Water Resources Division
South Dakota District Office
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Memorandum

To: Dave Rickert and Pete Rogerson

From: Joyce E. Williamson and Gregory C. Delzer

Subject: Results comparing VOC concentrations in samples preserved with HCl + 4° chill versus 4° chill only

INTRODUCTION

In the past, most volatile organic chemical (VOC) samples sent to the National Water-Quality Laboratory (NWQL) were chilled to 4°C without additional preservation. VOC samples analyzed by the NWQL are currently preserved in the field with 1:1 HCl and chilled to 4°C. The goal of this study was to document the effect of the standard operating procedure (SOP) change using HCl plus 4°C chill (hereafter referred to as "HCl" samples) as a VOC preservation agent in lieu of 4°C chill only (hereafter referred to as "no HCl" samples).

DESIGN

This study incorporated 13 sampling sites from a variety of settings and water types. Of these 13 sites, six were ground waters, three were surface waters, two were stormwaters, and two were sewage effluents (appendix 1). The sample preparation sequence and description of sample types collected at each site are listed in table 1. All samples were held for 14 days and analyzed at the NWQL in a random and sequential order. Statistical comparisons between HCl samples and no HCl samples were used to document the effect of the SOP change. Analytical results for the environmental samples, lab spikes, and DIW spikes are not presented herein but are contained in a South Dakota District data base. Additional information on these data and the sampling sites are available from Joyce Williamson or Greg Delzer.

Table 1. --Sample preparation sequence, type, and number of samples (N), and the type of preservation for each sample type

Sample Sequence	Sample Type	N	Type of Preservation
1	native water	3	Ascorbic acid, 2 drops of 1:1 HCl, 4° chill
2	HCl preserved + 4° chill	2	Ascorbic acid, 2 drops of 1:1 HCl, spike 5 ug/L, 4° chill (HCl samples)
3	4° chill only	2	4° chill (no HCl samples), spike 5 ug/L

STATISTICAL APPROACH AND DISCUSSION

All data were statistically analyzed using the sign test. This is a nonparametric analysis in which the sign of the difference population is examined. The average concentration of the 2-HCl samples minus the average concentration of the 2-no HCl samples was compared to zero. The null hypothesis is that the median of the difference population is equal to 0; the number of positive differences (x) is approximately the same as the negative differences (y). The alternate hypothesis is that $x > y$; VOC concentrations for HCl samples are greater than VOC concentrations for no HCl samples. For all tests, an α of 90 was used for determination of significant difference. The null hypothesis was rejected whenever the p-value was less than or equal to 0.10.

Statistical comparisons of average VOC concentrations were conducted on 3 different populations: 1) all 61 VOCs as a whole; 2) VOC subgroups; and 3) individual VOCs. Population 1 includes all 61 VOCs grouped together; population 2 includes VOCs grouped by type (halogenated alkanes, halogenated alkenes, etc.); and population 3 includes each individual VOC (no groups). All VOCs and VOC subgroups are listed by name in appendix 2. In addition, statistical comparisons of a subset of each of the 3 different populations were conducted. Subsets consisted of sites expected to have a greater chance of detectable levels of VOCs ("dirty" sites - 2 surface water, 2 NPDES, 2 effluents). VOC concentrations in the native water samples (sequence 1, table 1) were used to verify the selection of these "dirty" sites.

The sign test was selected so that all the data would be analyzed under the same test. Although other tests may have been statistically stronger for selected groups, the same test could not be used for all data divisions with the exception of the sign test. The sign test does not require a population to be normal or symmetric. Table 2 provides the statistical results from the 3 populations and subsets examined with the exception of individual VOCs. Other statistical tests were examined for some analyses when the data set met the necessary criteria and yielded similar results.

Table 2. -- Statistical summary of one-sided sign test for all VOCs, VOC subgroups, and individual VOCs

VOC Analytes	N	All Sites (n=13) Statistically Different	p-value	Median Difference (ug/L)	N	"Dirty" sites (n=6) Statistically Different	p-value	Median Difference (ug/L)
all 61 VOCs	806	yes	0.0000	0.10	372	yes	0.0029	0.15
VOC Subgroups (group number)								
- Halogenated Alkanes	338	yes	0.0006	0.09	156	yes	0.0152	0.11
- Halogenated Alkenes	130	yes	0.0793	0.08	60	no	0.2175	0.21
- Alkylated Benzenes	195	yes	0.0759	0.11	90	no	0.2992	0.21
- Halogenated Aromatics	117	yes	0.0130	0.14	54	yes	0.0380	0.18
- methyltert-butylether	13	no	0.5000	0.14	6	no	0.3438	0.15
- 2-Chloroethyl-vinylether	13	yes	0.01950	-0.09	6	no	0.1875	-1.24
Individual Analytes	13 ea	yes for 2 of 61 analytes: chloromethane, 2-chloroethylvinylether	appendix 3	appendix 3	6	no	appendix 3	appendix 3

