

Prospecting for Zones of Contaminated Ground-Water Discharge to Streams Using Bottom-Sediment Gas Bubbles

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Abstract

Decomposition of organic-rich bottom sediment in a tidal creek in Maryland results in production of gas bubbles in the bottom sediment during summer and fall. In areas where volatile organic contaminants discharge from ground water, through the bottom sediment, and into the creek, part of the volatile contamination diffuses into the gas bubbles and is released to the atmosphere by ebullition. Collection and analysis of gas bubbles for their volatile organic contaminant content indicate that relative concentrations of the volatile organic contaminants in the gas bubbles are substantially higher in areas where the same contaminants occur in the ground water that discharges to the streams. Analyses of the bubbles located an area of previously unknown ground-water contamination.

The method developed for this study consisted of disturbing the bottom sediment to release gas bubbles, and then capturing the bubbles in a polyethylene bag at the water-column surface. The captured gas was transferred either into sealable polyethylene bags for immediate analysis with a photoionization detector or by syringe to glass tubes containing wires coated with an activated-carbon adsorbent. Relative concentrations were determined by mass spectral analysis for chloroform and trichloroethylene.

Introduction

The presence in ground water of volatile organic contaminants (VOCs), such as chloroform and trichloroethylene, has created a widespread contamination problem (Giger and Schaffner, 1981; Zoetman, 1985; Fusillo et al., 1985; Fischer et al., 1987). Because the installation of observation wells at sites of ground-water contamination is expensive and proper placement of wells is necessary to ensure that suspected contaminant plumes are intercepted, reconnaissance methods that can detect and delineate possible areas of ground-water contamination are important to the design of a cost-efficient and functional monitoring network. This paper examines the utility of analyzing bubbles that originate from bottom sediment near zones of contaminated ground-water discharge as a reconnaissance tool for detecting the presence of VOCs.

The hypothesis that bottom-sediment gas bubbles within contaminated ground-water discharge zones may contain VOCs is based on the tendency of such contaminants to enter a vapor phase. The transport of VOCs across a water/vapor interface has been used extensively as the basis of soil-gas surveys to determine the possible areal distribution of VOCs in shallow ground water (Everett et al., 1984; Thompson and Marrin, 1987).

The source of the gas in the creek-bottom sediment is anaerobic bacterial decomposition of organic matter, a process that occurs in many types of anoxic organic-rich environments, including sediments of lakes, ponds, streams, oceans, estuaries, and marshes (Wetzel, 1975; Winfrey, 1984). A dominant gas-production process in fresh-water sediment is methanogenesis (Whiticar and Eckhard, 1985). Bubble formation occurs when the gas-production rates cause the partial pressure of the gas to exceed the ambient pore-water pressure in the sediments (Reeburgh, 1969; Wetzel, 1975; Martens and Klump, 1980). Bubbles generated by anaerobic decomposition of naturally occurring organic matter typically are composed of methane, ammonia, hydrogen sulfide, or carbon dioxide, and may contain mixtures of those gases (Carriker, 1967; Martens, 1976; Strayer and Tiedje, 1978).

Seasonal temperature variations and tidal cycles are dominant controls on the production and transport rates of

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gas bubbles. Zeikus and Winfrey (1976) have shown that methanogenic bacteria at ambient pressure are metabolically active from 4 to 45°C but that the optimum temperature for methanogenesis in sediment ranges from 35 to 42°C. Thus, production of methane bubbles increases during warm months and decreases during cold months (Martens and Klump, 1980; King and Wiebe, 1978; Baker-Blocker et al., 1977; Strayer and Tiedje, 1978).

Because flow velocity and turbulence of the water and vapor within the bottom sediment are minimal, the diffusion of volatile compounds from the ground water into the gas bubbles is controlled by the thermodynamic or physical properties of the compound. Such properties include the aqueous solubility, vapor pressure, Henry's law constant and diffusivity coefficient, and the presence of modifying materials such as absorbents, organic films, electrolytes, and emulsions (Thomas, 1982). Dissolved volatile constituents present in the sediment or pore water can diffuse into the bubbles across the vapor/water interface at the surface of the bubble. Such diffusion has been shown to account for removal of nitrogen and argon from the interstitial water of sediments in the Chesapeake Bay (Reeburgh, 1969) and Long Island Sound (Martens and Berner, 1977). The Henry's law constants of chloroform and trichloroethylene, compounds investigated in this study, likewise indicate a strong tendency to enter a vapor phase and that the rate-controlling factor is diffusion through the liquid (Thomas, 1982).

Description of Study Area

Canal Creek and the East and West Branches of Canal Creek (Figure 1) are located in the Edgewood area of Aberdeen Proving Ground in eastern Maryland near the head of the Chesapeake Bay. Canal Creek flows southward to the Gunpowder River, which drains to the Chesapeake Bay. In some areas, the main channel is separated from the shoreline by several hundred feet of marsh composed of soft organic-rich mud. In other areas, bends in the creek bring the main channel adjacent to the shoreline with little or no intervening marsh. The channel sediments are mostly fine-grained, organic-rich detritus overlying sands and clays. Canal Creek is tidal along most of the reach investigated. Tidal amplitudes range from 0.5 to 2 ft (0.1 to 0.6 m) in the Gunpowder River (Vroblesky et al., 1989) to near zero at the farthest upstream sampling point (site 15) in Canal Creek.

