Appendix 1. Quality-Assurance and Method Description for Volatile Organic Compounds

Quality assurance was conducted for both field and analytical procedures. Replicates and blanks were collected to assure the quality of field-sampling methods. Analytical quality assurance for VOC analysis was conducted by evaluating internal standard and surrogate areas and concentrations and by analyzing replicate samples. The first part of this Appendix describes the procedures that were followed. The second part is the Water Science Center Quality-Assurance Project Plan for methane and volatile organic compound (VOC) analyses at the MD-DE-DC Water Science Center Research Laboratory, in Baltimore, Maryland.

Quality Assurance of Field Methods

Field samples were collected in replicate using the same equipment and sampling procedures. For ferrous iron and methane samples, all replicate samples were analyzed. For VOCs, at least 20 percent of the replicate samples were analyzed.

In addition to replicate samples, field blanks were routinely collected and analyzed for VOCs. Blanks included source-water, equipment, trip, and deployment blanks. Explanations of these blanks and the sampling events during which they were collected are provided in the site-specific work plans for the field events (E. H. Majcher, U.S. Geological Survey, written commun., February 2002; February 2003).

Quality Assurance of Analytical Methods

As part of the USGS MD-DE-DC Water Science Center Research Laboratory internal quality-assurance and quality-control (QA/QC) procedures, a calibration check was performed daily to verify the standard calibration curve of the GC/MSD prior to processing VOC samples. A laboratory blank also was processed to ensure that there was no contamination caused by ambient laboratory conditions. In addition, internal standards and surrogate standards were injected into every blank and sample. The injection of internal standards was necessary to determine the relative response of each target compound. Concentrations of the target compounds were calculated on the basis of known internal standard responses and concentrations. Surrogate standards with similar properties to the analytes of interest were used to track possible variations in each analytical sample run. The surrogate concentrations were known values; therefore, the responses of the surrogates could be evaluated to detect variations in instrument performance. If a sample was processed and either the internal standard response was low or the surrogate detection was inconsistent with the known concentration, then the sample was reprocessed and/or the instrument was adjusted and re-calibrated before other samples were processed. Additional details of the laboratory QA/QC are described in Appendix 1B. A calibration check also was performed daily to verify the calibration curve of the GC/FID prior to and after processing samples for methane analyses.

The calibration of the GC/FID used to analyze the methane samples was verified daily using standard compressed gases before and after sample analyses. Air blanks were analyzed frequently to verify the absence of bias due to contamination from the sample vials or the laboratory equipment. Nearly all methane samples were collected in duplicate and all samples were analyzed. The lower reporting limit for aqueous phase methane analyses ranged from less than 28.7 micrograms per liter (µg/L) to less than 93.7 µg/L depending on the volume of sample in the vial. This method is described in Baedecker and Cozzarelli (1992).

Sampling and Quality-Assurance Data

Quality-assured data collected from ground water and surface water from 2002-03 are listed in Appendix 3. All VOC data reported in Appendix 3 passed all laboratory QA/QC. Samples that failed, as determined by the instrument response to the surrogate concentrations, are not reported in the data tables. Data considered to be marginal are qualified in the data tables. These data were independently verified by Thomas Imbrigiotta of the USGS Trenton, NJ, Water Science Center.

Quality Assurance of VOC Data

Field replicates were samples that were collected sequentially using the same equipment and sampling procedure. Replicate samples collected from the same location at the same time are referred to as replicate pairs. These pairs were analyzed to detect variability in the sampling and analytical procedures. Reproducibility of the replicate pairs can be determined by the average relative percent differences (RPDs) between sample pairs by use of the following calculation:

$$\frac{|c1-c2|}{(c1+c2)} * 100\% = \text{Average RPD}$$

where

c1 is the concentration in the first sample,

and

c2 is the concentration in the duplicate sample.

