

Supplementary Information

Electrochemical Detection with Preconcentration: Nitroenergetic Contaminants

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This supporting information includes sorbent details, additional calibration data, tables of complete data sets, and additional images of the prototype and sampling locations.

Synthesis of Sorbent. Bis(trimethoxysilyl)ethylbenzene (DEB) was obtained from Gelest, Inc. (Morrisville, PA, USA). 1,2-bis(Trimethoxysilyl)ethane 96% (BTE), hydrochloric acid 37% (HCl), nitric acid 70% (HNO₃), mesitylene (1,3,5-trimethylbenzene, TMB), dichloromethane $\geq 99.5\%$, 3,5-dinitrobenzoyl chloride $\geq 98\%$, and magnesium turnings were obtained from Sigma-Aldrich (St. Louis, MO, USA). Ethanol (200 proof) was obtained from the Warner-Graham Company (Cockeysville, MD, USA). Sodium bicarbonate (NaHCO₃) was purchased from Fisher (Hampton, NH, USA). Pluronic[®] P123 (P123) was donated generously by BASF (Jessup, MD, USA) (can be purchased from Sigma-Aldrich as poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) average Mn ~ 5800).

To prepare the sorbent, 1.66 g of P123 and 0.24 g of DNB-imprint P123 (see below) were dissolved with 0.6 g of TMB in 7.5 g of 0.1 M HNO₃ with magnetic stirring and heating *ca.* 60 °C. The stirring mixture was allowed to cool to room temperature and a silane mixture of 1.06 g BTE and 1.468 g DEB

(0.00784 mol total bis-silane with BTE: DEB ratio = 1) was added drop-wise. The mixture was stirred until homogeneous, transferred to a culture tube, sealed tightly, and heated at 60 °C overnight (≥ 18 h). A white gel formed during this initial heating and the culture tube was unsealed to dry for 2 d at 60 °C and 2 d at 80 °C. The monolithic material was refluxed in 1 M HCl in ethanol for at least 12 h three times to extract P123, a process that broke the material into a powder. It was collected by vacuum filtration, washed with ethanol and water, and dried at 110 °C.

The DNB-imprint P123 was prepared through esterification of P123 with 3,5-dinitrobenzoyl chloride. P123 (8 g), 3,5-dinitrobenzoyl chloride (1.27 g), and magnesium turnings were added to 60 mL of dichloromethane. The mixture was refluxed for 2 h. After refluxing, the mixture was shaken with 60 mL 2% aqueous NaHCO_3 . Following separation, the organic phase was collected. Evaporation of the solvent resulted in a yellow product, DNB-imprint P123.

Nitrogen adsorption experiments are used for characterization of sorbent batches prior to use in applications. A Micromeritics ASAP 2010 porosimeter at 77 K (Micromeritics Instrument Corporation, Norcross, GA, USA) is used to evaluate samples that are degassed to 1 μm Hg at 100 °C. Surface area is determined by the Brunauer-Emmett-Teller (BET) method, pore size by the Barrett-Joyner-Halenda (BJH) method from the adsorption branch of the isotherm, and total pore volume by the single point method at relative pressure (P/P_0) 0.97. The sorbent utilized in the studies described here had surface area 700 m^2/g , pore volume 0.75 cm^3/g , and average mesopore diameter 65 Å.

Figure S1. Calibration of electrochemical sensor against TNT 75% methanol with 75 mM KCl using peak area (x) and peak height (circle).

