SUPPORTING INFORMATION

Electrochemical Characterization of Natural Organic Matter by Direct Voltammetry in an Aprotic Solvent

*Ania S. Pavitt and Paul G. Tratnyek**

OHSU-PSU School of Public Health, Oregon Health & Science University
3181 SW Sam Jackson Park Road, Portland, OR 97239

*Corresponding author: Email: tratnyek@ohsu.edu

Contents

46 pages, 16 Figures, 7 Tables, 27 References

Table S1. Samples of natural organic matter (NOM) characterized in this study.[1]

No.	Name	Fraction [2]	Source [3]	Class [4]	Ref [5]
1	Bamboo	NOM	D. Macalady	T	
2	Bemidji	FA	G. Aiken	A	1, 2
3	Black River	NOM	D. Macalady	A	3
4	Cabbage Tree	NOM	D. Macalady	T	
5	Coal Creek	FA	G. Aiken	A	1, 4-7
6	Coal Creek	HA	G. Aiken	A	1, 7
7	Elliott Soil	FA Std II	IHSS	T	8-10
8	Elliott Soil	HA Std I	IHSS	T	8-13
9	Elliott Soil	HA Std IV	IHSS	T	9-13
10	Everglades 2BS	HPOA	USGS	A	6, 14, 15
11	Everglades F1	HPOA	USGS	A	6, 14-16
12	Everglades F1	TPIA	USGS	A	15
13	Everglades LOX8	HPOA	USGS	A	17
14	Georgetown	NOM	B. Gu	A	18, 19
15	Georgetown Carbohydrate	NOM	B. Gu	A	18-20
16	Georgetown Polyphenolic	NOM	B. Gu	A	18-20
17	Great Dismal Swamp	FA	Y. P. Chin	A	21, 22
18	Inangahua River	NOM	D. Macalady	A	3, 23
19	Kauri	NOM	D. Macalady	T	
20	Kitty Hawk	NOM	D. Macalady	A	24
21	Lake Fryxell	FA	G. Aiken	A	1, 4-6, 18
22	Leonardite[6]	HA Std I	IHSS	T	8, 10-12
23	Leonardite[6]	HA Std I	IHSS	T	8-13
24	MW-6	NOM	D. Macalady	A	3, 22 23
25	Nordic Reservoir	NOM	IHSS	A	10
26	North Sea	DOM	B. Koch	A	25
27	Ogeechee River	FA	G. Aiken	A	4, 6, 7, 15
28	Pacific Ocean	FA	USGS	A	6, 7, 14, 15
29	Pahokee Peat	FA Std II	IHSS	T	8-10, 12, 18
30	Pahokee Peat[6]	HA Std I	IHSS	T	8-13, 18

No.	Name	Fraction [2]	Source [3]	Class [4]	Ref [5]
31	Pahokee Peat[6]	HA Std I	IHSS	T	8-13, 18
32	Pine Barrens	NOM	Y. P. Chin	T	18
33	Pony Lake	FA	Y. P. Chin	A	7-9, 13, 21
34	Prairie Pothole P8	DOM	Y. P. Chin	A	26
35	Red Tussock	NOM	D. Macalady	T	
36	Rio Negro	NOM	D. Macalady	A	3, 23
37	Schönbuch Soil Anoxic	FA	A. Kappler	T	unpublished
38	Schönbuch Soil Anoxic	HA	A. Kappler	T	unpublished
39	Schönbuch Soil H_2O Anoxic	FA	A. Kappler	T	unpublished
40	Schönbuch Soil H_2O Anoxic	HA	A. Kappler	T	unpublished
41	Schönbuch Soil H_2O Oxic	HS	A. Kappler	T	unpublished
42	Schönbuch Soil Oxic	HA	A. Kappler	T	unpublished
43	Shelter Is. San Diego	HA	J. Coates	A	18
44	Soil	HA Ref	IHSS	T	18-20
45	Sutton Stream	NOM	D. Macalady	A	
46	Suwannee River	FA Std II	IHSS	A	1, 4-9, 12-14, 18
47	Suwannee River	HA Std III	IHSS	A	1, 6, 8-13, 15, 27
48	Suwannee River[7]	NOM	J. Needoba	A	8, 10, 13, 23
49	Suwannee River[7]	NOM	IHSS	A	8, 10, 13, 23
50	Suwannee River[7]	NOM	D. Macalady	A	8, 10, 13, 23
51	Toolik Lake	FA	Y. P. Chin	A	21
52	Walnut	NOM	D. Macalady	T	3, 22
53	Waskish Peat	HA Ref	IHSS	T	8-10
54	Williams Lake	HPOA	USGS	A	6, 14-16

[1]Order is alphabetical by common name. [2]Type of fraction NOM, DOM, HA, FA, HPOA, and TPIA. [3]Source is primary supplier. [4]Class equals aquatic (A) or terrestrial (T). [5]References: primary, authoritative, or most relevant to redox. [6]Samples 22, 23 and 30, 31 were from the same source and the same supplier, but samples 22 and 30 were obtained at a much earlier date (ca. 2002) than 23 and 31. [7]Samples 48-50 are from the same source, but were obtained from different suppliers.

Table S2. Model compounds.

No.	Name	CAS-RN	Source (Purity %)
1	Anthraquinone-2,6-disulfonic acid disodium salt (AQDS)	853-68-9	Combi Blocks (98)
2	5-hydroxy-1,4-naphthoquinone (juglone)	481-39-0	Acros (97)
3	2-hydroxy-1,4-naphthoquinone (lawsone)	83-72-7	Aldrich (97)
4	2-methyl-1,4-naphthoquinone (menadione)	58-27-5	Acros (98)
5	Menaquinone-4	863-61-6	Sigma-Aldrich
6	1,2-naphthoquinone-4-sulfonic acid sodium salt (o-NQS)	521-24-4	Sigma (99)
7	(E)-3-(4-hydroxyphenyl)pent-2-enedioic acid (SA)	57100-28-4	Exclusive Chemistry

Model compounds were chosen for their fast and reversible redox reactions and well documented redox potentials. Note: The following model compounds were not fully soluble: 7 in DMSO and 1, 2, 3, 4, 5 in H_2O.

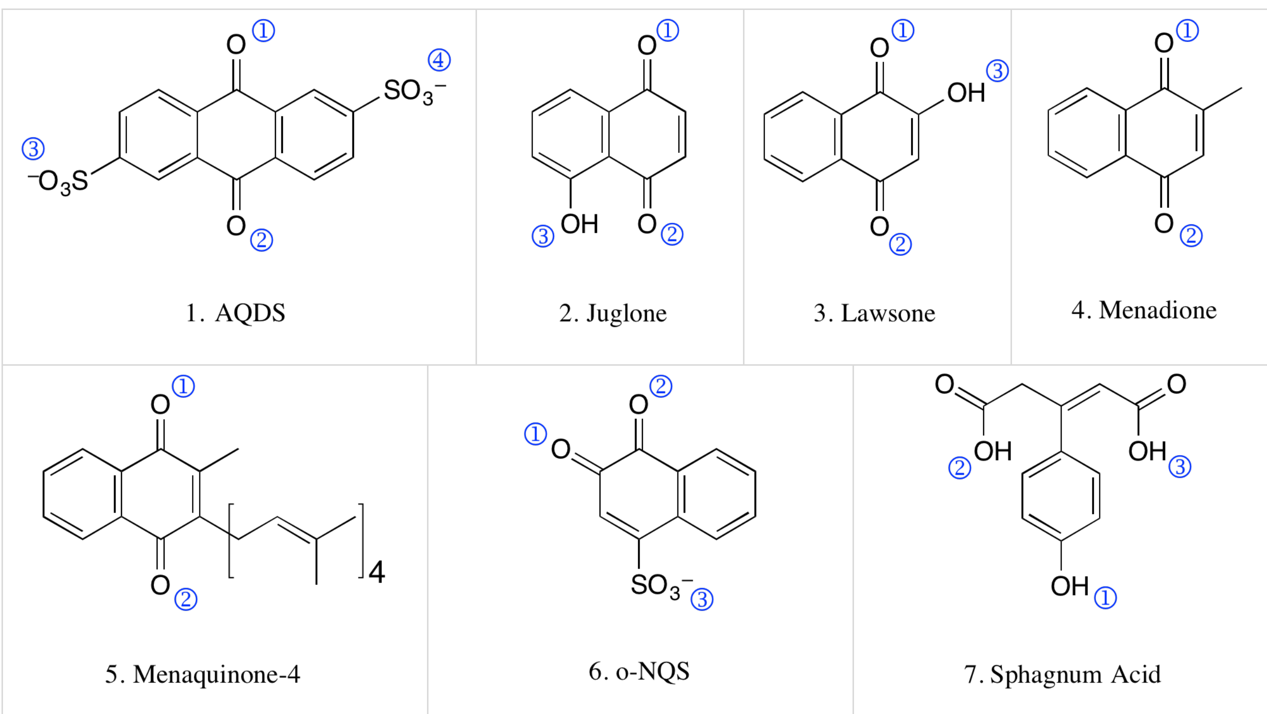


Figure S1. Chemical structures of model compounds. Numbers refer to pK_a's in Table S3.

Table S3. Calculated pK_a's of model compounds in DMSO and H_2O. [1]

No.	Name	pK_a1 O/R	pK_a2 O/R	pK_a3 O/R	pK_a4 O/R
			in H_2O		
1	AQDS	/7.17	/7.17	0.59/0.73	0.59/0.73
2	Juglone	/9.78	/9.63	9.42/9.51	
3	Lawsone	/9.32	/8.66	4.58/8.66	
4	Menadione	/10.29	/9.67		
5	Menaquinone-4	/17.01	/16.82		
6	o-NQS	/8.05	/8.38	0.55/0.93	
7	Sphagnum Acid	8.46/9.77	4.35/16.07	4.33/15.65	
			in DMSO		
1	AQDS	/10.51	/10.51	4.53/4.68	4.53/4.68
2	Juglone	/17.19	/17.12	17.48/16.96	
3	Lawsone	/16.72	/18.34	8.33/16.49	
4	Menadione	/18.17	/17.32		
5	Menaquinone-4	/28.55	/28.36		
6	o-NQS	/14.62	/12.17	4.4/5.23	
7	Sphagnum Acid	14.79/16.83	10.21/26.88	8.14/26.28	

[1]Numbers on pK_a's refer to positions labelled on the structures in **Figure S1**. pK_a's were calculated using ARChem's SPARC online calculator http://archemcalc.com/sparc-web/calc#/multiproperty accessed Sept 2018. O/R signifies oxidized or reduced form respectively. In cases where only the reduced form had a pK_a, a forward slash (/) precedes the value.

Table S4. Peak potentials of NOM.

No.	Name	E_{pa1}[1]	E_{pa2}[1]	E_{pc1}[2]	E_{pc2}[2]	E_{p1}[3]	E_{p2}[3]
1	Bamboo NOM	–0.887				–1.004	
2	Bemidji FA	–1.754	–0.915	–1.260		–0.810	
3	Black River NOM					–1.513	
4	Cabbage Tree NOM	–0.986				–0.803	
5	Coal Creek FA	–1.028		–1.278		–1.160	
6	Coal Creek HA			–1.353		–1.201	
7	Elliott Soil FA Std II	–0.853		–1.254		–0.824	
8	Elliott Soil HA Std I	–0.818		–1.359		–0.869	
9	Elliott Soil HA Std IV	–0.859		–1.457		–0.872	
10	Everglades 2BS HPOA	–0.851		–1.441		–0.822	
11	Everglades F1 HPOA	–0.844		–1.332		–0.820	
12	Everglades F1 TPIA	–0.820		–1.369		–0.820	
13	Everglades LOX8 HPOA	–0.832		–1.391		–0.819	
14	Georgetown NOM	–0.846		–1.353		–0.843	
15	Georgetown NOM CH	–0.794		–1.391		–0.780	
16	Georgetown NOM PP	–0.836		–1.345	–0.899	–0.767	
17	Great Dismal Swamp FA	–0.808		–1.357		–0.754	
18	Inangahua River NOM	–0.805				–0.797	
19	Kauri NOM	–1.002				–0.905	
20	Kitty Hawk NOM	–1.804	-0.846	–1.355		–0.834	
21	Lake Fryxell FA	–1.050		–1.258		–1.142	
22	Leonardite HA Std I	–0.863		–1.330		–0.867	
23	Leonardite HA Std I	–0.855		–1.387		–0.848	
24	MW-6 NOM	–0.838				–0.858	
25	Nordic Reservoir NOM	–0.863				–0.810	
26	North Sea DOM	–0.744		–1.443		–0.738	
27	Ogeechee River FA	–0.869		–1.266		–1.164	
28	Pacific Ocean FA	–0.846		–1.409		–0.832	
29	Pahokee Peat FA Std II	–0.857		–1.365		–0.854	
30	Pahokee Peat HA Std I	–0.863		–1.292		–0.854	
31	Pahokee Peat HA Std I	–0.863		–1.314		–0.862	
32	Pine Barrens NOM	–0.806		–1.334		–0.776	

No.	Name	E_{pa1}[1]	E_{pa2}[1]	E_{pc1}[2]	E_{pc2}[2]	E_{p1}[3]	E_{p2}[3]
33	Pony Lake FA	–0.955		–1.427		–0.891	
34	Prairie Pot Hole P8 DOM	–0.814		–1.381		–0.819	
35	Red Tussock NOM	–1.790	-0.844			–0.848	
36	Rio Negro NOM	–1.661	–0.857	–1.272		–0.880	
37	Schönbuch Anoxic FA	–0.867		–1.371	–0.972	–0.791	
38	Schönbuch Anoxic HA	–0.810		–1.316		–0.790	
39	Schönbuch H_2O Anoxic FA	–1.062				–0.948	
40	Schönbuch H_2O Anoxic HA	–0.830				–0.831	
41	Schönbuch H_2O Oxic HS	flat					
42	Schönbuch Oxic HA	–0.988		–1.090		-1.071	
43	Shelter Is. San Diego HA			–1.484		–0.959	
44	Soil HA Ref	–0.873		–1.286		–0.811	
45	Sutton Stream NOM	–0.832				–0.763	
46	Suwannee River FA Std II	–0.824		–1.385	–0.905	–0.817	
47	Suwannee River HA Std III			–1.395		–0.800	
48	Suwannee River NOM	–0.808		–1.349		–0.802	
49	Suwannee River NOM	–0.846		–1.363		–0.819	
50	Suwannee River NOM	–1.780	–0.859	–1.381		–0.836	
51	Toolik Lake FA	–0.824		–1.363		–0.778	
52	Walnut NOM	–0.969				–0.800	
53	Waskish Peat HA Ref	–0.798		–1.399		–0.817	
54	Williams Lake HPOA	–0.846		–1.431		–0.818	

Potentials reported in V vs Ag/Ag^+. Experiments performed in 0.1 M TBAFP in DMSO, with a Pt working electrode. NOM concentrations were 1.0 mg/mL except where NOM did not fully dissolve in DMSO. Scan rate was 25 mV s^{-1}, step size 2 mV, and amplitude 25 mV. [1]E_{pa} and [2]E_{pc} denote SCV anodic and cathodic peak respectively. [3]E_p denotes SWV peaks.

Table S5. Peak potentials of model compounds.

No.	Name	E_{pa1}[1]	E_{pa2}[1]	E_{pc1}[2]	E_{pc2}[2]	E_{p1}[3]	E_{p2}[3]
			in H_2O				
1	AQDS	–0.331		–0.459		–0.421	
2	Juglone	–0.177		–0.213		–0.215	
3	Lawsone	–0.274		–0.441		–0.308	
4	Menadione	–0.128		–0.302		–0.326	–0.131
5	Menaquinone-4	–0.282		–0.823	–0.431	–0.836	–0.315
6	o-NQS	0.169		–0.095		–0.093	0.145
7	Sphagnum acid	0.678				0.625	
			in DMSO				
1	AQDS	–1.673	–1.010	–1.786	–1.078	–1.720	–1.045
2	Juglone	–1.238	–0.633	–1.462	–0.711	–1.307	–0.672
3	Lawsone	–1.585		–1.786	–0.828	–1.681	–0.847
4	Menadione	–1.601	–0.887	–1.849	–0.961	–1.674	–0.921
5	Menaquinone-4	–1.681	–0.953	–1.923	–1.026	–1.799	–0.988
6	o-NQS	–1.300	–0.649	–1.397	–0.732	–1.339	–0.690
7	Sphagnum acid	–1.752	–0.766	–1.486		–0.825	

Potentials reported in V vs Ag/AgCl for H_2O and Ag/Ag^+ for DMSO. Potentials reported in H_2O are averages of all runs using NOVA 2.1 software, in DMSO values are the best run using Igor Multipeak fit. Aqueous runs were performed in a 0.1 M KCl/ 0.1 M Phosphate buffer (pH 7), using a Pt and GC working electrode. Aprotic runs were performed in 0.1 M TBAFP using a Pt working electrode. [1]E_{pa} and [2]E_{pc} denotes anodic and cathodic potentials respectively of staircase cyclic voltammograms and [3]E_p denotes peak potentials of square-wave voltammograms. Scan rate was 25 mV s^{-1}, step size 2 mV, and amplitude 25 mV.

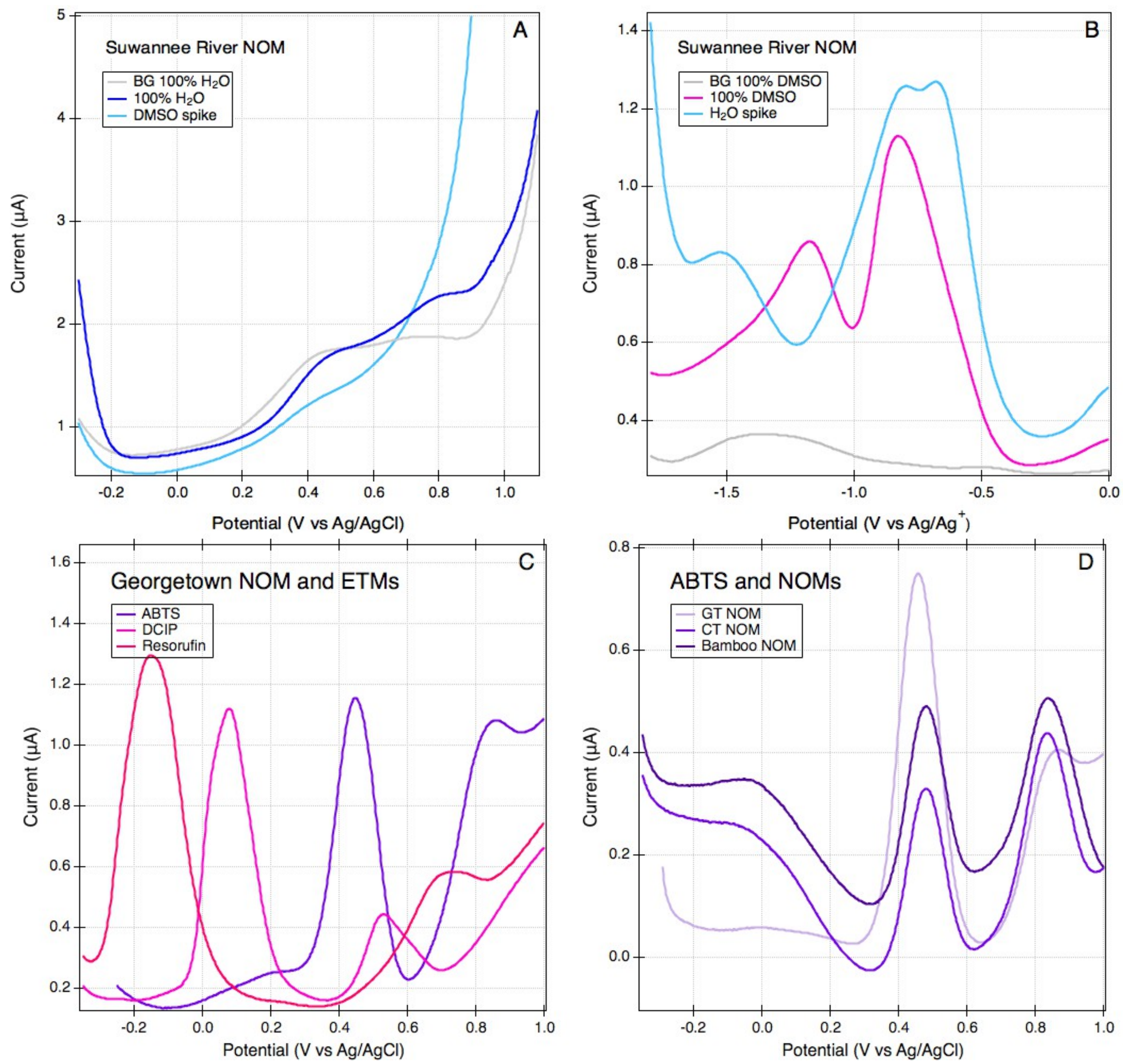
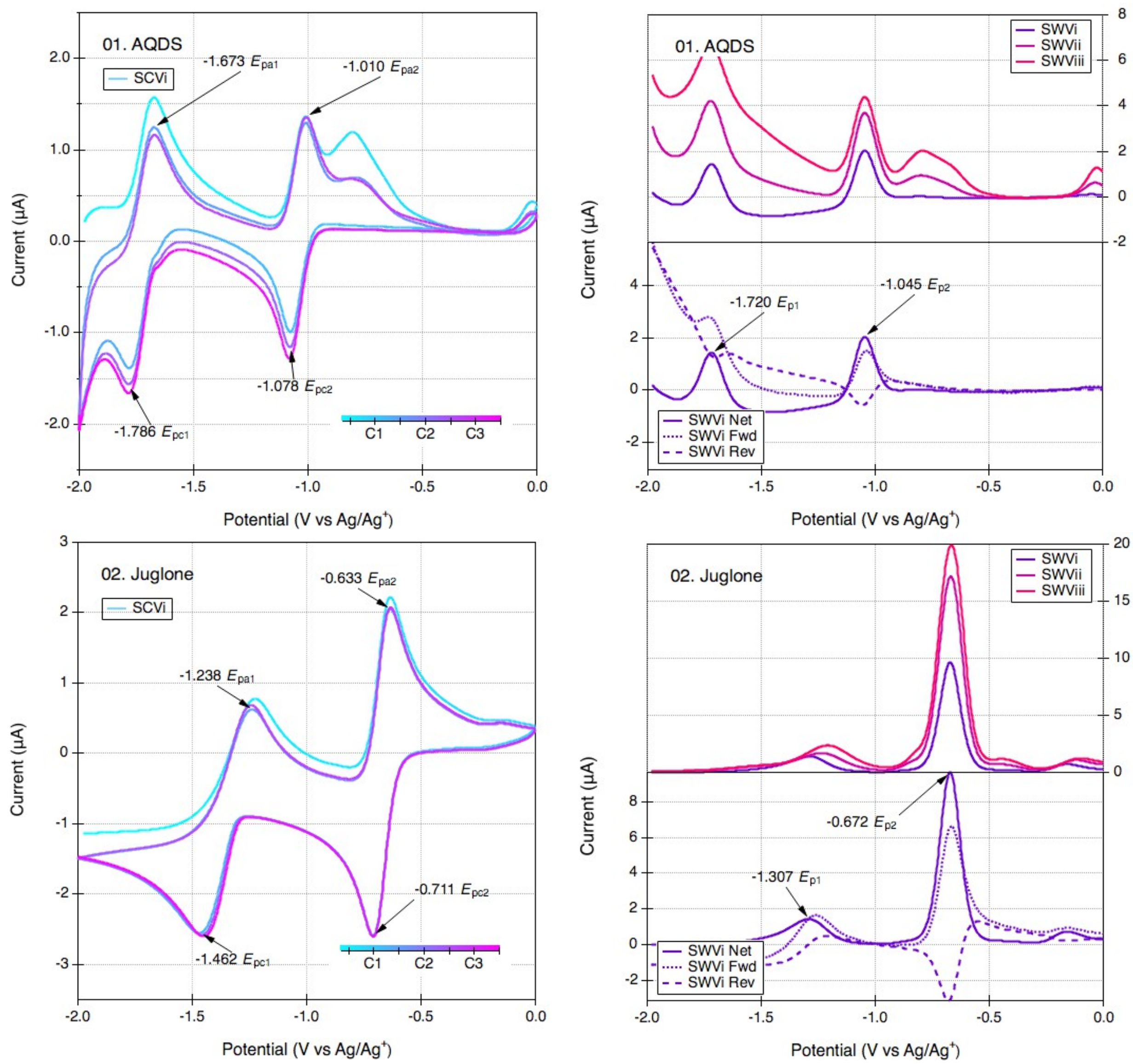


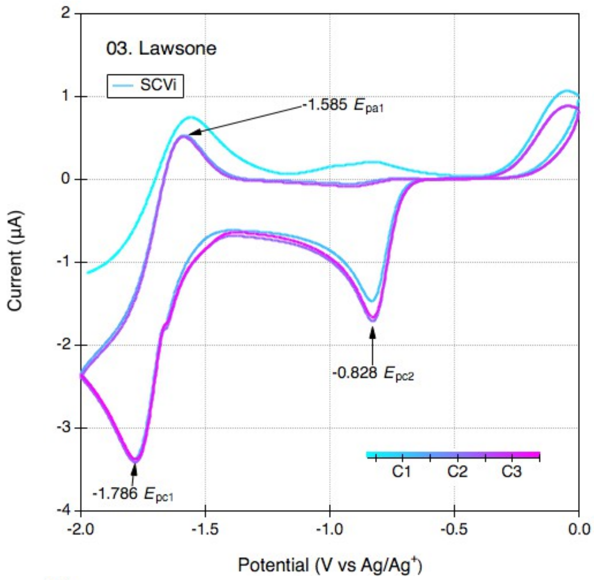
Figure S2. SWVs of control experiments. All SWVs at a scan rate of 25 mV/s, 2 mV step size, 25 mV amplitude, in 0.1 M KCl and phosphate buffer (pH 7.0) using a GC WE. (**A**) Suwannee River NOM in 100% H_2O (dark blue), 85% H_2O/15% DMSO (light blue), background (BG) (grey). (**B**) Suwannee River NOM in 100% DMSO (pink), 85% DMSO/15% H_2O (light blue), BG (grey). (**C**) SWV of Georgetown NOM using three mediators: ABTS (purple), DCIP (pink), and resorufin (red). (**D**) SWV of one mediator (ABTS) and three NOMs: Georgetown (light purple), Cabbage Tree (medium purple), and Bamboo (dark purple).

