Comparison of VOA Compositing Procedures

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SUMMARY

This report provides results produced by VOA grab and composite sampling procedures in studies conducted by the U.S. Environmental Protection Agency (EPA) in early 1994. In these studies, four individual grab samples of real-world effluents were collected over the course of a day. These samples were analyzed spiked or unspiked, composited and individually, by isotope dilution GC/MS, using Revision C of EPA Method 1624. Both manual and automated grab sampling procedures were employed. Compositing procedures employed included flask, purge device, and continuous. Analytes spiked were the volatile organic GC/MS fraction of the priority pollutants plus additional compounds routinely tested for in EPA's industrial surveys.

The objective of these studies was to compare the analytical results for manually collected individual grab samples to the analytical results for composited samples and automatically collected grab samples, to determine if bias occurred in the automated grab and compositing processes. Several compositing methods were investigated including: flask compositing and purge device compositing of automated and manual grab samples, and continuous compositing.

These tests showed that, for the samples tested, the mathematical average of the analytical results for hand collected grab samples were higher than results for composited samples. Conversely, mathematical averages of the analytical results for hand collected grab samples were marginally lower than results of automated grab samples. The cause of these slight differences is not known. However, the differences are not significant when compared to the variability in the analytical technique. It is not likely that these differences would have been found using a less sensitive analytical technique than isotope dilution GC/MS.

Background

Volatile Organic Compounds (VOCs)

The Federal Water Pollution Control Act of 1972 (PL 92-500) required EPA to control the discharge of toxic pollutants to the nation's waters. The act listed 65 compounds and compound classes for regulation as toxic pollutants. This list was later refined into an initial list of 129 "priority pollutants" and then a final priority pollutant list containing 126 individual compounds (Reference 1).

For determination of the priority pollutants, EPA separated the list of 126 compounds into groups based on the analytical technology that could be used to measure the pollutants. Those organic pollutants that could be determined by gas chromatography combined with mass spectrometry (GC/MS) were further categorized into volatile and acid/base/neutral extractable fractions.

The volatile fraction, also called the "purgeable" fraction, contains those compounds that boil below approximately 130°C and that are capable of being purged from water using a flowing gas stream (Reference 2). Analysis of this fraction is termed a "volatile organic analysis" (VOA) and the compounds in this fraction are termed "volatile organic compounds" (VOCs). Determination of VOCs in the VOA fraction of the list of priority pollutants is the subject of this study.

Pollutant Lists

A list of VOCs analyzed in this study is provided in Table 1. This table also provides a list of the stable isotopically-labeled analogs that were used for isotope dilution quantitation, and information concerning whether a given analyte is a priority pollutant or other pollutant associated with the 1976 Consent Decree (Reference 1). Chemical Abstracts Service Registry Numbers for the pollutants and their labeled analogs are given, where available.

The VOCs listed in Table 1 are separated into two groups. The first group contains VOCs that are determined by GC/MS using authentic standards; the second group contains VOCs determined by "reverse search." These latter compounds are considered identified when the chromatographic retention time and mass spectrum agree with those specified in the method. When a match is found, the compound is quantitated based on a response factor also given in the method. Although results produced by the reverse search technique are not as precise or accurate as results produced using authentic standards, the technique is useful for screening and provides approximate concentrations for VOCs in the reverse-search group. Furthermore, reverse search is more accurate in identifying compounds than a forward library search in which only the mass spectrum is tested against a large mass spectral file.

Table 1
Volatile Organic Compounds Analyzed

Compounds Determined by Isotope Dilution or Internal Standard

Compound	CAS Registry	Labeled Compound		Priority Pollutant
		Analog	CAS Registry	
Acetone	67-64-1	d_6	666-52-4	N
Acrolein	107-02-8	d_4	33984-05-3	Y
Acrylonitrile	107-13-1	d_3	53807-26-4	Y
Benzene	71-43-2	d_6	1076-43-3	Y
Bromodichloromethane	75-27-4	^{13}C	93952-10-4	Y
Bromoform	75-25-2	^{13}C	72802-81-4	Y
Bromomethane	74-83-9	d_3	1111-88-2	Y
Carbon tetrachloride	56-23-5	^{13}C	32488-50-9	Y
Chlorobenzene	108-90-7	d_5	3114-55-4	Y
Chloroethane	75-00-3	d_5	19199-91-8	Y
2-Chloroethylvinyl ether	110-75-8			Y
Chloroform	67-66-3	^{13}C	31717-44-9	Y
Chloromethane	74-87-3	d_3	1111-89-3	Y
Dibromochloromethane	124-48-1	^{13}C	93951-99-6	Y
1,1-Dichloroethane	75-34-3	d_3	56912-77-7	Y
1,2-Dichloroethane	107-06-2	d_4	17070-07-0	Y
1,1-Dichloroethene	75-35-4	d_2	22280-73-5	Y
trans-1,2-Dichloroethene	156-60-5	d_3	42366-47-2	Y
1,2-Dichloropropane	78-87-5	d_6	93952-08-0	Y
trans-1,3-Dichloropropene	10061-02-6	d_4	93951-86-1	Y
Diethyl ether	60-29-7	d_{10}	2679-89-2	N
p-Dioxane	123-91-1	d_8	17647-74-4	N
Ethylbenzene	100-41-4	d_{10}	25837-05-2	Y
Methylene chloride	75-09-2	d_2	1665-00-5	Y
Methyl ethyl ketone (MEK)	78-93-3	d_3	53389-26-7	N
1,1,2,2-Tetrachloroethane	79-34-5	d_2	33685-54-0	Y
Tetrachloroethene	127-18-4	$^{13}C_2$	32488-49-6	Y
Toluene	109-88-3	d_8	2037-26-5	Y
1,1,1-Trichloroethane	71-55-6	d_3	2747-58-2	Y
1,1,2-Trichloroethane	79-00-5	$^{13}C_2$	93952-09-1	Y
Trichloroethene	79-01-6	$^{13}C_2$	93952-00-2	Y
Vinyl chloride	75-01-4	d_3	6745-35-3	Y

Compounds Determined by Reverse Search

Compound	CAS Registry	Priority Pollutant
Carbon disulfide	75-15-0	N
cis-1,3-Dichloropropene	10061-01-5	Y
2-Hexanone	591-78-6	N
4-Methyl-2-pentanone	108-10-1	N
Trichlorofluoromethane	75-69-4	N
Vinyl acetate	108-05-4	N
m-Xylene	108-38-3	N
o- and *p*-Xylene	*	N

* O-xylene CAS Registry = 95-47-6
   P-xylene CAS Registry = 106-42-3

In addition to the priority pollutant VOCs, EPA has regulated other VOCs under the Safe Drinking Water Act (SDWA) and amendments, the Resource Conservation and Recovery Act (RCRA) and amendments, the Clean Air Act (CAA) and amendments, and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) and amendments. Although the VOCs listed in these lists are not identical to the list in Table 1, many of the compounds found on these other lists are included in Table 1, and, therefore, the results of this study are considered to be applicable to the VOCs found on these other lists.

"Gases" and "Water-Soluble" Compounds

Two groups of compounds present unique analytical problems in the determination of VOCs. These groups are the "gases" and "water-soluble compounds." The priority pollutant gases are chloromethane, bromomethane, chloroethane, and vinyl chloride. These gases boil below approximately 15° C and are readily lost from aqueous solutions. These losses make the analysis more variable than for compounds that are not lost as readily. Conversely, the water-soluble compounds present a separate set of analytical problems because they are not readily purged from water. In this study, the water-soluble priority pollutants tested are acrolein, acrylonitrile, and 2-chloroethylvinyl ether. Non-priority pollutant water-soluble compounds tested were acetone, 2-butanone (MEK), p-dioxane, and diethyl ether.

Control of Discharges

The Engineering and Analysis Division (EAD), within the Office of Science and Technology in EPA's Office of Water, is responsible for promulgating regulations controlling the discharge of pollutants to U.S. surface waters. EAD conducts surveys of the regulated industry to establish the best pollutant control strategies within various categories and subcategories

(Reference 3). In these surveys, EAD frequently samples and analyzes wastewaters to determine the presence and concentration of pollutants. Although these studies primarily focus on the 126 priority pollutants (40 *CFR* 423, Appendix A) and the five conventional pollutants (40 *CFR* 401.16), other "non-conventional" pollutants may also be determined and subsequently proposed for regulation.