Ground-water flow in the surficial aquifer (Figure 2) and the underlying Canal Creek aquifer is toward the creek (Oliveros and Vroblesky, 1989). Discharge occurs from the aquifers to Canal Creek and to the creek tributaries through streambanks, bottom sediments, and marshes. Recharge to the ground water is primarily from rainfall infiltration. Ground water is shallow (less than 10 ft) and unconfined. Tidal fluctuations in Canal Creek produce water-level changes of less than 0.5 ft (0.1 m) in the ground water near the creek (Oliveros and Vroblesky, 1989). Pumping stresses do not currently affect the aquifers in the study area.

The surficial aquifer consists of fine-grained, orange to brown, poorly sorted silty sand and gravel that range in size from silt to cobbles (Oliveros and Vroblesky, 1989). Thin

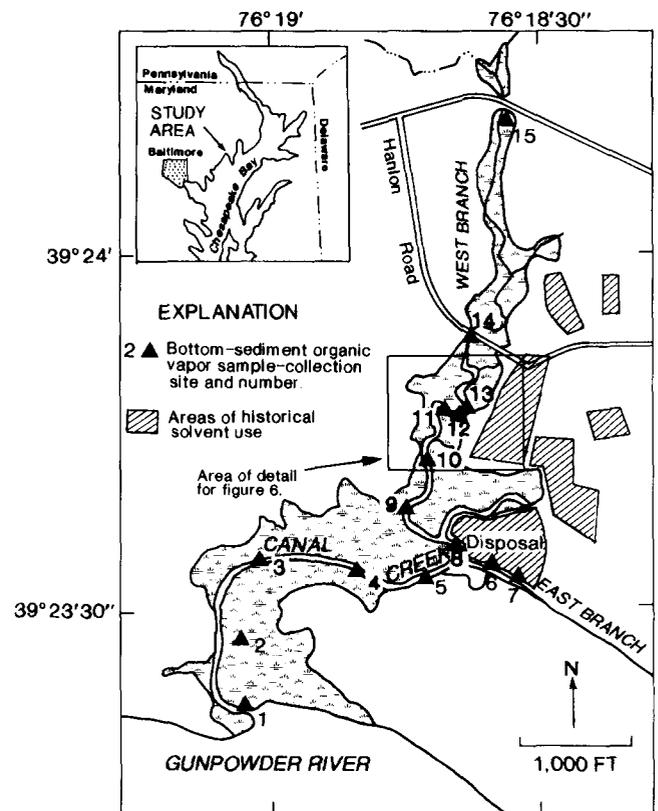


Fig. 1. Location of study area, sampling points, sites of historical chlorinated solvent use, and area of map detail for Figure 6.

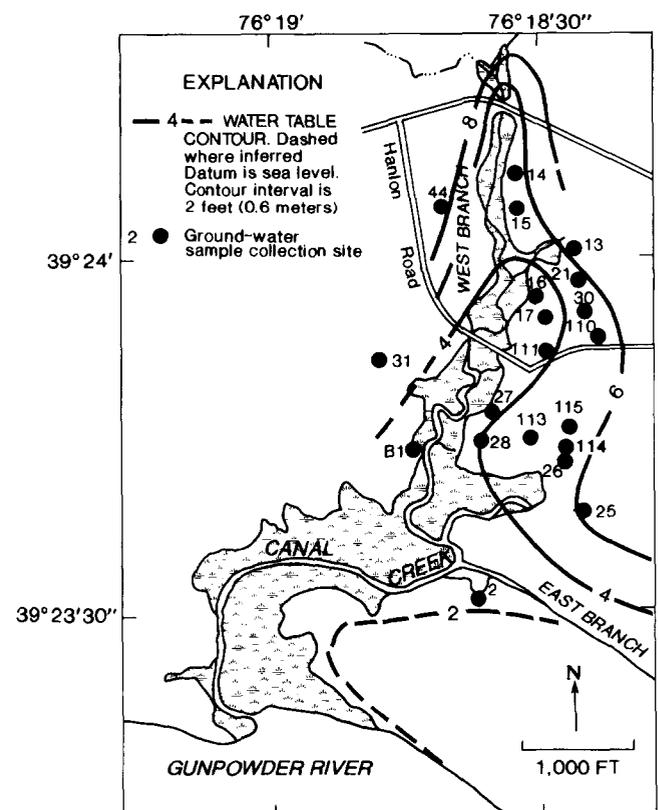


Fig. 2. Ground-water sampling sites and water-table contours, August 1987.

lenses (up to 6 in. thick) of gray and orange silty clay commonly are interfingered with the sand. The hydraulic conductivity of the aquifer ranges from 11 to 44 ft/day (3.3 to 13.4 m/day) (Oliveros and Vroblesky, 1989). The aquifer ranges from 10 to 35 ft (3 to 10.7 m) in thickness in the study area and dips to the southeast.