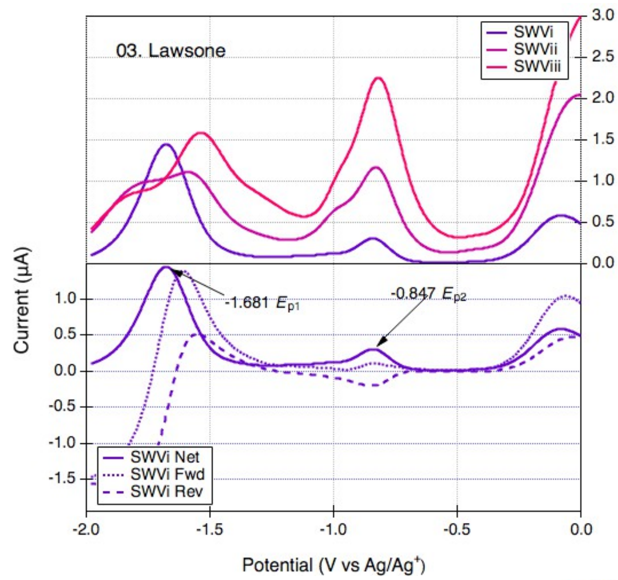
Caption for figures on pages S10-S12

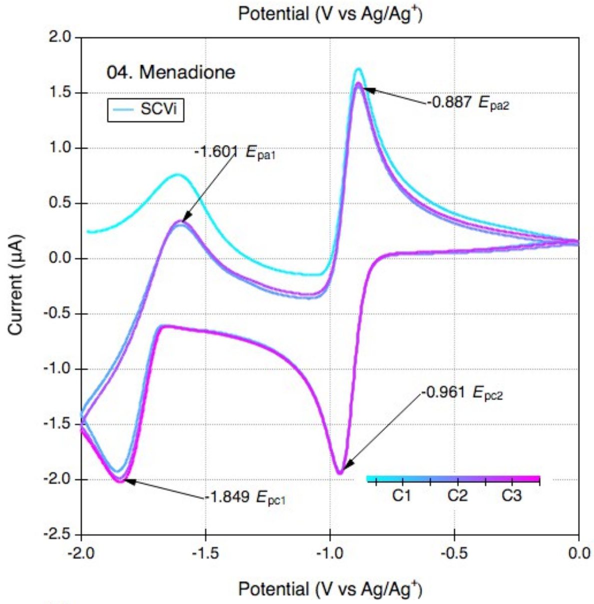
Figure S3. Primary SCV (left) and SWV (right) data for model compounds. Each row represents a model compound sample as listed in Table S2. Varying scan rate identified by *i*, *ii*, and *iii*.

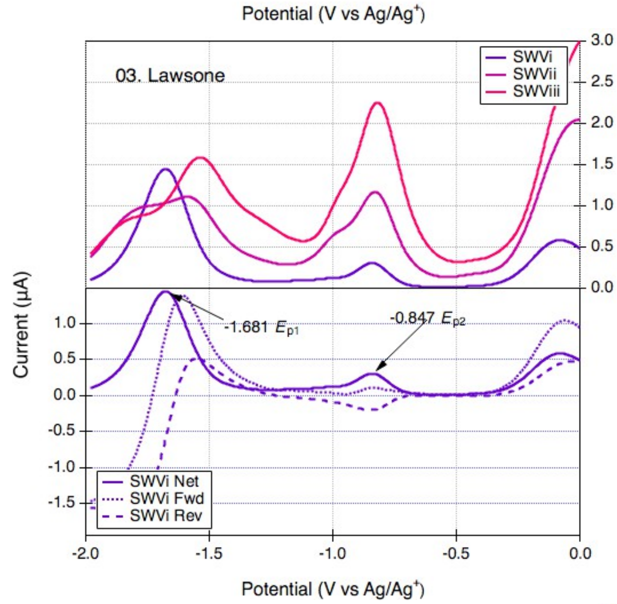
Conditions: 1.5 mM of model compound in 0.1 M TBAFP in DMSO, 1.6 mm Pt working electrode, Pt coil counter electrode and a Ag/Ag^+ reference electrode filled with 0.1 M TBAFP and 0.005 M $AgNO_3$ in DMSO. Scan rate: SWV*i* and SCV*i* 25 mV s^{-1}, SWV*ii* 125 mV s^{-1}, SWV*iii* 225 mV s^{-1}. Step size 2 mV, amplitude 25 mV.

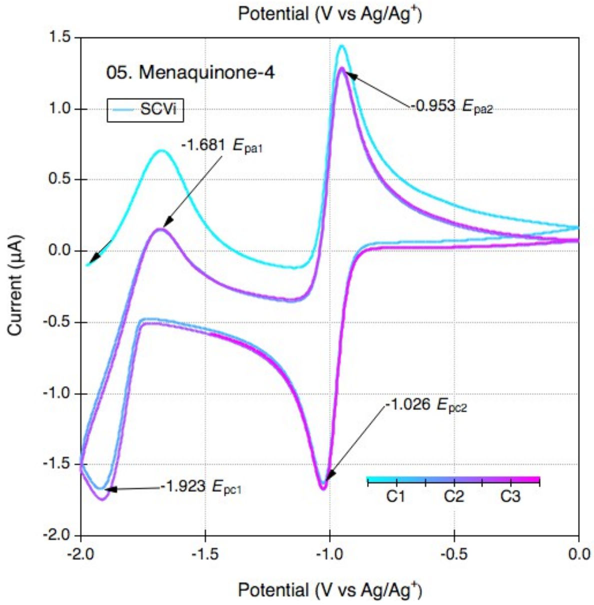


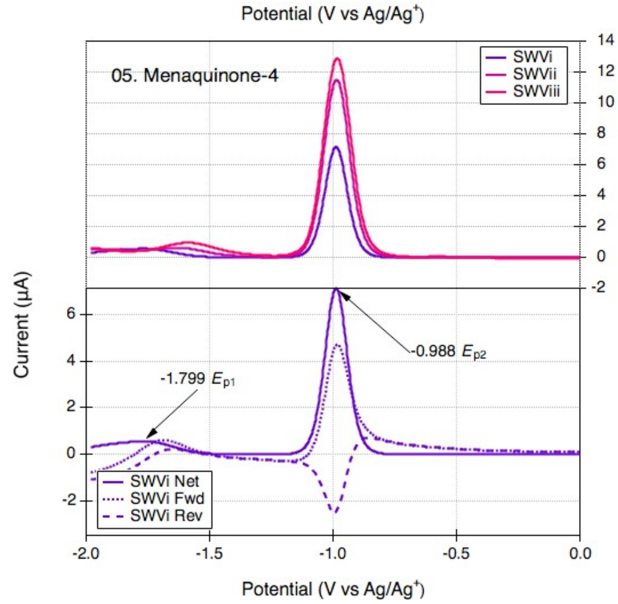

03. Lawsone
SCVi
-1.585 E_{pa1}
-0.828 E_{pc2}
-1.786 E_{pc1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

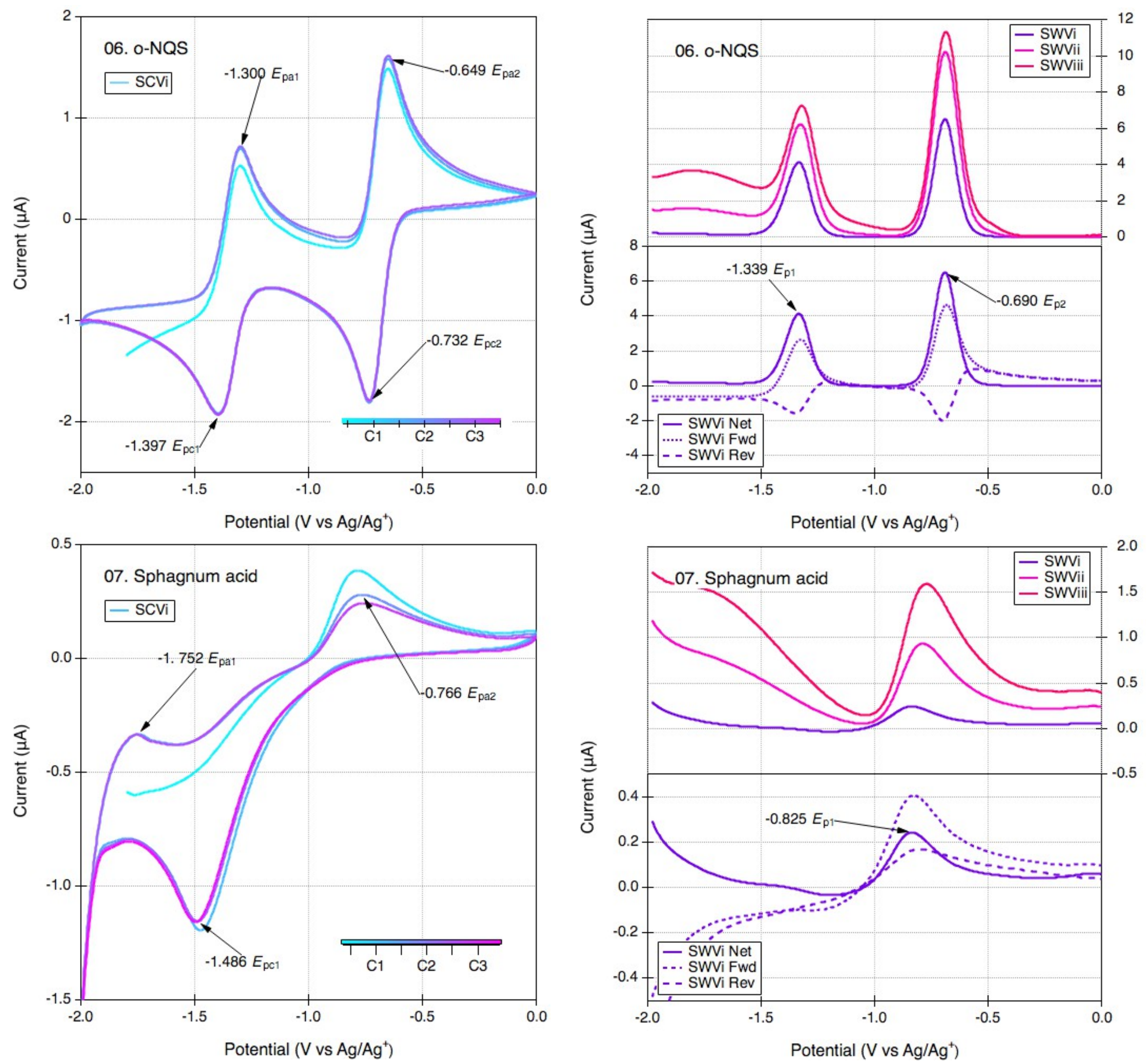

03. Lawsone
SWVi
SWVii
SWViii
-1.681 E_{p1}
-0.847 E_{p2}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)


04. Menadione
SCVi
-0.887 E_{pa2}
-1.601 E_{pa1}
-0.961 E_{pc2}
-1.849 E_{pc1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)


03. Lawsone
SWVi
SWVii
SWViii
-1.681 E_{p1}
-0.847 E_{p2}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)


05. Menaquinone-4
SCVi
-0.953 E_{pa2}
-1.681 E_{pa1}
-1.026 E_{pc2}
-1.923 E_{pc1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

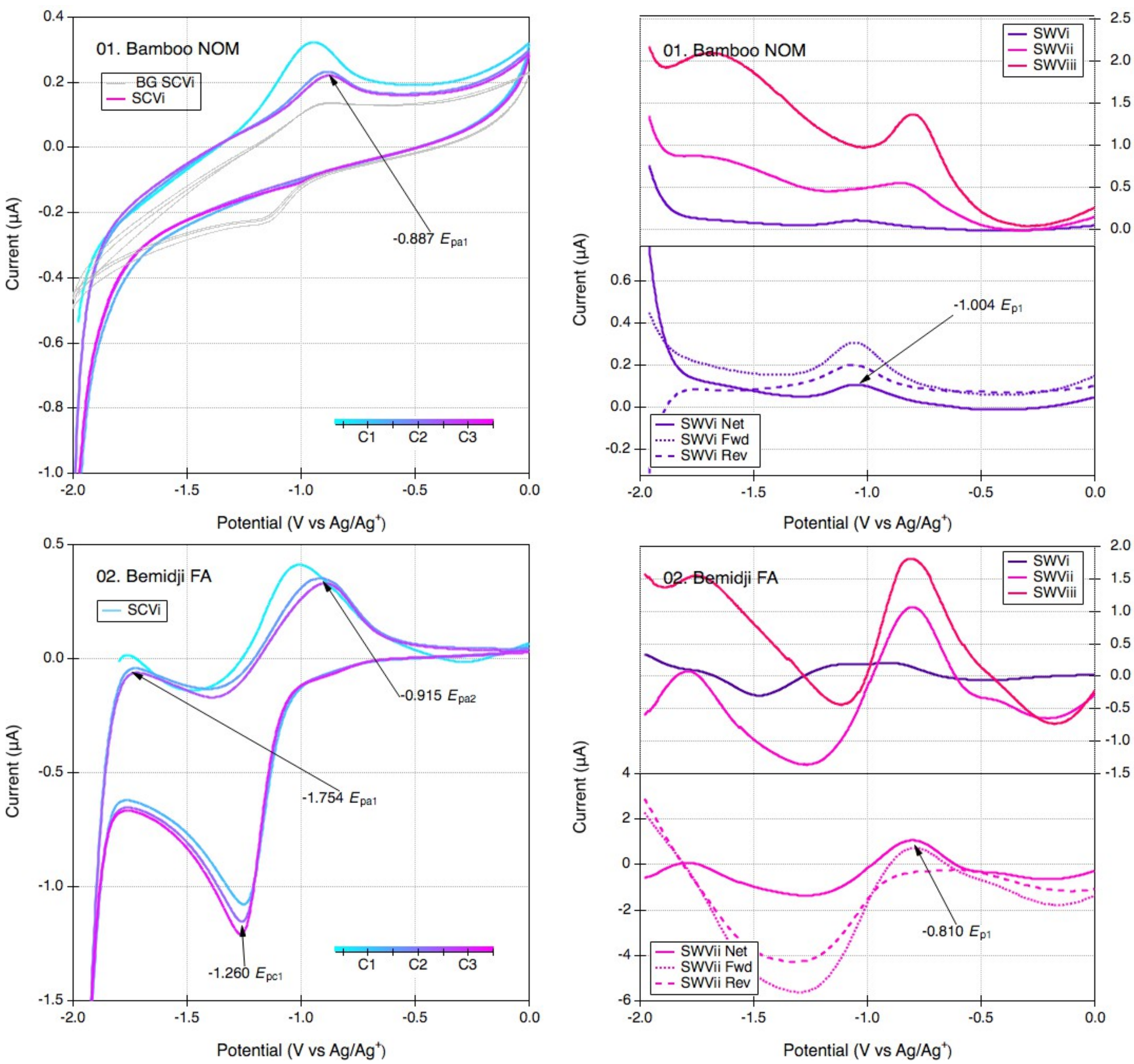

05. Menaquinone-4
SWVi
SWVii
SWViii
-0.988 E_{p2}
-1.799 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

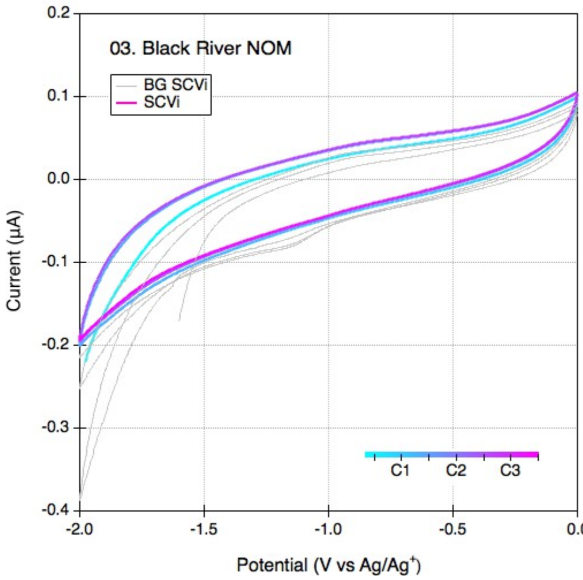

06. o-NQS
SCVi
-1.300 E_{pa1}
-0.649 E_{pa2}
-0.732 E_{pc2}
-1.397 E_{pc1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)
SWVi
SWVii
SWViii
-1.339 E_{p1}
-0.690 E_{p2}
SWVi Net
SWVi Fwd
SWVi Rev
07. Sphagnum acid
-1. 752 E_{pa1}
-0.766 E_{pa2}
-1.486 E_{pc1}
-0.825 E_{p1}

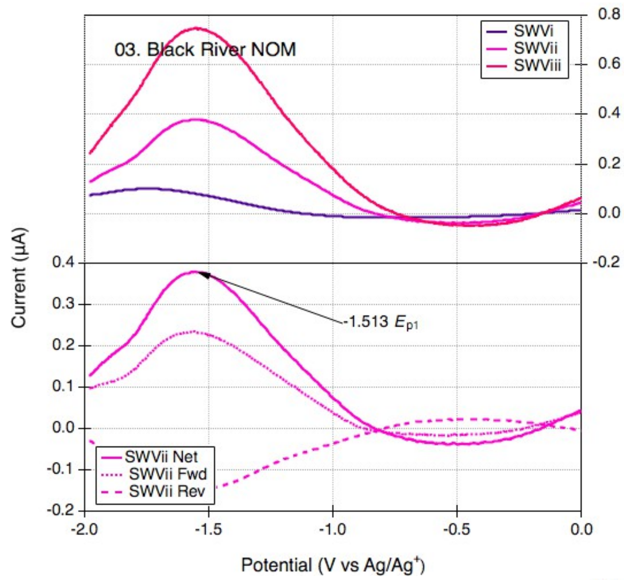
Caption for figures on pages S13-S31

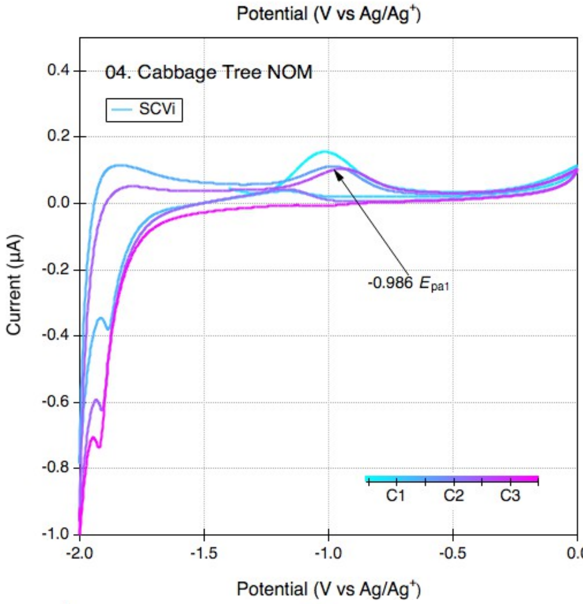
Figure S4. Primary SCV (left) and SWV (right) data for NOMs. Each row represents a NOM sample as listed in Table S1. Varying scan rate identified by *i, ii*, and *iii*.

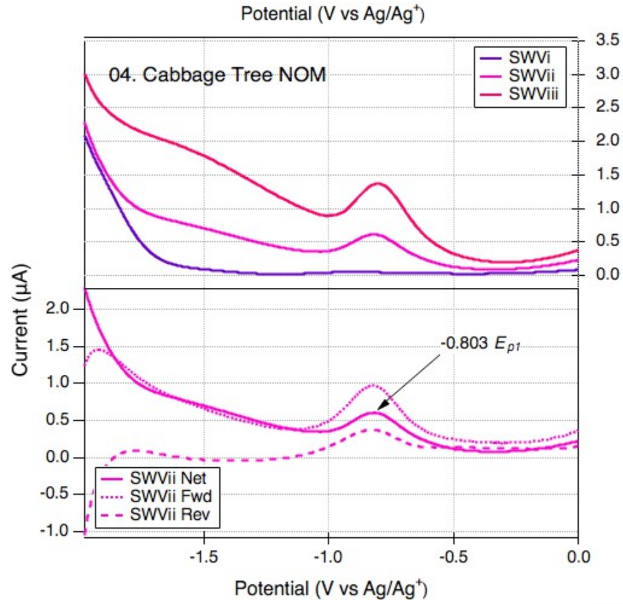
Conditions: 1.0 mg/mL (except for HS that did not fully dissociate in DMSO) of HS in 0.1 M TBAFP in DMSO, 1.6 mm Pt working electrode, Pt coil counter electrode and a Ag/Ag^+ reference electrode filled with 0.1 M TBAFP and 0.005 M $AgNO_3$ in DMSO. Scan rate: SWV*i* and SCV*i* 25 mV s^{-1}, SWV*ii* 125 mV s^{-1}, SWV*iii* 225 mV s^{-1}. Step size 2 mV, amplitude 25 mV.

