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**Stability of Purgeable VOCs in Water Samples
During
Pre-analytical Holding
*Part I. Analyses by a Commercial Laboratory***

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Environmental Sciences Division
Publication No. 4599

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*Part 1. Analyses by a Commercial Laboratory***

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EXECUTIVE SUMMARY

Analyte stability during pre-analytical storage is essential to the accurate quantification of contaminants in environmental samples. This is particularly true for volatile organic compounds (VOCs) which can easily volatilize and/or degrade during sample storage. To reduce the impact of potential analyte instability, regulatory programs require water samples be collected in vials without headspace and stored at 4°C, and that analyses be conducted within 14 days if samples are acid-preserved (7 days without acid preservation). Compliance with this 14-day holding time has been difficult for sample collectors, data users and analytical laboratories. Since the selection of a 14-day holding time was largely arbitrary and initially prescribed for a much more restricted analyte (and matrix) list than its current application, the appropriateness of this requirement must be re-evaluated.

This study was undertaken to examine the hypothesis that prevalent and priority purgeable VOCs in properly preserved water samples are stable for at least 28 days. For the purposes of this study, VOCs were considered functionally stable if concentrations measured after 28 days did not change by more than 10% from the initial values. An extensive stability experiment was performed on freshly-collected surface water spiked with a suite of 44 purgeable VOCs. The spiked water was then distributed into multiple 40-mL VOC vials with 0.010-in Teflon-lined silicone septum caps prefilled with 250 mg of NaHSO₄ (resulting pH of the water ~2). The samples were sent to a commercial [Analytical Resources, Inc. (ARI)] and EPA (Region IV) laboratory where they were stored at 4°C. On 1, 8, 15, 22, 29, 36, and 71 days after sample preparation, analysts from ARI took 4 replicate samples out of storage and analyzed these samples for purgeable VOCs following EPA/SW846 8260A. A similar analysis schedule was followed by analysts at the EPA laboratory. This document contains the results from the ARI analyses; the EPA results are described in a separate report.

For a majority of the 44 VOCs included in this study, concentration changes were <10% of the initial values after 28 days of storage. Practical reporting times (*PRTs*) were also calculated from the stability data using the method described by Bayne et al. (1993, 1994). In the *PRT* approach, a "significant change" in VOC concentration is statistically defined such that measurement variability is taken into account. However, aside from calculating *PRTs*, analytical validity with increasing holding times was evaluated using a

"practical" definition of an "acceptable" concentration change. Consideration of this additional criterion was necessary for certain compounds for which actual changes in concentration with time were relatively small but measurement variability was extremely low (4 to 7%) resulting in very short calculated *PRTs*. Ideally, specifications for "acceptable" concentration changes should be tied into the eventual use of the analytical data. For example, "acceptable" concentration changes for analytical data used in quantitative risk assessments can be determined by the sensitivity of the risk assessment results to changes in the input analytical data. Since, the selection of a generic "acceptable" concentration change is beyond the scope of this study, 10% was chosen to assess holding time effects on compounds in this study. An acceptable change of 10% is reasonable given the other sources of uncertainty in site characterization and risk assessment for which these analytical data are typically used. Examples of these uncertainty sources include: spatial and temporal variability of contaminant concentrations, use of simplified transport models to approximate exposure pathways, and extrapolation of laboratory toxicity data from animals to humans.

Based on an "acceptable" concentration change of 10% relative to initial values, the stability study showed that the measurement of 35 out of 44 purgeable VOCs in properly preserved water samples (4°C, 250 mg NaHSO₄, no headspace in 40-mL VOC vials with 0.010-in Teflon-lined silicone septum caps) will not be affected by sample storage for 28 days. Larger changes in concentration (>10%) and low *PRTs* were observed for a few analytes, e.g. acrolein, carbon disulfide, vinyl acetate, etc. However, analytical problems exist for these latter compounds (inconsistent purging, standards, etc) which can not be addressed by maintaining current holding time requirements alone.

This study demonstrates that a 28-day holding time for properly preserved VOC water samples would not jeopardize the measurement of target purgeable VOCs. A 28-day pre-analytical holding time would benefit the regulated community, particularly government agencies with large-scale compliance sampling programs such as the Departments of Defense and Energy. Stringent holding times result in logistical difficulties further complicated by additional requirements for sample screening (e.g., for radioactivity). The suggested 28-day holding time can also improve the efficiency of commercial laboratories through simplified sample management. Furthermore, application of currently available stability databases (including the one described in this report) to data review would improve the analytical data validation process. The results of this study can be used to assess the risks associated with accepting a measurement made

beyond the prescribed maximum holding time. This approach would be an alternative to unequivocally rejecting data when prescribed holding times are missed, a practice that is very costly but not technically defensible.

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1. INTRODUCTION

1.1 Objectives and Scope

Analyte stability during pre-analytical storage is essential to the accurate quantification of contaminant levels in environmental samples. This is particularly true for volatile organic compound (VOC) analysis, since some of these target analytes can volatilize and/or degrade during sample storage [Maskarinec et al. 1990, Minnich 1993]. To reduce the impact of these transformation mechanisms on VOC analyses, regulatory programs (e.g., Superfund, Resource Conservation and Recovery Act or RCRA) require that water samples be collected without headspace (to reduce volatilization) in 40-mL vials with Teflon-lined septum caps, acidified to pH~2 (to inhibit biodegradation), and stored at 4°C (to reduce volatilization and inhibit abiotic/biotic chemical degradation). Furthermore, analytical data are considered valid only if the analyses are conducted within 14 days of sample collection (7 days if samples are not acidified). This maximum holding time was arbitrarily set and specified in 40CFR Part 136 (1979), and has since been adopted by other regulatory programs and for application to other environmental media [40CFR Part 136, 1984; U.S. EPA, 1986]. The appropriateness of this requirement must be re-evaluated since compliance with this 14-day holding time can and has been difficult and costly for sample collectors, data users and analytical laboratories. Recent Superfund Guidance [U.S. EPA, 1994] attempts to address the problem by relying on data validators' judgment to assess the impact of missed holding times on analytical measurements. However, this has still led to unequivocal rejection of data when prescribed holding times are missed, and more specific guidance backed by scientific data is needed from regulatory agencies [Bottrell, 1995].

Previous stability studies [Maskarinec et al., 1989; Bottrell et al., 1989] have demonstrated that a majority of purgeable volatile organic compounds in properly preserved VOC water samples (acidified, no headspace, 4°C storage) are stable for time periods well over 14 days. This study was undertaken to examine the hypothesis that prevalent and priority VOCs in acidified water samples are stable for at least 28 days. Data from this study can be used as a scientific basis for establishing a 28-day holding time for VOC water samples.

1.2 Report Organization

An Environmental Protection Agency (EPA) regional laboratory (Region IV) and a commercial laboratory (Analytical Resources Inc.) participated in the holding time study described here. This report documents the results from the analyses by Analytical Resources, Inc.; the EPA results are contained in a separate document [West et al., 1996].

This report is organized as follows: Sect. 2 contains a description of the experimental methods used in this study. Sect. 3 begins with a presentation of calibration and laboratory control sample data supporting the validity of the VOC measurements. It also contains results of the stability study, regression analysis of the data to examine concentration trends with pre-analytical holding, comparisons of results with previous stability studies, and effects of acidification on microbial activity. The impact of this study on current practice and regulations are discussed in Sect. 4. Finally, conclusions are presented in Sect. 5.

2. EXPERIMENTAL APPROACH

2.1 VOC Sample Preparation and Analysis

The stability study was performed on surface water collected as 2-L grab samples from a tributary of the Clinch River in Oak Ridge, TN. The surface water was filtered through Whatman 4 coarse filter paper (GF/F, >20-25 μm particle retention) in order to avoid sample-to-sample inhomogeneity caused by varying levels of suspended solids. Basic water chemistry parameters were also measured prior to water spiking and sample preparation (Table 1). The water samples were prepared on the same day the surface water was collected.

Water samples (Table 2) were prepared following the procedure described by Maskarinec et al. [1989]. A clean 3-L Tedlar bag (SKC, Inc. Part No. 231-03) was filled with two liters of surface water. Measured aliquots of two VOC standard solutions (CRS M-8240B-R, CRS M-5751-M, purchased from Chromatography Research Supplies, see Table 3 for components) were injected into the water-filled Tedlar bag through the bag's septum port. For sample set W1, 200 μL and 20 μL of CRS M-8240B-R and CRS M-5751-M, respectively, were added to the water. For sample sets W2, 2000 μL and 200 μL of CRS M-8240B-R and CRS M-5751-M, respectively, were added to the water. The water-filled Tedlar bag was shaken for 1-min, and allowed to equilibrate at room temperature for 20 min. After equilibration, the spiked water was distributed into an appropriate number of pre-cleaned 40-mL VOA vials with Teflon-lined (0.010-in thick) silicone septum caps. Two hundred-fifty milligrams of NaHSO_4 were placed in each vial prior to filling for acidified samples. Each vial was completely filled (i.e., with no headspace) and stored at 4°C prior to analysis.

Immediately after sample preparation, the samples were shipped in coolers filled with blue ice for overnight delivery to Analytical Resources, Inc. (ARI), a laboratory located in Seattle, WA certified under the Contract Laboratory Program (CLP). This laboratory was chosen based on its ability to conduct the analysis according to the experimental schedule and to provide complete data packages. Upon receipt of the samples, personnel at ARI immediately stored these in a cooler maintained at 4°C. At 1, 8, 15, 22, 29, 36, and 71 days after sample preparation, four samples from each set were analyzed for VOCs. Analyses followed the purge-and-trap (PT) method in SW846-8260A [EPA, 1986], except that all calibrations were performed in reagent water that had

been acidified to pH~2 with reagent-grade NaHSO₄ (resulting pH was 2.4-2.6). In addition, matrix spike and matrix spike duplicate samples were not included in this study since the samples themselves are spiked samples.

A second set of 20-ppb and 200-ppb water samples were prepared as described above and sent to EPA's Region IV Laboratory for VOC analysis. The EPA results are described in a separate report [West et al., 1996].

Table 1. Characteristics of surface water used in VOC stability study

Parameter	Value
Alkalinity	71 mg CaCO ₃ /L
Total Solids ^a	0.015 mg/L
Dissolved Oxygen	6 mg/L
pH ^b	8.3
Total Microbial Plate Count	698 (CFUs/mL) ^c
VOCs listed in EPA/SW846 8260-A	none detected (5 ppb detection limit)

^a Measured after filtration of water through coarse filter paper (>20-25 µm particle retention).

^b pH was 2.4-2.6 after acidification with 250 mg NaHSO₄ per 40 mLs of sample water.

^c Colony forming units per mL of sample.

Table 2. Test conditions for VOC stability study

Sample Set	VOC Target Spiking Level ^a (µg/L)	Number of samples	Preservation	Analysis Days
W1	20	28 (4 replicates per day)	4°C no headspace 250 mg NaHSO ₄	1, 8, 15, 22, 29, 36, 71
W2	200	28 (4 replicates per day)	4°C no headspace 250 mg NaHSO ₄	1, 8, 15, 22, 29, 36, 71
		4 (2 replicates per day)	4°C no headspace	1, 36

^a Refer to Table 3 for VOCs in spiking solution.

Table 3. List of VOCs included in this stability study and concentrations (mg/mL) in standard solutions used for spiking water samples.

Compound ^a	Concentration in standard solution (mg/mL)	Compound ^a	Concentration in standard solution (mg/mL)
Acetone	0.2	Dichloropropane, 1,2-	0.2
Acrolein	0.2	Dichloropropene, cis-1,3-	0.212
Acrylonitrile	0.2	Dichloropropene, trans-1,3-	0.188
Benzene	0.2	Ethyl benzene	0.2
Bromodichloromethane	0.2	Hexanone, 2-	0.2
Bromoform	0.2	Methyl iodide	0.2
Bromomethane ^b	2.0	Methylene chloride	0.2
Butanone, 2-	0.2	Pentanone, 4-methyl-2-	0.2
Butene, trans-1,4-dichloro-2-	0.2	Styrene	0.2
Carbon disulfide	0.2	Tetrachloroethane, 1,1,2,2-	0.2
Carbon tetrachloride	0.2	Tetrachloroethene	0.2
Chlorobenzene	0.2	Toluene	0.2
Chlorodibromomethane	0.2	Trichloroethane, 1,1,1-	0.2
Chloroethane ^b	2.0	Trichloroethane, 1,1,2-	0.2
Chloroethylvinylether, 2-	0.2	Trichloroethene	0.2
Chloroform	0.2	Trichlorofluoromethane ^b	2.0
Chloromethane ^b	2.0	Trichloropropane, 1,2,3-	0.2
Dibromomethane	0.2	Vinyl acetate	0.2
Dichloroethane, 1,1-	0.2	Vinyl chloride ^b	2.0
Dichloroethane, 1,2-	0.2	Xylene, o-	0.2
Dichloroethene, 1,1-	0.2	Xylene, m-	0.2
Dichloroethene, trans-1,2-	0.2	Xylene, p-	0.2

^aEthanol, ethyl methacrylate, dichlorodifluoromethane and cis-1,4-dichloro-2-butene were included in the spike solutions but were not quantitated. The instrument was not calibrated for these compounds.

^bThese compounds were in the CRS M-5751-M stock solution (Chromatography Research Supplies). The rest of the compounds were in the CRS M-8240B-R stock solution (also from Chromatography Research Supplies).

2.2 Monitoring Microbial Populations in Water Samples

The purpose of acidifying water samples is to reduce or eliminate biodegradation of the analytes during sample storage. To verify the effects of acidification on bacterial activity, microbial populations were monitored in 3 acidified and 3 unacidified samples from sample set W1 (20-ppb spike), as well as in 2 unspiked, unacidified water samples prepared with the same batch of surface water used for samples sets W1 and W2. In addition, microbial growth was observed in 2 unacidified and 2 acidified sewage water samples obtained from the Oak Ridge Sewage Treatment Plant in Oak Ridge, TN. The sewage samples, which were not spiked with VOCs, were added to this component of the study in order to observe acidification effects on samples with very high microbial contents. Samples for microbial monitoring were stored at room temperature at ORNL. At 0, 1, 8, 15, 29, and 36 days after sample preparation, aliquots from these samples were transferred to agar-filled petri-dishes in which colony forming units (CFUs) were counted after at least two days of incubation at 37°C.

3. RESULTS AND DISCUSSION

3.1 Validation of VOC Measurements

Three 5-point (2, 10, 50, 100, 200-ppb) initial calibrations and five continuing calibrations were performed during the stability study. The percent relative standard deviations (%RSD, see Table 4) of the initial response factors were less than 15% for a majority of the compounds, and all of them were less than 30%, with the exception of 2-chloroethylvinylether. Compound quantitation was performed following Sects. 7.3.3 through 7.3.6 of SW846-8260A. For compounds with %RSDs less than 15%, concentrations were calculated from instrument responses as follows:

$$C = \frac{A_x I_s}{A_{IS} R_{IC}} \quad (1)$$

where A_x and A_{IS} are the characteristic ion areas for the target compound and the internal standard, respectively, I_s is the concentration of the internal standard, and R_{IC} is the average response factor obtained from the initial calibration. R_{IC} corresponds to the slope of a line with a zero-intercept that is fitted through the A_{CS}/A_{IS} vs. standard concentration data. A_{CS} is the standard area count for the target compound. For compounds with %RSDs greater than 15% but less than 30%, linear with non-zero intercepts and quadratic calibration curves of area ratio (A_{CS}/A_{IS}) versus concentration were fitted through the calibration data. All multiple correlation coefficient values (r^2) from all the calibration regressions were close to 1 ($r^2 > 0.99$). These calibration curves were then used to calculate sample concentrations from area ratios (A_x/A_{IS}) measured in the samples. Compounds for which calibration curves were constructed are marked in Tables 4 and 5.