In conducting these surveys, EPA collects aqueous samples in and around wastewater treatment plants and other locations. Unless treatment system characteristics dictate otherwise, VOA samples are composited to effect a cost savings over the analysis of individual grab samples. Normally, four individual grab samples are collected at approximately equal time intervals over the course of a 24-hour day. These samples are stored at 4° C, shipped under wet ice to the testing laboratory and composited in the laboratory. Results of these analyses are then used, in part, to develop, propose, and promulgate effluent guidelines and standards for the appropriate industrial category at 40 *CFR* Parts 403 - 499.

Theoretical Considerations and Prior Work

VOA compositing is used extensively by EPA for data gathering in regulatory development programs, and is used for compliance monitoring under EPA rules. The technical literature is replete with theoretical discussions of the effects that compositing may have on data integrity. Book chapters on the subject by Gilbert (Reference 4) and by Garner et al. (Reference 5) provide comprehensive evaluations of the concepts behind composite sampling and provide extensive bibliographies referencing the technical literature on sample compositing and statistical treatments of the compositing process.

Although the technical literature contains many theoretical discussions of VOA compositing, it is remarkably silent concerning data gathering designed to verify the theoretical work. A search of online databases revealed only one technical paper that presents actual results of a VOA compositing study (Reference 6).

Variability of Individual and Composite Measurements

Any empirical measurement process has inherent variability, and the measurement of each analyte in each analysis is accompanied by an analytical error. This error is normally characterized by replicate measurements and is expressed as the standard deviation of the concentration or is normalized to the concentration as the "relative standard deviation" or "coefficient of variation." For example, the concentration of chloroform may be determined by purge-and-trap GC/MS with a relative standard deviation of 10 percent.

The effect of measurement error on the result for a composite sample and on the average of individual grab samples can be understood most easily if it is assumed that the concentration of a pollutant is identical in all of the individual grab samples. Averaging the results for analysis of four individual samples requires determination of the concentration four separate times. Because measurement error is inversely proportional to the square root of the number of measurements, the measurement error associated with the four individual grab samples will be one-half of the error associated with any individual measurement. Because the determination of concentration in a composite sample is an individual measurement, the error associated with the average of four individual grab samples will be one-half of the error associated with the measurement of a composite sample.

Therefore, the most precise and accurate results will be produced if the individual grab samples are analyzed and the results averaged. The cost of analysis, however, will be four times as great as the cost for analysis of a single composite sample. Similar accuracy and precision could be achieved if the compositing process were replicated four times and the four composites analyzed separately, assuming that no error occurred in the compositing procedure. Pragmatic

considerations (e.g., cost and time) frequently outweigh the benefits acquired by measurement of grab samples individually; so discussions of error become moot, and the error associated with measuring concentration in a single composite sample becomes the only measurement error that must be considered.

Types Of Compositing

Time Compositing

Time compositing is the most common type of sample compositing. Samples are collected from a fixed sampling point over some fixed period of time, usually a 24-hour period beginning at midnight. Samples can be collected as discrete grab samples at intervals throughout the fixed time period, or continuously over the period.

Transients

The objective of sampling over time, whether the sampling is grab or continuous, is to attempt to capture the transient nature of compounds in the waste stream. Capture of transients requires a knowledge of the flow characteristics of each individual stream: system volumes, flow rates, and the nature of the transient wave. If the objective is to capture the concentration maximum, the ideal scheme is to collect a grab sample at the apex of the wave. Unfortunately, this scheme is frequently impractical. The next best scheme is to collect samples at frequent enough intervals to assure that some fraction of the transient will be captured. Although use of a continuous compositor will assure capture of the transient, the transient may be diluted by the stream before and after the passage of the wave. Therefore, if monitoring of transients in a waste stream is necessary to characterize treatment system operation, samples should be collected over the wave to model the wave. After the wave characteristics are known, the intervals for subsequent sampling can be determined.

Treatment System Detention Times

For treated effluents, a common mistake made by personnel unfamiliar with treatment system operation is to require grab samples at intervals more frequent than the detention time of the treatment system. For example, if the treatment system has a detention time of 6 hours, sampling the effluent from the system more frequently than every few hours is unnecessary, particularly if the samples are analyzed individually.

Spatial Compositing

Samples from different sampling points can be composited in an effort to save analysis costs. If an analyte is present in a composited sample, each sampling point can then be sampled individually to determine the point or points contributing to the level of the analyte in the sample. Spatial compositing of up to five streams is allowed, at the discretion of the States, under EPA drinking water regulations to reduce the total number of samples that small drinking water treatment system operators must analyze [40 *CFR* 141.24(f)(14)]. However, the analytical system must be capable of detecting one-fifth of the maximum contaminant level (MCL) required for an individual sample. This requirement can usually be met by compositing five 5-mL samples and purging a 25-mL composite, as suggested in the *CFR*.

Flow or Volume Compositing

As the name implies, flow or volume compositing involves proportioning the sample according to the flow rate or volume of the stream being sampled. The most common use of flow compositing is in stormwater sampling pursuant to EPA's stormwater rules [40 *CFR* 122.21(g)(7); Reference 7]. These rules require that the composited sample proportionately represent the runoff that occurs in a stormwater event. Because it is impossible to know beforehand the total discharge volume during the event, individual grab samples must be collected at time intervals throughout the event, and varying volumes from these individual grab samples must be composited to reflect the flow during the entire stormwater event. The details of stormwater sampling and analysis, along with an example of the compositing associated with a stormwater discharge event, have been described by Stanko (Reference 8).

Problems Unique to VOA Compositing

The high vapor pressure of VOAs, and particularly of the volatile gases, makes these analytes particularly susceptible to loss through evaporation during any manipulation, including collection and compositing.

Headspace During Sampling

Analyte loss to the headspace of a container has been documented by Cline and Severin (Reference 6). Therefore, it is imperative that headspace be eliminated during sampling and sample shipment. In this study, the loss of volatiles was not critical because the objective was to compare the results from analyses of individual grab samples with the results from analysis of a composited sample. If the loss of VOCs from the individual grab samples and from the samples that feed the composite are the same, there is no consequence to this loss.

Losses During Compositing

None of the existing compositing procedures requires that compositing be performed with zero headspace, and such a system in a laboratory is difficult to envision. Because such a system does not exist, exposure of the sample to the atmosphere can result in analyte losses through evaporation. Loss can be minimized by cooling the sample and minimizing the exposure time. In this study, all compositing (except continuous compositing) was performed rapidly with the VOA vials chilled to 0 - 4 C.

Compositing Procedures

Definitions

Sample: The water collected in a sample jug from a specific location at a specific time.

Individual grab sample: An aliquot poured from the sample jug.

Duplicate grab sample: A second aliquot poured from the same sample jug.

Replicate grab sample: Any aliquot poured from the sample jug.

Composite sample: The physical combination of four grab samples collected at different times on the same day.

Mathematical composite: The mathematical average of the analytical results of four individual grab samples.

Manual Compositing

Two types of manual compositing procedures were tested in this study: flask compositing and purge device compositing. Each of these procedures is described below. A third procedure, syringe compositing, is also described below but was not tested because of resource limitations.

Flask Compositing (44 *FR* 69555)

In the flask compositing procedure, a 300- to 500-mL round-bottom flask is immersed in an ice bath. The individual VOA grab samples, maintained at 0 - 4°C, are slowly poured into the round-bottom flask. The flask is swirled slowly to mix the individual grab samples. After mixing, multiple aliquots of the composited sample are poured into VOA vials and sealed for subsequent analysis. An aliquot can also be poured into a syringe for immediate analysis.

Purge Device Compositing [40 *CFR* 141.24(f)(1)(v)]

Equal volumes of individual grab samples are added to a purge device to a total volume of 5 or 25 mL. The sample is then analyzed.

Syringe Compositing [40 *CFR* 141.24(f)(14)(iv)]

In the syringe compositing procedure, equal volumes of individual grab samples at a temperature of 0 - 4° C are aspirated into a 25-mL syringe while maintaining zero headspace in the syringe. Either the total volume in the syringe or an aliquot is subsequently analyzed. The disadvantage of this technique is that the individual samples must be poured carefully in an attempt to achieve equal volumes of each. An alternate procedure uses multiple 5-mL syringes that are filled with the individual grab samples and then injected sequentially into the 25-mL syringe.

Automated Collection and Compositing

Two types of automated equipment are available for sample collection and/or compositing. These are: (1) automated grab collection; and (2) automated continuous collection/compositing. These devices are described below.

Automated Grab Collection

Automated grab collection can be accomplished using devices such as the Isco, Inc. Model 6000 automatic VOC sampler. With this system, a small bladder pump forces sample into a 40-mL VOA vial after rinsing the vial with three vial volumes as required by the method. In addition, the system overfills the vial to eliminate headspace. Up to 25 samples can be collected at a minimum of 5-minute and a maximum of 10-hour intervals. Samples are maintained at 0 - 4° C during collection.