Acceptable RPDs for individual constituents with concentrations greater than 5 µg/L are less than 25 percent. RPDs for duplicate samples with VOC concentrations less than 5 µg/L typically have higher RPDs when the actual concentrations are very close to each other. A greater range of RPDs is acceptable for values less than 5 µg/L. Duplicate pairs are said to be in agreement if (1) the concentration of one of the samples was greater than 5 µg/L and the RPD was less than 25 percent or (2) one of the duplicate concentrations that was detected was less than the detection limit of the associated replicate (or greater than the associated "greater than" value)—for example, if one value was less than 50 and the associated duplicate was 36 µg/L (or if one was greater than 250 and the other 253 µg/L). These cases are caused by the use of different dilution factors that are used to achieve values within the calibrated range of the instrument over a wide range of concentrations.

The variability of the VOC RPDs from peeper samples was greater in this investigation than that of VOC RPDs from PDS or surface-water samples and will be discussed separately. Duplicate VOC samples from peepers were collected from adjacent chambers rather than the same chambers because of the low volumes of water available in each. In previous investigations in the non-seep areas, duplicate VOCs from peepers showed low RPDs. In this investigation, peepers were placed in active seep areas and had much higher RPDs between duplicate samples. These higher RPDs may be from rapid ground-water flow in the seep areas that bias one side of the peeper over the other causing the greater variability in concentrations between the duplicate pairs. The distribution of RPDs in ground- and surface-water samples, and the distribution of RPDs in the peeper samples in seep areas are shown in figures A1 and A2.

Analyses from non-peeper samples had 858 duplicate combinations where at least one sample of the pair had a detectable concentration. Of those, 833 pairs were in agreement (RPDs less than 25 percent). Nine pairs of samples with concentrations greater than 5 µg/L had RPDs greater than 25 percent. Sixteen pairs of samples with concentrations greater than 5 µg/L were not in agreement, with 1 having an RPD greater than 60 percent, and 15 where one sample was determined to be less than a detection limit, and the associated value was greater than that limit (or one was greater than the calibrated limit and the associated value was less than that limit).

Analyses from peeper samples had 305 duplicate combinations. Of those, 175 were in agreement, but 94 had RPDs greater than 25 percent. Thirty-six sample pairs were not in agreement, where one sample was determined to be less than a detection limit, and the associated value was greater than that limit (or one was greater than the calibrated limit and the associated value was less than that limit). This high variability in peeper sample duplicates is attributed to greater vertical ground-water-flow rates in the seep along one side of the sampling device, rather than field sampling or analytical techniques.

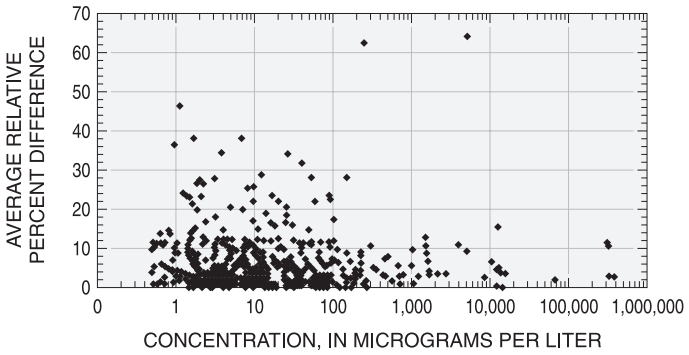

Figure A1. Average relative percent differences in ground- and surface- water samples West Branch Canal Creek, Aberdeen Proving Ground, Maryland.

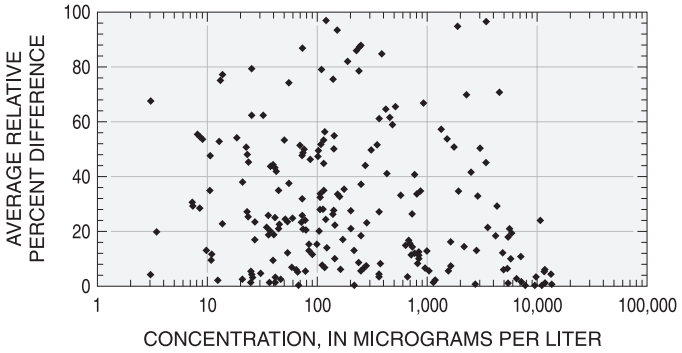

Figure A2. Average relative percent differences, West Branch Canal Creek, Peeper Samples, Aberdeen Proving Ground, Maryland.

