Modeling the Reduction Kinetics of Munition Compounds by Humic Acids

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Supplementary Information

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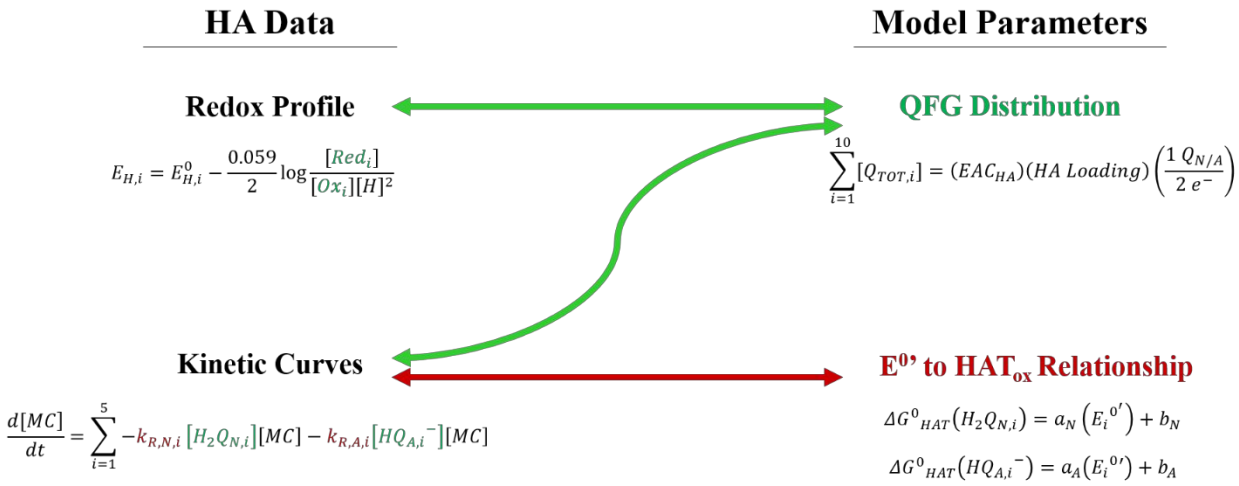
HA Model Framework Description

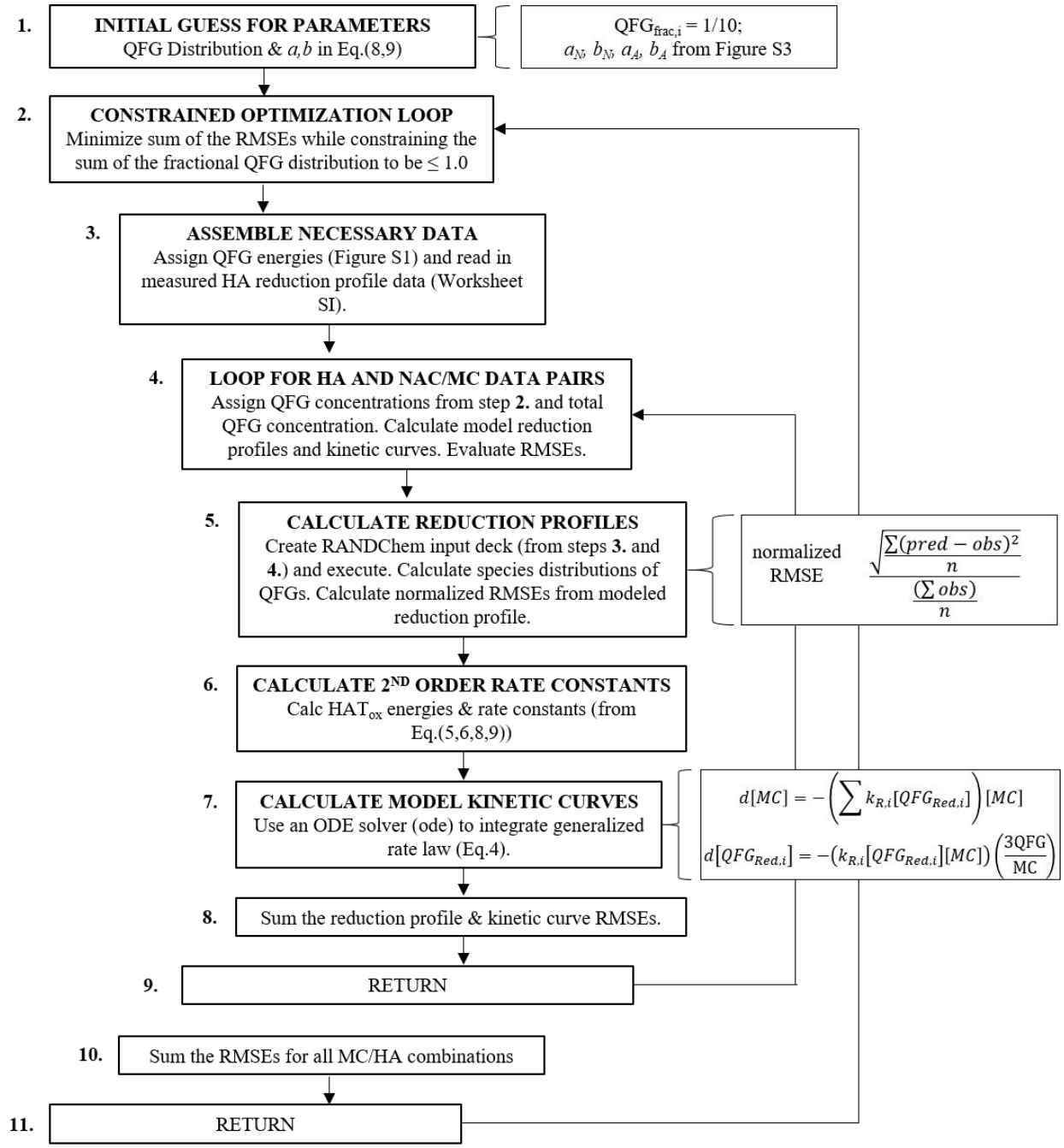
Scheme S1: *Relationships between the HA data being optimized and the model's fitted parameters. Arrows indicate links between model parameters and the optimized data. Equations shown are predominant, but not exhaustive, for each segment.*