Automated Continuous Collection/compositing

An automated system such as the Associated Design and Manufacturing Co. (ADM) automated continuous compositing system can be used to collect samples over a given sampling period. Sample is pushed into a bubble trap in the sampler via a peristaltic pump. The sample is then drawn into an air-tight glass syringe, the volume of which is controlled by a piston connected to a timer. The timer, and therefore the sampling frequency, is set by the user, or can be connected to a flow meter so that sampling frequency is dependent upon the flow rate. Upon completion of the sampling event, the syringe is capped with a Luer-Lok™ closure, and the entire syringe is delivered to the laboratory for sample analysis, thereby maintaining zero-headspace conditions.

Study Phases

The objective of these studies was to compare the analytical results for manually collected individual grab samples to the analytical results for composited samples and automatically collected grab samples, to determine if bias occurred in the automated grab or compositing processes. Several compositing methods were investigated including: flask compositing and purge device compositing of automated and manual grab samples, and continuous compositing.

The study reported here was divided into three phases: Phase I, a pilot phase with spiked reagent water and an unspiked field sample; Phase II, which used spiked field samples to compare flask or purge device compositing with mathematical compositing; and Phase III, which used spiked field samples to compare purge device compositing, automated compositing, automated grab collection, and mathematical compositing.

Sample Collection, Shipment, and Storage

All samples collected at industrial or municipal sites were preserved to pH < 2, refrigerated, and shipped to the laboratory under wet ice *via* overnight courier. If free chlorine was present in the sample, the sample was additionally preserved with sodium thiosulfate. Samples were stored in the laboratory at 0 - 4° C from the time of collection until analysis. All analyses were performed within the method-specified 14-day holding time.

Phase I and Phase II samples were collected by passage of a portion of the flowing sample stream through a coil of pre-cleaned polytetrafluoroethylene (PTFE) tubing that was immersed in a commercial picnic cooler filled with ice. This practice reduced the temperature of the sample to 0 - 4° C, thus reducing the volatility of the VOCs. The stream from the PTFE tubing was collected in a cooled one-liter glass jug. Samples were preserved to pH < 2 in this jug and free chlorine was removed, as required, using sodium thiosulfate.

After preservation, samples were allocated from the one-liter jug into 40-mL VOA vials. Vials were filled from the common jug, thus assuring that each replicate VOA vial in the set contained identical samples. The vials were filled to overflowing, then capped with a PTFE-faced silicone rubber septum. After capping, each VOA vial was inverted and inspected for an air bubble. If a bubble was present, the vial was uncapped and refilled to overflowing and re-capped until completely filled without an air bubble. Each vial was assigned a unique sample number. Sampling times were at approximately 9 a.m., noon, 3 p.m., and 6 p.m. Collection procedures for Phase III sampling are outlined in the Phase III study design section.

Analyses

All laboratory analyses were performed by Pacific Analytical, Inc., in Carlsbad, California. A single laboratory was chosen to perform this work because EPA desired to minimize analytical variability in order to increase the probability that differences between grab sampling and compositing procedures would be detected.

Calibration

All analyses were performed by isotope dilution GC/MS using Revision C of EPA Method 1624. Revision C is an updated version of the method promulgated for use in water programs (40 *CFR* 136, Appendix A). Revision C includes a "reverse-search" technique for identification and quantitation of pollutants other than the priority pollutants. In the promulgated version and in Revision C of Method 1624, the priority pollutants and certain additional compounds are determined using a 5-point calibration for quantitation. Nominal calibration points are 10, 20, 50, 100, and 200 µg/L. In addition, the list of "reverse search" compounds is determined from relative retention time data and response factors given in the method.

In this study, the method of quantitation was examined in relation to recovery of the VOCs for which the instrument was calibrated. The calibration procedures in Method 1624 require use of an average relative response or a calibration curve for isotope dilution calibration based on the five calibration points. However, because the analytes were spiked at known concentrations, it is possible to use the calibration point closest to each known concentration for calibration. This technique was used for calculation of all concentrations in Phases II and III of this study and reduced the analytical error to less than that obtained using the average of the five calibration points or a calibration curve. This practice of using the closest calibration point should only be employed when the concentration of a pollutant in a sample is known to be close to the calibration point. For samples containing unknown concentrations, such as the unspiked field samples in Phase I, the most accurate analyte concentrations will be found using the entire 5-point calibration curve.

Data Processing and Reporting

Data were received by the EPA Sample Control Center in the form of quantitation reports on diskette. These data included quality control (QC) data for each analysis. The QC data included recoveries for each labeled compound spiked. The QC data were tested against the QC acceptance criteria in the method using a modified version of QA Formaster™ supplied by Thermo-Finnigan Corp. Non-compliant data were resolved with the laboratory.

Phase I

Study Design

Two types of samples were analyzed in Phase I: an unspiked field sample set, and two spiked reagent water sample sets. Each set consisted of four aliquots representing a single sampling point and time. Reagent water was used to test compositing effects in the absence of matrix effects, and to eliminate any possible interference from native pollutants. Two concentrations were used to test whether compositing effects were concentration dependent.

In order to ensure complete solubility, each of the four aliquots per set was spiked with one-fourth of the total analyte list at either 100 µg/L or 600 µg/L , resulting in composite samples with nominal concentrations of 25 µg/L and 150 µg/L , respectively. However, the 600 µg/L individual aliquots exceeded the calibration range of the instrument, and so these aliquots were diluted 1:3 (sample:reagent water) prior to analysis. The low concentration spiking scheme for each aliquot is shown in Table 2. The analyte list was separated into the four groups on the basis of solubility in water. After spiking, each aliquot was then split: one split to be physically composited with splits from each of the other three aliquots, and one split to be analyzed separately. Each analyte was present at full concentration in one of the four aliqouts, and not present in the other three. This results in the analyte being present at the nominal concentration in the composite. The results of the four individually analyzed splits were than averaged to derive the mathematical composite value. If there were 100% recovery of the spike in the individually analyzed splits, the average concentration of each analyte would be

$$\frac{100\mu g/L + 0\mu g/L + 0\mu g/L + 0\mu g/L}{4} = 25\mu g/L \; ,$$

for the low concentration samples.

Table 2
Phase I VOC Spiking Groups*

Analyte	Conc. In Aliquot 1	Conc. In Aliquot 2	Conc. In Aliquot 3	Conc. In Aliquot 4	Conc. In Composite
Carbon tetrachloride	100 µg/L	0	0	0	25 µg/L
Chlorobenzene	100 µg/L	0	0	0	25 µg/L
trans-1,3-Dichloropropene	100 µg/L	0	0	0	25 µg/L
1,2-Dichloroethane	100 µg/L	0	0	0	25 µg/L
Ethylbenzene	100 µg/L	0	0	0	25 µg/L
Tetrachloroethene	100 µg/L	0	0	0	25 µg/L

Analyte	Conc. In Aliquot 1	Conc. In Aliquot 2	Conc. In Aliquot 3	Conc. In Aliquot 4	Conc. In Composite
1,1,2-Trichloroethane	100 µg/L	0	0	0	25 µg/L
1,1-Dichloroethene	100 µg/L	0	0	0	25 µg/L
trans-1,2-Dichloroethene	100 µg/L	0	0	0	25 µg/L
1,2-Dichloropropane	100 µg/L	0	0	0	25 µg/L
Benzene	0	100 µg/L	0	0	25 µg/L
Bromodichloromethane	0	100 µg/L	0	0	25 µg/L
Bromoform	0	100 µg/L	0	0	25 µg/L
Dibromochloromethane	0	100 µg/L	0	0	25 µg/L
1,1,2,2-Tetrachloroethane	0	100 µg/L	0	0	25 µg/L
Toluene	0	100 µg/L	0	0	25 µg/L
1,1,1-Trichloroethane	0	100 µg/L	0	0	25 µg/L
Trichloroethene	0	100 µg/L	0	0	25 µg/L
1,1-Dichloroethane	0	100 µg/L	0	0	25 µg/L
Methylene Chloride	0	100 µg/L	0	0	25 µg/L
Bromomethane	0	0	100 µg/L	0	25 µg/L
Chloroethane	0	0	100 µg/L	0	25 µg/L
Chloromethane	0	0	100 µg/L	0	25 µg/L
Vinyl chloride	0	0	100 µg/L	0	25 µg/L
Diethyl ether	0	0	100 µg/L	0	25 µg/L
Chloroform	0	0	100 µg/L	0	25 µg/L
Acetone	0	0	0	100 µg/L	25 µg/L
Acrolein	0	0	0	100 µg/L	25 µg/L
Acrylonitrile	0	0	0	100 µg/L	25 µg/L
2-Butanone	0	0	0	100 µg/L	25 µg/L
p-Dioxane	0	0	0	100 µg/L	25 µg/L

*For the high concentration group, each compound was spiked at 600 µg/L in the same pattern. Composite concentrations were 150 µg/L in each analyte.

