

COMPOSITING WATER SAMPLES FOR ANALYSIS OF VOLATILE ORGANIC COMPOUNDS

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Abstract: Accurate mean concentrations of volatile organic compounds (VOCs) can easily and economically be obtained from a single VOC analysis by using proven methods of collecting representative, discrete water samples and compositing them with a gas-tight syringe. The technique can be used in conjunction with chemical analysis by a conventional laboratory, field-portable equipment, or a mobile laboratory. The type of mean concentration desired depends on the objectives of monitoring. For example, flow-weighted mean VOC concentrations can be used to estimate mass loadings in wastewater and urban stormwater and spatially-integrated mean VOC concentrations can be used to assess sources of drinking water (e.g. reservoirs and rivers). The mean error in a discrete sample due to compositing is about 2 percent for most VOC concentrations greater than 0.1 µg/L. The total error depends on the number of discrete samples comprising the composite sample and precision of the chemical analysis.

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INTRODUCTION

Volatile organic compounds (VOCs) are among the more difficult and expensive contaminants to monitor in water. Because VOCs easily move between air and water, environmental samples can either lose VOCs by volatilization or become contaminated when VOCs in air partition into the sample during sample collection, processing, or analysis. Thus, surface waters usually are sampled for VOCs by manual, discrete grab sampling or with a proven point sampler (Shelton, 1997; Halde and others, 1999). However, some monitoring programs need mean VOC concentrations to calculate mass emissions, estimate exposures to aquatic organisms, and compare concentrations among sites. For example, spatially integrated mean VOC concentrations may be needed for a source of drinking water (e.g. reservoirs and rivers) and flow-weighted or time-weighted mean VOC concentrations may be needed for wastewater discharges and urban stormwater to estimate mass loadings and biologic effects. Multiple discrete samples yield the most information on the occurrence of contaminants and can be used to estimate mean concentrations; however, the analytical costs of discrete samples can be prohibitive. Recently, automatic VOC samplers have been developed to obtain discrete and composite water samples (ISCO Inc., 1995; Balogh and others, 1998). However, automatic VOC samplers are expensive, sometimes have uncertain reliability, and may have limited application (Balogh and others, 1998).

Urban streams are being monitored for VOCs and other contaminants as part of the U.S. Geological Survey's National Water-Quality Assessment Program (Lopes and Price, 1997). Urban streams are being sampled for VOCs during storms and during non-storm periods to characterize the occurrence and concentrations of VOCs during various flow conditions. VOCs are frequently detected in urban stormwater (Delzer and others, 1996), but detections can be sporadic (von Guerard and Weiss, 1995); therefore, a single discrete sample collected during a storm may not contain VOCs. A simple technique of compositing water samples for analysis of VOCs is needed to assess the occurrence of VOCs during storms while minimizing analytical costs. This paper presents such a technique and results of its performance.