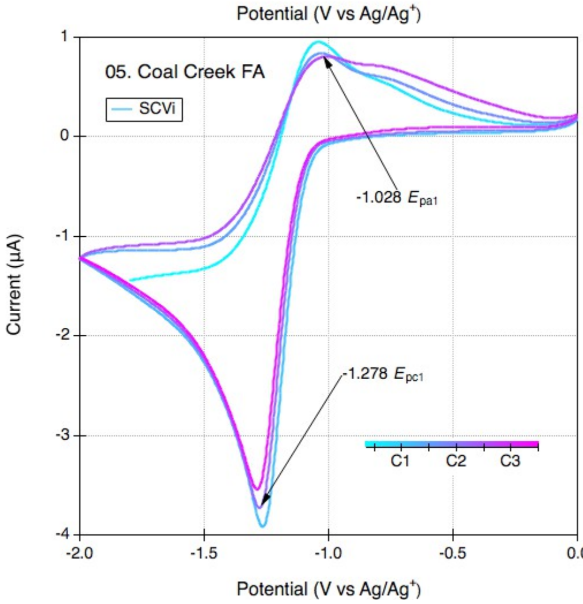


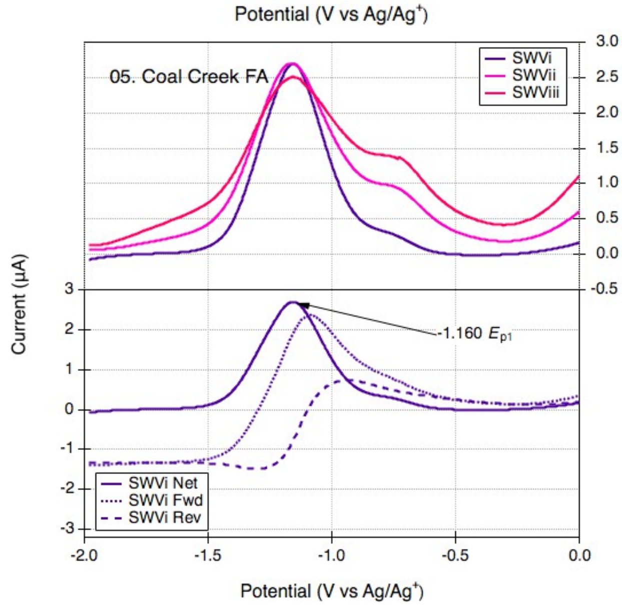

03. Black River NOM
BG SCVi
SCVi
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag+)

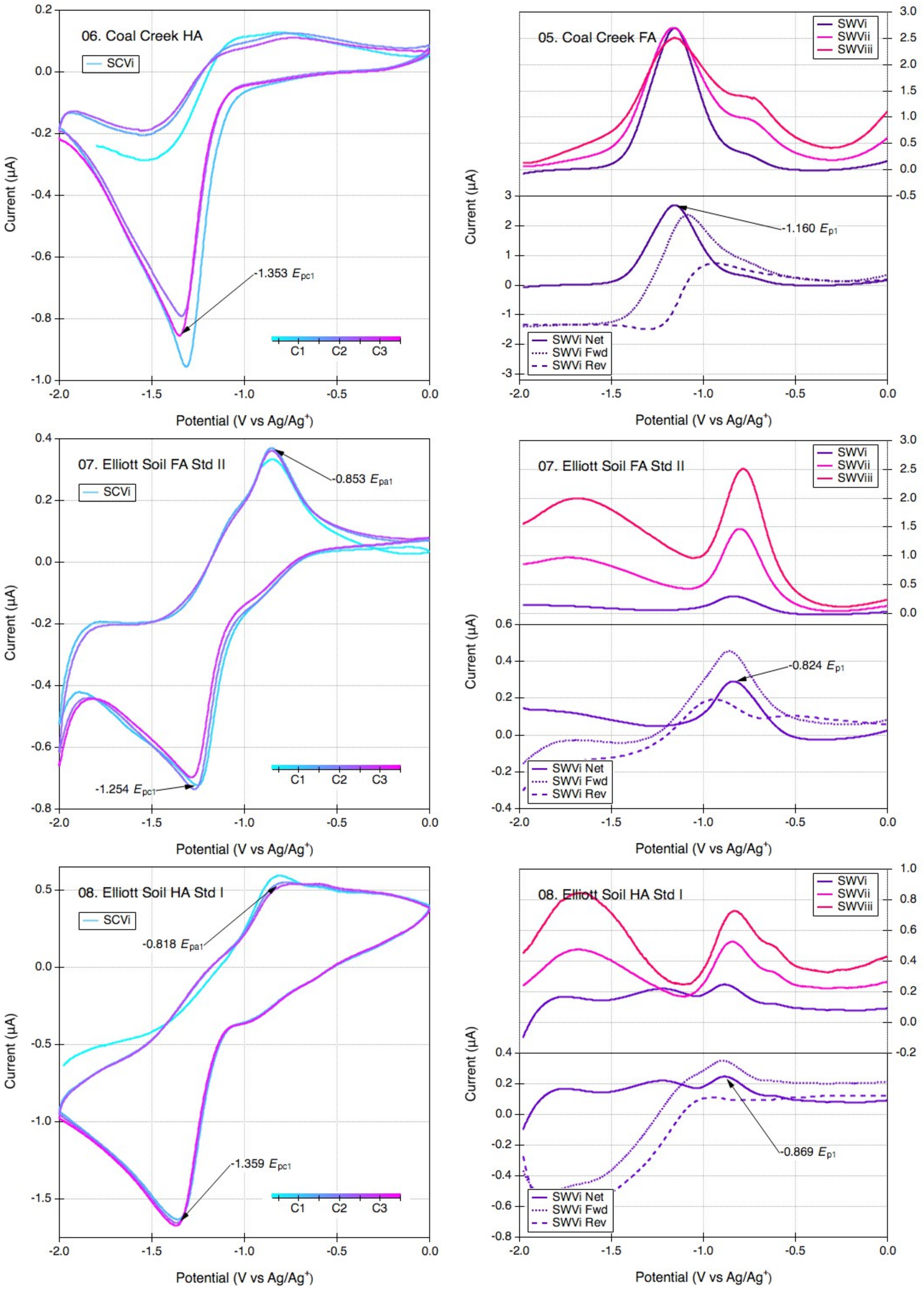

03. Black River NOM
SWVi
SWVii
SWViii
-1.513 Ep1
SWVii Net
SWVii Fwd
SWVii Rev
Current (µA)
Potential (V vs Ag/Ag+)


04. Cabbage Tree NOM
SCVi
-0.986 Epa1
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag+)

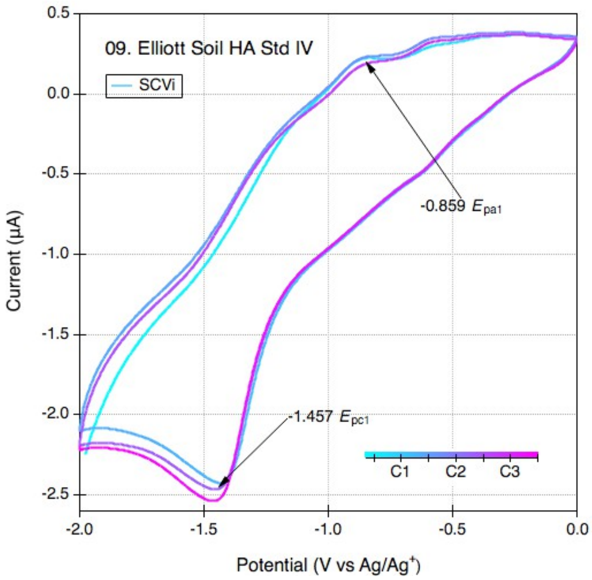

04. Cabbage Tree NOM
SWVi
SWVii
SWViii
-0.803 Ep1
SWVii Net
SWVii Fwd
SWVii Rev
Current (µA)
Potential (V vs Ag/Ag+)

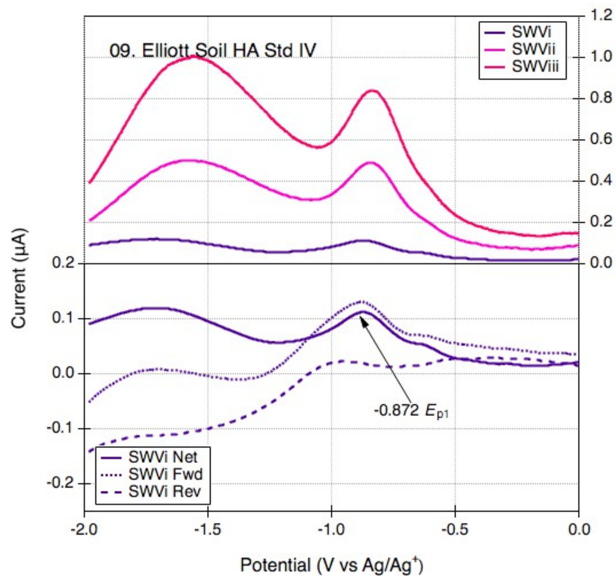

05. Coal Creek FA
SCVi
-1.028 Epa1
-1.278 Epc1
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag+)

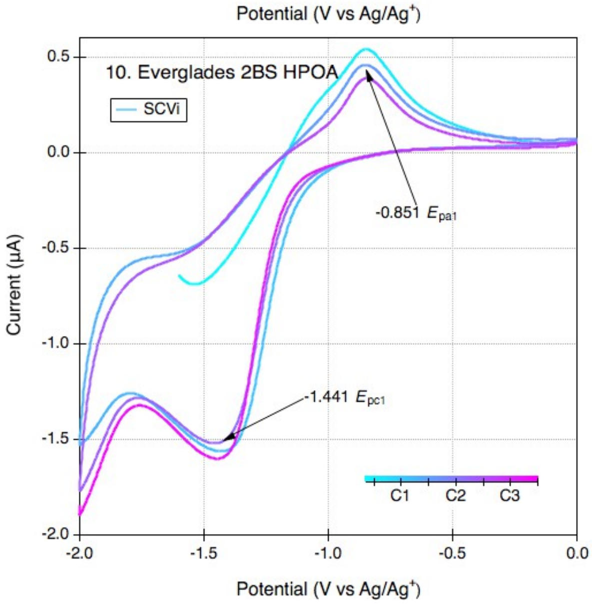

05. Coal Creek FA
SWVi
SWVii
SWViii
-1.160 Ep1
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag+)

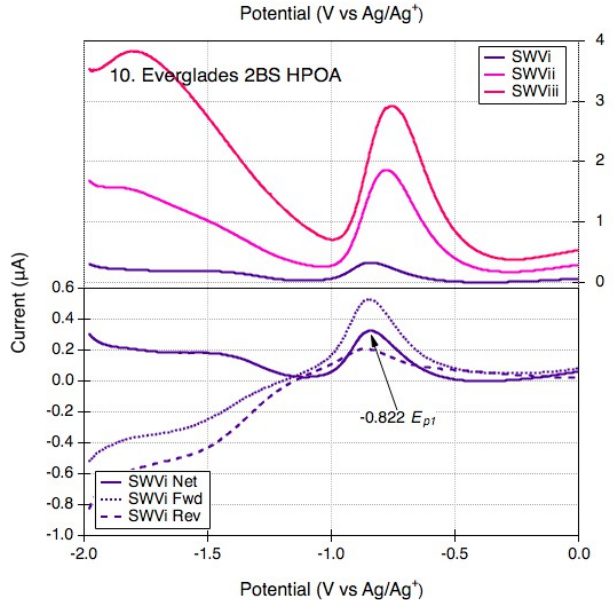


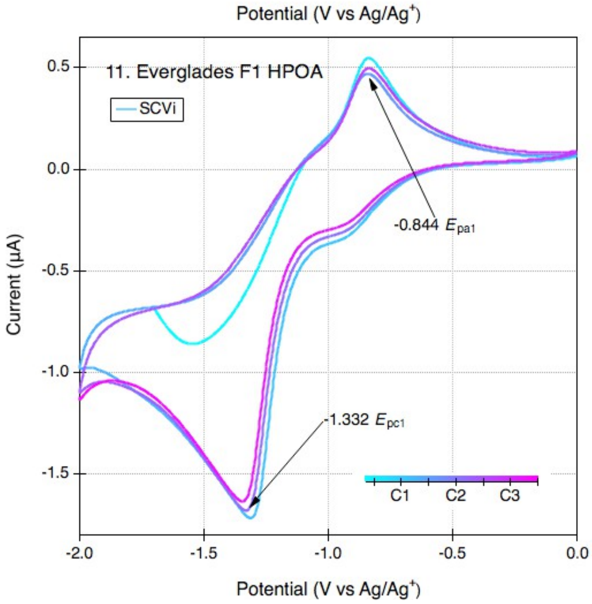
06. Coal Creek HA
SCVi
-1.353 E_{pc1}
C1 C2 C3
Current (μA)
Potential (V vs Ag/Ag⁺)
05. Coal Creek FA
SWVi
SWVii
SWViii
-1.160 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (μA)
Potential (V vs Ag/Ag⁺)
07. Elliott Soil FA Std II
SCVi
-0.853 E_{pa1}
-1.254 E_{pc1}
C1 C2 C3
Current (μA)
Potential (V vs Ag/Ag⁺)
07. Elliott Soil FA Std II
SWVi
SWVii
SWViii
-0.824 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (μA)
Potential (V vs Ag/Ag⁺)
08. Elliott Soil HA Std I
SCVi
-0.818 E_{pa1}
-1.359 E_{pc1}
C1 C2 C3
Current (μA)
Potential (V vs Ag/Ag⁺)
08. Elliott Soil HA Std I
SWVi
SWVii
SWViii
-0.869 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (μA)
Potential (V vs Ag/Ag⁺)

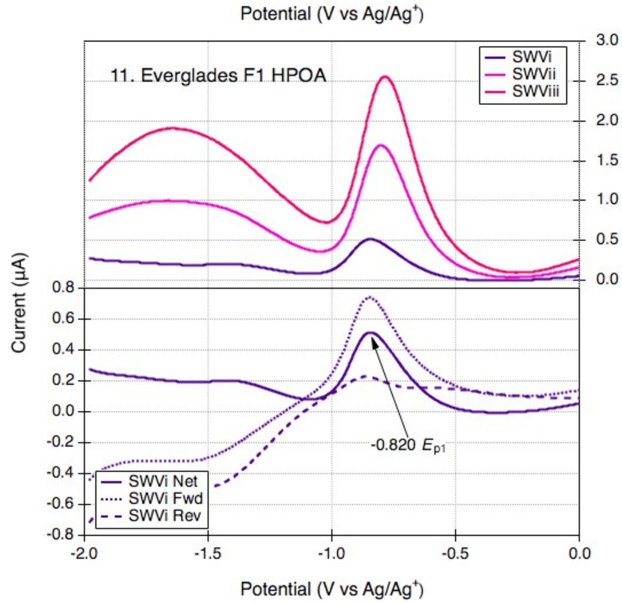

09. Elliott Soil HA Std IV
SCVi
-0.859 E_{pa1}
-1.457 E_{pc1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

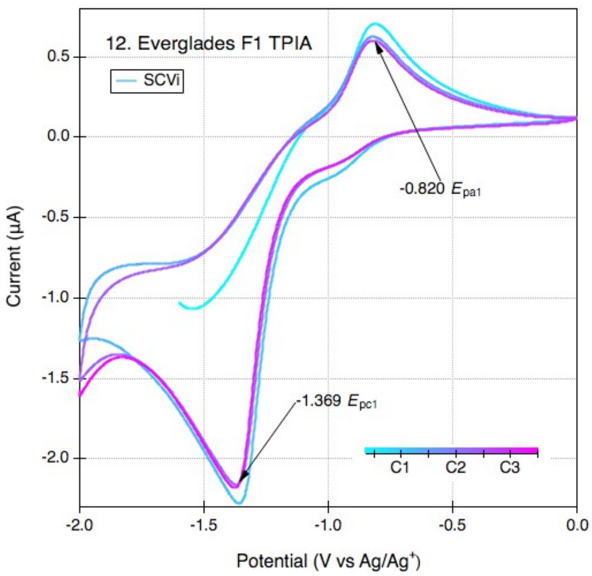

09. Elliott Soil HA Std IV
SWVi
SWVii
SWViii
-0.872 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

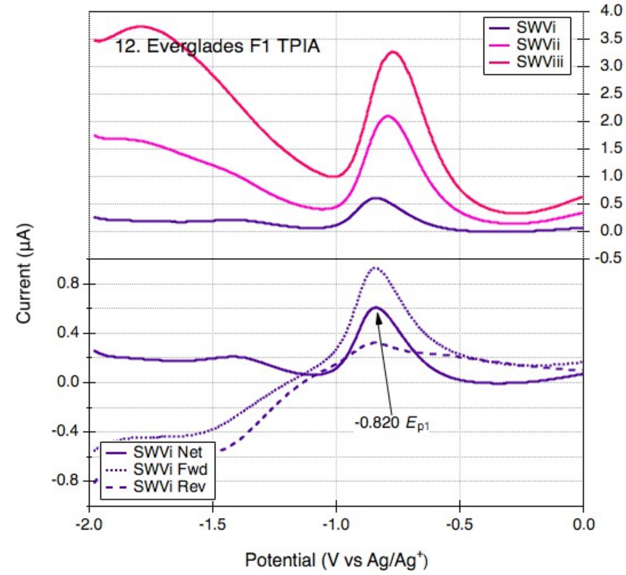

10. Everglades 2BS HPOA
SCVi
-0.851 E_{pa1}
-1.441 E_{pc1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

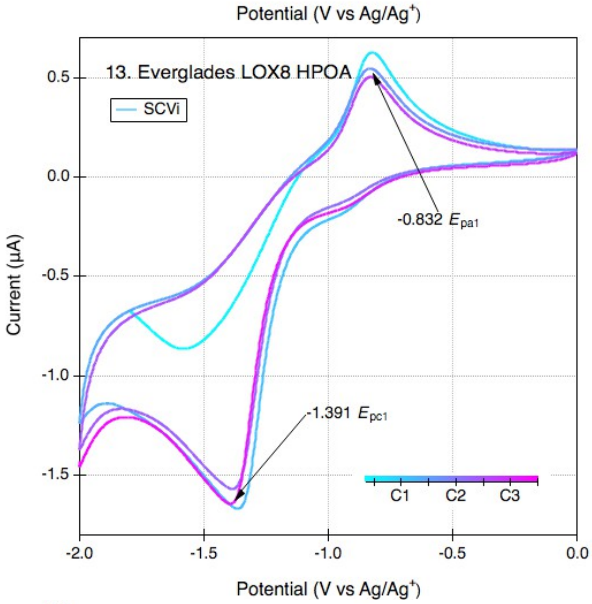

10. Everglades 2BS HPOA
SWVi
SWVii
SWViii
-0.822 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

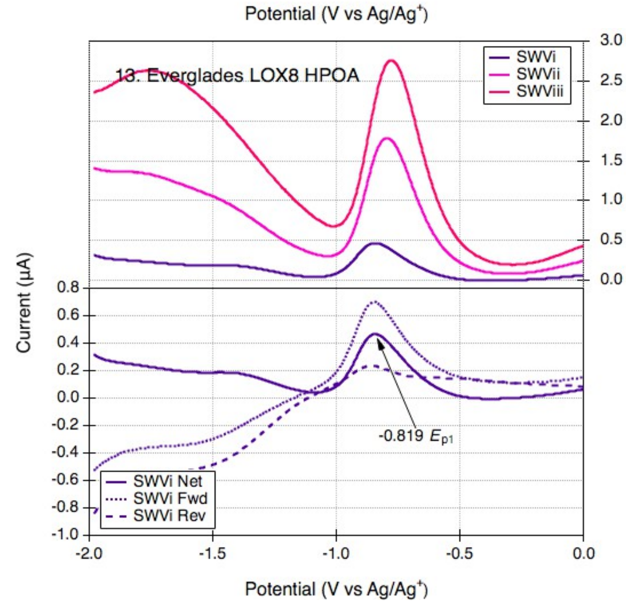

11. Everglades F1 HPOA
SCVi
-0.844 E_{pa1}
-1.332 E_{pc1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

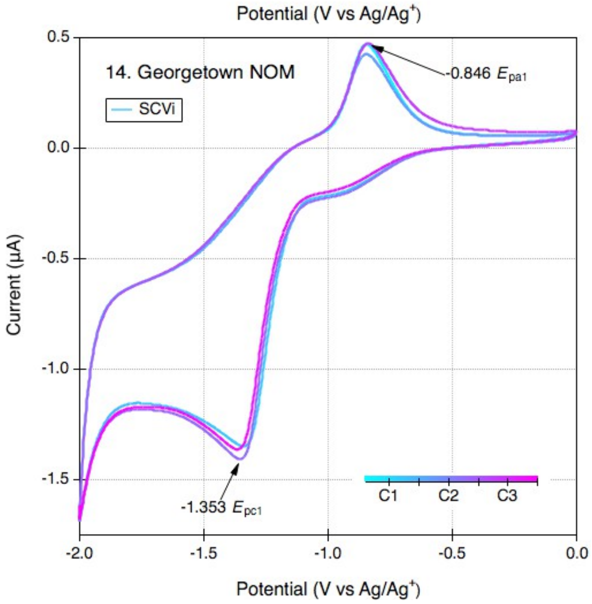

11. Everglades F1 HPOA
SWVi
SWVii
SWViii
-0.820 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

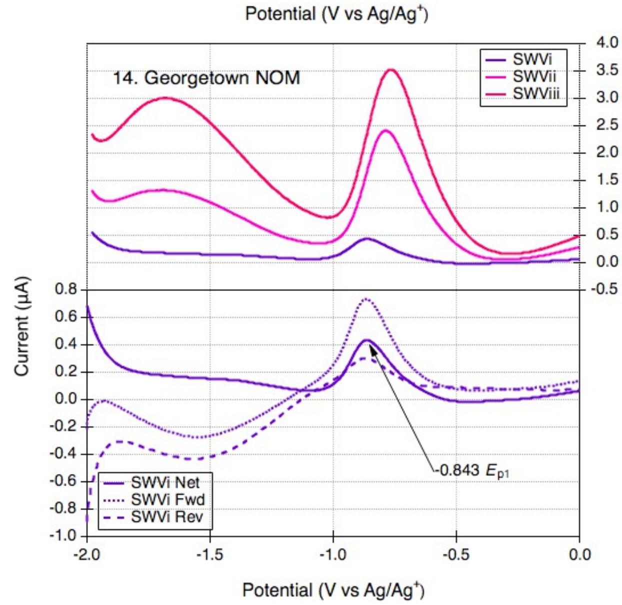

12. Everglades F1 TPIA
SCVi
-0.820 E_{pa1}
-1.369 E_{pc1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

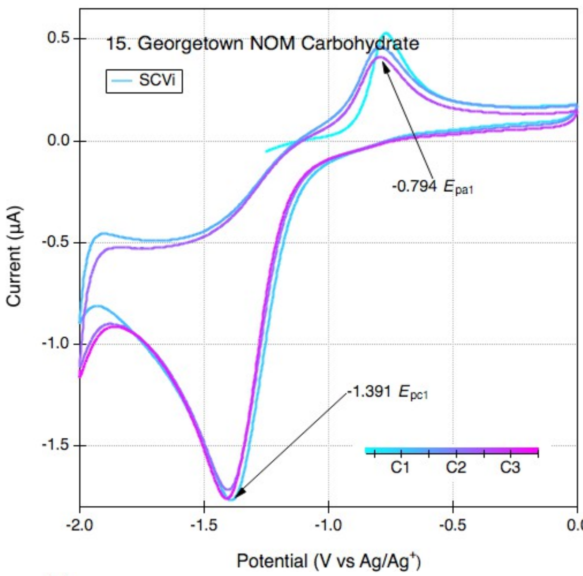

12. Everglades F1 TPIA
SWVi
SWVii
SWViii
-0.820 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

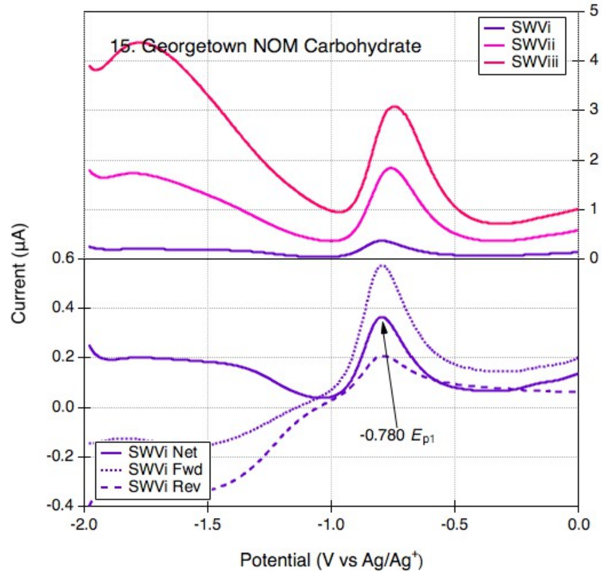

13. Everglades LOX8 HPOA
SCVi
-0.832 E_{pa1}
-1.391 E_{pc1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

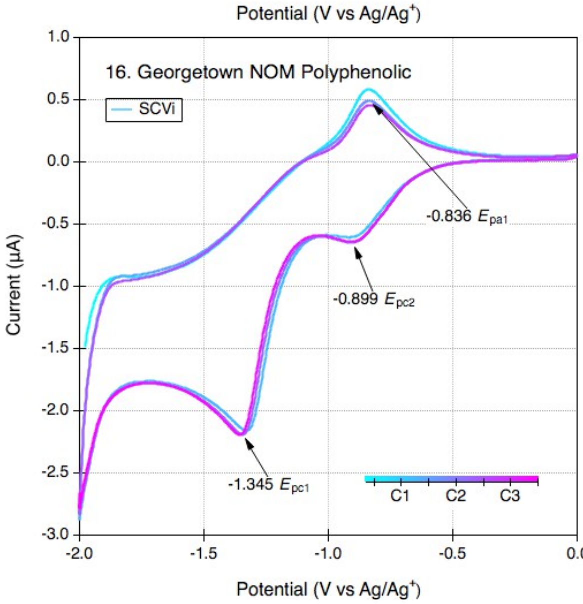

13. Everglades LOX8 HPOA
SWVi
SWVii
SWViii
-0.819 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

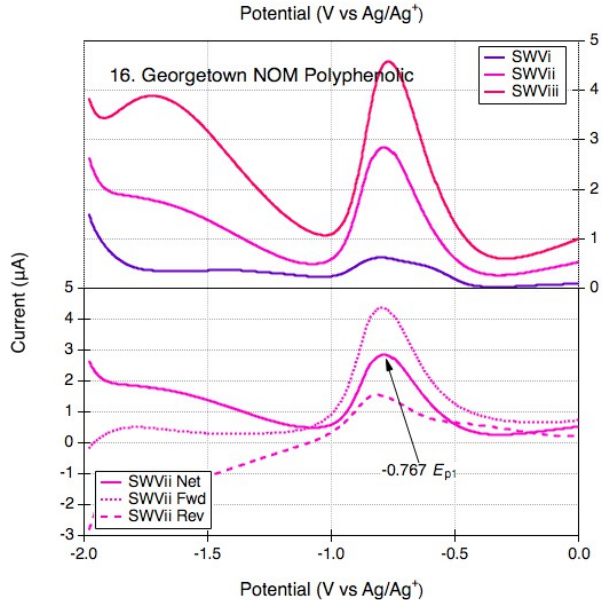

14. Georgetown NOM
SCVi
-0.846 E_{pa1}
-1.353 E_{pc1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

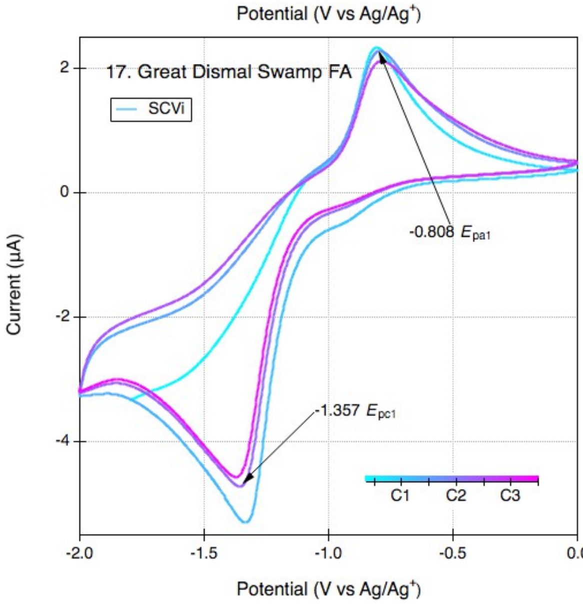

14. Georgetown NOM
SWVi
SWVii
SWViii
-0.843 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

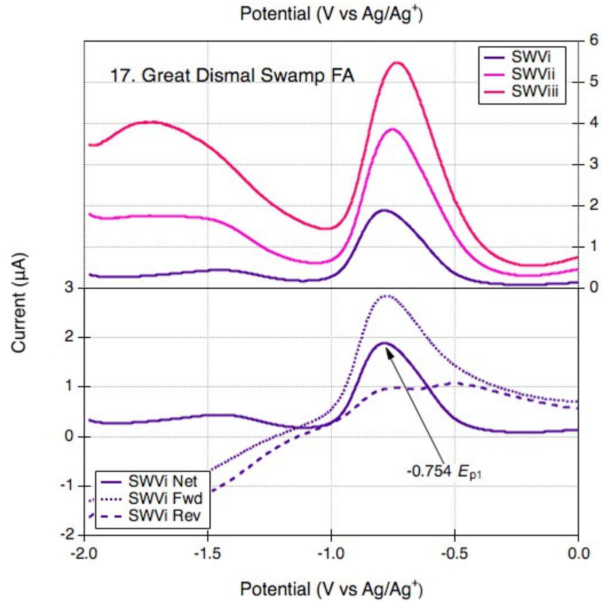

15. Georgetown NOM Carbohydrate
SCVi
-0.794 E_{pa1}
-1.391 E_{pc1}
C1 C2 C3
Current (μA)
Potential (V vs Ag/Ag$^+$)

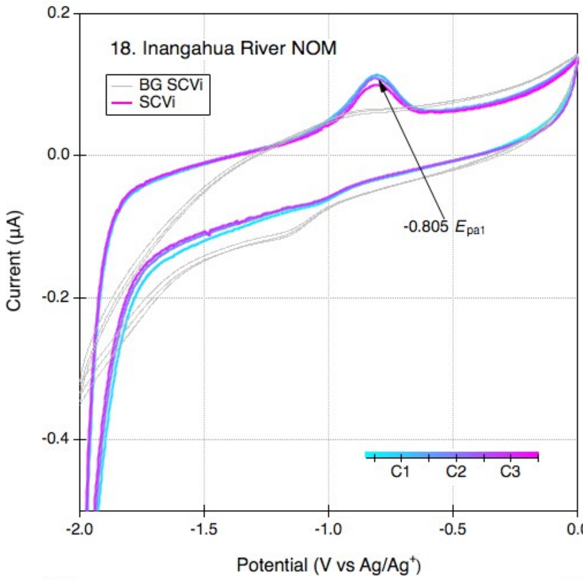

15. Georgetown NOM Carbohydrate
SWVi
SWVii
SWViii
SWVi Net
SWVi Fwd
SWVi Rev
-0.780 E_{p1}
Current (μA)
Potential (V vs Ag/Ag$^+$)

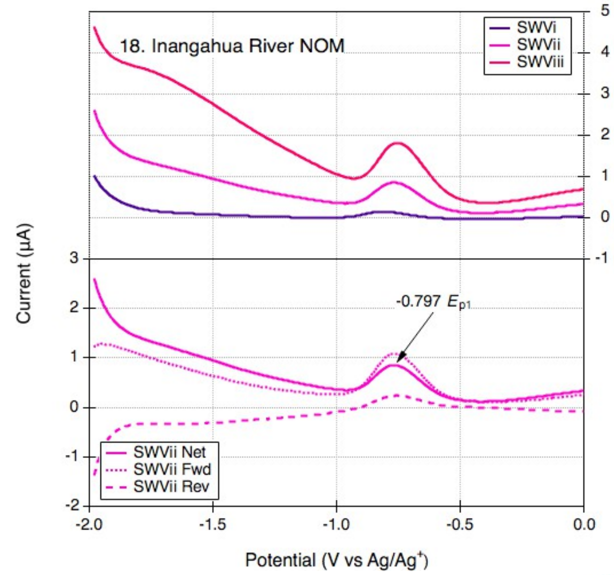

16. Georgetown NOM Polyphenolic
SCVi
-0.836 E_{pa1}
-0.899 E_{pc2}
-1.345 E_{pc1}
C1 C2 C3
Current (μA)
Potential (V vs Ag/Ag$^+$)

