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**Stability of Purgeable VOCs  
in Water Samples During  
Pre-analytical Holding  
*Part 2. Analyses by an EPA  
Regional Laboratory***

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**Stability of Purgeable VOCs in Water Samples During  
Pre-analytical Holding**  
*Part 2. Analyses by an EPA Regional 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 NaHSO<sub>4</sub> (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 EPA analyses; the ARI results are described in a separate report.

Of the 42 compounds quantified by the EPA laboratory, only vinyl acetate and the isomers of 1,3-dichloropropene were found to be unstable over a 28-day holding time. This was also observed in the samples sent to ARI [West et al., 1996]. Tetrachloroethene, carbon disulfide and trichlorofluoromethane appeared to be more stable in the EPA samples when compared to the ARI samples. Both sets of samples were prepared using identical procedures and the same source of surface water; slight changes in water chemistry may have caused discrepancies between the two sets of samples.

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 the EPA regional laboratory; the ARI 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 contains results of the stability study,

regression analysis of the data to examine concentration trends with pre-analytical holding, and comparisons with the ARI results. Conclusions are presented in Sect. 4.

## 2. EXPERIMENTAL APPROACH

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  $\mu\text{m}$  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 W3 (low-level spike), 200  $\mu\text{L}$  and 20  $\mu\text{L}$  of CRS M-8240B-R and CRS M-5751-M, respectively, were added to the water. For sample sets W4 (high-level spike), 1000  $\mu\text{L}$  and 200  $\mu\text{L}$  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  $\text{NaHSO}_4$  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. In order to assess the effect of acidification on analyte stability, unacidified samples were also prepared and stored at 4°C with no headspace. These samples were analyzed on Days 1 and 36 of the stability study.

Immediately after sample preparation, the samples were shipped in coolers filled with ice for overnight delivery to the EPA Region IV laboratory in Athens, GA. Upon receipt of the samples, personnel at EPA Region IV immediately stored these in a cooler maintained at 4°C. At 1, 8, 15, 22, 29, 36, 60, and 90 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]. Matrix spike and matrix spike duplicate samples were not included in this study since the samples themselves are spiked samples.

A second set of water samples were prepared as described above and sent to Analytical Resources, Inc. (ARI) in Seattle, WA. The ARI results are described in a separate report [West et al., 1996].

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

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

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

<sup>b</sup> pH was 2.4-2.6 after acidification with 250 mg NaHSO<sub>4</sub> per 40-mL vial.

<sup>c</sup> Colony forming units per mL of sample.

Table 2. Test conditions for VOC stability study

Sample Set	VOC Target Spiking Level <sup>a</sup> (µg/L)	Number of samples	Preservation	Analysis Days
W3	20	32 (4 replicates per day)	4°C no headspace 250 mg NaHSO <sub>4</sub>	1, 8, 15, 22, 29, 36, 60, 90
		4 (2 replicates per day)	4°C no headspace	1, 36
W4	100 - 200	32 (4 replicates per day)	4°C no headspace 250 mg NaHSO <sub>4</sub>	1, 8, 15, 22, 29, 36, 60, 90
		4 (2 replicates per day)	4°C no headspace	1, 36

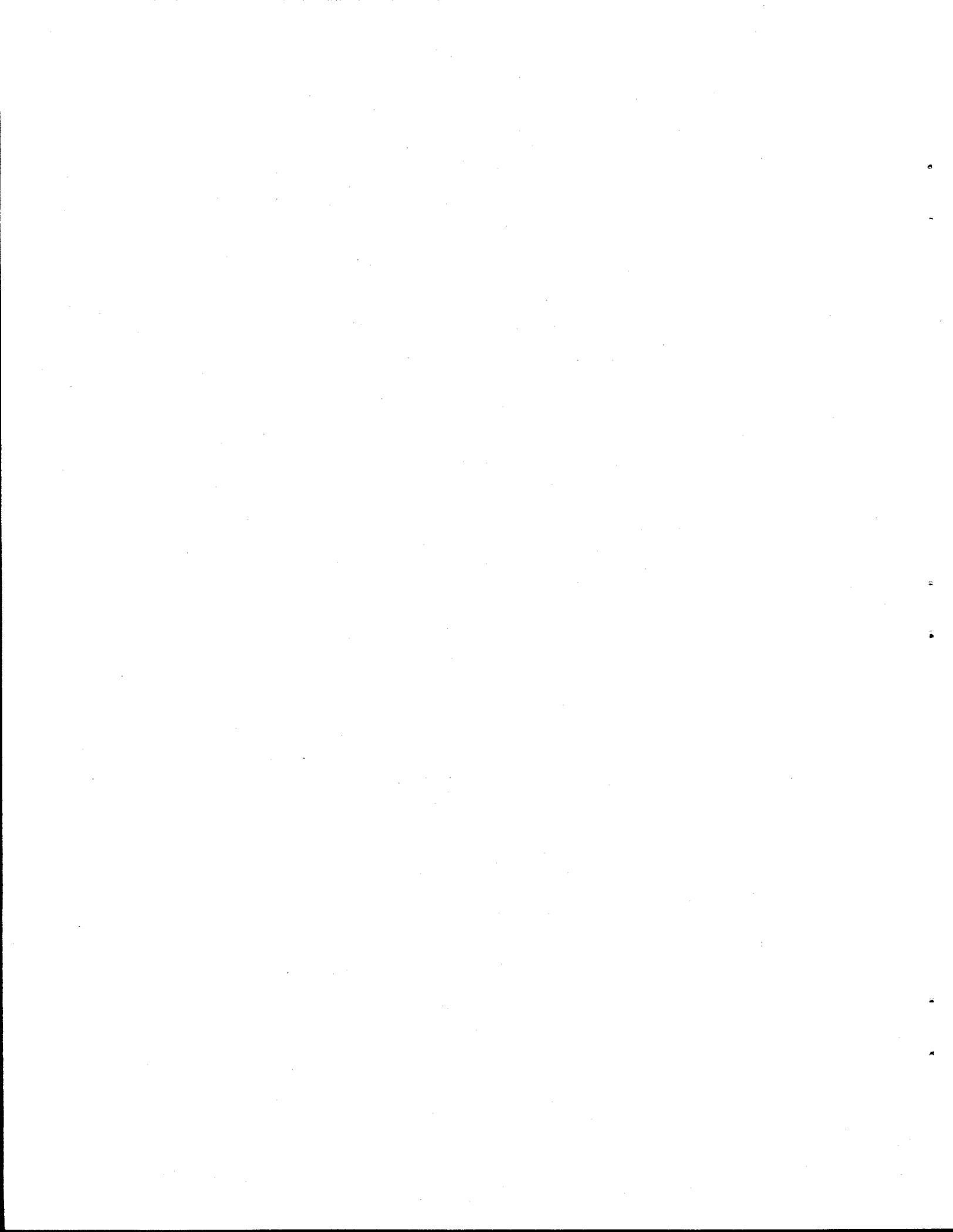
<sup>a</sup> Refer to Table 3 for VOCs in spiking solution.

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

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

<sup>a</sup> Acrolein, acrylonitrile, ethanol, 2-chloroethylvinylether, trans- 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.

<sup>b</sup> These 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).



### 3. RESULTS AND DISCUSSION

#### 3.1 Validation of VOC Measurements

Since the analyses described in this report were performed by an EPA regional laboratory (Region IV, Athens, GA), the measurements were presumed to be valid and a detailed description of instrument calibrations was deemed unnecessary.

#### 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 W3 (Table 4) and W2 (Table 5). Concentration measurements are given in the appendix. Measurement variability [i.e., relative measurement error (%RME)] for each compound within each sample set was estimated as follows:

$$\%RME = (S_o \times 100\%) / C_o \quad (1)$$

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 W3 and W4. 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.

The results of the EPA analyses were consistent with the stability observations noted from the ARI (commercial laboratory) data [West et. al, 1996]. 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 4 and 5). Furthermore, changes in concentration after 28 days of storage as predicted by the regression lines (see Tables 4 and 5) were predominantly low relative to the initial concentrations (estimated from the regression intercept). Out of 42 analytes, concentration changes exceeded 10% for only three compounds in both sets W3 and W4 [*vinyl acetate* (42%), *cis-1,3-dichloropropene* (16% and 17%), and *trans-1,4-dichloro-2-butene* (17% and 16%)].

Practical reporting times (PRTs) following the analysis described by Bayne et al. [1994] were calculated for the EPA regional data and are shown in Tables 4 and 5. Similar to PRT analysis results on the ARI data [West et. al, 1996], very short PRTs were calculated for some compounds even though the relative percent change after 28 days was less than 10% (e.g., *trans-1,2-dichloroethene* in Set W4). As noted in West et. al [1996],

factors other than calculated PRTs were considered in this study when assessing the effects of holding times on measurement validity. As such, statistical definitions of significant change such as the PRT approach must be complemented with "practical" definitions of "acceptable" concentration change. For this study, compounds with concentration changes less than 10% relative to initial concentrations were considered "functionally" stable. This criterion 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 distributions, 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].