The Canal Creek aquifer is coarser grained than the surficial aquifer and has a hydraulic conductivity of 11 to 180 ft/day (3.3 to 54.8 m/day) (Oliveros and Vroblesky, 1989). The aquifers are hydraulically connected near the West Branch of Canal Creek, and both aquifers contain VOC contamination (Lorah and Vroblesky, 1989).

The area adjacent to Canal Creek has been used to develop, test, and manufacture military-related chemicals since 1917. The chemicals produced included chlorine, mustard gas, tear gas, phosgene, clothing-impregnating material, chlorpicrin, white phosphorus, pyrotechnics, and arsenicals. Other relevant activities included filling of chemical munitions, landfilling of domestic and production wastes, and the use of degreasing solvents in machine and maintenance shops. Production and testing operations sharply declined after World War II.

Operations using chlorinated organic solvents near the West Branch of Canal Creek were located primarily on the eastern shore of the creek (Figure 1). The solvents were used as raw materials, decontaminating agents, and degreasers. As a result of inadequate controls on solvent recovery, chlorinated organic solvents were common waste products from chemical manufacturing, ordnance filling, and other miscellaneous activities (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). Releases of the waste products to the environment by spills and landfilling resulted in ground-water contamination (Lorah and Vroblesky, 1989).

Ground-water samples from the vicinity of the manufacturing operations collected between November 1986 and

September 1988 indicated the presence of VOCs (Lorah and Vroblesky, 1989). The major ground-water contaminants and their maximum concentrations near the east bank of the West Branch Canal Creek included chloroform (650 $\mu\text{g/l}$), trichloroethylene (760 $\mu\text{g/l}$), carbon tetrachloride (600 $\mu\text{g/l}$), 1,1,2,2-tetrachloroethane (5,800 $\mu\text{g/l}$), tetrachloroethylene (200 $\mu\text{g/l}$), and 1,2-trans dichloroethylene (1,000 $\mu\text{g/l}$). Although no wells were installed at the disposal area (Figure 1), due to the possibility of encountering buried mustard gas, manifests of the disposed material include chlorinated solvents (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986).

Prior to this investigation, little waste disposal was suspected to have occurred on the west side of Canal Creek. Of the two observation wells installed to the west of Canal Creek, a relatively low concentration of chloroform (24 $\mu\text{g/l}$) was detected in ground water from well 44, and no organic contaminants were detected in well 31 (Figure 2) (Lorah and Vroblesky, 1989).

Methods

Three sampling trips were made to collect gases released by gas ebullition from the bottom sediments of Canal Creek. Gas bubbles were collected at 14 sites (Figure 1) and surface-water samples were collected from four sites during the first trip on October 11, 1988. On November 2, 1988, gas samples again were collected at sites 10 and 12 and at one new site (site 11) (Figure 1), and surface-water samples were collected from two sites. Additional surface-water samples and a ground-water sample from site B1 were collected on November 21, 1988. Gas samples again were collected from four of the previous sites on October 23, 1989. With the exception of site B1, the ground-water data cited in this paper were obtained from samples collected during July and August 1988.

The gas-bubble sample-collection method developed for this study consisted of releasing bubbles from the bottom sediment and capturing the gas bubbles at the water surface. Bubble release was accomplished by gently pushing a flat wooden paddle into the sediment until gas bubbles escaped.

A simple device to capture the gas bubbles was constructed using a circular polyethylene sheet rimmed with thin plywood that kept the sheet on the surface of the water (Figure 3). Before the sediment was disturbed to release bubbles, the polyethylene bag was placed on the surface of the creek, and the trapped air was expelled from the bag. As gas bubbles rose to the surface, the gas was trapped beneath the polyethylene bag. During the time that the gas bubbles rise to the surface, part of the vapor phase is probably lost by diffusion into the water (Martens and Klump, 1980). In this study, however, the bubbles traveled through less than two feet of water before reaching the water surface, so loss of vapor phase would have been minor. Moreover, the depth of water was the same at all sampling sites. Therefore, if such vapor loss occurred, then the same amount would have been lost at all sites. Although not tested in this investigation, a possible approach to reducing such potential loss would be to collect the bubbles at the sediment-water interface.

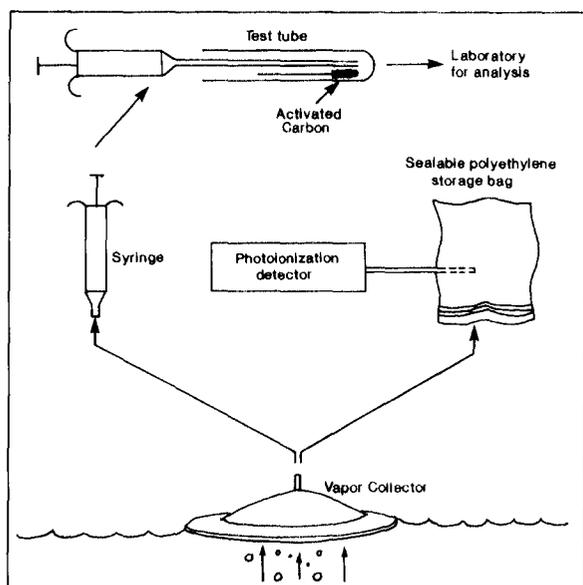


Fig. 3. Sample-collection apparatus.