Statistical Analyses and Results

Spiked Reagent Water Samples

When averaged across all compounds, the physical composite of the low concentration splits had 8% higher recoveries[1] than the mathematical composite of the low concentration splits. The physical composite of the high concentration splits had 17% higher recoveries than the mathematical composite of the high concentration splits. Because there was only one sample at each concentration, statistical analyses could not be performed. As both concentrations behaved similarly, their results were combined to allow statistical analysis, and paired t tests were performed for each analyte. Of the 29 analytes for which reliable data was received, a significant difference between the mathematical composite and the physical composite was seen for only one analyte. This result would be expected on the basis of chance alone, and therefore, the results of the physical and mathematical composites are not statistically different.

Unspiked Field Samples

The physically composited sample had analyte concentrations that were 13% lower than those for the mathematically composited sample. This result is the opposite of that seen in the reagent water sample. However, due to the fact that there was only one unspiked field sample, no statistical analyses could be performed, and therefore, the results cannot be considered statistically significant. Despite the attempt to find an industrial source with high levels of volatiles, only 10 analytes were present in measurable quantities. This lead to the decision to spike field samples in future studies.

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[1]Throughout this document, the term "recovery" refers to the percent of spike value following correction for labelled compound recovery.

Phase II

Study Design

Four samples were collected at different times over the course of a day from seven "real-world" sites. These sites are described in Table 3. Information about each site was recorded in an on-site log and included the EPA sample number, collection date and time, descriptions of sample and sampling location, sample pH and temperature, and preservatives used, if any.

Table 3
Description of Sites and Samples

Episode	Industrial Category	Sampling Point	pH
4559	Organic Chemicals	Primary Effluent	8.8
4561	Organic Chemicals	Primary Effluent	7.3
4563	Drum Reconditioning	Scrubber Water	8.6
4573	Shore Reception	Oily Wastewater	5.6
4575	Transportation	Separator Effluent	6.0
4593	Transportation	Separator Effluent	6.8
4595	MSW Landfill	Leachate	6.8

Sample sites were selected based on the expectation that the effluents would contain volatile organics. However, volatile organics were seldom found and, therefore, samples were spiked with VOAs. All spiking solutions were prepared in the laboratory and all spiking was performed in the laboratory. Samples from three episodes were flask composited and samples from four episodes were purge device composited. Schematic diagrams of the flask and purge device compositing procedures are shown in Figures 1 and 2, respectively. For the episodes that were flask composited, the grab sample from the first sample time was analyzed unspiked to determine the background concentrations of VOCs present. For the episodes that were purge device composited, the grab samples from all four time points were analyzed unspiked to determine the background concentrations present. This testing was done to determine the constancy of the background throughout the sampling period, and to remove the influence of background levels from statistical analyses.

Individual grab sample VOA vials from each of the four time points were spiked at concentrations of 20, 40, 80, and 40 µg/L, respectively, to produce an average concentration of 45 µg/L. An aliquot from these spiked VOA vials was analyzed and two other aliquots were used to make duplicate composites, thus assuring that the spike levels were identical for analyses of the individual and composited samples.
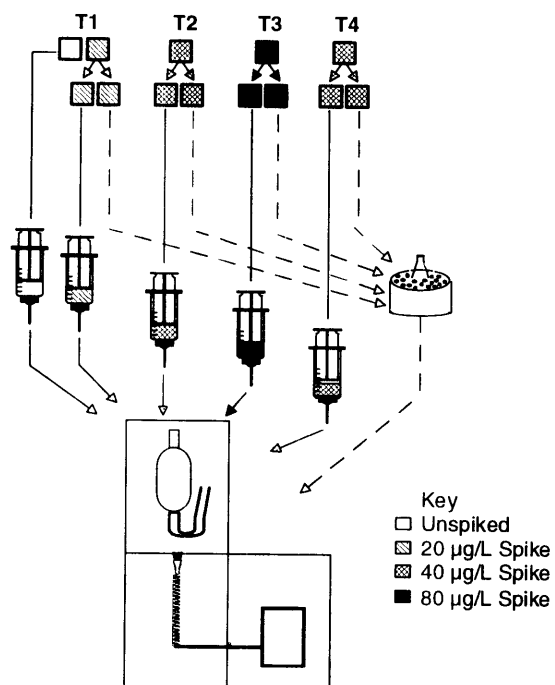
Figure 1. Flask Compositing Scheme
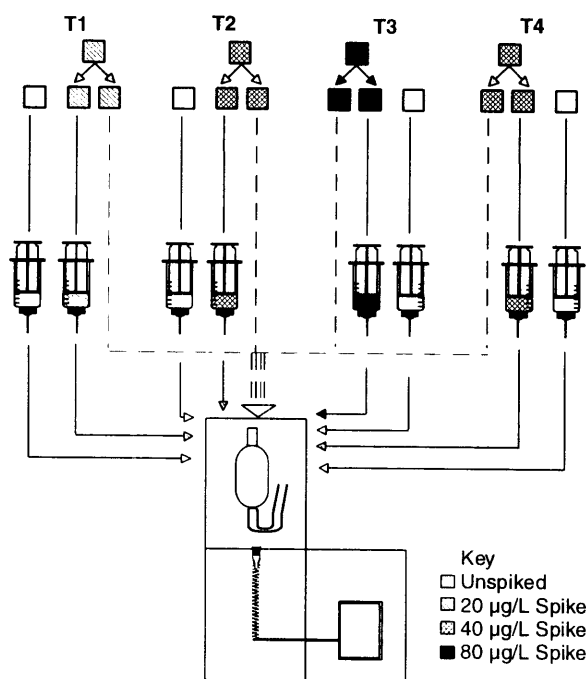
Figure 2. Purge Device Compositing Scheme

Statistical Analyses And Results

Analytes Tested

Data were evaluated with respect to QC requirements and three analytes were dropped from further analysis due to poor quantitation: 1,1,1-trichloroethane, 2-chloroethylvinyl ether, and trans-1-2-dichloroethene. All other analytes met QC requirements and were included in all statistical analyses.

Background Subtraction

The background level determined from the single, unspiked sample in each of the flask-composited episodes was subtracted from the result of all grab and composite samples for that episode. For each grab sample in the purge device-composited episode, the background level from the sample collected at the same point and time was subtracted from the analytical result. For each composite sample, the results of the four individual backgrounds were averaged, and the resulting value was subtracted from the composite results.

Statistical Analyses

For each analyte in each episode, the percent recoveries in the four grab samples were averaged, as were those of the two physical composites. The median recovery across all analytes and episodes was calculated. In addition, the ratio of mathematical composite recovery to physical composite recovery was calculated for each analyte in each episode, according to the formula

$$\text{Ratio} = \frac{\text{Mean mathematical composite recovery}}{\text{Mean physical composite recovery}}$$

A two-tailed Student's t test was performed to determine if this ratio was significantly different from 1.0, at the 5% level. In addition, a two-tailed Student's t-test was performed to determine if there were any differences between recoveries in samples composited in a flask and recoveries in samples composited in the purge device. When the number of samples in the two groups being compared are unequal, the Student's t test results are affected more severely by unequal variances for the two groups (Reference 10, p. 230). Since the variance for flask-composited samples was unequal to that for purge device-composited samples, and the sample sizes differed between the two groups, Satterthwaite's correction for unequal variances was applied to the t test calculations.

Results

The pollutants detected in the real-world samples were mainly the water-soluble compounds, resulting in high analytical variability. Statistically significant differences between the mathematically averaged results from analysis of the individual grab samples and the result from analysis of the physically composited sample were identified for a number of analytes. However, the size of the difference is small and may not be meaningful when compared to the

analytical variability. The two compositing methods, flask and purge device, provide analytical results for all analytes that are not statistically different.

Comparison of Grab and Composite Results

Table 4 compares composite recovery with grab recovery. These tests show that, for the analytes for which background subtraction was not required and from which the gases and water-soluble compounds were excluded, the median result for grab samples was 12.2 percent higher than the median result for the flask composites, and 7.3 percent higher than the median result for the purge device composites.

Depending on the analyte and analytical conditions, between 16% and 62% of the analytes show significantly lower concentrations in the composite samples than in the individual grab samples. The number of analytes showing these effects is much greater than would be expected by chance alone. In addition, the two compositing procedures show results in the same direction. The size of the effect, as a percent of the grab concentration, ranges up to 21, with the median across analytes showing the effect in the range of 6-13 percent. However, for routine VOA analyses this effect may not be significant compared to other sources of analytical variability.

