Attachment 1. Additional Guidance for Evaluating and Calculating Degradation Kinetics in Environmental Media

March 20, 2015

In 2013, the Environmental Fate and Effects Division (EFED) finalized the following guidance documents:

> Bohaty, R. F. H., Eckel, W., White, K., and Young, D. F. 2012. *Standard Operating Procedure for Using the NAFTA Guidance to Calculate Representative Half-life Values and Characterizing Pesticide Degradation*. November 30, 2012. Environmental Fate and Effects Division. Office of Pesticide Programs. United States Environmental Protection Agency
>
> NAFTA. 2012. *Guidance for Evaluating and Calculating Degradation Kinetics in Environmental Media*. December 2012. NAFTA Technical Working Group on Pesticides

Over the last year, USEPA evaluated results obtained using the above guidance documents to determine if adjustments need to be made to the approach. EFED compiled examples where the PestDF (version 0.8.4), the tool used most commonly by USEPA to conduct kinetic analysis following the NAFTA guidance, results required additional interpretation. A subsample of these examples, along with a brief explanation of some of the recurring issues observed are shown below. After completing the review, and considering comments received during the evaluation period, some updates in model fitting and interpretive rules were identified to improve the process. USEPA is recommending the following changes be made to the NAFTA guidance and summarized in an addendum to the initial NAFTA guidance document. Additionally, some changes to the model fitting tool are recommended.

The following parameter bounds are recommended to be utilized in the model fitting tool.

- The Double First Order in Parallel (DFOP) model parameter ‘f’ is the fraction of the total concentration that is subject to ‘k_0’ and one minus f is the fraction subject to ‘k_1.’ The ‘f parameter should be restricted to values between 0 and 1.
- The Indeterminate Order Rate Equation (IORE) model parameter ‘N’ should be restricted to values greater than 0. When N is less than 0 mass is created.
- All k values in the kinetics equations should be greater than or equal to 0. When k is less than 0, mass is created.

While the above parameter bounds were recommended by the USEPA degradation kinetics workgroup, it was found that it would not be possible to update the PestDF tool to include these bounds. Therefore, these limitations were not implemented in the PestDF tool. However, these parameter bounds should be considered when evaluating degradation kinetics results.

The following interpretive rules should be used when examining degradation kinetics following the NAFTA guidance.

- When the IORE parameter 'N' is less than one, the single-first order (SFO) model should be selected as the representative model input value. When N is less than one, the T_{IORE} will be less than the SFO half-life; therefore, use of a T_{IORE} as a representative half-life value is not conservative.
- When the DFOP k values are equal to the SFO k values, the SFO model should be selected as the representative model. Use of the simplest model to describe kinetics is preferred.
- Hydrolysis and aqueous photolysis studies are typically SFO. If SFO is not selected for one of these studies, the data should be further analyzed to determine why SFO was not the selected model.

These recommendations were made by the degradation kinetics workgroup.

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EXAMPLES

As part of the implementation evaluation of the NAFTA kinetics guidance, EFED compiled datasets where the kinetic analyses provided by PestDF (xxdeg 0.8.4) required additional interpretation in order to select a representative model input value. This evaluation focused specifically on those datasets that required additional analysis (*i.e.*, met the criteria listed below) and did not take a holistic approach and analyze every dataset that was fitted using PestDF following the NAFTA guidance. Nevertheless, the subset of datasets requiring additional analysis or fit the criteria below is thought to be low (<20%).

Criteria

1. **IORE PARAMETER ‘N’ IS LESS THAN 1**

2. **DFOP DID NOT CONVERGE OR YIELDED A NEGATIVE DT50 VALUE**

3. **DFOP PARAMETER ‘F’ IS GREATER THAN 1**

4. **DFOP PARAMETER ‘F’ IS LESS THAN 0**

5. **OBSERVED DT50 VALUE WAS DIFFERENT FROM THAT RECOMMENDED AS THE REPRESENTATIVE MODEL INPUT VALUE**

6. **SFO RESULTS WERE NOT SELECTED AS THE REPRESENTATIVE MODEL INPUT VALUE FOR AN ABIOTIC STUDY**

7. **DT50 WAS NOT OBSERVED DURING THE STUDY**

A subset of all the examples collected are organized by the criteria listed and provided on subsequent pages. A brief summary of the observations made as part of the evaluation are provided below.

In all the datasets except for two (see example on **Page 15**) where the IORE parameter ‘N’ was less than 1, PestDF selected SFO as the representative half-life value or the slow DFOP half-life value, which was equal to the SFO half-life value (see examples on **Page 12**). Based on this observation the degradation kinetics workgroup recommends that PestDF be updated to constrain the IORE parameter ‘N’ to positive values. In addition, the workgroup recommends when the IORE parameter ‘N’ less than 1 [*i.e.*, between greater than 0 (based on the recommended constraint) but less than 1], the results for SFO should be used.

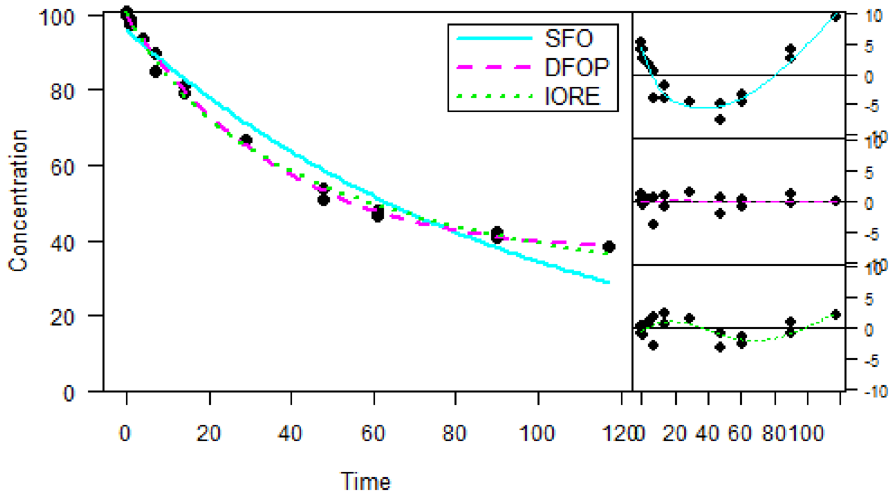
There is only one example where the DFOP parameter ‘f’ was observed to be greater than 1 using PestDF. In this case, the DFOP was selected as the representative model, and the second compartment DT50 value was equal to the SFO half-life value.

