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Decompositional Odor Analysis Database*

ABSTRACT: This study, conducted at the University of Tennessee's Anthropological Research Facility (ARF), describes the establishment of the Decompositional Odor Analysis (DOA) Database for the purpose of developing a man-portable, chemical sensor capable of detecting clandestine burial sites of human remains, thereby mimicking canine olfaction. This "living" database currently spans the first year and a half of burial, providing identification, chemical trends and semi-quantitation of chemicals liberated below, above and at the surface of graves 1.5 to 3.5 ft deep (0.45 to 1.0 m) for four individuals. Triple sorbent traps (TSTs) were used to collect air samples in the field and revealed eight major classes of chemicals containing 424 specific volatile compounds associated with burial decomposition. This research is the first step toward identification of an "odor signature" unique to human decomposition with projected ramifications on cadaver dog training procedures and in the development of field portable analytical instruments which can be used to locate human remains buried in shallow graves.

KEYWORDS: forensic science, human decomposition, odor analysis, cadaver dog, buried bodies

The detection of buried human remains is most often accomplished with the aid of ground-penetrating radar (GPR), manual probing techniques or "cadaver dogs"—canines trained to detect human remains (1,2). Of these methods, the means by which cadaver dogs locate human remains is least understood, as the chemicals the dogs detect and their relative ratios as they vary over time are uncharacterized.

Law enforcement agencies around the U.S. use specially trained canines for a variety of purposes. These canines have proven invaluable in such vital areas as explosive and accelerant detection, narcotics detection and tracking criminals as well as search-and-rescue efforts in the event of lost or missing persons (3,4). Recently, canines have been trained to locate human remains with mixed success. Certain canines have the ability to find historic human remains as well as an ability to discriminate between human remains and those of other mammals. Canines can differentiate between odors emitted by a live person and those from recently deceased individuals as well as those in various stages of decomposition, indicating that odor consists of multiple chemical signatures, which change over time. These abilities allow for their use in the area of human remains detection (HRD) (5–10), but they remain a minority in the law enforcement canine population primarily due to of the costs associated with the training, maintenance and care of the canine.

Many researchers would agree that canines still possess olfactory capabilities that are far more sensitive than our best analytical technology (11–13). It is speculated that this capability stems primarily from their ability to distinguish one complex scent profile from another. Unfortunately this assertion is difficult to test, validate, calibrate, and most importantly, standardize.

The purpose of the present study was to begin the difficult task of detecting and identifying volatile and semivolatile compounds that migrate upward from human burials to the soil surface during decomposition. Identification of these compounds with subsequent verification by HRD canines will provide a basis by which the HRD canine handlers can begin standardizing and optimizing their training procedures. Identification of these compounds is also important in the development of analytical instrumentation used to augment or supplant the canine (when they are unavailable). The results herein describe the development of the Decompositional Odor Analysis Database, which identifies chemicals associated with the decomposition of buried human remains (defined herein as a clandestine act where human remains are buried in hastily dug, shallow graves). The database contains a record of the volatile chemicals as they are produced near the body and follows their migration upward, through the soil column, to the surface. The compounds in the database are organized into eight separate classes with specific chemicals assigned to their respective classes. Because of the magnitude of the database, only those chemicals liberated from the decompositional process considered to be the most significant will be discussed here. The current database spans only the first 1.5 years of burial decomposition; however, it includes some preliminary data obtained from a 12-year-old grave site containing only skeletonized remains. The ultimate goal of this study is to define the chemical fingerprint produced by human decomposition over a span of many years in hopes of understanding human chemical decay processes and thereby enhancing canine training programs to improve performance as well

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as providing specific data necessary for the development of reliable detection instrumentation. Results to date provide an encouraging first step in attaining these goals.

Materials and Methods

A total of four cadavers were buried at the University of Tennessee's Anthropological Research Facility (ARF) in graves of various depths. This facility is located in a secluded, open-wooded area in Knoxville, Tennessee, dedicated to the study of the decomposition of human remains in a natural environment. This facility is located in a temperate region of the United States, possessing primarily broadleaf forests and averaging 40–60 in. (100–150 cm) of rainfall per year. This 3+ acre facility is surrounded by a chain-link fence to restrict intrusion by large carnivores and is under 24 hr surveillance to prevent unauthorized intruders. The soil type for the sampling area has been classified as a fine, mixed, thermic Typic Paleudalf according to U.S. Soil Taxonomy (Soil Survey Staff) (14).

The subjects were stored in morgue coolers or came directly from funeral homes prior to the onset of the decay study. Data concerning climatic conditions (temperature, humidity, and rainfall) were collected utilizing an electronic weather station (VWR Scientific) in the vicinity of the sampling area. Barometric pressure data were obtained from the Knoxville National Weather Service station located approximately 10 miles (16 km) from the facility.