Flask and Purge Device Compositing

Two-tailed Student's t-tests were used to determine the significance of differences between the two techniques for each analyte. Only 1 out of 20 analytes showed a significant effect on a two-tailed test at p=0.05; this could easily be due to chance variation. The two compositing procedures, therefore, give consistent results. Analytes tested were those with data for at least 3 samples by each method.

Table 4
Comparison of Composite Recovery with Grab Recovery

Composite Location	Background	Gas/H$_2$0 Soluble	Analytes Tested	Number Signif.	Median Effect*	Max. Effect*
Flask	Excluded	No	26	16	12.2%	21.0%
		Yes	11	5	13.0%	16.1%
	Subtracted	No	23	12	12.3%	21.0%
		Yes	9	4	13.1%	16.1%
Purge Device	Excluded	No	25	9	7.3%	12.5%
		Yes	11	5	9.0%	15.3%
	Subtracted	No	25	4	6.2%	11.1%
		Yes	11	5	9.3%	15.3%

* Effect = 100 x (grab concentration - composite concentration)/grab concentration.

"Background" indicates whether analytes present prior to spiking were background-subtracted or excluded from the analysis. Analytes tested were those with data for at least 3 samples; significance was tested at the p=0.05 level, two-tailed. As stated above, all significant differences were in the direction of lower composite concentration.

Phase III

Study Design

The purpose of this study phase was to compare manual grab, automated grab, mathematical compositing and automated compositing techniques. Two sites, with markedly different effluent matrices, were chosen for sampling: a POTW and a bus maintenance facility. Effluent from each site was collected, well mixed, and divided among four collapsible bags. Collapsible bags were used to minimize the amount of head space created as samples were withdrawn from the bags. Each bag was spiked with a different level of VOCs to simulate collection at different times. The spiking levels used were the same as those used in Phase II. Samples collected by all techniques at a single time were drawn from the same bag. The automated composite was drawn for the same length of time from each of the four bags.

The sampling scheme for Phase III is shown in Table 5 and Figure 3. From each bag, two grab samples were drawn manually and one drawn with an automated sampler. In addition, one sample from each site was drawn by an automated compositor. The automated compositor was set to draw a 0.3 mL sample every 40 seconds, until a total of approximately 10 mL was drawn (34 samples over a 23 minute period). This procedure was repeated in each of the four bags. One sample from each manually-drawn pair was assigned to the group to be analyzed directly and mathematically composited. The second manual grab sample was assigned to the group to be physically composited. Another single sample from each of the four bags was manually drawn prior to spiking, and was analyzed individually to assess the background levels of analytes present in the samples.

Table 5
Phase III Sampling Scheme

Bag (Time)	Samples				
1	Manual Grab	Automated Grab	Manual Grab	Back-ground	
2	Manual Grab	Automated Grab	Manual Grab	Back-ground	
3	Manual Grab	Automated Grab	Manual Grab	Back-ground	
4	Manual Grab	Automated Grab	Manual Grab	Back-ground	
Per Site	Mathematically Composited	Mathematically Composited	Physically Composited		Automated Composite

Figure 3. Phase III Compositing Scheme

Manual Grab
Automated Grab
Manual Composite
Automated Composite

Unspiked
20 µg/L Spike
40 µg/L Spike
80 µg/L Spike

Description of Sampling Equipment

Automated Grab Sampler

Automated grab samples were collected using an automated VOA sampler (Model 6000, Isco Environmental Division, Lincoln, NE). Sample is collected via a bladder pump that pushes the sample into the vial and does not expose the sample to a vacuum or partial vacuum. Prior to collection, the Model 6000 rinses the sample line and overfills the VOA vial three times, as required by the method and to eliminate headspace. The vials are filled *via* a syringe needle in a 360° stream designed to remove any air bubbles that may cling to the vials. The vials are covered with caps containing an air-tight valve that is opened for filling. When a vial is filled, the valve is closed.

Automated composite samples were collected using an automated VOA compositing sampler (AVOCS®-500, Associated Design and Manufacturing Co., Alexandria, VA). Sample is pushed into a bubble trap in the sampler via a peristaltic pump. The sample is then drawn into an air-

tight glass syringe, the volume of which is controlled by a piston connected to a timer. The timer, and therefore the sampling frequency, is set by the user, or can be connected to a flow meter so that sampling frequency can be coupled to the flow rate. Upon completion of the sampling event, the syringe is capped with a Luer-Lok™ closure, and the entire syringe is delivered to the laboratory for sample analysis, thereby maintaining zero-headspace conditions.

Statistical Analyses and Results

Statistical Analyses

Analyte concentrations detected at each sampling time (bag) were background-corrected using the concentrations found in the background sample for that time. For the automated composite, the background value used for correction was the average of the background values for each bag. For each analyte in each episode, the percent of spike recoveries in the manual grab samples were averaged, as were those of the automated grab samples. A Dunnett's test was performed using the mathematical composite of the manual grab as the control group. This test allows comparison of multiple techniques to a single control group. In addition, for each sampling technique, median and maximum effects were calculated. As in Phase II, effects are in terms of the difference between grab recovery and recovery by a particular technique, as a percentage of the grab recovery.

Results

The results are summarized in Table 6. For 11 of 30 analytes (37%), the physically composited samples had significantly lower recoveries than the mathematical composite of the manual grab samples. This percentage is far more than one would expect based on chance alone. Neither the automated compositor nor the automated sampler produced results which were statistically different from the mathematical composite of the manual grab sample for any analyte.

Table 6
Comparison of Alternative Sampling Techniques

Sampling Technique	Number of Analytes	Number Significantly Different	Median Effect* (%)	Maximum Effect* (%)
Automated Grab	30	0	- 4.6	- 29.8
Automated Composite	30	0	8.1	43.8
Physical Composite	30	11	15.0	- 42.0
* Effect = 100 x (Manual grab - technique) / Manual grab; a negative effect indicates that the technique resulted in higher recoveries than the manual grab.				

Conclusions and Discussion

Mathematical averages of the results from analyses of grab samples were found to be larger than the result from the analysis of either flask- or purge device-composited samples, although these differences are on the order of a few percent and would not be discernable except by isotope dilution quantitation procedures. In addition, the number of samples tested in this study (from 1 to 7, depending on the phase) was relatively small, even though the number of analytes per sample (29-40) was large. Because the behavior of one analyte can be expected to be correlated with that of other analytes in the sample, it is possible that the small number of samples results in differences that would be negated or lost in a larger study. For example, it is possible that the matrix for a particular sample contributed to the loss of analytes during compositing. If the behavior of analytes is correlated, then similar losses would be expected for many analytes in that sample. Because the primary metric in this study was the number of analytes that showed significant loss, a large difference in one sample out of the small number of samples could have a large impact on the study results. However, it is not know whether matrices have a differential effect on analyte loss.

The recoveries for the composited samples using reagent water in Phase I were greater than the average of the non-composited samples; in Phases II and III, the composited samples produced recoveries lower than the average of the non-composited samples. The reasons for these differences among the study phases are not known, but there are several possibilities. First, the results of the Phase I reagent water were not statistically significant, in part due to the small number of samples. Second, the individual reagent water aliquots were diluted 1:3 (sample:reagent water) while the composited reagent water aliquots were not. It is possible that some loss of analytes occurred during the dilution procedure. Third, it is possible that field samples have a greater loss of analyte during compositing due to the effects of the matrix or to interference by native analytes. Last, it is possible that the differences are due to measuring or compositing errors, even though calibrated syringes and volumetric glassware were used.

Compositing can be useful in some situations and will result in a cost savings over the analysis of individual grab samples. However, compositing may introduce some small systematic error in the analytical results. EPA plans to continue the use of VOA compositing in its effluent guidelines program and, after further studies, may promulgate compositing procedures for wastewaters.