METHODS

Streams Sampled

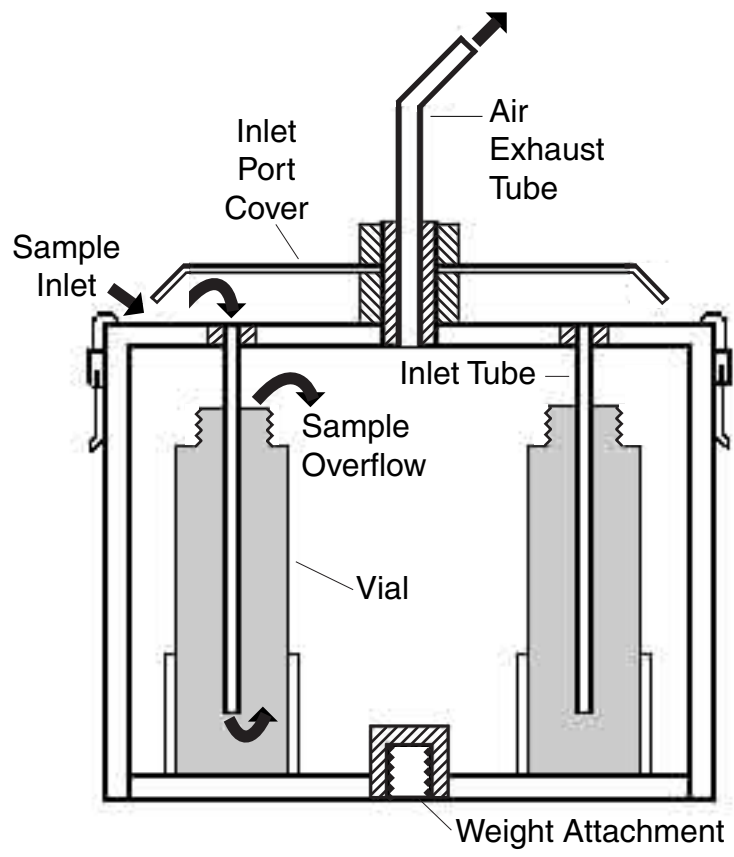
Two urban streams were selected to apply the technique of compositing water samples. Gills Creek in Columbia, South Carolina has a drainage area of 157 km² upstream of the streamflow-gaging station. Gills Creek originates from springs, flows through forested wetlands, flows through the urbanized portion of the basin, and then discharges into the Congaree River. In 1990, land use in the basin was 50 percent urban, 38 percent forested, 7 percent agriculture, and 5 percent other land uses (Hitt, 1994). Near the gaging station, the basin is a mix of rapidly developing residential and commercial land use.

Shingle Creek in the Twin Cities metropolitan area, Minnesota, has a drainage area of 73 km² upstream of the streamflow-gaging station and discharges into the Mississippi River. In the 4-km reach upstream from the gaging station, the stream flows through wetlands and a lake, under a highway, and through a golf course and residential/commercial areas. In 1990, land use in the basin was about 71 percent urban, 20 percent agriculture, 4 percent lakes, 1 percent forest, 1 percent wetlands, and 3 percent other land uses (Hitt, 1994). However, all agricultural lands have since been urbanized.

Stormwater Sampling

Stormwater samples were collected during 1996 and 1998 using two stainless steel and copper samplers specifically designed for sampling VOCs (fig. 1; Shelton, 1997). When the sampler is submerged, four 40-mL vials are flushed about seven times with stormwater and air is completely evacuated before the sample is collected. After submerging the sampler, the sample was removed with stainless steel tongs, quickly acidified with 1:1 hydrochloric acid, sealed with Teflon-lined septum caps, and chilled on ice. Two samplers were used to simultaneously collect a pair of discrete samples at approximately the same point in the stream. One discrete sample was used for a time-weighted storm composite and the other discrete sample was analyzed for VOCs.

Samplers were scrubbed with phosphate-free detergent, rinsed with deionized water, rinsed with a small amount of methanol, and then rinsed three times in the stream just before samples were collected. Analyses of quality



control samples indicated the samplers were not contaminating environmental samples at Gills Creek or Shingle Creek during 1996. However, analyses of field blanks indicated the sampler may have contaminated environmental samples with acetone and toluene at Shingle Creek on November 10, 1998. Thus, acetone and toluene data for these samples were not used in this paper.

On November 8, 1996, 1.24 cm of rain produced runoff with a peak discharge of $5.8 \text{ m}^3/\text{s}$ at Gills Creek. A total of six pairs of discrete samples were collected at Gills Creek including one of pre-storm baseflow, two on the rising limb of the hydrograph, one at peak discharge, and two on the receding limb of the hydrograph. Streamflow initially was green in color, changed to a milky beige-brown color with an oily sheen when samples on the rising limb were collected, and was less turbid and beige when the last sample was collected. During sampling, specific conductance varied between 37 and 45 $\mu\text{S}/\text{cm}$, pH varied between 6.2 and 6.3, water temperature varied between 18.3 and 19.3 $^{\circ}\text{C}$, and dissolved oxygen increased from 5.5 to 7.6 mg/L.