<u>HCl vs. no HCl -- all VOCs</u>

The difference population for all sites and all VOCs was analyzed. Since this population has a large N for statistical analysis, both the sign test and the paired t-test were applied. Results were similar for both tests, however only the sign test is presented in table 2, (t-test p-value = 0.000). The median of the difference population was small (0.10 ug/L). A boxplot of the difference population is presented in figure 1. The median is the middle value of the ranked concentration differences and the interquartile range is 50% of this distribution where 25% of the concentrations are greater than the difference median and 25% of the concentrations are less than the difference median. Outside and far outside points shown on figure 1 include 2-chloroethylvinylether (6 points), total xylene (5 points), dibromochloromethane (2 points), bromodichloromethane (2 points), naphthalene (2 points), dichlorodifluoromethane (1 point), chloromethane (1 point), chloroform (1 point), bromoform (1 point), p-isopropyltoluene (1 point), and n-butylbenzene (1 point).

As a subset of all sites, the dirty sites were evaluated. The statistical results were the same as for all sites, indicating that concentrations of HCl preserved samples were slightly higher than the concentrations of no HCl preserved samples.

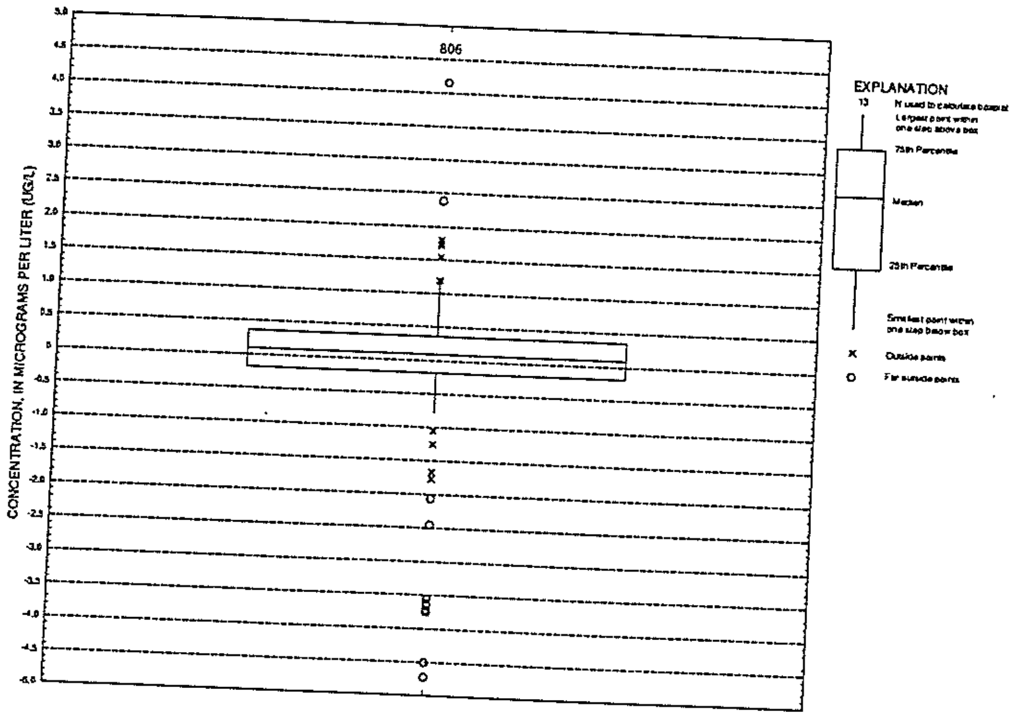

Figure 1.--Boxplot of difference population for all sites and VOCs.