During burial, a system of pipes was placed below and above the bodies, with (capture/sampling hoods) at the surface of the grave to facilitate sampling using sorbent traps as described below (Fig. 1). Air samples were collected on sorbent traps at various intervals (approximately twice a month) with a total of 374 samples collected for inclusion into the database. In-ground and in-corpse thermocouples allowed for accurate below-ground temperature recording and were used to determine burial accumulated degree days (BADDs) (15). The morphological state of decomposition was monitored via viewing ports placed around and within the corpses during the burial process. This included video and still capture imagery.

Subject Selection

Buried individuals were donations to the Anthropological Research Facility—having voluntarily donated their remains to the research facility or to science, or were donated by next-of-kin.

Individuals selected for this study were unautopsied and unembalmed. Only individuals who either exhibited no gross external decompositional changes, or were in the very early stages of decomposition (i.e., abdominal discoloration, slight bloating and/or livor or rigor mortis) were used. All subjects were buried without clothing or wrappings. Information concerning the age, ancestry, sex, cause of death, date of burial and interment information was recorded for all individuals (Tables 1*a*, 1*b*).

Triple Sorbent Traps (TSTs)

TSTs were composed of 14 mm sections of Carbotrap, Carbotrap-C and Carbosieve S-III sorbents (Supelco, Bellefonte, PA) packed (in that order) in the center of a 76 mm by 6 mm outside diameter by 4 mm inside diameter stainless steel tube. The tube was stamped with a number and an arrow indicating the sampling flow direction. TSTs were cleaned prior to spiking (described below) by heating at 380°C for at least three to four hours with a helium flow of 50 to 100 mL/min. A stainless steel manifold able to accept 18 traps was used to process the traps in a batch fashion. The clean traps were spiked with 10 ng of bromobenzene as a performance verification standard and stored in a freezer at −18°C until use. Traps

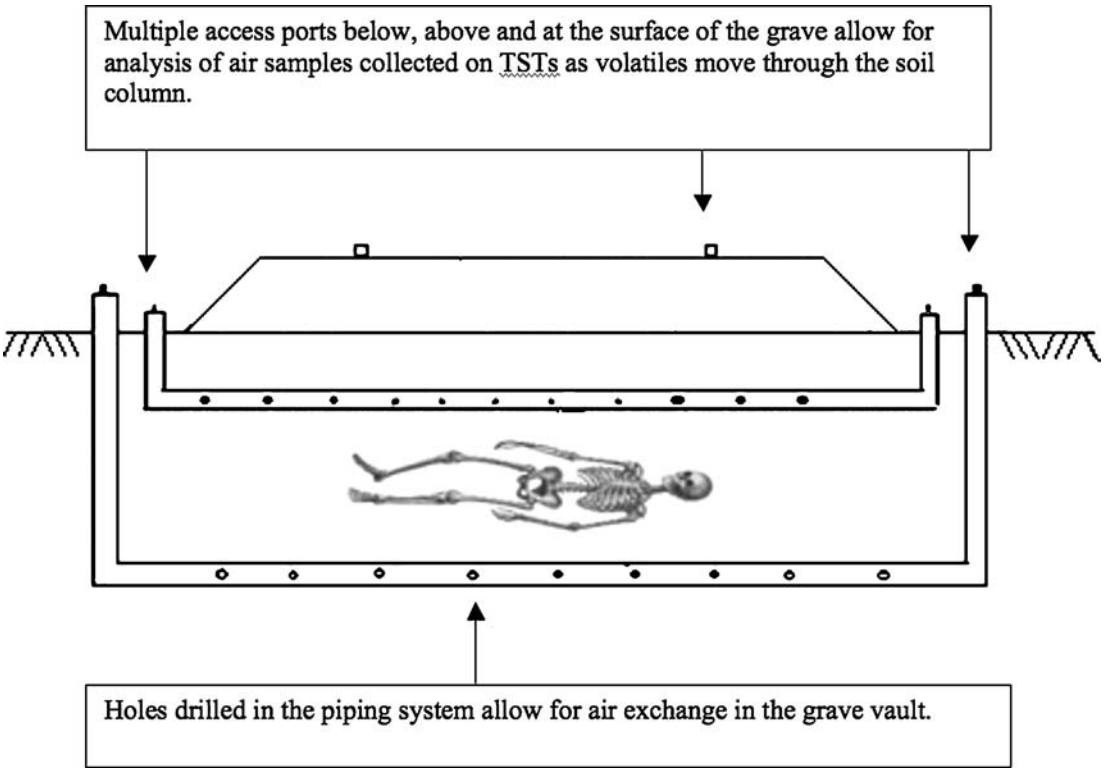

FIG. 1—*Representation of graves and respective sampling locations—below body, above body, and surface hood. For clarity, viewing ports and thermocouple placements were not included (not to scale).*

TABLE 1*a*—*Summary of available information on test subjects.*

Subject	Sex	Ancestry	Age	Weight (lb)*	Cause of Death	Burial Date (mo-day-yr)	Date of Death (mo-day-yr)
1	M	C	27	132	drowning	9-14-90	09-02-90
2	M	C	71	130	lymphoma	5-13-02	05-09-02
3	F	C	71	150	leukemia	11-13-02	11-09-02
4	M	C	67	221	ASCVD	12-02-02	11-25-02

C = Caucasian, ASCVD = atherosclerosis cardiovascular disease.
*1 lb = 0.45 kg.