Runoff was sampled at Shingle Creek on August 5 and September 3, 1996, and on November 9-10, 1998. On August 5, 1996, 1.32 cm of rain produced runoff with a peak discharge of $1.3 \text{ m}^3/\text{s}$. A total of four pairs of discrete samples were collected during the August 5 storm including one at peak discharge and three on the receding limb of the hydrograph. Stream color was difficult to determine because the storm occurred at night. However, the water appeared turbid, with trash, seeds, and tree branches observed near peak discharge. The stream became slightly less turbid with each successive sample. During sampling, conductance dropped from 957 to 309 $\mu\text{S}/\text{cm}$, water temperature varied from 22.5 to 25.5 $^{\circ}\text{C}$, and pH was 8.0, and dissolved oxygen was 7.4 mg/L.

On September 3, 1996, 2.03 cm of rain produced runoff with a peak discharge of $0.29 \text{ m}^3/\text{s}$ on Shingle Creek. A total of five pairs of discrete samples were collected during the September 3 storm including two on the rising limb of the hydrograph, one sample at peak discharge, and two on the receding limb of the hydrograph. Streamflow was slightly turbid on the rising and receding limbs of the hydrograph and very turbid at peak discharge. Brown, oily spots about 5 cm in diameter appeared on the water during the rising limb of the hydrograph, became smaller (about 1 cm in diameter) and less numerous near peak discharge, and were not observed when the last sample was collected. Specific conductance was 1,020 $\mu\text{S}/\text{cm}$ when the first sample was collected, decreased to 782 $\mu\text{S}/\text{cm}$ near

peak discharge, and rebounded to 943 $\mu\text{S}/\text{cm}$ during the recession. Water temperature initially was 22.0 °C, decreased to 21.5 °C, and then rose to 23.5 °C. Dissolved oxygen continually decreased from 4.8 to 3.3 mg/L and pH varied from 7.4 to 7.6.

On November 9-10, 1998, 2.95 cm of rain produced a peak discharge of 2.4 m^3/s on Shingle Creek. A total of seven pairs of discrete samples were collected including 4 samples on the rising limb of the hydrograph, one near peak discharge, and two on the receding limb of the hydrograph. It was difficult to judge the appearance of the stream water on November 9 because of darkness. On November 10, the water was turbid during the peak discharge and flow recession; however, no oil sheen was observed. Specific conductance varied from 1,130 to 890 $\mu\text{S}/\text{cm}$ and water temperature ranged from 5.5 to 3.5 °C. Dissolved oxygen and pH were not measured.

Sample compositing

Discrete samples were transported to the office and composited using a Hamilton Series 1000 Leur lock, gas-tight, 100-mL syringe. Compositing also can be done in the field and samples analyzed with field-portable equipment or a mobile laboratory. The syringe was fitted with a 13-gauge, 90-mm, point style 5 needle that had a conical point and a side hole that minimized plugging by the septum. The 13-gauge needle reduced the amount of bubbles that formed in the syringe compared to when a smaller diameter needle was used. A 16-gauge, 25-mm disposable needle was inserted into the septum to allow air to enter the vial when aliquots were withdrawn with the syringe. This prevented a vacuum from forming in the vial and made it easy to withdraw aliquots. The syringe was cleaned with phosphate-free detergent, rinsed with deionized water, rinsed again with a small amount of methanol, and air dried before each use. Analysis of an equipment blank indicated the syringe was not contaminating water samples. Discrete samples were composited using the following steps:

1. The percentage of the runoff period represented by each discrete sample (PRP_{ds}) was calculated:

$$PRP_{ds} = 100 * (T_{ds} - T_{pds}) / T_{total} \quad (1)$$

where T_{ds} is the time of the discrete sample, T_{pds} is the time of the previous discrete sample, and T_{total} is the total time of the storm event that was sampled. For example, discrete samples were collected at 20, 50, 90, 120, and 180 minutes from the start of runoff. PRP_{ds} for the 5 samples were 11, 17, 22, 17, 33 percent, respectively.