<u>HCl vs. no HCL -- VOC subgroups</u>

VOC subgroups (appendix 2) were examined to determine if differences occurred for one or more groups of VOCs. Results of statistical analyses and difference medians are presented in table 2, with all groups except group 5 (methyltertbutylether) being statistically different. All had difference medians of less than 0.14 micrograms per liter (ug/L). Boxplots showing the distribution of each group are presented in figure 2. It should be noted that group 6, which shows a large reduction in concentration for HCl preserved samples, includes only 1 VOC (2-Chloroethylvinylether). This compound is known to be unstable in the presence of HCl at a lower pH. When only the 6 "dirty" sites were analyzed, only groups 1 (halogenated alkanes) and 4 (halogenated aromatics) were statistically different, with difference medians of 0.11 and 0.18, respectively (table 2).

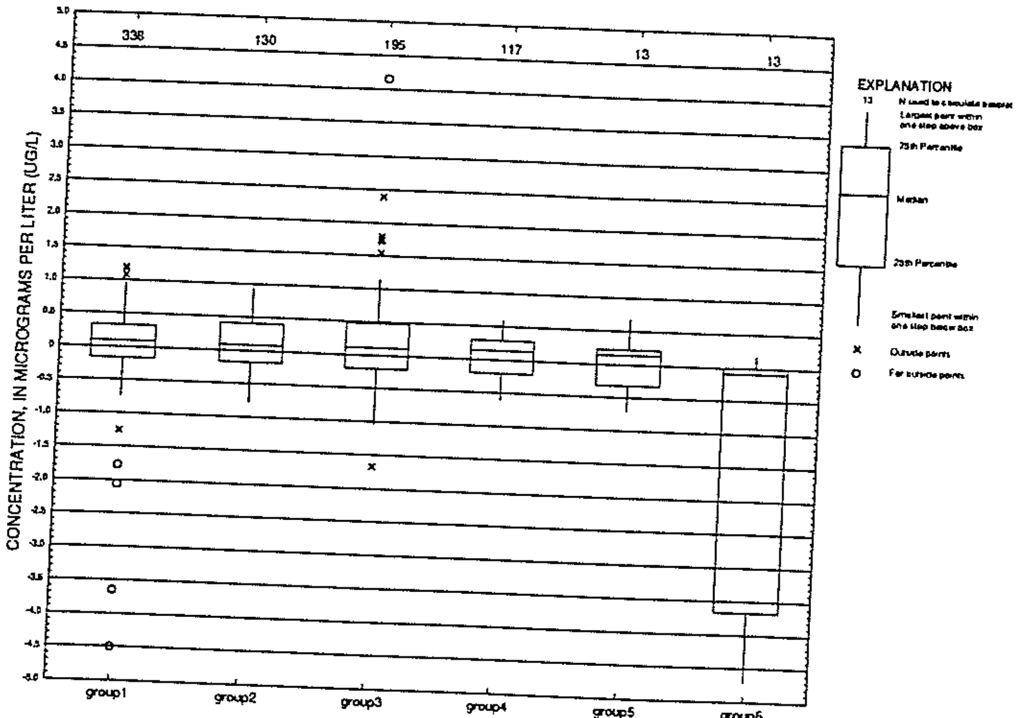

Figure 2.--Boxplots of difference population by analyte group.

HCl vs. no HCl -- individual VOCs

Each individual VOC was analyzed to determine if one VOC responded differently than another VOC. Appendix 3 presents the results of all the individual VOC statistical analysis in addition to means and medians. Differences between means and medians are an indication of outliers. Only chloromethane and 2-chloroethylvinylether were statistically different (HCl preserved samples greater than no HCl preserved samples and no HCl preserved samples greater than HCl preserved samples, respectively). Chloromethane is a known by-product of the HCl preservative and 2-chloroethylvinylether is known to degrade at lower pHs in the presence of HCl. Means and medians varied slightly for most VOCs but the mean and median had a difference of more than 1.5 ug/L for 2-chloroethylvinylether.

None of the individual VOCs were statistically different for the "dirty" sites. It is important to note the sample size of the "dirty" sites is 6 and that all differences have to be either positive or negative to reject the null hypothesis with N this small.

OBSERVATIONS

As with any study, there are some variables that can effect or influence the results. Samples were spiked using a micropipettor by 13 different people, of which some had experience using a pipettor and others did not. The precision of the micropipettor has yet to be documented. Recoveries for all 60 VOCs combined were very low; the theoretical concentration spiked was 5 ug/L and the median recoveries ranged from 3.21 ug/L to 3.45 ug/L (64% to 69%). It is now known that low VOC recoveries are due to the operational manner of the micropipettor, not from other loss mechanisms.

