DECOMPOSITIONAL ODOR ANALYSIS DATABASE – PHASE I

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Running Title: Odor of decomposition

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ABSTRACT: This study, conducted at the University of Tennessee's Anthropological Research Facility (ARF), describes the development of the Decompositional Odor Analysis (D.O.A.) Database and seeks to establish the chemical basis for canine's scenting ability when detecting human remains. This database is composed of chemicals that are liberated during the decompositional process from buried human remains. 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 1.5 - 2.5 ft graves for three individuals (two males and one female). A fourth male individual (buried in 1990) was also sampled to provide possible 'endpoint' information. In-ground, in-corpse thermocouples provided temperature information which can be used to correlate accumulated degree days (ADDs) to surface decompositional events and indicated an approximate 12 hour lag between equilibration of grave temperature with the surface air. Clear, sealed, hollow pipes were also placed in the grave vault providing viewing ports by which the burial decompositional process could be monitored. Results confirm that burial decomposition is approximately eight times slower than surface decomposition. Movement of these chemicals through the soil column significantly reduces the chemical species which might be available to detection devices, including canines. Triple sorbent traps (TSTs) were used to collect air samples in the field. The TSTs were thermally desorbed in the laboratory and analyzed on a GC-MS system revealing eight major classes of chemicals containing 424 specific volatile compounds associated with the decompositional process of burials. This research furthers our understanding of human decomposition and has profound ramifications on cadaver dog training procedures and in the development of field portable analytical instruments which can be used to locate buried human remains.

KEYWORDS: forensic science, human decomposition, odor analysis, cadaver dog, burials

The detection of buried human remains is most often accomplished with the aid of ground-penetrating radar (GPR), manual probing techniques or trained 'cadaver dogs' - canines that 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 are unknown.

The success of canines has expanded the science of odorology to encompass forensic applications of dogs able to successfully discriminate scent. Law enforcement agencies around the country use specially trained dogs for a variety of purposes. These dogs have proved invaluable in such vital areas as explosive and accelerant detection, narcotics detection, and searching for criminals as well as lost or missing persons (3,4). More recently, canines have been trained to detect human remains with mixed success. Certain canines have the ability to find historic human remains and the 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 with time. These abilities allow for their use in the area of Human Remains Detection (HRD) (5-10), but they remain as a minority in the law enforcement canine population primarily because of the cost associated with the training, care and purchase of the canine. Many would agree that canines still possess olfactory capabilities that are far more sensitive than our best analytical technology (11, 12, 13). It is currently believed that this capability stems primarily from their ability to distinguish one complex scent from another. Unfortunately this assertion is difficult to test, validate, calibrate and most importantly, standardize.

The purpose of this study was to begin the difficult task of identifying volatile compounds which migrate upward to the surface of soil (allowing for detection by cadaver dogs) from burials during the decompositional process. Identification of these compounds with subsequent verification by HRD canines will provide a basis by which the HRD canine handlers can begin standardizing their training. Identification of these compounds is also important in the development of instrumentation used to augment or replace the canine (when they are unavailable). The results herein describe this task – the development of the Decompositional Odor Analysis Database which identifies chemicals associated with burial decomposition. The database records volatile chemicals as they are produced near the body and follows their migration upward 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 what are considered the most important chemicals liberated from the decompositional process will be discussed in this report. The current database spans only the first 1.5 years of burial decomposition with some preliminary data obtained from a 12 year-old grave site containing only skeletonized material. It is the ultimate goal of this study to define the chemical fingerprint produced by human decomposition over a span of many years in hopes of understanding and enhancing canine performance and in producing reliable detection instrumentation. Results to date are 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, TN, 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 inches (100 - 150 cm) of rainfall per year. This 3+ acre facility is surrounded by a chain-link fence to restrict large carnivores and is under 24 hr surveillance to prevent unauthorized intrusions. 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 was obtained from the Knoxville National Weather Service station located approximately 10 miles 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 (Figure 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

The subjects used in this study were donations to the Anthropology Research Facility. The individuals had either voluntarily donated their remains to the center for research purposes, had signed papers to donate their remains to science, or had been donated by family members.