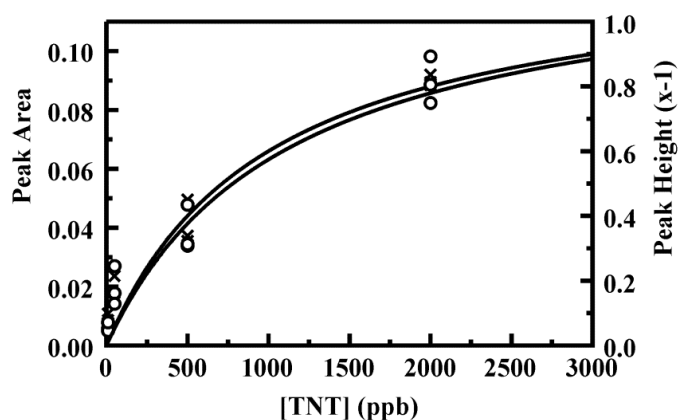


Figure S2. Analysis of mixed target samples. Points here represent the results for quantification of samples using the prototype system with analysis by HPLC (x-axis) and EC (y-axis): **(A)** TNT and **(B)** DNT. EC results presented use the peak height analysis. The line indicates the expected results based on HPLC analysis of the spiked samples. The complete data set is provided in the Supporting Information, Table S7.

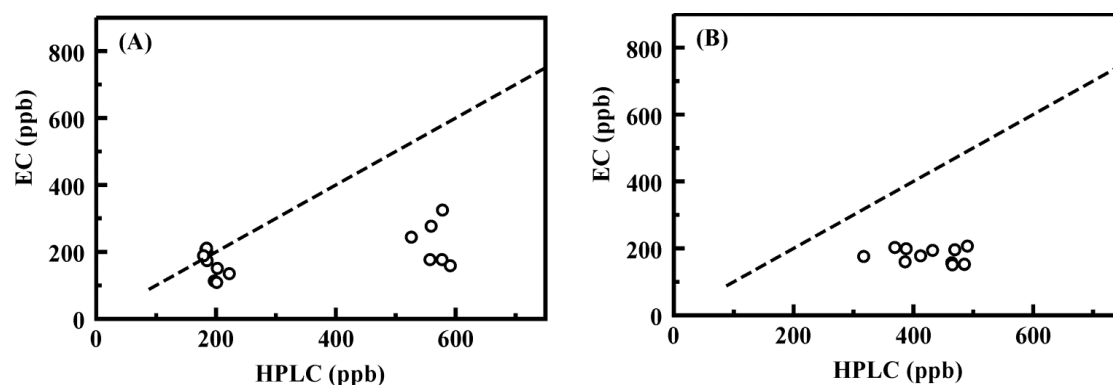


Table S1. Complete data set for calibration of electrochemical sensor against TNT in 75% methanol with 75 mM KCl. TNT reduction peaks appeared between 0.57 and 0.61 V.

[Prepared] (ppb)	Peak Height (μA)	Peak Area (μAV)
9	−0.08	5.75×10^{-3}
9	−0.07	5.00×10^{-3}
9	−0.10	7.85×10^{-3}
50	−0.22	2.70×10^{-2}
50	−0.15	1.78×10^{-2}
50	−0.13	1.42×10^{-2}
500	−0.45	4.78×10^{-2}
500	−0.32	3.39×10^{-2}
500	−0.34	3.44×10^{-2}
2000	−0.81	9.82×10^{-2}
2000	−0.80	8.86×10^{-2}
2000	−0.84	8.24×10^{-2}

Table S2. Complete data set for calibration of electrochemical sensor against TNT in 50% methanol with 100 mM KCl.