The population 1 analysis (group of all VOCs and all sites) resulted in a significant difference between the HCl and no HCl samples. However, the median of the differences was generally 0.10 ug/L, suggesting that although the statistical method determined that the populations are different, the difference in concentration is relatively small. Other variables may account for some differences, especially when the median difference is small.

The population 2 analysis (VOC subgroups) resulted in a significant difference between 5 of 6 groups, but only two of the subgroups of "dirty" sites were significantly different. All medians of the differences are less than 0.14 ug/L for all sites and less than or equal to 0.21 for the "dirty" sites with the exception of group 6 (2-chloroethylvinylether). Again, other variables may account for some differences.

The population 3 analysis (individual VOCs) resulted in only chloromethane and 2-chloroethylvinylether as being statistically different. Chloromethane yielded higher concentrations in 11 of the 13 samples preserved with HCl in comparison to those without the addition of HCl. Chloromethane is, however, a known by-product of the HCl preservative. 2-chloroethylvinylether was either found in much lower concentrations or was absent from samples preserved with HCl. 2-chloroethylvinylether is known to degrade at lower pHs in the presence of HCl.

Analyses were again completed on populations 1 (group of all VOCs and all sites) and 2 (VOC subgroups) excluding chloromethane and 2-chloroethylvinylether resulting in similar findings. Thus, these two compounds don't appear to affect these analyses.

A statistical difference in VOC concentrations was evident when individual VOCs were grouped together (populations 1 and 2), however, this difference was small and typically ≤ 0.10 ug/L. A statistical difference in VOC concentrations was not evident when VOCs were examined individually (population 3) with the exception of the 2 VOCs noted above (chloromethane and 2-chloroethylvinylether). Though a statistical difference between VOC concentrations may have been evident, the median difference between HCl and no HCl samples was not environmentally important. Based upon the results of this study, the SOP change of adding HCl for preservation does not appear to result in a marked effect on the concentrations of VOCs in spiked environmental samples.

Appendix 1

Site number, name, matrix and sample types collected [X indicates sample was collected and analyzed]

Site number	Site name	Site Matrix	Native sample, preserved with HCl, unspiked	Lab Spike of native water preserved with HCl	Field spike in native water with no HCl preservation (chilled only)	Field spike in native water with no HCl preservation (chilled only) Replicate	Field spike in native water with HCl preservation	Field spike in native water with HCl preservation Replicate	Syringe spiked DIW, preserved with HCl	Pipettor spiked DIW, preserved with HCl
1	Connecticut	GW	X	X	X	X	X	X	X	
3	Atlanta, GA	GW	X	X	X	X	X	X	X	X
4	Austin, TX	GW	X	X	X	X	X	X	X	X
5	Lakewood, CO	GW	X	X	X	X	X	X	X	X
6	Tacoma, WA	GW	X	X	X	X	X	X	X	X
7	Raleigh, NC	GW	X	X	X	X	X	X	X	
8	Rapid City, SD Canyon Lake	SW	X		X	X	X	X	X	X
9	Baton Rouge, LA Miss. River	SW	X		X	X	X	X	X	X
11	Baton Rouge, LA L Calcasieu R.	SW	X	X	X	X	X	X	X	X
15	Tuscaloosa, AL	NPDES	X		X	X	X	X	X	X
16	Lincoln, NE	NPDES	X		X	X	X	X	X	X
19	Rapid City, SD WWTP	Effluent	X		X	X	X	X	X	X
21	San Antonio, TX	Effluent	X	X	X	X	X	X	X	X