TABLE 1*b*—*Summary of interment information.*

Subject	Interment Information
1	Burial depth: 3.5 ft*. A sampling tube was placed between and slightly above the legs and another placed about 1.5 ft above the body on 11-14-02.
2	Burial depth 1.5 ft. Sampling tubes placed perpendicular to body: one below upper chest region, one above upper chest region and one below buttocks region.
3	Burial depth 2.5 ft. Sampling tubes placed parallel to length of body. The 1½ in.* i.d. sampling tube was placed below the body in a shallow depression covered with gravel. The ¾ in. i.d. sampling tube was placed 1 ft above the body.
4	Burial depth 2.5 ft. Sampling tubes placed parallel to length of body. The 1½ in. i.d. sampling tube was placed below the body in a shallow depression covered with gravel. The ¾ in. i.d. sampling tube was placed 1 ft above the body.

* 1 ft = 0.30 m; 1 in. = 2.54 cm.

were sealed during storage and transport using ¼ in. (0.635 cm) stainless steel Swagelok caps.

Bromobenzene peak detection during sample analyses confirms that the instrument is working properly and allows for the comparison of different TSTs based on the amount of bromobenzene detected. Assuming a response factor of one for all compounds compared to bromobenzene, an estimate of the analyte mass present on any given TST can be obtained. Measuring the air volume sampled allows for an estimation of the analyte concentration in the sampled zone.

The spiking method was a static dilution technique utilizing amber dilution bottles equipped with screw-on vapor-lock valved caps maintained at 70°C throughout the spiking process. A master stock bottle was prepared by spiking 8.4 μL of bromobenzene through the pushbutton vapor-lock cap into dry, hydrocarbon-free air. This was allowed to equilibrate for at least 10 min after which time 250 μL of the master stock was removed using a heated (70°C) gastight syringe and transferred to another dilution bottle to create a working standard. The working standard was allowed to equilibrate for at least 10 min before proceeding to the spiking step. During the trap spiking step, the TST was mounted into a Swagelok tee equipped with a Cajon® septum fitting and connected to a purified helium stream which was preheated to 70°C. Each trap was spiked with 200 μL of the working standard using a VICI gastight syringe (Valco, Houston, TX) with a Pressure-Lok valve to effect a mass loading of 10 ng per trap. At least one trap from each batch was analyzed by thermal desorption/gas chromatograph/mass spectrometry (TD/GC/MS) to confirm spiking effectiveness and trap purity for the batch (16).

Sampling Tubes for Graves

Three tube designs were used in this study. The initial tube design (0.1 L volume) consisted of 18 in. (45.7 cm) sections of ¾ in. o.d. stainless steel tubing perforated with thirty-four ¼ in. (0.635 cm) holes alternating between a vertical and horizontal alignment down the length of the tube. The tubing was welded shut at one end and connected to a 2 ft (0.6 m) section of ¼ in. o.d. stainless steel tubing through a 90-deg fitting elbow at the other. The ¼ in. (0.635 cm) stainless steel tubing terminated in a fitting union sealed with a plug. Subsequent tubes for vapor sampling of graves in the study were constructed of ¾ in. o.d. (1.9 cm) and 1½ in. o.d. (3.81 cm) stainless steel tubing and were implemented to avoid plugging concerns from liquids and remnants of tissue seen in the smaller tubes. The larger-diameter tubes (2.9 L volume) were each fabricated from a 10 ft (3.0 m) section of 1½ in. o.d. (3.81 cm) by 0.065 in. (1.65 mm) wall stainless steel tubing by bending 2½ ft (0.762 m) vertical sections at each end. This design left a 5 ft (1.5 m) horizontal section in the middle of the tube. The smaller-diameter tubes (0.4 L volume) were each fabricated from a 6 ft (1.82 m) section of ¾ in. o.d. (1.9 cm) by 0.035 in. (0.889 mm) wall stainless steel tubing by bending 8 in. (20.32 cm) vertical sections at each end (Fig. 1). Each tube was washed with hexane and methanol and heated to 200°C by passing air from a heat gun through the tube. The interior of the tube was then sampled with a TST to ensure its cleanliness. When the tube was determined to be clean, 42 holes were drilled through its horizontal section. The holes were on 2 in. and 2½ in. (5.08 and 6.35 cm) centers for the small and large tubes, respectively, and alternated between a vertical and horizontal alignment. Swagelok reducers (1½ × ¼ [3.8 × 0.635 cm] or ¾ × ¼ in. o.d. [1.9 × 0.635 cm]) were placed on each end of the tubes for sampling ports.