During the 1988 trips, the captured gas bubbles were immediately extracted from the gas collector using 20-ml syringes to draw gas from a small tubular outlet that was opened at the center of the polyethylene sheet. A small-diameter Teflon tube was then attached to the syringe and the gas sample was injected into a test tube containing activated-carbon absorbent on a ferromagnetic wire. The vapor sample was injected into the test tube at the end distal from the opening, near the activated-carbon adsorbent (Figure 3). An 80-ml gas-bubble sample was collected at each site. The sampling tubes were sealed immediately with screw-on caps lined with a Teflon septum.

All vapor samplers were sent for analysis to the PETREX Division of Northeast Research Institute, Inc., a commercial supplier of the tubes. Sorbed constituents were removed from the activated carbon and were analyzed using an Extranuclear Quadrupole Mass Spectrometer equipped with a Curie-point pyrolysis/thermal desorption inlet. Identification of individual compounds was made by comparison of mass-spectral signatures. (Use of firm names and trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.)

The relative intensities of the mass-spectral indicator peaks for specific compounds were calculated in terms of ion counts. The ion counts represent relative concentrations of the identified compounds. Further quantification was not attempted because of potential minor losses of vapor as the bubbles rise through the water column and during injection into the test tubes. However, to minimize sampling variations resulting from such processes, all aspects of the sampling technique, including depth of the water column, were held constant among the sampling sites.

Duplicate samples were collected from two sites using two different techniques. A duplicate sample was collected at site 7 by repeating the entire sampling process at a site immediately adjacent to site 7, and a duplicate sample was collected at site 10 using a sampling tube that contained two wires coated with the activated-carbon adsorbent rather than one. Sample replication at site 7 was good: both the sample and duplicate contained 3,000 $\mu\text{g}/\text{l}$ of chloroform and 4,000 $\mu\text{g}/\text{l}$ of trichloroethylene.

Ion counts of chloroform detected on the two wires at site 10 showed differences (one wire from site 10 contained 122,000 ion counts and the other contained 133,000 ion counts); however, both values were substantially greater than the range of relative concentrations of chloroform found in uncontaminated areas (1,400 to 16,000 ion counts). Similarly, one wire from site 10 contained 6,000 ion counts and the other contained 7,000 ion counts of trichloroethylene, but both values were substantially greater than the range of relative concentrations found in uncontaminated areas (0 to 1,400 ion counts). Therefore, the analytical results were adequate to indicate areas of substantially greater and lesser concentrations of volatile contaminants in vapor bubbles.

Ambient air samples were collected in addition to duplicate bottom-sediment gas samples for quality control and assurance on the October and November field trips. At

five sites, a sampling tube was kept uncapped for approximately 5 to 10 minutes to determine the degree of influence that contaminants in ambient air may have on the sample collection. The tubes were open slightly longer than the amount of time required to collect the bottom-sediment vapor samples. In addition, two trip blanks, which were not opened in the field, were sent to the laboratory for analysis with the other samples.

The sampling tubes that were left open to the atmosphere contained zero or extremely low ion counts of VOCs. The highest ion count observed in these background air samples was 220 for chloroform at site 12 on November 2, and this ion count is negligible compared to the amount (33,500 ion counts) measured in the gas-bubble sample at the site.

Three additional samples were collected to determine if VOCs were stripped from the water column or from the atmosphere during the procedure used to obtain gas-bubble samples. To determine the contribution from the water column, the polyethylene sheet was placed on the water surface for approximately 5 minutes, and a headspace sample was collected prior to disturbing the sediment to release gas bubbles. VOCs were detected in the headspace sample at certain sites, but the detected amounts were substantially less than found in bottom-sediment gas bubbles from the corresponding sites. The greatest amount of chlorinated hydrocarbon measured in a headspace sample was approximately 10 percent of that measured in the bottom-sediment gas bubbles from the site.

Nitrogen gas was bubbled through the water column and collected at site 12, where previous analyses had shown the presence of VOCs in the surface water. The purpose of the test was to determine whether a significant amount of the VOCs detected in the gas bubbles was derived from exchange with VOCs in the surface water. The analysis showed higher relative concentrations (by a factor of 3 to 36) of VOCs in the bottom-sediment gas bubbles than in the nitrogen gas bubbled through the water column. Thus, VOCs added to the gas bubbles as they rise through the surface-water column appear to be negligible compared to VOCs added to the gas bubbles while still within the bottom sediment.

During the sample-collecting trip in October 1989, an alternative method was used to collect samples. The captured gas was forced from the polyethylene vapor collector (by pushing the collector slightly beneath the water surface) into 0.0027-in. (2.7 mil) thick, 1 gallon sealable freezer bags (Ziplock brand) (Figure 3). The bags were sealed and the sampling probe of a photoionization detector was used to pierce the side of the bags and extract a vapor sample. The photoionization detector was zeroed relative to ambient atmospheric vapor, so the data were recorded as parts per million organic vapor relative to atmospheric vapor. The reported accuracy of the instrument is about 10 to 15 percent at concentrations less than 100 parts per million (ppm) (Photovac, Inc., 1988).