Appendix 2

VOC elusion order, name, and subgroup

VOC elusion order	VOC name	VOC elusion order	VOC name
	GROUP 1 -- HALOGENATED ALKANES		
06	Dichlorodifluoromethane	07	Chloromethane
09	Bromomethane	10	Chloromethane
11	Trichlorofluoromethane	14	Trichlorotrifluoroethane
15	Methylene chloride	19	1,1-Dichloroethane
20	2,2-Dichloropropane	22	Bromochloromethane
23	Chloroform	24	1,1,1-Trichloroethane
26	Carbon tetrachloride	28	1,2-Dichloroethane
30	1,2-Dichloropropane	31	Dibromomethane
32	Dibromochloromethane	37	1,1,2-Trichloroethane
39	1,3-Dichloropropane	40	Bromodichloromethane
41	1,2-Dibromoethane (EDB)	43	1,1,1,2-Tetrachloroethane
48	Bromoform	51	1,1,2,2-Tetrachloroethane
52	1,2,3-Trichloropropane	67	1,2-Dibromo-3-chloropropane
71	Hexachlorobutadiene		
	GROUP 2 -- HALOGENATED ALKENES		
08	Vinyl chloride	13	1,1-Dichloroethene
17	trans-1,2-Dichloroethene	21	cis-1,2-Dichloroethene
25	1,1-Dichloropropene	29	Trichloroethene
34	cis-1,3-Dichloropropene	36	trans-1,3-Dichloropropene
38	Tetrachloroethene		
	GROUP 3 -- ALKYLATED BENZENES		
27	Benzene	35	Toluene
44	Ethylbenzene	45	Xylenes (total)
46	o-Xylene	47	Styrene
49	Isopropylbenzene	53	N-Propylbenzene

VOC elusion order, name, and subgroup

VOC elusion order	VOC name	VOC elusion order	VOC name
56	1,3,5-Trimethylbenzene	58	tert-Butylbenzene
59	1,2,4-Trimethylbenzene	60	sec-Butylbenzene
62	p-Isopropyltoluene	66	N-Butylbenzene
72	Naphthalene		
	GROUP 4 -- HALOGENATED AROMATICS		
42	Chlorobenzene	50	Bromobenzene
54	2-Chlorotoluene	55	4-Chlorotoluene
61	1,3-Dichlorobenzene	63	1,4-Dichlorobenzene
65	1,2-Dichlorobenzene	70	1,2,4-Trichlorobenzene
73	1,2,3-Trichlorobenzene		
	GROUP 5 -- METHYL TERT-BUTYL ETHER		
18	Methyl tert-butyl ether		
	GROUP 6 -- 2-CHLOREOTHYLVINYLETHER		
33	2-Chloroethylvinylether		

Appendix 3

Results of one-sided sign test and mean and median for the difference population (average of 2 HCl preserved samples minus average of 2 no HCl preserved samples) for each individual VOC at all sites and for all "dirty" sites

Compound name	All Sites (n=13)			"Dirty" sites (n=6)		
	One-sided P value results of sign test	Mean	Median	One-sided P value results of sign test	Mean	Median
Dichlorodifluoromethane	0.2905	0.236	0.075	0.6563	0.322	0.173
Chloromethane	0.0112	0.253	0.170	0.3438	0.287	0.158
Vinyl chloride	0.2905	0.157	0.065	0.6563	0.209	0.115
Bromomethane	0.1334	0.199	0.135	0.3438	0.330	0.353
Chloromethane	0.5000	0.125	0.080	0.6563	0.178	0.103
Trichlorofluoromethane	0.2905	0.119	0.140	0.6563	0.138	0.123
1,1-Dichloroethene	0.5000	0.098	0.015	0.6563	0.143	0.103
Trichlorotrifluoroethane	0.2905	0.117	0.105	0.6563	0.158	0.140
Methylene chloride	0.5000	0.097	0.030	0.6563	0.092	0.070
trans-1,2-Dichloroethene	0.5000	0.107	0.020	0.6563	0.141	0.095
Methyl tert-butyl ether	0.5000	0.011	0.135	0.3438	0.080	0.148
1,1-Dichloroethane	0.5000	0.103	0.015	0.6563	0.161	0.155
2,2-Dichloropropane	0.5000	0.021	-0.050	0.6563	0.103	0.048
cis-1,2-Dichloroethene	0.3872	0.092	0.040	0.5000	0.121	0.140
Bromochloromethane	0.5000	-0.025	0.075	0.6563	-0.092	0.028
Chloroform	0.5000	-0.268	0.050	0.6563	-0.647	0.125
1,1,1-Trichloroethane	0.5000	0.122	0.030	0.6563	0.138	0.115
1,1-Dichloropropene	0.5000	0.096	0.010	0.6563	0.123	0.098
Carbon tetrachloride	0.5000	0.051	-0.030	0.3438	-0.075	-0.200
Benzene	0.5000	0.073	0.025	0.6563	0.103	0.108
1,2-Dichloroethane	0.2905	0.060	0.180	0.3438	0.098	0.105
Trichloroethene	0.5000	0.086	0.030	0.6563	0.126	0.103

Results of one-sided sign test and mean and median for the difference population (average of 2 HCl preserved samples minus average of 2 no HCl preserved samples) for each individual VOC at all sites and for all "dirty" sites