Sampling Hoods

Two low-volume sampling hoods (18 × 54 × 2 in. [~46 × 137 × 5 cm]) were fabricated from 1/16-in.-thick (1.58 mm) stainless steel. A divider in the center separated the hood into two discrete sampling zones. Swagelok fittings (¼ in. [0.635 cm]) were located in the top of the hood on each side for sampling. The total volume of the hood, when in place over the grave, was about 14 L.

A high-volume sampling hood (18 × 54 × 10 in. [~46 × 137 × 25 cm]) was also fabricated from 1/16-in.-thick (1.58 mm) stainless steel with one ¼ in. (0.635 cm) Swagelok fitting in the center of the hood for sampling. The total volume of the hood, when placed on top of the grave, was approximately 130 L.

All hoods were heated (~50 to 54°C) with strip heaters to eliminate condensation of water vapor on the interior surfaces of the hoods because many of the compounds could potentially partition

into a condensate layer and, if this occurred, would therefore not be truly represented in a vapor phase.

Viewing Tubes

Viewing tubes made of glass (1½ in. o.d. [3.8 cm] by 1¼ in. i.d. [3.17 cm]) and polycarbonate (1½ in. o.d. [3.8 cm] by 1¼ in. i.d. [3.17 cm]) of varying lengths were constructed for placement in the graves. The glass tubes were sealed on one end and plugged on the other with a rubber stopper, while the polycarbonate tubes were capped with polycarbonate plugs on each end. These viewing ports were placed around and within two of the bodies to allow long-term monitoring of the decay state. External ports were placed in direct contact with various body interfaces (i.e., palm, abdomen, cheek, buttocks, and foot) and internally inserted through scalpel-incised entries. The internal port of the first body was inserted laterally from left to right mid-abdomen while the port for the second was inserted laterally from left to right in the thoracic region at the approximate level of the seventh through ninth ribs.

Chemicals

Analytical-grade chemicals, including bromobenzene, were purchased from Sigma Chemical Corporation (St. Louis, MO).

Instrumentation

Thermal desorption analyses of the TST samples acquired during the study were conducted on either a Hewlett-Packard 5890/5972 GC/MSD or a Varian 3400/Saturn 2000 GC/MS. Both instruments were modified for sample introduction via thermal desorption of TST samples. Thermal desorption was performed with a flow opposite that of sample collection. Each gas chromatograph was equipped with a J&W Scientific (part #123-1063) DB-1 phase (1.0 μm film thickness), 0.32 mm i.d. by 60 m length capillary column.

Two different cryofocusing techniques were explored in this study. The first technique utilized liquid nitrogen to cool the GC oven to −50°C so that the entire GC column functioned as the cryofocusing element. It was determined that this technique was subject to plugging due to freezing of water vapor or an excess of volatile components. In an effort to avoid the freezing problem, a second technique was adopted which used a short loop (between 5 and 6 in. [12.7 and 15.4 cm] in length) of 0.063 in. o.d. (1.6 mm) stainless steel tubing with an inside diameter of 0.030 in. (0.762 mm) connected to a low-dead-volume 1/16 in. (1.58 mm) stainless steel "tee" connector. The "tee" outlet flow passed either to an atmospheric vent (during desorption) or, when this was closed, to the analytical column. The cryofocusing loop was manually immersed in liquid nitrogen during desorption.

Operating conditions for the HP instrument were as follows:

- Thermal desorption (column cryofocusing):
  The helium carrier gas was set at 11 mL/min. A coil heater was used to heat the TST to 350°C during a five-minute desorption period. The GC split and septum purge flow was off during desorption.
- Thermal desorption (loop cryofocusing):
  The helium carrier was set at 40 mL/min and vented to the atmosphere after the cryofocusing loop. A coil heater was used to heat TST to 350°C during a five-minute desorption period. The GC split and septum purge flow were off during desorption.
- GC oven parameters (column cryofocusing):

initial temperature	−50°C
initial hold time	5.5 min
initial rate	70°C per min
first temperature	25°C
first hold time	3.0 min
first rate	4°C per min
second temperature	70°C
second hold time	0.0 min
second rate	10°C per min
final temperature	280°C
final hold time	10.0 min
total run time	51.0 min

- GC oven parameters (loop cryofocusing):

initial temperature	35°C
initial hold time	1.0 min
initial rate	4°C per min
first temperature	80°C
first hold time	0.0 min
first rate	10°C per min
final temperature	280°C
final hold time	10 min
total run time	50 min

Carrier gas: helium at 1.5 mL/min

Operating conditions for the Varian instrument were as follows:

A single cryofocusing technique used a short loop (between 5 and 6 in. [12.7 and 15.4 cm] in length) of 0.063 in. o.d. (1.6 mm) stainless steel tubing with an inside diameter of 0.030 in. (0.762 mm) connected to a low-dead-volume 1/16 in. (1.58 mm) stainless steel "tee" connector. The "tee" outlet flow passed either to an atmospheric vent (during desorption) or, when this was closed, to the analytical column. The cryofocusing loop was immersed in liquid nitrogen during desorption. Thermal desorption: The helium carrier at 40 mL/min was vented to the atmosphere after the cryofocusing loop. A coil heater was used to heat the TSTs to 350°C during a five-minute desorption period. The GC split and septum purge flow were off during desorption.