[Prepared] (ppb)	Potential (V)	Peak Height (μA)	Peak Area (μAV)
62.5		No Peak	
125		No Peak	
187.5	−0.63	-3.92×10^{-2}	2.27×10^{-2}
187.5	−0.64	-3.11×10^{-2}	3.01×10^{-3}
187.5	−0.62	-3.03×10^{-2}	3.04×10^{-3}
187.5	−0.625	-3.25×10^{-2}	3.17×10^{-3}
250	−0.615	-1.01×10^{-1}	1.68×10^{-2}
250	−0.62	-9.38×10^{-2}	1.41×10^{-2}
250	−0.62	-7.98×10^{-2}	1.15×10^{-2}
250	−0.605	-7.26×10^{-2}	1.07×10^{-2}
325	−0.625	-1.83×10^{-1}	2.97×10^{-2}
325	−0.615	-1.90×10^{-1}	3.43×10^{-2}
325	−0.62	-2.07×10^{-1}	3.72×10^{-2}
325	−0.625	-1.80×10^{-1}	2.93×10^{-2}
400	−0.625	-2.44×10^{-1}	3.80×10^{-2}
400	−0.625	-2.45×10^{-1}	4.25×10^{-2}
400	−0.62	-2.45×10^{-1}	5.06×10^{-2}
400	−0.625	-2.75×10^{-1}	5.31×10^{-2}
450	−0.625	-2.79×10^{-1}	4.97×10^{-2}
450	−0.62	-2.74×10^{-1}	5.38×10^{-2}
450	−0.625	-2.86×10^{-1}	5.32×10^{-2}
450	−0.625	-2.82×10^{-1}	5.40×10^{-2}
500	−0.63	-3.07×10^{-1}	5.34×10^{-2}
500	−0.63	-3.20×10^{-1}	5.70×10^{-2}
500	−0.625	-2.90×10^{-1}	5.43×10^{-2}
500	−0.63	-3.13×10^{-1}	5.61×10^{-2}
700	−0.615	-3.55×10^{-1}	-3.71×10^{-2}
700	−0.615	-3.53×10^{-1}	-4.37×10^{-2}
700	−0.615	-3.71×10^{-1}	-4.11×10^{-2}
700	−0.615	-3.76×10^{-1}	-4.18×10^{-2}
1000	−0.63	-4.78×10^{-1}	7.10×10^{-2}
1000	−0.63	-4.91×10^{-1}	7.35×10^{-2}
1000	−0.63	-4.88×10^{-1}	7.27×10^{-2}
1000	−0.635	-4.89×10^{-1}	6.89×10^{-2}
2500	−0.625	-7.48×10^{-1}	9.98×10^{-2}
2500	−0.625	-6.95×10^{-1}	9.37×10^{-2}
2500	−0.625	-7.08×10^{-1}	9.55×10^{-2}
2500	−0.625	-7.86×10^{-1}	1.05×10^{-1}

Table S3. Complete data set for calibration of electrochemical sensor against DNT in 50% methanol with 100 mM KCl.

[Prepared] (ppb)	Potential (V)	Peak Height (μA)	Peak Area (μAV)
62.5	No Peak		
125	No Peak		
187.5	−0.77	-8.63×10^{-2}	2.58×10^{-2}
187.5	−0.77	-1.10×10^{-1}	6.46×10^{-2}
187.5	−0.77	-8.70×10^{-2}	3.69×10^{-2}
187.5	−0.775	-8.18×10^{-2}	2.77×10^{-2}
187.5	−0.77	-7.91×10^{-2}	3.73×10^{-2}
250	−0.77	-8.54×10^{-2}	2.69×10^{-2}
250	−0.77	-9.36×10^{-2}	3.76×10^{-2}
250	−0.77	-1.01×10^{-1}	4.25×10^{-2}
250	−0.77	-9.10×10^{-2}	3.99×10^{-2}
250	−0.765	-1.47×10^{-1}	5.64×10^{-2}
325	−0.77	-1.71×10^{-1}	5.05×10^{-2}
325	−0.77	-1.41×10^{-1}	2.48×10^{-2}
325	−0.77	-1.36×10^{-1}	2.79×10^{-2}
325	−0.77	-1.18×10^{-1}	3.61×10^{-2}
325	−0.765	-1.76×10^{-1}	5.84×10^{-2}
350	−0.765	-2.13×10^{-1}	4.74×10^{-2}
350	−0.765	-2.25×10^{-1}	8.43×10^{-2}
350	−0.765	-2.08×10^{-1}	6.26×10^{-2}
350	−0.77	-2.22×10^{-1}	6.98×10^{-2}
350	−0.77	-1.66×10^{-1}	4.65×10^{-2}
400	−0.77	-1.62×10^{-1}	3.57×10^{-2}
400	−0.77	-1.54×10^{-1}	4.29×10^{-2}
400	−0.77	-2.01×10^{-1}	6.82×10^{-2}
400	−0.77	-2.20×10^{-1}	6.98×10^{-2}
400	−0.77	-2.37×10^{-1}	7.92×10^{-2}
450	−0.77	-2.73×10^{-1}	6.43×10^{-2}
450	−0.77	-2.76×10^{-1}	6.35×10^{-2}
450	−0.77	-2.73×10^{-1}	6.50×10^{-2}
450	−0.77	-2.62×10^{-1}	7.61×10^{-2}
450	−0.765	-2.72×10^{-1}	5.86×10^{-2}
500	−0.77	-2.86×10^{-1}	8.76×10^{-2}
500	−0.77	-2.94×10^{-1}	9.39×10^{-2}
500	−0.765	-2.96×10^{-1}	7.67×10^{-2}
500	−0.77	-2.93×10^{-1}	8.08×10^{-2}
500	−0.77	-2.92×10^{-1}	7.45×10^{-2}
700	−0.77	-3.80×10^{-1}	8.71×10^{-2}
700	−0.765	-3.71×10^{-1}	9.13×10^{-2}
700	−0.765	-3.70×10^{-1}	9.86×10^{-2}
700	−0.765	-3.74×10^{-1}	9.74×10^{-2}
700	−0.765	-3.14×10^{-1}	7.20×10^{-2}