The general framework for the humic acid (HA) model is shown in Scheme S1. The HA reduction profiles and NAC/MC kinetic curves serve as the thermodynamic and kinetic characteristics of a given HA source and are used to calibrate the quinone-like functional groups (QFGs) that comprise the HA model. The unique parameters being fit through this calibration are the QFG distribution and the formal reduction potential ($E^{0'}$) to HAT_{ox} energy relationships, as shown in Scheme S1.

The optimization procedure used for HA model calibration is shown in Scheme S2. The program was written and executed in R and utilizes an additional equilibrium speciation program (RANDChem), which was written and compiled in Fortran. The optimization program minimizes the root mean square errors (RMSEs) associated with both the HA reduction profiles and the NAC/MC kinetic curves concurrently through fitting the model parameters outlined in Scheme S1. It does this through a constrained optimization (constrOptim) which ensures that the sum of the QFG fractions does not exceed 1.0.

Scheme S2: *Program schematic for optimization procedure. Written in R programming language with the use of RandChem equilibrium speciation program (Fortran).*



Thermodynamic Description of Model Quinone-like Functional Groups

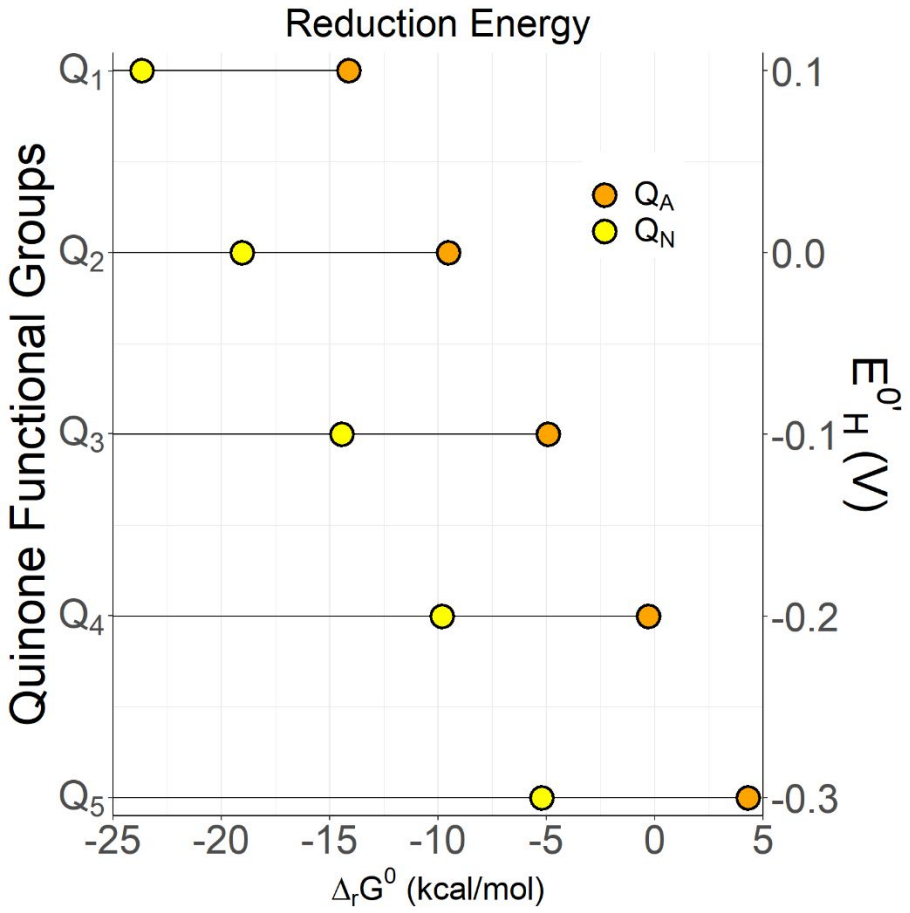


Figure S1: *Energy Distribution of the ten model functional groups. Reduction energies were distributed evenly between the energy boundaries provided by the reduction profile.* $E^{0}{}'_{H}$ *is the formal potential (pH = 7) relative to the standard hydrogen electrode.* Q_N *and* Q_A *are the neutral and anionic function groups respectively.* $\Delta_r G^0$ *corresponds to the standard state Gibbs free energy (pH= 0) of the reduction reactions for the QFGs (Eqs.1,2 in manuscript) and are used as their formation energies in the speciation calculations.*