Using the 10% criterion for functional stability, the EPA analytical results show that 39 out of 42 compounds did not exhibit a significant change in concentration over a 28-day holding time. Only vinyl acetate exhibited a relatively large change over the duration of the holding time study, while the isomers of 1,3-dichloropropene showed consistent changes on the order of 16 to 17% at 28 days in both sets W3 and W4. It was shown in [West et. al, 1996] that microbial activity is significantly reduced in 40-mL water samples that had been acidified with 250 mg of NaHSO<sub>4</sub>. Therefore, it is improbable that the instability of vinyl acetate and the isomers of 1,3-dichloropropene is due to biodegradation. It is more likely that these compounds are either volatilizing or undergoing abiotic chemical degradation at higher rates when compared to the other compounds in the samples.

Table 4. Linear regression and practical reporting time analysis results on stability data from sample set W3.

	<u>Regression parameters</u>		Significant negative slope (1-sided 5% significance)	Relative meas. error <sup>b</sup>	Change in conc. at 28 days <sup>c</sup>	%Change in conc. at 28 days <sup>d</sup>	Practical reporting time (Days) <sup>e</sup>
	Intercept <sup>a</sup>	Slope <sup>a</sup>					
Acetone	18.4	-0.0685	no	44%	-	-	90
Benzene	18.0	-0.0041	no	3%	-	-	90
Bromodichloromethane	18.4	0.0055	no	4%	-	-	90
Bromoform	17.8	-0.0021	no	5%	-	-	90
Bromomethane	20.3	-0.0179	yes	6%	-0.5	-2%	49
Butanone, 2-	15.6	-0.0108	no	15%	-	-	90
Carbon Disulfide	15.7	-0.0127	yes	5%	-0.4	-2%	42
Carbon Tetrachloride	16.4	-0.0007	no	4%	-	-	90
Chlorobenzene	17.7	-0.0043	no	3%	-	-	90
Chloroethane	19.4	0.0223	no	6%	-	-	90
Chloroform	18.9	-0.0024	no	4%	-	-	90
Chloromethane	12.2	0.0489	no	15%	-	-	90
Dibromochloromethane	19.3	0.0133	no	3%	-	-	90
Dibromomethane	20.5	-0.0042	no	4%	-	-	90
Dichlorodifluoromethane	9.4	0.0662	no	42%	-	-	90
Dichloroethane, 1,1-	20.1	-0.0003	no	3%	-	-	90
Dichloroethane, 1,2-	19.2	-0.0070	no	4%	-	-	90
Dichloroethene, 1,1-	16.7	-0.0024	no	4%	-	-	90
Dichloroethene, trans-1,2-	17.1	-0.0208	yes	4%	-0.6	-3%	23
Dichloropropane, 1,2-	20.2	-0.0088	yes	3%	-0.2	-1%	51
Dichloropropene, cis-1,3-	16.6	-0.0940	yes	4%	-2.6	-16%	5
Dichloropropene, trans-1,3-	14.3	-0.0848	yes	9%	-2.4	-17%	10
Ethyl Benzene	16.9	-0.0059	no	4%	-	-	90
Ethyl Methacrylate	9.8	0.0002	no	7%	-	-	90
Hexanone, 2-	16.5	0.0048	no	12%	-	-	90
Iodomethane	5.9	0.0018	no	7%	-	-	90
Methylene Chloride	20.9	-0.0293	no	15%	-	-	90
Pentanone, 4-methyl 2-	20.5	-0.0041	no	6%	-	-	90

<sup>a</sup> Intercept of regression line corresponds to extrapolated Day 0 concentration. Slope of regression line corresponds to change in concentration per day.

<sup>b</sup> 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.

<sup>c</sup> Calculated from regression line.

<sup>d</sup> Percent change relative to the intercept of the regression line (extrapolated Day 0 concentration).

<sup>e</sup> Practical reporting time calculated using method described in [Bayne et. al, 1993; 1994].

Table 4 (continued). Linear regression and practical reporting time analysis results on stability data from sample set W3.

	Regression parameters		Significant negative slope (1-sided 5% significance)	Relative Meas. Error <sup>b</sup>	Change in conc. at 28 days <sup>c</sup>	%Change in conc. at 28 days <sup>d</sup>	Practical Reporting Time (Days) <sup>e</sup>
	Intercept <sup>a</sup>	Slope <sup>a</sup>					
Styrene	18.3	-0.0093	yes	4%	-0.3	-1%	55
Tetrachloroethane,1,1,2,2-	18.2	-0.0118	no	6%	-	-	90
Tetrachloroethene	15.4	-0.0222	yes	5%	-0.6	-4%	22
Toluene	16.8	0.0025	no	3%	-	-	90
Trichloroethane,1,1,1-	15.7	0.0045	no	4%	-	-	90
Trichloroethane,1,1,2-	20.1	-0.0001	no	4%	-	-	90
Trichloroethene	18.0	-0.0162	yes	3%	-0.5	-3%	27
Trichlorofluoromethane	23.4	0.0086	no	5%	-	-	90
Trichloropropane,1,2,3-	20.3	-0.0018	no	6%	-	-	90
Vinyl Acetate	5.5	-0.0829	yes	36%	-2.3	-42%	17
Vinyl Chloride	17.0	0.0323	no	9%	-	-	90
Xylene,(m- and/or p-)	35.6	-0.0228	yes	3%	-0.6	-2%	31
Xylene,o-	18.2	-0.0083	yes	3%	-0.2	-1%	48

<sup>a</sup> Intercept of regression line corresponds to extrapolated Day 0 concentration. Slope of regression line corresponds to change in concentration per day.

<sup>b</sup> Estimated by  $So/Co \times 100\%$  where  $So$  and  $Co$  are the mean squared error and the intercept of the regression line, respectively.

<sup>c</sup> Calculated from regression line.

<sup>d</sup> Percent change relative to the intercept of the regression line (extrapolated Day 0 concentration).

<sup>e</sup> Practical reporting time calculated using method described in [Bayne et. al, 1993; 1994].

Table 5. Linear regression and practical reporting time analysis results on stability data from sample set W4

	Regression parameters		Significant negative slope (1-sided 5% significance)	Relative Meas. Error <sup>b</sup>	Change in conc. at 28 days <sup>c</sup>	%Change in conc. at 28 days <sup>d</sup>	Practical Reporting Time (Days) <sup>e</sup>
	Intercept <sup>a</sup>	Slope <sup>a</sup>					
Acetone	75.1	-0.1301	yes	16%	-3.6	-5%	61
Benzene	94.2	-0.0660	yes	4%	-1.8	-2%	41
Bromodichloromethane	99.3	-0.0172	no	2%	-	-	90
Bromoform	108.3	-0.1263	yes	5%	-3.5	-3%	28
Bromomethane	175.4	-0.1849	no	10%	-	-	90
Butanone, 2-	86.0	-0.0956	no	10%	-	-	90
Carbon Disulfide	78.5	-0.1263	yes	8%	-3.5	-5%	36
Carbon Tetrachloride	81.3	-0.0354	yes	3%	-1.0	-1%	41
Chlorobenzene	96.4	-0.0970	yes	3%	-2.7	-3%	20
Chloroethane	181.5	0.0683	no	8%	-	-	90
Chloroform	98.3	-0.0342	yes	2%	-1.0	-0%	47
Chloromethane	113.7	0.3673	no	18%	-	-	90
Dibromochloromethane	106.1	-0.0440	no	5%	-	-	90
Dibromomethane	111.9	-0.1268	yes	3%	-3.5	-3%	19
Dichlorodifluoromethane	75.4	0.3925	no	39%	-	-	90
Dichloroethane, 1,1-	105.2	-0.0255	no	5%	-	-	90
Dichloroethane, 1,2-	99.9	-0.0405	yes	2%	-1.1	-1%	28
Dichloroethene, 1,1-	79.5	-0.0483	yes	4%	-1.4	-2%	41
Dichloroethene, trans-1,2-	86.8	-0.1559	yes	3%	-4.4	-5%	12
Dichloropropane, 1,2-	110.4	-0.1186	yes	4%	-3.3	-3%	24
Dichloropropene, cis-1,3-	93.7	-0.5832	yes	3%	-16.3	-17%	4
Dichloropropene, trans-1,3-	89.6	-0.5054	yes	7%	-14.2	-16%	9
Ethyl Benzene	88.8	-0.0824	yes	3%	-2.3	-3%	21
Ethyl Methacrylate	53.6	0.0135	no	21%	-	-	90
Hexanone, 2-	93.9	-0.0574	no	10%	-	-	90
Iodomethane	30.5	-0.0044	no	6%	-	-	90
Methylene Chloride	104.4	-0.1557	yes	12%	-4.4	-4%	54
Pentanone, 4-methyl 2-	115.9	-0.0766	yes	5%	-2.1	-2%	51

<sup>a</sup> Intercept of regression line corresponds to extrapolated Day 0 concentration. Slope of regression line corresponds to change in concentration per day.