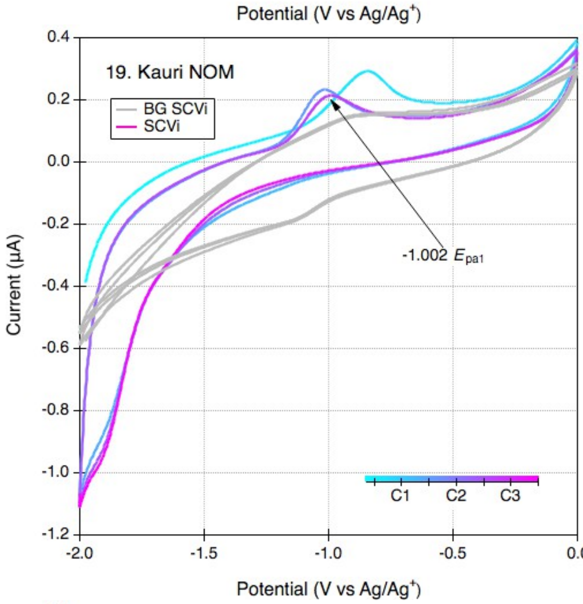

16. Georgetown NOM Polyphenolic
SWVi
SWVii
SWViii
SWVii Net
SWVii Fwd
SWVii Rev
-0.767 E_{p1}
Current (μA)
Potential (V vs Ag/Ag$^+$)

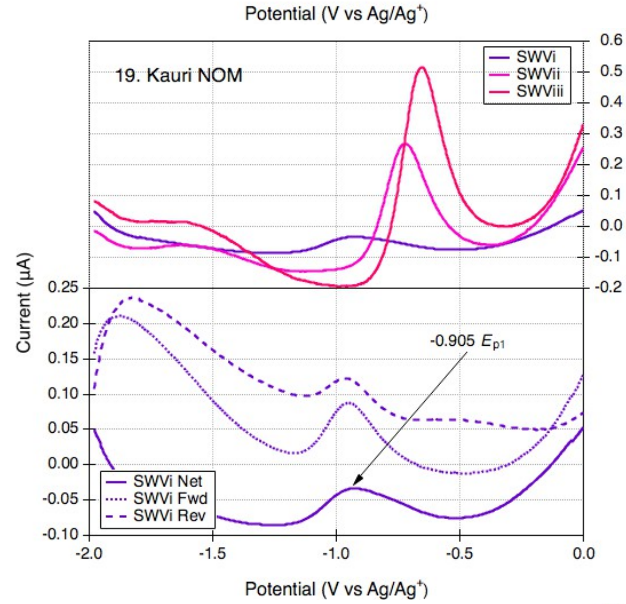

17. Great Dismal Swamp FA
SCVi
-0.808 E_{pa1}
-1.357 E_{pc1}
C1 C2 C3
Current (μA)
Potential (V vs Ag/Ag$^+$)

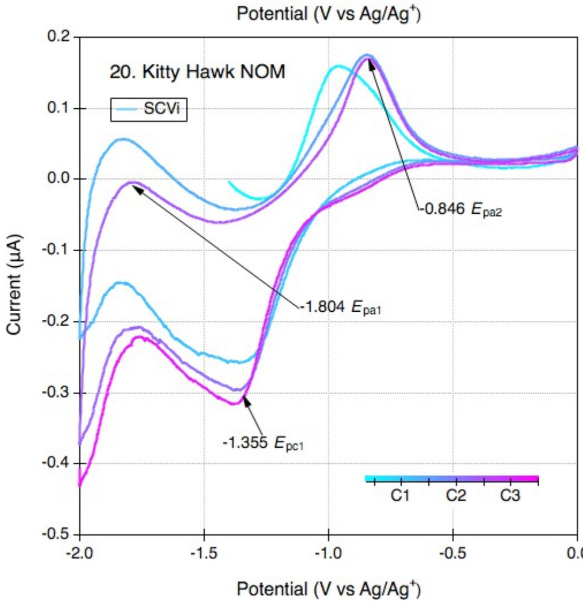

17. Great Dismal Swamp FA
SWVi
SWVii
SWViii
SWVi Net
SWVi Fwd
SWVi Rev
-0.754 E_{p1}
Current (μA)
Potential (V vs Ag/Ag$^+$)

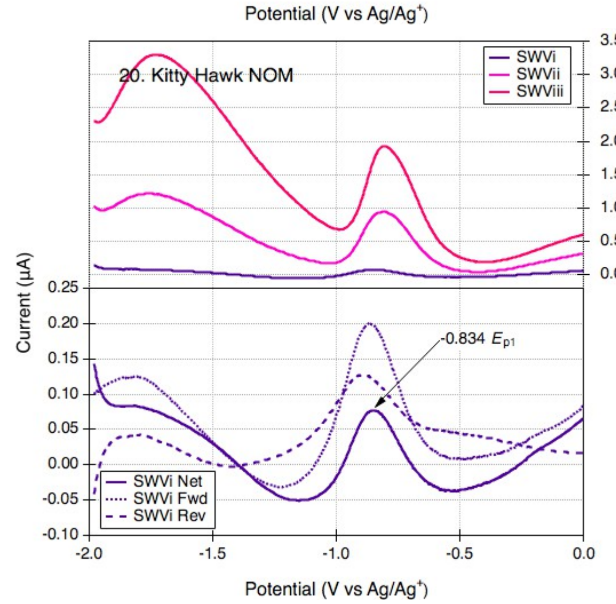

18. Inangahua River NOM
BG SCVi
SCVi
-0.805 E_{pa1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

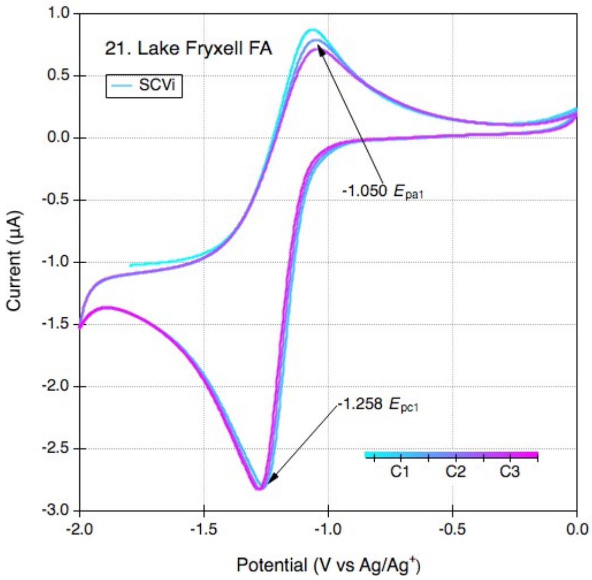

18. Inangahua River NOM
SWVi
SWVii
SWViii
-0.797 E_{p1}
SWVii Net
SWVii Fwd
SWVii Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

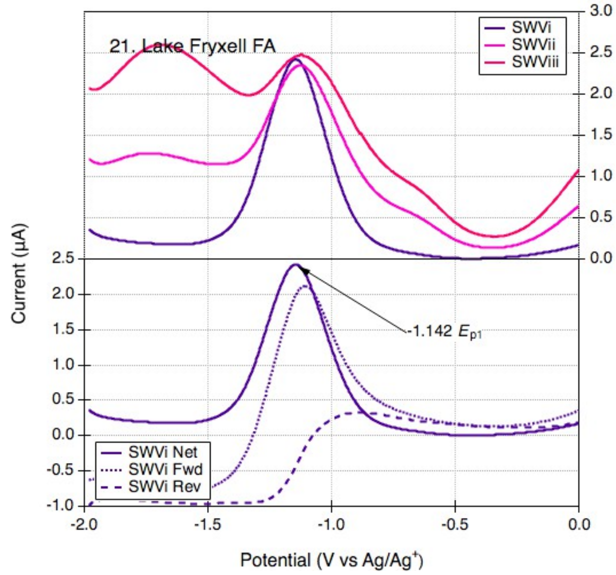

19. Kauri NOM
BG SCVi
SCVi
-1.002 E_{pa1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

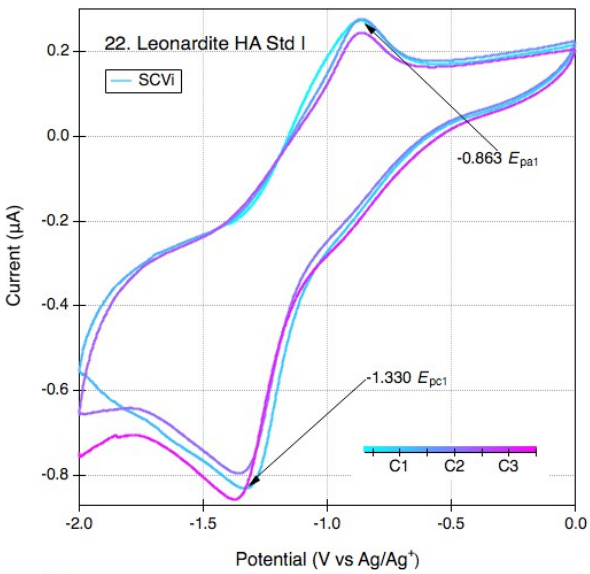

19. Kauri NOM
SWVi
SWVii
SWViii
-0.905 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

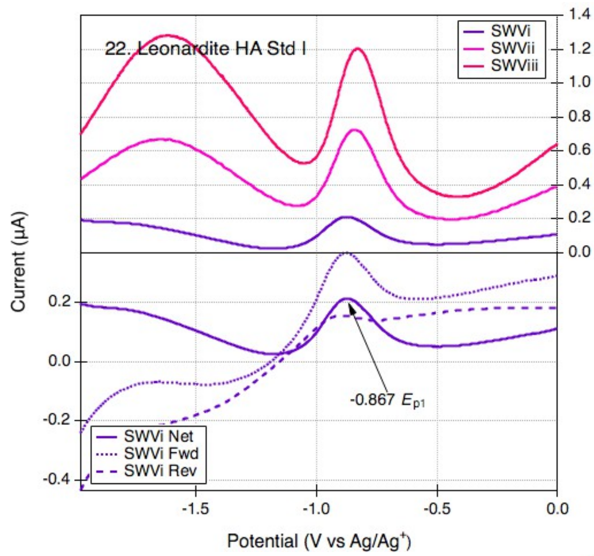

20. Kitty Hawk NOM
SCVi
-0.846 E_{pa2}
-1.804 E_{pa1}
-1.355 E_{pc1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

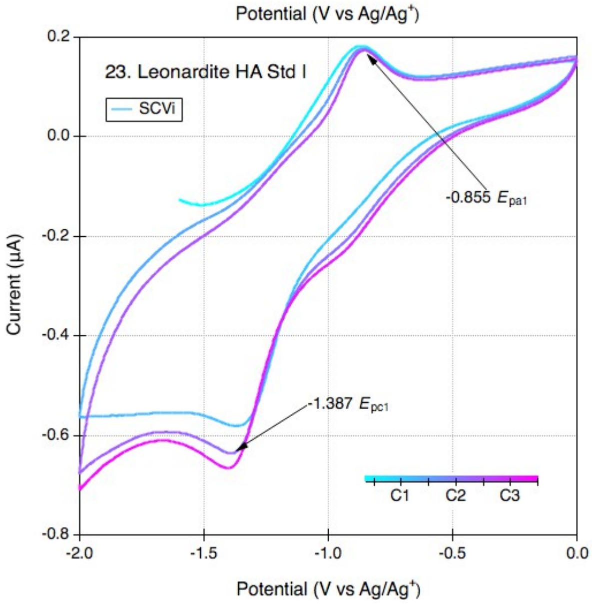

20. Kitty Hawk NOM
SWVi
SWVii
SWViii
-0.834 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

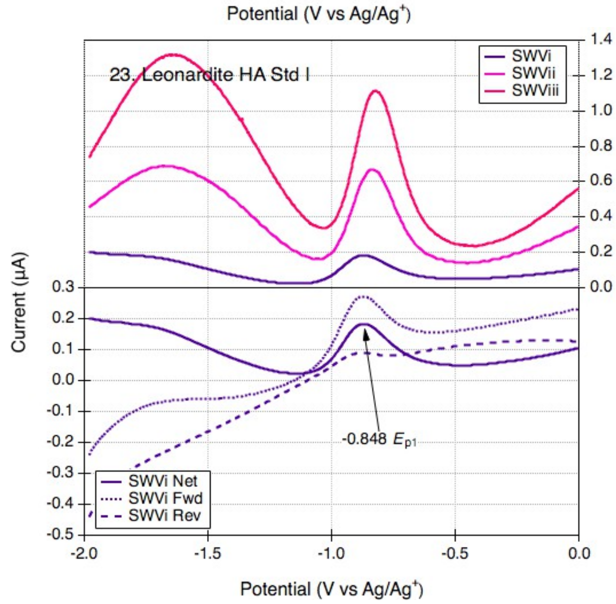

21. Lake Fryxell FA
SCVi
-1.050 E_{pa1}
-1.258 E_{pc1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

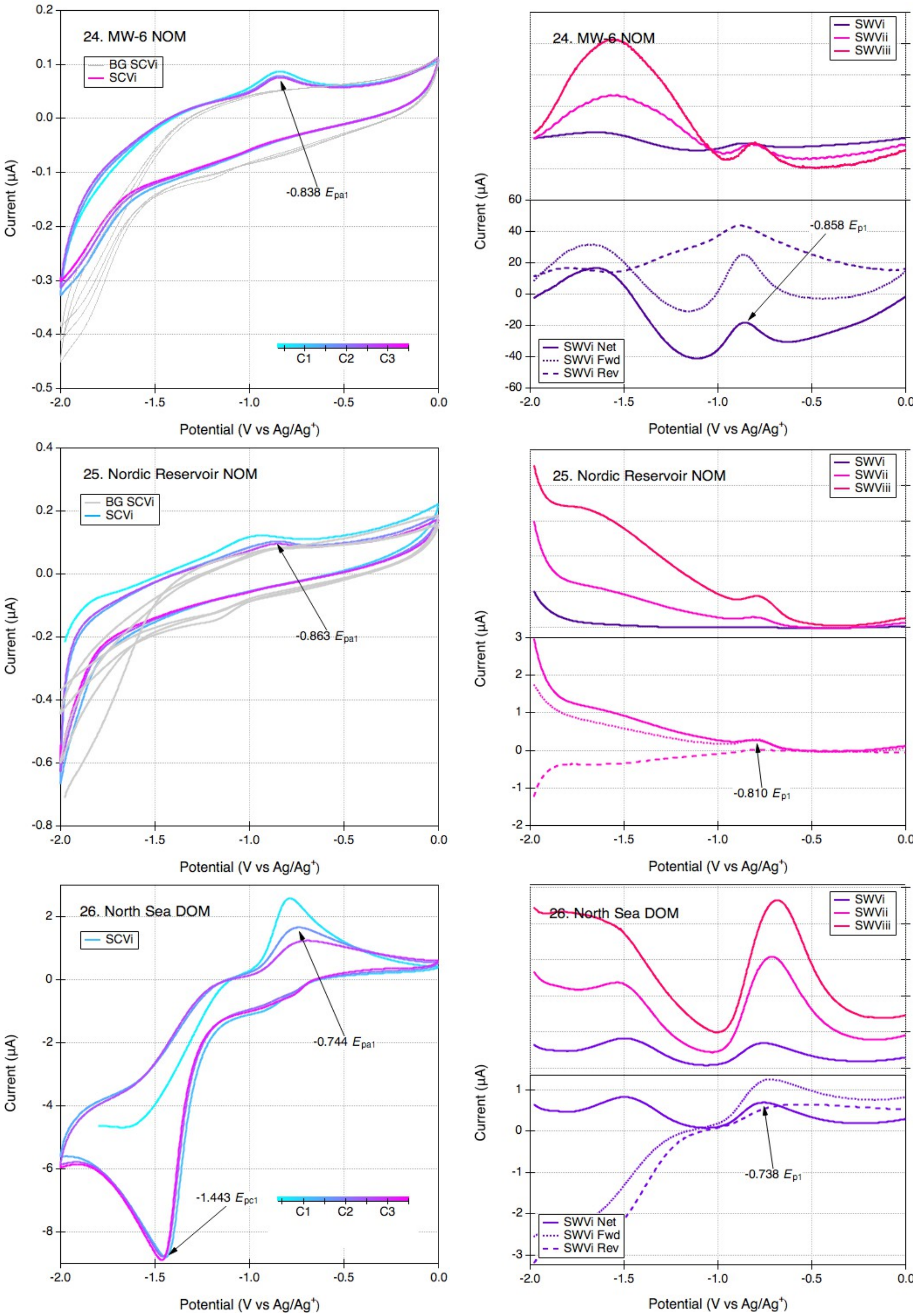

21. Lake Fryxell FA
SWVi
SWVii
SWViii
-1.142 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

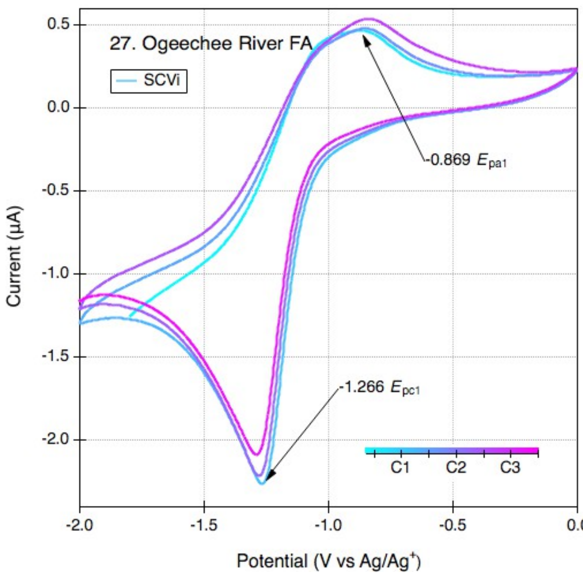

22. Leonardite HA Std I
SCVi
-0.863 E_{pa1}
-1.330 E_{pc1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

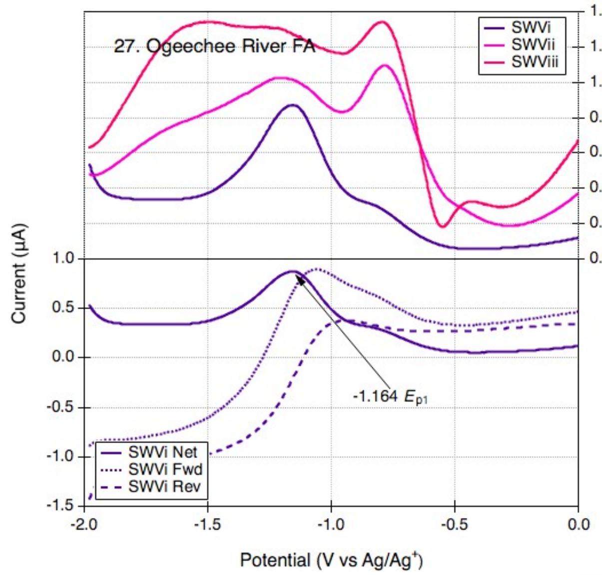

22. Leonardite HA Std I
SWVi
SWVii
SWViii
-0.867 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

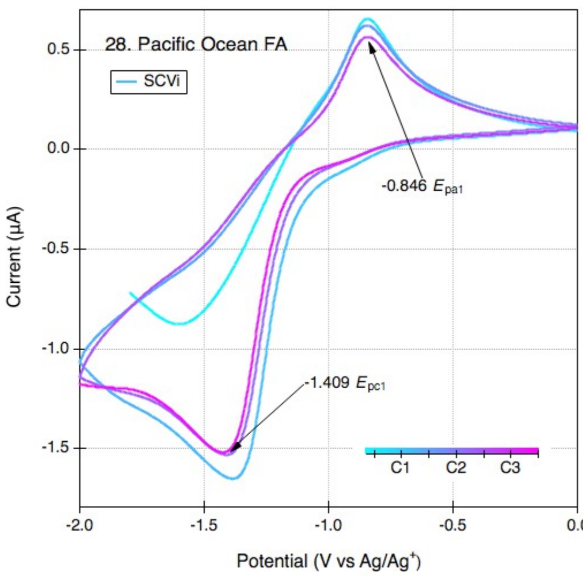

23. Leonardite HA Std I
SCVi
-0.855 E_{pa1}
-1.387 E_{pc1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

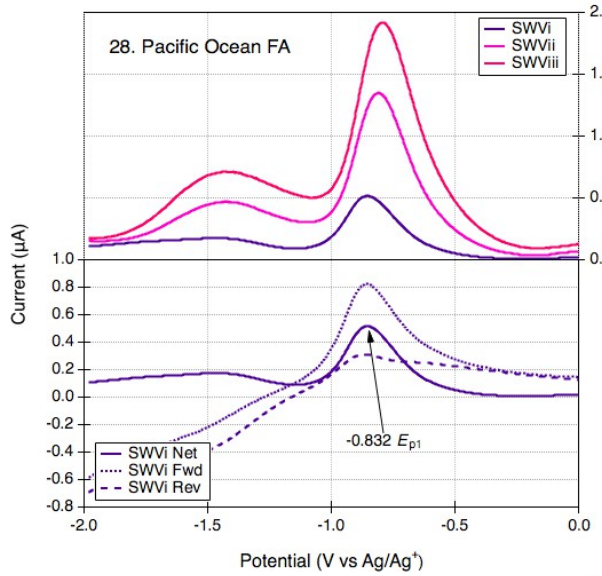

23. Leonardite HA Std I
SWVi
SWVii
SWViii
-0.848 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

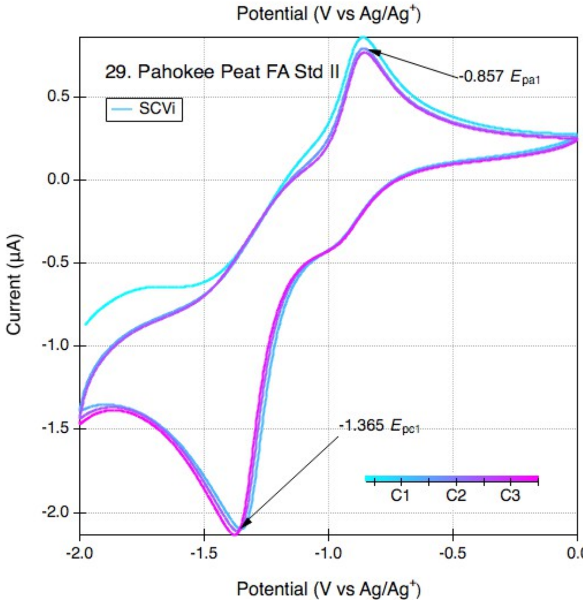

24. MW-6 NOM
BG SCVi
SCVi
-0.838 E_{pa1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag+)
SWVi
SWVii
SWViii
-0.858 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
25. Nordic Reservoir NOM
-0.863 E_{pa1}
-0.810 E_{p1}
26. North Sea DOM
-0.744 E_{pa1}
-1.443 E_{pc1}
-0.738 E_{p1}