Individuals selected for this study were unautopsied and unembalmed. Individuals having known bloodborne pathogens were excluded from this study. Additionally, 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 for this study. All subjects were buried without clothing or wrappings. Information concerning the age, ancestry, gender, cause of death, date of burial and interment information was recorded for all individuals (Tables 1a, 1b).

Triple Sorbent Traps (TSTs)

TSTs were composed of 14 mm sections of Carbotrap, Carbotrap-C and Carbosieve S-III sorbents packed (in that order) in the center of a 76 mm x 6 mm o.d. x 4 mm i.d. stainless steel tube. The tube was stamped with a number and an arrow indicating the sampling 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.

Bromobenzene peak detection during sample analyses confirms that the instrument is working properly and allows comparison of different TSTs based on the amount of bromobenzene detected. Assuming a response factor of one for all compounds compared to bromobenzene, we can obtain an estimate of the analyte mass present on any given TST. Determining 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 μ L of bromobenzene through the push button vapor-lock cap. This was allowed to equilibrate for at least 10 minutes after which time 250 μ L of the master stock was removed using a heated (70°C) gas-tight syringe and transferred to another dilution bottle to make a working standard. The working standard was allowed to equilibrate for at least 10 minutes 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 μ L of the working standard using a VICI gas-tight syringe with Pressure-Lok valve to affect a mass loading of 10 ng per trap. At least one trap from each batch was analyzed by 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" sections of 34" stainless steel tubing perforated with thirty-four 1/4" 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 foot section of ¹/₄" stainless steel tubing through a 90° fitting elbow at the other. The ¹/₄" 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 ³/₄" and 1 ¹/₂" stainless steel tubing. The larger diameter tubes (2.9 L volume) were each fabricated from a 10 ft. section of 1 ¹/₂" x 0.065" wall stainless steel tubing by bending $2\frac{1}{2}$ ft. vertical arms at each end. This left a five foot horizontal section in the middle of the tube. The smaller diameter tubes (0.4 L volume) were each fabricated from a 6 ft. section of ³/₄" x 0.035" wall stainless steel tubing by bending 8" vertical arms at each end. This left a 4 1/2 ft. horizontal section in the middle of the tube. 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 the horizontal section of the tube. The holes were on 2" and $2\frac{1}{2}$ " centers for the small and large tubes, respectively, and alternated between a vertical and

horizontal alignment. Swagelok reducers $(1 \frac{1}{2} x \frac{1}{4})$ or $\frac{3}{4} x \frac{1}{4}$ were placed on each end of the tubes for sampling ports.

Sampling hoods

Two low volume sampling hoods (18"x 54"x 2") were fabricated from 1/16" stainless steel. A divider in the center separated the hood into two discrete sampling zones. Swagelok fittings (1/4") were located in the top of the hood on each side for sampling. The total volume of the hood, when in place on the grave, was about 14 L.

A high volume sampling hood (18"x 54"x 10") was also fabricated from 1/16" stainless steel, with one $\frac{1}{4}$ " Swagelok fitting in the center of the hood for sampling. The total volume of the hood, when placed on the grave, was approximately 130 L.

Viewing tubes

Viewing tubes of glass (1 $\frac{1}{2}$ " o.d. x 1.2" i.d.) and polycarbonate (1 $\frac{1}{2}$ " o.d. x 1 $\frac{1}{4}$ " i.d.) 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.

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. Each gas chromatograph was equipped with a J&W Scientific (part #123-1063) DB-1 phase (1.0 um film thickness), 0.32 mm ID by 60 m length capillary column.

