |
| <b>kinfit</b> | no fit |           |          |                  |                  |

Table 11: Results of fitting the FOMC model to the water phase data from example dataset F ([FOCUS Work Group on Degradation Kinetics, 2006](#)), as given in the report, in comparison to the results obtained by **kinfit**.

| Package       | $M_0$  | $\alpha$  | $\beta$   | DT <sub>50</sub> | DT <sub>90</sub> |
|---------------|--------|-----------|-----------|------------------|------------------|
| Kinetica      | 100.51 | 1.26e+03  | 2.27E+04  | 12.51            | 41.58            |
| Madonna       | 100.55 | 3.76e+06  | 6.83E+07  | 12.59            | 41.81            |
| Mathematica   | 100.55 | 1.86e+06  | 3.39E+07  | 12.58            | 41.80            |
| MatLab        | 100.73 | 4.79e+01  | 8.55E +02 | 12.47            | 42.13            |
| MMaker        | 100.60 | 1.20e+02  | 2.18E+03  | 12.60            | 42.15            |
| ModelManager  | 100.55 | 2.14e+03  | 3.89E+04  | 12.58            | 41.81            |
| PRISM         | 100.50 | 9.78e+04  | 1.77E+06  | 12.55            | 41.68            |
| Median        | 100.55 | 2140.0000 | 3.39E+07  | 12.58            | 41.81            |
| <b>kinfit</b> | no fit |           |           |                  |                  |

Table 12: Results of fitting the DFOP model to the example dataset A ([FOCUS Work Group on Degradation Kinetics, 2006](#)), as given in the report, in comparison to the results obtained by **kinfit**.

| Package       | $M_0$  | $f$  | $k_1$  | $k_2$  | DT <sub>50</sub> | DT <sub>90</sub> |
|---------------|--------|------|--------|--------|------------------|------------------|
| ACSL          | 109.30 | 1.00 | 0.0376 | 0.0000 | 18.43            | 61.24            |
| Madonna       | 109.15 | 0.54 | 0.0372 | 0.0372 | 18.62            | 61.87            |
| Mathematica   | 109.15 | 0.58 | 0.0372 | 0.0372 | 18.62            | 61.87            |
| MatLab        | 109.15 | 0.50 | 0.0372 | 0.0372 | 18.62            | 61.86            |
| ModelMaker    | 109.10 | 0.07 | 0.0369 | 0.0371 | 18.70            | 62.10            |
| PRISM         | 109.16 | 0.50 | 0.0372 | 0.0372 | 18.65            | 61.88            |
| Tablecurve    | 109.14 | 0.79 | 0.0372 | 0.0373 | 18.63            | 61.86            |
| Median        | 109.15 | 0.54 | 0.0372 | 0.0372 | 18.62            | 61.87            |
| <b>kinfit</b> | no fit |      |        |        |                  |                  |

Table 13: Results of fitting the DFOP model to the example dataset B ([FOCUS Work Group on Degradation Kinetics, 2006](#)), as given in the report, in comparison to the results obtained by **kinfit**.

| Package       | $M_0$ | $f$  | $k_1$  | $k_2$  | DT <sub>50</sub> | DT <sub>90</sub> |
|---------------|-------|------|--------|--------|------------------|------------------|
| ACSL          | 99.59 | 0.82 | 0.0890 | 0.0439 | 8.70             | 30.60            |
| Madonna       | 99.65 | 0.67 | 0.0959 | 0.0526 | 8.64             | 30.34            |
| Mathematica   | 99.65 | 0.67 | 0.0958 | 0.0525 | 8.68             | 30.79            |
| MatLab        | 99.61 | 0.80 | 0.0903 | 0.0452 | 8.69             | 30.71            |
| ModelMaker    | 99.70 | 0.68 | 0.0955 | 0.0517 | 8.70             | 30.90            |
| PRISM         | 99.65 | 0.67 | 0.0958 | 0.0525 | 8.68             | 30.79            |
| Statistica    | 99.65 | 0.67 | 0.0958 | 0.0526 | 8.64             | 30.74            |
| Tablecurve 2D | 99.65 | 0.67 | 0.0958 | 0.0526 | 8.68             | 30.79            |
| Median        | 99.65 | 0.67 | 0.0958 | 0.0525 | 8.68             | 30.77            |
| <b>kinfit</b> | 99.65 | 0.67 | 0.0958 | 0.0525 | 8.68             | 30.79            |