The photoionization detector used was sensitive to the cumulative signal of many of the VOCs present in ground water at the site but was not sensitive to the vapors forming

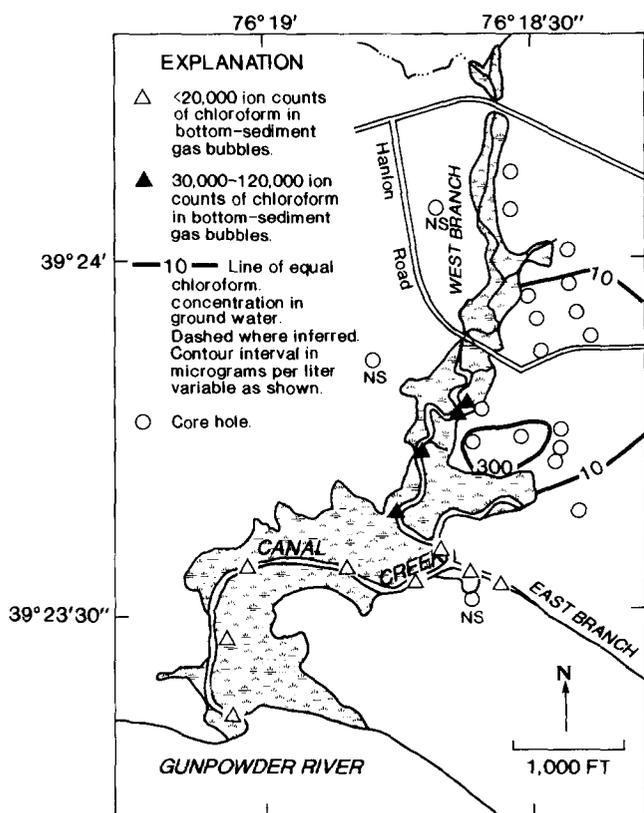


Fig. 4. Distribution of chloroform in bottom-sediment methane bubbles, October 1988, and in the adjacent shallow ground water, July through August 1988. Although no samples were collected from the wells labeled NS, samples collected from those wells during 1986 contained no chloroform, except well 44 which contained 24 µg/l (Lorah and Vroblesky, 1989).

gas bubbles in uncontaminated areas. Therefore, the recorded concentration refers to the organic contaminants within the gas bubbles.

Ground-water samples were collected from observation wells during July and August of 1989. Sampling methodology consisted of purging the wells and bottling the samples to be sent to a contract laboratory for analysis. A minimum of two well volumes was purged from each well. The water level in the well was allowed to recover before samples were collected using a bottom-discharge, Teflon bailer. Decontamination of bailers between sites included washing with detergent and distilled water and rinsing at least three times with distilled water. The VOC samples were collected by discharging a slow, steady stream of well water into two 40-ml glass vials and allowed to overflow several times. The vials were sealed with caps lined with a Teflon septum and inspected for bubbles. If bubbles were noted, the sample was discarded and recollected.

Ground-water samples were collected from well clusters screened in the surficial aquifer and the Canal Creek aquifer. Because both aquifers discharge to Canal Creek, in this paper the concentrations of VOCs in ground water east of the creek represent an average of the concentrations in both aquifers.

Surface-water samples for VOCs were collected by slowly submerging two 40-ml glass vials below the water surface and capping them under water. If bubbles were noted, the sample was discarded and recollected.

Results

VOCs were detected in bottom-sediment gas bubbles collected at several sites along Canal Creek (Figures 4 and 5). The most commonly detected chlorinated VOCs in the gas bubbles and the nearby shallow ground water were chloroform and trichloroethylene.

The sites where elevated relative concentrations of VOCs were found in the bottom-sediment gas bubbles corresponded closely to areas of elevated concentrations of the same VOCs in the adjacent shallow ground water. Ion counts for chloroform, which showed a wider range of ion counts along Canal Creek than the other chlorinated VOCs, were less than 20,000 in gas bubbles collected where chloroform was not known to be present in the nearby ground water (Figure 4). Ion counts were less than 2,000 for trichloroethylene at sites where ground-water contamination was not suspected adjacent to the creek (Figure 5). Compared to these background relative concentrations, ion counts for chloroform and trichloroethylene in the gas bub-