Two different cryofocusing techniques have been used with this instrument. The first technique utilized liquid nitrogen to cool the GC oven to -50° C so that the GC column functioned as the cryofocusing element. It was determined that this technique was subject to plugging due to freezing. In an effort to avoid the freezing problem, a second technique was adopted which used a short loop (between five and six inches in length) of 0.063" O.D. stainless steel tubing with an I.D. of 0.030" connected to a low dead volume 1/16" stainless steel "tee" connector. The "tee" outlet was 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.

Operating conditions for the HP instrument are as follows:

Thermal Desorption (column cryofocusing):

helium carrier at 11 ml/min

coil heater used to heat TST to 350° C during a five minute desorption period GC split and septum purge flow off during desorption

Thermal Desorption (loop cryofocusing):

helium carrier at 40 ml/min vented to the atmosphere after the cryofocusing loop coil heater used to heat TST to 350° C during a five minute desorption period GC split and septum purge flow 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

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

Carrier Gas: helium at 1.5 ml/min

Operating conditions for the Varian instrument are as follows:

A single cryofocusing technique used a short loop (between five and six inches in length) of 0.063" O.D. stainless steel tubing with an I.D. of 0.030" connected to a low dead volume 1/16" stainless steel "tee" connector. The "tee" outlet was 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:

helium carrier at 40 ml/min vented to the atmosphere after the cryofocusing loop coil heater used to heat TST to 350° C during a five minute desorption period

GC split and septum purge flow 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.

<u>Sampling</u>

A four port manifold was constructed using Parker fittings, toggle valve, and Porter fine metering valves 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 ¹/4" 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 mLs/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" 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.

Control pipes (pipes placed at a depth of ~2ft. and buried in a new, previously unused area of the research facility, ~200 feet 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

HP GC/MS data were transferred to a satellite pc for processing. The HP analytical method (Version B.01.00) was used to calculate the peaks and areas using the HP quantitation database generated from aggregate data reviews. After identification and quantitation was complete, the data were reviewed manually using the QEdit Quant Result feature of the HP software. In this review, individual compounds were identified, if present in the sample, 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 database. 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. Only the columns containing the compound name, retention time, and integrated area were used. This file was saved back into the same text file name. The file was then imported into the Microsoft Access database, where it was associated with the experimental data from the sample.

Varian GC/MS data were transferred to a satellite pc for processing, where the quantitation method developed for the study was used to both quantitate and review the data. Because of the greater sophistication of the Varian software (Saturnview, Version 5.52), 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 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 compounds of interest, 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 mass spectroscopic analysis. Observed 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). Discrete decompositional stages (neither visual nor chemical) were readily apparent and 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 hours. The apparent cutoff (soil inversion point) is approximately 15°C. Burial temperatures tend to be approximately 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 post-mortem interval (PMI) determinations.

This study has identified 424 specific volatile chemicals liberated from the 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 separate 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. The seven primary categories and the environmental factors which influence them are described in Table 2. The compounds produced during the decompositional process were exposed to many factors including: barometric pressure, partial pressure oxygen 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 making interpretation of the results a difficult task. Figure 2 is used to illustrate the extreme complexity of the effects of environmental factors on the spectrum of volatiles detected and shows the need to condense this data into tabular form. Table 2 ranks the most important environmental factors (barometric pressure, temperature and rainfall) which affected the movement of chemical classes through the soil column. This was derived through careful plotting of data in a stepwise progression comparing compound class time points possessing a similar concentration using one specific factor (e.g. temperature) and determining the effect on the classes as the other environmental factors changed (Figure 2). For this reason only obvious effects of the various factors are described. 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. These trends will be analyzed statistically as more subjects become available for this study.