Table 14: Results of fitting the HS model to the example dataset A ([FOCUS Work Group on Degradation Kinetics, 2006](#)), as given in the report, in comparison to the results obtained by **kinfit**.

| Package            | $M_0$  | $t_b$ | $k_1$  | $k_2$  | DT <sub>50</sub> | DT <sub>90</sub> |
|--------------------|--------|-------|--------|--------|------------------|------------------|
| Excel <sup>a</sup> | 102.31 | 10.92 | 0.0167 | 0.0544 | 20.29            | 49.86            |
| Excel <sup>a</sup> | 100.75 | 5.11  | 0.0006 | 0.0456 | 20.22            | 55.49            |
| Kinetica           | 101.24 | 5.96  | 0.0066 | 0.0462 | 20.13            | 54.99            |
| Madonna            | 102.31 | 10.91 | 0.0167 | 0.0544 | 20.29            | 49.86            |
| Mathematica        | 100.26 | 5.33  | 0.0462 | 0      | 20.33            | 49.56            |
| ModelMaker         | 102.30 | 10.90 | 0.0167 | 0.0543 | 20.31            | 49.95            |
| ModelManager       | 102.31 | 10.91 | 0.0167 | 0.0545 | 20.29            | 49.85            |
| PRISM              | 102.30 | 10.91 | 0.0167 | 0.0545 | 20.29            | 49.85            |
| Statistica         | 102.31 | 10.92 | 0.0167 | 0.0544 | 20.31            | 49.89            |
| Median             | 102.30 | 10.91 | 0.0167 | 0.0544 | 20.29            | 49.86            |
| <b>kinfit</b>      | no fit |       |        |        |                  |                  |
| <b>kinfit</b>      | 101.24 | 5.97  | 0.0066 | 0.0462 | 20.12            | 54.95            |
| <b>kinfit</b>      | 102.31 | 10.91 | 0.0167 | 0.0544 | 20.29            | 49.85            |

Table 15: Results of fitting the HS model to the example dataset B ([FOCUS Work Group on Degradation Kinetics, 2006](#)), as given in the report, in comparison to the results obtained by **kinfit**.

| Package            | $M_0$  | $t_b$ | $k_1$  | $k_2$  | DT <sub>50</sub> | DT <sub>90</sub> |
|--------------------|--------|-------|--------|--------|------------------|------------------|
| Excel <sup>a</sup> | 99.33  | 26.00 | 0.0788 | 0.0592 | 8.79             | 30.27            |
| Excel <sup>a</sup> | 100.42 | 7.00  | 0.0848 | 0.0702 | 8.42             | 31.36            |
| Kinetica           | 100.14 | 7.00  | 0.0833 | 0.071  | 8.55             | 31.23            |
| Madonna            | 100.19 | 7.00  | 0.0839 | 0.0704 | 8.50             | 31.37            |
| Mathematica        | 98.62  | 26.26 | 0.0744 | NA     | 8.93             | 29.05            |
| ModelManager       | 99.34  | 26.01 | 0.0789 | 0.0592 | 8.79             | 30.26            |
| PRISM              | 99.20  | 35.03 | 0.0783 | 0.0538 | 8.86             | 29.42            |
| Statistica         | 99.33  | 26.00 | 0.0789 | 0.0592 | 8.79             | 30.26            |
| Median             | 99.335 | 26.00 | 0.0789 | NA     | 8.79             | 30.27            |
| <b>kinfit</b>      | no fit |       |        |        |                  |                  |

Table 16: Results of fitting the HS model to the example dataset C ([FOCUS Work Group on Degradation Kinetics, 2006](#)), as given in the report, in comparison to the results obtained by **kinfit**.