There are several datasets where DFOP did not converge or yielded a negative DT50 value for the second compartment. For many of these datasets, the DT50 was not observed during the study (see the example provided on **Page 11**) or it was observed at the end of the study (examples provided on **Page 5**). For some datasets, there is a higher amount of radioactivity observed at the end of the study than at previous sampling intervals (see example on **Page 11**) during the course of the study. This result may be due to normal variability in the data.

1. DFOP DID NOT CONVERGE OR YIELDED A NEGATIVE DT50 VALUE

Aerobic Soil Metabolism Study

Day	Applied Radioactivity
0	101.
0	99.8
1	98.8
1	97.5
4	93.8
4	93.6
7	89.7
7	85.1
14	81.0
14	79.2
29	66.7
29	66.6
48	51.1
48	53.7
61	47.8
61	46.7
90	42.2
90	40.6
117	38.4
117	38.4

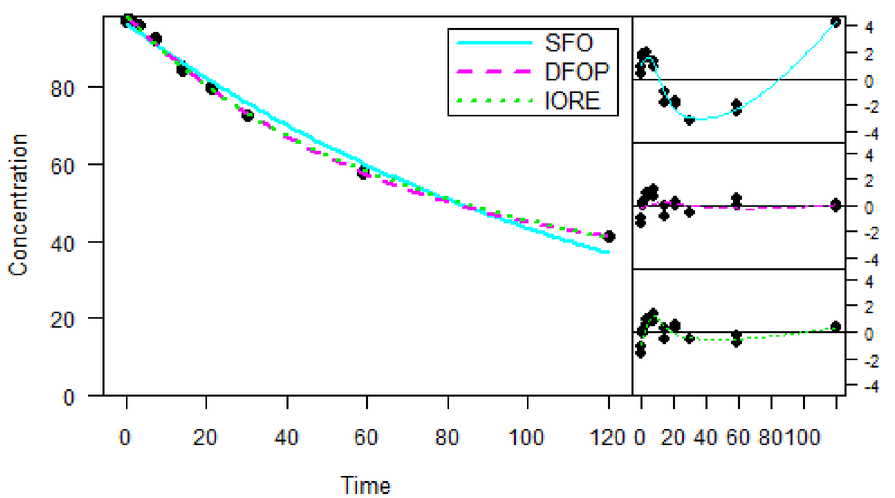


	DT_{50}	DT_{90}	χ^2	C_0	Parameters
SFO	67.7	225	5.4	95.8	k = 0.0102
DFOP	NA	NA	0.98	99.8	f = 0.725, k_0 = 0.0238, k_1 = -0.00186
IORE	58.2	1068	1.6	101	N = 2.57, k = 1.54e-05

S_C	64.4
S_{SFO}	465
Slow $t_{1/2}$	-374
$t_{R\ IORE}$	322

Aerobic Soil Metabolism Study

Day	Applied Radioactivity
0	96.9
0	97.4
1	97.3
1	97.6
3	95.8
3	96.2
7	92.1
7	92.6
14	84.4
14	85.2
21	79.6
21	79.9
30	72.7
30	72.7
59	57.6
59	58.2
120	41.1
120	41.3

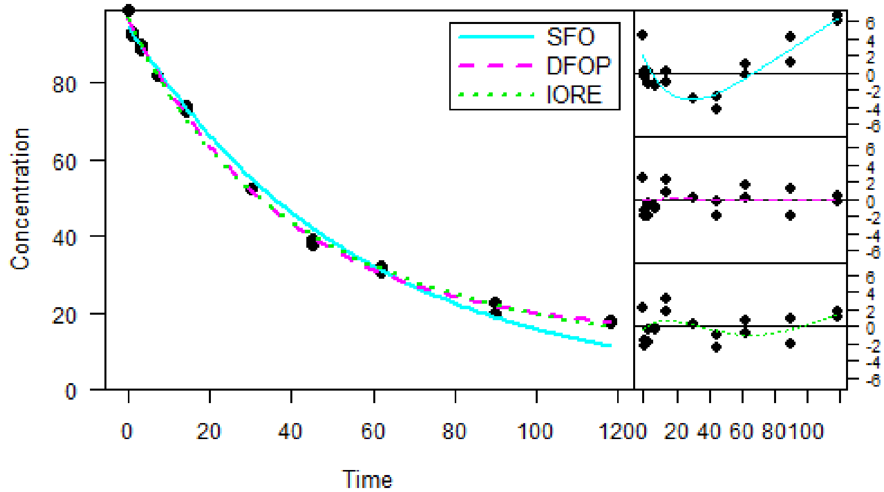


	DT_{50}	DT_{90}	χ^2	C_0	Parameters
SFO	86.6	288	2.3	96.5	k = 0.008
DFOP	NA	NA	0.68	98.3	f = 0.774, k_0 = 0.0141, k_1 = -0.00168
IORE	85.5	717	0.75	98.5	N = 1.94, k = 0.000153