Extremely low instrument response to 2-chloroethylvinylether was observed in the acidified calibration standards as well as in the water samples. Matrix acidification using sodium bisulfate had a severe negative impact to 2-chloroethylvinylether, possibly causing it to degrade very rapidly. Because of the inability to obtain a reliable calibration curve for this compound, it has not been included in the subsequent presentation and discussion of stability study results.

Table 4. Results of initial five-point calibrations performed during holding time study.

Volatile organic compound	August 15, 1995 Day 1		August 29, 1995 Day 15		October 23, 1996 Day before Day 71	
	Ave. Response Factor	%RSD	Ave. Response Factor	%RSD	Ave. Response Factor	%RSD
Acetone	0.418	6.5	0.357	6.4	0.297	6.6
Acrolein	0.132	6.1	0.177	16.1 ^b	0.157	2.6
Acrylonitrile	0.283	7.5	0.358	12.3	0.33	5.1
Benzene	1.534	6.9	1.664	10.7	1.803	3.3
Bromodichloromethane	0.769	11.4	0.615	12.3	0.583	7.9
Bromoform	0.444	21.2 ^b	0.388	20.7 ^b	0.295	24.0 ^b
Bromomethane	0.407	10.5	0.453	8.6	0.39	7.4
Butanone, 2-	0.79	7	0.698	9.3	0.59	4.3
Butene, trans-1,4-dichloro-2-	0.493	4.7	0.506	17.9 ^b	0.478	10.2
Carbon disulfide	1.227	8.2	1.736	14.1	2.09	6.4
Carbon tetrachloride	0.79	9.7	0.602	12.3	0.481	9.4
Chlorobenzene	1.11	7.6	1.168	13.6	1.091	11.4
Chloroethane	0.431	13.7	0.49	6.8	0.438	4.5
Chloroethylvinylether, 2-	0.074	128.3 ^c	0.077	56.7 ^c	0.002	NC ^c
Chloroform (CCC) ^a	1.27	5.7	1.085	8.3	1.213	3.9
Chloromethane	0.895	8	0.889	12.8	1.128	10
Dibromochloromethane	0.525	17.1 ^b	0.525	16.9 ^b	0.432	17.4 ^b
Dibromomethane	0.342	6.4	0.29	12.4	0.289	8.4
Dichloroethane, 1,1-	1.355	6.6	1.327	8.8	1.458	4.3
Dichloroethane, 1,2-	1.123	6	0.782	8.7	0.689	3.2
Dichloroethene, 1,1- (CCC) ^a	0.385	6.5	0.491	8.8	0.562	3.8
Dichloroethene, trans-1,2-	0.447	5.7	0.549	9	0.632	4.5
Dichloropropane, 1,2- (CCC) ^a	0.567	7.3	0.578	14.2	0.61	6.7
Dichloropropene, cis-1,3-	0.874	8.7	0.783	13.2	0.805	8.7
Dichloropropene, trans-1,3-	0.921	7.6	0.736	13.3	0.731	9.1
Ethylbenzene (CCC) ^a	2.067	9.2	2.17	14.7	2.01	9.9
Hexanone, 2-	0.715	13.1	0.714	12	0.606	16.6 ^b
Methyl iodide	0.61	5	0.642	9.7	0.69	3.8
Methylene chloride	0.491	5	0.629	6.4	0.711	3
Pentanone, 4-Methyl-2-	0.265	8.7	0.247	12.3	0.25	13.5

^a Calibration check compounds (CCCs) as specified in EPA-SW846 Method 8260A [EPA, 1994].

^b For %RSD>15%, calibration curves constructed from area ratio vs std. concentration data were used to calculate sample concentrations, instead of average response factors.

^c Instrument response to 2-chloroethylvinylether in acidified water samples was extremely low. Analytical data for this compound not considered valid. NC = not calculated.

*** continued ***

Table 4 (continued). Results of initial five-point calibrations performed during holding time study.

Volatile organic compound	August 15, 1995		August 29, 1995		October 23, 1996	
	Day 1		Day 15		Day before Day 71	
	Ave. Response Factor	%RSD	Ave. Response Factor	%RSD	Ave. Response Factor	%RSD
Styrene	1.239	9.8	1.187	18.0 ^b	1.177	17.4 ^b
Tetrachloroethane, 1,1,2,2-	0.942	8.7	1.261	15.4 ^b	1.331	8.8
Tetrachloroethene	0.514	7.6	0.58	15.2 ^b	0.458	14
Toluene (CCC) ^a	1.045	5.4	0.922	13.3	1.003	7.8
Trichloroethane, 1,1,1-	1.227	6.8	0.883	11.3	0.925	7.9
Trichloroethane, 1,1,2-	0.406	6.8	0.364	11.3	0.37	7
Trichloroethene	0.487	5.4	0.443	12.6	0.434	7.6
Trichlorofluoromethane	1.009	7.8	0.775	8.6	0.739	4.4
Trichloropropane, 1,2,3-	0.308	9.6	0.356	9.5	0.329	6.4
Vinyl acetate	1.132	3.2	1.026	11.8	0.832	6.3
Vinyl chloride (CCC) ^a	2.091	10.9	0.723	14.9	0.536	11.5
Xylene, m,p- ^c	0.725	8.4	0.756	20.3 ^b	0.735	14.6
Xylene, o-	0.731	8.3	0.724	18.4 ^b	0.722	14.8
(Surrogates)						
1,2-Dichloroethane-d4	1.147	7.9	0.740	10.5	0.858	4.4
Toluene-d8	1.400	4.9	1.352	11.6	1.383	5.6
4-Bromofluorobenzene	0.691	12.7	0.622	13.2	0.642	13.2
1,2-Dichlorobenzene-d4	0.962	5.4	1.063	11.3	1.117	8.1

^a Calibration check compounds (CCCs) as specified in EPA-SW846 Method 8260A [EPA, 1994].

^b For %RSD>15%, calibration curves constructed from area ratio vs std. concentration data were used to calculate sample concentrations, instead of average response factors.

^c m- and p- xylene were not chromatographically separated.

ARI ran a continuing calibration every 12-hours, following specifications in SW846-8260A (see Table 5 for results). According to this method, the initial calibration can be considered valid if the %drift (%D) of the calibration check standard is within $\pm 20\%$ for the calibration check compounds (CCC). %D is calculated as follows:

$$\%D = \frac{C_I - C_c}{C_I} \times 100 \quad (2)$$

where C_I is the calibration check standard concentration (50 ppb) and C_c is the measured concentration. The calculated %D for the CCCs were within $\pm 20\%$ for all the continuing calibrations, although %D for a few other compounds exceeded $\pm 20\%$ (see Table 5). As a precaution against including invalid measurements in the stability data set, the analysis results for any compound on a given day were eliminated from the data set when the %D for that compound in that day's continuing calibration was outside $\pm 20\%$.

Laboratory control samples were analyzed on each day of the stability study as an additional check on quality control. These laboratory control samples were prepared by ARI analysts from acidified reagent-water spiked to 50 ppb (250 ppb for acrolein) on the same day of analysis, using stock solutions separate from those used in the calibration standards. Percentage recoveries were predominantly between 85 and 115% [see Table 6(a) and (b)]. *Vinyl acetate* recoveries were consistently greater than 150%, indicating that quantitation of this compound in the stability samples may not be reliable. As in the calibration standards, response for *2-chloroethyvinylether* was extremely low leading to inconsistent measurements in the laboratory control samples. Occasionally low recoveries were also noted for the most volatile compounds (e.g., *chloromethane*, *vinyl chloride*, *chloroethane*) as well as for the poorly purgeable analytes (e.g., *acrolein* and the ketones).

Additional quality control data are contained in the appendices. These include: 4-bromoflourobenzene checks, system performance checks, internal standard area summaries, surrogate recoveries, and method blanks.

Table 5. Results of continuing calibration checks performed during holding time study.

Initial Calibration Date----->	Day 8		Day 22		Day 29		Day 36		Day 71	
	Aug. 22, 1995 (Aug. 15, 1995)		Sept. 5, 1995 (Aug. 29, 1995)		Sept. 12, 1995 (Aug. 29, 1995)		Sept. 19, 1995 (Aug. 29, 1995)		Oct. 24, 1995 (Oct. 23, 1995)	
Volatile organic compound	Check Std. Conc.	%D	Check Std. Conc.	%D	Check Std. Conc.	%D	Check Std. Conc.	%D	Check Std. Conc.	%D
Acetone	37.1	25.8	39.1	21.8	40.1	19.9	38.8	22.4	49	2
Acrolein	36.4	27.3	39.9 ^a	20.2	39.0 ^a	22	35.6 ^a	28.8	51.9	-3.8
Acrylonitrile	35.5	29	40.8	18.4	41.6	16.8	36.6	26.8	51.5	-3
Benzene	48	3.9	48.1	3.8	47.4	5.1	44.5	11	49.1	1.8
Bromodichloromethane	46.4	7.2	51.5	-3.1	51.5	-2.9	49.8	0.5	48	3.9
Bromoform	50	0	50.8 ^a	-1.6	47.5 ^a	5	49.5 ^a	1	52.7 ^a	-5.4
Bromomethane	36.9	26.3	49.8	0.4	46.1	7.7	46.4	7.3	59	-17.9
Butanone, 2-	31.6	36.7	40.5	18.9	39	21.9	37	26.1	46.1	7.8
Butene, trans-1,4-dichloro-2-	39.1	21.7	45.4 ^a	9.2	48.4 ^a	3.2	43.7 ^a	12.6	45.8	8.4
Carbon disulfide	48.8	2.4	53.1	-6.3	52.5	-5.1	42.9	14.2	51.2	-2.4
Carbon tetrachloride	52.8	-5.6	53	-6	51.7	-3.3	52.8	-5.6	48	4
Chlorobenzene	50	0.1	47.1	5.8	44.6	10.9	44.2	11.6	48.3	3.5
Chloroethane	32.1	35.7	50.5	-1	47	5.9	46.7	6.5	61.9	-23.7
Chloroethylvinylether, 2- ^b	28.4	43.2	64.3	-28.6	29.9	40.3	41.6	16.9	60.3	-20.6
Chloroform (CCC)	42.8	14.3	50.5	-1	49.7	0.6	47.2	5.6	48.8	2.5
Chloromethane	30.1	39.8	50.2	-0.4	44.7	10.6	48.1	3.7	49.7	0.6
Dibromochloromethane	49.7 ^a	0.6	50.4 ^a	-0.8	48.1 ^a	3.8	48.6 ^a	2.8	50.4 ^a	-0.8
Dibromomethane	46.9	6.1	48.3	3.4	48.6	2.8	46.7	6.6	47.1	5.9
Dichloroethane, 1,2-	45.4	9.2	50.3	-0.6	48.3	3.5	49.1	1.8	47.8	4.5
Dichloroethane, 1,1-	40.7	18.7	46.8	6.4	46.8	6.5	43.7	12.5	50	0
dichloroethene, trans-1,2-	49.6	0.9	49	2	48.5	3.1	44.4	11.3	49.8	0.5
Dichloroethene, 1,1- (CCC)	48.3	3.4	50.1	-0.2	47.8	4.5	45.6	8.8	52.9	-5.9
Dichloropropane, 1,2- (CCC)	41.2	17.6	46.2	7.6	45.6	8.8	42	16.1	48.1	3.8
Dichloropropene, cis-1,3-	42.3	15.3	49.4	1.1	48.3	3.4	45.1	9.8	48.1	3.7
Dichloropropene, trans-1,3-	41.3	17.5	50.2	-0.4	48.9	2.2	48	4.1	47.6	4.8
Ethylbenzene (CCC)	47.7	4.6	47.5	5.1	44.6	10.8	43.7	12.6	50.5	-1
Hexanone, 2-	39.8	20.4	44.5	11.1	43.4	13.2	41.6	16.8	46.6 ^a	6.8
Methyl iodide	48.4	3.1	45.9	8.3	57.9	-15.9	55.7	-11.4	49.6	0.9
Methylene chloride	47.4	5.3	49	1.9	49.8	0.5	44.9	10.2	50.9	-1.8
Pentanone, 4-methyl-2-	38.3	23.4	47	6.1	47.8	4.5	43.3	13.4	48.4	3.2

^a For %RSD>15%, calibration curves constructed from area ratio vs std. concentration data were used to calculate sample concentrations, instead of average response factors.

^b Instrument response to 2-chloroethylvinylether in acidified water samples was extremely low. Analytical data for this compound not considered valid.

*** continued ***

Table 5 (continued). Results of continuing calibration checks performed during holding time study.

Initial Calibration Date----->	Day 8		Day 22		Day 29		Day 36		Day 71	
	Aug. 22, 1995 (Aug. 15, 1995)		Sept. 5, 1995 (Aug. 29, 1995)		Sept. 12, 1995 (Aug. 29, 1995)		Sept. 19, 1995 (Aug. 29, 1995)		Oct. 24, 1995 (Oct. 23, 1995)	
Volatile organic compound	Check Std. Conc. (ppb)	%D	Check Std. Conc. (ppb)	%D	Check Std. Conc. (ppb)	%D	Check Std. Conc. (ppb)	%D	Check Std. Conc.	%D
Styrene	47.6	4.8	47.9 ^a	4.2	44.7 ^a	10.6	44.4 ^a	11.2	50.1 ^a	-0.2
Tetrachloroethane, 1,1,2,2-	45.1	9.8	45.0 ^a	10	46.8 ^a	6.4	42.7 ^a	14.6	46.9	6.2
Tetrachloroethene	57.1	-14.2	48.1	3.8	43.5	13	46.3	7.4	47.8	4.4
Toluene (CCC)	44	12	48.3	3.4	46.7	6.6	44.5	11.1	47.8	4.5
Trichloroethane, 1,1,1-	44.4	11.2	52.1	-4.2	50.9	-1.8	48.8	2.5	47.7	4.5
Trichloroethane, 1,1,2-	44.3	11.3	48.6	2.7	47.3	5.5	46	8	47.6	4.9
Trichloroethene	47.9	4.1	49.7	0.7	47.9	4.3	46.4	7.2	46.8	6.5
Trichlorofluoromethane	52.7	-5.5	55.2	-10.3	44.4	11.2	53.4	-6.8	55.2	-10.4
Trichloropropane, 1,2,3-	47.9	4.2	45.2	9.6	47.3	5.3	46.5	7	45.9	8.2
Vinyl acetate	36.1	27.7	45	9.9	43.7	12.7	38.8	22.3	48	4
Vinyl chloride (CCC)	47.1	5.9	56.8	-13.7	52.2	-4.4	59.4	-18.8	51.5	-3
Xylene, m,p- ^b	101.7	-1.7	96.3 ^a	3.7	88.8 ^a	11.2	89.0 ^a	11	98	2
Xylene, o- (Surrogates)	49.1	1.8	48.4 ^a	3.2	44.3 ^a	11.4	44.3 ^a	11.4	48.3	3.5
1,2-Dichloroethane-d4	35.7	28.6	46.1	7.7	46.6	6.9	46.2	7.6	43.5	12.9
Toluene-d8	41.4	17.1	44.2	11.6	43.7	12.6	43.5	13.1	43.9	12.3
4-Bromofluorobenzene	41.8	16.4	44.6	10.8	43.0	14.0	45.5	9.0	43.7	12.6
1,2-Dichlorobenzene-d4	48.0	4.1	44.0	11.9	44.7	10.6	43.7	12.6	42.0	16.0

^a For %RSD>15%, calibration curves constructed from area ratio vs std. concentration data were used to calculate sample concentrations, instead of average response factors.