<sup>b</sup> Estimated by  $S_0/C_0 \times 100\%$  where  $S_0^2$  and  $C_0$  are the mean squared error and the intercept of the regression line, respectively.

<sup>c</sup> Calculated from regression line.

<sup>d</sup> Percent change relative to the intercept of the regression line (extrapolated Day 0 concentration).

<sup>e</sup> Practical reporting time calculated using method described in [Bayne et. al, 1993; 1994].

Table 5 (continued). Linear regression and practical reporting time analysis results on stability data from sample set W4

	Regression parameters		Significant negative slope (1-sided 5% significance)	Relative Meas. Error <sup>b</sup>	Change in conc. at 28 days <sup>c</sup>	%Change in conc. at 28 days <sup>d</sup>	Practical Reporting Time (Days) <sup>e</sup>
	Intercept <sup>a</sup>	Slope <sup>a</sup>					
Styrene	98.6	-0.0967	yes	3%	-2.7	-3%	19
Tetrachloroethane,1,1,2,2-	109.3	-0.1573	yes	5%	-4.4	-4%	25
Tetrachloroethene	79.3	-0.1564	yes	4%	-4.4	-6%	14
Toluene	90.8	-0.0628	yes	3%	-1.8	-2%	31
Trichloroethane,1,1,1-	83.2	-0.0258	no	4%	-	-	90
Trichloroethane,1,1,2-	111.0	-0.0491	yes	3%	-1.4	-1%	46
Trichloroethene	93.2	-0.1147	yes	3%	-3.2	-3%	15
Trichlorofluoromethane	206.7	-0.0704	no	5%	-	-	90
Trichloropropane,1,2,3-	118.2	-0.0793	yes	4%	-2.2	-2%	46
Vinyl Acetate	36.6	-0.5105	yes	28%	-14.3	-39%	14
Vinyl Chloride	156.7	0.1963	no	13%	-	-	90
Xylene,(m- and/or p-)	186.2	-0.1507	yes	4%	-4.2	-2%	31
Xylene,o-	98.0	-0.0901	yes	3%	-2.5	-3%	21

<sup>a</sup> Intercept of regression line corresponds to extrapolated Day 0 concentration. Slope of regression line corresponds to change in concentration per day.

<sup>b</sup> Estimated by  $S_0/C_0 \times 100\%$  where  $S_0^2$  and  $C_0$  are the mean squared error and the intercept of the regression line, respectively.

<sup>c</sup> Calculated from regression line.

<sup>d</sup> Percent change relative to the intercept of the regression line (extrapolated Day 0 concentration).

<sup>e</sup> Practical reporting time calculated using method described in [Bayne et. al, 1993; 1994].

### 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 Tables 6 and 7). 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.

Tables 6 and 7 show 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:

$$P.I. = C_o + BD \pm t(N-2, 0.025)(\text{var}(C_o) + D^2\text{var}(B) + 2D\text{covar}(C_o, B) + S_o^2)0.5 \quad (2)$$

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 36 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 unacidified samples on a given day fell outside the prediction intervals were: 1,1,2,2-tetrachloroethane and trichloroethene. 1,1,2,2-Tetrachloroethane was lower in the unacidified samples while trichloroethene levels were higher (see Table 6). This observation is consistent with the ARI data [West, et. al, 1996] and is attributed to the possible hydrolysis of 1,1,2,2-tetrachloroethane under neutral or basic pH conditions [Haag and Mill, 1988]. The higher trichloroethene levels in the unacidified samples are consistent with the fact that this compound is the by-product of 1,1,2,2-tetrachloroethane hydrolysis [Haag and Mill, 1988]. The degradation of 1,1,2,2-tetrachloroethane may have been inhibited by low pH in the acidified samples.

The stability of biodegradable VOCs (e.g. benzene, styrene) even without acidification is not surprising because the bacteria present in the surface water may not be acclimated to these compounds. The benefits of acidification were shown in [West et. al, 1996], where it was demonstrated that acidification leads to significant decreases in active microbial populations.

Table 6. Comparison between prediction intervals from acidified sample analyses and VOC levels in unacidified water samples from set W3

	Day 1		Day 1 Unacidified		Day 36 Prediction		Day 36 Unacidified	
	Prediction Interval <sup>a</sup>		Samples <sup>b</sup>		Interval <sup>a</sup>		Samples <sup>b</sup>	
	Lower Limit	Upper Limit	W3-0	W3-12	Lower Limit	Upper Limit	W3-37	W3-28
Acetone	0	38.1	13.0	14.0	0	35.2	13	11
Benzene	16.6	19.4	18.0	18.0	16.5	19.2	17	17
Bromodichloromethane	16.6	20.1	19.0	19.0	16.9	20.3	18	18
Bromoform	15.5	20.1	17.0	18.0	15.5	20.0	19	18
Bromomethane	17.2	23.5	19.0	19.0	16.6	22.8	19	17
Carbon Disulfide	13.8	17.6	16.0	16.0	13.4	17.1	16	13
Carbon Tetrachloride	14.9	17.9	18.0	17.0	14.9	17.8	16	15
Chlorobenzene	16.3	19.1	19.0	18.0	16.2	18.9	17	17
Chloroethane	16.7	22.1	20.0	19.0	17.5	22.8	20	19
Chloroform	16.9	20.8	19.0	19.0	16.8	20.7	18	18
Chloromethane	7.7	16.7	12.0	11.0	9.5	18.4	12	11
Dibromochloromethane	17.7	20.8	19.0	18.0	18.2	21.3	19	19
Dibromomethane	18.7	22.4	20.0	20.0	18.6	22.2	20	20
Dichlorodifluoromethane	-0.4	19.2	7.8	7.7	2.2	21.4	7.1	6.6
Dichloroethane,1,1-	18.5	21.8	21.0	21.0	18.5	21.7	20	19
Dichloroethane,1,2-	17.2	21.1	19.0	19.0	17.0	20.8	18	18
Dichloroethene,1,1-	15.2	18.2	18.0	17.0	15.2	18.1	16	16
Dichloroethene,trans-1,2-	15.3	18.8	17.0	17.0	14.6	18.0	16	16
Dichloropropane,1,2-	18.6	21.8	22.0	21.0	18.3	21.4	20	19
Dichloropropene,cis-1,3-	14.9	18.3	18.0	17.0	11.6	14.9	14	13
Dichloropropene,trans-1,3-	11.2	17.4	14.0	14.0	8.2	14.3	14	11
Ethyl Benzene	15.3	18.4	18.0	17.0	15.2	18.2	16	16
Ethyl Methacrylate	8.0	11.6	10.0	10.0	8.1	11.6	3	7
Iodomethane	4.9	7.0	9.0	6.0	4.9	7.1	6	6
Hexanone, 2-	11.6	21.4	15.0	16.0	11.8	21.5	16	16
Butanone, 2-	9.9	21.3	15.0	16.0	9.7	20.8	15	14
Pentanone, 2-, 4-methyl	17.5	23.5	18.0	18.0	17.4	23.3	21	21
Methylene Chloride	13.2	28.5	20.0	20.0	12.3	27.3	17	18
Styrene	16.4	20.1	19.0	18.0	16.1	19.7	17	16
Tetrachloroethane,1,1,2,2-	15.5	20.8	15.0	16.0	15.1	20.4	8.6	7.2
Tetrachloroethene	13.7	17.1	17.0	16.0	12.9	16.3	14	14
Toluene	15.3	18.2	19.0	18.0	15.5	18.2	16	16
Trichloroethane,1,1,1-	14.1	17.2	17.0	16.0	14.3	17.4	16	14
Trichloroethane,1,1,2-	18.2	22.0	21.0	20.0	18.2	21.9	20	20
Trichloroethene	16.5	19.6	21.0	20.0	16.0	18.9	24	23
Trichlorofluoromethane	20.8	26.1	25.0	24.0	21.2	26.3	22	21
Trichloropropane,1,2,3-	17.4	23.3	18.0	20.0	17.4	23.2	22	20
Vinyl Acetate	0.6	10.4	N/D	N/D	0	7.3	N/D	N/D
Vinyl Chloride	13.1	20.9	17.0	16.0	14.3	22.0	16	16
Xylene,m- and/or p-	33.1	38.1	37.0	35.0	32.3	37.2	33	32
Xylene,o-	16.8	19.6	19.0	18.0	16.5	19.3	17	16