- GC oven parameters:

initial temperature	35°C
initial hold time	1.0 min
initial rate	4°C per min
first temperature	80°C
first hold time	0.0 min
first rate	10°C per min
final temperature	280°C
final hold time	10 min
total run time	42 min

Carrier gas: helium at 1.5 mL/min

Grave Sampling

A four-port manifold was constructed using Parker fittings, toggle valve, and fine metering valves (Parker Hannifin, Columbus, OH) to allow independent control of four different TST samples. A Gast Model DOA-P104B-AA diaphragm pump was used to provide vacuum to the manifold. TSTs were connected to the sampling manifold via sections of ¼ in. o.d. (0.635 cm) PTFE tubing. Flow rates were determined before and after sampling using an ADM 3000 flowmeter (J&W Scientific). Flow rates were intentionally

kept low (20–100 mL/min) to avoid rapid volume depletion in the pipes. TSTs were connected to the sampling ports of either the sampling tubes or the sampling hoods with 1/4 in. o.d. (0.635 cm) tube fittings. Sample start times and stop times were recorded and used with the average flow rate to calculate the total sample volume. TSTs were handled with nylon gloves to avoid sample contamination by the operator.

Sample control pipes (placed at a depth of ~2 ft [0.6 m] and buried in a new, previously unused area of the research facility, ~200 ft [61 m] from the nearest corpse) were also sampled using TSTs at regular intervals. Sample hoods, when first brought out to the research facility, were also placed in this general area to establish a baseline for control purposes.

A VistaCam Omni® dental camera from Air Techniques, Inc. was used for imaging of the bodies in the graves through the viewing tubes previously mentioned. Both still pictures and video images were collected after sampling sessions.

Data Reduction

Hewlett Packard (HP) GC/MS data were transferred to a satellite computer for processing. The HP analytical method (Software Version B.01.00) was used to locate the peaks and calculate the areas using the HP quantitation database generated from aggregate data reviews. Compounds were identified by comparing the baseline subtracted spectra with the NIST mass spectral database using a probability-based matching algorithm to supply the compounds with the highest match qualities. Qualities were generally greater than 80%. After identification and quantitation was complete, the data were reviewed manually by experienced mass spectroscopists using the QEdit Quant Result feature of the HP software. In this review, individual compounds were identified and the total ion chromatogram (TIC) quantitated manually. Unknowns with a peak height of greater than 50,000 were also reviewed and either added to the quantitation database or listed as unknowns if no identification was possible from the software databases (Wiley 138, NBS 75K). When the QEdit review was complete, the results were saved, and both a file and screen summary report were generated. The screen report was saved as a text file, which was then imported into Excel™ (Microsoft, Belleview, WA). Only the data fields containing the compound name, retention time, and integrated area were selected. This file was saved back into the same text file name. The file was then imported into the Microsoft Access database where it was manually associated with the experimental data from the sample.

Varian GC/MS data were transferred to a satellite computer for processing, where the quantitation method developed for the study was used to both quantitate and review the data. Using the Varian software (Saturnview, Version 5.52, NIST 98 MS database), the individual compounds were quantitated using selected ions rather than TICs. Unknowns were treated similarly to those identified in the HP analyses. ASCII files of the sample report were then generated from the software, the header and extraneous information from the file were removed in a text editor, and the file was then imported into the Microsoft Access database where it was manually associated with the experimental data from the sample.

Incorporation into MS Access Database

A relational database was developed in Microsoft Access™ for compilation of the data from this study. Data entered into the database included identities and integrated area counts of all identified compounds, correlated to the sample they were found in, as well as the sampling and analysis conditions for each sample. To permit direct comparison of results, 10 ng of bromobenzene were added to sample traps prior to TD/GC/MS analysis. Measured counts for each compound in a sample were divided by the count for bromobenzene. These normalized counts were then divided by the sample volume (determined at the time of collection) to provide relative concentrations that can be used to compare results from different samples.

Results

The results of this study demonstrate that burial decomposition is much more complex than previously thought (17–20). Neither visual nor chemical decompositional stages were readily apparent. While many chemicals were identified in this study, their origin remains unclear. In-ground and in-corpse thermocouple data indicate that shallow burial temperatures tend to mimic surface temperature, but lag behind surface temperatures by about 12 h. The apparent cutoff (soil inversion point) is approximately 15°C. Burial temperatures tend to be 3.3°C cooler than surface temperatures above this cutoff and 4.4°C warmer below this cutoff. These values were calculated by averaging the surface and burial temperature differences over the course of a year. This is an important observation when attempting to determine BADDs useful for postmortem interval (PMI) determinations.