Multiple Analyses from the Same VOC Vials

VOC samples are analyzed at different dilutions based on the anticipated concentrations so that the results will be within the calibrated range of the instrument. The wide range of VOC concentrations in water samples from the site often makes it difficult to anticipate the correct dilutions, and multiple analyses from the same sample vials are sometimes required to determine concentrations that are in range for different analytes. The following section describes the QA results from these multiple analyses.

Multiple samples from 37 VOC vials were analyzed for 61 different organic constituents. Twelve of the 37 samples were run at the same dilution, and the remaining 25 sample sets were analyzed at different dilutions. Of the 139 data pairs where two or more concentrations were above the detection limit, the average RPD was 5.6 percent. The RPD from only

three concentration pairs exceeded 25 percent (between 28 and 33 percent), and each of the three were from samples that were run at different dilutions.

There were 81 cases where there was one concentration in the calibrated range and the associated duplicate from the vial was above or below the calibrated range. Of those 81 instances, 69 pairs were in agreement, where the concentration was less than the associated "less than" value or the concentration was greater than the associated "greater than" value. Of the 12 that did not agree, 10 had concentrations close to the associated "less than" value. The remaining two pairs had RPDs of less than 30 percent when comparing the actual value to the maximum reported value for the "less than" value. The pairs with the greatest differences were associated with large differences in dilutions between the two samples. These results indicate little difference between analyses after multiple aliquots were collected from a VOC vial.

Results of Field Blanks

Seventy-seven blank samples were collected during the 2002-03 field efforts and included equipment, pre-deployment, source water, trip, tubing, and peeper blanks. The types and number of blank samples collected are listed in table A1. Of the 77 samples, 10 had low-level detections of benzene compounds, with a maximum detection of 2.3 µg/L. In 7 of these 10 samples, benzene compounds were the only detections in the sample. Benzene compounds are not compounds of interest in this investigation, but benzene compound concentrations below 2 µg/L may be from sources other than the field site2

Of the three blank samples that had detections other than benzene, one was carryover from a previous sample in the GS/MS and is qualified with a "v" in Appendix 3. The remaining two blanks with detections were a PDS pre-deployment blank and a source-water blank with a total of three values that ranged from 1 to 6.3 µg/L. Field values from the sampling round when these two blanks were collected showed no bias with the compounds detected in the blanks (1,2 dichloroethane (12DCA), trichloroethane (TCE), and 1,1,2,2 tetrachloroethane (1122TCA).

Summary of Quality Assurance

Based on the results of the preceding sections, the data presented in this report are of good quality. Individual data values that may be suspect are qualified in Appendix 3. An "x" code after a value indicates that the recommended 14-day holding time was exceeded for this sample, which could result in losses for some or all compounds. A "V" code after a value indicates possible positive bias due to suspected laboratory contamination as indicated by instrument blanks. An "H" code after a value indicates possible positive bias based on an unacceptably high response for this compound in one or more calibration checks for this batch of samples, while a "L" code indicates a low response. An "e" code indicates estimated concentrations that may be above or below calibrated ranges of the instrument.

Table A1. Summary of field blanks collected during 2002-03 West Branch Canal Creek field work, Aberdeen Proving Ground, Maryland.

[< D.L., less than the detection limit; PDS, Passive diffusion samplers]

Number of blanks collected	Type of blank	Number of blanks with detections	Number of blanks with only benzene compounds detected
	GROUND-WATER BLANKS		
17	Equipment blanks	4	4
16	Pre-deployment PDS blanks	2	1
8	Source-water blanks	1	0
21	Trip blanks	3	
1	Peeper tank blank	all < D.L.	
	SURFACE-WATER BLANKS		
7	Equipment Blanks	all < D.L.	
2	Source-water blanks	all < D.L.	
5	Tubing Blanks	all < D.L.	
77	Total		

Quality-Assurance Project Plan for Methane and VOC Analyses at the MD-DE-DC Water Science Center Research Laboratory

Methane Analysis Methods

1. Instrumentation used—The instrument used in the laboratory is a Hewlett Packard HP5890 Series II gas-chromatograph flame-ionization detector (GC-FID) system with a fused silica capillary column [column inner diameter of 0.53 millimeters, column length of 15 meters, film thickness 50 micrometers, and a phase ratio of 2.65] (HP part number 19085P-MS9). Peak retention times and areas are recorded and printed by a Hewlett Packard HP 3396 Series II integrator.