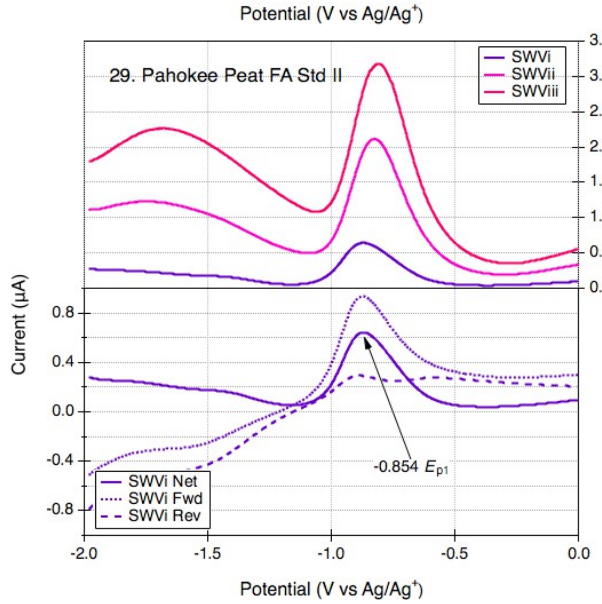

27. Ogeechee River FA
SCVi
-0.869 E_{pa1}
-1.266 E_{pc1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

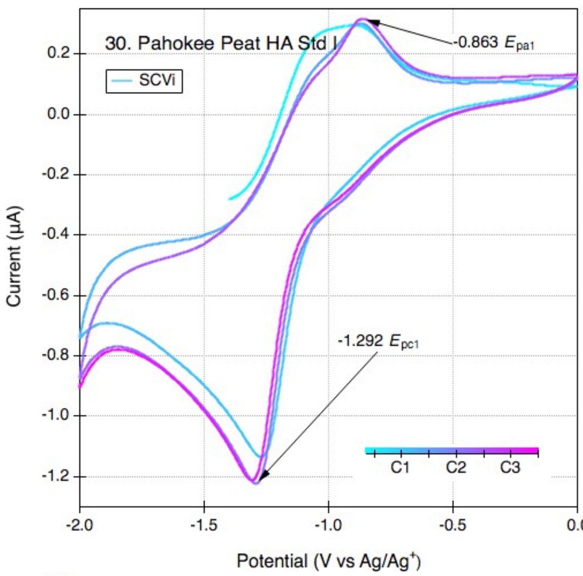

27. Ogeechee River FA
SWVi
SWVii
SWViii
SWVi Net
SWVi Fwd
SWVi Rev
-1.164 E_{p1}
Current (µA)
Potential (V vs Ag/Ag$^+$)

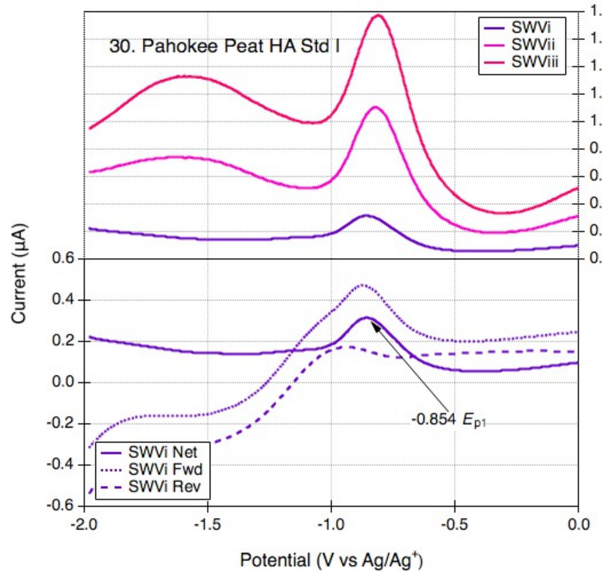

28. Pacific Ocean FA
SCVi
-0.846 E_{pa1}
-1.409 E_{pc1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

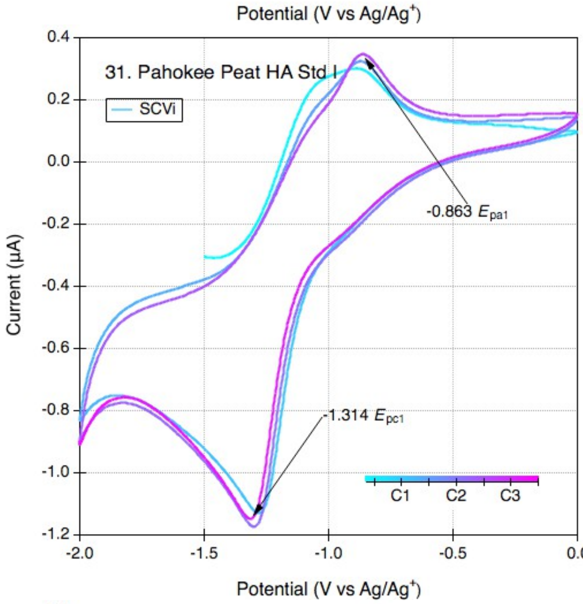

28. Pacific Ocean FA
SWVi
SWVii
SWViii
SWVi Net
SWVi Fwd
SWVi Rev
-0.832 E_{p1}
Current (µA)
Potential (V vs Ag/Ag$^+$)

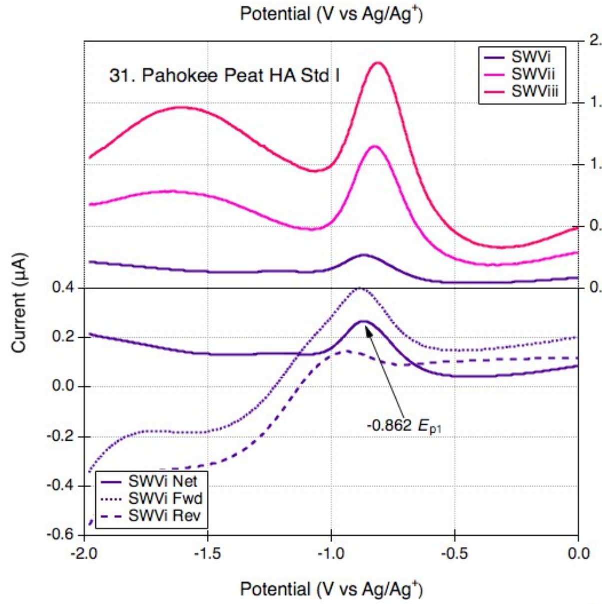

29. Pahokee Peat FA Std II
SCVi
-0.857 E_{pa1}
-1.365 E_{pc1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

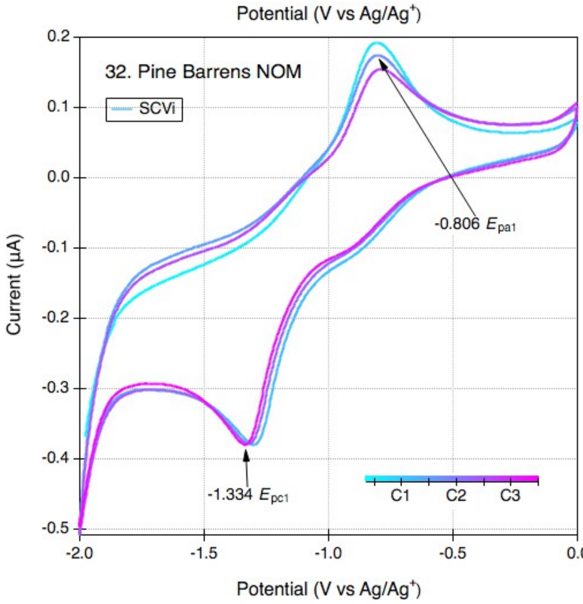

29. Pahokee Peat FA Std II
SWVi
SWVii
SWViii
SWVi Net
SWVi Fwd
SWVi Rev
-0.854 E_{p1}
Current (µA)
Potential (V vs Ag/Ag$^+$)

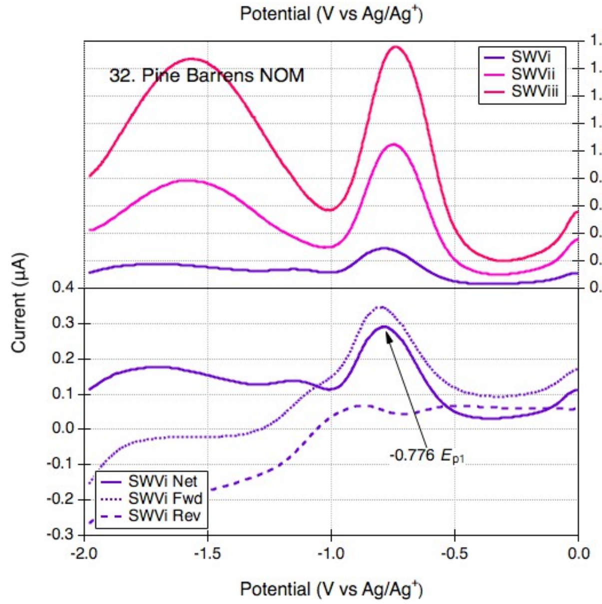

30. Pahokee Peat HA Std I
SCVi
-0.863 E_{pa1}
-1.292 E_{pc1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

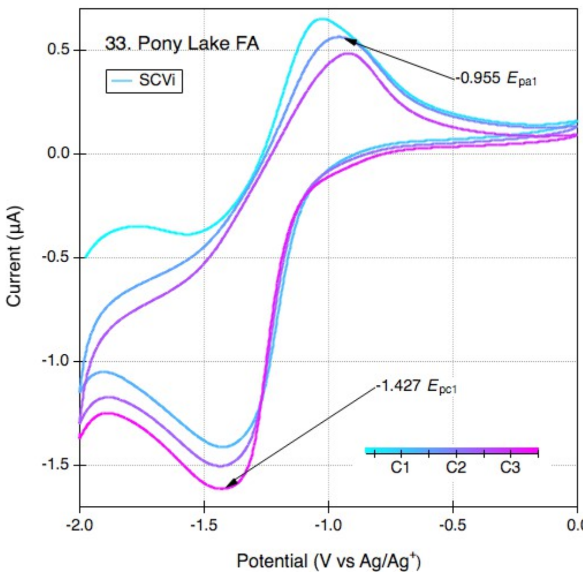

30. Pahokee Peat HA Std I
SWVi
SWVii
SWViii
-0.854 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)


31. Pahokee Peat HA Std I
SCVi
-0.863 E_{pa1}
-1.314 E_{pc1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

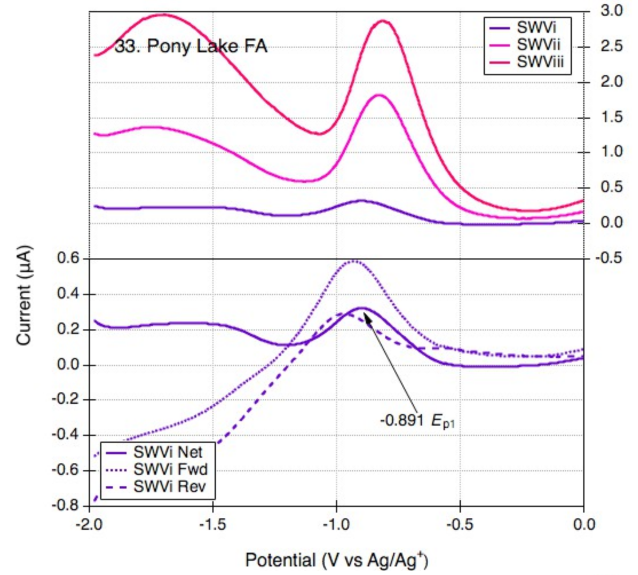

31. Pahokee Peat HA Std I
SWVi
SWVii
SWViii
-0.862 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)


32. Pine Barrens NOM
SCVi
-0.806 E_{pa1}
-1.334 E_{pc1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

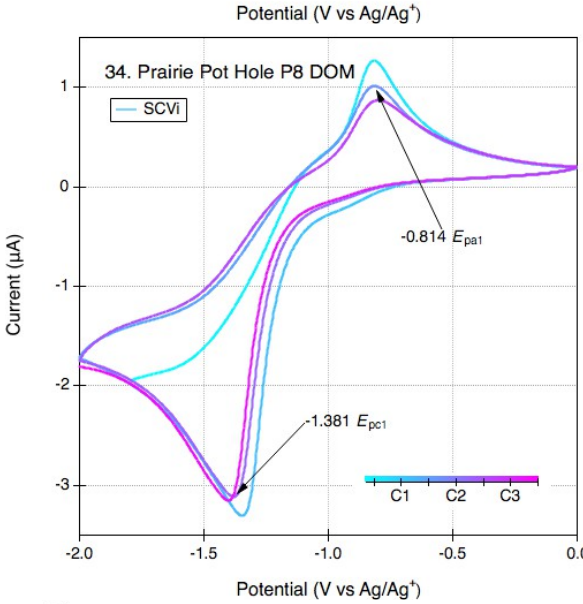

32. Pine Barrens NOM
SWVi
SWVii
SWViii
-0.776 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)



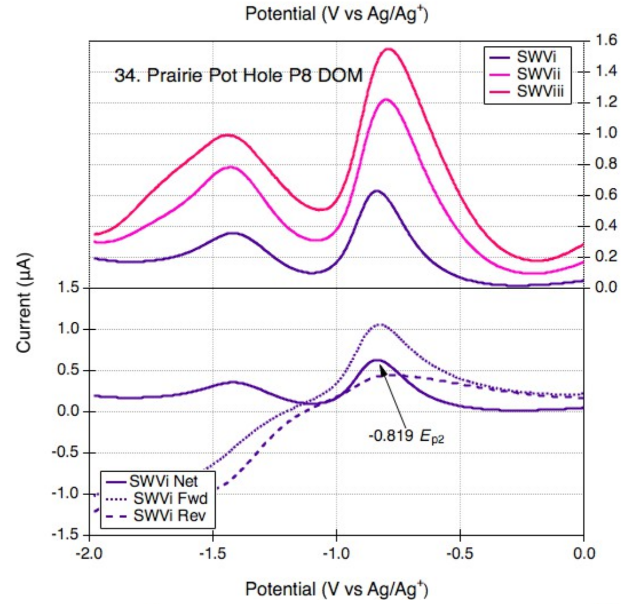
33. Pony Lake FA
SCVi
-0.955 E_{pa1}
-1.427 E_{pc1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)



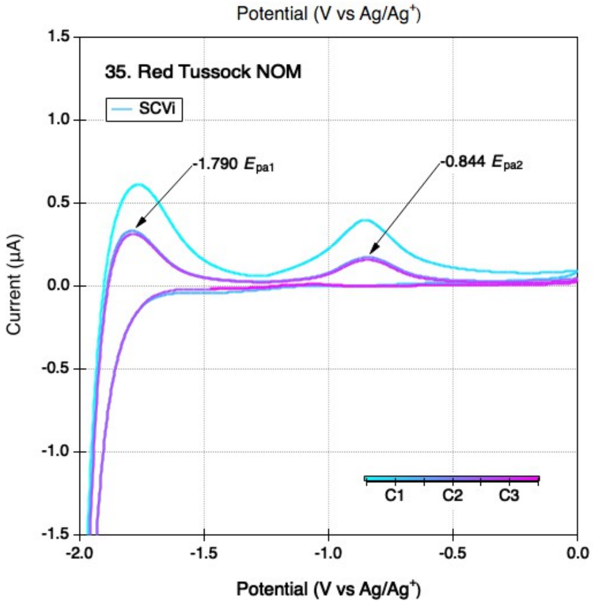
33. Pony Lake FA
SWVi
SWVii
SWViii
SWVi Net
SWVi Fwd
SWVi Rev
-0.891 E_{p1}
Current (µA)
Potential (V vs Ag/Ag$^+$)



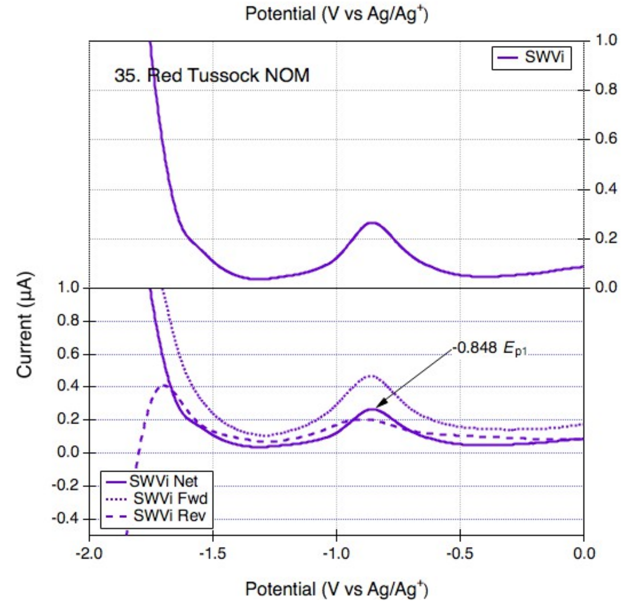
34. Prairie Pot Hole P8 DOM
SCVi
-0.814 E_{pa1}
-1.381 E_{pc1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)



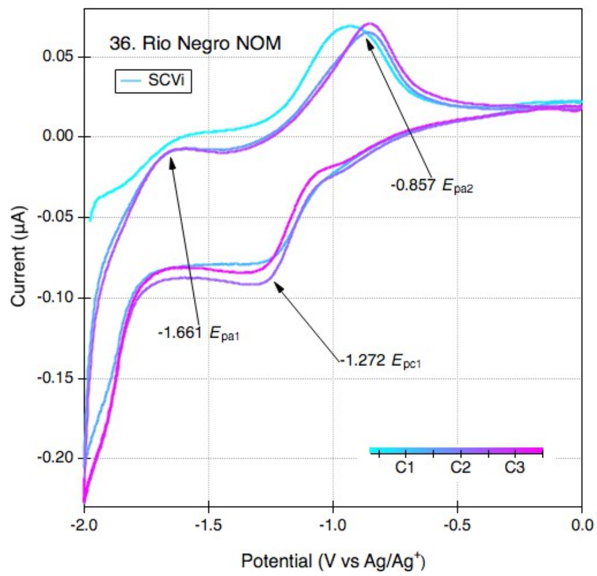
34. Prairie Pot Hole P8 DOM
SWVi
SWVii
SWViii
SWVi Net
SWVi Fwd
SWVi Rev
-0.819 E_{p2}
Current (µA)
Potential (V vs Ag/Ag$^+$)

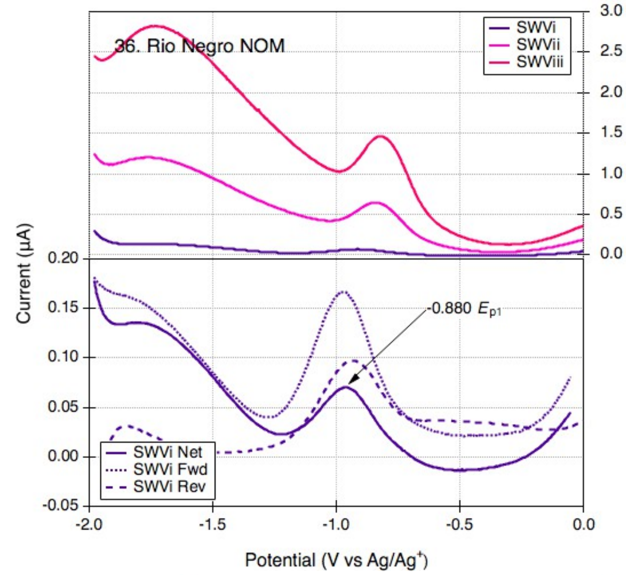


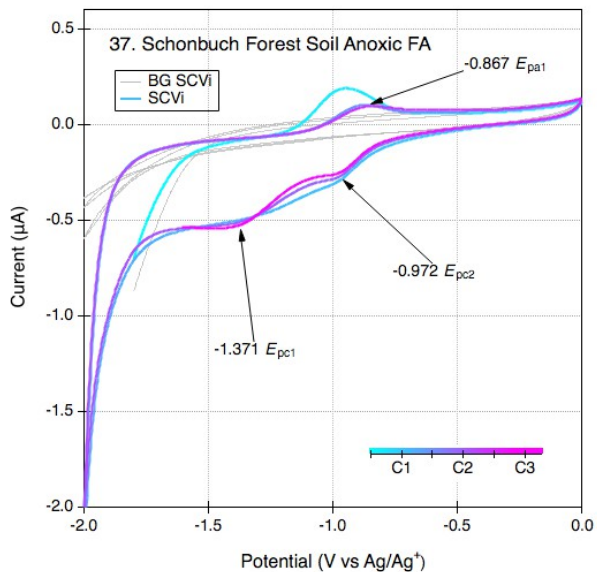
35. Red Tussock NOM
SCVi
-1.790 E_{pa1}
-0.844 E_{pa2}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

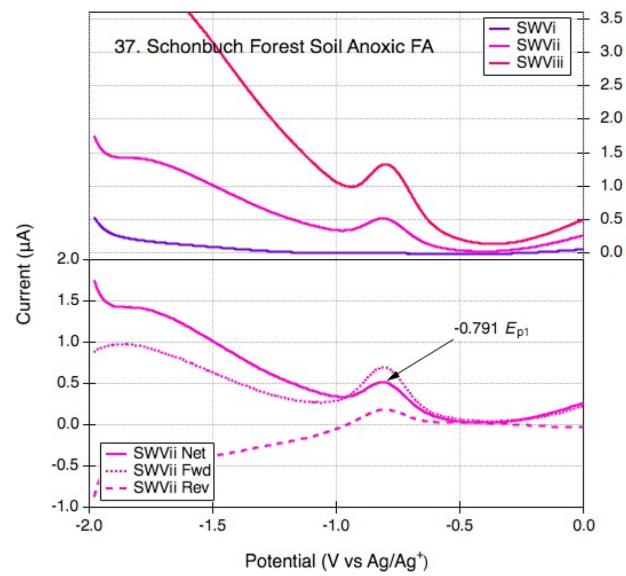


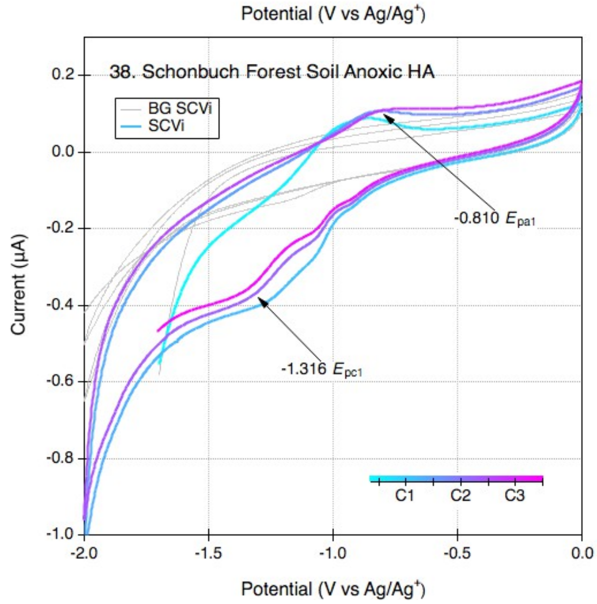
35. Red Tussock NOM
SWVi
SWVi Net
SWVi Fwd
SWVi Rev
-0.848 E_{p1}
Current (µA)
Potential (V vs Ag/Ag$^+$)

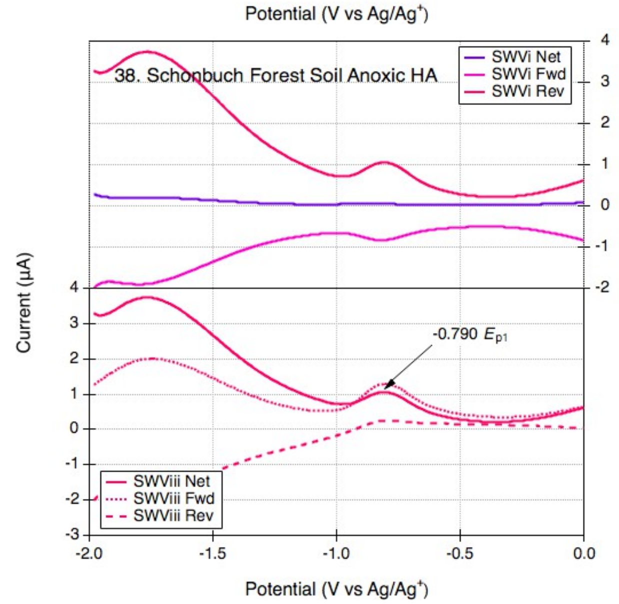

36. Rio Negro NOM
SCVi
-0.857 E_{pa2}
-1.661 E_{pa1}
-1.272 E_{pc1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

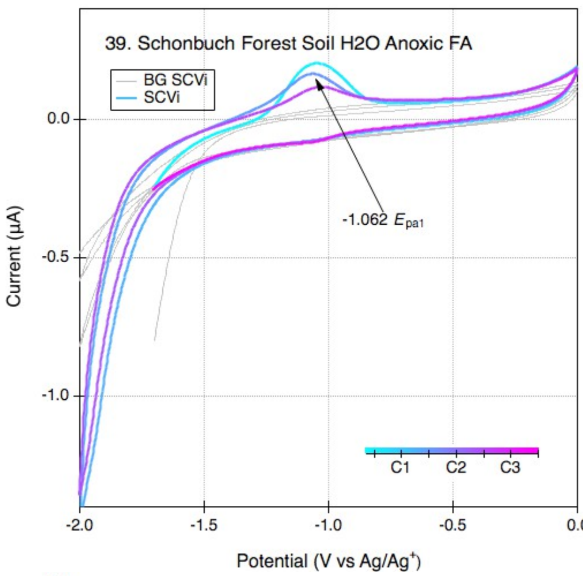

36. Rio Negro NOM
SWVi
SWVii
SWViii
-0.880 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

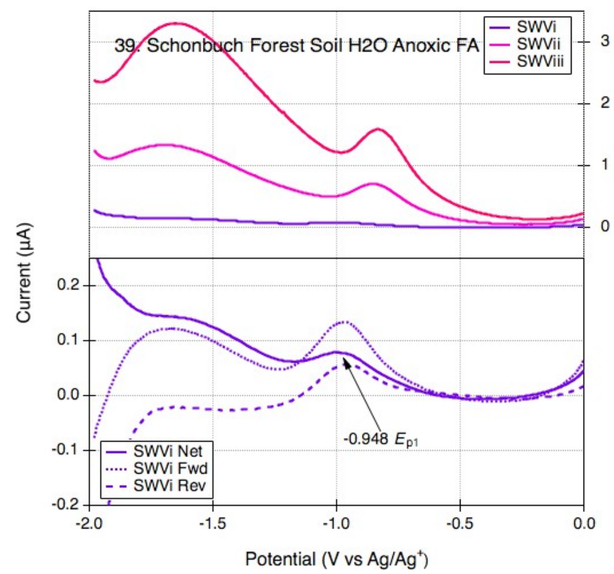

37. Schonbuch Forest Soil Anoxic FA
BG SCVi
SCVi
-0.867 E_{pa1}
-0.972 E_{pc2}
-1.371 E_{pc1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

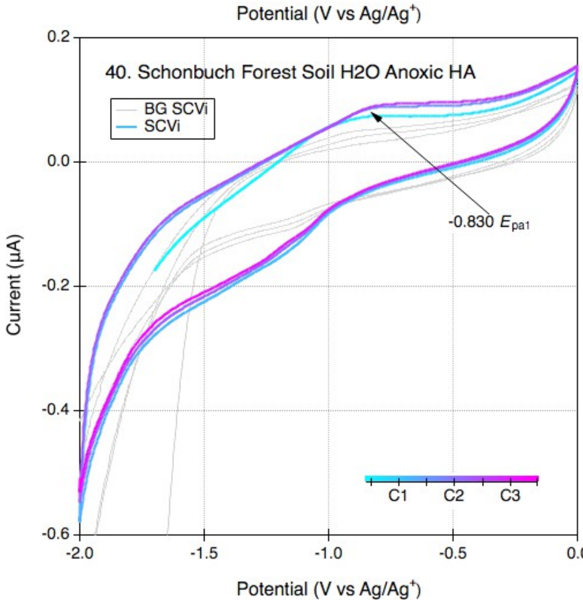

37. Schonbuch Forest Soil Anoxic FA
SWVi
SWVii
SWViii
-0.791 E_{p1}
SWVii Net
SWVii Fwd
SWVii Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

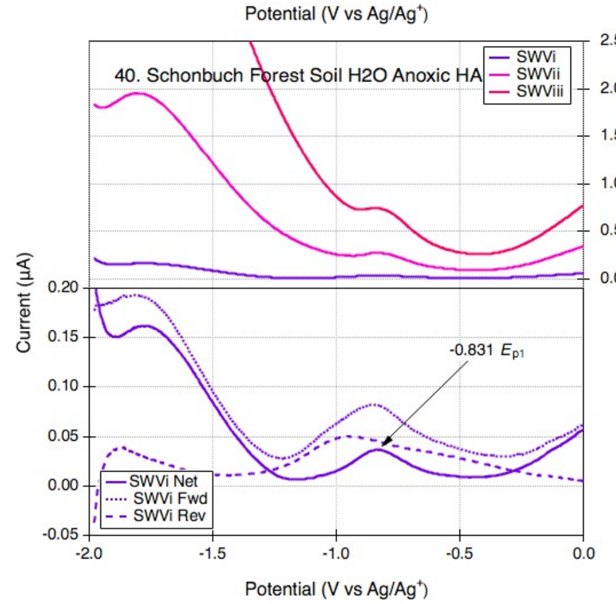

38. Schonbuch Forest Soil Anoxic HA
BG SCVi
SCVi
-0.810 E_{pa1}
-1.316 E_{pc1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