This study has identified 424 specific volatile chemicals liberated from the human decompositional process of burials. Several additional compounds, which are not discussed in this paper, could not be positively identified. Identified chemicals have been grouped into eight distinct categories. The eighth category (*Others*) is a compilation of miscellaneous chemicals assumed to be related to the burial process, but more likely are products of decaying vegetation (21). The seven primary categories and the environmental factors which influence them are listed in Table 2. The compounds produced during the decompositional process were exposed to many factors including: barometric pressure, partial pressure oxygen

TABLE 2—*Possible environmental influences on appearance of compound classes at grave surface for soft tissue burials within first year of decomposition.*

Compound Class	Does *Barometric Pressure (BP)* Affect Class?	Does *Air Temperature* Affect Class?	Does *Rainfall* Affect Class?	Optimal Surface Detection Factors	Is Production Below Body Burial Dependent on:	
					Temperature	Precipitation
Cyclic hydrocarbons	yes	no	no	high BP	yes	yes
Noncyclic hydrocarbons	no	yes	no	warm	yes	yes
Nitrogen compounds	unclear	unclear	unclear	. . .	no	no
Oxygen compounds	no	no	no	. . .	yes	no
Acids/esters	yes	no	no	high BP	yes	no
Halogen compounds	no	no	no	. . .	no	no
Sulfur compounds	no	no	no	. . .	yes	no

atmospheres (burial), rainfall (moisture), soil binding, temperature changes and an acidic environment, all of which may affect their rate and direction of migration through the soil column. None of these factors were controlled in order to simulate a real-life scenario; however, as such, interpretation of the results was more difficult. As illustrated in Fig. 2, the extreme complexity of the effects of environmental factors on the spectrum of volatiles detected shows the need to condense these data into tabular form. Table 2 gives preliminary results of the possible environmental factors (barometric pressure, temperature and rainfall) which could have affected the movement of volatile chemicals through the soil column. Investigation of the influence of environmental factors on compound class concentration using statistical regression analysis was accomplished. The initial focus for these analyses was on the data for the two bodies buried at approximately the same time and at the same depth. For each compound class, a model was fit to the logarithm of concentration versus the measured environmental temperature, precipitation, barometric pressure and all cross products. The model allowed for differences between the two bodies in the form of a constant shift upward or downward independent of the environmental factors. The goal of these analyses was to identify potentially important environmental factors and interactions. The factors listed in Table 2 and the type of effect they have on concentration were determined from fitted models; statistically significant explanatory variables at the 0.10 alpha level were selected for inclusion (R Foundation for Statistical Computing, Vienna, Austria). The type of effect, increasing or decreasing, was determined by the sign of the coefficient. Since it is unknown whether a hydrophobic compound would be driven downward or upward after a heavy rain, information such as this was not used in this determination.

Table 3 lists the primary time frame (BADDs and days since burial) in which these chemicals are liberated at the surface during the first 1 to 1.5 years of burial decomposition, indicating that oxygen containing compounds, acids/esters and sulfur compounds are liberated first in shallow burials. Interestingly, it took 17 days for the first compounds to become detectable at the surface of the 1.5 ft (0.45 m) grave using TSTs, with a majority of compounds becoming apparent only after the first month. Deeper burials (2.5 ft [0.76 m]) tended to produce slightly different liberation profiles in that halogens were the first class of compounds to be detected at the surface with the majority of classes being detected after two months. This may be an artifact based on the seasonality of the burial, since calculating this effect based on BADDs gave similar results. Nevertheless, the depth of the burial had a significant effect on the production of various classes of chemicals, most likely due to the greater partial pressure of oxygen in the shallower grave, which affects the microflora as well as the formation of compounds. Not surprisingly, several classes of compounds were detected more prominently below body at certain times of the year and appear to be related to the progression of decomposition. Light alcohols, hydrocarbon acids/esters, and sulfur compounds were detected early in the decomposition of the corpse interred during the summer