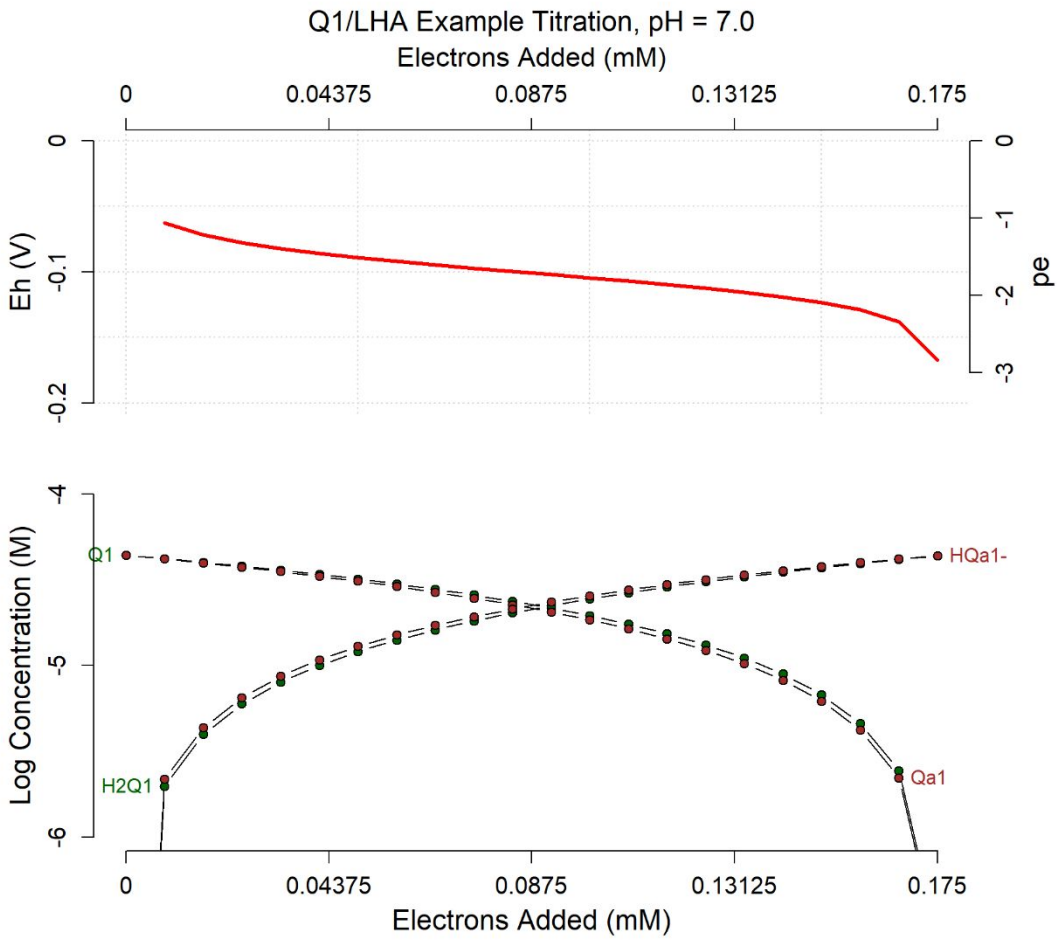


Figure S2: *Results of example tableau in table 1. Model HA is comprised of one neutral (Q_{N1}) and one anionic (Q_{A1}) functional group at a 50/50 concentration ratio. Total functional group concentration is 88 µM as calculated from the EAC of LHA. The QN1/QA1 reduction energies were selected as Q3 in Figure S1 simply to bisect the measured values. Top: Red line is model output. Bottom: Concentration of the oxidized and reduced form of the two functional groups as a function of electrons titrated, or reduction extent.*

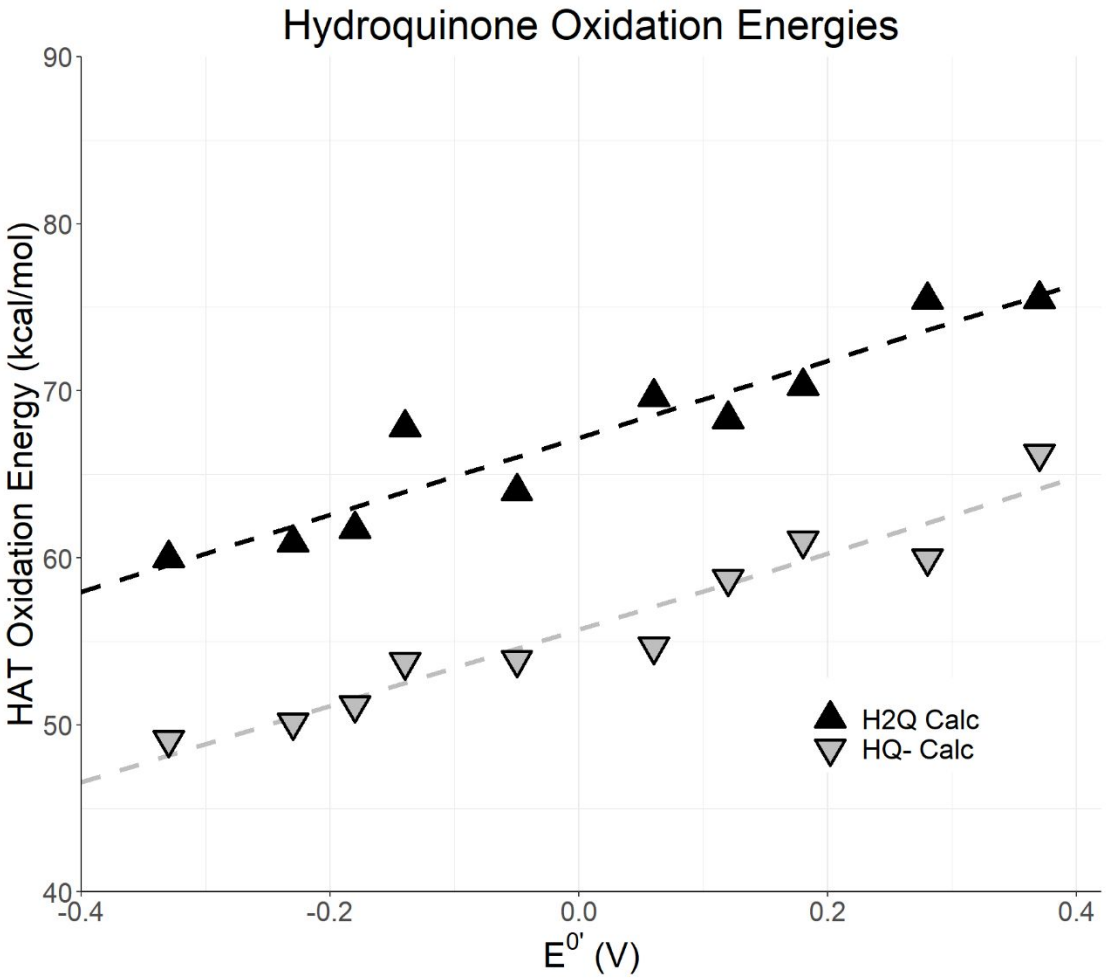


Figure S3: *Calculated HAT oxidation energies as a function of reported formal potential for ten selected hydroquinones.*