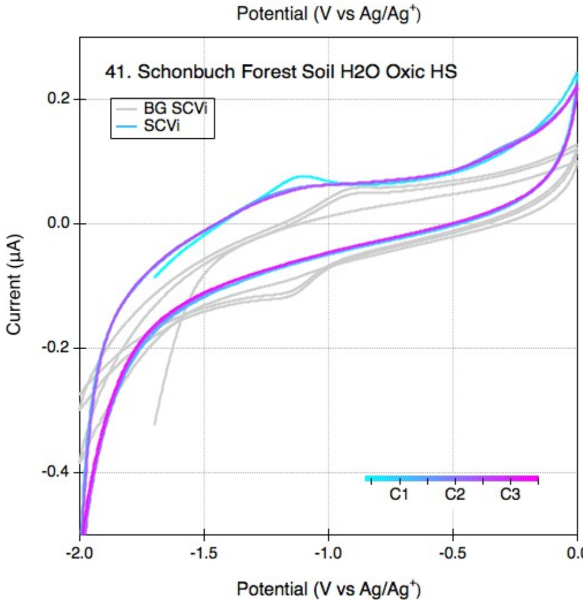

38. Schonbuch Forest Soil Anoxic HA
SWVi Net
SWVi Fwd
SWVi Rev
-0.790 E_{p1}
SWViii Net
SWViii Fwd
SWViii Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

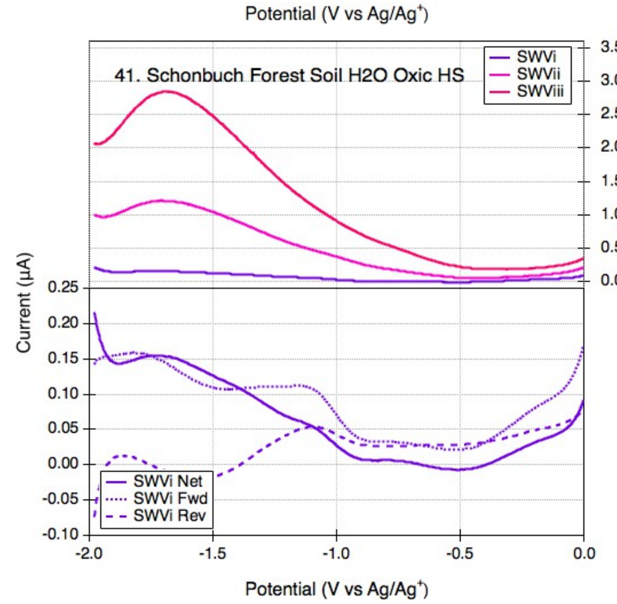

39. Schonbuch Forest Soil H2O Anoxic FA
BG SCVi
SCVi
-1.062 E_{pa1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

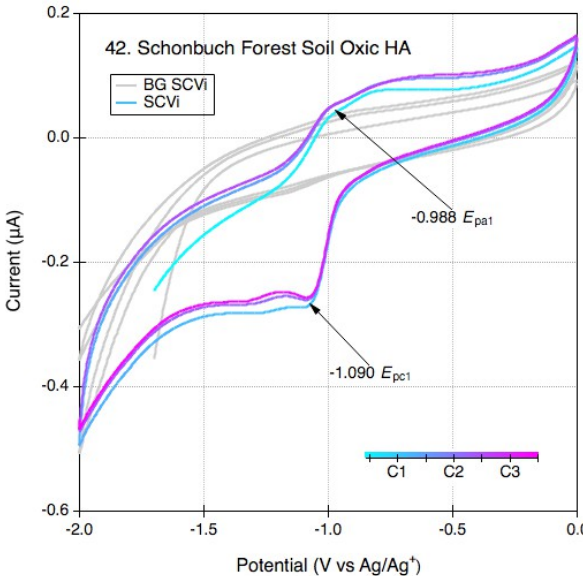

39. Schonbuch Forest Soil H2O Anoxic FA
SWVi
SWVii
SWViii
-0.948 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

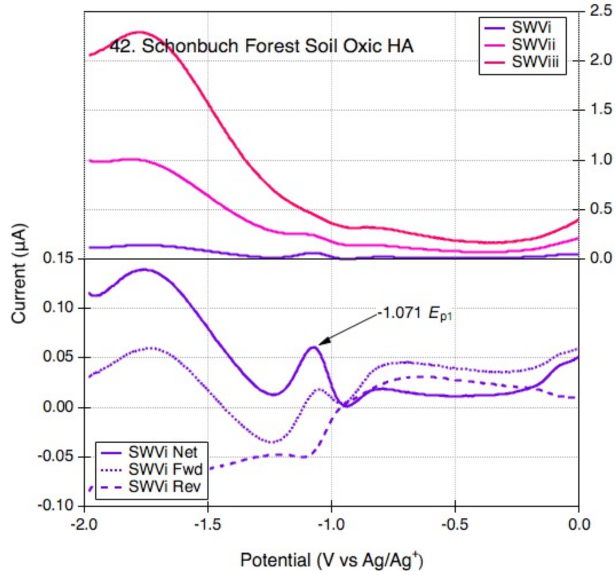

40. Schonbuch Forest Soil H2O Anoxic HA
BG SCVi
SCVi
-0.830 E_{pa1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

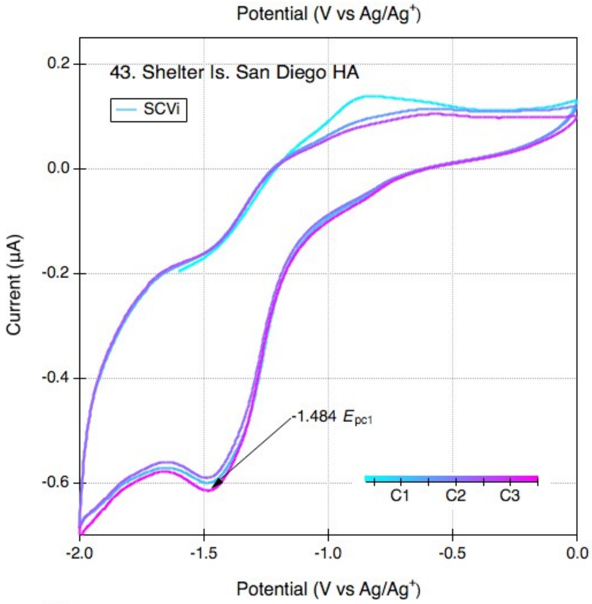

40. Schonbuch Forest Soil H2O Anoxic HA
SWVi
SWVii
SWViii
-0.831 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

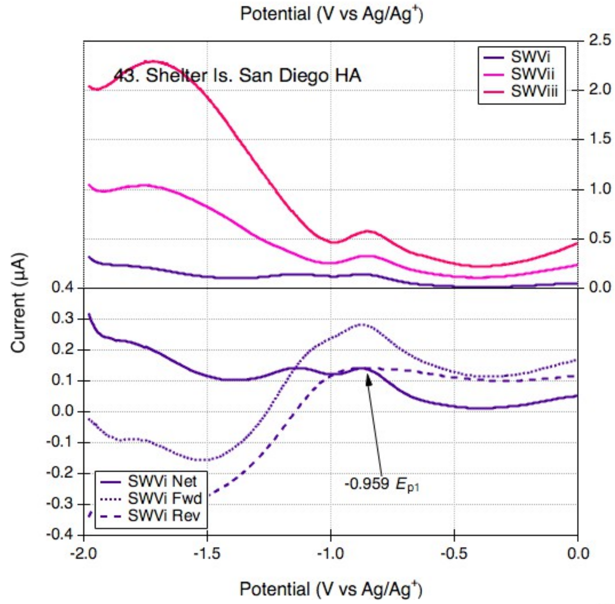

41. Schonbuch Forest Soil H2O Oxic HS
BG SCVi
SCVi
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

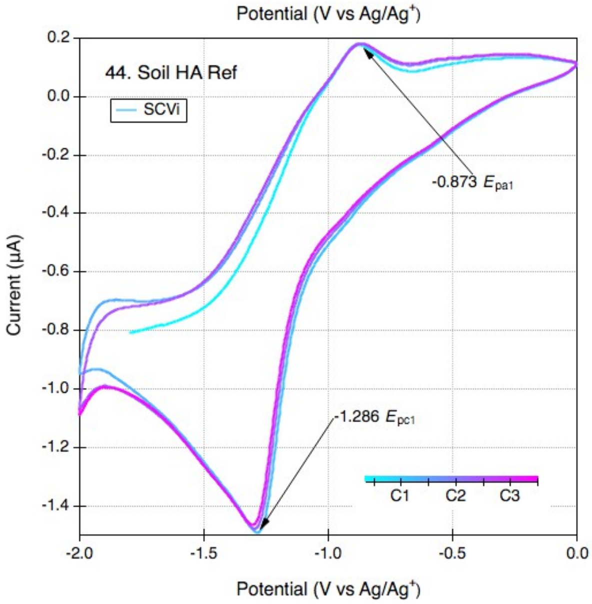

41. Schonbuch Forest Soil H2O Oxic HS
SWVi
SWVii
SWViii
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

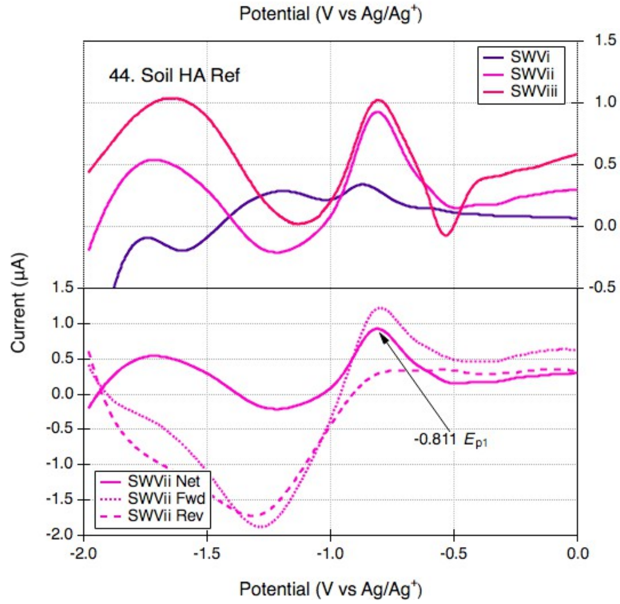

42. Schonbuch Forest Soil Oxic HA
BG SCVi
SCVi
-0.988 E_{pa1}
-1.090 E_{pc1}
C1
C2
C3
Current (μA)
Potential (V vs Ag/Ag$^+$)

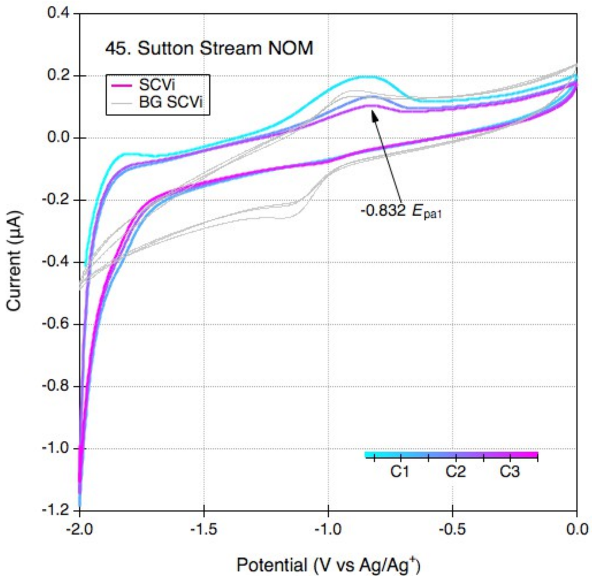

42. Schonbuch Forest Soil Oxic HA
SWVi
SWVii
SWViii
-1.071 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (μA)
Potential (V vs Ag/Ag$^+$)

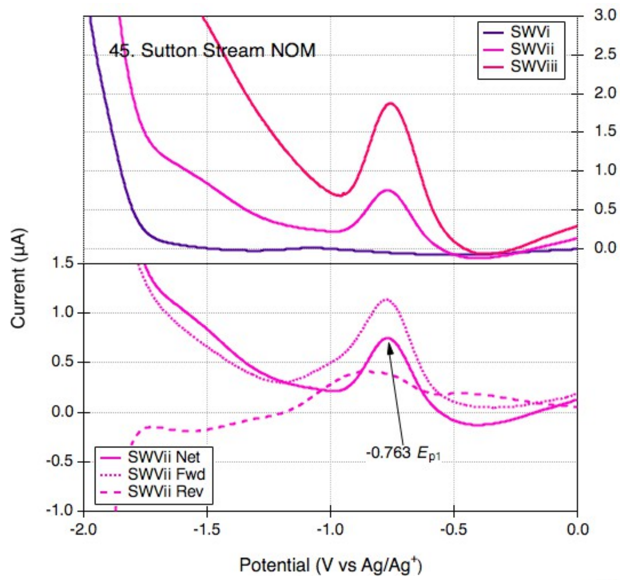

43. Shelter Is. San Diego HA
SCVi
-1.484 E_{pc1}
C1
C2
C3
Current (μA)
Potential (V vs Ag/Ag$^+$)

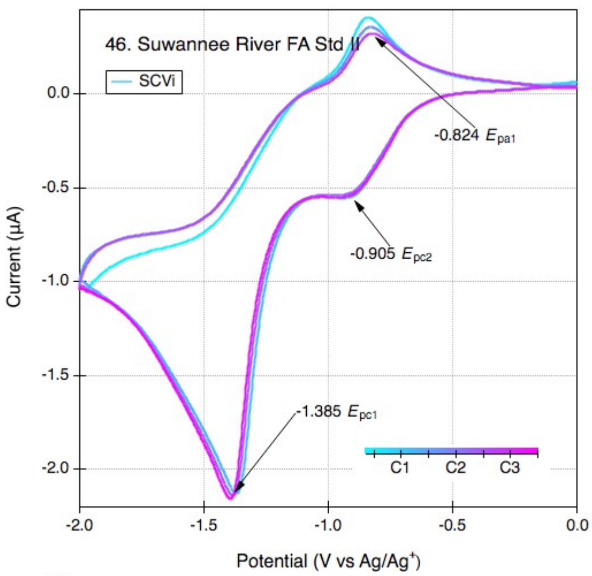

43. Shelter Is. San Diego HA
SWVi
SWVii
SWViii
-0.959 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (μA)
Potential (V vs Ag/Ag$^+$)

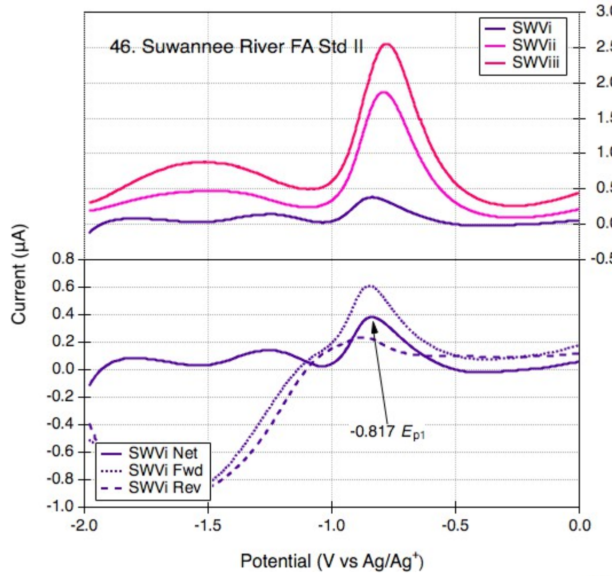

44. Soil HA Ref
SCVi
-0.873 E_{pa1}
-1.286 E_{pc1}
C1
C2
C3
Current (μA)
Potential (V vs Ag/Ag$^+$)

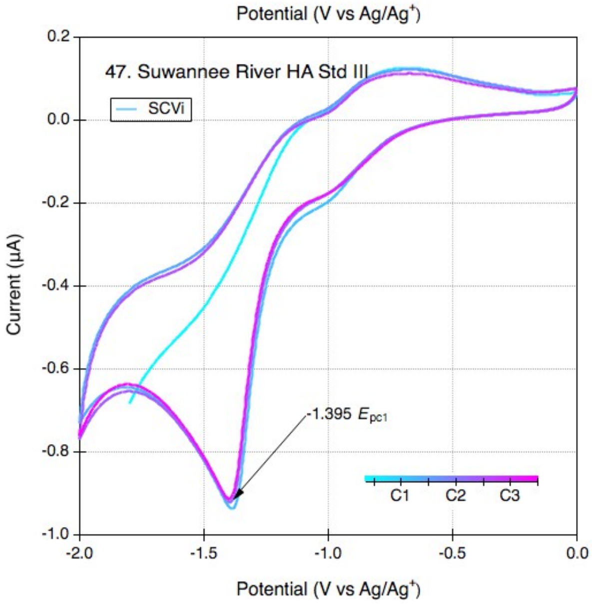

44. Soil HA Ref
SWVi
SWVii
SWViii
-0.811 E_{p1}
SWVii Net
SWVii Fwd
SWVii Rev
Current (μA)
Potential (V vs Ag/Ag$^+$)

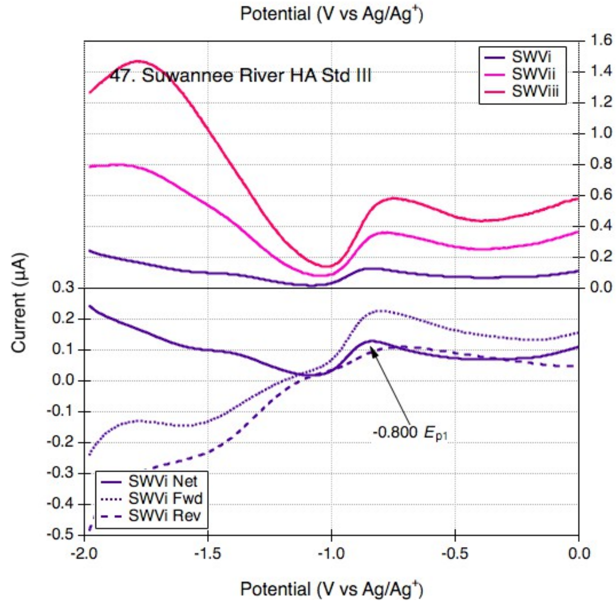

45. Sutton Stream NOM
SCVi
BG SCVi
-0.832 E_{pa1}
C1
C2
C3
Current (μA)
Potential (V vs Ag/Ag$^+$)

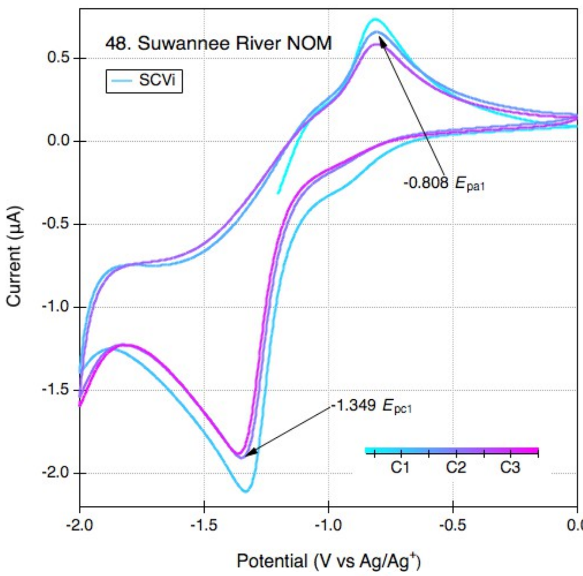

45. Sutton Stream NOM
SWVi
SWVii
SWViii
SWVii Net
SWVii Fwd
SWVii Rev
-0.763 E_{p1}
Current (μA)
Potential (V vs Ag/Ag$^+$)

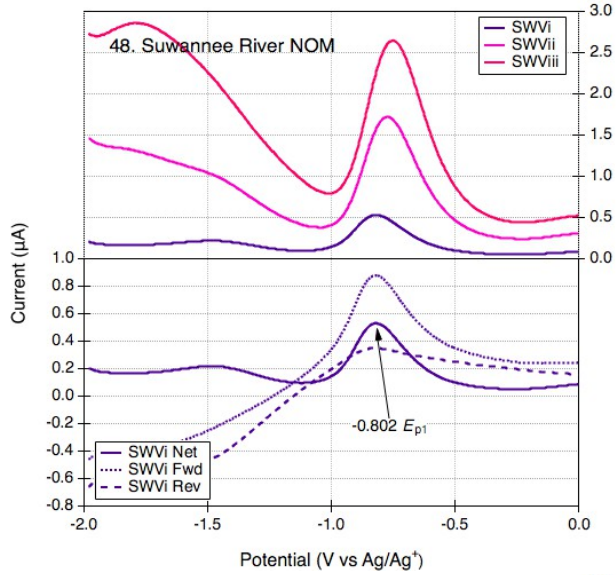

46. Suwannee River FA Std II
SCVi
-0.824 E_{pa1}
-0.905 E_{pc2}
-1.385 E_{pc1}
C1
C2
C3
Current (μA)
Potential (V vs Ag/Ag$^+$)

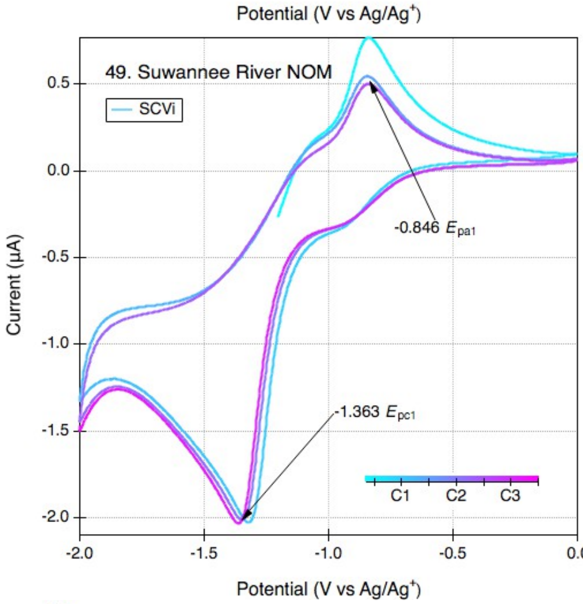

46. Suwannee River FA Std II
SWVi
SWVii
SWViii
SWVi Net
SWVi Fwd
SWVi Rev
-0.817 E_{p1}
Current (μA)
Potential (V vs Ag/Ag$^+$)

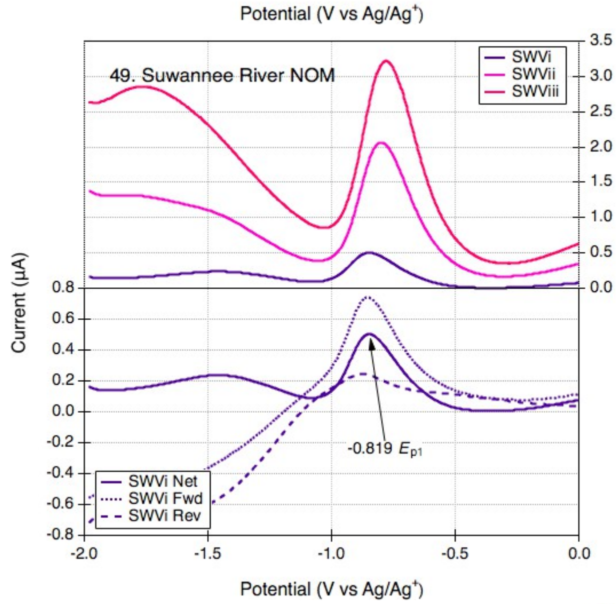

47. Suwannee River HA Std III
SCVi
-1.395 E_{pc1}
C1
C2
C3
Current (μA)
Potential (V vs Ag/Ag$^+$)

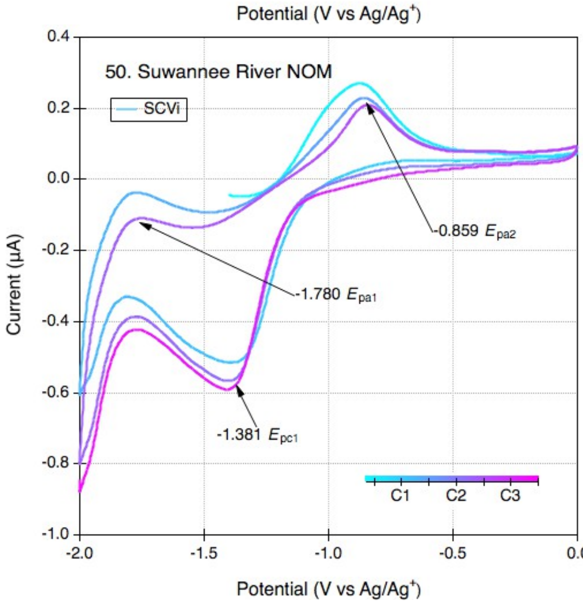

47. Suwannee River HA Std III
SWVi
SWVii
SWViii
SWVi Net
SWVi Fwd
SWVi Rev
-0.800 E_{p1}
Current (μA)
Potential (V vs Ag/Ag$^+$)