2. A number of milliliters equal to PRP_{ds} was withdrawn from each discrete sample to fill the syringe (e.g. 11 mL from the first sample, 17 mL from the second, etc).
3. The composited sample was slowly injected into the bottom of a new 40-mL vial. The vial was overfilled with about 40 mL of the composited sample, acidified, capped, and chilled on ice.
4. Chilled discrete and composite samples were shipped overnight to the National Water-Quality Laboratory in Denver, Colorado, for analysis.

Concentrations measured in the n discrete samples (C_{ds}) and PRP_{ds} were used to calculate the time-weighted concentrations of VOCs (C_{calc}) in the composite sample:

$$C_{calc} = \sum_1^n (PRP_{ds} * C_{ds}) / 100 \quad (2)$$

The calculated time-weighted concentrations were compared to the concentrations measured in the composite sample ($C_{composite}$) to determine the percent difference (PD) between values:

$$PD = 100 * (C_{calc} - C_{composite}) / C_{composite} \quad (3)$$

Analytical Methods

Runoff water samples were analyzed for 86 VOCs by purge and trap capillary-column gas chromatography/mass spectrometry (Connor and others, 1998). Stream water spiked at concentrations of 1 to 100 $\mu\text{g/L}$ had recoveries between 85 and 115 percent for the VOCs detected runoff (Connor and others, 1998). Long-term method detection limits (LTMDL) for most VOCs are less than 0.1 micrograms per liter ($\mu\text{g/L}$); however, acetone and 2-butanone have LTMDLs of 2.45 and 1.65 $\mu\text{g/L}$, respectively. The LTMDL is a statistically defined

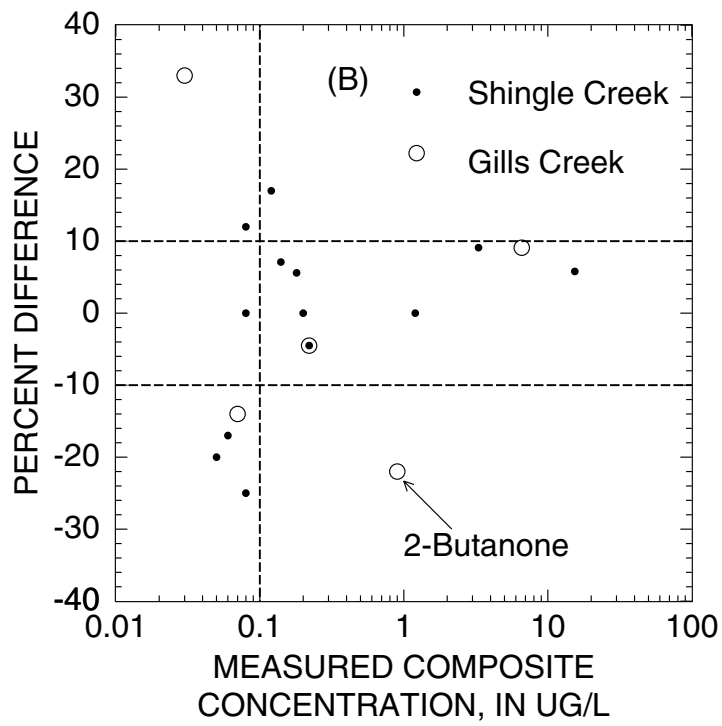
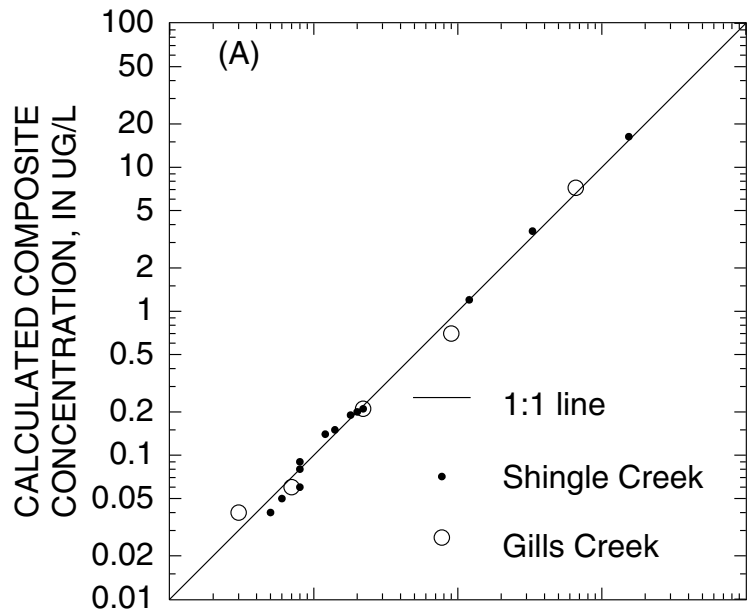
concentration that limits false positive detections to 1 percent (Connor and others, 1998). The LTMDL accounts for long-term variance of multiple instruments, multiple operators, and multiple calibrations over an extended period.