Table 7. Comparison between prediction intervals from acidified sample analyses and VOC levels in unacidified water samples from set W4

	Day 1		Day 1 Unacidified		Day 36 Prediction		Day 36 Unacidified	
	Prediction Interval <sup>a</sup>		Samples <sup>b</sup>		Interval <sup>a</sup>		Samples <sup>b</sup>	
	Lower Limit	Upper Limit	W4-9	W4-35	Lower Limit	Upper Limit	W4-32	W4-36
Acetone	46.4	103.9	81.0	84.0	42.3	98.7	69	64
Benzene	84.6	103.8	85.0	90.0	82.4	101.2	89	88
Bromodichloromethane	95.2	103.4	94.0	98.0	94.7	102.7	98	94
Bromoform	95.9	120.8	99.0	100.0	91.7	116.1	110	97
Bromomethane	131.3	219.5	150.0	160.0	125.7	212.1	150	140
Carbon Disulfide	62.3	94.7	68.0	73.0	58.2	90.0	70	68
Carbon Tetrachloride	76.2	86.5	74.0	82.0	75.0	85.2	78	80
Chlorobenzene	89.7	103.2	92.0	97.0	86.4	99.7	90	88
Chloroethane	144.1	219.0	160.0	160.0	147.2	220.6	170	170
Chloroform	92.6	104.0	93.0	98.0	91.5	102.7	94	92
Chloromethane	64.8	162.6	94.0	98.0	78.6	174.4	97	97
Dibromochloromethane	93.9	118.4	100.0	110.0	92.6	116.6	100	100
Dibromomethane	103.1	120.7	110.0	110.0	98.8	116.1	110	110
Dichlorodifluoromethane	3.4	147.4	57.0	62.0	18.6	159.7	56	54
Dichloroethane,1,1-	91.7	118.7	98.0	100.0	91.1	117.5	97	96
Dichloroethane,1,2-	95.9	104.0	98.0	110.0	94.6	102.5	97	93
Dichloroethene,1,1-	72.5	86.6	73.0	77.0	70.9	84.7	74	74
Dichloroethene,trans-1,2-	80.2	93.4	82.0	86.0	74.9	87.8	79	78
Dichloropropane,1,2-	100.2	120.6	100.0	110.0	96.3	116.3	100	99
Dichloropropene,cis-1,3-	85.9	101.4	85.0	90.0	65.7	80.8	71	68
Dichloropropene,trans-1,3-	74.0	105.2	76.0	81.0	56.6	87.1	72	58
Ethyl Benzene	82.4	95.1	84.0	89.0	79.7	92.1	83	86
Ethyl Methacrylate	25.5	81.8	60.0	60.0	26.5	81.7	20	30
Iodomethane	26.1	34.8	30.0	30.0	26.0	34.6	30	30
Methyl Butyl Ketone	70.8	117.0	100.0	100.0	69.3	114.5	91	93
Methyl Ethyl Ketone	64.1	107.9	98.0	96.0	61.2	104.1	86	84
Methyl Isobutyl Ketone	102.0	129.9	120.0	120.0	99.6	126.9	120	120
Methylene Chloride	73.9	134.9	95.0	100.0	69.1	128.8	86	86
Styrene	92.0	105.1	94.0	100.0	88.8	101.6	92	90
Tetrachloroethane,1,1,2,2-	95.3	123.2	93.0	88.0	90.1	117.4	46	39
Tetrachloroethene	71.2	87.4	79.0	86.0	65.9	81.8	70	72
Toluene	83.9	97.7	85.0	93.0	81.8	95.4	84	86
Trichloroethane,1,1,1-	74.4	92.0	74.0	80.0	73.6	90.9	80	74
Trichloroethane,1,1,2-	102.9	119.1	110.0	110.0	101.3	117.2	110	100
Trichloroethene	87.1	99.4	93.0	100.0	83.2	95.3	120	130
Trichlorofluoromethane	181.9	231.4	190.0	210.0	180.0	228.4	190	190
Trichloropropane,1,2,3-	105.3	131.1	120.0	110.0	102.8	128.1	120	110
Vinyl Acetate	11.3	62.0	40.0	40.0	-6.1	43.6	N/D	N/D
Vinyl Chloride	105.5	207.9	130.0	140.0	113.4	213.8	140	130
Xylene,m- and/or p-	169.5	202.9	180.0	190.0	164.5	197.2	170	180
Xylene,o-	91.2	104.8	92.0	96.0	88.2	101.5	91	90

### **3.4 Comparison between Stability Study Results from Commercial and EPA Laboratories**

The stability study results were generally consistent between the analyses by the commercial (ARI, West et al., 1996) and EPA regional laboratories (see Table 8). In both sets of samples, a majority of the target VOCs were found to be functionally stable based on an "acceptable" relative concentration change of 10%. Fewer compounds failed this criterion in the samples sent to EPA; these compounds were vinyl acetate and the isomers of 1,3-dichloropropane. Tetrachloroethene, carbon disulfide and trichlorofluoromethane also failed the 10% relative change criterion in the ARI samples but were found to be functionally stable in the EPA samples. It is difficult to ascertain the reason behind this discrepancy since the same source of surface water (Clinch River) and the same sample preparation procedures (see Section 2) were used. Because the samples were prepared in separate batches and on different days, slight changes in water chemistry from one batch of surface water to the other may have led to differences in behavior between the two sets of samples.

Table 8. Changes in concentration after 28 days relative to initial levels in stability study samples analyzed by a commercial (Analytical Resource Inc., ARI) and an EPA laboratory.

Compound	Sample Set W1 20 ppb (ARI)	Sample Set W2 200 ppb (ARI)	Sample Set W3 20 ppb (EPA)	Sample Set W4 200 ppb (EPA)
Acetone	* <sup>a</sup>	*	*	-5%
Acrolein	-- <sup>b</sup>	-25%	N.A. <sup>c</sup>	N.A.
Acrylonitrile	*	*	N.A.	N.A.
Benzene	*	*	*	-2%
Bromodichloromethane	*	-3%	*	*
Bromoform	*	-6%	*	-3%
Bromomethane	-4%	-9%	-2%	*
Carbon Disulfide	-9%	-17%	-2%	-5%
Carbon Tetrachloride	-3%	-10%	*	-1%
Chlorobenzene	-2%	-6%	*	-3%
Chloroethane	*	-6%	*	*
Chloroform	*	*	*	-1%
Chloromethane	-5%	-10%	*	*
Chlorovinylethylether,2-	-- <sup>d</sup>	-- <sup>d</sup>	N.A.	N.A.
Dibromochloromethane	*	-6%	*	*
Dibromomethane	*	*	*	-3%
Dichlorodifluoromethane	N.A.	N.A.	*	*
Dichloroethane,1,1-	*	*	*	*
Dichloroethane,1,2-	*	*	*	-1%
Dichloroethene,1,1-	*	*	*	-2%
Dichloroethene,trans-1,2-	-4%	-9%	-3%	-5%
Dichloropropane,1,2-	*	*	-1%	-3%
Dichloropropene,cis-1,3-	-11%	-14%	-16%	-17%
Dichloropropene,trans-1,3-	-9%	-12%	-17%	-16%
Ethyl Benzene	-2%	-8%	*	-3%
Ethyl Methacrylate	N.A.	N.A.	*	*
Iodomethane (Methyl iodide)	*	*	*	*
Methyl Butyl Ketone (2-Hexanone)	*	-9%	*	*
Methyl Ethyl Ketone (2-Butanone)	*	*	*	*
Methyl Isobutyl Ketone (4-Methyl-2-Pentanone)	*	*	*	-2%
Methylene Chloride	*	*	*	-4%
Styrene	*	-10%	-1%	-3%

<sup>a</sup> "\*" indicates that regression did not have a negatively significant slope.

<sup>b</sup> Spike level in sample set W1 below detection limit for acrolein (50 ppb).

<sup>c</sup> "N.A." indicates the compound was not quantitated.

<sup>d</sup> Instrument response to 2-chloroethylvinylether in acidified water samples was extremely low.

\*\*\* continued \*\*\*

Table 8 (continued). Changes in concentration after 28 days relative to initial levels in stability study samples analyzed by a commercial (Analytical Resource Inc., ARI) and an EPA laboratory.