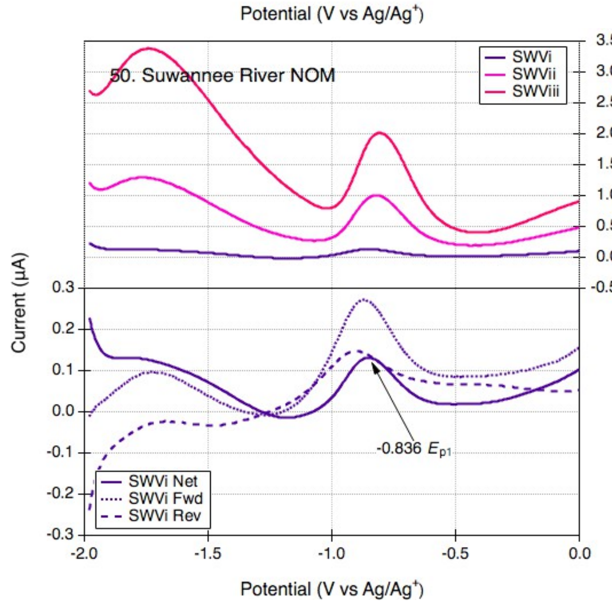

48. Suwannee River NOM
SCVi
-0.808 E_{pa1}
-1.349 E_{pc1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)

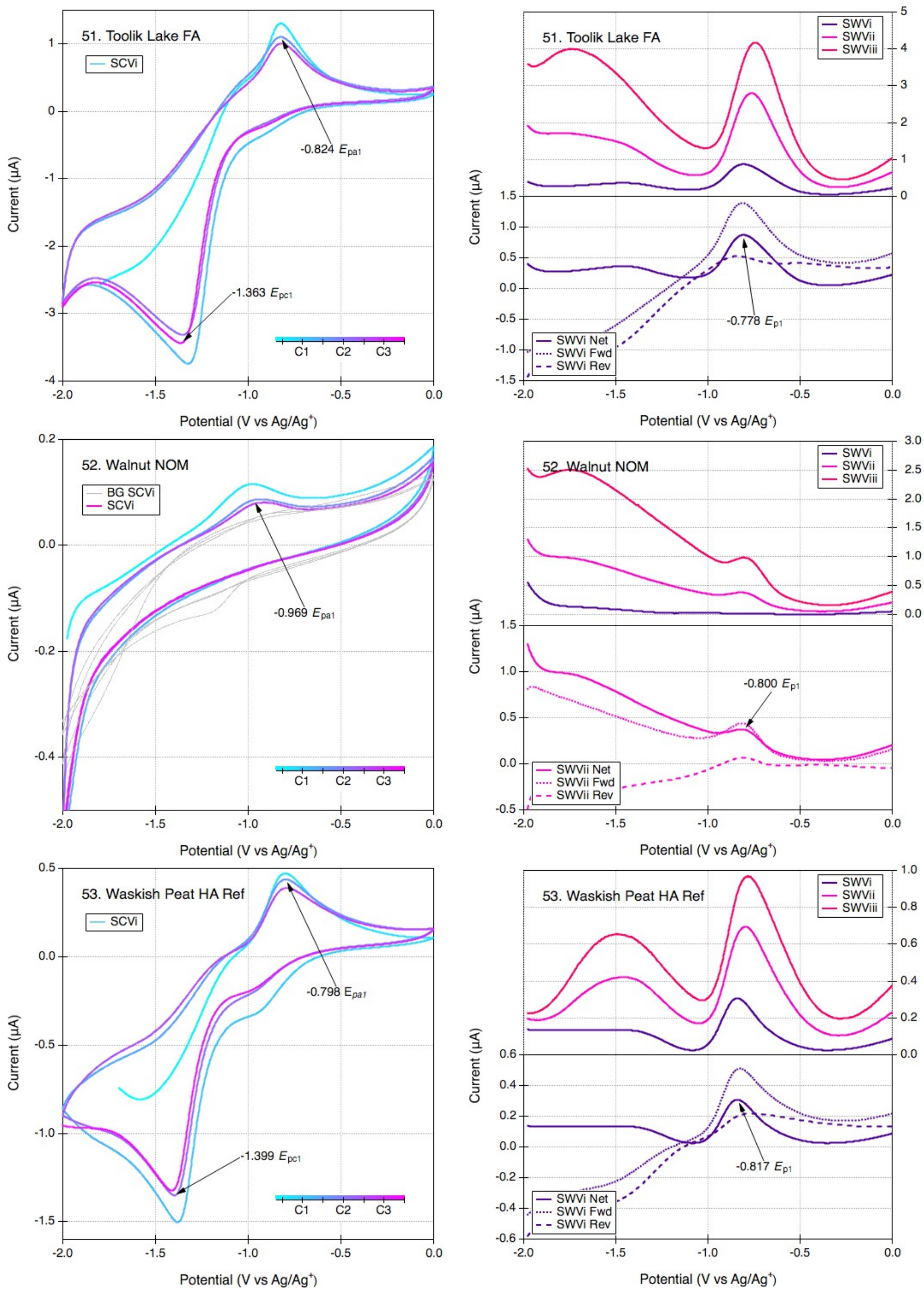

48. Suwannee River NOM
SWVi
SWVii
SWViii
SWVi Net
SWVi Fwd
SWVi Rev
-0.802 E_{p1}
Current (µA)
Potential (V vs Ag/Ag$^+$)

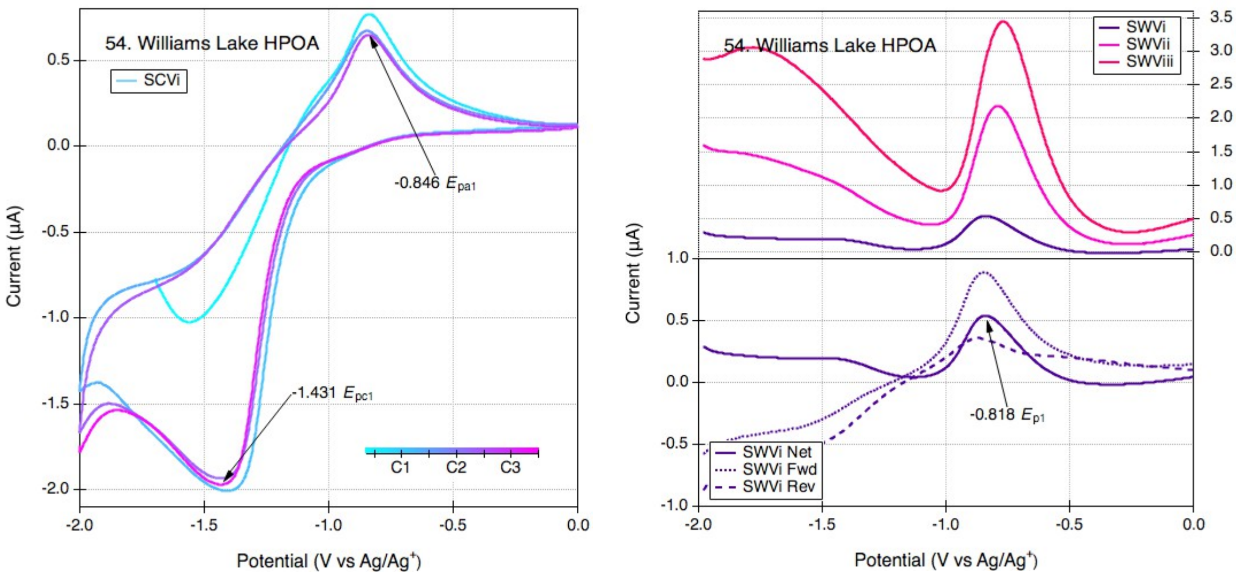

49. Suwannee River NOM
SCVi
-0.846 E_{pa1}
-1.363 E_{pc1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)


49. Suwannee River NOM
SWVi
SWVii
SWViii
SWVi Net
SWVi Fwd
SWVi Rev
-0.819 E_{p1}
Current (µA)
Potential (V vs Ag/Ag$^+$)


50. Suwannee River NOM
SCVi
-0.859 E_{pa2}
-1.780 E_{pa1}
-1.381 E_{pc1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)


50. Suwannee River NOM
SWVi
SWVii
SWViii
SWVi Net
SWVi Fwd
SWVi Rev
-0.836 E_{p1}
Current (µA)
Potential (V vs Ag/Ag$^+$)


51. Toolik Lake FA
SCVi
-0.824 E_{pa1}
-1.363 E_{pc1}
C1 C2 C3
Current (µA)
Potential (V vs Ag/Ag+)
SWVi
SWVii
SWViii
-0.778 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
52. Walnut NOM
BG SCVi
SCVi
-0.969 E_{pa1}
SWVii Net
SWVii Fwd
SWVii Rev
-0.800 E_{p1}
53. Waskish Peat HA Ref
-0.798 E_{pa1}
-1.399 E_{pc1}
-0.817 E_{p1}


54. Williams Lake HPOA
SCVi
-0.846 E_{pa1}
-1.431 E_{pc1}
C1
C2
C3
Current (µA)
Potential (V vs Ag/Ag$^+$)
54. Williams Lake HPOA
SWVi
SWVii
SWViii
-0.818 E_{p1}
SWVi Net
SWVi Fwd
SWVi Rev
Current (µA)
Potential (V vs Ag/Ag$^+$)

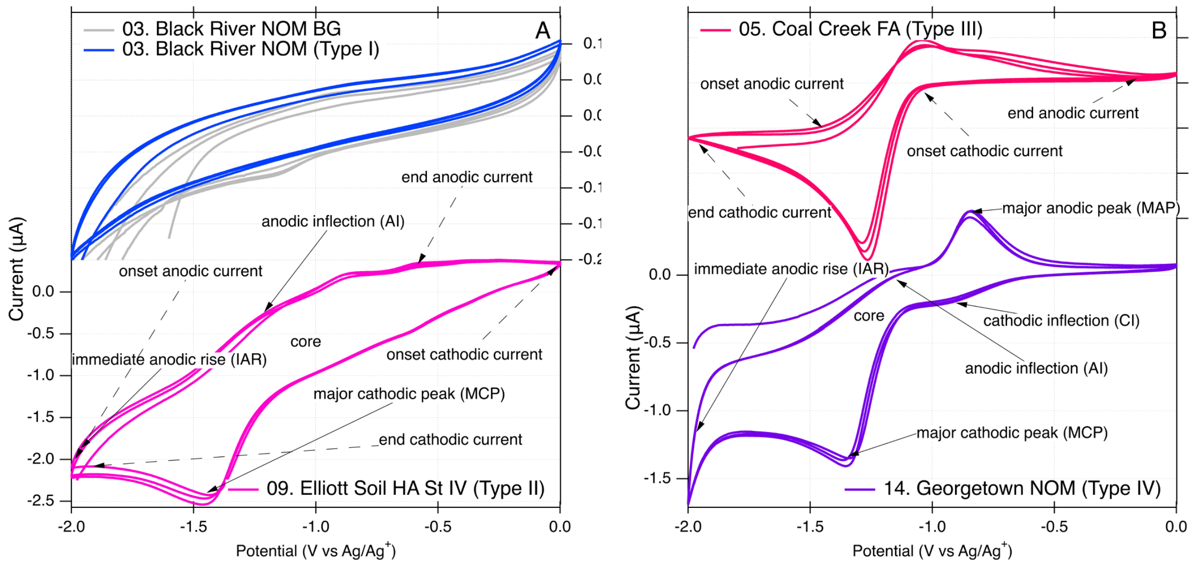


Figure S5. Four types of SCV responses and definition of current breadth. **(A)** type I, mostly flat; type II, mostly core; **(B)** type III, model compound like; type IV, typical NOM response. Teal annotations signify onset and end of current responses (current breadth) as shown in **Figure 6**. Green annotations signify the six types of characteristics of all the NOMs as tabulated in **Table S6**. Conditions: 1.0 mg/mL (except for HS, which did not fully dissociate in DMSO) of HS in 0.1 M TBAFP in DMSO, 1.6 mm Pt working electrode, Pt coil counter electrode, and a Ag/Ag$^+$ reference electrode filled with 0.1 M TBAFP and 0.005 M $AgNO_3$ in DMSO. Scan rate: SCV*i* 25 mV s^{-1}.

Table S6. Ranking of Characteristics for NOM SCVs.

No.	Name	*Cat*	*Type*	*Core*	IAR	*AI*	MAP	*CI*	*MCP*	*Sum*
1	Bamboo NOM	2	1	2	2	0	1	0	0	6
2	Bemidji FA	3	4	2	3	3	3	1	3	19
3	Black River NOM	1	1	2	1	0	0	0	0	4
4	Cabbage Tree NOM	2	1	1	2	2	1	0	0	7
5	Coal Creek FA	3	3	1	0	0	3	0	3	10
6	Coal Creek HA	5	3	1	0	0	1	1	3	9
7	Elliott Soil FA Std II	4	4	3	2	1	3	1	3	17
8	Elliott Soil HA Std I	6	2	3	3	1	2	1	3	15
9	Elliott Soil HA Std IV	6	2	3	3	1	1	1	2	13
10	Everglades 2BS HPOA	7	4	1	3	1	3	0	2	14
11	Everglades F1 HPOA	7	4	2	2	1	3	2	3	17
12	Everglades F1 TPIA	7	4	1	2	1	3	2	3	16
13	Everglades LOX8 HPOA	7	4	1	2	1	3	2	3	16
14	Georgetown NOM	1	4	1	2	1	3	2	3	16
15	Georgetown NOM CH	1	4	1	2	1	3	0	3	14
16	Georgetown NOM PP	1	4	2	2	1	3	3	3	18
17	Great Dismal Swamp FA	3	4	1	2	1	3	1	3	15
18	Inangahua River NOM	1	1	2	2	0	2	0	0	7
19	Kauri NOM	2	1	2	2	0	2	0	0	7
20	Kitty Hawk NOM	1	4	1	2	0	3	1	2	13
21	Lake Fryxell FA	3	3	1	1	0	3	0	3	11
22	Leonardite HA Std I	6	2	3	3	0	2	1	2	13
23	Leonardite HA Std I	6	2	3	3	0	2	1	2	13
24	MW-6 NOM	1	1	2	2	0	1	0	0	6
25	Nordic Reservoir NOM	1	1	1	2	0	1	0	0	5
26	North Sea DOM	1	4	1	2	2	2	1	3	15
27	Ogeechee River FA	3	3	2	2	0	2	0	3	12
28	Pacific Ocean FA	3	4	1	3	1	3	1	3	16
29	Pahokee Peat FA Std II	4	4	2	2	1	3	2	3	17
30	Pahokee Peat HA Std I	6	4	3	2	1	3	1	3	17
31	Pahokee Peat HA Std I	6	4	3	2	1	3	1	3	17
32	Pine Barrens NOM	2	4	3	2	1	3	2	3	18

No.	Name	*Cat*	*Type*	*Core*	IAR	*AI*	MAP	*CI*	*MCP*	*Sum*
33	Pony Lake FA	3	4	2	2	0	3	0	3	14
34	Prairie Pot Hole P8 DOM	1	4	1	2	1	3	0	3	14
35	Red Tussock NOM	2		1	3	0	2	0	0	6
36	Rio Negro NOM	1	4	2	3	0	3	1	2	15
37	Schönbuch Anoxic FA	4	1	2	2	0	1	2	1	9
38	Schönbuch Anoxic HA	6	1	2	2	0	1	1	1	8
39	Schönbuch H_2O Anoxic FA	4	1	1	2	0	2	0	0	6
40	Schönbuch H_2O Anoxic HA	6	1	2	2	0	1	0	1	7
41	Schönbuch H_2O Oxic HS	2	1	2	2	0	1	0	0	6
42	Schönbuch Oxic HA	6	1	2	2	0	1	0	2	8
43	Shelter Is. San Diego HA	5	2	2	3	1	1	1	2	12
44	Soil HA Ref	6	4	2	2	0	2	0	3	13
45	Sutton Stream NOM	1	1	1	2	0	1	0	0	5
46	Suwannee River FA Std II	3	4	2	1	2	3	3	3	18
47	Suwannee River HA Std III	5	4	2	2	2	2	2	3	17
48	Suwannee River NOM	1	4	1	2	1	3	1	3	15
49	Suwannee River NOM	1	4	2	2	1	3	2	3	17
50	Suwannee River NOM	1	4	1	2	0	3	0	3	13
51	Toolik Lake FA	3	4	1	2	1	3	1	3	15
52	Walnut NOM	2	1	2	2	0	1	0	0	6
53	Waskish Peat HA Ref	6	4	1	3	2	3	2	3	18
54	Williams Lake HPOA	7	4	1	3	1	3	0	3	15

NOM category, type, characteristics, and sum of type and characteristics. *Categories*: NOM/A (1), NOM/T (2), FA/A (3) FA/T (4), HA/A (5), HA/T (6), HPOA/TPIA (7), where A and T are aqueous and terrestrial respectively. *Types*: no response (1), mostly core (2), model like (3), typical NOM behavior (4). *Characteristics* within type; Core, immediate anodic rise (IAR), anodic inflection (AI), major anodic peak (MAP), cathodic inflection (CI), major cathodic peak (MCP), where 0, 1, 2, 3 are lack of, small, medium and large response respectively. *Sum* is the sum of all columns excluding category.

Table S7. Estimated Potential Breadths for NOM SCVs and SWVs.

No.	Name	*SCVas*[1]	*SCVae*[1]	*SCVcs*[2]	*SCVce*[2]	*SWVs*[3]	*SWVe*[3]
1	Bamboo NOM	−2.000	−0.689			−1.258	−0.554
2	Bemidji FA	−2.000	−1.373	−1.746	−0.681	−1.230	−0.502
3	Black River NOM					−1.978	−0.685
4	Cabbage Tree NOM	−1.979	−0.726			−1.000	−0.467
5	Coal Creek FA	−1.526	−0.096	−1.960	−1.000	−1.508	−0.546
6	Coal Creek HA	−1.516	−0.193	−1.998	−0.978	−1.512	−1.012
7	Elliott Soil FA Std II	−1.918	−0.143	−1.829	−0.635	−1.155	−0.481
8	Elliott Soil HA Std I	−1.978	−0.012	−1.978	−0.012	−1.036	−0.679
9	Elliott Soil HA Std IV	−1.996	−0.526	−1.978	−0.014	−1.234	−0.689
10	Everglades 2BS HPOA	−1.996	−0.324	−1.756	−0.996	−1.064	−0.471
11	Everglades F1 HPOA	−1.992	−0.227	−1.871	−0.534	−1.082	−0.439
12	Everglades F1 TPIA	−1.994	−0.119	−1.820	−0.701	−1.054	−0.449
13	Everglades LOX8 HPOA	−1.996	−0.227	−1.816	−0.760	−1.064	−0.504
14	Georgetown NOM	−1.994	−0.481	−1.681	−0.653	−1.060	−0.508
15	Georgetown NOM CH	−1.960	−0.356	−1.843	−0.719	−1.008	−0.479
16	Georgetown NOM PP	−1.990	−0.415	−1.736	−1.052	−1.012	−0.393
17	Great Dismal Swamp FA	−1.994	−0.046	−1.863	−0.673	−1.032	−0.369
18	Inangahua River NOM	−1.946	−0.573			−0.943	−0.481
19	Kauri NOM	−1.956	−0.689			−1.179	−0.477
20	Kitty Hawk NOM	−1.998	−1.462	−1.750	−0.691	−1.137	−0.538
21	Lake Fryxell FA	−1.990	−0.286	−1.861	−0.968	−1.536	−0.647
22	Leonardite HA Std I	−1.996	−0.619	−1.742	−0.008	−1.143	−0.574
23	Leonardite HA Std I	−1.998	−0.633	−1.673	−0.028	−1.105	−0.526
24	MW−6 NOM	−1.972	−0.582			−1.115	−0.643
25	Nordic Reservoir NOM	−1.046	−0.707			−0.911	−0.609
26	North Sea DOM	−1.994	−0.046	−1.871	−0.617	−1.014	−0.366
27	Ogeechee River FA	−1.964	−0.300	−1.806	−0.978	−1.512	−0.522
28	Pacific Ocean FA	−1.988	−0.078	−1.847	−0.719	−1.171	−0.425
29	Pahokee Peat FA Std II	−1.994	−0.096	−1.829	−0.637	−1.157	−0.481
30	Pahokee Peat HA Std I	−1.986	−0.546	−1.812	−0.479	−1.036	−0.512
31	Pahokee Peat HA Std I	−1.990	−0.536	−1.808	−0.510	−1.036	−0.508

No.	Name	*SCVas*[1]	*SCVae*[1]	*SCVcs*[2]	*SCVce*[2]	*SWVs*[3]	*SWVe*[3]
32	Pine Barrens NOM	−1.978	−0.346	−1.687	−0.052	−1.004	−0.429
33	Pony Lake FA	−1.994	−0.453	−1.843	−0.903	−1.175	−0.522
34	Prairie Pot Hole P8 DOM	−1.988	−0.096	−1.960	−1.080	−1.054	−0.429
35	Red Tussock NOM	−1.968	−1.508			−1.092	−0.498
36	Rio Negro NOM	−1.994	−1.429	−1.673	−0.195	−1.230	−0.504
37	Schönbuch Anoxic FA	−1.974	−0.726	−1.708	−1.121	−0.984	−0.449
38	Schönbuch Anoxic HA	−1.976	−0.560	−1.982	−0.060	−0.994	−0.401
39	Schönbuch H_2O Anoxic FA	−1.950	−0.776			−1.185	−0.494
40	Schönbuch H_2O Anoxic HA	−1.982	−0.504			−1.161	−0.508
41	Schönbuch H_2O Oxic HS						
42	Schönbuch Oxic HA	−1.990	−0.046	−1.960	−0.018	−1.258	−0.945
43	Shelter Is. San Diego HA	−1.998	−0.494	−1.673	−0.044	−1.449	−0.471
44	Soil HA Ref	−1.986	−0.637	−1.867	−0.024	−1.165	−0.508
45	Sutton Stream NOM	−1.996	−0.088			−0.967	−0.435
46	Suwannee River FA Std II	−1.996	−0.235	−1.978	−1.076	−1.032	−0.463
47	Suwannee River HA Std III	−1.996	−0.165	−1.802	−0.570	−1.064	−0.485
48	Suwannee River NOM	−1.986	−0.068	−1.816	−0.719	−1.074	−0.425
49	Suwannee River NOM	−1.990	−0.139	−1.857	−0.643	−1.070	−0.449
50	Suwannee River NOM	−1.986	−1.508	−1.774	−0.566	−1.137	−0.536
51	Toolik Lake FA	−1.998	−0.248	−1.816	−0.617	−1.068	−0.443
52	Walnut NOM	−1.990	−0.102			−0.971	−0.633
53	Waskish Peat HA Ref	−1.998	−0.123	−1.778	−0.482	−1.068	−0.443
54	Williams Lake HPOA	−1.986	−0.185	−1.829	−0.732	−1.088	−0.485

Estimated start and end of current response for SCV and SWV for all NOM samples. [1]Anodic start (*as*) and end (*ae*), [2]cathodic start (*cs*) and end (*ce*) of current response for SCV. [3]Start (*s*) and end (*e*) of current response for SWV. In the event there were more than one area of onset and end of current (2 peaks in a few of the NOMs) we only used the first peaks for comparison (E_{pa1}, E_{pc1}). It should be noted that the onset of potentials was not always easy to ascertain. For example, it was not immediately clear whether to choose the immediate start of current, or the current rise after the initial plateau. We chose the former, as the responses differed between NOMs from large plateaus (N07, N12, N15, N16) to no plateaus (N08, N09, N23). The difference in behavior between NOM samples suggests response is in excess of non-faradaic processes and therefore was important to include.

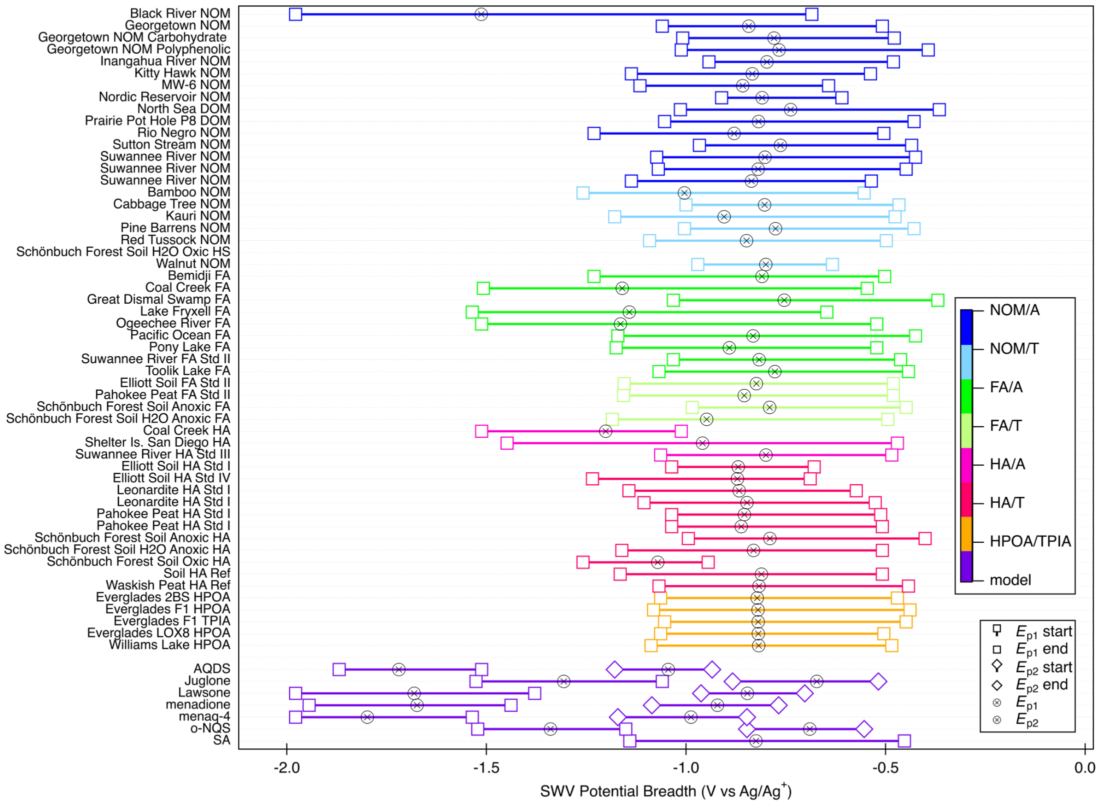


Figure S6. Summary of the breadth of potential response and the peak potentials for SWV for all NOMs and model compounds. Conditions: 1.0 mg/mL (except for HS, which did not fully dissociate in DMSO) of HS in 0.1 M TBAFP in DMSO, 1.6 mm Pt working electrode, Pt coil counter electrode and a Ag/Ag$^+$ reference electrode filled with 0.1 M TBAFP and 0.005 M $AgNO_3$ in DMSO. Scan rate: 25 mV s^{-1}.

Discussion for Figures S7-S16.

Some groups of NOM samples may be of particular interest for various reasons. To facilitate comparisons within these groups, selected SCV and SWV data (from Figures S3 and S4, respectively) were rearranged into the summary plots below. The groups include: sample category (NOM, FA, and HA in **Figure S7-S9**), source region (Antarctic in **Figure S10**; Everglades in **Figure S11**), component fraction (**Figure S12**), differences for Suwannee River NOM categories (**Figure S13**) and source (**Figure S14**), aging effects on Georgetown NOM (**Figure S15**), and our own extractions of plant material (**Figure S16)**.

In all three category groups (**Figure S7-S9**), the more positive SWV peak potential values are similar (~ −0.800 V vs Ag/Ag^+), while currents vary significantly. Comparing the current scale (y-axis) among the three groups shows that their response follows the trend FA > NOM > HA. In a few cases, the SWV data show a second peak at a more negative potential (~ −1.350 V), which may correspond to a prominent cathodic SCV peak around the same potential. This is especially evident for Prairie Pot Hole and Suwannee River NOMs (**Figure S7**).