S_C	11.8
S_{SFO}	94.8
Slow $t_{1/2}$	-414
$t_{R\ IORE}$	216

Aerobic Soil Metabolism Study

Day	Applied Radioactivity
0	99.2
0	99.2
1	92.5
1	93.2
3	88.5
3	90.0
7	82.0
7	82.2
14	73.9
14	72.5
30	52.2
30	52.2
45	37.9
45	39.4
62	30.7
62	32.0
90	19.9
90	22.9
118	17.3
118	18.1

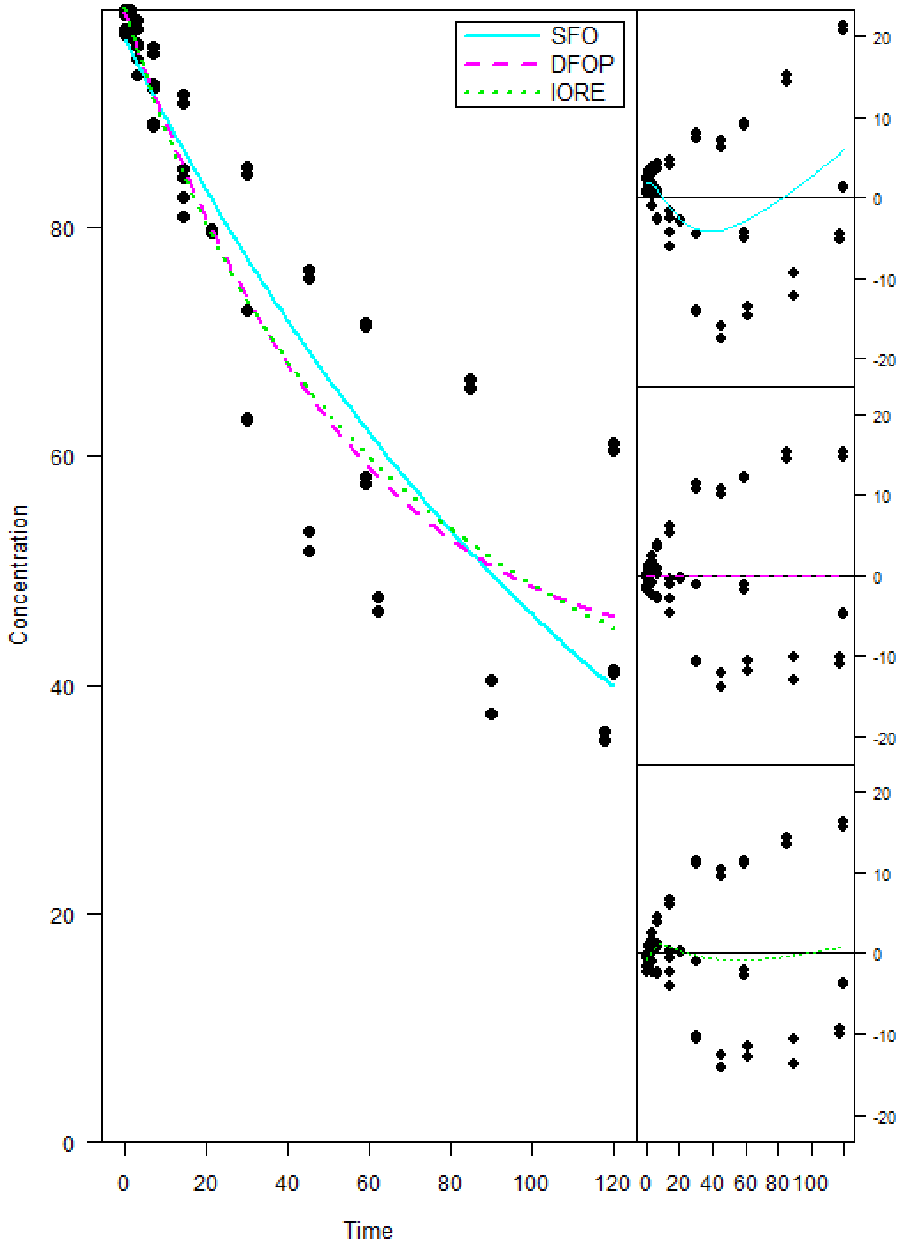


	DT_{50}	DT_{90}	χ^2	C_0	Parameters
SFO	38.6	128	4.1	94.8	k = 0.018
DFOP	34	NA	1.9	96.6	f = 0.875, k_0 = 0.0252, k_1 = -0.000788
IORE	33.8	177	2	97.2	N = 1.5, k = 0.00246

S_C	58
S_{SFO}	192
Slow $t_{1/2}$	-879
$t_{R\ IORE}$	53.3

Aerobic Soil Metabolism Study

Day	Applied Radioactivity
0	96.9
0	97.4
1	97.3
1	97.6
3	95.8
3	96.2
7	92.1
7	92.6
14	84.4
14	85.2
21	79.6
21	79.9
30	72.7
30	72.7
59	57.6
59	58.2
120	41.1
120	41.3
0	98.6
0	98.8
1	96.6
1	96.7
3	93.3
3	94.7
7	88.9
7	89.1
14	82.7
14	80.9
30	63.4
30	63.1
45	51.7
45	53.4
62	46.4
62	47.7
90	37.5
90	40.4
118	35.2
118	36.0
0	98.9
0	99.0
1	99.0
1	98.6
3	97.3
3	98.1
7	95.2
7	95.8
14	90.9
14	91.7
30	85.3
30	84.7
45	76.3
45	75.5
59	71.4
59	71.7
85	66.8
85	65.9
120	61.2
120	60.6