Table 3 describes the primary time frame (BADDs and days since burial) in which these chemicals are liberated at the surface during the first 1 - 1.5 years of burial decomposition indicating that oxygen, 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 1.5ft grave using TSTs, with a majority of compounds becoming apparent only after the first month. Deeper burials (2.5 ft) 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 2 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 decompositional progress. Light alcohols, hydrocarbon acids/esters, and sulfur compounds were detected early in the decomposition of the corpse interred during the summer 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 describe the most significant 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 seen 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 detected at the surface. Although the reason for this is unknown, it is possible that there is a concentration of the gases occurring at the surface (possibly by surface moisture which may not penetrate far into the soil column) which allows for their detection, but this tends to be class dependant and is seen to a lesser extent in halogen and non-cyclic compounds. It is also possible that the amounts of chemicals present are below our detection limits, which was roughly in the parts per trillion range. This was not dependant 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 surface with nearly a 75% recovery for all chemical classes. As the corpse ages, the cyclic/non-cyclic 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 this data in tabular form and also confirms the results of Table 6. Not only are more compounds produced in certain classes (sulfur, non-cyclic), but they are also produced in greater concentration dependent 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 dependant on many factors including: temperature, rainfall, barometric pressure, season of burial, soil type, burial depth (decreased partial pressure of oxygen) and possibly even the peri-mortem weight of the individual. All these factors contribute to an ever changing pattern in the liberation (and detection) of decompositional products from a burial. One of the more interesting observations of this study has been the role of temperature in burial decomposition. Temperature has always played the dominant role in above ground decomposition, but it tends to be less important than rainfall in burials. Visual observation of the burials tended to support an eight-fold slower decompositional rate than what is typically seen at the surface (based on visual observations using images obtained from the viewing ports (21)), 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 – something 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 the grave vault.

Of all the classes of volatile compounds detected during the decompositional cycle, the fluorinated compounds are the most interesting and unexpected. Determining the source of the fluorinated compounds still remains a mystery. It is assumed that since much of the water in this country 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 (22-23). 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, we sampled the morgue 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, pers. comm.) and are generated by refrigeration type units such as those found in morgues. While fluorinated compounds were detected in small amounts, they were, in most cases, different compounds than what was detected at the graves. Areas of the world which do not have fluorinated drinking water do not show fluorinated compounds present in decompositional samples (Bart Smedts, Koninklijke Militaire School, Brussels, pers. comm.) giving credence to this hypothesis. It is interesting to note that dichlorodifluoroethane was not detected in below body samples, but only appeared above body and at the surface indicating: 1) that it was not a natural background component, and 2) that is was most likely formed after the primary decompositional process had occurred.

For the cyclic and non-cyclic hydrocarbons, halogens and 'other' categories, many of the compounds which were produced during decomposition were able to migrate to the surface at detectable levels. While a few specific chemicals were no longer detectable, others such as substituted benzene compounds, cyclohexanes, substituted naphthalenes, long chain hydrocarbon acids and substituted ethane compounds appear to have been generated by microbial modification of the various base compounds as they moved up the soil column (24).

Another interesting finding was the complete absence of detectable levels of diamines. Putrescine and cadaverine have long been associated with human decomposition and it has always been assumed that these two chemicals are key in cadaver dog alerting. Previous studies have relied on derivatization of tissue samples in order to detect their presence (25). Several explanations are possible: 1) Diamine compounds are not volatile in a burial situation, 2) diamine compounds in a burial are metabolized by bacteria soon after generation, 3) these compounds are thermally labile and therefore were instrumentally destroyed before they could be detected (this is currently under investigation using high performance liquid chromatography, but these compounds have previously been detectable (without derivatization) using gas chromatography (26)) and, 4) these compounds are not produced in partial pressure oxygen atmospheres. The answer to this puzzle is quite important and could point to an entire new class of thermally labile compounds which were undetected using this current

detection system or could lead to a new understanding of the way in which dogs detect scent.

The results of this study indicate that defining the chemical fingerprint produced by human decomposition is an attainable goal. Success in this undertaking will advance our understanding of canines' scenting ability and allow for the development of training aids capable of enhancing the canines' performance. This database is also the first step in developing reliable detection instrumentation which can be used to aid law enforcement in search and recovery efforts.

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

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