^b Combined spiked concentration of m- and p-xylene was 100 ppb.

Table 6a. Analysis of laboratory control samples for Days 1, 8, 15 and 22 of holding time study. Samples were prepared from reagent water, acidified with 250 mg NaHSO₄ per 40-mL sample, and spiked to 50 ppb with target VOCs, except for acrolein (250 ppb).

Volatile organic compound	August 15, 1995; Day 1		August 22, 1995; Day 8		August 29, 1995; Day 15		September 5, 1995; Day 22	
	Conc. (ppb)	%Rec. ^a	Conc. (ppb)	%Rec. ^a	Conc. (ppb)	%Rec. ^a	Conc. (ppb)	%Rec. ^a
Acetone	52.1	104%	35.4	71%	47.5	95%	38.1	76%
Acrolein	264.9	106%	178.7	71%	211.1	84%	191.2	76%
Acrylonitrile	51.9	104%	36.4	73%	48.7	97%	45.2	90%
Benzene	51.7	103%	45.3	91%	47.5	95%	43.1	86%
Bromodichloromethane	54.3	109%	45.8	92%	47.9	96%	48	96%
Bromoform	50.9	102%	50.9	102%	48.4	97%	51	102%
Bromomethane	48.9	98%	30.7	61%	48.5	97%	39.8	80%
Butanone, 2-	42.7	85%	29.2	58%	41.6	83%	37.4	75%
Butene, trans-1,4-dichloro2-	41.8	84%	31	62%	37.7	75%	38.9	78%
Carbon disulfide	52.2	104%	45.5	91%	39.7	79%	46.5	93%
Carbon tetrachloride	56.2	112%	50.3	101%	49.1	98%	48	96%
Chlorobenzene	53.2	106%	51.2	102%	48.2	96%	44.3	89%
Chloroethane	50.3	101%	27.4	55%	51.5	103%	39.9	80%
Chloroethylvinylether, 2- ^b	nd	NC	6.2	12%	12.7	25%	18.1	36%
Chloroform	54	108%	43.1	86%	48.7	97%	46.9	94%
Chloromethane	54.4	109%	25.5	51%	55.5	111%	33.2	66%
Dibromochloromethane	49.9	100%	50.9	102%	47.3	95%	48.2	96%
Dibromomethane	55.6	111%	46.5	93%	48.2	96%	46.5	93%
Dichloroethane, 1,2-	54.2	108%	43.9	88%	48.8	98%	46.3	93%
Dichloroethane, 1,1-	54.2	108%	38.7	77%	49	98%	42.6	85%
dichloroethene, trans-1,2-	53.2	106%	46.5	93%	48.3	97%	42.7	85%
Dichloroethene, 1,1-	51.9	104%	43	86%	48.3	97%	42.4	85%
Dichloropropane, 1,2-	54.1	108%	41.2	82%	49.8	100%	44.3	89%
Dichloropropene, cis-1,3-	54.1	108%	40.6	81%	48.3	97%	45.2	90%
Dichloropropene, trans 1,3-	53.5	107%	39.9	80%	48.4	97%	46.5	93%
Ethylbenzene	54.7	109%	48.3	97%	48	96%	44.6	89%
Hexanone, 2-	47.9	96%	40.9	82%	47.6	95%	47.7	95%
Methyl iodide	53.6	107%	47.2	94%	48.2	96%	43.5	87%
Methylene chloride	53.7	107%	45.6	91%	48.6	97%	43.5	87%
Pentanone, 4-methyl-2-	51.2	102%	37.2	74%	49.1	98%	48.1	96%
Styrene	52	104%	47.7	95%	47.2	94%	44.1	88%
Tetrachloroethane, 1,1,2,2-	54	108%	45.5	91%	47.5	95%	44.8	90%
Tetrachloroethene	55.2	110%	57.8	116%	48	96%	45.9	92%
Toluene	52.1	104%	42.8	86%	46.8	94%	44	88%
Trichloroethane, 1,1,1-	54.2	108%	42.7	85%	47.4	95%	46.7	93%
Trichloroethane, 1,1,2-	54.5	109%	43.5	87%	48.5	97%	45.9	92%
Trichloroethene	53.9	108%	45.9	92%	47.7	95%	44.5	89%
Trichlorofluoromethane	57.2	114%	46.6	93%	50.5	101%	44	88%
Trichloropropane, 1,2,3-	55.6	111%	47.7	95%	47.5	95%	44.8	90%
Vinyl acetate	102.6	205%	65.2	130%	85.9	172%	84.5	169%
Vinyl chloride	55.6	111%	35.3	71%	67.2	134%	42.1	84%
Xylene, m,p- b	105.1	105%	101.8	102%	95.6	96%	89.1	89%
Xylene, o-	53	106%	50.7	101%	47.7	95%	45.2	90%

^a %Recovery = (Measured concentration in ppb/spike concentration in ppb)*100% .

^b Instrument response to 2-chloroethylvinylether in acidified water samples was extremely low. Analytical data for this compound not considered valid. nd = not detected. NC = not calculated.

Table 6b. Analysis of laboratory control samples for Days 29, 36, and 71 of holding time study. Samples were prepared from reagent water, acidified with 250 mg NaHSO₄ per 40-mL sample, and spiked to 50 ppb with target VOCs, except for acrolein (250 ppb).

Compound	September 12, 1995; Day 29		September 19, 1995; Day 36		October 24, 1995; Day 71	
	Conc. (ppb)	%Rec. ^a	Conc. (ppb)	%Rec. ^a	Conc. (ppb)	%Rec. ^a
Acetone	38.4	77%	38.4	77%	42.9	86%
Acrolein	174.8	70%	168.8	68%	244	98%
Acrylonitrile	44.1	88%	40.9	82%	50.7	101%
Benzene	48.8	98%	44.7	89%	50.9	102%
Bromodichloromethane	51.7	103%	51.6	103%	51.3	103%
Bromoform	51.8	104%	49.8	100%	51.9	104%
Bromomethane	47.8	96%	41.8	84%	44.2	88%
Butanone, 2-	35.8	72%	34.2	68%	43.3	87%
Butene, trans-1,4-dichloro-2-	39.3	79%	37.5	75%	37.2	74%
Carbon disulfide	45.7	91%	40.2	80%	43.6	87%
Carbon tetrachloride	53.1	106%	54.3	109%	50.3	101%
Chlorobenzene	48.1	96%	45.1	90%	50.8	102%
Chloroethane	50.8	102%	43.7	87%	50	100%
Chloroethylvinylether,2-b	9.5	19%	8.5	17%	0	0%
Chloroform	53.1	106%	48.7	97%	50.7	101%
Chloromethane	55.5	111%	43.7	87%	47	94%
Dibromochloromethane	49.4	99%	48.7	97%	50.3	101%
Dibromomethane	50.6	101%	48.6	97%	51.1	102%
Dichloroethane, 1,2-	50.3	101%	51.8	104%	49.9	100%
Dichloroethane,1,1-	49.8	100%	45.1	90%	51.9	104%
dichloroethene, trans-1,2-	49.6	99%	44.7	89%	51.7	103%
Dichloroethene,1,1-	48.1	96%	43.8	88%	50.4	101%
Dichloropropane, 1,2-	50.7	101%	44.5	89%	52.2	104%
Dichloropropene,cis-1,3-	52	104%	46.3	93%	50.8	102%
Dichloropropene,trans-1,3-	52.6	105%	47.6	95%	50.7	101%
Ethylbenzene	47.7	95%	45.5	91%	52.2	104%
Hexanone,2-	43.3	87%	42.8	86%	43.6	87%
Methyl iodide	58.8	118%	57.7	115%	45.5	91%
Methylene chloride	48.7	97%	45	90%	50.5	101%
Pentanone,4-methyl-2-	46.7	93%	41.8	84%	45.8	92%
Styrene	47.7	95%	44.9	90%	49.9	100%
Tetrachloroethane, 1,1,2,2-	47.6	95%	43.4	87%	51.9	104%
Tetrachloroethene	47.5	95%	46.2	92%	50.7	101%
Toluene	49	98%	43.7	87%	50.3	101%
Trichloroethane, 1,1,1-	53.4	107%	49.2	98%	50.8	102%
Trichloroethane,1,1,2-	50.5	101%	46.5	93%	52.1	104%
Trichloroethene	50.2	100%	49.1	98%	51.5	103%
Trichlorofluoromethane	47	94%	50.7	101%	49	98%
Trichloropropane, 1,2,3-	47.6	95%	43.4	87%	51.5	103%
Vinyl acetate	83.3	167%	77.2	154%	98	196%
Vinyl chloride	64.9	130%	56.3	113%	45.6	91%
Xylene, m,p-	93.9	94%	91	91%	100.9	101%
Xylene, o-	47.3	95%	46	92%	50.3	101%

^a %Recovery = (Measured concentration in ppb/spike concentration in ppb)*100% .

^b Instrument response to 2-chloroethylvinylether in acidified water samples was extremely low. Analytical data for this compound not considered valid. nd = not detected. NC = not calculated.

3.2 Trends in VOC Concentration vs Pre-analytical Holding Time

Regression lines were fitted to the data for concentration vs analysis day from samples sets W1 (20 ppb spike, Table 7) and W2 (200 ppb spike, Table 8). Graphs of concentration vs pre-analytical holding time are given in the Appendix G. Measurement variability [i.e., relative measurement error (%RME)] for each compound within each sample set was estimated as follows:

$$\%RME = \frac{S_o \times 100\%}{C_o}, \quad (3)$$

where S_o is the square root of the mean-square error for the linear regression residuals, and C_o is the extrapolated concentration on Day 0 (the regression intercept). Calculated values for %RME were predominantly less than 15% in both sets W1 and W2, with values being lower in set W1 (20 ppb spike). These low values indicate that scatter in the data was generally minimal, and that concentration trends with time were less likely masked by measurement variability. Such masking of concentration trends may have occurred with *vinyl chloride*, which exhibited the highest %RME in both sample sets (43% and 33%). Changes in *vinyl chloride* concentration with time, which were found statistically insignificant, may have been confounded by large measurement variability. However, a statistically significant negative slope was observed in *vinyl acetate* in both sets W1 and W2, despite a relatively large %RME (21% and 29%). For this compound, the concentration change with time was large enough to offset the masking effects of data scatter.

A large number of VOCs exhibited slopes that were not significantly negative (e.g., these VOCs were not decreasing with pre-analytical holding time, see Tables 7 and 8). For some compounds with significantly negative slopes, changes in concentration after 28 days of storage as predicted by the regression lines (last column in Tables 7 and 8) were predominantly low relative to the initial concentrations (estimated from the regression intercept). Analytes also appeared to be more stable in sample set W1, indicated by the smaller number of compounds with statistically-significant negative slopes (Table 7). Out of 44 analytes, concentration changes exceeded 10% for only three compounds in set W1 [*vinyl acetate* (42%), *cis-1,3-dichloropropene* (11%), and *trans-1,4-dichloro-2-butene* (20%)]. Concentration changes exceeded 10% for a larger number of compounds in set W2, including *trichlorofluoromethane* (15%), *acrolein* (25%), *carbon disulfide* (17%),

vinyl acetate (42%), *cis*-1,3-dichloropropene (14%), *trans*-1,3-dichloropropene (12%), tetrachloroethene (16%), and *trans*-1,2-dichloro-2-butene (26%).

Table 7. Summary of linear regression on stability data from sample set W1 (20 ppb spike).

Volatile organic compound	No. of data points ^a	Regression parameters		Significant Negative Slope (1-sided 5% significance)	Relative Meas. Error ^d	Change in conc. at 28 days ^e (ppb)	%Change in conc. at 28 days ^f
		Intercept ^b (ppb)	Slope ^c (ppb/day)				
Acetone	16	21.2	0.0124	NO	10%	—	—
Acrolein ^g	—	—	—	—	—	—	—
Acrylonitrile	20	18.8	0.0336	NO	10%	—	—
Benzene	28	16.1	0.0033	NO	5%	—	—
Bromodichloromethane	28	17.1	0.0140	NO	7%	—	—
Bromoform	28	19	0.0201	NO	10%	—	—
Bromomethane	24	15.9	-0.0221	YES	5%	-0.6	-4%
Butanone, 2-	16	16.3	0.0566	NO	9%	—	—
Butene, <i>trans</i> -1,4-dichloro-2-	24	8.4	-0.0600	YES	16%	-1.7	-20%
Carbon disulfide	28	15.2	-0.0501	YES	6%	-1.4	-9%
Carbon tetrachloride	28	16.6	-0.0168	YES	6%	-0.5	-3%
Chlorobenzene	28	16.8	-0.0134	YES	5%	-0.4	-2%
Chloroethane	24	18.2	0.0278	NO	6%	—	—
Chloroform	28	18	0.0056	NO	6%	—	—
Chloromethane	24	10.9	-0.0201	YES	7%	-0.6	-5%
Dibromochloromethane	28	21.3	-0.0231	NO	7%	—	—
Dibromomethane	28	18.8	0.0028	NO	4%	—	—
Dichloroethane, 1,2-	28	17.9	0.0114	NO	6%	—	—
Dichloroethane, 1,1-	28	16.6	0.0153	NO	8%	—	—
dichloroethene, <i>trans</i> -1,2-	28	15.6	-0.0211	YES	5%	-0.6	-4%
Dichloroethene, 1,1-	28	15.5	-0.0187	YES	5%	-0.5	-3%
Dichloropropane, 1,2-	28	16.6	0.0227	NO	7%	—	—
Dichloropropene, <i>cis</i> -1,3-	28	14.8	-0.0587	YES	7%	-1.6	-11%
Dichloropropene, <i>trans</i> -1,3-	28	14.9	-0.0497	YES	8%	-1.4	-9%
Ethylbenzene	28	15.4	-0.0135	YES	5%	-0.4	-2%
Hexanone, 2-	24	17.5	0.0408	NO	7%	—	—
Methyl iodide	28	19.8	-0.0123	NO	8%	—	—
Methylene chloride	28	17.5	-0.0007	NO	5%	—	—

^a Some data points were eliminated due to aborted analyses or unsatisfactory calibration (%D outside of $\pm 20\%$ limits).

^b Intercept of regression line corresponds to extrapolated Day 0 concentration.

^c Slope of regression line corresponds to change in concentration per day.

^d Estimated by $S_o/C_o \times 100\%$ where S_o^2 and C_o are the mean squared error and the intercept of the regression line, respectively.

^e Calculated from the regression line.

^f Percent change relative to the intercept of the regression line (extrapolated Day 0 concentration).

^g Spike level in sample set W1 below detection limit for acrolein (50 ppb).

*** continued ***

Table 7 (continued). Summary of linear regression on stability data from sample set W1
(20 ppb spike).

Volatile organic compound	No. of data points ^a	Regression parameters		Significant Negative Slope (1-sided 5% significance)	Relative Meas. Error ^d	Change in conc. at 28 days ^e (ppb)	%Change in conc. at 28 days ^f
		Intercept ^b (ppb)	Slope ^c (ppb/day)				
Pentanone, 4-methyl-2-	24	18.3	0.0082	NO	7%	—	—
Styrene	28	17.7	0.0099	NO	12%	—	—
Tetrachloroethane, 1,1,2,2	28	17.5	0.0052	NO	5%	—	—
Tetrachloroethene	28	18.1	-0.0654	YES	9%	-1.8	-10%
Toluene	28	15.2	-0.0005	NO	6%	—	—
Trichloroethane, 1,1,1-	28	15.6	0.0034	NO	8%	—	—
Trichloroethane, 1,1,2-	28	18	0.0079	NO	6%	—	—
Trichloroethene	28	16.9	-0.0103	NO	5%	—	—
Trichlorofluoromethane	28	27.9	-0.0778	YES	6%	-2.2	-8%
Trichloropropane, 1,2,3-	28	19.9	0.0001	NO	4%	—	—
Vinyl acetate	20	23.5	-0.3486	YES	21%	-9.8	-42%
Vinyl chloride	24	10.9	0.0915	NO	43%	—	—
Xylene, m,p-	28	37.4	-0.0752	YES	10%	-2.1	-6%
Xylene, o-	28	18.7	-0.0268	NO	11%	—	—

^a Some data points were eliminated due to aborted analyses or unsatisfactory calibration (%D outside of $\pm 20\%$ limits).