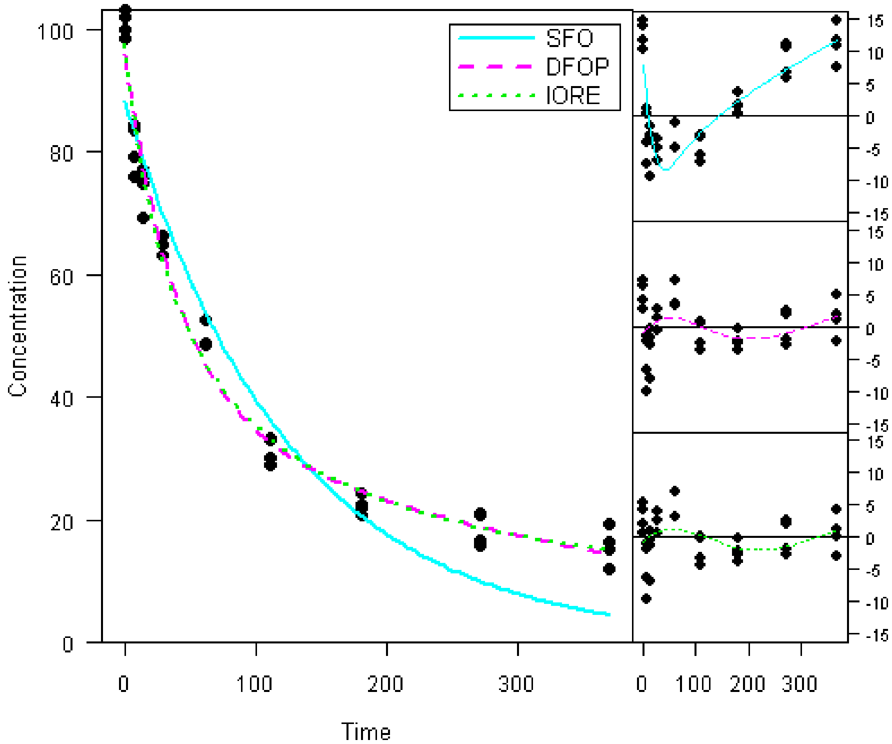
	DT_{50}	DT_{90}	χ^2	C_0	Parameters
SFO	94.3	313	7.6	96.4	k = 0.00735
DFOP	NA	NA	7.6	98.8	f = 0.734, k_0 = 0.0153, k_1 = -0.00226
IORE	96.7	1510	7.4	99.2	N = 2.45, k = 1.6e-05

S_C	3.33e+03
S_{SFO}	3.66e+03
Slow $t_{1/2}$	-307
$t_{R\ IORE}$	455

2. OBSERVED DT50 VALUE WAS DIFFERENT FROM THAT RECOMMENDED AS THE REPRESENTATIVE MODEL INPUT VALUE

Aerobic Soil Metabolism Study

Day	Applied Radioactivity
0	99.8
0	102.
0	98.5
0	103.
7	76.0
7	79.2
7	84.6
7	83.7
14	74.9
14	69.4
14	75.9
14	77.2
29	65.0
29	65.0
29	66.4
29	63.0
62	48.8
62	48.6
62	48.6
62	52.5
111	29.0
111	30.1
111	33.0
111	33.3
181	22.4
181	22.0
181	24.3
181	20.9
272	20.7
272	21.2
272	16.8
272	15.9
370	16.3
370	19.2
370	15.3
370	12.1



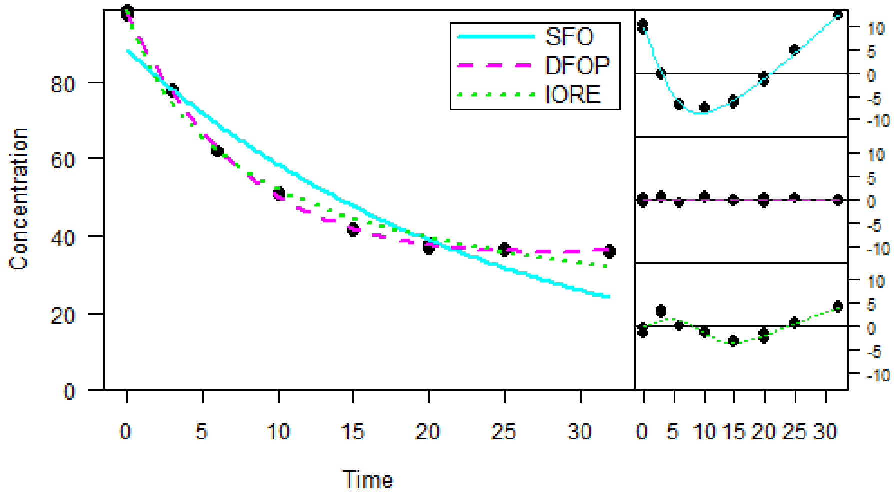
	DT_{50}	DT_{90}	χ^2	C_0	Parameters
SFO	86.3	287	11	88.2	k= 0.00803
DFOP	55.6	518	5.6	95.7	f = 0.589, k_0 = 0.025, k_1 = 0.00273
IORE	53.4	669	4.5	97.7	N = 2.27, k = 6.1e-05

S_C	477
S_{SFO}	2e+03
Slow $t_{1/2}$	254
$t_{R\ IORE}$	201

3. SFO RESULTS WERE NOT SELECTED AS THE REPRESENTATIVE MODEL INPUT VALUE FOR AN ABIOTIC STUDY

Hydrolysis Study

Day	Applied Radioactivity
0	98.6
0	97.5
3	78.0
3	77.4
6	62.1
6	62.0
10	51.1
10	50.7
15	41.7
15	41.2
20	38.0
20	36.9
25	36.4
25	36.6
32	36.2
32	35.9