| Package       | $M_0$ | $t_b$ | $k_1$  | $k_2$  | DT <sub>50</sub> | DT <sub>90</sub> |
|---------------|-------|-------|--------|--------|------------------|------------------|
| ACSL          | 84.50 | 5.10  | 0.3562 | 0.0247 | 1.95             | 24.76            |
| Kinetica      | 84.50 | 5.16  | 0.3562 | 0.0225 | 1.95             | 25.84            |
| Madonna       | 84.50 | 5.15  | 0.3562 | 0.0227 | 1.95             | 25.78            |
| Mathematica   | 91.45 | -0.33 | 0.3060 | 0      | 1.93             | 7.10             |
| ModelMaker    | 84.51 | 5.15  | 0.3555 | 0.0225 | 1.95             | 26.12            |
| PRISM         | 84.50 | 5.15  | 0.3562 | 0.0227 | 1.95             | 25.77            |
| Median        | 84.50 | 5.15  | 0.3562 | 0.0226 | 1.95             | 25.77            |
| <b>kinfit</b> | 84.5  | 5.15  | 0.3562 | 0.0227 | 1.95             | 25.78            |

Table 17: Comparison of  $\chi^2$  error levels in percent calculated for model fits by the KinGUI and **kinfit** packages.

| Dataset  | SFO     |               | FOMC    |               | DFOP    |               | HS     |               |
|----------|---------|---------------|---------|---------------|---------|---------------|--------|---------------|
|          | KinGUI  | <b>kinfit</b> | KinGUI  | <b>kinfit</b> | KinGUI  | <b>kinfit</b> | KinGUI | <b>kinfit</b> |
| A        | 8.3852  | 8.3848        | 9.3116  |               | 9.66    |               | 4.1106 |               |
| B        | 4.4562  | 4.4555        | 4.6641  | 4.5886        | 4.9562  | 4.9527        | 4.4535 |               |
| C        | 15.8456 | 15.844        | 6.6574  | 6.6568        | 2.6613  | 2.6621        | 4.6963 | 4.6952        |
| D        | 6.4539  | 6.4524        | 6.808   | 6.7792        | 7.2751  |               | 5.8196 |               |
| F system | 12.5386 | 12.5379       | 13.4533 |               | 14.1524 |               | 3.2178 |               |
| F water  | 10.8069 | 10.8055       | 11.6682 |               | 12.1821 |               | 1.6558 |               |

Table 18: Comparison of model efficiency (EF) values calculated by KinGUI and  $R^2$  values calculated by **kinfit**.

| Dataset | SFO    |               | FOMC   |               | DFOP   |               | HS     |               |
|---------|--------|---------------|--------|---------------|--------|---------------|--------|---------------|
|         | KinGUI | <b>kinfit</b> | KinGUI | <b>kinfit</b> | KinGUI | <b>kinfit</b> | KinGUI | <b>kinfit</b> |
| A       | 0.9845 | 0.9845        | 0.9831 |               | 0.9845 |               | 0.9972 |               |
| B       | 0.9971 | 0.9971        | 0.9973 | 0.9973        | 0.9973 | 0.9973        | 0.9972 |               |
| C       | 0.9714 | 0.9714        | 0.9955 | 0.9955        | 0.9994 | 0.9994        | 0.998  | 0.998         |
| D       | 0.9919 | 0.9919        | 0.992  | 0.992         | 0.9919 |               | 0.9945 |               |

$$R^2 = 1 - RSS/TSS \quad (1)$$

where RSS is the sum of squares of the residuals and TSS is the sum of squares of the deviations from the mean value is compared to the model efficiency EF calculated by KinGUI based on the same formula (FOCUS 2006, p. 99) as shown in Table 18. This exercise was done for FOCUS datasets A to D only.

The comparison shows that whenever the comparison was possible, the  $R^2$  value calculated by the **kinfit** package was equal to the model efficiency calculated by KinGUI, both rounded to four digits.

## 4 Conclusion

The **kinfit** package for R gives access to the possibility to fit the kinetic models recommended by the FOCUS group (FOCUS Work Group on Degradation Kinetics, 2006) from within R. Comparison with the results obtained with other software packages shows that **kinfit** produces kinetic endpoints that are within the variability and even very close to the median of results obtained with other packages, except for some cases where **kinfit** does not produce results and the results obtained with other software packages are strongly divergent.

## 5 Acknowledgements

This package would not have been written without me being introduced to regulatory fate modelling of pesticides by Adrian Gurney during my time at Harlan Laboratories Ltd (formerly RCC Ltd). Parts of the package were written during my employment at Harlan.

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