^b Intercept of regression line corresponds to extrapolated Day 0 concentration.

^c Slope of regression line corresponds to change in concentration per day.

^d Estimated by $S_o/C_o \times 100\%$ where S_o^2 and C_o are the mean squared error and the intercept of the regression line, respectively.

^e Calculated from the regression line.

^f Percent change relative to the intercept of the regression line (extrapolated Day 0 concentration).

Table 8. Summary of linear regression on stability data from sample set W2 (200 ppb spike).

Volatile organic compound	No. of data points ^a	Regression parameters		Significant negative slope (1-sided 5% significance)	Relative meas. error ^d	Change in conc. at 28 days ^e (ppb)	%Change in conc. at 28 days ^f
		Intercept ^b (ppb)	Slope ^c (ppb/day)				
Acetone	16	194.5	-0.2472	NO	9%	—	—
Acrolein	12	37.9	-0.3371	YES	6%	-9.4	-25%
Acrylonitrile	19	202.9	-0.0034	NO	8%	—	—
Benzene	27	177.7	-0.2523	NO	10%	—	—
Bromodichloromethane	27	200.8	-0.2503	YES	8%	-7	-3%
Bromoform	27	184.3	-0.4126	YES	5%	-11.6	-6%
Bromomethane	23	157.1	-0.5205	YES	9%	-14.6	-9%
Butanone, 2-	15	175.1	0.1160	NO	7%	—	—
Butene,trans-1,4-dichloro-2-	23	71.8	-0.6622	YES	4%	-18.5	-26%
Carbon disulfide	27	200.8	-1.2258	YES	8%	-34.3	-17%
Carbon tetrachloride	27	199	-0.6786	YES	13%	-19	-10%
Chlorobenzene	27	182	-0.3897	YES	9%	-10.9	-6%
Chloroethane	23	189	-0.4214	YES	10%	-11.8	-6%
Chloroform	27	194	-0.3069	YES	10%	-8.6	-4%
Chloromethane	23	115.1	-0.4242	YES	11%	-11.9	-10%
Dibromochloromethane	27	188.2	-0.4348	YES	5%	-12.2	-6%
Dibromomethane	27	215.9	-0.0654	NO	9%	—	—
Dichloroethane, 1,2-	27	190.7	-0.1154	NO	10%	—	—
Dichloroethane,1,1-	27	186.4	-0.2999	NO	11%	—	—
dichloroethene, trans-1,2-	27	176.5	-0.5698	YES	9%	-16	-9%
Dichloroethene,1,1-	27	178.8	-0.6263	YES	11%	-17.5	-10%
Dichloropropane, 1,2-	27	194.7	-0.0645	NO	11%	—	—
Dichloropropene,cis-1,3-	27	172.2	-0.8444	YES	9%	-23.6	-14%
Dichloropropene,trans1,3-	27	173.8	-0.7595	YES	10%	-21.3	-12%
Ethylbenzene	27	171.7	-0.4825	YES	10%	-13.5	-8%
Hexanone,2-	23	216.1	-0.7084	YES	4%	-19.8	-9%
Methyl iodide	27	244.1	-0.5562	YES	12%	-15.6	-6%
Methylene chloride	27	179.3	-0.1591	NO	9%	—	—

^a Some data points were eliminated due to aborted analyses or unsatisfactory calibration (%D outside of $\pm 20\%$ limits).

^b Intercept of regression line corresponds to extrapolated Day 0 concentration.

^c Slope of regression line corresponds to change in concentration per day.

^d Estimated by $S_o/C_o \times 100\%$ where S_o^2 and C_o are the mean squared error and the intercept of the regression line, respectively.

^e Calculated from the regression line.

^f Percent change relative to the intercept of the regression line (extrapolated Day 0 concentration).

*** continued ***

Table 8 (continued). Summary of linear regression on stability data from sample set W2 (200 ppb spike).

Volatile organic compound	No. of data points ^a	Regression parameters		Significant Negative Slope (1-sided 5% significance)	Relative Meas. Error ^d	Change in conc. at 28 days ^e (ppb)	%Change in conc. at 28 days ^f
		Intercept ^b (ppb)	Slope ^c (ppb/day)				
Pentanone,4-methyl-2-	23	210.6	-0.0675	NO	5%	—	—
Styrene	27	174.7	-0.6391	YES	5%	-17.9	-10%
Tetrachloroethane,1,1,2,2	27	169.7	-0.1062	NO	7%	—	—
Tetrachloroethene	27	166.5	-0.9265	YES	8%	-25.9	-16%
Toluene	27	178.6	-0.1996	NO	16%	—	—
Trichloroethane, 1,1,1-	27	182.3	-0.5152	YES	12%	-14.4	-8%
Trichloroethane,1,1,2-	27	194.5	0.0947	NO	10%	—	—
Trichloroethene	27	193.7	-0.5018	YES	11%	-14.1	-7%
Trichlorofluoromethane	27	273.3	-1.5012	YES	11%	-42	-15%
Trichloropropane, 1,2,3-	27	219.1	-0.4670	YES	4%	-13.1	-6%
Vinyl acetate	19	235.4	-3.5267	YES	19%	-98.7	-42%
Vinyl chloride	23	144	-0.0040	NO	33%	—	—
Xylene, m,p-	27	343.6	-1.1289	YES	7%	-31.6	-9%
Xylene, o-	27	172.2	-0.4257	YES	6%	-11.9	-7%

^a Some data points were eliminated due to aborted analyses or unsatisfactory calibration (%D outside of $\pm 20\%$ limits).

^b Intercept of regression line corresponds to extrapolated Day 0 concentration.

^c Slope of regression line corresponds to change in concentration per day.

^d Estimated by $S_o/C_o \times 100\%$ where S_o^2 and C_o are the mean squared error and the intercept of the regression line, respectively.

^e Calculated from the regression line.

^f Percent change relative to the intercept of the regression line (extrapolated Day 0 concentration).

Maximum holding times have been derived from past stability studies using methods prescribed by Bayne et al. [1994], by the Association for Testing Materials [ASTM 1986] or by Prentice and Bender [1987]. All three methods implicitly or explicitly define a significant change in concentration relative to a statistical measure of measurement variability. For example, for a set of concentration vs holding time data through which a regression line has been fitted, ASTM prescribes that the holding time (*HT*) be calculated as follows:

$$HT = t(df, 0.005) \frac{S_{C_o}}{|b|} \quad (4)$$

where *df* is the number of degrees of freedom in the regression, $t(df, 0.005)$ is the 99.5% percentile point of the *t*-distribution, S_{C_o} is the standard deviation of the regression line's

intercept, and b is the regression line's slope. High values for b (large changes in concentration with time) can be offset by large measurement variability (high values for S_{C_0}). On the other hand, very tight measurements can result in short holding times, even if concentration changes are relatively small.

A similar trend was observed for the "practical reporting time" method described by Bayne et al. (1993, 1994). Using this approach, the "practical reporting time" or PRT is calculated based on a statistical definition of when a "significant change" in VOC concentration has occurred. The concept is illustrated in Fig. 1 using a linear model for concentration vs. holding time, and assuming that measurement variation follows a normal distribution. In this approach, a critical concentration C_{crit} is determined at time 0 of the stability study; it is the concentration at which there is only a 5% risk due to measurement variability that the measured value will be less than this concentration. At increasing holding times, the risk that the measured concentration will be below C_{crit} increases (see Fig. 1). By definition, a "significant change" has occurred when the risk of measuring a concentration below C_{crit} increases from 5% to 15%; this point in time is referred to as the practical reporting time (PRT).

The risk of measuring a concentration below C_{crit} increases very rapidly with increasing pre-analytical holding time for compounds with low measurement variability (e.g., %RME < 10%). This is illustrated in Fig. 2, using the stability data from sample set W2 (200 ppb spike) for styrene and carbon tetrachloride. These compounds were selected because the slopes for their respective stability regressions were comparable (0.639 ppb/day for styrene vs 0.679 ppb/day for carbon tetrachloride). However, the variability for the styrene measurements was significantly smaller than the variability in the carbon tetrachloride values ($S_0^2 = 75.48$ and 702.45 for styrene and carbon tetrachloride, respectively). As Fig. 2 shows, the risk of measuring a concentration below C_{crit} increases much more rapidly for styrene. This resulted in a calculated PRT for styrene that is approximately a third of the PRT for carbon tetrachloride, even though the relative change in concentration on the 28th day was 10% for both compounds (see Table 8).

For analytes with low measurement variability, factors other than calculated PRT s were considered in this study when assessing the effects of holding times on measurement validity. Statistical definitions of significant concentration change, on which current methods for calculating holding times are based, must be complemented with "practical"

definitions of "acceptable" concentration change. Ideally, specifications for "acceptable" concentration changes should be tied into the eventual use of the analytical data. For example, "acceptable" concentration changes for analytical data used in quantitative risk assessments can be determined by the sensitivity of the risk assessment results to the input analytical data. Since, the selection of a generic "acceptable" concentration change is beyond the scope of this study, 10% was chosen to assess the holding time effects on compounds in this study. An acceptable change of 10% is reasonable given the other sources of uncertainty in site characterization and health risk assessment for which these analytical data are typically used. Examples of these uncertainty sources include spatial and temporal variability of contaminant concentrations, use of simplified contaminant transport models to approximate exposure pathways, and extrapolation of laboratory toxicity data from animals to humans [Cox and Ricci 1990; NRC 1994].

Table 9 shows the list of VOCs which were found to be functionally stable over a 28-day holding time based on a criterion of <10% concentration change relative to initial values. *PRTs* and *%RMEs* are also shown in this table for compounds exhibiting negative slopes (e.g., decreasing concentration with holding time). The *%RMEs* were included in this table to qualify the value of the calculated *PRT*; compounds with low calculated *PRTs* but with low *%RMEs* were still considered functionally stable if the concentration change on the 28th day is relatively small.

Table 10 shows the VOCs which did not meet the criterion for functional stability. Low *PRTs* were also calculated for these compounds despite *%RMEs* which were predominantly greater than 10%. The analysis of water samples containing these compounds may be negatively impacted by a 28-day holding time. Concentration changes in *vinyl acetate* were the highest and were found to be statistically significant despite the relatively large measurement error (19 to 21%, see Tables 7 and 8) observed for this compound. Although the absolute quantitation of *vinyl acetate* in the samples may be problematic due to abnormally high percentage recoveries in the laboratory control samples [Tables 6(a) and (b)], the decreasing trends observed in the stability samples are probably real.

Figure 1. Schematic illustration of practical reporting time analysis of stability data.

Figure 2. Effects of measurement variability on risk of measured concentration being below the critical concentration and calculated maximum holding time.

Table 9. List of functionally stable VOCs based on percentage changes <10% relative to initial levels. Also includes practical reporting times and relative measurement errors.

Compound	%Change in concentration after 28 days ^a		Practical reporting time (days) ^b ; Relative measurement error (%RME)	
	Sample Set W1 (20 ppb spike)	Sample Set W2 (200 ppb spike)	Sample Set W2 (20 ppb spike)	Sample Set W2 (200 ppb spike)
Acetone	N.S. ^c	N.S.	— ^d	—
Acrylonitrile	N.S.	N.S.	—	—
Benzene	N.S.	N.S.	—	—
Bromomethane	N.S.	N.S.	—	—
2-Butanone	N.S.	N.S.	—	—
Dichloroethane, 1,1-	N.S.	N.S.	—	—
Dichloroethane, 1,2-	N.S.	N.S.	—	—
Dichloroethene, 1,1-	N.S.	N.S.	—	—
Dichloropropane, 1,2-	N.S.	N.S.	—	—
Dibromomethane	N.S.	N.S.	—	—
Pentanone, 4-methyl-2-	N.S.	N.S.	—	—
Tetrachloroethane, 1,1,2,2-	N.S.	N.S.	—	—
Toluene	N.S.	N.S.	—	—
Trichloroethane, 1,1,2-	N.S.	N.S.	—	—
Vinyl chloride	N.S.	N.S.	—	—
Bromodichloromethane	N.S.	-3%	—	45, 8%
Bromoform	N.S.	-6%	—	15, 5%
Bromomethane	-4%	-9%	25, 5%	20, 9%
Carbon tetrachloride	-3%	-10%	43, 6%	28, 13%
Chlorobenzene	-2%	-6%	41, 5%	29, 9%
Chloroethane	N.S.	-6%	—	34, 10%
Chloroform	N.S.	N.S.	—	44, 10%
Chloromethane	-5%	-10%	26, 7%	22, 11%
Dibromochloromethane	N.S.	-6%	—	14, 5%
Dichloroethene, trans-1,2-	-4%	-9%	24, 5%	20, 9%
Ethylbenzene	-2%	-8%	40, 5%	26, 10%
2-Hexanone	N.S.	-9%	—	8, 4%
Trichloroethane, 1,1,1-	N.S.	-8%	—	30, 12%
Trichloroethene	N.S.	-7%	—	31, 11%
Trichloropropane, 1,2,3-	N.S.	-6%	—	13, 4%
Methyl iodide	N.S.	N.S.	—	37, 12%
Styrene	N.S.	-10%	—	9, 5%
Xylene, m,p-	N.S.	-9%	36, 10%	15, 7%
Xylene, o-	N.S.	-7%	—	18, 6%

^a Relative change in concentration calculated at 28 days computed from regression line (see Tables 7 and 8).

^b Practical reporting times calculated following method described in [Bayne, 1993; 1994].

^c N.S. = slope of regression line on stability data not significantly negative at a 5% significance level.

^d Practical reporting times were not calculated for compounds with non-significant slopes.

Table 10. List of VOCs with concentration changes at 28 days greater than 10% relative to initial levels. Practical reporting times and relative measurement errors are also included.

Compound	%Change in concentration after 28 days ^a		Practical reporting time (Days); Relative Measurement Error (%RME) ^b	
	Sample Set W1 (20 ppb spike)	Sample Set W2 (200 ppb spike)	Sample Set W2 (20 ppb spike)	Sample Set W2 (200 ppb spike)
Acrolein ^c	—	-25%	—	5, 6%
Butene,trans-1,4-dichloro-2-	-20%	-26%	16, 16%	3, 4%
Carbon disulfide	-9%	-17%	13, 6%	9, 8%
Dichloropropene, cis-1,3-	-11%	-14%	13, 7%	13, 9%
Dichloropropene, trans-1,3-	-9%	-12%	17, 8%	17, 10%
Tetrachloroethene	-10%	-16%	17, 9%	10, 8%
Trichlorofluoromethane	-8%	-15%	16, 6%	15, 11%
Vinyl acetate	-42%	-42%	10, 21%	9, 19%

^a Relative change in concentration calculated at 28 days computed from regression line (see Tables 7 and 8).

^b Practical reporting times calculated following method described in [Bayne, 1993; 1994].

^c Spike level in sample set W1 below detection limit for acrolein (50 ppb).