References

1. Keith, L.H. and Telliard, W.A. <u>Env. Sci. & Tech.</u>, 1979, 13(4) 416 - 423.
2. Bellar, T.A., Lichtenberg, J.J., and Kroner,R.C. <u>J. Am. Water Works Assoc.</u>, 1974, 66, 703 - 706.
3. Telliard, W.A., Rubin, M.B., and Rushneck, D.R. <u>J. Chromatog. Sci.</u>, 1987, 25, 322 - 327.
4. "Compositing and Three-Stage Sampling", from <u>Statistical Methods for Environmental Monitoring</u>, Gilbert, R.O. Editor. D. Van Nostrand, New York, 1987.
5. Garner, F.C., Stapanian, M.A., and Williams, L.R., "Composite Sampling for Environmental Monitoring", from <u>Principles of Environmental Sampling</u>, Keith, L.H. Editor, American Chemical Society, Washington DC, 1988.
6. Cline, S.M., and Severin, B.F. <u>Water Res.</u>, 1989, 23(4) 407 - 412.
7. EPA 833-B-92-001, 1992
8. Stanko,G.H. <u>Environmental Lab</u>, 1994, 6(2) 10 - 15.
9. Hoaglin, D.C., Mosteller, F., and Tukey, J.S. <u>Understanding Robust and Exploratory Data Analysis</u>, John Wiley and Sons, New York, 1983.
10. Snedecor, G.W. and Cochran, W.G. Statistical Methods (eighth edition). Iowa State University Press, Ames, 1989.

Appendix A
Phase I Data

Phase I - Unspiked Field Sample Data
Analyte Concentration (µg/L)

ANALYTE	Mathematical Composite	Physical Composite
2-BUTANONE	357.14	178.53
2-PROPANONE	10744.84	7459.43
4-METHYL-2-PENTANONE	105.78	67.03
CHLOROFORM	180.08	161.71
ETHYLBENZENE	22.74	21.21
ISOBUTYL ALCOHOL	26.30	.
M-XYLENE	41.82	47.19
O+P XYLENE	29.94	31.77
TETRACHLOROETHENE	45.82	41.70
TOLUENE	181.85	161.41
TRICHLOROFLUOROMETHANE	32.90	34.40

Phase I - Spiked Reagent Water Data
Percent Recovery of Spikes

------------------------ High Concentration ------------------------

ANALYTE NAME	Mathematical Composite	Physical Composite
1,1,1-TRICHLOROETHANE	65.090	84.630
1,1,2,2-TETRACHLOROETHANE	186.322	104.438
1,1,2-TRICHLOROETHANE	101.457	112.564
1,1-DICHLOROETHENE	33.839	71.735
1,2-DICHLOROETHANE	74.214	81.336
1,2-DICHLOROPROPANE	90.028	101.859
1,4-DIOXANE	70.086	98.706
2-BUTANONE	68.824	82.143
2-PROPANONE	66.402	82.180
2-PROPENAL	56.863	65.999
ACRYLONITRILE	93.371	92.072
BENZENE	63.462	78.418
BROMODICHLOROMETHANE	83.349	97.070
BROMOMETHANE	60.393	58.326
CHLOROBENZENE	74.594	86.913
CHLOROETHANE	48.000	38.372
CHLOROFORM	78.140	71.504
CHLOROMETHANE	51.208	38.725
DIBROMOCHLOROMETHANE	87.038	96.361
DIETHYL ETHER	86.957	84.197
ETHYLBENZENE	66.712	87.389
METHYLENE CHLORIDE	79.693	97.755
TETRACHLOROETHENE	63.577	78.527
TETRACHLOROMETHANE	48.719	96.309
TOLUENE	76.557	94.174
TRANS-1,2-DICHLOROETHENE	36.805	50.857
TRANS-1,3-DICHLOROPROPENE	8.392	7.890
TRICHLOROETHENE	86.775	120.956
VINYL CHLORIDE	38.895	21.150

Phase I - Spiked Reagent Water Data
Percent Recovery of Spikes

---------------------- Low Concentration ----------------------

ANALYTE NAME	Mathematical Composite	Physical Composite
1,1,1-TRICHLOROETHANE	33.288	65.347
1,1,2,2-TETRACHLOROETHANE	167.883	127.389
1,1,2-TRICHLOROETHANE	106.369	124.057
1,1-DICHLOROETHENE	45.451	57.013
1,2-DICHLOROETHANE	77.358	86.549
1,2-DICHLOROPROPANE	91.312	101.143
1,4-DIOXANE	76.002	159.430
2-BUTANONE	80.217	98.540
2-PROPANONE	90.481	159.593
2-PROPENAL	64.039	62.613
ACRYLONITRILE	99.959	144.573
BENZENE	48.498	70.288
BROMODICHLOROMETHANE	80.002	105.830
BROMOMETHANE	50.303	55.540
CHLOROBENZENE	78.741	89.123
CHLOROETHANE	35.325	41.987
CHLOROFORM	69.5035	74.761
CHLOROMETHANE	38.9250	38.700
DIBROMOCHLOROMETHANE	82.1605	114.159
DIETHYL ETHER	85.3305	85.413
ETHYLBENZENE	74.1770	84.400
METHYLENE CHLORIDE	72.8565	109.240
TETRACHLOROETHENE	70.4925	80.151
TETRACHLOROMETHANE	63.4920	71.291
TOLUENE	57.1250	82.931
TRANS-1,2-DICHLOROETHENE	39.6740	51.291
TRANS-1,3-DICHLOROPROPENE	10.7310	.
TRICHLOROETHENE	54.9185	96.264
VINYL CHLORIDE	23.0345	21.433

Appendix B
Phase II Data

Phase II Data - Percent of Spike Recoveries

---------------------- Flask Compositing ----------------------

EPISODE	ANALYTE	Mathematical Composite	Physical Composite
4559	1,1,2,2-TETRACHLOROETHANE	99.4	109.2
4561	1,1,2,2-TETRACHLOROETHANE	104.2	102.0
4563	1,1,2,2-TETRACHLOROETHANE	102.8	90.9
4559	1,1,2-TRICHLOROETHANE	103.4	109.6
4561	1,1,2-TRICHLOROETHANE	105.9	102.6
4563	1,1,2-TRICHLOROETHANE	103.5	96.1
4559	1,1-DICHLOROETHANE	108.4	101.4
4561	1,1-DICHLOROETHANE	106.0	95.9
4563	1,1-DICHLOROETHANE	103.6	91.9
4559	1,1-DICHLOROETHENE	124.8	113.7
4561	1,1-DICHLOROETHENE	101.9	90.9
4563	1,1-DICHLOROETHENE	100.8	86.7
4559	1,2-DICHLOROETHANE	100.3	101.9
4561	1,2-DICHLOROETHANE	102.4	99.9
4563	1,2-DICHLOROETHANE	100.6	92.5
4559	1,2-DICHLOROPROPANE	106.3	101.0
4561	1,2-DICHLOROPROPANE	104.9	99.0
4563	1,2-DICHLOROPROPANE	99.6	91.4
4559	2-HEXANONE	1003.2	987.2
4561	2-HEXANONE	351.3	311.3
4563	2-HEXANONE	295.1	266.0
4559	4-METHYL-2-PENTANONE	198.3	199.9
4561	4-METHYL-2-PENTANONE	184.8	173.3
4563	4-METHYL-2-PENTANONE	883.5	781.3
4559	ACETONE	356.6	371.3
4561	ACETONE	386.7	418.1
4563	ACETONE	821.6	668.1
4559	ACROLEIN	52.8	65.5
4561	ACROLEIN	67.3	76.2
4563	ACROLEIN	66.6	64.4
4559	ACRYLONITRILE	108.1	120.7
4561	ACRYLONITRILE	95.5	104.2
4563	ACRYLONITRILE	96.0	100.2
4559	BENZENE	160.4	130.5
4561	BENZENE	105.0	93.7
4563	BENZENE	103.5	90.5
4559	BROMODICHLOROMETHANE	105.7	107.6
4561	BROMODICHLOROMETHANE	109.2	103.8
4563	BROMODICHLOROMETHANE	102.8	91.2
4559	BROMOFORM	105.8	105.8
4561	BROMOFORM	136.5	127.9
4563	BROMOFORM	103.2	98.7
4559	BROMOMETHANE	179.7	171.8
4561	BROMOMETHANE	105.5	91.3
4563	BROMOMETHANE	101.8	86.2