When compounds were not detected, the analysis was reported as less than the laboratory reporting level (LRL). The LRL is a statistically defined concentration which limits false negative detections to 1 percent (Connor and others, 1998). Positive detections that are less than the LRL or lowest daily calibration standard are reported as estimated concentrations because of decreased confidence in the quantitation. This reporting approach provides information on the positive occurrence of a VOC but qualifies the concentration accuracy. The concentrations of detections that are above the LRL are not qualified. Equation 2 was used assuming that C_{ds} values reported as less than the LRL were equal to zero. Estimated and nonqualified C_{ds} values both were used directly in equation 2 as the values reported by the laboratory.

RESULTS AND DISCUSSION

VOCs detected in discrete and composite water samples are listed in table 1. In general, more VOCs were detected at higher concentrations at Shingle Creek than at Gills Creek. The mean and median percent differences between the 18 calculated and measured composite concentrations were -0.5 and 0 percent, respectively. The mean and median of the absolute percent differences were 11 and 9.1 percent, respectively. The largest percent differences generally occurred with estimated concentrations and when VOCs were not detected in several discrete samples comprising the composite.

A signrank test (Helsel and Hirsch, 1992) between the measured and calculated composite concentrations indicated that differences were not significantly different from zero (two-sided p-value = 0.51), indicating that compositing does not bias the results. The measured and calculated composite concentrations plot close to a 1:1 line (Fig. 2a). Percent differences generally are less than 10 percent at concentrations greater than 0.1 $\mu\text{g/L}$ and greater than 10 percent at concentrations less than 0.1 $\mu\text{g/L}$ (Fig. 2b). The value of -22 percent at 0.9 $\mu\text{g/L}$ is for 2-butanone, which has a LTMDL of 1.65 $\mu\text{g/L}$. The higher percent differences at lower concentrations suggest that precision of



the chemical analysis decreases at concentrations near or less than the LTMDL. Overall, these results indicate the compositing technique performs well.

The error in a discrete sample due to compositing can be estimated by assuming the errors in the technique and in the chemical analysis are random and independent. With this assumption, the error in a composite sample (i.e. the percent difference) is equal to the quadratic sum of errors in the discrete samples (Taylor, 1982). The error in a discrete sample is comprised of the error from compositing (q) and the error in the chemical analysis, as measured by the percent relative standard deviation (RSD):

$$PD = \sqrt{q_1^2 + q_2^2 + \dots + RSD_1^2 + RSD_2^2 + \dots} \quad (4)$$

Assuming q and RSD are equal for each discrete sample, the error from summing n discrete samples is:

$$PD = \sqrt{n * q^2 + n * RSD^2} \quad (5)$$

Solving for q :

$$q = \sqrt{(PD^2 / n) - RSD^2} \quad (6)$$

RSD values for the 12 VOCs in table 1 ranged from 1 to 3.1 percent (Connor and others, 1998). Values were determined from 7 replicates of stream water spiked at concentrations between 1 to 100 $\mu\text{g/L}$. A ranksum test indicated no significant difference (two-sided p-value of 0.09) in RSD values between spikes at low concentrations (1 or 2 $\mu\text{g/L}$) and high concentrations (10, 20, or 100 $\mu\text{g/L}$). Thus, the average of the low- and high-concentration RSD values for each VOC and PD values were used in equation 6 to calculate q values.