Compound	Sample Set W1 20 ppb (ARI)	Sample Set W2 200 ppb (ARI)	Sample Set W3 20 ppb (EPA)	Sample Set W4 200 ppb (EPA)
Tetrachloroethane,1,1,2,2-	* <sup>a</sup>	*	*	-4%
Tetrachloroethene	-10%	-16%	-4%	-6%
Toluene	*	*	*	-2%
Trichloroethane,1,1,1-	*	-8%	*	*
Trichloroethane,1,1,2-	*	*	*	-1%
Trichloroethene	*	-7%	-3%	-3%
Trichlorofluoromethane	-8%	-15%	*	*
Trichloropropane,1,2,3-	*	-6%	*	-2%
Vinyl Acetate	-42%	-42%	-42%	-39%
Vinyl Chloride	*	*	*	*
Xylene,m- and/or p-	*	-9%	-2%	-2%
Xylene,o-	*	-7%	-1%	-3%

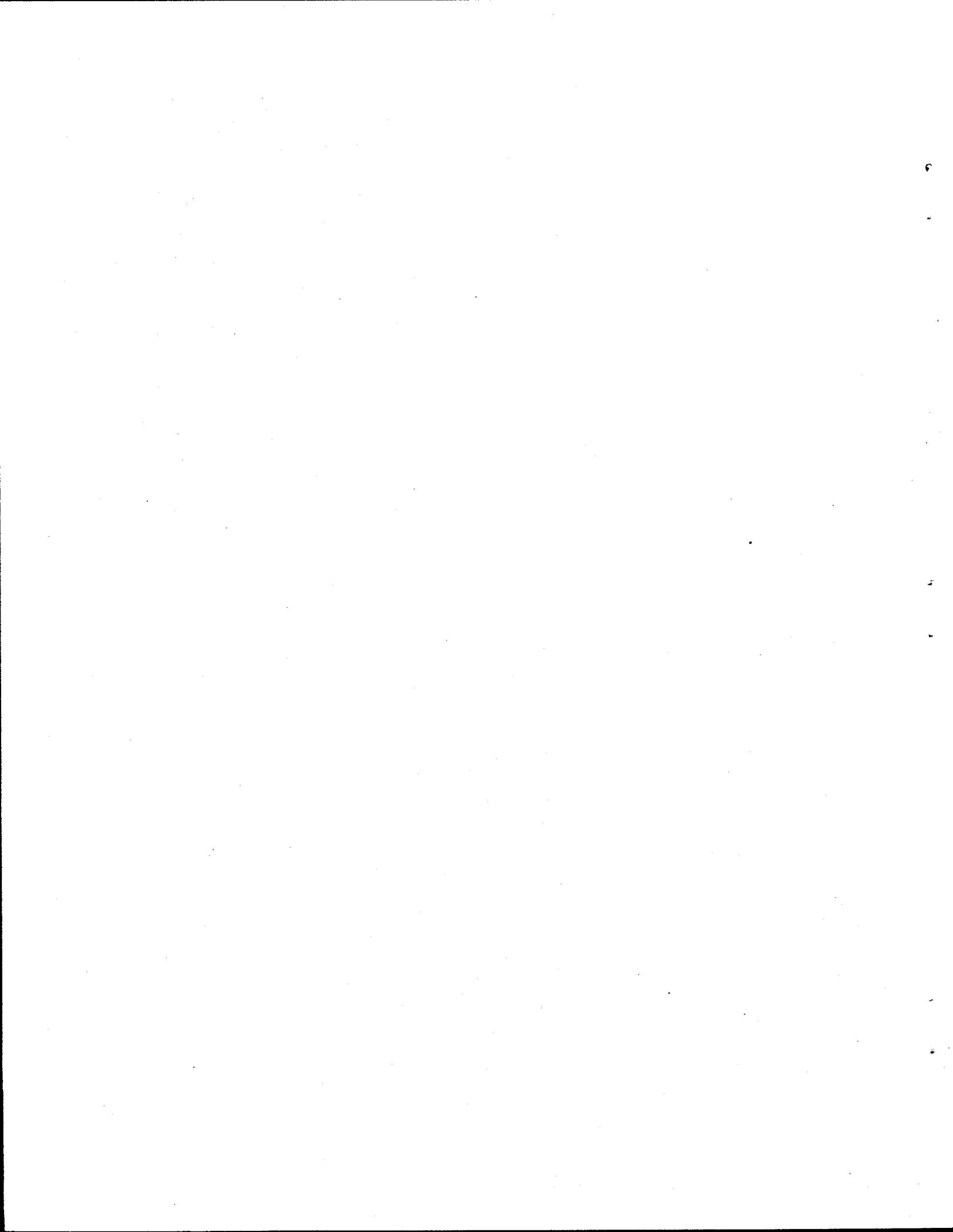
<sup>a</sup> '\*' indicates that regression had a did not have a negatively significant slope.

## 5. CONCLUSIONS

The stability study results from samples sent to an EPA regional laboratory (Region IV) showed that the measurement of 39 out of 42 purgeable VOCs in properly preserved water samples will not be affected by sample storage for 28 days. In this study, analytes were considered functionally stable if concentration changes on the 28th day were less than 10% of the initial levels. This criterion is reasonable given the other sources of uncertainty in site characterization and health risk assessment for which these analytical data are typically used.

Of the 42 compounds analyzed by the EPA laboratory, only vinyl acetate and the isomers of 1,3-dichloropene were found to be unstable over a 28-day holding time. This was also observed in the samples sent to ARI [West et al., 1996]. Tetrachloroethene, carbon disulfide and trichlorofluoromethane appeared to be more stable in the EPA samples when compared to the ARI samples. Both sets of samples were prepared using identical procedures and the same source of surface water; slight changes in water chemistry may have caused discrepancies between the two sets of samples.

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.



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**APPENDIX**  
EPA Region IV Analyses of Stability Study Samples

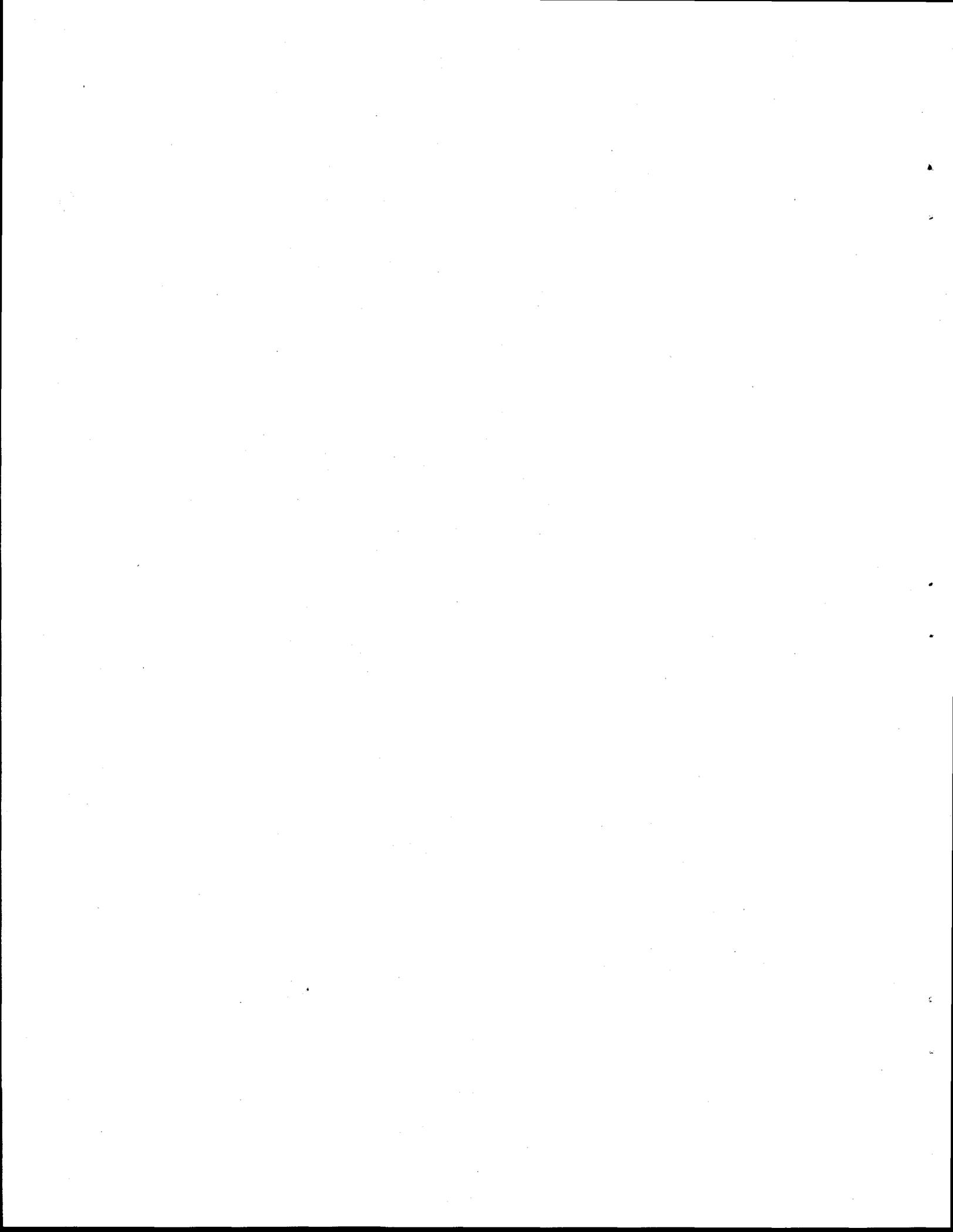


Tabla A1. Concentrations (ppb) of volatile organic compounds measured by EPA Region IV laboratory in acidified samples from set W3 (20 ppb spike)