[Prepared] (ppb)	Potential (V)	Peak Height (μA)	Peak Area (μAV)
1000	−0.765	-4.00×10^{-1}	6.88×10^{-2}
1000	−0.77	-4.05×10^{-1}	7.92×10^{-2}
1000	−0.765	-3.94×10^{-1}	7.05×10^{-2}
1000	−0.765	-3.91×10^{-1}	7.43×10^{-2}
1000	−0.765	-3.96×10^{-1}	7.26×10^{-2}
2500	−0.76	-5.40×10^{-1}	6.67×10^{-2}
2500	−0.755	-6.02×10^{-1}	7.31×10^{-2}
2500	−0.755	-6.32×10^{-1}	7.66×10^{-2}
2500	−0.755	-5.92×10^{-1}	7.04×10^{-2}
2500	−0.755	-6.02×10^{-1}	7.18×10^{-2}

Table S4. Analysis of samples in deionized water. All concentrations provided in parts per billion (ppb).

Target	[Prepared] ¹	[HPLC]	Height (μA)	[Height]	St. Dev. [Height]	Area (μAV)	[Area]	St. Dev [Area]
TNT ²	1	63			Not Detected			
TNT ²	1	67			Not Detected			
TNT ²	3	213	−0.025	36	8	0.002	13	4
TNT ²	3	188	−0.064	94	17	0.006	46	10
TNT ²	5	160	−0.182	298	49	0.022	181	31
TNT ²	5	222	−0.158	253	81	0.020	162	66
TNT	20	205	−0.115	177	43	0.018	146	64
TNT	20	156	−0.111	171	22	0.015	122	18
TNT	20	142	−0.119	185	25	0.017	138	10
TNT	20	108	−0.060	89	9	0.007	53	6
TNT	20	100	−0.069	103	42	0.008	60	28
TNT	20	109	−0.080	120	6	0.009	72	4
TNT	50	323	−0.230	394	121	0.031	279	136
TNT	50	303	−0.203	340	78	0.029	262	74
TNT	125	737	−0.250	437	48	0.035	325	86
TNT ²	125	834	−0.381	762	159	0.083	1354	879
TNT ²	125	784	−0.366	720	182	0.041	410	104
TNT	125	717	−0.273	488	69	0.039	379	55
TNT	125	764	−0.273	489	286	0.039	374	219
TNT	125	818	−0.368	724	47	0.051	554	41
TNT	200	1080	−0.456	992	152	0.054	598	134
TNT	200	1074	−0.472	1050	160	0.057	660	96
TNT	250	1466	−0.803	2992	731	0.106	2625	831
TNT	250	1618	−0.757	2575	1079	0.102	2311	1369
TNT	250	1573	−0.818	3140	1303	0.111	3165	2339
TNT	250	1296	−0.525	1248	213	0.075	1072	209
TNT	250	1318	−0.634	1755	407	0.090	1609	456
TNT	250	1378	−0.662	1913	683	0.094	1808	779
DNT ²	1	97			Not Detected			
DNT ²	1	75			Not Detected			
DNT ²	5	153	−0.201	376	39	0.025	105	28
DNT ²	5	60	−0.142	246	38	0.020	82	18
DNT ²	5	240			Not Detected			
DNT	20	99			Not Detected			
DNT	20	99			Not Detected			
DNT	20	98			Not Detected			
DNT	50	340	−0.167	298	64	0.018	70	22
DNT	50	456	−0.192	355	41	0.027	117	19
DNT	50	206			Not Detected			
DNT	50	249			Not Detected			
DNT	50	240			Not Detected			
DNT	125	578	−0.205	385	61	0.021	88	24
DNT	125	619	−0.260	528	38	0.030	137	20
DNT	125	672	−0.241	476	23	0.025	105	5