For the 10 measured VOC concentrations greater than 0.1 $\mu\text{g/L}$ (excluding 2-butanone at Gills Creek), the error in a discrete sample due to compositing has a mean of 2.3 percent, a median of 2.0 percent, and a maximum of 6.2 percent. The percent difference at concentrations near or less than the LTMDL is due to decreased precision of the chemical analysis in addition to errors from compositing. Thus, for these samples, the RSD values determined from spiked stream water cannot be used in equation 6. The RSD values for concentrations near the LTMDL can be approximated by using the 8 PD values at concentrations near the LTMDL (including 2-butanone from Gills Creek) and by assuming the mean error due to compositing (2.3 percent) is the same at these concentrations. Estimated RSD

values at concentrations near the LTMDL have a mean of 7.4 percent, a median of 6.6 percent, and a maximum of 15 percent.

CONCLUSIONS

Accurate mean concentrations of VOCs can easily and economically be obtained from a composited water sample by using a gas-tight syringe and proven methods of collecting representative, discrete water samples. This technique can be used in conjunction with analysis by a conventional laboratory, field-portable analytical equipment, or a mobile laboratory. Compositing has many applications, such as determining time-weighted, flow-weighted, or spatially integrated mean VOC concentrations in wastewaters, urban stormwater, rivers, and reservoirs. The mean error in a discrete sample due to compositing is about 2 percent for most VOC concentrations greater than about 0.1 $\mu\text{g/L}$. The total error due to compositing is the quadratic sum of errors in each discrete sample comprising the composite and, therefore, depends on the number of discrete samples used to prepare the composite sample. The analytical method used for this study estimated concentrations less than about 0.1 $\mu\text{g/L}$. The errors associated with estimated concentrations have a mean of 7.4 percent and a maximum of 15 percent compared to about 1 to 3 percent for concentrations greater than 1 $\mu\text{g/L}$. These results indicate that, although precision is lower, estimated concentrations are still accurate.

APPENDIX I. REFERENCES

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Figure Caption

Figure 1. Schematic diagram of the VOC sampler.

Figure 2. Measured composite VOC concentrations as a function of (A) calculated VOC concentration and (B) percent difference between calculated and measured VOC concentration

Table 1. VOC composite data [t, time since start of runoff; min, minutes; PRP_{ds} , percent of runoff period represented by discrete sample; 1-I-4-MB, 1-isopropyl-4-methylbenzene; TMB, trimethylbenzene; e, estimated value; ---, VOC not detected or value not applicable; Calculated, calculated composite concentration; PD , percent difference; RSD , percent relative standard deviation; q , percent error due to compositing; a 2.3, mean q for concentrations greater than 0.1 $\mu\text{g/L}$ (or greater than 1 $\mu\text{g/L}$ for 2-butanone) was used to estimate RSD for concentrations <0.1 $\mu\text{g/L}$ (or <1 $\mu\text{g/L}$ for 2-butanone)]