Sample No. ->	Day 1				Day 8				Day 15			
	3-8	3-13	3-25	3-40	3-3	3-6	3-18	3-39	3-10	3-17	3-30	3-PH
Acetone	16	15	16	14	12	23	12	31	10	13	14	23
Benzene	18	18	17	18	18	18	18	19	16	18	18	18
Bromodichloromethane	18	18	18	18	19	19	19	19	17	18	19	19
Bromoform	17	18	17	18	19	18	19	18	16	18	19	18
Bromomethane	19	19	18	20	20	20	20	20	19	20	21	21
Carbon Disulfide	16	16	15	16	15	16	16	16	15	15	16	16
Carbon Tetrachloride	17	17	16	16	16	16	16	17	15	16	17	16
Chlorobenzene	18	19	17	18	17	18	18	18	17	18	17	18
Chloroethane	19	19	18	19	19	19	19	20	18	19	19	19
Chloroform	20	19	18	18	18	19	20	19	17	18	20	20
Chloromethane	12	11	11	11	11	12	12	12	12	13	13	13
Dibromochloromethane	19	19	19	20	19	20	20	19	18	20	20	20
Dibromomethane	21	20	20	20	21	20	22	21	19	21	20	20
Dichlorodifluoromethane	7.6	7.6	7.7	7.5	7.9	8.1	7.7	8.1	9.5	10	11	11
Dichloroethane,1,1-	21	21	20	20	20	20	21	20	19	20	21	21
Dichloroethane,1,2-	20	19	19	19	19	19	19	20	17	19	19	20
Dichloroethene,1,1-	16	16	17	17	16	17	17	17	16	16	18	17
Dichloroethene,trans-1,2-	17	18	16	18	17	18	18	18	15	17	17	17
Dichloropropane,1,2-	21	21	21	19	20	20	20	20	18	19	20	21
Dichloropropene,cis-1,3-	17	18	16	17	16	16	16	16	14	16	15	15
Dichloropropene,trans-1,3-	17	18	17	14	13	13	13	13	12	12	13	13
Ethyl Benzene	17	18	16	17	16	17	17	16	16	17	17	17
Ethyl Methacrylate	10	10	10	10	10	10	10	10	9	10	10	10
Iodomethane	6	6	6	5	6	6	6	7	5	6	6	6
Methyl Butyl Ketone	18	18	18	14	16	16	17	16	13	15	15	16
Methyl Ethyl Ketone	17	17	18	13	15	14	15	16	12	12	14	14
Methyl Isobutyl Ketone	20	21	20	19	22	21	22	21	18	20	20	22
Methylene Chloride	24	23	22	27	16	16	15	15	22	29	19	26
Styrene	18	19	17	18	18	19	18	18	17	19	19	18
Tetrachloroethane,1,1,2,2-	18	20	19	18	20	18	20	19	16	17	17	17
Tetrachloroethene	16	17	16	16	15	16	16	16	14	15	15	15
Toluene	17	18	17	17	16	17	17	16	16	17	17	17
Trichloroethane,1,1,1-	16	16	16	16	16	16	16	16	14	15	16	16
Trichloroethane,1,1,2-	21	21	20	20	19	20	20	20	19	21	20	20
Trichloroethene	18	18	17	18	18	18	18	19	16	18	19	18
Trichlorofluoromethane	24	23	24	23	24	24	24	23	21	22	25	24
Trichloropropane,1,2,3-	20	20	21	19	22	20	23	21	19	21	21	22
Vinyl Acetate	10	10	10	7	6	5	5	5	4	4	3	3
Vinyl Chloride	16	16	16	17	16	16	16	17	17	18	18	18
Xylene,m- and/or p-	35	37	34	36	34	36	36	34	33	35	36	36
Xylene,o-	18	18	18	18	18	19	18	18	17	19	18	18

Tabla A1 (continued). Concentrations (ppb) of volatile organic compounds measured by EPA Region IV laboratory in acidified samples from set W3 (20 ppb spike)

Sample No. ->	Day 22				Day 29				Day 36			
	3-26	3-27	3-32	3-4	3-1	3-16	3-22	3-33	3-23	3-24	3-31	3-36
Acetone	19	18	54	19	15	13	15	14	12	13	12	13
Benzene	18	17	19	18	18	18	18	18	18	18	18	18
Bromodichloromethane	19	18	19	18	19	19	19	20	18	18	18	19
Bromoform	18	17	17	17	19	17	19	18	18	17	17	19
Bromomethane	21	21	21	21	21	21	21	22	19	18	17	19
Carbon Disulfide	15	14	16	15	15	16	15	16	15	14	14	15
Carbon Tetrachloride	16	16	16	16	17	17	18	17	16	17	16	16
Chlorobenzene	18	17	18	18	17	17	18	18	17	17	17	17
Chloroethane	22	20	22	22	21	21	20	22	19	20	19	20
Chloroform	19	19	20	19	19	19	19	19	18	18	18	18
Chloromethane	14	14	15	14	16	16	17	16	12	11	11	12
Dibromochloromethane	20	19	20	20	20	19	20	21	19	20	19	19
Dibromomethane	20	20	22	21	21	20	21	20	21	21	20	20
Dichlorodifluoromethane	13	13	13	12	16	16	16	16	6.7	7.1	6.8	6.9
Dichloroethane,1,1-	19	19	20	20	21	20	21	20	20	20	19	20
Dichloroethane,1,2-	19	18	20	19	20	19	20	20	18	18	18	19
Dichloroethene,1,1-	17	16	17	16	18	17	17	17	16	17	16	16
Dichloroethene,trans-1,2-	16	16	16	16	16	17	16	16	17	16	16	16
Dichloropropane,1,2-	20	20	21	20	20	20	20	20	20	20	19	20
Dichloropropene,cis-1,3-	14	15	14	14	14	14	14	15	13	13	12	14
Dichloropropene,trans-1,3-	12	12	12	12	10	11	11	11	10	11	10	13
Ethyl Benzene	17	17	18	17	16	16	17	18	17	17	16	16
Ethyl Methacrylate	10	10	10	10	10	10	10	10	10	10	10	6
Iodomethane	6	6	7	6	6	6	6	6	6	6	6	6
Methyl Butyl Ketone	19	19	21	19	18	16	18	18	17	16	15	15
Methyl Ethyl Ketone	18	18	22	18	18	15	16	16	15	14	13	14
Methyl Isobutyl Ketone	20	20	22	21	20	18	21	20	22	22	20	20
Methylene Chloride	19	19	21	21	20	20	20	20	18	18	17	18
Styrene	19	18	19	18	18	18	18	20	17	17	17	17
Tetrachloroethane,1,1,2,2-	18	17	19	17	18	17	18	18	17	17	17	19
Tetrachloroethene	15	14	15	14	14	14	15	15	14	14	13	14
Toluene	17	17	17	17	16	16	17	18	16	17	17	16
Trichloroethane,1,1,1-	16	15	16	16	16	16	16	16	16	15	14	16
Trichloroethane,1,1,2-	21	20	21	20	19	19	20	22	20	20	19	20
Trichloroethene	17	17	18	18	18	18	18	18	17	17	17	17
Trichlorofluoromethane	24	23	25	24	24	25	24	25	23	22	22	22
Trichloropropane,1,2,3-	20	19	21	19	21	19	21	20	20	20	19	21
Vinyl Acetate	2	2	2	2	2	1	1	1	0.8	0.9	1	2
Vinyl Chloride	18	18	19	18	20	20	20	21	16	16	16	17
Xylene,m- and/or p-	37	35	35	35	34	36	36	37	35	35	34	34
Xylene,o-	19	18	19	18	18	18	18	19	17	17	17	18

Tabla A1 (continued). Concentrations (ppb) of volatile organic compounds measured by EPA Region IV laboratory in acidified samples from set W3 (20 ppb spike)