Functional Group Distribution and Energies

Table S1: *Model fitted functional group distribution for the mean HA model.*

Group	Composition (Fraction)
H_2Q_{N1}	0.043919
H_2Q_{N2}	0.01959
H_2Q_{N3}	0.111252
H_2Q_{N4}	0.410781
H_2Q_{N5}	0.147647
HQ_{A1}^-	0.002697
HQ_{A2}^-	0.089338
HQ_{A3}^-	0.045164
HQ_{A4}^-	0.085892
HQ_{A5}^-	0.043541

Table S2: *Formal potentials and HAT oxidation energies for ten real hydroquinones and five model quinone-like functional groups. HAT energies for real hydroquinones are calculated quantum chemically, while the energies for the functional groups are calculated from Eq.8 with slopes and intercepts fitted through the mean HA model.*

	Quinone Functional Group	$E^{0'}$	HAT_{ox} Energies[a]	
			Neutral Form[b]	Anionic Form[c]
		(V)	(kcal/mol)	(kcal/mol)
Existing Hydroquinones	1,2-benzoquinone	0.37	75.508	66.254
	1,4-benzoquinone	0.28	75.454	59.971
	2-hydroxy-1,4-benzoquinone	0.18	70.288	61.036
	1,4-naphthoquinone-2-sulfonate	0.12	68.317	58.766
	1,4-naphthoquinone	0.06	69.645	54.693
	5,8-dihydroxy-1,4-naphthoquione	-0.05	63.989	53.904
	2-hydroxy-1,4-naphthoquione	-0.14	67.818	53.765
	9,10-anthraquinone-2,6-disulfonate	-0.18	61.731	51.189
	9,10-anthraquinone-2-sulfonate	-0.23	60.922	50.163
	9,10-anthraquinone	-0.33	59.991	49.120
Model Functional Groups	Q_1	0.10	84.220	73.371
	Q_2	0.00	78.931	67.417
	Q_3	-0.10	73.647	61.475
	Q_4	-0.20	68.348	55.534
	Q_5	-0.30	63.061	49.592

[a] $HAT_{ox} = a(E^{0'}) + b$
[b] a = 52.89; b = 78.98
[c] a = 59.44; b = 67.45

Table S3: *Conditions of NAC/MC reduction with HA experiments.*

HA/NAC	pH	HA Loading (g/L)	EAC (mmol e^- /g_{HA})
LHA/NTO	6.5, 8.0	0.5	1.7
LHA/DNAN	6.5	0.5	1.7
LHA/NB	7.5	0.1	1.7
ESHA/NTO	7.0	0.5	1.96
SRHA/NTO	7.0	0.5	0.8
PPHA/NTO	7.0	0.5	1.7