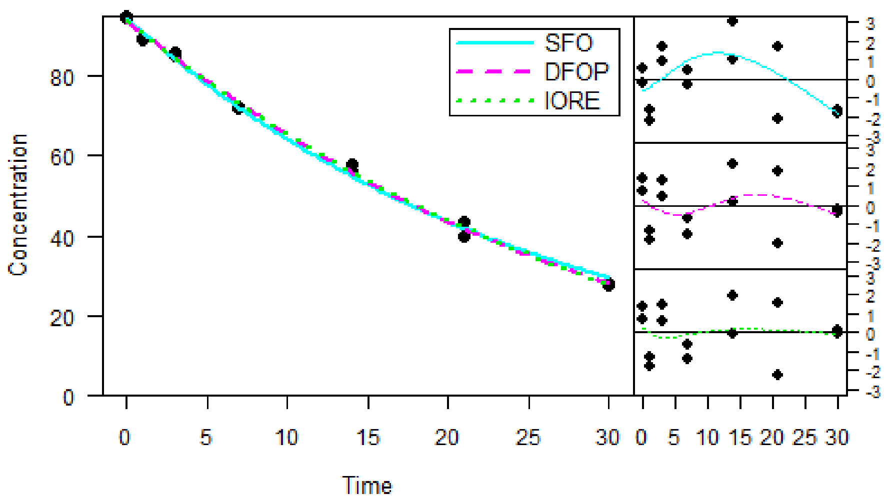


	DT_{50}	DT_{90}	χ^2	C_0	Parameters
SFO	16.9	56.3	10	88.2	k = 0.0409
DFOP	10.5	NA	0.69	98.2	f = 0.74, k_0 = 0.118, k_1 = -0.00942
IORE	11.6	337	3.6	98.9	N = 2.91, k = 1.93e-05

S_C	106
S_{SFO}	839
Slow $t_{1/2}$	-73.6
$t_{R\ IORE}$	101

Hydrolysis Study

Day	Applied Radioactivity
0	94.5
0	95.2
1	88.9
1	89.4
3	86.0
3	85.2
7	72.6
7	71.8
14	56.0
14	58.0
21	39.7
21	43.5
30	27.9
30	27.7

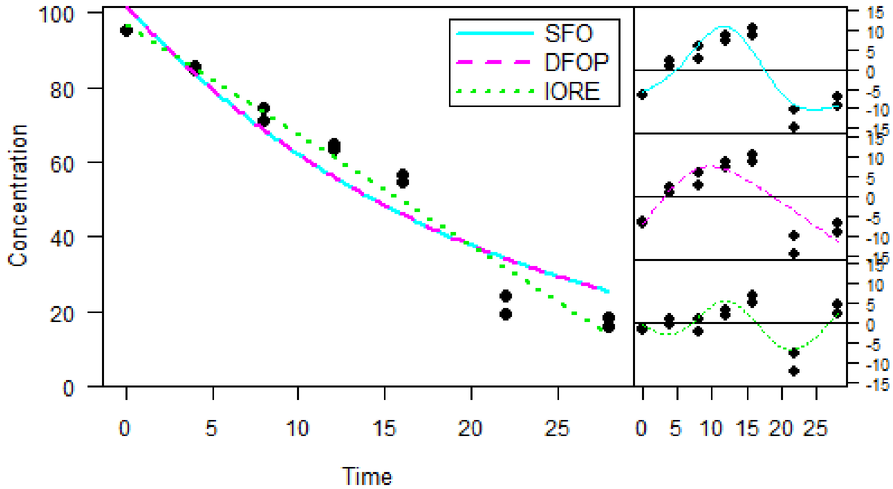


	DT_{50}	DT_{90}	χ^2	C_0	Parameters
SFO	17.8	59.2	1.6	94.7	k = 0.0389
DFOP	18.2	53.6	1.4	93.8	f = -0.816, k_0 = 0.0746, k_1 = 0.0515
IORE	18.4	49.2	1.2	93.9	N = 0.711, k = 0.127

S_C	28.5
S_{SFO}	35.6
Slow $t_{1/2}$	13.5
$t_{R\ IORE}$	14.8

Aquatic Photolysis Study

Day	Applied Radioactivity
0	95.3
0	95.0
4	84.4
4	85.7
8	71.0
8	74.3
12	63.2
12	64.7
16	56.6
16	54.8
22	19.6
22	24.0
28	16.1
28	18.3



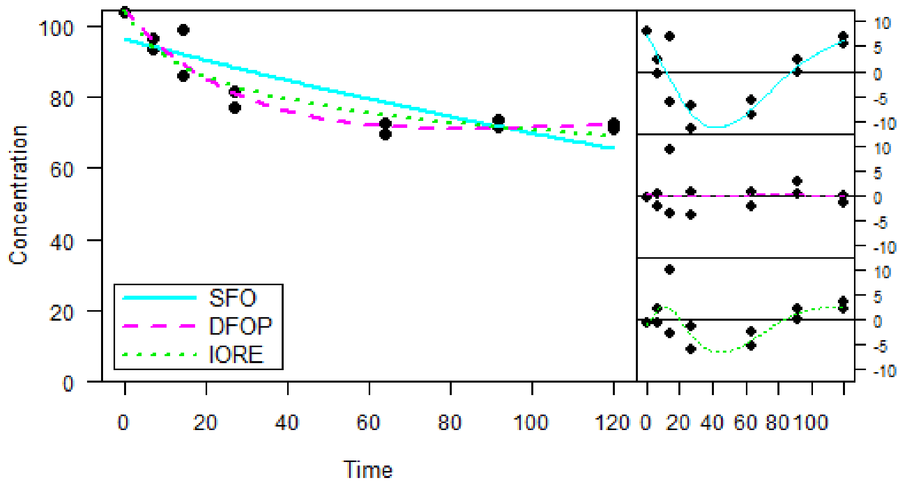
	DT_{50}	DT_{90}	χ^2	C_0	Parameters
SFO	14	46.5	11	102	k= 0.0495
DFOP	14	46.5	13	102	f= 0.435, k_0= 0.0495, k_1= 0.0495
IORE	16.4	29.4	6.9	96.7	N= -0.0161, k= 3.15