3.3 Unacidified Samples

The behavior of most VOCs in the unacidified samples was not significantly different from that observed in the acidified samples. This was inferred from comparisons between the measured VOC levels in the unacidified samples to corresponding 95% prediction intervals calculated from the acidified sample data (see Table 11). Since both acidified and unacidified water samples were prepared from the same batch of spiked surface water, the initial VOC levels in both types of samples are expected to be the same, and any differences observed will most likely be due to acidification effects.

Table 11 shows that a majority of the measured VOC levels in the unacidified samples fell within the 95% prediction intervals from the acidified sample analyses. The 95% prediction interval (*P.I.*) is defined as follows:

$$P.I. = C_o + BD \pm t(N-2, 0.025) \sqrt{\text{var}(C_o) + D^2 \text{var}(B) + 2D \text{covar}(C_o, B) + S_o^2} \quad (5)$$

where C_o and B are the intercept and slope from the regression on the acidified stability data, D is the holding time of interest (1 or 35 days), $\text{var}(C_o)$ and $\text{var}(B)$ are the variances of C_o and B , respectively, $\text{covar}(C_o, B)$ is the covariance of C_o and B , $t(N-2, 0.025)$ is the

97.5% point of the t -distribution with $N-2$ degrees of freedom, N is the number of data points in the regression and S_o^2 is the mean squared error of the regression line. Compounds for which analyses of both samples on a given day fell outside the prediction intervals were *acrolein*, *vinyl acetate*, *trichloroethene*, *2-chloroethylvinylether*, and *1,1,2,2-tetrachloroethane*. The adverse effect of acidification on *2-chloroethylvinylether* was already noted earlier (Sect. 3.1). In the Day 1 samples, *acrolein* was higher in the unacidified samples, but this trend was reversed in the Day 36 analyses. Reasons for this trend are unclear; however, it is apparent that *acrolein* is unstable regardless of whether samples are acidified or not. For *vinyl acetate*, the VOC levels in the unacidified samples are consistently below the prediction intervals on Day 1 and Day 36. Acidification seems to have improved the stability of this compound, although the change in concentration at 28 days was >10% for *vinyl acetate* in acidified samples and calculated PRT was only 9 to 10 days (see Table 10).

The levels of 1,1,2,2,-tetrachloroethane in the Day 1 unacidified samples were within the 95% prediction interval from the acidified sample analyses (see Table 11). However, the Day 36 measured concentrations were below what would have been predicted from the acidified data. Haag and Mill [1988] have observed the abiotic neutral and base-catalyzed hydrolysis of 1,1,2,2,-tetrachloroethane, with trichloroethylene as the major by-product of degradation. 1,1,2,2,-Tetrachloroethane may have been undergoing hydrolysis in the unacidified samples; this would be consistent with the observed increase in trichloroethylene levels after 36 days (see Table 11). The reaction may be inhibited under low pH conditions; Haag and Mill [1988] reported a decreasing trend in 1,1,2,2,-tetrachloroethane hydrolysis with decreasing pH. However, their experiments did not include pH values as low as the levels observed in the acidified samples (2.4-2.6).

Table 11. Comparison between prediction intervals from acidified sample analyses and VOC levels in unacidified water sample analyses (set W2, 200 ppb).

	Day 1		Day 1 Unacidified		Day 35 Prediction		Day 35 Unacidified	
	Prediction Interval ^a		Samples ^b		Interval ^a		Samples ^b	
	Lower Limit	Upper Limit	W2-9	W2-35	Lower Limit	Upper Limit	W2-32	W2-36
Acetone	154.9	233.5	213.2	216.2	147.8	223.8	159.1	179.2
Acrolein	32.5	42.6	45.1	48.2	21.2	31.0	20.9	22.8
Acrylonitrile	167.7	238.0	205.2	210.7	168.6	236.9	169.1	191.7
Benzene	137.9	217.1	164.4	173.3	130.1	207.7	188.7	195.8
Bromodichloromethane	165.2	235.9	194.7	205.6	157.4	226.6	214.0	221.9
Bromoform	164.5	203.3	178.0	180.0	150.9	188.9	173.3	184.4
Bromomethane	125.1	188.0	137.8	147.0	108.5	169.3	148.3	157.6
2-Butanone	146.9	203.6	178.4	179.3	151.7	206.7	144.9	164.9
trans-1,4-Dichloro-2-butene	64.5	77.7	70.5	73.4	42.3	55.0	46.2	47.8
Carbon disulfide	164.8	234.3	222.5	235.5	123.9	191.8	172.5	181.1
Carbon tetrachloride	141.4	255.2	184.0	190.1	119.6	230.8	214.5	219.7
Chlorobenzene	147.4	215.8	168.1	172.1	134.9	201.8	182.9	190.8
Chloroethane	145.8	231.4	168.7	172.3	132.9	215.7	176.7	190.7
2-Chloroethylvinylether	N.C. ^c	N.C.	198.0	200.0	N.C.	N.C.	225.0	244.0
Chloroform	151.6	235.7	194.5	206.4	142.1	224.4	196.3	212.4
Chloromethane	86.5	142.9	98.1	103.0	73.0	127.5	102.1	109.8
Dibromochloromethane	169.0	206.6	182.0	191.0	154.6	191.4	179.5	187.9
Dibromomethane	174.9	256.9	205.2	215.3	173.5	253.8	228.0	243.9
1,1-Dichloroethane	142.7	229.5	198.1	210.9	133.5	218.4	180.2	197.7
1,2-Dichloroethane	150.7	230.4	188.0	196.9	147.6	225.6	206.2	217.0
1,1-Dichloroethene	134.2	222.1	178.2	184.1	113.9	199.9	171.5	183.4
trans-1,2-dichloroethene	141.0	210.9	177.4	185.2	122.3	190.8	165.9	175.6
1,2-Dichloropropane	149.8	239.4	188.0	200.9	148.5	236.3	207.3	219.0
cis-1,3-Dichloropropene	137.3	205.5	172.0	183.9	109.4	176.0	154.2	160.5
trans-1,3-Dichloropropene	134.3	211.8	177.1	185.9	109.3	185.1	164.0	171.7
Ethylbenzene	133.3	209.2	156.7	159.8	117.7	192.0	171.3	177.4
2-Hexanone	198.2	232.7	213.3	212.4	174.7	208.0	179.7	195.5
Methyl iodide	180.6	306.5	232.6	244.6	163.1	286.2	256.2	279.5
Methylene chloride	145.7	212.5	182.8	194.5	141.1	206.4	177.9	194.0
4-Methyl-2-Pentanone	185.5	235.6	202.6	209.2	184.0	232.5	193.2	204.5
Styrene	155.5	192.8	176.6	182.6	134.1	170.6	158.3	163.0
1,1,2,2-Tetrachloroethane	144.4	194.9	155.0	156.0	141.3	190.7	90.0	89.5
Tetrachloroethene	138.2	193.0	162.1	165.2	107.3	160.9	141.6	145.3
Toluene	118.0	238.7	160.6	171.5	112.6	230.6	194.8	201.9

^a Prediction interval calculated from the W2 acidified sample data.

^b Measurements outside of prediction intervals are bold-faced and italicized.

^c Instrument not calibrated for 2-chloroethylvinylether in acidified samples.

Table 11. (continued) Comparison between prediction intervals from acidified sample analyses and VOC levels in unacidified water sample analyses (set W2, 200 ppb).

	Day 1		Day 1 Unacidified		Day 35 Prediction		Day 35 Unacidified	
	Prediction Interval ^a		Samples ^b		Interval ^a		Samples ^b	
	Lower Limit	Upper Limit	W2-9	W2-35	Lower Limit	Upper Limit	W2-32	W2-36
1,1,1-Trichloroethane	134.6	229.1	176.1	184.0	118.1	210.5	190.1	204.8
1,1,2-Trichloroethane	154.8	234.3	185.5	195.5	158.9	236.6	208.0	220.0
Trichloroethene	145.6	240.8	191.6	204.4	129.6	222.7	280.2	295.0
Trichlorofluoromethane	204.5	339.2	284.4	283.4	154.9	286.7	253.2	267.1
1,2,3-Trichloropropane	200.7	236.5	204.3	215.3	185.2	220.3	196.2	206.4
Vinyl acetate	130.7	333.1	71.9	64.6	13.8	210.2	<i>n.d.</i>	<i>n.d.</i>
Vinyl chloride	39.9	248.2	116.1	119.0	42.6	245.2	188.9	198.4
m,p-Xylene	291.0	394.0	350.1	362.0	253.7	354.5	316.6	323.5
o-Xylene	148.6	194.9	178.4	179.4	134.7	179.9	155.4	161.8

^a Prediction interval calculated from the W2 acidified sample data.

^b Measurements outside of prediction intervals are bold-faced and italicized.

The stability of biodegradable VOCs (e.g., benzene, styrene) even without acidification in this study is not surprising because the bacteria present in the surface water may not be acclimated to these compounds. Biodegradation of these compounds will more likely occur in field-contaminated groundwater samples since the bacteria would have been acclimated to the contaminants. The benefits of acidification will be more apparent when the negative impacts on microbial growth are shown in Section 3.5.

3.4 Comparison with Previous Holding Time Studies

Sodium bisulfate (NaHSO₄) was first evaluated as a VOC water sample preservative by Maskarinec, et al. [1986]. In this previous study, the stability of several VOCs over a 112-day period was monitored in spiked water samples (prepared from distilled, ground and surface water) preserved with sodium bisulfate (250 mg) contained in 40-mL VOA vials (with no headspace) and stored at 4°C. The VOCs included in this previous study (see Table 12) were found to be stable over a 28-day holding time, based on calculated *PRTs* approach and an "acceptable" 28-day concentration change of 10%. The same conclusion for these VOCs were made from the current study except for carbon disulfide and tetrachloroethene (see Table 12). The shorter *PRTs* for carbon disulfide in the current study were probably due to the lower relative measurements errors (%*RMEs*) observed (6.3 and 8.1%) when compared to the previous study (15.1% to 20.4%, see Table 13). As noted earlier, lower %*RMEs* result in reduced *PRTs*. For

tetrachloroethylene, %RMEs were comparable between the previous and current studies, except for surface water in the previous study which had a %RME of 17.4% (see Table 11). Lower PRTs for tetrachloroethylene in the current study may be due to factors other than lower relative measurement errors, including tetrachloroethene being more susceptible to chemical degradation in the surface water used for the current study.

Table 12. Comparison between calculated practical reporting times and 28-day relative concentration changes in the current and previous stability studies.

Compound	Previous Study [Maskarinec et al. 1986]						This Study			
	Distilled H ₂ O 150 ppb spike		Ground H ₂ O 150 ppb spike		Surface H ₂ O 150 ppb spike		Surface H ₂ O 20 ppb spike (W1)		Surface H ₂ O 200 ppb spike (W2)	
	PRT ^a	Conc. Change in 28 days (%) ^b	PRT ^a	Conc. Change in 28 days (%) ^b	PRT ^a	Conc. Change in 28 days (%) ^b	PRT ^a	Conc. Change in 28 days (%) ^b	PRT ^a	Conc. Change in 28 days (%) ^b
Acetone	112		112		112		71		71	
Benzene	112		112		27	-3%	71		71	
Bromoform	112		112		112		71		15	-6%
Bromomethane	112		112		112		25	-4%	20	-9%
2-Butanone	112		112		112		71		71	
Carbon Disulfide	31		39		39		13	-9%	9	-17%
Carbon Tetrachloride	57		112		112		43		28	
Chlorobenzene	112		112		53		41		29	
Chloroethane	112		112		112		71		34	
Chloroform	112		112		112		71		44	
Chloromethane	112		112		112		26	-5%	22	-10%
1,1-Dichloroethane	112		112		112		71		71	
1,1-Dichloroethene	112		51		112		30		23	-10%
1,2-Dichloropropane	41		112		45		71		71	
Ethyl benzene	112		112		112		40		26	-8%
2-Hexanone	112		112		112		71		8	-9%
Methylene Chloride	19	-6%	22	-6%	40		71		71	
4-Methyl-2-pentanone	112		112		112		71		71	
Styrene	112		112		112		71		9	-10%
1,1,2,2-Tetrachloroethane	112		112		112		71		71	
Tetrachloroethene	48		112		40		17.2	-10%	10	-16%
Toluene	42		112		34		71		71	
1,1,2-Trichloroethane	36		112		32		71		71	
Trichloroethene	112		112		57		71		31	
o-Xylene	112		112		112		71		17	-7%

^a PRT = practical reporting time calculated using method described by Bayne et al. (1993; 1994).

^b Relative concentration change on the 28th day calculated from slope and intercept of regression on stability data.

Table 13. Comparison between relative measurement errors (%RME) in the current and previous stability studies.

	Previous Study [Maskarinec et al. 1986]			This Study	
	Distilled H2O 150 ppb spike	Ground H2O 150 ppb spike	Surface H2O 150 ppb spike	Surface H2O 20 ppb spike (W1)	Surface H2O 200 ppb spike (W2)
Acetone	13.9%	14.6%	15.9%	10.4%	8.9%
Benzene	5.0%	16.5%	4.0%	4.8%	10.4%
Bromoform	4.9%	7.8%	5.3%	9.7%	4.9%
Bromomethane	13.1%	20.0%	13.5%	4.9%	9.1%
2-Butanone	12.3%	11.6%	30.5%	8.7%	7.0%
Carbon Disulfide	15.2%	20.4%	16.7%	6.3%	8.1%
Carbon Tetrachloride	6.3%	19.5%	7.7%	6.3%	13.3%
Chlorobenzene	3.8%	15.2%	5.1%	4.7%	8.8%
Chloroethane	14.7%	24.2%	15.9%	5.9%	10.3%
Chloroform	7.4%	18.0%	9.5%	6.0%	10.1%
Chloromethane	41.5%	39.9%	37.9%	6.6%	11.2%
1,1-Dichloroethane	8.7%	18.3%	9.2%	8.0%	10.8%
1,1-Dichloroethene	10.8%	19.4%	11.4%	5.2%	11.5%
1,2-Dichloropropane	5.9%	15.2%	5.4%	7.3%	10.7%
Ethyl benzene	5.8%	20.9%	4.6%	5.0%	10.3%
2-Hexanone	13.8%	13.6%	13.9%	7.5%	3.6%
Methylene Chloride	5.6%	6.2%	6.0%	4.8%	8.7%
4-Methyl-2-pentanone	9.6%	6.6%	5.4%	7.3%	5.4%
Styrene	5.8%	33.6%	5.8%	11.9%	5.0%
1,1,2,2-Tetrachloroethane	5.9%	5.0%	2.1%	5.5%	6.9%
Tetrachloroethene	9.2%	17.1%	8.1%	8.9%	7.7%
Toluene	4.4%	9.8%	4.1%	5.9%	15.8%
1,1,2-Trichloroethane	5.1%	16.3%	6.6%	5.9%	9.5%
Trichloroethene	5.3%	21.7%	5.4%	4.8%	11.5%
o-Xylene	4.5%	31.0%	6.4%	10.6%	6.2%

* Relative measurement error (%RME) estimated by $S_o/C_o \times 100\%$ where S_o^2 and C_o are the mean squared error and the intercept of the regression line, respectively.

3.5 Effects of Sodium Bisulfate Acidification on Microbial Activity in Water Samples

The purpose of preserving VOC water samples by acidification is to reduce biodegradation of target analytes during sample storage. The short- and long-term effectiveness of this preservation technique was evaluated by monitoring microbial activity in unacidified and acidified water samples for 36 days [Figs. 3 and 4]. These figures clearly demonstrate that bacterial counts in water samples acidified with 250 mg of sodium bisulfate were dramatically reduced. In addition, bacterial counts in the acidified surface and sewage water samples remained low for 36 days. Low reproduction rates for microbes are an indication of a bacterial population under stress; biodegradation of target analytes are expected to be very slow under these conditions.