Reduction Profile of All HAs in Study

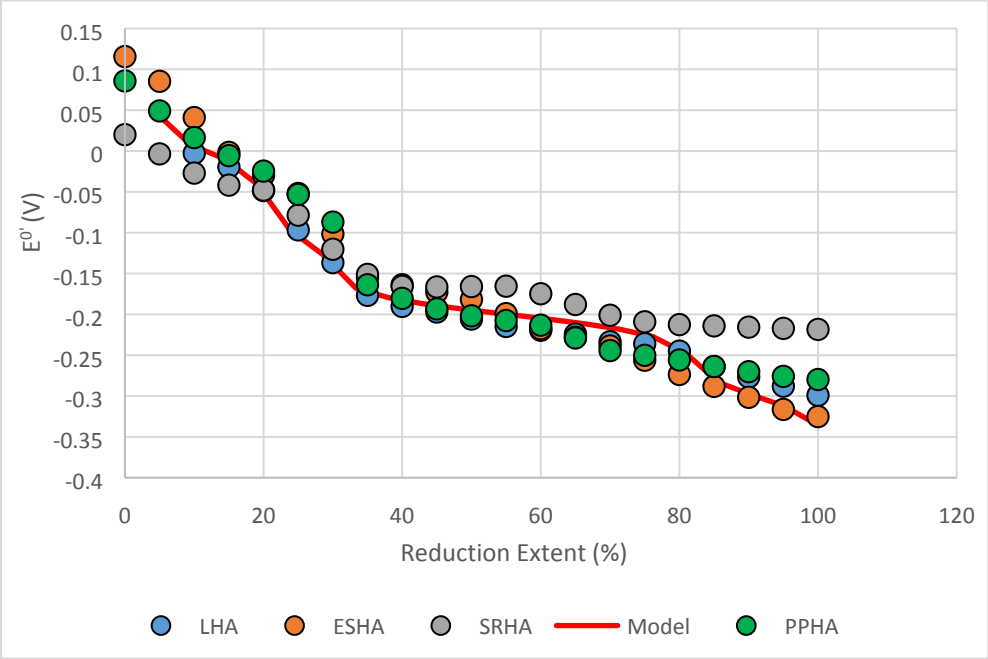


Figure S4: *Measured reduction profiles for Leonardite Humic Acid (LHA), Eliot Soil Humic Acid (ESHA), Suwanee River Humic Acid (SRHA), and Pahokee Peat Humic Acid (PPHA), as well as the Mean HA model fit.*

Independent ESHA/NTO Optimization

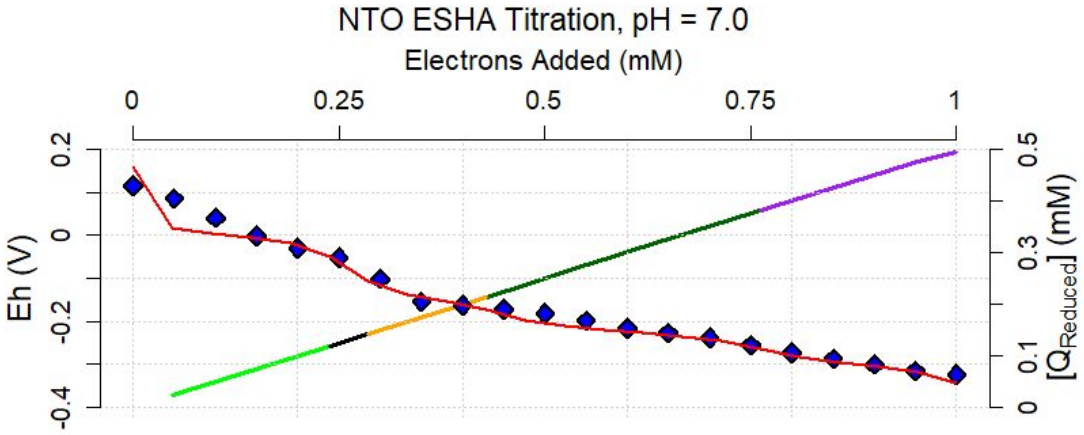


Figure S5: *Reduction profile as potential vs. HA reduction extent for ESHA (blue diamonds) and the model fit (red line). Colored line on base indicates the active or redox controlling functional group as a function of reduction extent (right Y axis).*