Phase II Data - Percent of Spike Recoveries

----------------- Flask Compositing (Cont')--------------------

EPISODE	ANALYTE	Mathematical Composite	Physical Composite
4559	CARBON DISULFIDE	284.3	251.8
4561	CARBON DISULFIDE	258.3	226.4
4563	CARBON DISULFIDE	254.6	198.0
4559	CARBON TETRACHLORIDE	116.0	101.1
4561	CARBON TETRACHLORIDE	98.8	92.6
4563	CARBON TETRACHLORIDE	97.5	78.6
4559	CHLOROBENZENE	105.5	100.3
4561	CHLOROBENZENE	224.2	183.1
4563	CHLOROBENZENE	105.4	94.6
4559	CHLOROETHANE	137.0	116.3
4561	CHLOROETHANE	99.9	86.9
4563	CHLOROETHANE	100.9	82.9
4559	CHLOROFORM	123.3	116.0
4561	CHLOROFORM	108.1	99.4
4563	CHLOROFORM	103.6	88.1
4559	CHLOROMETHANE	302.3	286.6
4561	CHLOROMETHANE	107.7	93.5
4563	CHLOROMETHANE	100.1	84.5
4559	CIS-1,3-DICHLOROPROPENE	331.1	336.9
4561	CIS-1,3-DICHLOROPROPENE	307.8	298.9
4563	CIS-1,3-DICHLOROPROPENE	306.4	261.6
4559	DIBROMOCHLOROMETHANE	112.5	112.2
4561	DIBROMOCHLOROMETHANE	114.0	108.7
4563	DIBROMOCHLOROMETHANE	105.6	97.0
4559	DIETHYL ETHER	107.1	110.4
4561	DIETHYL ETHER	101.5	101.5
4563	DIETHYL ETHER	99.8	93.5
4559	ETHYL BENZENE	106.0	98.8
4561	ETHYL BENZENE	199.1	170.6
4563	ETHYL BENZENE	163.1	129.0
4559	M-XYLENE	65.3	62.3
4561	M-XYLENE	363.9	279.3
4563	M-XYLENE	137.0	123.2
4559	METHYL ETHYL KETONE	100.7	104.2
4561	METHYL ETHYL KETONE	103.3	109.1
4563	METHYL ETHYL KETONE	184.5	157.5
4559	METHYLENE CHLORIDE	120.2	114.4
4561	METHYLENE CHLORIDE	98.1	91.7
4563	METHYLENE CHLORIDE	140.3	121.6
4559	O- + P-XYLENE	73.7	70.9
4561	O- + P-XYLENE	213.6	178.8
4563	O- + P-XYLENE	84.5	79.3
4559	P-DIOXANE	79.9	76.3
4561	P-DIOXANE	96.6	89.3
4563	P-DIOXANE	373.0	214.5
4559	TETRACHLOROETHENE	115.0	102.2

Phase II Data - Percent of Spike Recoveries

----------------- Flask Compositing (Cont')-------------------

EPISODE	ANALYTE	Mathematical Composite	Physical Composite
4561	TETRACHLOROETHENE	108.0	99.7
4563	TETRACHLOROETHENE	105.6	95.3
4559	TOLUENE	110.3	102.6
4561	TOLUENE	104.7	96.0
4563	TOLUENE	121.6	103.9
4559	TRANS-1,3-DICHLOROPROPENE	102.0	101.0
4561	TRANS-1,3-DICHLOROPROPENE	93.8	84.6
4563	TRANS-1,3-DICHLOROPROPENE	95.6	81.1
4559	TRICHLOROETHENE	118.6	109.9
4561	TRICHLOROETHENE	163.2	144.4
4563	TRICHLOROETHENE	105.4	93.3
4559	TRICHLOROFLUOROMETHANE	77.5	65.7
4561	TRICHLOROFLUOROMETHANE	63.2	54.5
4563	TRICHLOROFLUOROMETHANE	59.1	47.8
4559	VINYL CHLORIDE	210.1	187.0
4561	VINYL CHLORIDE	105.2	93.0
4563	VINYL CHLORIDE	99.0	85.7

Phase II Data - Percent of Spike Recoveries

------------------- Purge Device Compositing -------------------

EPISODE	ANALYTE	Mathematical Composite	Physical Composite
4573	1,1,2,2-TETRACHLOROETHANE	91.5	94.4
4575	1,1,2,2-TETRACHLOROETHANE	97.9	99.6
4593	1,1,2,2-TETRACHLOROETHANE	116.6	117.6
4595	1,1,2,2-TETRACHLOROETHANE	99.2	94.4
4573	1,1,2-TRICHLOROETHANE	97.5	85.1
4575	1,1,2-TRICHLOROETHANE	90.7	88.6
4593	1,1,2-TRICHLOROETHANE	101.2	93.7
4595	1,1,2-TRICHLOROETHANE	89.8	81.7
4573	1,1-DICHLOROETHANE	97.1	79.3
4575	1,1-DICHLOROETHANE	92.0	86.4
4593	1,1-DICHLOROETHANE	98.7	90.4
4595	1,1-DICHLOROETHANE	108.4	89.8
4573	1,1-DICHLOROETHENE	98.3	77.1
4575	1,1-DICHLOROETHENE	88.7	79.2
4593	1,1-DICHLOROETHENE	96.8	87.0
4595	1,1-DICHLOROETHENE	92.4	76.2
4573	1,2-DICHLOROETHANE	96.3	83.0
4575	1,2-DICHLOROETHANE	91.9	87.9
4593	1,2-DICHLOROETHANE	98.4	92.4
4595	1,2-DICHLOROETHANE	97.2	85.2
4573	1,2-DICHLOROPROPANE	94.5	81.0
4575	1,2-DICHLOROPROPANE	93.2	90.7
4593	1,2-DICHLOROPROPANE	102.6	95.8
4595	1,2-DICHLOROPROPANE	94.9	83.8
4573	2-HEXANONE	341.9	301.8
4575	2-HEXANONE	316.6	317.1
4593	2-HEXANONE	457.8	423.7
4595	2-HEXANONE	330.6	316.6
4573	4-METHYL-2-PENTANONE	205.5	182.6
4575	4-METHYL-2-PENTANONE	167.4	159.1
4593	4-METHYL-2-PENTANONE	263.6	229.2
4595	4-METHYL-2-PENTANONE	169.6	170.4
4573	ACETONE	68.2	62.3
4575	ACETONE	135.2	120.5
4593	ACETONE	79.2	90.8
4595	ACETONE	58.0	44.6
4573	ACROLEIN	63.5	71.9
4575	ACROLEIN	16.2	9.6
4593	ACROLEIN	23.3	12.2
4595	ACROLEIN	140.7	5.2
4573	ACRYLONITRILE	103.4	96.2
4575	ACRYLONITRILE	106.0	108.0
4593	ACRYLONITRILE	111.3	103.9
4595	ACRYLONITRILE	98.3	98.8
4573	BENZENE	90.5	73.0
4575	BENZENE	91.7	83.6

Phase II Data - Percent of Spike Recoveries

------------------ Purge Device Compositing (Cont') -----------------

EPISODE	ANALYTE	Mathematical Composite	Physical Composite
4593	BENZENE	98.9	92.7
4595	BENZENE	90.4	76.2
4573	BROMODICHLOROMETHANE	92.8	80.1
4575	BROMODICHLOROMETHANE	92.6	83.7
4593	BROMODICHLOROMETHANE	97.0	89.4
4595	BROMODICHLOROMETHANE	92.1	81.8
4573	BROMOFORM	99.0	89.4
4575	BROMOFORM	98.7	77.9
4593	BROMOFORM	101.2	74.6
4595	BROMOFORM	113.3	83.7
4573	BROMOMETHANE	97.3	83.8
4575	BROMOMETHANE	94.7	86.6
4593	BROMOMETHANE	110.2	97.2
4595	BROMOMETHANE	101.2	83.4
4573	CARBON DISULFIDE	240.2	183.3
4575	CARBON DISULFIDE	217.7	196.9
4593	CARBON DISULFIDE	241.4	221.8
4595	CARBON DISULFIDE	225.0	185.9
4573	CARBON TETRACHLORIDE	101.1	81.7
4575	CARBON TETRACHLORIDE	94.9	81.7
4593	CARBON TETRACHLORIDE	99.5	87.0
4595	CARBON TETRACHLORIDE	198.6	181.7
4573	CHLOROBENZENE	115.3	82.3
4575	CHLOROBENZENE	94.4	86.6
4593	CHLOROBENZENE	131.5	118.1
4595	CHLOROBENZENE	95.9	83.0
4573	CHLOROETHANE	98.7	79.2
4575	CHLOROETHANE	88.2	82.2
4593	CHLOROETHANE	96.0	88.9
4595	CHLOROETHANE	104.5	86.2
4573	CHLOROFORM	97.1	78.7
4575	CHLOROFORM	83.9	78.8
4593	CHLOROFORM	103.0	95.7
4595	CHLOROFORM	91.2	78.6
4573	CHLOROMETHANE	102.6	80.0
4575	CHLOROMETHANE	95.6	81.7
4593	CHLOROMETHANE	105.0	95.3
4595	CHLOROMETHANE	101.4	82.3
4573	CIS-1,3-DICHLOROPROPENE	317.8	271.8
4575	CIS-1,3-DICHLOROPROPENE	280.0	259.5
4593	CIS-1,3-DICHLOROPROPENE	292.4	247.3
4595	CIS-1,3-DICHLOROPROPENE	296.0	255.2
4573	DIBROMOCHLOROMETHANE	96.2	84.4
4575	DIBROMOCHLOROMETHANE	89.2	84.4
4593	DIBROMOCHLOROMETHANE	97.8	89.1
4595	DIBROMOCHLOROMETHANE	97.0	87.3