Based on the microbial monitoring results, the concentration changes observed for some compounds in the stability study were unlikely due to biodegradation. Volatilization, either through permeation through the septum cap or leakage around the rim of the glass vial, is possible particularly for the compounds which have high vapor pressures. Sparingly-soluble compounds with low vapor pressures may have adsorbed to the glass vial. Finally, acidification with sodium bisulfate can bring about favorable conditions for abiotic chemical reactions. However, the latter was only clearly observed for *2-chloroethylvinylether* which appeared to have rapidly degraded only in the acidified samples and standards.

Figure 3. Bacterial populations vs sample holding times in uncontaminated surface water (BGA, BGB, BGC), spiked surface water (W1-7,20 and 28) and acidified, spiked surface water samples (W1-4,5,38).

Figure 4. Bacterial populations vs sample holding times in uncontaminated sewage water (SS-3,4), and acidified water samples (SS-1,2).

4. IMPLICATIONS FOR PRACTICE

The technical quality and legal defensibility of analytical data is essential when the data serves as input for making decisions regarding human health and/or environmental protection. However, quality standards for analytical data must be specified relative to how the data will actually be used. Extremely stringent standards on the analytical process can be costly (e.g., very short sample holding times) and may not add much value in light of other sources of uncertainty that go into any quantitative or qualitative decision-making process. For example, in quantitative risk assessment, human exposure pathways and laboratory animal-based toxicity studies are "order-of-magnitude" estimates of reality at best [Cox and Ricci, 1990, Fairless and Bates, 1989; Korte and Brown, 1993]. Given these uncertainties, a 10% decrease in analyte concentration due to losses during sample holding (e.g., from 100 ppb to 90 ppb) is not of any "practical" significance. For simpler decisions based on comparisons between sample concentrations and "threshold levels", a 4.5 ppb level may still be considered as exceeding a "threshold" level of 5 ppb. The professional judgment and past experience of regulators would most likely influence decisions in such cases.

The current practice of disregarding data from VOC water analyses performed after 14 days of sample holding is unnecessary, in view of the practically insignificant concentration changes observed over at least a 28 day holding time for a majority of the target VOCs in this study. A 28-day holding time, versus a 14-day holding for VOCs in properly preserved water samples would benefit the regulated community, particularly government agencies with large-scale compliance sampling programs such as the Departments of Defense and Energy. Overly stringent holding times result in logistical difficulties further complicated by additional requirements for sample screening (e.g., for radioactivity). The suggested 28-day holding time can also improve the efficiency of commercial laboratories through simplified sample management. Furthermore, application of currently available stability databases (including the one described in this report) to data review would improve the analytical data validation process. The results of this study can be used to assess the risks associated with accepting a measurement made beyond the prescribed maximum holding time. It allows the data end-user to consider these risks in light of the other uncertainties that go into the decision-making process. This approach would be an alternative to the current unequivocal rejection of data when prescribed holding times are missed, a practice that is very costly but not technically defensible.

5. CONCLUSIONS

For a majority of the 44 VOCs included in this study, concentration changes were <10% of the initial values after 28 days of storage. Practical reporting times (*PRTs*) were calculated using the method described in [Bayne et al., 1993; 1994]. In the *PRT* approach, a "significant change" in VOC concentration is statistically defined such that measurement variability is taken into account. However, aside from calculating *PRTs*, measurement validity with increasing holding times was evaluated using a "practical" definition of an "acceptable" concentration change. Consideration of this additional criterion was necessary for certain compounds for which actual changes in concentration with time were relatively small but measurement variability was extremely low (<10%) resulting in very short calculated *PRTs*. Ideally, specifications for "acceptable" concentration changes should be tied into the eventual use of the analytical data. For example, "acceptable" concentration changes for analytical data used in quantitative risk assessments can be determined by the sensitivity of the risk assessment results to variations in the input analytical data. Since, the selection of a generic "acceptable" concentration change is beyond the scope of this study, 10% was chosen to assess the holding time effects on compounds in this study. An acceptable change of 10% is reasonable given the other sources of uncertainty in site characterization and risk assessment for which these analytical data are typically used.

Based on an "acceptable" concentration change of 10%, the stability study showed that the measurement of 35 out of 44 purgeable VOCs in properly preserved water samples will not be affected by sample storage for 28 days. These compounds include:

Acetone
Acrylonitrile
Benzene
Bromodichloromethane
Bromoform
Bromomethane
2-Butanone
Carbon tetrachloride
Chlorobenzene
Chloroethane
Chloroform
Chloromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-dichloroethene
trans-1,2-Dichloroethene

Dibromochloromethane
Dibromomethane
1,2-Dichloropropane
Ethylbenzene
2-Hexanone
Methyl iodide
4-Methyl-2-Pentanone
Styrene
1,1,2,2-Tetrachloroethane
Toluene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
1,2,3-Trichloropropane
m- and p-Xylene
o-Xylene
vinyl chloride

Larger changes in concentration ($>10\%$) and low *PRTs* were observed for a few analytes, including:

Acrolein
Trichlorofluoromethane
Carbon disulfide
Chloroethylvinylether, 2-
Vinyl acetate
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
Tetrachloroethene
trans-1,4-Dichloro-2-butene

However, analytical problems exist for these latter compounds (inconsistent purging, standards, etc) which can not be addressed by maintaining current holding time requirements alone.

This study demonstrates that a 28-day holding time for properly preserved VOC water samples would not jeopardize the measurement of a majority of target VOCs. This holding time extension would benefit the regulated community, particularly government agencies with large-scale compliance sampling programs such as the Departments of Defense and Energy. Stringent holding times result in logistical difficulties further complicated by additional requirements for sample screening (e.g., for radioactivity). The suggested 28-day holding time can also improve the efficiency of commercial laboratories through simplified sample management. Furthermore, application of currently available stability databases (including the one described in this report) to data review would improve the analytical data validation process. The results of this study can be used to

assess the risks associated with accepting a measurement made beyond the prescribed maximum holding time. This approach would be an alternative to unequivocally rejecting data when prescribed holding times are missed, a practice that is very costly but not technically defensible.

This study also demonstrated a methodology for conducting a stability study for obtaining site-specific holding times which, depending on the compounds of interest, can be longer than 28 days.

6. REFERENCES

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7. APPENDICES

APPENDIX A.
List of Samples and Analysis Days

Day	Date	Samples ^a
1	August 15, 1996	W1-8, W1-13, W1-24, W1-40 W2-5, W2-10, W2-21, W2-34 W2-9, W2-35 (unpreserved)
8	August 22, 1996	W1-3, W1-6, W1-18, W1-39 W2-3, W2-4, W2-15, W2-33
15	August 29, 1995	W1-10, W1-17, W1-19, W1-30 W2-7, W2-14, W2-24, W2-37
22	September 5, 1995	W1-11, W1-26, W1-27, W1-32 W2-22, W2-23, W2-27, W2-38 ^a
29	September 12, 1995	W1-1, W1-16, W1-22, W1-33 W2-1, W2-13, W2-18, W2-28
36	September 19, 1995	W1-23, W1-24, W1-31, W1-36 W2-19, W2-20, W2-26, W2-31, W2-32, W2-36 (unpreserved)
71	October 24, 1995	W1-2, W1-35, W1-14, W1-20 W2-2, W-24, W2-30, W2-11

^a All samples preserved with 250 mg of NaHSO₄ unless otherwise indicated.

^b No VOC results for this sample. Power outage occurred in the middle of analysis.

APPENDIX B.
Gas Chromatograph/Mass Spectrometer Tuning: Bromofluorobenzene Checks

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**VOLATILE ORGANIC GC/MS TUNING AND MASS
CALIBRATION - BROMOFLUOROBENZENE (BFB)**

Lab File ID: F3BFB0815
Instrument ID: FINN 3

Client: L443 - Oak Ridge Nat. Lab
Project: Holding Studies

Matrix: Water

Column: Cap

Data Release Authorized:
Report: 10/17/95 MAC: MNS

BFB Injection Date: 08/15/95
BFB Injection Time: 10:12

m/e	Ion Abundance Criteria	% Relative Abundance
50	8.0-40.0% of mass 95	34.0
75	30.0-66.0% of mass 95	57.1
95	Base peak, 100% relative abundance	100
98	5.0-9.0% of mass 95	6.8
173	Less than 2.0% of mass 174	0.0 (0.0)1
174	50.0-120.0% of mass 95	85.9
175	4.0-9.0% of mass 174	6.7 (7.8)1
176	93.0-101.0% of mass 174	84.4 (98.2)1
177	5.0-9.0% of mass 176	5.7 (6.8)2

1-Value is % mass 174 2-Value is % mass 176

THIS TUNE APPLIES TO THE FOLLOWING SAMPLES, MS MSD, BLANKS, AND STANDARDS:

Client Sample ID	ARI Sample ID	Lab File ID	Date Analyzed	Time Analyzed
VSTD050	50 NG/ML VOA STD	F30500815	08/15/95	12:57
LCS (spike blank) 8/15	SB0815	F3SB0815	08/15/95	14:15
Method Blank 8/15	MB0815	F3MB0815	08/15/95	14:50
W1-8	L443A	F3L443A	08/15/95	15:53
W1-13	L443B	F3L443B	08/15/95	16:16
W1-25	L443C	F3L443C	08/15/95	16:46
W1-40	L443D	F3L443D	08/15/95	17:16
W2-5	L443E	F3L443E	08/15/95	17:46
W2-9	L443F	F3L443F	08/15/95	18:16
W2-10	L443G	F3L443G	08/15/95	18:47
W2-21	L443H	F3L443H	08/15/95	19:17
W2-34	L443I	F3L443I	08/15/95	19:47
W2-35	L443J	F3L443J	08/15/95	20:18

FORM V VOA-W

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**VOLATILE ORGANIC GC/MS TUNING AND MASS
CALIBRATION - BROMOFLUOROBENZENE (BFB)**

Lab File ID: F3BFB0822C
Instrument ID: FINN 3

Client: L443 - Oak Ridge Nat. Lab
Project: Holding Studies

Matrix: Water

Column: Cap

Data Release Authorized: MM
Report: 09/11/95 MAC: MNS

BFB Injection Date: 08/22/95
BFB Injection Time: 13:21

m/e	Ion Abundance Criteria	% Relative Abundance
50	8.0-40.0% of mass 95	30.1
75	30.0-66.0% of mass 95	56.7
95	Base peak, 100% relative abundance	100
96	5.0-9.0% of mass 95	7.4
173	Less than 2.0% of mass 174	0.0 (0.0)1
174	50.0-120.0% of mass 95	94.2
175	4.0-9.0% of mass 174	7.1 (7.5)1
176	93.0-101.0% of mass 174	92.3 (98.0)1
177	5.0-9.0% of mass 176	6.3 (6.8)2

1-Value is % mass 174 2-Value is % mass 176

THIS TUNE APPLIES TO THE FOLLOWING SAMPLES, MS MSD, BLANKS, AND STANDARDS:

Client Sample ID	ARI Sample ID	Lab File ID	Date Analyzed	Time Analyzed
VSTD050	50 NG/ML VOA STD	F30500822	08/22/95	13:35
LCS (spike blank) 8/22	SB0822	F3SB0822	08/22/95	14:19
Method Blank 8/22	MB0822	F3MB0822	08/22/95	14:59
W1-3	L443K	F3L443K	08/22/95	15:41
W1-6	L443L	F3L443L	08/22/95	16:24
W1-18	L443M	F3L443M	08/22/95	16:54
W1-39	L443N	F3L443N	08/22/95	17:25
W2-3	L443O	F3L443O	08/22/95	17:55
W2-4	L443P	F3L443P	08/22/95	18:25
W2-15	L443Q	F3L443Q	08/22/95	18:56
W2-33	L443R	F3L443R	08/22/95	19:26

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VOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION - BROMOFLUOROBENZENE (BFB)

Lab File ID: F38FB0826
Instrument ID: FINN 3

BFB Injection Date: 08/26/95
BFB Injection Time: 10:09

Matrix Init. Calibration

Level: NA
Column: Cap

Data Release Authorized: _____
Report: 08/28/95 **MAC:** MNS

m/e	Ion Abundance Criteria	% Relative Abundance
50	8.0-40.0% of mass 95	23.9
75	30.0-66.0% of mass 95	48.1
95	Base peak, 100% relative abundance	100
96	5.0-9.0% of mass 95	7.0
173	Less than 2.0% of mass 174	0.0 (0.0)1
174	50.0-120.0% of mass 95	83.5
175	4.0-9.0% of mass 174	5.7 (6.9)1
176	93.0-101.0% of mass 174	82.2 (98.4)1
177	5.0-9.0% of mass 176	5.9 (7.2)2

1-Value is % mass 174 2-Value is % mass 176

THIS TUNE APPLIES TO THE FOLLOWING SAMPLES, MS MSD, BLANKS, AND STANDARDS:

[illegible]

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**VOLATILE ORGANIC GC/MS TUNING AND MASS
CALIBRATION - BROMOFLUOROBENZENE (BFB)**

Lab File ID: F3BFB0829
Instrument ID: FINN 3

Client: Oak Ridge National Lab.
Project: Holding Studies

Matrix: Water

Column: Cap

Data Release Authorized:
Report: 10/17/95 MAC: CSP

BFB Injection Date: 08/29/95
BFB Injection Time: 09:15

m/e	Ion Abundance Criteria	% Relative Abundance
50	8.0-40.0% of mass 95	25.0
75	30.0-66.0% of mass 95	49.1
95	Base peak, 100% relative abundance	100
96	5.0-9.0% of mass 95	7.7
173	Less than 2.0% of mass 174	0.0 (0.0)1
174	50.0-120.0% of mass 95	85.5
175	4.0-9.0% of mass 174	6.2 (7.2)1
176	93.0-101.0% of mass 174	82.7 (96.7)1
177	5.0-9.0% of mass 176	5.8 (7.0)2

1-Value is % mass 174. 2-Value is % mass 176

THIS TUNE APPLIES TO THE FOLLOWING SAMPLES, MS MSD, BLANKS, AND STANDARDS:

Client Sample ID	ARI Sample ID	Lab File ID	Date Analyzed	Time Analyzed
VSTD050	50 NG/ML VOA STD	F30500829	08/29/95	09:32
LCS (spike blank) 8/29	SB0829	F3SB0829	08/29/95	13:53
Method Blank 8/29	MB0829	F3MB0829	08/29/95	14:29
W1-10	L443S	F3L443S	08/29/95	15:41
W1-17	L443T	F3L443T	08/29/95	16:03
W1-19	L443U	F3L443U	08/29/95	16:34
W1-30	L443V	F3L443V	08/29/95	17:04
W2-7	L443W	F3L443W	08/29/95	17:34
W2-14	L443X	F3L443X	08/29/95	18:04
W2-25	L443Y	F3L443Y	08/29/95	18:34
W2-37	L443Z	F3L443Z	08/29/95	19:05

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**VOLATILE ORGANIC GC/MS TUNING AND MASS
CALIBRATION - BROMOFLUOROBENZENE (BFB)**

Lab File ID: F3BFB0905
Instrument ID: FINN 3

Client: Oak Ridge National Lab.
Project: Holding Studies

Matrix: Water

Column: Cap

Data Release Authorized: MM
Report: 09/08/95 MAC: CSP

BFB Injection Date: 09/05/95
BFB Injection Time: 07:45

m/e	Ion Abundance Criteria	% Relative Abundance
50	8.0-40.0% of mass 95	26.1
75	30.0-66.0% of mass 95	50.3
95	Base peak, 100% relative abundance	100
96	5.0-9.0% of mass 95	7.0
173	Less than 2.0% of mass 174	0.0 (0.0)1
174	50.0-120.0% of mass 95	79.5
175	4.0-9.0% of mass 174	6.7 (8.4)1
176	93.0-101.0% of mass 174	78.2 (98.4)1
177	5.0-9.0% of mass 176	5.5 (7.0)2