2. Methods used—The method used for methane analysis is documented in Baedecker and Cozzarelli (1992). During 1996, Isabelle Cozzarelli (USGS) analyzed 20 split samples, and the average variability between the split samples (determined at relative percent difference) was less than 30 percent, with no observable trend in the residuals. The variability between the split samples was comparable to the typical variability observed between field replicates analyzed at one laboratory or the other. The analysis of dissolved methane involves collecting air samples from the headspace in the vial and injecting the air into the GC-FID to analyze for the concentration of methane. Methane has a retention time of approximately 0.43 minutes. Water samples collected for methane analyses are collected in the field using 10-mL (milliliter) sterile glass syringes, and injected into 20-mL sterile serum vials without introducing ambient air. The vials have been cleaned, baked, sterilized, sealed, purged with nitrogen, and weighed prior to field sampling. Aqueous sample volumes typically range from 2 mL to 5 mL depending on the anticipated concentrations of methane in the headspace sample.

3. Laboratory Quality Controls (QC—The instrument calibration is performed at the beginning and end of each day of use. Calibration standards include air blanks, and 10 ppm (parts per million), 100 ppm, and 1,000 ppm methane standards. Integration values read from the printer output should be within 25 percent of the calculated value predicted for that range. Air blanks are analyzed periodically through the day to check if drift is occurring.

4. Laboratory Quality-Assurance (QA) data—Copies of the instrument printout are stored in the laboratory. All data are transcribed from printouts to an electronic form for analysis. Data are entered into the spreadsheet and double-checked against original values. Relative percent differences are calculated for each sample pair.

   In the laboratory, the retention times, integrated area, and temperature of each sample are written in a bound logbook. After analyses, sample identification information and the following values are entered into a spreadsheet to determine the gas and aqueous phase methane concentrations:

   - Three weights of the vials including empty, with sample, and filled vial,
   - The retention time and area integrated by the instrument, and
   - Temperature of the sample at time of analysis.

   Quantitative sample results, including quality-assured sample results, are archived on the MD-DE-DC Water Science Center server. Environmental samples will be incorporated into the project Excel and Access databases.

5. Field QA/QC protocols are documented in the USGS peer-reviewed data reports in which the data are presented. To date, these data reports include OFR 97-560 (Olsen and others, 1997), OFR 00-282 (Spencer and others, 2000), and OFR 01-420 (Spencer and others, 2002).

VOC Analysis Methods

VOC analyses were conducted in the MD-DE-DC Water Science Center research laboratory by a senior analyst (hydrologist) and hydrologic technician with specialized training. Analyses at this laboratory have supported research projects conducted for scientific investigations on military installations, including Aberdeen Proving Ground, Maryland, and Dover Air Force Base, Delaware.

1. Instrumentation used—Instruments used in this laboratory include two OI Analytical DPM-16 multisamplers (in tandem), one OI Analytical 4560 sample concentrator, one Hewlett Packard 5973 mass-selective detector, and one Hewlett Packard 6890-series gas-chromatograph system. These instruments are controlled through a computer workstation equipped with Hewlett Packard G1701BA analytical software and the NIST 98 mass-spectral library.

2. Methods used—This laboratory analyzes microcosm samples, porewater, ground-water, and surface-water VOCs. All water samples are analyzed using a modified version of USEPA Method 524.2 (U.S. Environmental Protection Agency, 1998). Most modifications to this method are described in Rose and Schroeder (1995). Additional modifications to the method include the following:

- Dibromofluoromethane is substituted for 1,2–dichloroethane-d4 as the earliest eluting surrogate standard. This compound has a shorter retention time than 1,2-dichloroethane-d4, and thus provides better coverage of early eluting compounds (such as vinyl chloride, *cis*-1,2-dichloroethene, and *trans*-1,2-dichloroethene) that are of central interest to the research supported by these analyses. The use of dibromofluoromethane as an acceptable surrogate for VOCs analyzed by purge and trap gas chromatography/mass spectrometry is documented in USEPA Method 8260.