Table S4. Cont.

Target	[Prepared] ¹	[HPLC]	Height (μA)	[Height]	St. Dev. [Height]	Area (μAV)	[Area]	St. Dev [Area]
DNT	200	604	−0.233	454	83	0.030	138	68
DNT	200	660	−0.278	578	35	0.035	176	19
DNT	250	1238	−0.368	887	232	0.051	336	148
DNT	250	1015	−0.307	668	53	0.044	251	39
DNT	250	1271	−0.493	1514	273	0.063	554	265

¹ Prepared sample concentration prior to preconcentration. Preconcentration involved passing 30 mL of the sample through the system with elution in 2 mL methanol. The eluant was then diluted into 2 mL of 0.15 M KCl in water. ² Preconcentration of samples at less than 10 ppb involved passing 300 mL of the sample through the system with elution into 2 mL methanol. The eluant was then diluted into 2 mL of 0.15 M KCl in water.

Table S5. Analysis of samples in ground water. All concentrations provided in parts per billion (ppb).

Target	[Prepared] ¹	[HPLC]	Height (μA)	[Height]	St. Dev. [Height]	Area (μAV)	[Area]	St. Dev [Area]
TNT ²	3	213	−0.025	36	8	0.002	13	4
TNT ²	3	188	−0.064	94	17	0.006	46	10
TNT	20	108	−0.060	89	9	0.007	53	6
TNT	20	100	−0.069	103	42	0.008	60	28
TNT	20	109	−0.080	120	6	0.009	72	4
TNT	125	717	−0.273	488	69	0.039	379	55
TNT	125	764	−0.273	489	286	0.039	374	219
TNT	125	818	−0.368	724	47	0.051	554	41
TNT	250	1296	−0.525	1248	213	0.075	1072	209
TNT	250	1318	−0.634	1755	407	0.090	1609	456
TNT	250	1378	−0.662	1913	683	0.094	1808	779
DNT ²	7	492	−0.061	96	5	0.005	19	1
DNT ²	7	498	−0.057	89	4	0.005	16	1
DNT	70	364	−0.066	105	13	0.006	21	3
DNT	70	383	−0.083	135	27	0.008	27	6
DNT	70	397	−0.091	149	11	0.008	29	3
DNT	125	668	−0.281	587	147	0.032	149	48
DNT	125	672	−0.293	626	156	0.032	154	47
DNT	125	717	−0.378	925	192	0.043	247	68
DNT	250	1281	−0.485	1466	326	0.057	425	106
DNT	250	1346	−0.599	2407	504	0.068	669	181
DNT	250	1615	−0.539	1843	1026	0.091	3191	3336

¹ Prepared sample concentration prior to preconcentration. Preconcentration involved passing 30 mL of the sample through the system with elution in 2 mL methanol. The eluant was then diluted into 2 mL of 0.15 M KCl in water. ² Preconcentration of samples at less than 10 ppb involved passing 300 mL of the sample through the system with elution into 2 mL methanol. The eluant was then diluted into 2 mL of 0.15 M KCl in water.

Table S6. Analysis of mixed target samples. All concentrations provided in parts per billion (ppb).