1-Value is % mass 174 2-Value is % mass 176

THIS TUNE APPLIES TO THE FOLLOWING SAMPLES, MS MSD, BLANKS, AND STANDARDS:

Client Sample ID	ARI Sample ID	Lab File ID	Date Analyzed	Time Analyzed
VSTD050	50 NG/ML VOA STD	F30500905	09/05/95	08:07
LCS (spike blank) 9/5	S80905	F3S80905	09/05/95	08:52
Method Blank 9/5	M80905	F3M80905	09/05/95	09:45
W1-11	L443AA	F3L443AA	09/05/95	10:14
W1-26	L443AB	F3L443AB	09/05/95	10:45
W1-27	L443AC	F3L443AC	09/05/95	11:16
W1-32	L443AD	F3L443AD	09/05/95	11:46
W2-22	L443AE	F3L443AE	09/05/95	12:16
W2-23	L443AF	F3L443AF	09/05/95	12:47
W2-27	L443AG	F3L443AG	09/05/95	13:17

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**VOLATILE ORGANIC GC/MS TUNING AND MASS
CALIBRATION - BROMOFLUOROBENZENE (BFB)**

Lab File ID: F3BFB0912
Instrument ID: FINN 3

Client: Oak Ridge National Lab.
Project: Holding Studies

Matrix: Water

Column: Cap

Data Release Authorized: MP
Report: 09/14/95 MAC: MNS

BFB Injection Date: 09/12/95
BFB Injection Time: 08:36

m/e	Ion Abundance Criteria	% Relative Abundance
50	8.0-40.0% of mass 95	27.0
75	30.0-66.0% of mass 95	53.5
95	Base peak, 100% relative abundance	100
96	5.0-9.0% of mass 95	7.4
173	Less than 2.0% of mass 174	0.0 (0.0)1
174	50.0-120.0% of mass 95	80.5
175	4.0-9.0% of mass 174	6.2 (7.7)1
176	93.0-101.0% of mass 174	77.1 (95.8)1
177	5.0-9.0% of mass 176	5.2 (6.7)2

1-Value is % mass 174 2-Value is % mass 176

THIS TUNE APPLIES TO THE FOLLOWING SAMPLES, MS MSD, BLANKS, AND STANDARDS:

Client Sample ID	ARI Sample ID	Lab File ID	Date Analyzed	Time Analyzed
VSTD050	50 NG/ML VOA STD	F30500912	09/12/95	09:01
LCS (spike blank) 9/12	SB0912	F3SB0912	09/12/95	09:46
Method Blank 9/12	MB0912	F3MB0912	09/12/95	10:26
W1-1	L443AJ	F3L443AJ	09/12/95	11:14
W1-16	L443AJ	F3L443AJ	09/12/95	11:47
W1-22	L443AK	F3L443AK	09/12/95	12:18
W1-33	L443AL	F3L443AL	09/12/95	12:48
W2-1	L443AM	F3L443M	09/12/95	13:19
W2-13	L443AN	F3L443AN	09/12/95	13:49
W2-18	L443AO	F3L443AO	09/12/95	14:19
W2-28	L443AP	F3L443AP	09/12/95	14:49

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**VOLATILE ORGANIC GC/MS TUNING AND MASS
CALIBRATION - BROMOFLUOROBENZENE (BFB)**

Lab File ID: F3BFB0919
Instrument ID: FINN 3

Client: L443-Oak Ridge National Lab.
Project: Holding Studies

Matrix: Water

Column: Cap

Data Release Authorized: AK

BFB Injection Date: 09/19/95

BFB Injection Time: 09:00

Report: 09/22/95 MAC: MNS

m/e	Ion Abundance Criteria	% Relative Abundance
50	8.0-40.0% of mass 95	25.8
75	30.0-66.0% of mass 95	52.6
95	Base peak, 100% relative abundance	100
96	5.0-9.0% of mass 95	7.0
173	Less than 2.0% of mass 174	0.0 (0.0)1
174	50.0-120.0% of mass 95	83.3
175	4.0-9.0% of mass 174	6.8 (8.2)1
176	93.0-101.0% of mass 174	81.1 (97.4)1
177	5.0-9.0% of mass 176	6.3 (7.8)2

1-Value is % mass 174

2-Value is % mass 176

THIS TUNE APPLIES TO THE FOLLOWING SAMPLES, MS MSD, BLANKS, AND STANDARDS:

Client Sample ID	ARI Sample ID	Lab File ID	Date Analyzed	Time Analyzed
VSTD050	50 NG/ML VOA STD	F30500919	09/19/95	09:13
LCS (spike blank)	SB0919	F3SB0919	09/19/95	10:04
Method Blank	MB0919	F3L443MB0919	09/19/95	10:47
W1-23	L443AQ	F3L443AQ	09/19/95	11:28
W1-24	L443AR	F3L443AR	09/19/95	12:01
W1-31	L443AS	F3L443AS	09/19/95	12:32
W1-36	L443AT	F3L443AT	09/19/95	13:02
W2-19	L443AU	F3L443AU	09/19/95	13:32
W2-20	L443AV	F3L443AV	09/19/95	14:03
W2-26	L443AW	F3L443AW	09/19/95	14:33
W2-31	L443AX	F3L443AX	09/19/95	15:03
W2-32	L443AY	F3L443AY	09/19/95	15:34
W2-36	L443AZ	F3L443AZ	09/19/95	16:04

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**VOLATILE ORGANIC GC/MS TUNING AND MASS
CALIBRATION - BROMOFLUOROBENZENE (BFB)**

Lab File ID: F3BFB1024
Instrument ID: FINN 3

Client: Oak Ridge National Laboratory
Project: Holding Study

Matrix: Water
Level: NA

BFB Injection Date: 10/24/95
BFB Injection Time: 10:13

Data Release Authorized: *SP*
Report: 10/31/95 MAC: MNS

Column: Cap

m/e	Ion Abundance Criteria	% Relative Abundance
50	8.0-40.0% of mass 95	26.6
75	30.0-66.0% of mass 95	49.2
95	Base peak, 100% relative abundance	100
96	5.0-9.0% of mass 95	7.0
173	Less than 2.0% of mass 174	0.0 (0.0)1
174	50.0-120.0% of mass 95	72.6
175	4.0-9.0% of mass 174	5.3 (7.3)1
176	93.0-101.0% of mass 174	70.9 (97.6)1
177	5.0-9.0% of mass 176	4.7 (6.6)2

1-Value is % mass 174 2-Value is % mass 176

THIS TUNE APPLIES TO THE FOLLOWING SAMPLES, MS, MSD, BLANKS, AND STANDARDS:

Client Sample ID	ARI Sample ID	Lab File ID	Date Analyzed	Time Analyzed
VSTD050	50 NG/ML VOA STD	F30501024	10/24/95	10:51
Method Blank	MB1024	F3MB1024	10/24/95	12:27
Lab. Sample Control	SB1024	F3SB1024	10/24/95	11:29
W2-2	M041B	F3M041B	10/24/95	13:36
W2-24	M041C	F3M041C	10/24/95	14:09
W1-2	M041D	F3M041D	10/24/95	14:40
W1-35	M041E	F3M041E	10/24/95	15:11
W1-14	M041F	F3M041F	10/24/95	15:42
W1-20	M041G	F3M041G	10/24/95	16:13
W2-30	M041H	F3M041H	10/24/95	17:14
W2-11	M041A3	F3M041A3	10/24/95	17:54

APPENDIX C.
System Monitoring Compound Summary: Surrogate Recoveries

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WATER VOLATILE SYSTEM MONITORING COMPOUND SUMMARY

Matrix: Water

Date: 8/15/95

QC Report No: L443

Lab ID	Client ID	DCE	TOL	BFB	DCB	TOT OUT
MB	Method Blank	99%	95%	87%	94%	0
L443A	W1-8 Day 1	99%	95%	88%	93%	0
L443LCS	Lab Cntrl Sample	95%	96%	92%	94%	0
L443B	W1-13	101%	97%	90%	92%	0
L443C	W1-25	100%	95%	88%	90%	0
L443D	W1-40	102%	95%	88%	92%	0
L443E	W2-5	98%	94%	94%	92%	0
L443F	W2-9	98%	94%	98%	93%	0
L443G	W2-10	102%	96%	92%	92%	0
L443H	W2-21	100%	93%	97%	91%	0
L443I	W2-34	101%	97%	97%	91%	0
L443J	W2-35	101%	96%	95%	92%	0

	LCS/MB LIMITS	QC LIMITS
(DCE) = 1,2-Dichloroethane-d4	(80-120)	(77-123)
(TOL) = Toluene-d8	(88-110)	(87-115)
(BFB) = Bromofluorobenzene	(86-115)	(86-113)
(DCB) = 1,2-Dichlorobenzene-d4	(80-120)	(90-113)

Column to be used to flag recovery values

• Values outside of required QC limits

D System Monitoring Compound diluted out

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WATER VOLATILE SYSTEM MONITORING COMPOUND SUMMARY

Matrix: Water

Date: 8/22/95
QC Report No: L443

Lab ID	Client ID	DCE	TOL	BFB	DCB	TOT OUT
MB	Method Blank	106%	99%	98%	104%	0
L443K	W1-3	107%	96%	98%	103%	0
L443LCS	Lab Cntrl Sample	98%	98%	104%	104%	0
L443L	W1-6	107%	100%	100%	103%	0
L443M	W1-18	107%	98%	96%	103%	0
L443N	W1-39	103%	98%	97%	102%	0
L443O	W2-3	110%	104%	109%	103%	0
L443P	W2-4	109%	101%	109%	102%	0
L443Q	W2-15	102%	101%	107%	99%	0
L443R	W2-33	99%	99%	109%	100%	0

	LCS/MB LIMITS	QC LIMITS
(DCE) = 1,2-Dichloroethane-d4	(80-120)	(77-123)
(TOL) = Toluene-d8	(88-110)	(87-115)
(BFB) = Bromofluorobenzene	(86-115)	(86-113)
(DCB) = 1,2-Dichlorobenzene-d4	(80-120)	(90-113)

Column to be used to flag recovery values

* Values outside of required QC limits

D System Monitoring Compound diluted out

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WATER VOLATILE SYSTEM MONITORING COMPOUND SUMMARY

Matrix: Water

Date: 8/29/95
QC Report No: L443

Lab ID	Client ID	DCE	TOL	BFB	DCB	TOT OUT
MB	Method Blank	107%	98%	100%	97%	0
L443S	W1-10	102%	97%	100%	97%	0
L443LCS	Lab Cntrl Sample	102%	98%	100%	97%	0
L443T	W1-17	105%	97%	97%	98%	0
L443U	W1-19	103%	95%	99%	99%	0
L443V	W1-30	103%	97%	99%	96%	0
L443W	W2-7	104%	98%	96%	97%	0
L443X	W2-14	104%	97%	97%	97%	0
L443Y	W2-25	106%	96%	97%	97%	0
L443Z	W2-37	104%	96%	97%	98%	0

	LCS/MB LIMITS	QC LIMITS
(DCE) = 1,2-Dichloroethane-d4	(80-120)	(77-123)
(TOL) = Toluene-d8	(88-110)	(87-115)
(BFB) = Bromofluorobenzene	(86-115)	(86-113)
(DCB) = 1,2-Dichlorobenzene-d4	(80-120)	(90-113)

Column to be used to flag recovery values

* Values outside of required QC limits

D System Monitoring Compound diluted out

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WATER VOLATILE SYSTEM MONITORING COMPOUND SUMMARY

Matrix: Water

Date: 9/5/95
QC Report No: L443

Lab ID	Client ID	DCE	TOL	BFB	DCB	TOT OUT
MB	Method Blank	99%	96%	98%	98%	0
L443AA	W1-11	97%	96%	95%	98%	0
L443LCS	Lab Cntrl Sample	99%	98%	99%	99%	0
L443AB	W1-26	99%	98%	98%	98%	0
L443AC	W1-27	99%	98%	98%	98%	0
L443AD	W1-32	100%	97%	96%	97%	0
L443AE	W2-22	101%	98%	96%	99%	0
L443AF	W2-23	96%	97%	97%	97%	0
L443AG	W2-27	99%	96%	96%	99%	0
L443AH	W2-38	Not Entered	Not Entered	Not Entered	Not Entered	0

	LCS/MB LIMITS	QC LIMITS
(DCE) = 1,2-Dichloroethane-d4	(80-120)	(77-123)
(TOL) = Toluene-d8	(88-110)	(87-115)
(BFB) = Bromofluorobenzene	(86-115)	(86-113)
(DCB) = 1,2-Dichlorobenzene-d4	(80-120)	(90-113)

Column to be used to flag recovery values

* Values outside of required QC limits

D System Monitoring Compound diluted out

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WATER VOLATILE SYSTEM MONITORING COMPOUND SUMMARY

Matrix: Water

Date: 9/12/95
QC Report No: L443

Lab ID	Client ID	DCE	TOL	BFB	DCB	TOT OUT
MB	Method Blank	99%	99%	100%	96%	0
L443AI	W1-1	99%	96%	100%	97%	0
L443LCS	Lab Cntrl Sample	102%	102%	103%	97%	0
L443AJ	W1-16	103%	101%	102%	96%	0
L443AK	W1-22	101%	99%	102%	99%	0
L443AL	W1-33	99%	99%	103%	99%	0
L443AM	W2-1	101%	100%	99%	97%	0
L443AN	W2-13	99%	101%	101%	97%	0
L443AO	W2-18	103%	100%	105%	97%	0
L443AP	W2-28	99%	100%	100%	97%	0

	LCS/MB LIMITS	QC LIMITS
(DCE) = 1,2-Dichloroethane-d4	(80-120)	(77-123)
(TOL) = Toluene-d8	(88-110)	(87-115)
(BFB) = Bromofluorobenzene	(86-115)	(86-113)
(DCB) = 1,2-Dichlorobenzene-d4	(80-120)	(90-113)

- # Column to be used to flag recovery values
- Values outside of required QC limits
- D System Monitoring Compound diluted out

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WATER VOLATILE SYSTEM MONITORING COMPOUND SUMMARY

Matrix: Water

Date: 9/19/95
QC Report No: L443

Lab ID	Client ID	DCE	TOL	BFB	DCB	TOT OUT
MB	Method Blank	102%	96%	95%	98%	0
L443AQ	W1-23	101%	99%	97%	97%	0
L443LCS	Lab Cntrl Sample	100%	99%	99%	99%	0
L443AR	W1-24	102%	98%	97%	100%	0
L443AS	W1-31	104%	99%	96%	100%	0
L443AT	W1-36	102%	101%	97%	98%	0
L443AU	W2-19	102%	98%	96%	99%	0
L443AV	W2-20	104%	98%	97%	100%	0
L443AW	W2-26	100%	98%	98%	98%	0
L443AX	W2-31	101%	99%	95%	98%	0
L443AY	W2-32	100%	98%	96%	98%	0
L443AZ	W2-36	106%	100%	98%	101%	0

	LCS/MB LIMITS	QC LIMITS
(DCE) = 1,2-Dichloroethane-d4	(80-120)	(77-123)
(TOL) = Toluene-d8	(88-110)	(87-115)
(BFB) = Bromofluorobenzene	(86-115)	(86-113)
(DCB) = 1,2-Dichlorobenzene-d4	(80-120)	(90-113)

- # Column to be used to flag recovery values
- Values outside of required QC limits
- D System Monitoring Compound diluted out