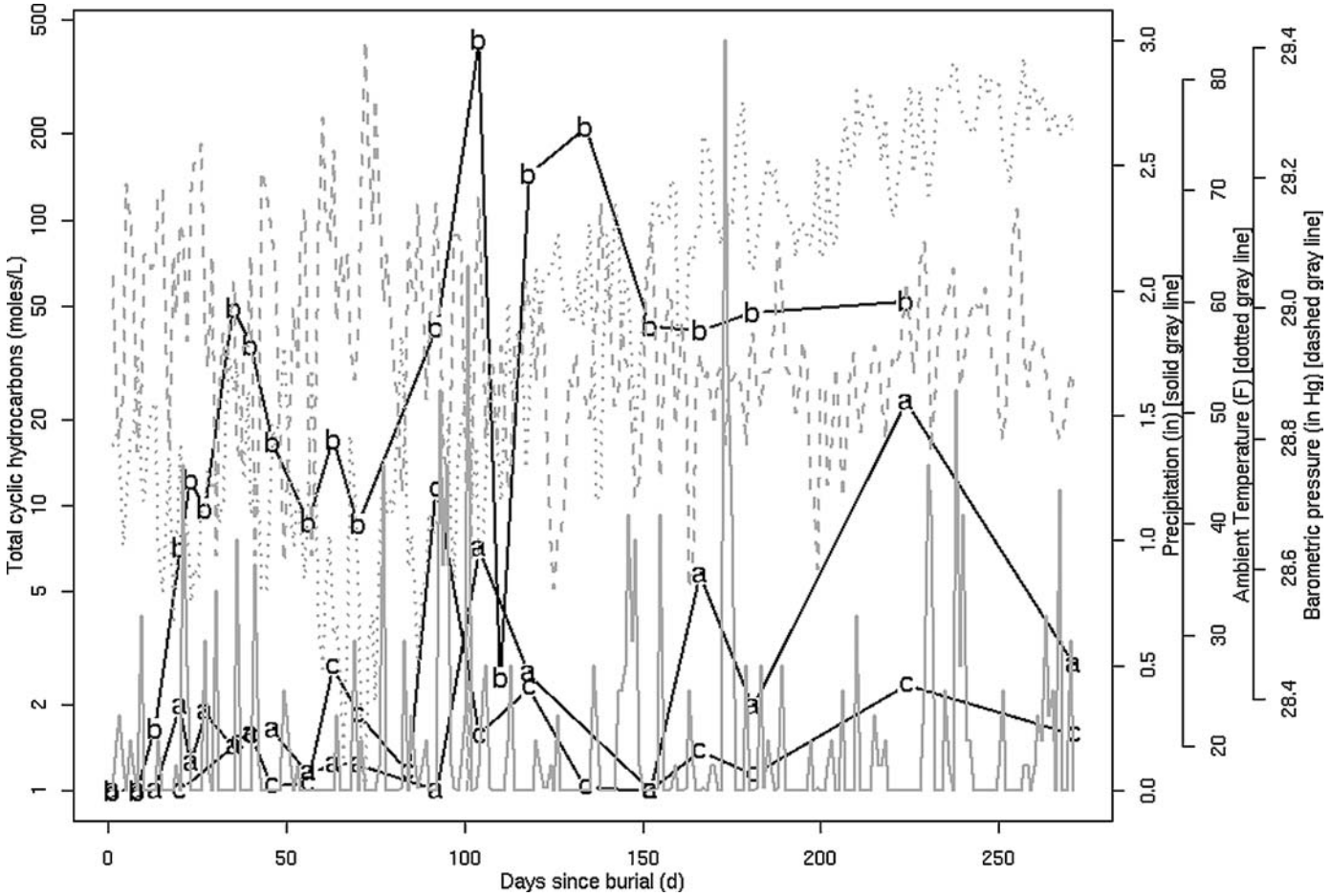

FIG. 2—*Total cyclic hydrocarbons detected below, above, and at surface of 2.5 ft (0.76 m) grave showing complexity of production in relation to environmental factors:* (a) *above corpse,* (b) *below corpse,* (c) *capture hood (at surface).*

TABLE 3—*Approximate time of primary appearance of compound classes at soil surface in relation to below-body production for 1-to-1.5-year burials.*

	Approximate Range of Primary Production Summer Burial at Depth of 1.5 ft		Approximate Range of Primary Production Fall/Winter Burial at Depth of 2.5 ft	
Compound Class	BADDs	Days Since Burial	BADDs	Days Since Burial
Cyclic hydrocarbons	1000–3000	50–150	500–3000+	60–230+
Noncyclic hydrocarbons	500–3000	30–150	750–3000+	90–230+
	4000–6000	250–400		
Nitrogen compounds	2500–5000	128–350	500–1000	60–115
Oxygen compounds	250–3000	17–150	500–3000+	60–230+
Acids/esters	250–3000+	17–150+	500–3000+	60–230+
Halogen compounds	1500–3000	75–150	200–2000	25–185
	3500–5000	200–350		
Sulfur compounds	250–3000	17–150	750–3000+	90–230+

(+) indicates significant production of compounds in the various classes as monitoring for this phase of the project ended.

months. Acids and esters were detected again from the same body during the subsequent summer. Sulfur compounds were also detected early in the decompositional process for the two individuals buried during the fall/winter months with alcohols and hydrocarbon acids/esters only appearing during the first spring following burial.

Tables 4 and 5 list the most prevalent volatile chemicals detected at the surface of burials sorted by compound class and indicate that cyclic hydrocarbons, oxygen compounds and halogen compounds are of significant importance when interpreting burial decomposition. Sulfur compounds are more significant only during the early stages (first few years) of decomposition.