Sample No. ->	Day 60				Day 90			
	3-2	3-14	3-29	3-35	3-9	3-11	3-19	3-34
Acetone	11	9.9	11	11	14	14	14	15
Benzene	17	18	18	18	17	17	18	18
Bromodichloromethane	18	18	18	18	19	18	20	20
Bromoform	17	16	17	16	18	18	18	19
Bromomethane	20	20	20	22	17	18	18	18
Carbon Disulfide	16	16	16	17	14	14	14	14
Carbon Tetrachloride	16	16	16	17	16	16	17	16
Chlorobenzene	17	17	18	18	17	17	18	18
Chloroethane	21	21	21	22	20	20	21	22
Chloroform	19	19	18	19	18	18	19	20
Chloromethane	17	17	18	18	15	14	16	15
Dibromochloromethane	19	20	20	20	20	21	21	21
Dibromomethane	20	19	20	19	20	20	21	21
Dichlorodifluoromethane	22	20	19	19	11	11	12	11
Dichloroethane,1,1-	20	20	20	19	20	20	21	21
Dichloroethane,1,2-	18	18	19	19	18	18	20	19
Dichloroethene,1,1-	17	17	17	17	16	16	16	17
Dichloroethene,trans-1,2-	16	16	15	16	15	15	16	16
Dichloropropane,1,2-	20	20	20	20	19	19	19	20
Dichloropropene,cis-1,3-	9.7	10	10	11	8.8	8.8	8.7	8.8
Dichloropropene,trans-1,3-	8.9	8.8	9	9	7.3	7.5	7.6	7.6
Ethyl Benzene	16	16	17	16	16	16	17	17
Ethyl Methacrylate	10	10	10	10	10	10	10	10
Iodomethane	6	6	6	5	6	6	7	6
Methyl Butyl Ketone	14	14	14	14	18	19	18	19
Methyl Ethyl Ketone	13	12	13	12	16	16	16	16
Methyl Isobutyl Ketone	19	19	20	18	20	21	20	22
Methylene Chloride	19	19	19	19	19	18	20	19
Styrene	17	18	18	18	17	17	18	18
Tetrachloroethane,1,1,2,2-	17	16	17	16	17	18	18	19
Tetrachloroethene	14	14	14	14	14	14	14	14
Toluene	16	17	17	17	17	17	17	18
Trichloroethane,1,1,1-	15	16	16	17	16	16	17	16
Trichloroethane,1,1,2-	20	19	20	19	20	20	21	21
Trichloroethene	17	17	17	18	16	16	17	17
Trichlorofluoromethane	24	25	25	25	23	24	25	24
Trichloropropane,1,2,3-	19	18	20	18	21	21	21	22
Vinyl Acetate	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Vinyl Chloride	20	22	21	21	18	18	19	19
Xylene,m- and/or p-	33	34	34	35	33	33	34	34
Xylene,o-	17	18	18	18	17	17	18	18

Tabla A2. Concentrations (ppb) of volatile organic compounds measured by EPA Region IV laboratory in unacidified samples from set W3 (20 ppb spike)

Sample No.->	Day 1		Day 36	
	W3-0	W3-12	W3-37	W3-28
Acetone	13	14	13	11
Benzene	18	18	17	17
Bromodichloromethane	19	19	18	18
Bromoform	17	18	19	18
Bromomethane	19	19	19	17
Carbon Disulfide	16	16	16	13
Carbon Tetrachloride	18	17	16	15
Chlorobenzene	19	18	17	17
Chloroethane	20	19	20	19
Chloroform	19	19	18	18
Chloromethane	12	11	12	11
Dibromochloromethane	19	18	19	19
Dibromomethane	20	20	20	20
Dichlorodifluoromethane	7.8	7.7	7.1	6.6
Dichloroethane,1,1-	21	21	20	19
Dichloroethane,1,2-	19	19	18	18
Dichloroethene,1,1-	18	17	16	16
Dichloroethene,trans-1,2-	17	17	16	16
Dichloropropane,1,2-	22	21	20	19
Dichloropropene,cis-1,3-	18	17	14	13
Dichloropropene,trans-1,3-	14	14	14	11
Ethyl Benzene	18	17	16	16
Ethyl Methacrylate	10	10	3	7
Iodomethane	9	6	6	6
Methyl Butyl Ketone	15	16	16	16
Methyl Ethyl Ketone	15	16	15	14
Methyl Isobutyl Ketone	18	18	21	21
Methylene Chloride	20	20	17	18
Styrene	19	18	17	16
Tetrachloroethane,1,1,2,2	15	16	9	7
Tetrachloroethene	17	16	14	14
Toluene	19	18	16	16
Trichloroethane,1,1,1-	17	16	16	14
Trichloroethane,1,1,2-	21	20	20	20
Trichloroethene	21	20	24	23
Trichlorofluoromethane	25	24	22	21
Trichloropropane,1,2,3-	18	20	22	20
Vinyl Acetate	N/D	N/D	N/D	N/D
Vinyl Chloride	17	16	16	16
Xylene,m- and/or p-	37	35	33	32
Xylene,o-	19	18	17	16

Tabla A3. Concentrations (ppb) of volatile organic compounds measured by EPA Region IV laboratory in acidified samples from set W4 [200 ppb spike for compounds in CRS M-5751-M stock (see Table 3); 100 ppb spike for other compounds]

Sample No. ->	Day 1				Day 8				Day 15			
	4-5	4-10	4-21	4-34	4-3	4-4	4-15	4-33	4-7	4-14	4-25	4-37
Acetone	76	86	87	53	69	82	67	63	62	71	72	110
Benzene	86	92	86	90	92	94	94	96	93	98	94	94
Bromodichloromethane	96	100	97	99	100	100	100	100	99	100	100	100
Bromoform	97	110	99	98	110	110	110	110	110	110	110	110
Bromomethane	160	160	150	170	160	160	160	160	180	180	180	180
Carbon Disulfide	71	72	68	75	73	77	76	77	77	81	78	77
Carbon Tetrachloride	76	82	78	81	80	82	82	81	81	83	85	80
Chlorobenzene	92	100	94	100	91	95	96	95	93	96	96	96
Chloroethane	160	170	160	170	170	180	180	180	180	190	190	180
Chloroform	96	98	96	96	97	99	98	98	97	100	100	100
Chloromethane	98	100	95	100	100	110	110	110	120	130	120	120
Dibromochloromethane	100	110	100	110	110	110	110	100	100	100	110	110
Dibromomethane	110	110	110	110	110	110	110	110	100	110	110	110
Dichlorodifluoromethane	59	59	59	63	62	62	62	62	79	79	83	76
Dichloroethane,1,1-	100	100	100	100	100	110	110	100	100	110	110	110
Dichloroethane,1,2-	100	100	100	100	100	100	100	100	97	100	100	100
Dichloroethene,1,1-	78	79	75	80	76	79	78	78	80	80	82	77
Dichloroethene,trans-1,2-	84	87	84	88	83	86	86	86	83	86	88	84
Dichloropropane,1,2-	110	110	110	100	110	110	110	110	110	110	110	110
Dichloropropene,cis-1,3-	90	94	87	92	87	88	90	89	86	90	86	88
Dichloropropene,trans-1,3-	77	82	75	77	88	89	90	90	86	87	85	90
Ethyl Benzene	85	89	86	93	84	86	88	87	87	90	88	88
Ethyl Methacrylate	70	70	70	70	50	60	60	50	40	50	50	50
Iodomethane	30	30	30	30	30	30	30	30	30	30	30	30
Methyl Butyl Ketone	100	110	110	78	96	88	94	91	85	84	83	89
Methyl Ethyl Ketone	95	100	98	66	88	82	88	83	74	79	74	81
Methyl Isobutyl Ketone	110	130	110	100	120	120	120	120	110	110	110	120
Methylene Chloride	110	120	120	100	86	86	84	84	120	140	99	120
Styrene	95	100	95	98	94	96	97	97	97	98	100	100
Tetrachloroethane,1,1,2,2-	100	120	100	96	110	110	110	110	110	110	100	110
Tetrachloroethene	83	86	81	86	74	77	77	77	75	75	78	75
Toluene	87	95	89	91	86	88	89	90	89	91	92	91
Trichloroethane,1,1,1-	76	78	77	79	83	85	84	84	84	86	87	84
Trichloroethane,1,1,2-	110	120	110	110	110	110	110	110	110	110	110	110
Trichloroethene	89	93	89	94	91	92	94	93	90	95	95	93
Trichlorofluoromethane	200	210	200	200	200	210	210	210	200	210	200	190
Trichloropropane,1,2,3-	110	120	120	110	120	120	120	120	120	110	110	120
Vinyl Acetate	40	70	40	20	50	40	40	40	30	30	30	30
Vinyl Chloride	140	140	130	140	150	150	150	150	160	170	160	160
Xylene,m- and/or p-	180	190	180	190	180	180	180	180	180	190	190	190
Xylene,o-	94	97	94	99	94	96	97	96	96	98	100	98

Tabla A3 (continued). Concentrations (ppb) of volatile organic compounds measured by EPA Region IV laboratory in acidified samples from set W4.