Sample Number	Target	[Prepared] ¹	HPLC ID	[HPLC]	EC ID	[Height]	St. Dev. [Height]	[Area]	St. Dev [Area]
1	TNT	21	TNT/RDX	185/270	TNT	199	8	222	19
	RDX	85		183/272		209	3	239	10
				184/279		211	8	247	6
2	DNT	65	DNT/RDX	317/268	DNT	176	5	58	1
	RDX	95		369/297		203	26	70	14
				388/306		199	15	67	9
3	TNT	79	TNT/DNT	557/464	TNT/ DNT	177/157	18/3	145/48	12/3
	DNT	77		577/465		177/151	22/5	143/40	19/2
				591/485		159/152	13/5	121/40	11/2
4	DNT	74	DNT/NG	485/523	DNT	153	12	42	5
	NG	103		469/525		196	26	60	11
				490/569		207	17	65	8
5	TNT	77	TNT/NG	526/630	TNT	244	15	223	15
	NG	103		559/599		277	24	271	29
				578/626		325	15	366	15
6	TNT	20	TNT/DNT	222/386	TNT/ DNT	135/160	6/3	117/50	14/3
	DNT	75		197/412		113/178	15/15	93/58	32/8
				201/432		109/194	3/8	83/64	5/5
7	TNT	31	TNT	202	TNT	151	10	131	17
				185		174	12	171	26
				179		189	5	197	18

¹ Prepared sample concentration prior to preconcentration as determined by HPLC. Preconcentration involved passing 30 mL of the sample through the system with elution in 2 mL methanol. The eluant was then diluted into 2 mL of 0.15 M KCl in water.

Table S7. Analysis of blind samples. All concentrations provided in parts per billion (ppb). Samples were analyzed in numerical order in triplicate.

Sample Number	Target	[Prepared] ¹	HPLC ID	[HPLC]	EC ID	[Height]	St. Dev. [Height]	[Area]	St. Dev [Area]
1	None	-	-	-	-	-	-	-	-
					-	-	-	-	-
					-	-	-	-	-
2	TNT	250	TNT	1034	TNT	719	37	660	49
				1193	TNT	1308	214	1290	157
				1247	TNT	840	128	713	96
3	None	-	TNT	94	-	-	-	-	-
			TNT	55	-	-	-	-	-
			-	-	-	-	-	-	-
4	RDX	250	RDX	684	-	-	-	-	-
				711	-	-	-	-	-
				763	-	-	-	-	-

Table S7. Cont.

Sample Number	Target	[Prepared] ¹	HPLC ID	[HPLC]	EC ID	[Height]	St. Dev. [Height]	[Area]	St. Dev [Area]
5	DNT	250	DNT	908	DNT	755	60	179	14
				1046	DNT	1317	291	345	101
				1216	DNT	1635	197	429	74
6	None	-	-	-	DNT	505	85	111	21
					-	-	-	-	-
					-	-	-	-	-
7	None	-	-	-	-	-	-	-	-
					-	-	-	-	-
					-	-	-	-	-
8	TNT	250	TNT	1328	TNT	974	128	707	93
				1546	TNT	1336	371	1006	278
					DNT	362	68	83	14
				1686	TNT	1613	216	1423	179
					DNT	362	50	80	11
9	NG	125	NG	997	TNT	351	14	323	17
				783	TNT	367	6	342	7
				731	TNT	361	5	331	6
10	None	-	-	-	-	-	-	-	-
					-	-	-	-	-
					-	-	-	-	-
11	TNT	30	TNT	147	TNT	383	20	405	17
			TNT	159	TNT	424	7	480	10
12	DNT	125	DNT	644	-	-	-	-	-
				706	-	-	-	-	-
				751	-	-	-	-	-
13	None	-	DNT	116	-	-	-	-	-
			-	-	-	-	-	-	-
			-	-	-	-	-	-	-
14	TNT	50	TNT	314	TNT	422	40	361	57
				333	TNT	462	21	412	31
				337	TNT	515	35	472	40
15	DNT	250	DNT	1282	DNT	352	32	81	11
				1446	-	-	-	-	-
				1503	-	-	-	-	-

¹ Prepared sample concentration prior to preconcentration. Preconcentration involved passing 30 mL of the sample through the system with elution in 2 mL methanol. The eluant was then diluted into 2 mL of 0.15 M KCl in water. ² Preconcentration of samples at less than 10 ppb involved passing 300 mL of the sample through the system with elution into 2 mL methanol. The eluant was then diluted into 2 mL of 0.15 M KCl in water.