S_C	413
S_{SFO}	899
Slow $t_{1/2}$	14
$t_{R\ IORE}$	8.84

4. DT50 WAS NOT OBSERVED DURING THE STUDY

Aerobic Soil Metabolism Study

Day	Applied Radioactivity
0	104.
0	104.
7	96.3
7	93.6
14	85.8
14	98.7
27	76.9
27	81.5
64	72.4
64	69.7
92	73.8
92	71.4
120	72.5
120	71.1



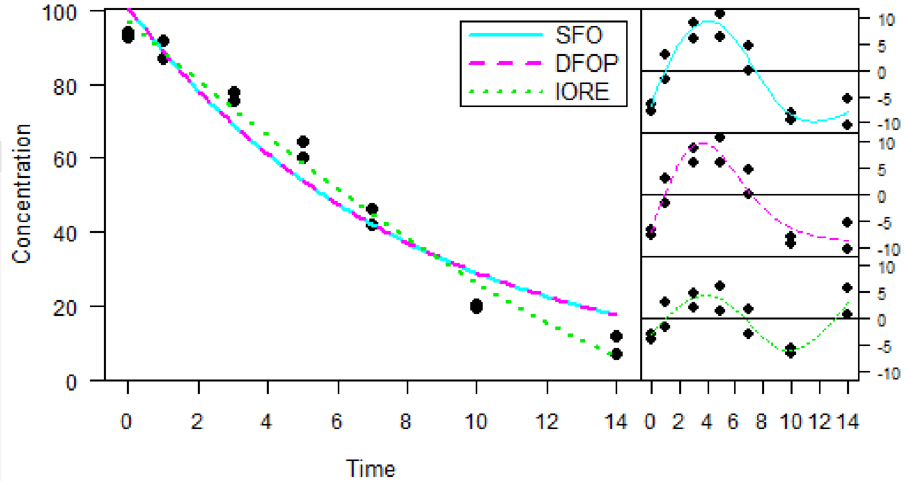
	DT_{50}	DT_{90}	χ^2	C_0	Parameters
SFO	216	718	5.5	96.2	k = 0.00321
DFOP	NA	NA	1.7	104	f = 0.415, k_0 = 0.0331, k_1 = -0.00134
IORE	973	136690933	2.7	105	N = 8.36, k = 3.11e-17

S_C	252
S_{SFO}	580
Slow $t_{1/2}$	-518
$t_{R\ IORE}$	4.11e+07

5. IORE PARAMETER ‘N’ IS LESS THAN 1 AND THE DFOP REPRESENTATIVE HALF-LIFE VALUE EQUALS THE SFO HALF-LIFE VALUE

Aerobic Soil Metabolism Study

Day	Applied Radioactivity
0	92.8
0	93.9
1	91.8
1	87.0
3	78.0
3	75.3
5	64.7
5	60.1
7	42.0
7	46.6
10	19.6
10	20.8
14	7.27
14	12.1

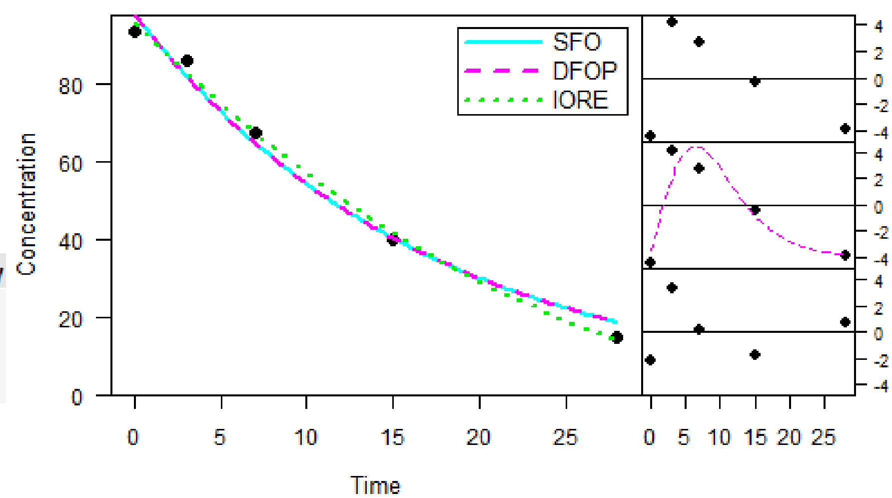


	DT_{50}	DT_{90}	χ^2	C_0	Parameters
SFO	5.58	18.5	9.5	101	k = 0.124
DFOP	5.58	18.5	11	101	f = 0.74, k_0 = 0.124, k_1 = 0.124
IORE	6.49	13.2	5.3	96.8	N = 0.263, k = 2.44

S_C	270
S_{SFO}	695
Slow $t_{1/2}$	5.58
$t_{R\ IORE}$	3.99

Aerobic Aquatic Metabolism Study

Day	Applied Radioactivity
0	93.3
3	86.0
7	67.4
15	40.0
28	14.9

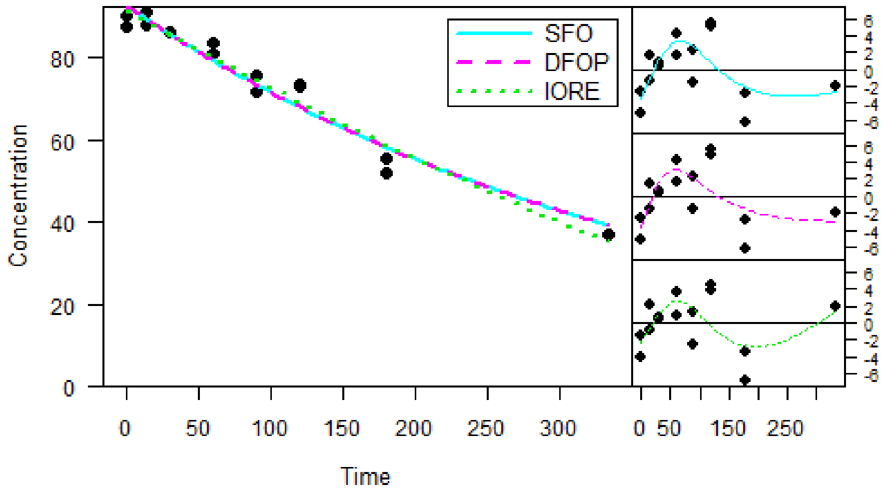


	DT_{50}	DT_{90}	χ^2	C_0	Parameters
SFO	11.8	39.1	4.6	97.7	k = 0.0589
DFOP	11.8	39.1	6.5	97.7	f = 0.621, k_0 = 0.0589, k_1 = 0.0589
IORE	12.9	31.4	3	95.5	N = 0.568, k = 0.333