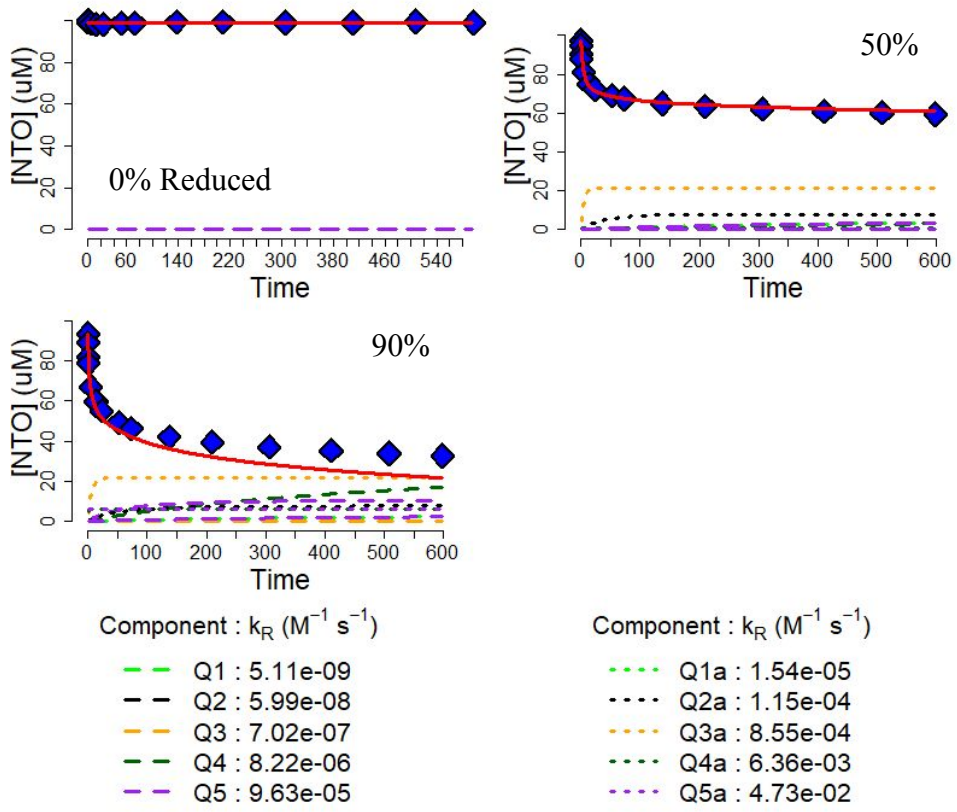


Figure *S6*: *NTO concentration as a function of time for reduction with Eliot Soil Humic Acid (ESHA). Dashed and dotted lines correspond to the contribution of NTO loss from individual QFGs (dashed = neutral, dotted = anionic).*