Phase II Data - Percent of Spike Recoveries

---------------- Purge Device Compositing (Cont') ----------------

EPISODE	ANALYTE	Mathematical Composite	Physical Composite
4573	DIETHYL ETHER	94.6	82.9
4575	DIETHYL ETHER	101.2	100.6
4593	DIETHYL ETHER	112.8	102.0
4595	DIETHYL ETHER	91.3	71.3
4573	ETHYL BENZENE	97.7	74.6
4575	ETHYL BENZENE	93.5	83.7
4593	ETHYL BENZENE	56.3	48.8
4595	ETHYL BENZENE	95.8	78.1
4573	M-XYLENE	46.8	34.1
4575	M-XYLENE	32.4	33.7
4593	M-XYLENE	141.5	78.9
4595	M-XYLENE	56.8	44.9
4573	METHYL ETHYL KETONE	79.1	74.3
4575	METHYL ETHYL KETONE	103.2	103.0
4593	METHYL ETHYL KETONE	99.8	100.8
4595	METHYL ETHYL KETONE	102.5	103.2
4573	METHYLENE CHLORIDE	86.0	72.4
4575	METHYLENE CHLORIDE	76.3	72.6
4593	METHYLENE CHLORIDE	93.8	88.1
4595	METHYLENE CHLORIDE	84.8	72.5
4573	O- + P-XYLENE	43.3	37.5
4575	O- + P-XYLENE	40.9	40.0
4593	O- + P-XYLENE	120.9	79.4
4595	O- + P-XYLENE	58.7	48.8
4573	P-DIOXANE	87.1	83.0
4575	P-DIOXANE	100.0	110.2
4593	P-DIOXANE	98.7	98.7
4595	P-DIOXANE	126.6	117.8
4573	TETRACHLOROETHENE	92.4	80.4
4575	TETRACHLOROETHENE	84.8	76.2
4593	TETRACHLOROETHENE	95.3	83.6
4595	TETRACHLOROETHENE	92.6	81.1
4573	TOLUENE	94.8	72.1
4575	TOLUENE	91.3	82.9
4593	TOLUENE	54.7	49.5
4595	TOLUENE	100.6	48.9
4573	TRANS-1,3-DICHLOROPROPENE	96.4	81.1
4575	TRANS-1,3-DICHLOROPROPENE	80.0	78.9
4593	TRANS-1,3-DICHLOROPROPENE	93.1	91.1
4595	TRANS-1,3-DICHLOROPROPENE	84.8	102.7
4573	TRICHLOROETHENE	103.2	81.6
4575	TRICHLOROETHENE	83.8	77.0
4593	TRICHLOROETHENE	93.6	83.1
4595	TRICHLOROETHENE	95.4	81.4
4573	TRICHLOROFLUOROMETHANE	.	.
4575	TRICHLOROFLUOROMETHANE	.	.
4593	TRICHLOROFLUOROMETHANE	.	.

Phase II Data - Percent of Spike Recoveries

--------------- Purge Device Compositing (Cont') ----------------

EPISODE	ANALYTE	Mathematical Composite	Physical Composite
4595	TRICHLOROFLUOROMETHANE	.	.
4573	VINYL ACETATE	240.0	217.9
4573	VINYL CHLORIDE	97.1	74.9
4575	VINYL CHLORIDE	91.0	81.4
4593	VINYL CHLORIDE	104.1	92.9
4595	VINYL CHLORIDE	103.3	84.3

Appendix C
Phase III Data

Phase III Data - Percent of Spike Recoveries

EPISODE	ANALYTE	Mathematical Composite	Automated Sampler	Automated Compositor	Physical Composite
4617	1,1,1-TRICHLOROETHANE	76.1	78.9	63.9	61.4
4618	1,1,1-TRICHLOROETHANE	67.7	72.4	61.4	55.5
4617	1,1,2,2-TETRACHLOROETHANE	102.4	115.9	87.7	86.4
4618	1,1,2,2-TETRACHLOROETHANE	107.4	111.4	107.1	106.8
4617	1,1,2-TRICHLOROETHANE	86.8	93.7	82.0	85.8
4618	1,1,2-TRICHLOROETHANE	88.4	91.1	90.5	77.3
4617	1,1-DICHLOROETHANE	79.5	80.7	73.0	62.8
4618	1,1-DICHLOROETHANE	73.2	77.3	71.3	61.9
4617	1,1-DICHLOROETHENE	72.5	79.4	62.4	60.6
4618	1,1-DICHLOROETHENE	66.7	70.6	57.7	52.5
4617	1,2-DICHLOROETHANE	93.8	95.5	87.6	83.2
4618	1,2-DICHLOROETHANE	88.2	94.1	88.7	85.0
4617	1,2-DICHLOROPROPANE	83.7	81.6	75.3	68.5
4618	1,2-DICHLOROPROPANE	78.2	82.0	78.0	70.9
4617	2-CHLOROETHYLVINYL ETHER	90.4	117.3	71.8	112.6
4618	2-CHLOROETHYLVINYL ETHER	101.9	121.0	113.3	109.6
4617	ACRYLONITRILE	100.7	109.5	96.6	106.5
4618	ACRYLONITRILE	110.5	114.1	113.2	114.8
4617	BENZENE	101.7	107.4	97.3	82.8
4618	BENZENE	74.2	77.8	73.1	62.5
4617	BROMODICHLOROMETHANE	72.4	72.7	59.2	61.2
4618	BROMODICHLOROMETHANE	89.6	92.5	85.7	80.2
4617	BROMOFORM	46.6	33.7	26.2	.
4618	BROMOFORM	89.3	81.5	97.5	126.8
4617	BROMOMETHANE	78.4	81.3	69.6	64.2
4618	BROMOMETHANE	79.0	82.9	77.2	65.9
4617	CARBON TETRACHLORIDE	55.8	56.0	38.9	48.2
4618	CARBON TETRACHLORIDE	66.1	67.2	37.1	54.6
4617	CHLOROBENZENE	91.2	95.9	76.1	78.2
4618	CHLOROBENZENE	79.2	80.1	63.9	70.3
4617	CHLOROETHANE	82.5	88.6	75.7	66.3
4618	CHLOROETHANE	78.0	81.9	74.3	60.3
4617	CHLOROFORM	89.5	97.8	91.4	75.4
4618	CHLOROFORM	83.6	86.1	80.2	70.2
4617	CHLOROMETHANE	84.2	91.1	80.1	67.3
4618	CHLOROMETHANE	80.5	85.3	78.2	61.9
4617	DIBROMOCHLOROMETHANE	55.1	54.6	36.4	55.3
4618	DIBROMOCHLOROMETHANE	85.0	90.7	84.9	86.6
4617	DIETHYL ETHER	106.3	112.2	106.8	92.6
4618	DIETHYL ETHER	106.5	111.2	111.6	100.0
4617	ETHYL BENZENE	77.6	81.1	60.4	72.1
4618	ETHYL BENZENE	70.2	71.3	55.6	59.7
4617	METHYL ETHYL KETONE	103.8	96.9	120.3	92.7
4618	METHYL ETHYL KETONE	126.0	125.1	128.6	132.0
4617	METHYLENE CHLORIDE	104.6	101.3	93.5	91.4
4618	METHYLENE CHLORIDE	85.8	90.4	86.3	73.8
4617	P-DIOXANE	62.7	52.0	57.6	73.4
4618	P-DIOXANE	102.1	108.0	101.4	109.9
4617	TETRACHLOROETHENE	69.6	74.9	52.0	69.4
4618	TETRACHLOROETHENE	63.0	62.8	40.6	49.7
4617	TOLUENE	75.9	77.8	54.5	48.5
4618	TOLUENE	71.9	73.8	60.1	58.9
4617	TRANS-1,2-DICHLOROETHENE	77.2	92.2	68.1	66.6
4618	TRANS-1,2-DICHLOROETHENE	71.1	75.0	68.3	58.4
4617	TRANS-1,3-DICHLOROPROPENE	79.3	83.6	54.8	71.8
4618	TRANS-1,3-DICHLOROPROPENE	82.4	82.1	71.1	65.1
4617	TRICHLOROETHENE	72.3	69.4	55.0	61.5
4618	TRICHLOROETHENE	65.6	67.1	51.2	51.7
4617	VINYL CHLORIDE	78.2	85.1	68.7	60.2
4618	VINYL CHLORIDE	75.1	79.0	69.5	57.9