Table 6 tracks the fate of volatile chemicals as they move from the site of production (the corpse) to the surface. As illustrated in Table 6, depth plays a vital role in determining which compounds are generated during the decompositional process, with nitrogen compounds being the most severely affected, followed closely by acid/ester compounds. Interestingly, many of the above corpse samples are significantly lower than the below or surface values. Within the first 1.5 years of burial decomposition, only about 47% of the total chemicals liberated at the body (below sample) are detected above the body, whereas 69% are detectable at the surface. Although the reason for this is unknown, it is possible that there is a surface concentration effect occurring for the gases (possibly by surface moisture which may not penetrate far into the soil column) that allows for their detection, but this tends to be class dependent and is observed to a lesser extent in halogen and noncyclic compounds. It is also possible that the concentrations of chemicals present are below the method detection limit, which was roughly in the parts-per-trillion range. This was not dependent on the orientation of the upper pipe (perpendicular or parallel) since both burials displayed similar patterns. The 12-year-old burial provides some evidence that what remains of the chemical classes at, or near, the body, do make it to the surface with nearly a 75% recovery for all compounds. As the corpse ages, the cyclic/noncyclic hydrocarbons and halogen compounds tend to have the greatest longevity and stability. This percentage varies depending on the class of compound and environmental conditions. As a general rule, of the chemicals liberated at the corpse, only about 0.1% of the below-body concentration is detectable at the surface. Table 7 presents these data in tabular form and also confirms the results of Table 6. Not only are more compounds produced in certain classes (sulfur, noncyclic), but they are also produced in greater concentration depending on the depth of the burial. The opposite is true of other classes (e.g., nitrogen). This also varies tremendously depending on environmental factors (Table 2).

Discussion

Burial decomposition, even when insects are for the most part excluded, is extremely complex and dependent on many factors, including temperature, insect exclusion, rainfall/humidity, barometric pressure, season of burial, soil type, burial depth (decreased partial pressure of oxygen) and possibly even the peri-mortem weight or diet of the individual. All these factors contribute to an ever-changing pattern in the liberation (and detection) of decompositional products from a burial. One interesting observation of this study has been the role of temperature in burial decomposition. Surface temperature has always played the dominant role in above-ground decomposition and also influences the production of compounds at the body in a burial, but has a diminished role in promoting the liberation of chemicals at the soil surface (Table 2). Shallow burials tended to support an eightfold slower decompositional rate than what is typically observed at the surface (22,23) (based on visual observations using images obtained from the viewing ports), while BADDs indicate that decomposition should be more similar to surface rates. This implies that temperature is not the only significant environmental factor in burial decomposition. Soil types may also play a significant role in the production and eventual liberation of the compounds at the surface. The soils in this study had a significant clay content (considered a "worst case scenario" because of the dense nature of clay). This could affect the permeability of compounds through the soil column and could affect the penetration of water into and out of the grave vault.

Of all the classes of volatile compounds detected during the decompositional cycle, the fluorinated compounds are the most interesting and unexpected. The source of the fluorinated compounds still remains a mystery. It is assumed that since much of the water in the United States is fluorinated, the ingested fluoride is principally incorporated into bone and, to a lesser extent, soft tissue, being slowly liberated during soft tissue decomposition and skeletal diagenesis (24,25). Microbial modification could also be taking place, since halogenated compounds are known for their stability and the halogenated compounds detected in this study are not normally found in drinking water. Chlorinated hydrocarbons (and chloro-fluoro compounds) may also be formed by similar mechanisms from the significant amounts of chloride ions present in the body. Since the subjects in this study were briefly stored in the Knoxville Medical Examiner's morgue, the morgue was sampled for the presence of these compounds since it has been observed that fluorinated compounds easily adhere to surfaces for long time periods (Dr. Marcus Wise, Oak Ridge National Laboratory, personal communication) and are generated by refrigeration-type units such

TABLE 4—*Most significant volatile chemicals detected at the surface of one-year-old burials sorted by compound class.*

Cyclic Hydrocarbons	Non-Cyclic Hydrocarbons	Nitrogen Compounds	Sulfur Compounds	Acid/ester Compounds	Oxygen Compounds	Halogen Compounds	Others
1,4 dimethyl benzene	heptane	methenamine	sulfur dioxide	hexadecanoic acid, methyl ester	decanal	trichloromonofluoromethane	1-methyl naphthalene
1,2 dimethyl benzene	2-methyl pentane	benzonitrile	carbon disulfide	...	benzene methanol, a,a dimethyl	chloroform	naphthalene
Ethyl benzene	undecane	...	benzothiazole	...	1-hexanol, 2-ethyl	trichloroethene	...
Toluene	...	...	2,4-dimethylthiane, S,S-dioxide	...	benzaldehyde	tetrachloroethene	...
Styrene	...	...	dimethyl trisulfide	...	nonanal	dichlorodifluoromethane	...
1-methyl-2-ethyl benzene	...	...	dimethyl disulfide	...	benzene (1-methoxypropyl)	dichlorotetrafluoroethane	...
C4-benzene	...	...	...	...	2-propanone	trichloroethane	...
...	...	...	...	...	...	carbon tetrachloride	...

The current version of the database is presently being archived at the Federal Bureau of Investigation, Counterterrorism and Forensic Science Research Unit, Quantico, Virginia. The database includes all detectable chemicals, relative abundances, chemical trends, experimental information, methodologies, and weather data related to sampling.

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