Sample No. ->	Day 22				Day 29				Day 36			
	4-22	4-23	4-27	4-38	4-1	4-13	4-18	4-28	4-19	4-20	4-26	4-31
Acetone	81	83	82	85	67	65	70	74	61	55	60	68
Benzene	94	96	99	98	90	95	96	97	88	88	92	88
Bromodichloromethane	100	100	100	100	97	100	100	100	97	94	99	96
Bromoform	110	110	110	110	100	100	110	110	100	98	100	100
Bromomethane	180	190	200	190	180	190	190	200	150	140	160	150
Carbon Disulfide	79	79	84	82	74	76	79	78	70	68	74	70
Carbon Tetrachloride	82	81	83	81	79	80	82	82	78	78	82	77
Chlorobenzene	96	98	97	97	90	93	95	96	90	91	92	89
Chloroethane	190	190	210	200	190	200	200	210	170	160	180	170
Chloroform	98	100	100	100	96	99	99	100	93	92	96	92
Chloromethane	130	140	150	140	140	150	150	150	100	98	100	100
Dibromochloromethane	110	110	110	110	100	100	110	110	100	100	100	100
Dibromomethane	110	110	110	110	110	110	110	120	110	110	110	110
Dichlorodifluoromethane	100	99	110	100	120	120	120	130	55	53	58	53
Dichloroethane,1,1-	110	110	110	110	100	100	110	110	98	96	100	98
Dichloroethane,1,2-	100	100	100	100	97	100	100	100	97	93	97	96
Dichloroethene,1,1-	81	80	85	82	77	79	81	80	72	76	76	72
Dichloroethene,trans-1,2-	84	84	88	85	80	82	84	84	77	76	80	78
Dichloropropane,1,2-	110	110	110	110	100	110	110	110	100	100	110	100
Dichloropropene,cis-1,3-	84	86	84	85	74	77	79	81	70	66	71	69
Dichloropropene,trans-1,3-	84	86	84	84	75	77	80	81	72	56	71	70
Ethyl Benzene	88	90	92	90	83	86	88	88	83	86	85	82
Ethyl Methacrylate	50	50	30	50	30	50	60	60	50	50	60	60
Iodomethane	30	30	40	30	30	30	30	30	30	30	30	30
Methyl Butyl Ketone	100	100	110	100	90	90	97	100	88	89	84	88
Methyl Ethyl Ketone	91	94	98	96	81	82	85	89	81	71	79	78
Methyl Isobutyl Ketone	110	120	120	120	110	110	120	120	110	110	110	110
Methylene Chloride	96	100	100	110	96	100	100	100	88	86	88	87
Styrene	100	100	100	100	92	96	98	98	92	92	95	92
Tetrachloroethane,1,1,2,2-	110	110	110	110	98	100	110	110	110	94	100	110
Tetrachloroethene	75	73	79	76	71	73	75	74	69	69	73	70
Toluene	91	92	94	92	86	90	92	93	84	88	86	83
Trichloroethane,1,1,1-	85	86	88	85	82	85	86	86	80	74	84	78
Trichloroethane,1,1,2-	110	110	110	110	110	110	110	110	110	100	110	110
Trichloroethene	90	92	94	92	88	90	90	92	86	87	88	85
Trichlorofluoromethane	210	210	220	210	210	210	220	220	190	190	200	180
Trichloropropane,1,2,3-	120	120	130	120	110	110	120	120	120	110	110	120
Vinyl Acetate	20	20	20	20	10	20	10	10	10	5	20	10
Vinyl Chloride	170	180	190	190	170	180	190	190	140	130	150	140
Xylene,m- and/or p-	190	190	190	190	170	180	180	190	170	180	180	170
Xylene,o-	98	100	100	100	92	96	98	99	92	93	94	91

Tabla A3 (continued). Concentrations (ppb) of volatile organic compounds measured by EPA Region IV laboratory in acidified samples from set W4.

Sample No. ->	Day 60				Day 90			
	4-2	4-11	4-24	4-30	4-6	4-8	4-16	4-29
Acetone	54	77	55	57	67	67	73	70
Benzene	91	91	93	97	86	82	86	88
Bromodichloromethane	98	97	100	100	100	96	97	98
Bromoform	100	100	100	110	94	92	97	99
Bromomethane	160	180	180	200	140	140	150	150
Carbon Disulfide	80	79	82	88	59	57	59	61
Carbon Tetrachloride	78	79	79	84	78	76	77	79
Chlorobenzene	92	89	92	95	87	83	87	92
Chloroethane	190	190	200	220	180	170	180	170
Chloroform	96	95	99	100	95	93	95	96
Chloromethane	150	160	160	170	130	130	130	130
Dibromochloromethane	100	100	100	100	110	100	100	110
Dibromomethane	100	100	100	110	100	98	100	100
Dichlorodifluoromethane	150	140	140	150	81	79	77	83
Dichloroethane,1,1-	110	110	110	110	100	97	100	100
Dichloroethane,1,2-	99	96	98	100	98	94	98	96
Dichloroethene,1,1-	78	77	78	82	76	72	74	74
Dichloroethene,trans-1,2-	80	78	80	84	73	68	71	74
Dichloropropane,1,2-	110	100	110	110	100	94	98	98
Dichloropropene,cis-1,3-	55	56	56	57	43	42	42	44
Dichloropropene,trans-1,3-	56	56	57	58	40	44	44	47
Ethyl Benzene	84	83	84	88	80	78	80	85
Ethyl Methacrylate	30	50	50	50	70	60	60	70
Iodomethane	30	30	30	30	30	30	30	30
Methyl Butyl Ketone	78	77	77	81	100	96	94	98
Methyl Ethyl Ketone	71	69	71	73	87	79	83	87
Methyl Isobutyl Ketone	110	110	110	110	110	110	110	110
Methylene Chloride	96	96	97	100	93	92	92	92
Styrene	92	92	93	97	90	86	88	93
Tetrachloroethane,1,1,2,2-	98	98	100	100	96	89	96	97
Tetrachloroethene	71	71	74	77	67	63	63	68
Toluene	87	86	88	91	84	83	83	89
Trichloroethane,1,1,1-	82	81	83	86	78	78	79	82
Trichloroethane,1,1,2-	110	100	110	110	110	100	110	110
Trichloroethene	90	86	87	92	82	80	80	85
Trichlorofluoromethane	210	210	210	220	200	190	200	190
Trichloropropane,1,2,3-	110	110	110	110	110	110	110	120
Vinyl Acetate	N/D	2	N/D	2	N/D	N/D	N/D	N/D
Vinyl Chloride	190	190	190	210	160	150	150	160
Xylene,m- and/or p-	180	180	180	190	170	160	170	180
Xylene,o-	92	92	93	97	89	86	87	94

Tabla A4. Concentrations (ppb) of volatile organic compounds measured by EPA Region IV laboratory in unacidified samples from set W4 [200 ppb spike for compounds in CRS M-5751-M stock (see Table 3); 100 ppb spike for other compounds]

Sample No.->	Day 1		Day 36	
	4-9	4-35	4-32	4-36
Acetone	81	84	69	64
Benzene	85	90	89	88
Bromodichloromethane	94	98	98	94
Bromoform	99	100	110	97
Bromomethane	150	160	150	140
Carbon Disulfide	68	73	70	68
Carbon Tetrachloride	74	82	78	80
Chlorobenzene	92	97	90	88
Chloroethane	160	160	170	170
Chloroform	93	98	94	92
Chloromethane	94	98	97	97
Dibromochloromethane	100	110	100	100
Dibromomethane	110	110	110	110
Dichlorodifluoromethane	57	62	56	54
Dichloroethane,1,1-	98	100	97	96
Dichloroethane,1,2-	98	110	97	93
Dichloroethene,1,1-	73	77	74	74
Dichloroethene,trans-1,2-	82	86	79	78
Dichloropropane,1,2-	100	110	100	99
Dichloropropene,cis-1,3-	85	90	71	68
Dichloropropene,trans-1,3-	76	81	72	58
Ethyl Benzene	84	89	83	86
Ethyl Methacrylate	60	60	20	30
Iodomethane	30	30	30	30
Methyl Butyl Ketone	100	100	91	93
Methyl Ethyl Ketone	98	96	86	84
Methyl Isobutyl Ketone	120	120	120	120
Methylene Chloride	95	100	86	86
Styrene	94	100	92	90
Tetrachloroethane,1,1,2,2	93	88	46	39
Tetrachloroethene	79	86	70	72
Toluene	85	93	84	86
Trichloroethane,1,1,1-	74	80	80	74
Trichloroethane,1,1,2-	110	110	110	100
Trichloroethene	93	100	120	130
Trichlorofluoromethane	190	210	190	190
Trichloropropane,1,2,3-	120	110	120	110
Vinyl Acetate	40	40	N/D	N/D
Vinyl Chloride	130	140	140	130
Xylene,m- and/or p-	180	190	170	180
Xylene,o-	92	96	91	90