Sample time or other variable	t (min)	PRP_{ds} (%)	Concentration, in $\mu\text{g/L}$, or PD , RSD , or q in percent											
			Acetone	Toluene	Chloro-methane	2-Butanone	1-I-4-MB	Dichloro-methane	M+P Xylenes	O-Xylene	1,3,5-TMB	2-Ethyl toluene	1,2,4 TMB	1,2,3 TMB
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)
0945	0	0	4.8	<0.1	e0.06	e0.7	e0.01	---	---	---	---	---	---	---
1010	25	7.6	5.7	<0.1	e0.06	<10	e0.01	---	---	---	---	---	---	---
1110	85	18.5	9.4	e0.1	<0.4	e0.8	e0.02	---	---	---	---	---	---	---
1215	150	20.0	9.1	0.68	e0.1	e0.8	e0.1	---	---	---	---	---	---	---
1410	265	35.4	6.1	e0.1	e0.06	e0.7	e0.03	---	---	---	---	---	---	---
1510	325	18.5	5.4	e0.09	e0.05	e0.6	e0.02	---	---	---	---	---	---	---
Composite	---	---	6.6	0.22	e0.07	e0.9	e0.03	---	---	---	---	---	---	---
Calculated	---	---	7.2	0.21	0.06	0.7	0.04	---	---	---	---	---	---	---
PD	---	---	9.0	-4.5	-14	-22	33	---	---	---	---	---	---	---
RSD	---	---	2.3	1.4	5.8	9.6	15	---	---	---	---	---	---	---
q	---	---	3.3	1.4	a 2.3	a 2.3	a 2.3	---	---	---	---	---	---	---

Gills Creek, November 8, 1996

Table 1. VOC composite data (Continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)
Shingle Creek, September 3, 1996														
0706	36	9.7	23.2	7.4	e0.4	5.4	---	e0.22	---	---	---	---	---	---
0728	58	6.0	12.6	3.1	e0.17	e2.7	---	<0.4	---	---	---	---	---	---
0748	78	5.4	6.7	e0.38	e0.12	e1.4	---	e0.22	---	---	---	---	---	---
0918	168	24.3	10.7	e0.4	e0.11	e2.1	---	e0.25	---	---	---	---	---	---
1240	370	54.6	18.9	e0.37	e0.13	4.2	---	e0.2	---	---	---	---	---	---
Composite	---	---	15.4	1.2	e0.14	3.3	---	e0.2	---	---	---	---	---	---
Calculated	---	---	16.3	1.2	0.15	3.6	---	0.2	---	---	---	---	---	---
<i>PD</i>	---	---	5.8	0	7.1	9.1	---	0	---	---	---	---	---	---
<i>RSD</i>	---	---	2.3	1.4	1.7	2.9	---	1.6	---	---	---	---	---	---
<i>q</i>	---	---	1.2	1.4	2.7	2.8	---	1.6	---	---	---	---	---	---

Table 1. VOC composite data (Continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)
Shingle Creek, November 9-10, 1998														
11.09 1710	85	6.7	---	---	---	---	---	---	<0.12	<0.12	<0.09	<0.2	<0.11	<0.24
11.09 1745	120	2.8	---	---	---	---	---	---	<0.12	<0.12	<0.09	<0.2	<0.11	<0.24
11.09 1820	155	2.8	---	---	---	---	---	---	<0.12	<0.12	<0.09	<0.2	<0.11	<0.24
11.09 2130	345	15.0	---	---	---	---	---	---	<0.12	<0.12	<0.09	<0.2	<0.11	<0.24
11.10 0955	1,090	58.9	---	---	---	---	---	---	0.20	0.14	e0.08	e0.05	0.31	e0.09
11.10 1210	1,225	10.7	---	---	---	---	---	---	e0.14	e0.08	e0.05	e0.04	0.20	e0.08
11.10 1250	1,265	3.2	---	---	---	---	---	---	e0.13	e0.09	e0.04	e0.05	0.21	e0.09
Composite	---	---	---	---	---	---	---	---	e0.12	e0.08	e0.06	e0.05	0.22	e0.08
Calculated	---	---	---	---	---	---	---	---	0.14	0.09	0.05	0.04	0.21	0.06
<i>PD</i>	---	---	---	---	---	---	---	---	17	12	-17	-20	-4.5	-25
<i>RSD</i>	---	---	---	---	---	---	---	---	1.6	3.9	6.0	7.2	1.9	9.2
<i>q</i>	---	---	---	---	---	---	---	---	6.2	^a 2.3	^a 2.3	^a 2.3	0.0	^a 2.3