S_C	51.5
S_{SFO}	58.9
Slow $t_{1/2}$	11.8
$t_{R\ IORE}$	9.46

Aerobic Soil Metabolism Study

Day	Applied Radioactivity
0	90.1
0	87.5
14	91.0
14	88.0
30	86.2
30	86.5
60	83.7
60	81.0
90	75.8
90	72.0
120	73.0
120	73.6
180	55.5
180	52.0
333	37.2



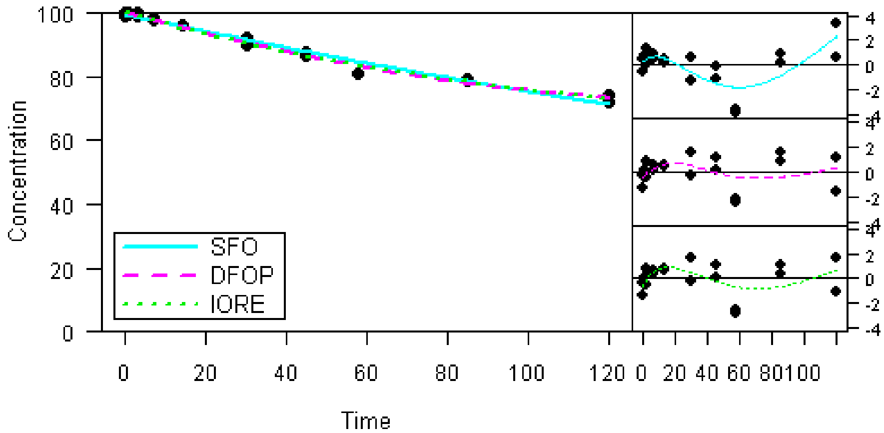
	DT_{50}	DT_{90}	χ^2	C_0	Parameters
SFO	269	892	3.3	92.7	k = 0.00258
DFOP	269	892	3.8	92.7	f = 0.441, k_0 = 0.00258, k_1 = 0.00258
IORE	261	560	3.1	91.6	N = 0.354, k = 0.0396

S_C	172
S_{SFO}	175
Slow $t_{1/2}$	269
$t_{R\ IORE}$	169

6. DT50 WAS NOT OBSERVED DURING THE STUDY AND DFOP DID NOT CONVERGE OR YIELDED A NEGATIVE DT50 VALUE

Aerobic Soil Metabolism Study

Day	Applied Radioactivity
0	98.9
0	100.
1	99.5
1	100.
3	98.7
3	100.
7	98.4
7	98.0
14	96.1
14	95.9
30	92.1
30	90.2
45	86.6
45	87.6
58	80.7
58	81.0
85	79.4
85	78.7
120	71.8
120	74.5



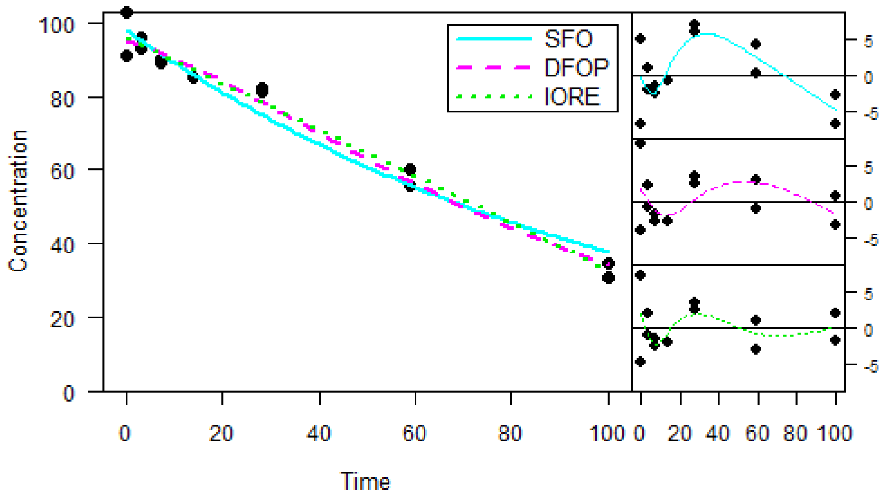
	DT_{50}	DT_{90}	χ^2	C_0	Parameters
SFO	248	825	1.3	99.5	k = 0.00279
DFOP	NA	NA	0.94	100	f = 0.963, k_0 = 0.00409, k_1 = -0.0112
IORE	434	22248	0.95	100	N = 3.31, k = 9.44e-08

S_C	32.8
S_{SFO}	48.4
Slow $t_{1/2}$	-61.6
$t_{R\ IORE}$	6.7e+03

7. IORE PARAMETER ‘N’ IS LESS THAN 1 AND DFOP PARAMETER ‘F’ IS LESS THAN 0

Aerobic Sediment Metabolism Study

Day	Applied Radioactivity
0	103.
0	91.0
3	93.0
3	96.0
7	89.0
7	90.0
14	85.0
14	85.0
28	81.0
28	82.0
59	60.0
59	56.0
100	31.0
100	35.0