Compound name	All Sites (n=13)			"Dirty" sites (n=6)		
	One-sided P value results of sign test	Mean	Median	One-sided P value results of sign test	Mean	Median
1,2-Dichloropropane	0.2905	0.089	0.090	0.3438	0.134	0.160
Dibromomethane	0.5000	-0.053	0.060	0.3438	-0.101	0.077
Dibromochloromethane	0.5000	-0.082	0.020	0.3438	-0.168	0.060
2-Chloroethylvinylether	0.0195	-1.673	-0.090	0.1875	-1.578	-1.235
cis-1,3-Dichloropropene	0.2905	0.157	0.165	0.3438	0.181	0.190
Toluene	0.5000	0.097	0.005	0.6563	0.173	0.148
trans-1,3-Dichloropropene	0.1334	0.182	0.235	0.1094	0.250	0.263
1,1,2-Trichloroethane	0.1334	0.058	0.165	0.1094	0.097	0.150
Tetrachloroethene	0.5000	0.110	0.105	0.6563	0.092	0.045
1,3-Dichloropropane	0.1334	0.085	0.180	0.1094	0.127	0.218
Bromodichloromethane	0.5000	-0.272	-0.010	0.3438	-0.594	-0.022
1,2-Dibromoethane (EDB)	0.1334	0.091	0.235	0.1094	0.127	0.222
Chlorobenzene	0.2905	0.090	0.100	0.3438	0.114	0.145
1,1,1,2-Tetrachloroethane	0.2905	0.122	0.140	0.3438	0.127	0.178
Ethylbenzene	0.5000	0.108	0.090	0.6563	0.139	0.123
Xylenes (total)	0.5000	0.298	0.325	0.6563	0.412	0.420
o-Xylene	0.5000	0.084	0.115	0.6563	0.115	0.142
Styrene	0.5000	0.078	0.125	0.6563	0.131	0.140
Bromoform	0.2905	-0.145	-0.110	0.1094	-0.257	-0.232
Isopropylbenzene	0.5000	0.143	0.075	0.6563	0.108	0.073
Bromobenzene	0.2905	0.087	0.130	0.3438	0.130	0.182
1,1,2,2-Tetrachloroethane	0.1334	0.088	0.235	0.1094	0.158	0.250
1,2,3-Trichloropropane	0.1334	0.043	0.150	0.1094	0.138	0.243
N-Propylbenzene	0.5000	0.193	0.060	0.6563	0.168	0.123

Results of one-sided sign test and mean and median for the difference population (average of 2 HCl preserved samples minus average of 2 no HCl preserved samples) for each individual VOC at all sites and for all "dirty" sites

Compound name	All Sites (n=13)			"Dirty" sites (n=6)		
	One-sided P value results of sign test	Mean	Median	One-sided P value results of sign test	Mean	Median
2-Chlorotoluene	0.5000	0.091	0.135	0.6563	0.091	0.110
4-Chlorotoluene	0.5000	0.062	0.055	0.6563	0.103	0.118
1,3,5-Trimethylbenzene	0.5000	0.104	0.135	0.6563	0.108	0.095
tert-Butylbenzene	0.5000	0.100	0.090	0.6563	0.095	0.078
1,2,4-Trimethylbenzene	0.5000	0.125	0.120	0.6563	0.146	0.140
sec-Butylbenzene	0.5000	0.152	0.070	0.6563	0.083	0.018
1,3-Dichlorobenzene	0.2905	0.071	0.135	0.3438	0.083	0.115
p-Isopropyltoluene	0.2905	0.254	0.190	0.3438	0.420	0.295
1,4-Dichlorobenzene	0.2905	0.085	0.135	0.3438	0.105	0.172
1,2-Dichlorobenzene	0.1334	0.072	0.170	0.3438	0.077	0.180
N-Butylbenzene	0.2905	0.225	0.280	0.3438	0.189	0.323
1,2-Dibromo-3-chloropropane	0.5000	0.039	0.025	0.3438	0.212	0.287
1,2,4-Trichlorobenzene	0.2905	0.026	0.065	0.3438	0.053	0.140
Hexachlorobutadiene	0.5000	0.004	-0.010	0.6563	-0.094	-0.102
Naphthalene	0.2905	0.561	0.190	0.3438	0.190	0.187
1,2,3-Trichlorobenzene	0.2905	0.029	0.150	0.3438	0.039	0.207