Example of NAC/MC Reduction kinetic Curves in Linear-Linear Scale

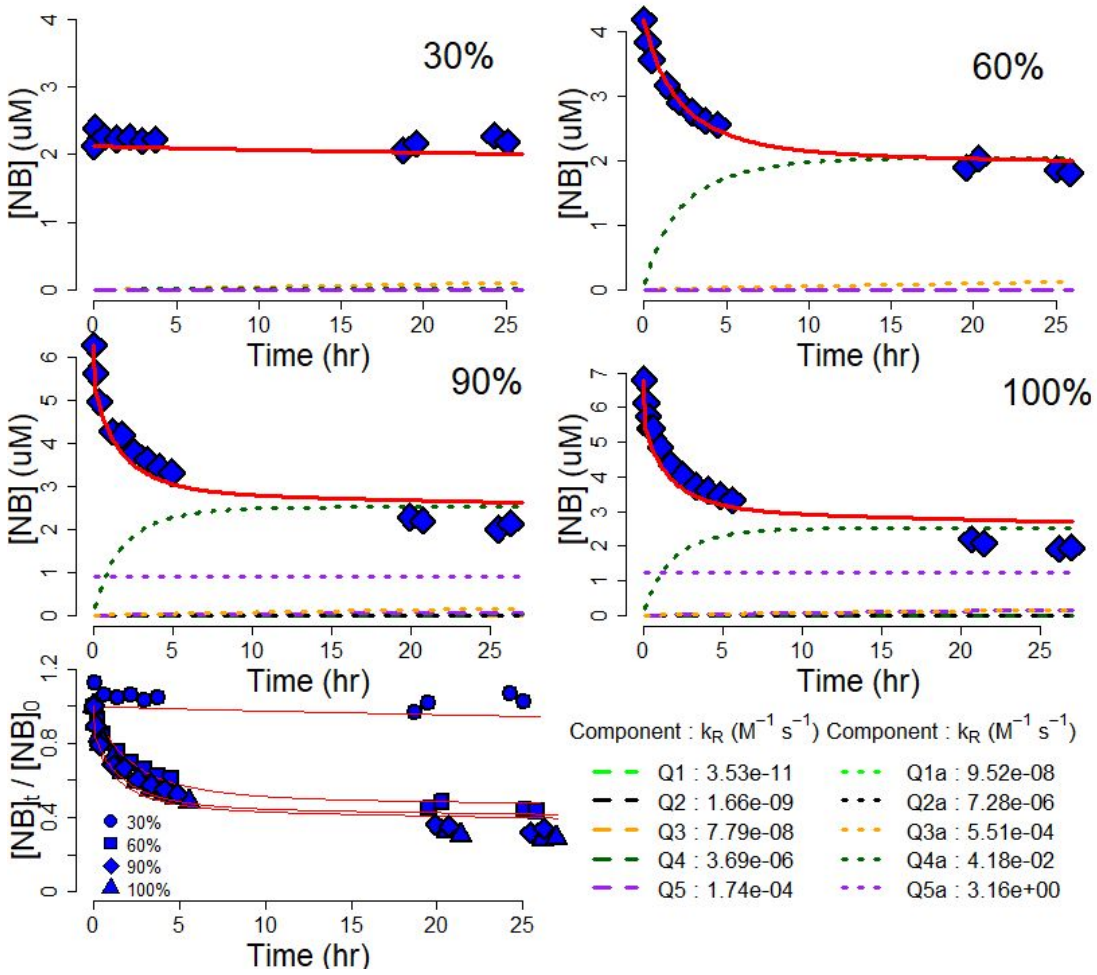


Figure S7*: NB concentration as a function of time for reduction with Leonardite Humic Acid (LHA) at 30%, 60%, 90% and 100% reduced LHA. Same data presented in Figure 4, row A but plotted on a linear-linear scale. Dashed and dotted lines correspond to the contribution of NB loss from individual QFGs (dashed = neutral, dotted = anionic).*

Example LHA Input Deck

```
LHA_DNAN_10Q
LITER
1.0
MULTIPLIERS


RT
25.
LIMIT
1000
ROWS
H2O    1
    .000     .000     .000     .000
Hp     0
    .000     .000     .000     .000
Em     0
    .000     .000     .000     .000
Q1     0
    .000     .000     .000     .000
Q2     0
    .000     .000     .000     .000
Q3     0
    .000     .000     .000     .000
Q4     0
    .000     .000     .000     .000
Q5     0
    .000     .000     .000     .000
Qd1    0
    .000     .000     .000     .000
Qd2    0
    .000     .000     .000     .000
Qd3    0
    .000     .000     .000     .000
Qd4    0
    .000     .000     .000     .000
Qd5    0
    .000     .000     .000     .000
END

MATRIX
Aqueou          .00     .00     .00                    .0
    H2O       -56.69     .00     .00  1.0H2O               .0
    OHm       -37.59     .00     .00  1.0H2O    -1.0Hp     .0
    Hp          .00     .00     .00  1.0Hp                .0
    O2         3.92     .00     .00  2.0H2O    -4.0Hp    -4.0Em
    H2        4.207     .00     .00  2.0Hp      2.0Em
    Q1        0.000     .00     .00  1.0Q7
    H2Q1      -12.63     .00     .00  1.0Q7     2.0Hp     2.0Em