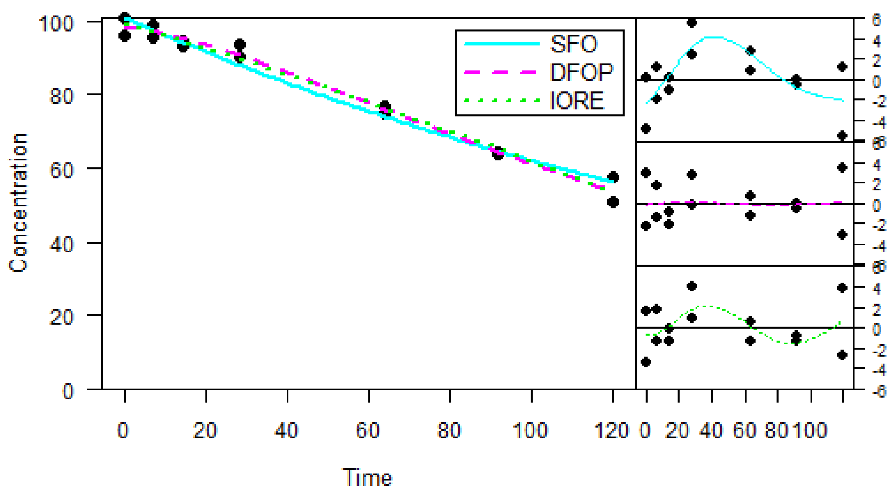


	DT_{50}	DT_{90}	χ^2	C_0	Parameters
SFO	72.8	242	3.4	98	k = 0.00952
DFOP	74.3	193	2.5	95	f = -0.692, k_0 = 0.0298, k_1 = 0.0145
IORE	76.6	135	1.9	95.8	N = -0.0463, k = 0.762

S_C	166
S_{SFO}	246
Slow $t_{1/2}$	47.7
$t_{R\ IORE}$	40.7

Aerobic Soil Metabolism Study

Day	Applied Radioactivity
0	101.
0	95.9
7	95.6
7	98.7
14	94.4
14	93.1
28	93.5
28	90.4
64	76.7
64	74.8
92	64.4
92	63.9
120	57.4
120	50.8



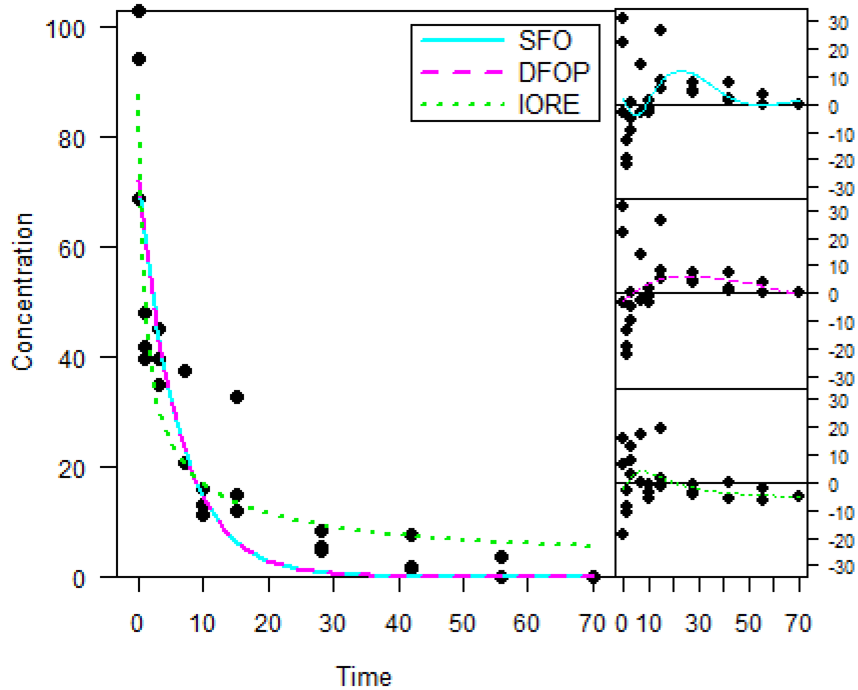
	DT_{50}	DT_{90}	χ^2	C_0	Parameters
SFO	143	474	2	101	k = 0.00486
DFOP	134	367	0.88	98.2	f = -0.304, k_0 = 0.0257, k_1 = 0.007
IORE	129	202	1.2	99.4	N = -0.36, k = 1.81

S_C	80.3
S_{SFO}	107
Slow $t_{1/2}$	99
$t_{R\ IORE}$	60.7

8. DFOP PARAMETER ‘F’ IS GREATER THAN 1 AND THE DFOP REPRESENTATIVE HALF-LIFE VALUE EQUALED THE SFO HALF-LIFE VALUE

Terrestial Field Dissipation Study

Day	Applied Radioactivity
0	94.0
1	39.5
3	45.1
7	20.7
10	11.3
15	15.0
28	8.46
42	1.88
56	0.100
70	0.100
0	68.6
1	47.9
3	34.8
7	37.6
10	16.0
15	32.9
28	5.64
42	1.41
56	3.76
70	0.100
0	103.
1	41.8
3	39.5
7	20.7
10	13.2
15	12.2
28	4.70
42	7.52
56	3.76
70	0.100



	DT_{50}	DT_{90}	χ^2	C_0	Parameters
SFO	4.35	14.4	31	72	$k = 0.159$
DFOP	4.35	14.4	34	72	$f = 1.11$, $k_0 = 0.159$, $k_1 = 0.16$
IORE	1.48	32.1	18	87.4	$N = 2.7$, $k = 0.000455$

S_C	2.25e+03
S_{SFO}	3.83e+03
Slow $t_{1/2}$	4.35
$t_{R\ IORE}$	9.67