The Antarctic FAs (**Figure S10**) show some unusual discrepancies between the SWVs and the SCV results. Lake Fryxell FA had the largest current response in the SWV, but the largest SCV response was from Toolik Lake FA (anodic and cathodic). The E_{p1} for Lake Fryxell FA and E_{pa1} for Toolik Lake differed notably from the corresponding peak potentials of the other two FAs; wheres all three FAs gave similar E_{pc1}. All of the Everglades HPOA and TPIA samples gave similar potentials for SCV and SWV (**Figure S11**), so their potential was not significatly affected by the differences in their sulfur content. However, the current varied in the SWV data, with the high S oxidized and the intermediate S having the highest and lowest current responses respectively. The high S oxidized sample also had the highest E_{pc1}, consistent with the more oxidized sample having more reduction capacity.

Georgetown NOM samples (**Figure S12**), include fractions that were enriched for carbohydrate and polyphenolic components. As expected, and supported by our previous work with these samples,[18] this fractionation affected both the SCV and SWV data. The polyphenolic fraction had the largest SWV current response, the largest SCV cathodic response, and the largest SCV initial anodic rise. Carbohydrate enriched GT NOM, had a medium response and the GT NOM (not enriched) was the least responsive.

Of all the sources, Suwannee River was represented by the most samples, including multiple categories and components. **Figure S13** shows Suwannee River sourced samples by category, and **Figure S14** compares multiple instances of the same material obtained from different providers. **Figure S13** shows that Suwannee River NOM gave similar peak potentials, but larger peak currents compared with the HA and somewhat larger compared with FA samples, this is in slight contrast to the samples in **Figures S7-S9**, where FA had the largest current response followed by NOM and HA. The comparison of Suwannee River NOM from three providers (**Figure S14**) shows very consistent peak potentials in all three NOMs, but the current response was much larger for N48 and N49 than N50. This might be consistent with the samples being nominally identical material, but the sample from Macalady was roughly a decade older. The aging of the dry material over a very long time span (years) is hard to compare to **Figure S15,** which shows Georgetown NOM in DMSO over the time span of 6 days. However, the aging in DMSO was similar in response in that only the current was affected (only for SWV), but the potential remained the same.

Figure S16 shows SWVs of our own extracted plant material (desribed in MT). Both the black walnut hull and pau d'arco bark potentials were similar in value as with our NOM samples. The black walnut hull had a pronounced response for the non-extracted (dry), and the water extracted sample, but when DMSO was used for extraction the peaks were not as pronounced and had a greater variety in potentials. For the pau d'arco bark the 24 h DMSO extraction sample had the most resolved peak, while the water extracted samples had more shouldering, indicating possible redox activity in that area that was not obtained with the DMSO only and the DMSO/ H_2O extracted samples.

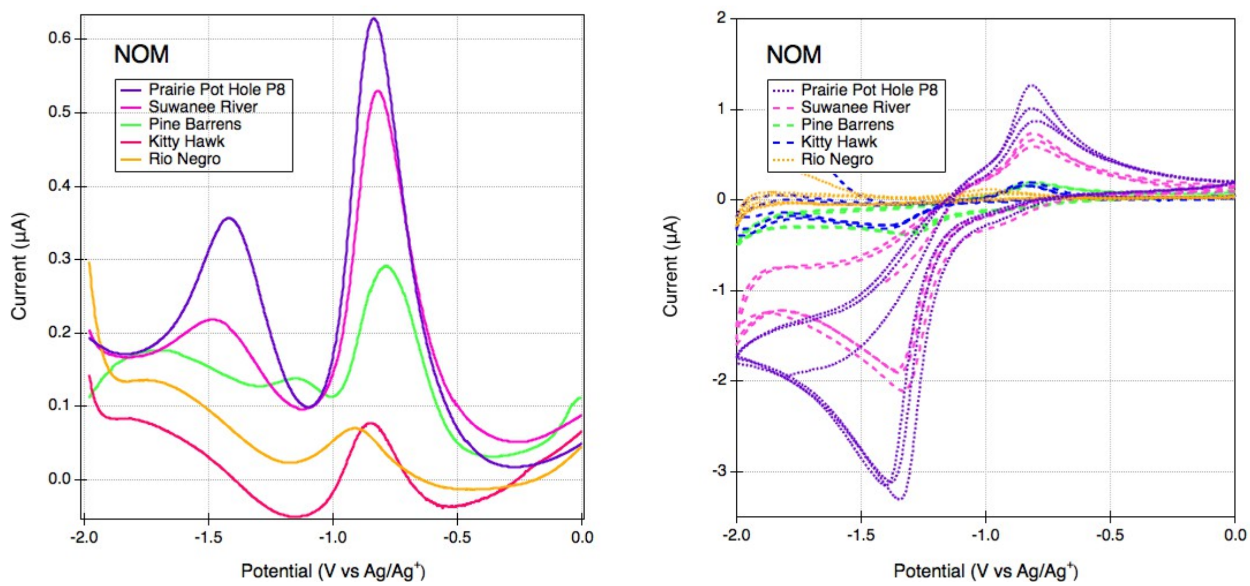


Figure S7. Comparison of SWV*i* (**A**) and SCV*i* (**B**) of NOMs from different sources. Primary data Figures S4.34, 4.48, 4.32, 4.20, 4.36.

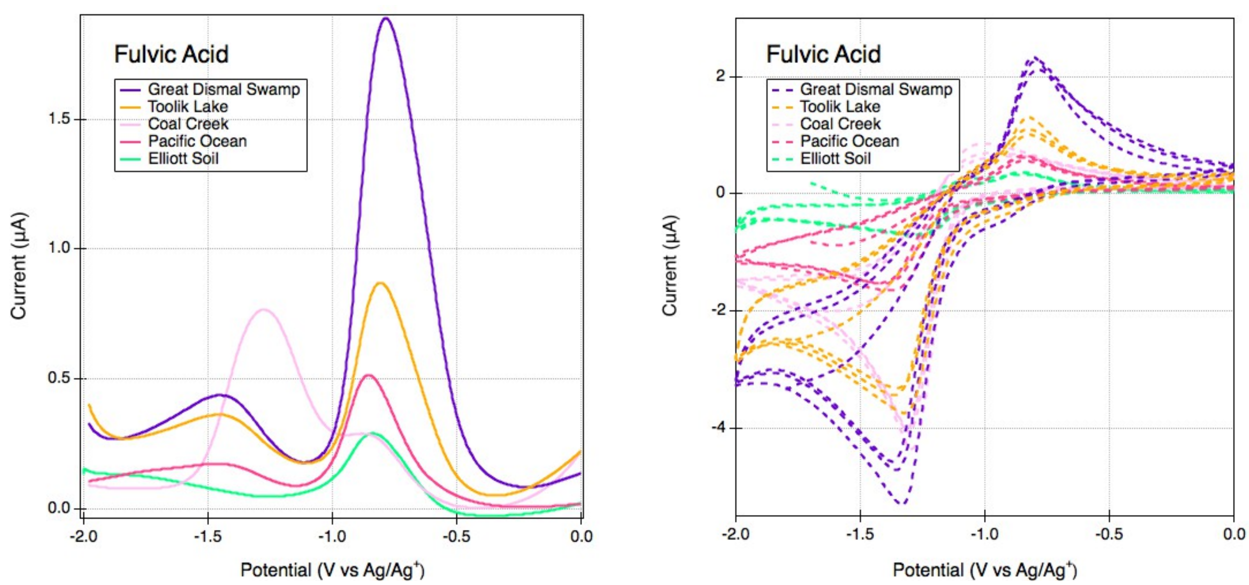


Figure S8. Comparison of SWV*i* (**A**) and SCV*i* (**B**) of FAs from different sources. Primary data Figures S4.17, 4.51, 4.05, 4.28, 4.07.

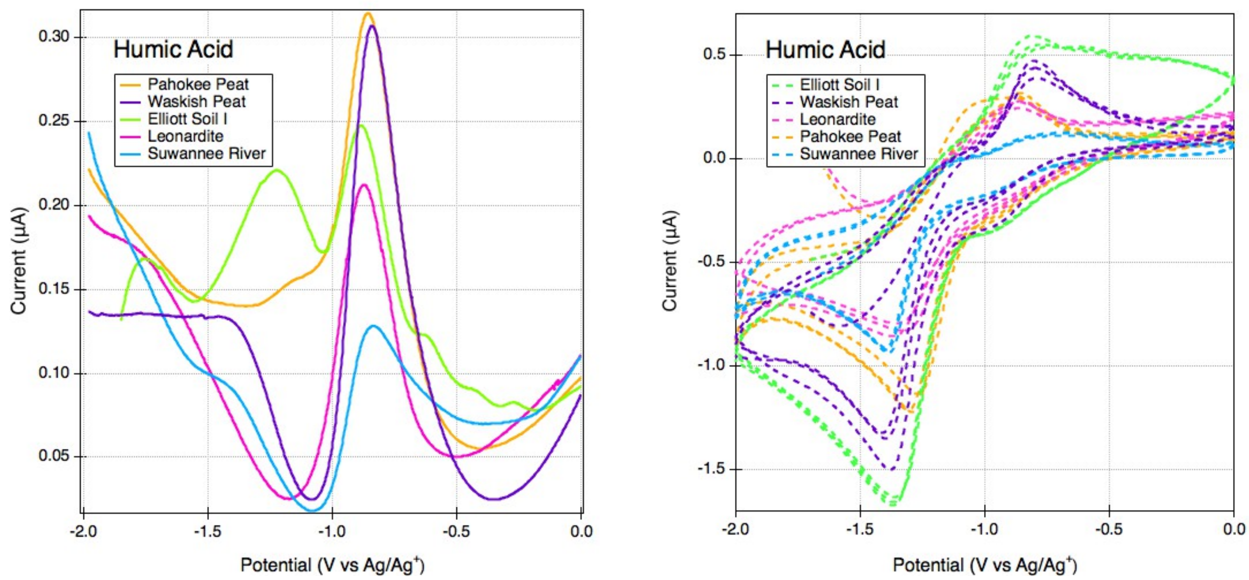


Figure S9. Comparison of SWV*i* (**A**) and SCV*i* (**B**) of HAs from different sources. Primary data Figures S4.30, 4.53, 4.08, 4.22, 4.47.

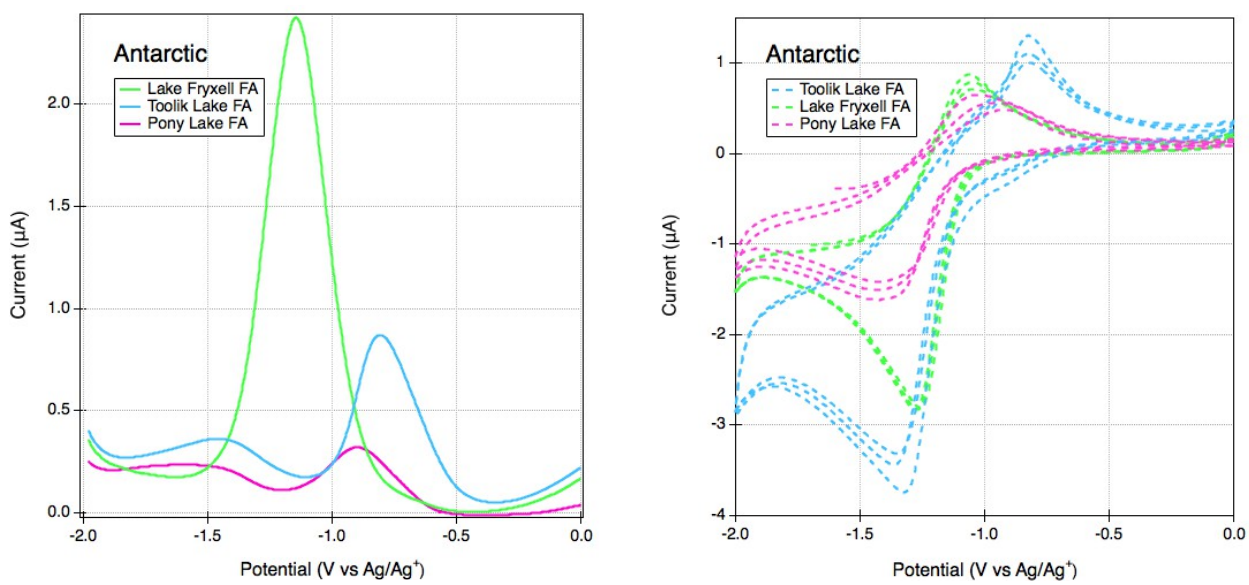


Figure S10. Comparison of SWV*i* (**A**) and SCV*i* (**B**) of microbially derived FAs. Primary data Figures S4.21, 4.51, 4.33.

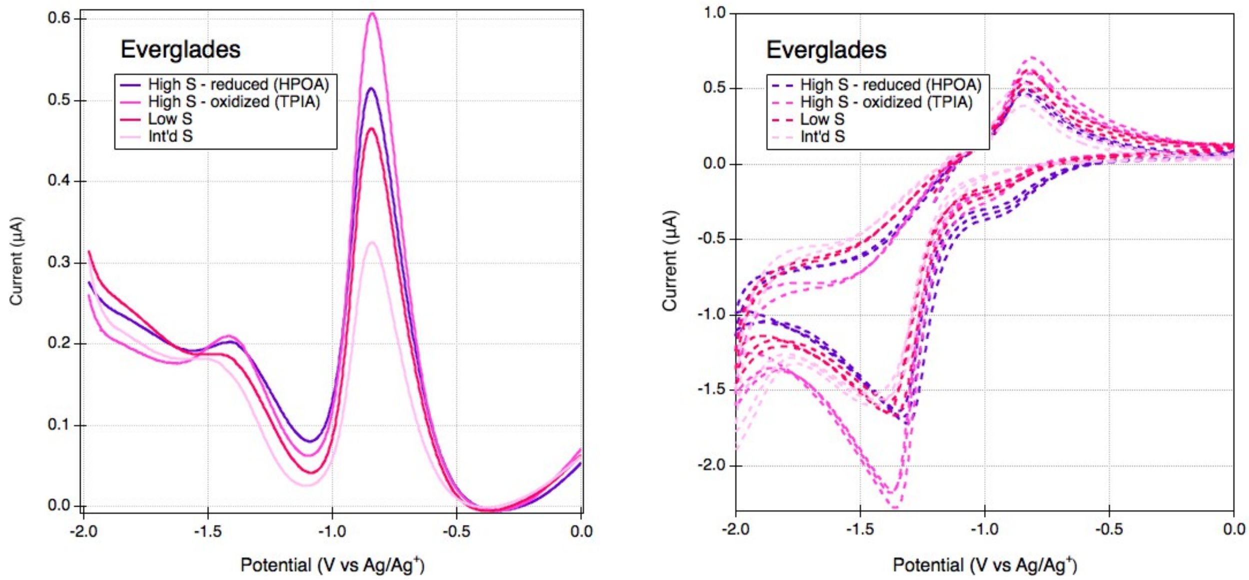


Figure S11. Comparison of SWV*i* (**A**) and SCV*i* (**B**) of USGS samples from the Everglades with varying amounts of sulfur. Primary data Figures S4.11, 4.12, 4.13, 4.10.

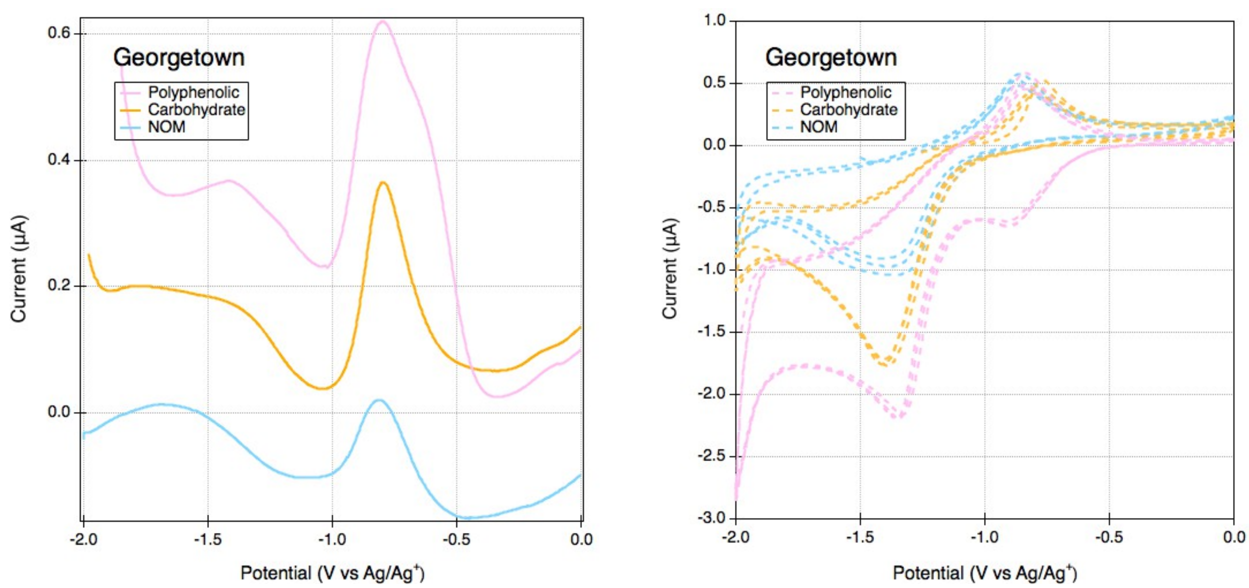


Figure S12. Comparison of SWV*i* (**A**) and SCV*i* (**B**) of Georgetown NOM (blue) and fractions enriched in carbohydrate (yellow) and polyphenols (pink). Primary data Figures S4.16, 4.15, 4.14.

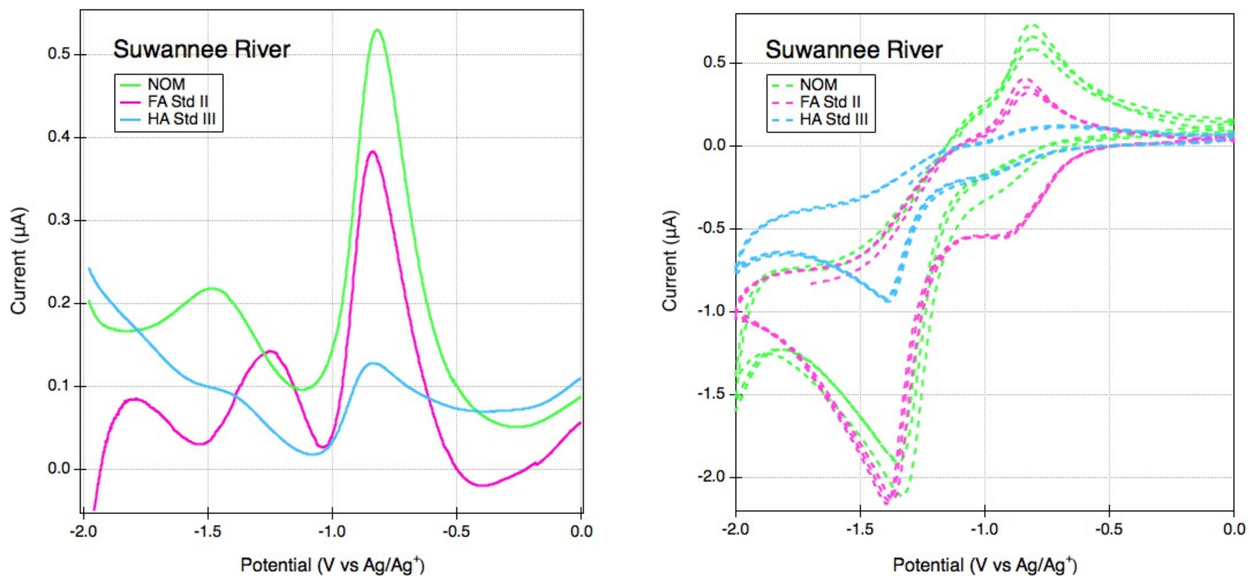


Figure S13. . Comparison of SWV*i* (**A**) and SCV*i* (**B**) of Suwannee River NOM (green), FA (pink) and HA (blue). Primary data Figures S4.48, 4.46, 4.47.

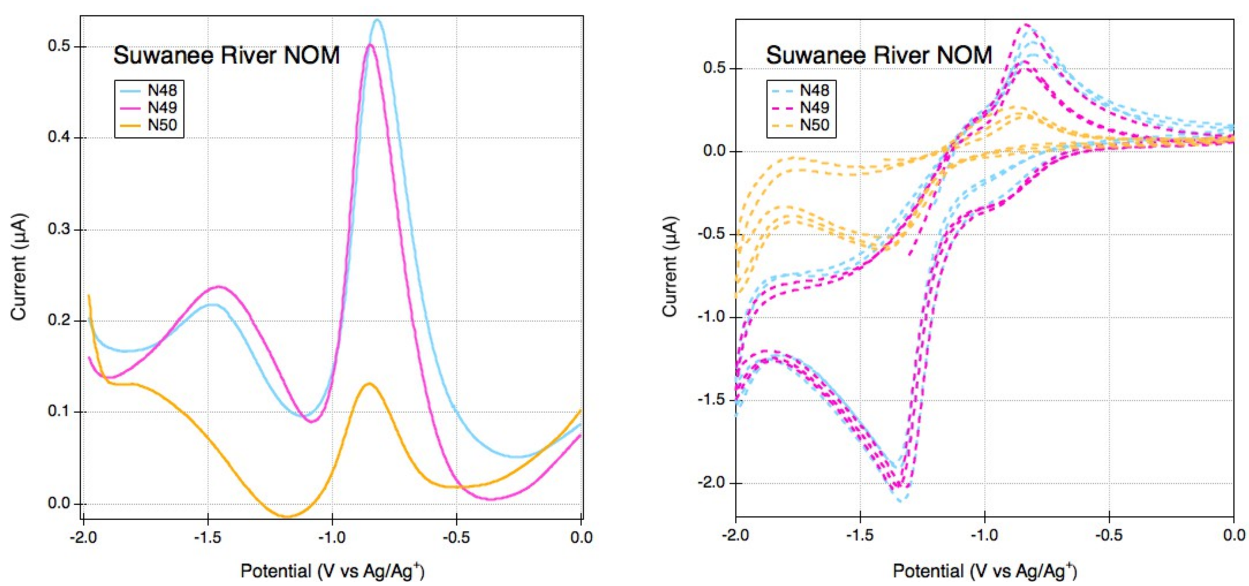


Figure S14. Comparison of SWV*i* (**A**) and SCV*i* (**B**) of Suwannee River NOM obtained from different suppliers: J. Needoba, N48 (blue), IHSS, N49 (pink) and D. Macalady, N50 (yellow). Primary data Figures S4.48, 4.49, 4.50.

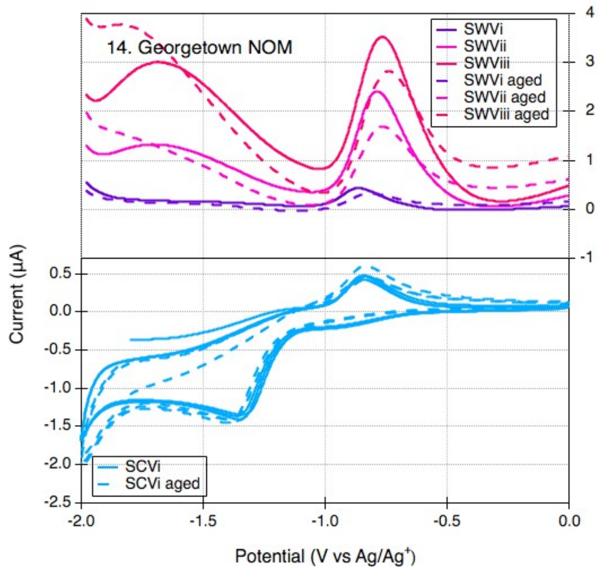


Figure S15. The effects of aging on Georgetown NOM. Aged samples were left in an amber bottle in DMSO for ~6 days.

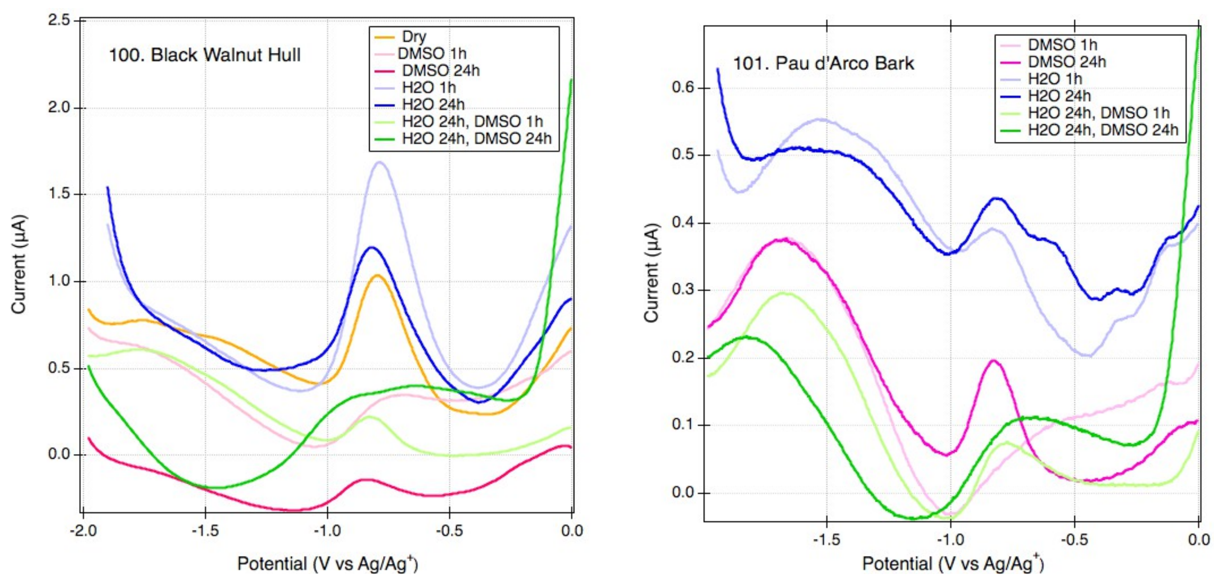


Figure S16. *SWV*i of black walnut hull and pau d'arco bark extracted using H_2O and DMSO. Conditions: 2.0 mg/mL of sample in 0.1 M TBAFP in DMSO, 1.6 mm Pt working electrode, Pt coil counter electrode and a Ag/Ag+ reference electrode filled with 0.1 M TBAFP and 0.005 M $AgNO_3$ in DMSO. Scan rate: 25 mV s^{-1}.

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