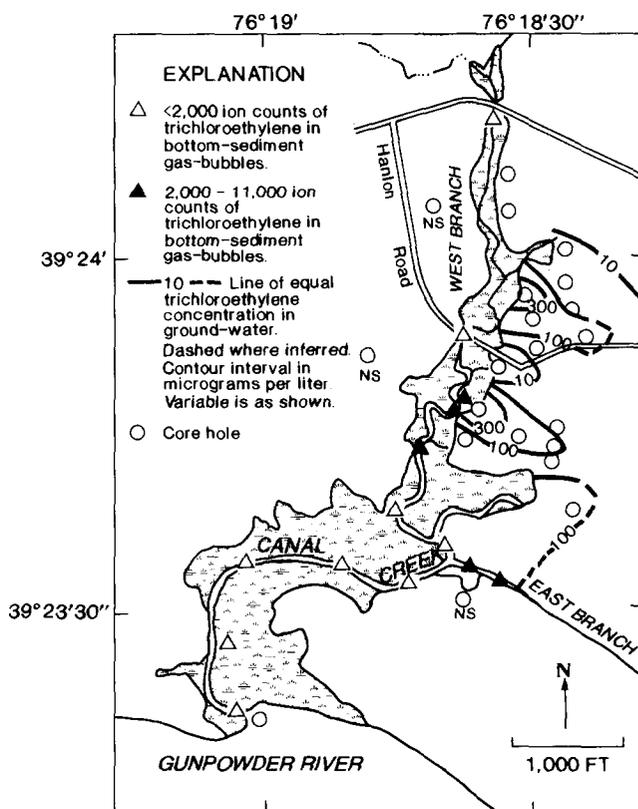


Fig. 5. Distribution of trichloroethylene in bottom-sediment methane bubbles, October 1988, and in the adjacent shallow ground water, July through August 1988. Although no samples were collected from the wells labeled NS, samples collected from those wells during 1986 contained no trichloroethylene (Lorah and Vroblesky, 1989).

bles collected at sites adjacent to areas of known ground-water contamination along Canal Creek were substantially greater (34,000 to 122,000 and 2,000 to 11,000, respectively).

The most elevated relative concentrations of VOCs were found in the gas bubbles collected from the reach of the creek between the Hanlon Rd. bridge and the junction of the East and West Branches of the creek at sites 10 and 13 (Figure 1). Manufacturing and waste disposal mainly took place along the eastern bank of this area of Canal Creek (Figure 1). The highest elevated relative concentration of trichloroethylene (11,000 ion counts) and second highest relative concentration of chloroform (112,000 ion counts) were found in this area at site 13. The highest relative concentration of chloroform (122,000 ion counts) and the second highest relative concentration of trichloroethylene (6,000 ion counts), however, were found adjacent to the western shoreline (site 10) where no previous use of solvents had been recorded. Trichloroethylene was detected in concentrations greater than 2,000 ion counts in the bottom-sediment gas bubbles adjacent to the disposal area at the junction of the East and West Branches of Canal Creek where chlorinated solvents reportedly were disposed (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986).

Low relative concentrations of VOCs (less than 15 percent of the maximum measured) in the bottom-sediment gas bubbles were found in the extreme upper and lower reaches of Canal Creek outside of the manufacturing and disposal area. Gas-bubble samples were not collected in the upper reach of Canal Creek between sites 14 and 15 (Figure 1) because low water and the narrow creek channel made this area inaccessible by canoe. Sites 14 and 15 were accessible from bridges.

During November 1988 sampling, samples of bottom-sediment gas bubbles again were collected from sites 10 and 12 (Figure 6). Relative concentrations of chloroform at site 12 (33,500 ion counts) were similar to those found at the same site in October 1988 (34,000 ion counts). Relative concentrations of chloroform at site 10 (67,000 ion counts) were less than during the previous month (122,000 ion counts) but were still greater than at site 12. However, bottom-sediment gas bubbles collected from an additional site (site 11) between sites 10 and 12 showed an area of relatively low ion counts (3,000 ion counts) (Figure 6). A similar distribution was found for trichloroethylene (Figure 6).

Collection and analysis of bottom-sediment gas bubbles one year later at sites 10, 11, 12, and 13 using the photoionization detector (Figure 6) showed a distribution of VOCs similar to the distributions of individual VOCs found the previous year. Where elevated relative concentrations of VOCs had been found the previous year using the activated-carbon vapor collectors (sites 10, 12, and 13), concentrations of organic vapor measured with the photoionization detector ranged from 6 to 40 ppm. At site 11, where the previous year's work had shown only low relative concentrations (3,000 ion counts or less) of VOCs, the photoionization detector indicated -6 ppm organic vapor relative to ambient atmospheric conditions.

Discussion

The ground water discharging to Canal Creek contains the same VOCs found in the creek water, indicating that ground-water contaminants discharge to the creek. Because the discharging contaminants must pass through the organic-rich creek-bottom sediment, part of the contaminant mass would be expected to diffuse into gas bubbles within the sediment. If so, then subsequent bubble ebullition would transport the captured VOCs past sorption sites in the organic-rich sediment to the water surface and release them to the atmosphere. The relatively large amounts of chloroform (33,000 ion counts at site 12 and 112,000 ion counts at site 13) and trichloroethylene (2,000 ion counts at site 12 and 11,000 ion counts at site 13) detected in the bottom-sediment gas bubbles adjacent to areas where chloroform was known to be present (40 to 315 $\mu\text{g}/\text{l}$) in the ground water appear to indicate that such a diffusion occurs.

An initially surprising result was the elevated relative concentrations of chloroform found in the bottom-sediment gas bubbles along the western shoreline (Figure 4) (41,000 and 122,000 ion counts, at sites 9 and 10, respectively in October 1988) adjacent to a forested area where historical records showed no indication of previous activity involving VOC use or disposal. In fact, one of the sites, site 10, contained the highest relative concentrations of chloroform found in gas bubbles anywhere in the creek. Subsequent visual inspection of the wooded area showed that the site had been used as a dumping area in the past. The evidence included the presence of rusted drums, unlabeled cans, and building debris.