    Q2        0.000     .00     .00  1.0Qa
    H2Q2      -12.00     .00     .00  1.0Qa     2.0Hp     2.0Em
    Q3        0.000     .00     .00  1.0Qb
    H2Q3      -11.25     .00     .00  1.0Qb     2.0Hp     2.0Em
    Q4        0.000     .00     .00  1.0Q8
    H2Q4      -10.79     .00     .00  1.0Q8     2.0Hp     2.0Em
    Q5        0.000     .00     .00  1.0Q9
    H2Q5      -8.482     .00     .00  1.0Q9     2.0Hp     2.0Em
    Qd1       0.000     .00     .00  1.0Qd7
    H2Qd1     -12.63     .00     .00  1.0Qd7    1.0Hp     2.0Em
    Qd2       0.000     .00     .00  1.0Qda
```

```
    H2Qd2      -12.00     .00     .00   1.0Qda     1.0Hp      2.0Em
    Qd3         0.000     .00     .00   1.0Qdb
    H2Qd3      -11.25     .00     .00   1.0Qdb     1.0Hp      2.0Em
    Qd4         0.000     .00     .00   1.0Qd8
    H2Qd4      -10.79     .00     .00   1.0Qd8     1.0Hp      2.0Em
    Qd5         0.000     .00     .00   1.0Qd9
    H2Qd5      -8.482     .00     .00   1.0Qd9     1.0Hp      2.0Em
pH              .000     .00     .00
    HPLUS       .000     .00     .00   1.0Hp
END

NOMESSAGES
RETURN
  21            Aqueou
H2O       1.000    1.000    1.0
Em        1.0e-9   8.5e-4   1.0
Q1        3.6e-5   3.6e-5   1.0
Q2        3.6e-5   3.6e-5   1.0
Q3        3.6e-5   3.6e-5   1.0
Q4        3.6e-5   3.6e-5   1.0
Q5        3.6e-5   3.6e-5   1.0
Qd1       3.6e-5   3.6e-5   1.0
Qd2       3.6e-5   3.6e-5   1.0
Qd3       3.6e-5   3.6e-5   1.0
Qd4       3.6e-5   3.6e-5   1.0
Qd5       3.6e-5   3.6e-5   1.0
HPLUS      1.0      1.0     1.0
pH         7.0      7.0     1.0
END

EXIT
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