- Sample volumes are 5 mL instead of 25 mL. The volumes of sparge tubes, gas-tight syringes, luer-lock syringes, volumetric flasks, and other glassware have been adjusted accordingly. Potential reduction of analyte response due to the lower sample volume is offset by the improved purge efficiency associated with purging a smaller sample volume.

- Method detection limits (MDLs) have not been statistically determined for the instrumentation that is currently in use. A lower reporting limit of 0.5 µg/L is used for all analytes of interest. Non-detections and detections that are less than 0.5 µg/L are reported as "<0.5 µg/L" with no additional qualifiers. The water samples analyzed in this laboratory come from sites of known contamination and usually are very high in concentration (>20,000 µg/L for some analytes). The analytical results are used for research and screening purposes only, not for determining regulatory compliance; therefore, a less rigorous determination of lower reporting limits is considered acceptable for the current uses of the data. The lower reporting limit of 0.5 µg/L corresponds to a signal-to-noise ratio of 10 or higher for analytes of interest, and is sufficiently larger (typically by a factor of 10 or more) than the MDLs that are attainable using the same instrument configuration, for example, those reported in USGS OFR 97-829 (Connor and others, 1998).

- Calibration is performed using 12 to 14 calibration standards with concentrations ranging from 0.1 to 250.0 µg/L. Calibration curves are constructed for each analyte of interest, using the set of standards that provides the widest concentration range while achieving a relative standard deviation (RSD) of less than or equal to 20 percent. The highest calibration level accepted for each analyte is used as the upper reporting limit for that analyte. Data exceeding the upper reporting limit are reported as ">" the reporting limit value.

- Frequently, samples analyzed in this laboratory exceed the upper reporting limit for some of the analytes, but not others. Replicate samples are diluted using volumetric glassware and gas-tight syringes and are analyzed to determine the concentrations of the analytes that exceeded the upper reporting level in the original sample. Concentrations of analytes that do not exceed the upper calibration level in the original sample are determined from the original sample, not the diluted sample.

- Samples from microcosm experiments or other non-standard media are sometimes diluted prior to analysis to mitigate interferences that could be harmful to the instruments (for example, formaldehyde used to sterilize microcosm samples may be present at concentrations of up to 4 percent). The lower reporting limits for these samples are adjusted accordingly by multiplying by the dilution factor used for the sample.

3. Laboratory QC protocols are documented in USEPA Method 524.2 (U.S. Environmental Protection Agency, 1988) and are similar to those documented in USGS Open-File Report 94-708 (Rose and Schroeder, 1995). Ground-water samples from wells and standard drive-point piezometers are analyzed with full QA, including matrix spikes. Sometimes, a number of these samples are collected as split samples for comparison between laboratories (e.g., with USGS National Water Quality Laboratory). Microcosm experiments, porous-membrane sampling devices (peepers), passive-diffusion-bag samplers, ¼-inch inverted-screen piezometers, multi-level sampling devices, and Hoverprobe sampling activities do not yield sufficient water volume to allow a full suite of QA to be analyzed, so matrix-spike samples are rarely analyzed for these media. "Separate stock" standards or performance evaluation standards obtained from a different vendor than the supplier of the calibration standards are periodically analyzed to verify overall system performance.

4. Laboratory QA data are documented and archived as paper copies that are inserted into the instrument performance log book (BFB tune reports, matrix-spike recovery reports) or are bundled with the data (daily QC logs, blank reports, continuing calibration verification reports) and put into data books. Daily QA logs are completed and signed by the analyst and are reviewed by a senior project member. Electronic copies of all of the data, including the raw GC-MSD files, are stored on CDs in fireproof filing cabinets. Quantitative sample results, including QA sample results, are archived on the Water Science Center server, and data collected between 1994 and 1999 have been published in an Access database (Smith and Lesniewski, 2001).

5. Field QA/QC protocols are documented in the USGS peer-reviewed data reports in which the data are presented. To date, these data reports include OFR 97-560 (Olsen and others, 1997),

OFR 00-282 (Spencer and others, 2000), and OFR 01-420 (Spencer and others, 2002).

6. Laboratory and field methods and quality assurance of VOC data collected were also reviewed by the assistant to the Water Science Center Water-Quality Specialist and the former senior analyst. Their comments are on file in the MD-DE-DC Water Science Center office in Baltimore, MD.

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