As a further investigation of the area, a hole was dug to the water table on the land adjacent to site 10, where the

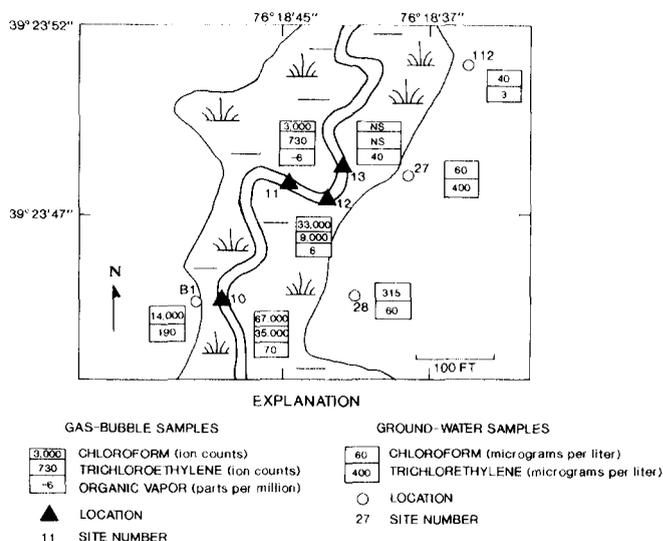


Fig. 6. Detailed area of Canal Creek, West Branch, showing distribution of chloroform and trichloroethylene in bottom-sediment bubbles (November 1988), concentrations of organic vapors, as measured with a photoionization detector, in bottom-sediment bubbles (October 1989), and distribution of chloroform and trichloroethylene in ground water (1988). NS indicates that no sample was collected.

elevated relative concentrations of chloroform were detected in the gas bubbles. A ground-water sample collected from the hole (site B1) and analyzed by a commercial laboratory showed the presence of higher concentrations of chloroform (14,000 $\mu\text{g}/\text{l}$) than were found in the ground water elsewhere near the creek. Other VOCs also were present. Thus, analysis of the VOC content of the bottom-sediment gas bubbles was useful in locating an area of previously unknown ground-water contamination.

The substantially lower ion counts detected at site 11, relative to sites 10 and 12, probably reflect the configuration of the creek channel (Figure 6). Site 11 is separated from either shoreline by over 100 ft (304 m) of marsh. Moreover, there are bends in the creek near both shorelines that would be expected to intercept much of the shallow ground water discharging from onshore areas. In addition, the reach of the creek in which site 11 is located is oriented perpendicular to both shorelines, providing additional areas to intercept shallow ground-water flow. Thus, from a hydrologic view, it is highly unlikely that site 11 receives significant subsurface discharge from the shallow ground-water system underlying onshore areas.

Examination of sites 10 to 13 the following year using a photoionization detector showed a similar distribution of VOCs among the sampling sites (Figure 6). Once again, the largest amounts of VOCs were found at site 10 (70 ppm organic vapor), and positive values were found at sites 12 and 13 (6 and 40 ppm organic vapor, respectively). Moreover, the -6 ppm organic vapor found at site 11, where the previous year's investigation showed only small amounts of VOCs, indicated that there were more compounds to which the photoionization detector was sensitive in the ambient air than were present in the gas bubbles. Thus, sufficient information can be obtained on-site using a photoionization detector to allow delineation of areas where ground water contaminated with VOCs is discharging to surface water.

There are several benefits of using gas-bubble collection and analysis as a reconnaissance method. Samples can be collected relatively rapidly; two people were able to collect the samples for the present study in approximately four hours on each trip. Required materials and equipment are simple and inexpensive, and analytical costs are relatively low. In addition, the analytical technique can measure a broad range of halogenated organic compounds and petroleum hydrocarbons that readily partition into a vapor phase.

The gas-bubble samples also gave more information on nearby ground-water contamination than the information that was obtained by collecting surface-water samples along Canal Creek. Although concentrations of VOCs were detected in the surface water, the source area of these concentrations could not be determined because of the dilution and lateral transport of the VOCs within the creek. The concentrations of VOCs measured in surface-water samples from Canal Creek often were only slightly above the detection limits of the analytical method. In contrast, for most VOCs, the amount sorbed from the gas bubbles onto the activated carbon ranged from less than 100 ion counts to greater than 10,000 ion counts. For chloroform, sorbed amounts ranged from less than 2,000 ion counts to greater

than 120,000 ion counts. Moreover, the gas bubbles were collected from the site of their formation, allowing site-specific conclusions to be drawn.

One drawback of the gas bubble method is that the method can be applied only in areas of anoxic bottom sediments where gas is being produced. Gas-bubble production is seasonal, occurring primarily when high temperatures increase gas production rates. In addition, the extent of ground-water contamination away from the creek cannot be determined because VOC relative concentrations are being measured only at the ground-water discharge point. Collection and analysis of bottom-sediment gas bubbles, however, can provide a rapid, inexpensive tool for preliminary investigations at suspected ground-water contamination sites where gas production is active.

Conclusions

The close correspondence between areas where high relative concentrations of VOCs were found in bottom-sediment gas bubbles and areas where the same VOCs occur in ground water indicate that VOCs can diffuse into naturally occurring gas bubbles in contaminated ground-water discharge zones. The captured VOCs are then transported by bubble ebullition to the water surface, where they are released to the atmosphere. Analysis of the gas bubbles for their VOC content was used to locate an area of previously unknown ground-water contamination, demonstrating that such analyses are effective for identifying zones of contaminated ground-water discharge to surface water. In areas where species-specific information is not needed, the photoionization detector can be used.