Figure S3. Photographs of the NRL bench-scale prototype preconcentration system: (1) 0.7 μm filter for particulate removal; (2) filtered sample solution; (3) solenoid valves for flow direction control powered by DC source (4); (5) peristaltic pump powered by 9 V battery (6); sorbent column (7); (8) eluted sample collection and electrochemical sensor; (9) PalmSens device.

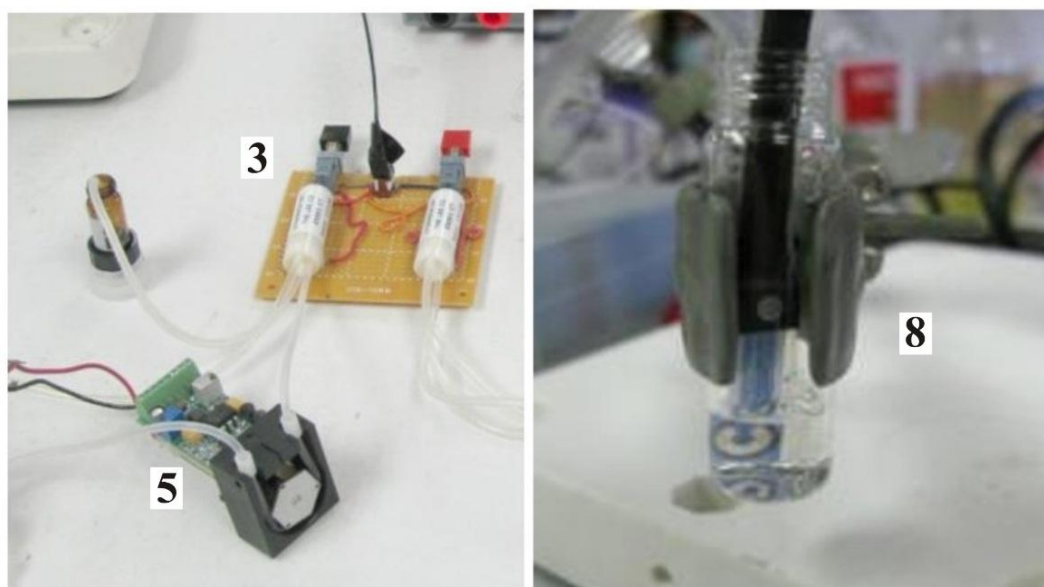
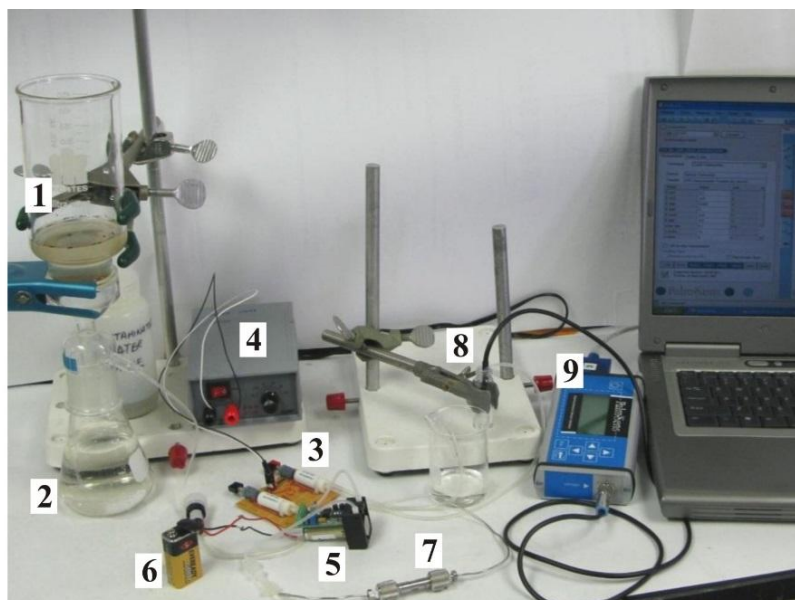


Figure S4. Photographs of the SubChem Systems, Inc. prototype preconcentration system and user control interface: (1) manifold; (2) LFYA valves; (3) GA series pump; (4) printed circuit board.