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WATER VOLATILE SYSTEM MONITORING COMPOUND SUMMARY

Matrix: Water

Date: 10/24/95
QC Report No: M041

Lab ID	Client ID	DCE	TOL	BFB	DCB	TOT OUT
M041A	W2-11	95%	101%	94%	94%	0
MB	Method Blank	99%	99%	96%	98%	0
M041B	W2-2	98%	103%	97%	96%	0
M041LCS	Lab Cntrl Sample	98%	101%	98%	100%	0
M041C	W2-24	101%	101%	96%	98%	0
M041D	W1-2	100%	101%	96%	96%	0
M041E	W1-35	99%	99%	95%	97%	0
M041F	W1-14	102%	101%	97%	97%	0
M041G	W1-29	98%	100%	94%	97%	0
M041H	W2-30	97%	102%	94%	96%	0

	LCS/MB LIMITS	QC LIMITS
(DCE) = 1,2-Dichloroethane-d4	(80-120)	(77-123)
(TOL) = Toluene-d8	(88-110)	(87-115)
(BFB) = Bromofluorobenzene	(86-115)	(86-113)
(DCB) = 1,2-Dichlorobenzene-d4	(80-120)	(90-113)

Column to be used to flag recovery values

• Values outside of required QC limits

D System Monitoring Compound diluted out

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APPENDIX D.
Internal Standard Area Summary

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VOLATILE INTERNAL STANDARD AREA SUMMARY

Lab File ID: F30500919
Instrument ID: FINN 3

Client: L443-Oak Ridge National Lab.
Project: Holding Studies

Matrix: Water
Level: NA

Date Analyzed: 09/19/95
Time Analyzed: 09:13

Data Release Authorized: AS
Report: 09/22/95 MAC:MNS

Column: Cap

	IS1 (PFB) AREA	RT	IS2 (DCB) AREA	RT	IS3 (DFB) AREA	RT	IS4 (CLB) AREA	RT
12 HOUR STD	107074	7.45	60112	15.03	124464	8.32	109520	11.90
UPPER LIMIT	214148		120224		248928		219040	
LOWER LIMIT	53537		30056		62232		54760	
CLIENT SAMPLE ID								
Method Blank	118271	7.45	56638	15.03	133218	8.32	110438	11.90
Lab. Sample Control	109046	7.47	58402	15.05	123782	8.33	105100	11.92
W1-23	111538	7.45	58380	15.05	126264	8.32	111537	11.92
W1-24	109290	7.48	53384	15.07	122907	8.33	107300	11.93
W1-31	102248	7.48	54572	15.07	117192	8.35	104298	11.93
W1-36	105228	7.45	55682	15.03	118486	8.32	106362	11.90
W2-19	101766	7.47	53600	15.07	116316	8.33	103569	11.93
W2-20	99910	7.47	57516	15.05	114340	8.33	105734	11.92
W2-26	103372	7.48	57992	15.07	116068	8.33	105574	11.93
W2-31	105766	7.45	58632	15.03	119088	8.32	109944	11.90
W2-32	105966	7.48	60422	15.07	120196	8.33	111844	11.93
W2-36	94280	7.48	56998	15.07	111374	8.35	103572	11.93

IS1 (PFB)=Pentafluorobenzene
IS2 (DCB)=1,4-Dichlorobenzene-d4
IS3 (DFB)=1,4-Difluorobenzene
IS4 (CLB)=Chlorobenzene-d5

Upper Limit = +100% of Internal Standard area
Lower Limit = -50% of Internal Standard area
Asterisked values outside limits

000028

APPENDIX E.
Method Blank Summary

VOLATILE METHOD BLANK SUMMARY

ARI Job No: L443
Lab Sample ID: F3MB0919

Client: Oak Ridge National Lab.
Project: Holding Studies

Instrument ID: FINN 3
Matrix: Water

Date Analyzed: 09/19/95
Time Analyzed: 10:47

Data Release Authorized: 1181
Report: 08/22/95 **MAC:** MNS

Level: NA

THIS METHOD BLANK APPLIES TO THE FOLLOWING SAMPLES, MS,MSD:

[illegible]**Comments:**

APPENDIX F.

Practical Reporting Time Analysis

Practical reporting times are calculated from stability data using the following procedure [Bayne et al., 1993; 1994]: (1) an approximating model representing "concentration vs. holding time" is fitted to the data by the method of least squares [Draper 1981], (2) the one-sided 95% prediction limit for the concentration at time zero is located for the approximating model (this limit is the critical concentration); (3) a horizontal line is drawn from the critical concentration until it intersects with the one-sided 85% prediction limit; and (4) a vertical line is drawn from the intersection described in (3) to the time axis (see Fig. 1). An analytical expression for PRT may be obtained if a linear model:

$$C_j = C_o + \beta D_j \quad (\text{F.1})$$

or a first-order kinetic model:

$$\ln(C_j) = \ln(C_o) + \beta D_j \quad (\text{F.2})$$

is applied to the data, where C_j is the concentration at holding time D_j , C_o is the concentration at time 0 and β is a rate constant. Let A and B be the estimated values for C_o (or $\ln(C_o)$) and β respectively. Then the practical reporting time (PRT) is calculated as follows:

$$PRT = \frac{-\Delta \pm (\Delta^2 + 4\Lambda\Gamma)^{1/2}}{2\Lambda} \quad (\text{F.3})$$

where

$$\Lambda = B^2 - t^2(0.15, df) \text{var}(B) \quad (\text{F.4})$$

$$\Delta = 2[Bt(0.05, df)(\text{var}(A) + S_o^2)^{1/2} - t^2(0.15, df)\text{cov}(A, B)] \quad (\text{F.5})$$

$$\Gamma = [t^2(0.05, df) - t^2(0.15, df)][\text{var}(A) + S_o^2]. \quad (\text{F.6})$$

In Eqs. (F.4) through (F.5), $t(p, df)$ is the $(1-p)$ percentile point of the t -distribution with df = degrees of freedom = (number of points in the regression - number of estimated model

parameters); S_o is estimated as the square root of the mean-square error for the regression residuals, $\text{var}(A) = a_{11}S_o^2$, $\text{var}(B) = a_{22}S_o^2$, $\text{cov}(A,B) = a_{12}S_o^2$ where a_{ii} refers to the elements of the 2x2 covariance matrix. PRT is equal to the smallest positive root of eq. (F.3).

APPENDIX G.
Concentration vs Holding Time Graphs for Individual VOCs

Figure G-1a. Linear regression through concentration vs pre-analytical holding time for acetone (W1-20 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$).

Figure G-1b. Linear regression through concentration vs pre-analytical holding time for acetone (W2-200 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$).

Figure G-2a. Linear regression through concentration vs pre-analytical holding time for acrolein (W1-20 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$). Spike level below detection limit for this compound (50 ppb).

Figure G-2b. Linear regression through concentration vs pre-analytical holding time for acrolein (W2-200 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$).

Figure G-3a. Linear regression through concentration vs pre-analytical holding time for acrylonitrile (W1-20 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$).

Figure G-3b. Linear regression through concentration vs pre-analytical holding time for acrylonitrile (W2-200 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$), and aborted analysis of a sample due to a power outage (Day 22).

Figure G-4a. Linear regression through concentration vs pre-analytical holding time for benzene (W1-20 ppb spike).

Figure G-4b. Linear regression through concentration vs pre-analytical holding time for benzene (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-5a. Linear regression through concentration vs pre-analytical holding time for bromodichloromethane (W1-20 ppb spike).

Figure G-5b. Linear regression through concentration vs pre-analytical holding time for bromodichloromethane (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-6a. Linear regression through concentration vs pre-analytical holding time for bromoform (W1-20 ppb spike).

Figure G-6b. Linear regression through concentration vs pre-analytical holding time for bromoform (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-7a. Linear regression through concentration vs pre-analytical holding time for bromomethane (W1-20 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration (%D > 20%).

Figure G-7b. Linear regression through concentration vs pre-analytical holding time for bromomethane (W2-200 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration (%D > 20%), and to aborted analyses of a sample due to a power outage (Day 22).

Figure G-8a. Linear regression through concentration vs pre-analytical holding time for 2-butanone (W1-20 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$).

Figure G-8b. Linear regression through concentration vs pre-analytical holding time for 2-butanone (W2-200 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$), and aborted analysis of a sample due to power outage (day 22).

Figure G-9a. Linear regression through concentration vs pre-analytical holding time for carbon disulfide (W1-20 ppb spike).

Figure G-9b. Linear regression through concentration vs pre-analytical holding time for carbon disulfide (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-10a. Linear regression through concentration vs pre-analytical holding time for carbon tetrachloride (W1-20 ppb spike).

Figure G-10b. Linear regression through concentration vs pre-analytical holding time for carbon tetrachloride (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-11a. Linear regression through concentration vs pre-analytical holding time for chlorobenzene (W1-20 ppb spike).

Figure G-11b. Linear regression through concentration vs pre-analytical holding time for chlorobenzene (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-12a. Linear regression through concentration vs pre-analytical holding time for chloroethane (W1-20 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$).

Figure G-12b. Linear regression through concentration vs pre-analytical holding time for chloroethane (W2-200 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$), and to aborted analysis of a sample due to a power outage (day 22).

Figure G-13a. Linear regression through concentration vs pre-analytical holding time for chloroform (W1-20 ppb spike).

Figure G-13b. Linear regression through concentration vs pre-analytical holding time for chloroform (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-14a. Linear regression through concentration vs pre-analytical holding time for chloromethane (W1-20 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$).

Figure G-14b. Linear regression through concentration vs pre-analytical holding time for chloromethane (W2-200 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$) and to aborted analysis of a sample due to a power outage.

Figure G-15a. Linear regression through concentration vs pre-analytical holding time for dibromochloromethane (W1-20 ppb spike).

Figure G-15b. Linear regression through concentration vs pre-analytical holding time for dibromochloromethane (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-16a. Linear regression through concentration vs pre-analytical holding time for dibromomethane (W1-20 ppb spike).

Figure G-16b. Linear regression through concentration vs pre-analytical holding time for dibromomethane (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-17a. Linear regression through concentration vs pre-analytical holding time for trans-1,4-dichloro-2-butene (W1-20 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$).

Figure G-17b. Linear regression through concentration vs pre-analytical holding time for trans-1,4-dichloro-2-butene (W2-200 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$), and to aborted analysis of a sample due to a power outage (day 22).

Figure G-18a. Linear regression through concentration vs pre-analytical holding time for 1,1-dichloroethane (W1-20 ppb spike).

Figure G-18b. Linear regression through concentration vs pre-analytical holding time for 1,1-dichloroethane (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-19a. Linear regression through concentration vs pre-analytical holding time for 1,2-dichloroethane (W1-20 ppb spike).

Figure G-19b. Linear regression through concentration vs pre-analytical holding time for 1,2-dichloroethane (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-20a. Linear regression through concentration vs pre-analytical holding time for 1,1-dichloroethene (W1-20 ppb spike).

Figure G-20b. Linear regression through concentration vs pre-analytical holding time for 1,1-dichloroethene (W1-20 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-21a. Linear regression through concentration vs pre-analytical holding time for trans-1,2-dichloroethene (W1-20 ppb spike).

Figure G-21b. Linear regression through concentration vs pre-analytical holding time for trans-1,2-dichloroethene (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-22a. Linear regression through concentration vs pre-analytical holding time for 1,2-dichloropropane (W1-20 ppb spike).

Figure G-22b. Linear regression through concentration vs pre-analytical holding time for 1,2-dichloropropane (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-23a. Linear regression through concentration vs pre-analytical holding time for cis-1,3-dichloropropene (W1-20 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration (%D > 20%).

Figure G-23b. Linear regression through concentration vs pre-analytical holding time for cis-1,3-dichloropropene (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-24a. Linear regression through concentration vs pre-analytical holding time for trans-1,3-dichloropropene (W1-20 ppb spike).

Figure G-24b. Linear regression through concentration vs pre-analytical holding time for trans-1,3-dichloropropene (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-25a. Linear regression through concentration vs pre-analytical holding time for ethylbenzene (W1-20 ppb spike).

Figure G-25b. Linear regression through concentration vs pre-analytical holding time for ethylbenzene (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-26a. Linear regression through concentration vs pre-analytical holding time for 2-hexanone (W1-20 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$).

Figure G-26b. Linear regression through concentration vs pre-analytical holding time for 2-hexanone (W2-200 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$), and to aborated analysis of a sample due to a power outage (day 22).

Figure G-27a. Linear regression through concentration vs pre-analytical holding time for methyl iodide (W1-20 ppb spike).

Figure G-27b. Linear regression through concentration vs pre-analytical holding time for methyl iodide (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-28a. Linear regression through concentration vs pre-analytical holding time for 4-methyl-2-pentanone (W1-20 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration (%D > 20%).

Figure G-28b. Linear regression through concentration vs pre-analytical holding time for 4-methyl-2-pentanone (W2-200 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration (%D > 20%), and to aborted analysis of a sample due to a power outage (day 22).

Figure G-29a. Linear regression through concentration vs pre-analytical holding time for methylene chloride (W1-20 ppb spike).

Figure G-29b. Linear regression through concentration vs pre-analytical holding time for methylene chloride (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-30a. Linear regression through concentration vs pre-analytical holding time for styrene (W1-20 ppb spike).

Figure G-30b. Linear regression through concentration vs pre-analytical holding time for styrene (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-31a. Linear regression through concentration vs pre-analytical holding time for 1,1,2,2-tetrachloroethane (W1-20 ppb spike).

Figure G-32a. Linear regression through concentration vs pre-analytical holding time for tetrachloroethene (W1-20 ppb spike).

Figure G-32b. Linear regression through concentration vs pre-analytical holding time for tetrachloroethene (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-34a. Linear regression through concentration vs pre-analytical holding time for 1,1,1-trichloroethane (W1-20 ppb spike).

Figure G-34b. Linear regression through concentration vs pre-analytical holding time for 1,1,1-trichloroethane (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-35a. Linear regression through concentration vs pre-analytical holding time for 1,1,2-trichloroethane (W1-20 ppb spike).

Figure G-35b. Linear regression through concentration vs pre-analytical holding time for 1,1,2-trichloroethane (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-36a. Linear regression through concentration vs pre-analytical holding time for trichloroethene (W1-20 ppb spike).

Figure G-36b. Linear regression through concentration vs pre-analytical holding time for trichloroethene (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-37a. Linear regression through concentration vs pre-analytical holding time for trichlorofluoromethane (W1-20 ppb spike).

Figure G-37b. Linear regression through concentration vs pre-analytical holding time for trichlorofluoromethane (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-38a. Linear regression through concentration vs pre-analytical holding time for vinyl acetate (W1-20 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$).

Figure G-38b. Linear regression through concentration vs pre-analytical holding time for vinyl acetate (W-200 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$), and aborted analysis of a sample due to a power outage.

Figure G-39a. Linear regression through concentration vs pre-analytical holding time for vinyl chloride (W1-20 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$).

Figure G-39b. Linear regression through concentration vs pre-analytical holding time for vinyl chloride (W2-200 ppb spike). Points along x-axis correspond to data deleted due to unsatisfactory calibration ($\%D > 20\%$), and to aborted analysis of a sample due to a power outage (day 22).

Figure G-40a. Linear regression through concentration vs pre-analytical holding time for m,p-xylene (W1-20 ppb spike).

Figure G-40b. Linear regression through concentration vs pre-analytical holding time for m,p-xylene (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

Figure G-41a. Linear regression through concentration vs pre-analytical holding time for o-xylene (W1-20 ppb spike).

Figure G-41b. Linear regression through concentration vs pre-analytical holding time for o-xylene (W2-200 ppb spike). Point on x-axis corresponds to aborted analysis of a sample due to a power outage.

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