References

- Baker-Blocker, A., T. M. Donahue, and K. H. Mancy. 1977. Methane flux from wetlands areas. *Tellus*. v. 29, no. 3, pp. 245-250.
- Carriker, M. R. 1967. Ecology of estuarine benthic invertebrates: A perspective. In: Lauff, G. H., ed., *Estuaries: American Assoc. for the Advancement of Science*. Washington, DC. Publication no. 83. pp. 442-487.
- Everett, L. G., E. W. Hoylman, L. G. Wilson, and L. G. McMillon. 1984. Constraints and categories of vadose-zone monitoring devices. *Ground Water Monitoring Review*. v. 4, no. 1, pp. 26-32.
- Fischer, A. J., E. A. Rowan, and R. F. Spalding. 1987. VOCs in ground water influenced by large scale withdrawals. *Ground Water*. v. 25, no. 4, pp. 407-414.
- Fusillo, T. V., J. J. Hochreiter, Jr. and D. G. Lord. 1985. Distribution of volatile organic compounds in a New Jersey Coastal Plain aquifer system. *Ground Water*. v. 23, no. 3, pp. 354-360.
- Giger, W. and C. Schaffner. 1981. Groundwater pollution by volatile organic chemicals. In: W. van Duijvenbooden, P. Glasbergen, and H. van Lelyveld (eds.), *Quality of Groundwater*. Elsevier, Amsterdam. pp. 517-522.
- King, G. M. and W. J. Wiebe. 1978. Methane release from soils of a Georgia salt marsh. *Geochimica et Cosmochimica Acta*. v. 42, pp. 343-348.
- Lorah, M. M. and D. A. Vroblesky. 1989. Inorganic and organic ground-water chemistry in the Canal Creek area of Aberdeen Proving Ground, Maryland. U.S. Geological Survey Water-Resources Investigation Report 89-4022. 97 pp.

- Martens, C. S. 1976. Control of methane sediment-water bubble transport by macroinfaunal irrigation in Cape Lookout Blight, North Carolina. *Science*. v. 192, pp. 998-1000.
- Martens, C. S. and R. A. Berner. 1977. Interstitial water chemistry of anoxic Long Island Sound sediments. I. Dissolved gases. *Limnology and Oceanography*. v. 22, no. 1, pp. 10-25.
- Martens, C. S. and J. Val Klump. 1980. Biogeochemical cycling in an organic-rich coastal marine basin—I. Methane sediment-water exchange processes. *Geochimica et Cosmochimica Acta*. v. 44, pp. 471-490.
- Oliveros, J. P. and D. A. Vroblesky. 1989. Hydrogeology of the Canal Creek area, Aberdeen Proving Ground, Maryland. U.S. Geological Survey Water-Resources Investigation Report 89-4021. 50 pp.
- Reeburgh, W. S. 1969. Observations of gases in Chesapeake Bay sediments. *Limnology and Oceanography*. v. 14, pp. 368-375.
- Photovac, Inc. 1988. Users Manual for TIP II. Huntington, NY. 33 pp.
- Strayer, R. F. and J. M. Tiedje. 1978. In situ methane production in a small, hypereutrophic, hard-water lake: Loss of methane from sediments by vertical diffusion and ebullition. *Limnology and Oceanography*. v. 23, no. 6, pp. 1201-1206.
- Thomas, R. G. 1982. Volatilization from water. In: Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt, eds., *Handbook of Chemical Property Estimation Methods*. McGraw-Hill, New York. pp. 15-1 to 15-34.
- Thompson, G. M. and D. L. Marrin. 1987. Soil gas contaminant investigations: A dynamic approach. *Ground Water Monitoring Review*. v. 7, no. 3, pp. 88-93.
- Vroblesky, D. A., M. M. Lorah, and J. P. Oliveros. 1989. Ground-water, surface-water, and bottom-sediment contamination in the O-Field area, Aberdeen Proving Ground, Maryland, and the possible effects of selected remedial actions. U.S. Geological Survey Open-File Report 89-399. 399 pp.
- Wetzel, R. G. 1975. *Limnology*. W. B. Saunders Company, Philadelphia. 743 pp.
- Whiticar, M. J. and Faber Eckhard. 1985. Methane oxidation in sediment and water-column environments—Isotopic evidence. *Advances in Organic Chemistry*. v. 10, pp. 759-768.
- Winfrey, M. R. 1984. Microbial production of methane. In: R. M. Atlas (ed.), *Petroleum Microbiology*. Macmillan Publishing Company, New York. pp. 153-219.
- Zeikus, J. G. and M. R. Winfrey. 1976. Temperature limitation of methanogenesis in aquatic sediments. *Applied Environmental Microbiology*. v. 31, pp. 99-107.
- Zoeteman, B.C.J. 1985. Overview of contaminants in ground water. In: C. H. Ward, W. Giger, and P. L. McCarty, *Ground Water Quality*. John Wiley and Sons, New York. pp. 27-37.

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