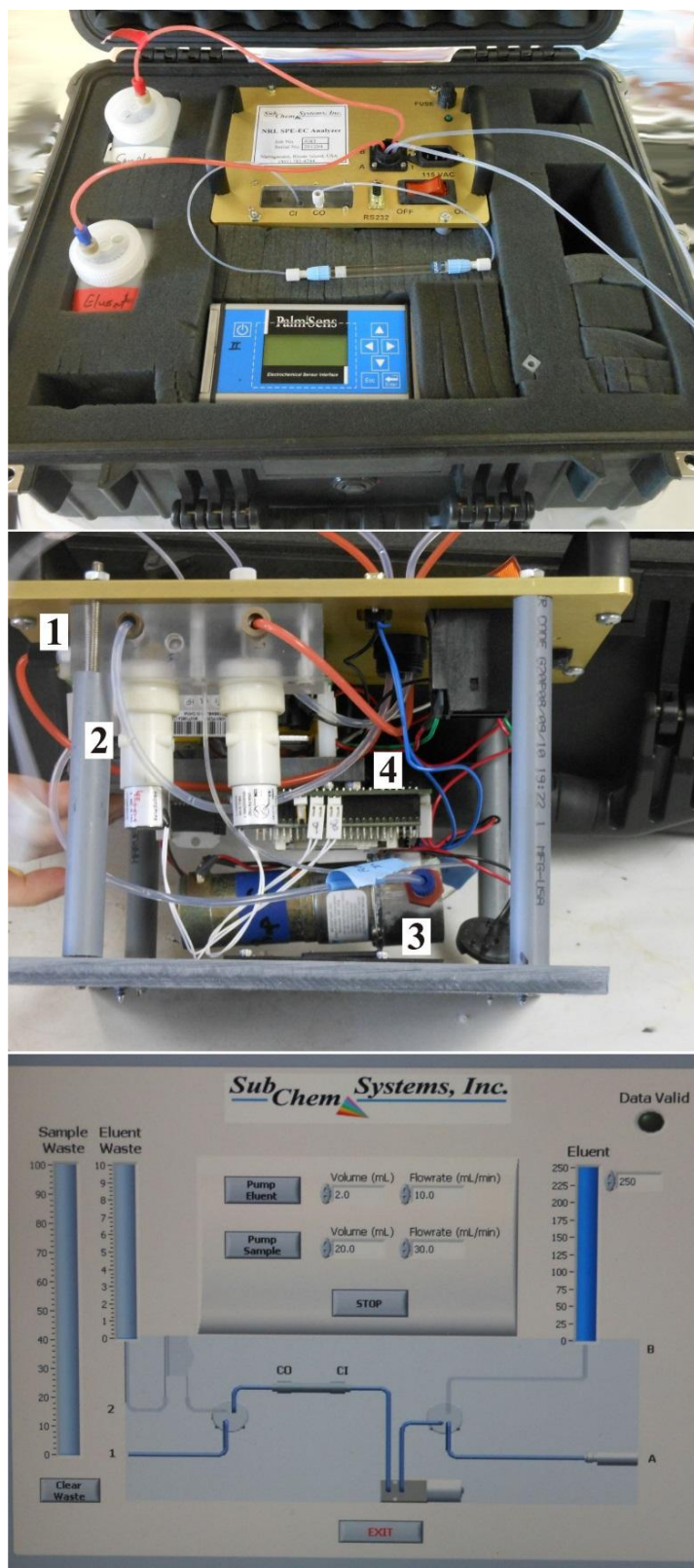


Figure S5. Photographs of the sites utilized for field trials in Cherokee County, OK, USA. (a) prototype system at site #1; (b) site #1, pond at residential site; (c) site #2, Ranger Creek; (d and e) site #3, Double Spring Creek; (f) site #4, Hulbert Landing.

