Supplementary Materials

The Limits of Validity of Kinetic Models in Field Trials of Bioremediation of Oil-Contaminated Soils

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The tables below were computed with the scripts kinetic_analysis.py and numerical_experiment.py, which are openly available together with the field data in figshare (https://doi.org/10.6084/m9.figshare.33514384, version 2).

Table S1. Sensitivity analysis with the control-plot TPH subtracted: oil-derived excess over the control (1C) in each treatment.

Treatment	Excess on day 0, mg kg^{-1}	Excess on day 83, mg kg^{-1}	Change over 83 d	k ± SE, d^{-1}
2O — natural attenuation	6,241	3,707	−40.6%	0.00869 ± 0.00377
3F — biostimulation	7,853	8,508	+8.3%	−0.00066 ± 0.00155
4R — reintroduction	6,813	7,041	+3.3%	−0.00039 ± 0.00252
5B — biopreparation	6,661	6,743	+1.2%	−0.00126 ± 0.00168
6BC — biochar	7,623	7,560	−0.8%	0.00001 ± 0.00211

Excess = TPH of the treatment minus TPH of the control on the same sampling date. k is the first-order constant fitted to the excess series (seven sampling dates), with its standard error; a negative value means that the excess did not decline. The control was a single plot whose weathered residues need not behave like the background in the amended plots, so this correction is a sensitivity analysis and not the primary result (Section 3.1).

Table S2. Relative error of K_N (treatment 5B) in subsets of the seven-date series that retain day 0.

Held fixed	Varied	Number of subsets	Median relative error of K_N	Subsets with relative error < 50%
5 dates	duration 55 d	1	286%	0
5 dates	duration 69 d	4	121%	0
5 dates	duration 83 d	10	110%	1
duration 83 d	4 dates	10	150%	1
duration 83 d	5 dates	10	110%	1
duration 83 d	6 dates	5	106%	0
duration 83 d	7 dates	1	88%	0

The nitrogen-limited model (Equation (6)) was refitted to every subset of the sampling dates (days 0, 13, 27, 41, 55, 69, 83) that includes day 0 and has the stated number of dates or duration; the relative error is the standard error divided by the estimate.

Table S3. Noise-free control for the Haldane model: recovery of all three parameters from a single loading level.

C_0, mg kg^{-1}	Degradation depth	Random starting points	Starts with V_{max}, K_s and K_i all within ±5% of the true values
18,600	20%	30	100%
18,600	50%	30	100%
18,600	90%	30	100%
30,000	20%	30	100%
30,000	50%	30	100%
30,000	90%	30	100%

True values K_s = 5,000 mg kg^{-1} and K_i = 30,000 mg kg^{-1}; eight equally spaced sampling dates; no noise added. Recovery from every starting point shows that the Haldane model is structurally identifiable from a single loading level, so its non-identifiability in the field data is practical (Sections 3.8 and 3.13).

Table S4. Monte Carlo series for the nitrogen-limited model: successful recovery of K_N.

Error in N, %	Varied	Sampling dates	Duration, d	Degradation depth	Median K_N, mg kg^{-1}	Recovery
5	sampling dates	5	83	37%	18.8	45.5%
5	sampling dates	7	83	37%	18.8	35%
5	sampling dates	10	83	37%	21	43%
5	sampling dates	13	83	37%	19.3	41.5%
5	sampling dates	16	83	37%	16.8	39.5%
5	duration	7	55	29.2%	19.6	31%
5	duration	7	120	46%	16	46%
5	duration	7	180	57.9%	13.2	57.5%
15	sampling dates	7	83	37%	18.3	45.5%
15	sampling dates	16	83	37%	17.5	53%
15	duration	7	180	57.9%	13.6	54.5%

True values k_{max} = 0.0145 d^{-1} and K_N = 20 mg kg^{-1}; nitrate declining from 53 to 8 mg kg^{-1} with a time constant of 12 d, as in treatment 5B, and interpolated linearly between sampling dates; 3% proportional noise on TPH; 200 replicates per design; success = estimate within ±50% of the true value. The 80% criterion was not reached in any design.

Table S5. GC–MS biodegradation ratios: *n*-C17/pristane and, in brackets, *n*-C18/phytane.

Treatment	Day 0	Day 13	Day 27	Day 41	Day 55	Day 69
1C — control (no oil)	1.20 (2.43)	1.13 (—)	— (—)	1.20 (2.03)	1.05 (2.09)	0.95 (1.79)
2O — natural attenuation	2.31 (4.66)	2.26 (3.86)	2.36 (4.22)	2.18 (3.85)	1.91 (4.27)	2.29 (4.39)
3F — biostimulation	1.96 (3.97)	1.94 (4.53)	1.80 (4.21)	1.89 (3.84)	1.79 (3.61)	1.88 (3.95)
4R — reintroduction	1.97 (3.92)	1.88 (4.01)	1.93 (4.67)	1.86 (4.33)	1.82 (3.71)	1.91 (4.33)
5B — biopreparation	1.76 (3.37)	1.77 (3.33)	1.58 (—)	1.87 (4.21)	1.72 (3.02)	1.70 (2.90)
6BC — biochar	2.12 (4.56)	1.93 (4.18)	1.88 (3.86)	1.98 (3.92)	1.85 (3.67)	1.91 (3.81)

Ratios of relative peak areas (semi-quantitative). Peaks were assigned by retention time on the HP-5MS column: *n*-C17 33.45 min, pristane 33.61 min, *n*-C18 36.10 min, phytane 36.36 min. "—", peak not identified. GC–MS data are available up to day 69.