Forensic Science International 217 (2012) 39–49

Contents lists available at SciVerse ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Dust as a collection media for contaminant source attribution

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ARTICLE INFO

Article history:
Received 10 November 2010
Received in revised form 21 September 2011
Accepted 26 September 2011
Available online 21 October 2011

Keywords:
Dust
Source attribution
Principal components analysis
Mass spectrometry
Organophosphate pesticides
Nerve agents

ABSTRACT

Dust was investigated for its ability to retain source attribution profiles (SAPs) after chemical exposure. Three distinct sources of the organophosphate pesticide acephate were investigated as a proof-of-concept model. In addition, attribution profiles were created and tested using compounds related to chemical warfare agents (CWAs), specifically VX and G-series agents: *O*-ethyl methylphosphonothioate (EMPTA), *N*,*N*-diisopropylmethylamine (DIPMA), *N*,*N*-diisopropylethylamine (DIEA), diisopropylamine (DIPA), diethyl aniline (DEA), diethyl ethyl phosphonate (DEEP), trimethyl phosphite (TMP), dimethyl hydrogen phosphite (DMHP), diethyl hydrogen phosphite (DEHP), triethyl phosphate (TEP), ethyl methylphosphonate (EMPA), and diisopropyl methylphosphonate (DIMP). Dust was collected from a storage shed, aliquots deposited on carpet and loaded with distinct chemical profiles using an exposure chamber and aerosolizer. After a given period of time (1 h, 24 h, or 72 h), the dust was extracted and its SAP analyzed by gas chromatography–mass spectrometry (GC–MS) and/or liquid chromatography–tandem mass spectrometry (LC–MS/MS). Principal components analysis (PCA) was used to determine the association of dust exposed to the same and different chemical sources. PCA results demonstrate that dust samples exposed to distinct chemical sources are clearly differentiated from one another across all collection times. Furthermore, dust aliquots exposed to the same source can be clearly associated with one another across all collection times. When the CWA-related compounds were subjected to elevated temperature (90 °C) conditions, it was found that the signature was stable at the 1 h and 24 h collections. At 72 h and elevated temperature, larger deviations from the control were observed for some compounds. Elevated pH (10) affected the profile to a lesser degree than elevated temperature. Overall, dust is found to be an effective media for the *in situ* collection of source attribution profiles.

1. Introduction

The source attribution profile (SAP) of a given substance is the unique "fingerprint" consisting of all the chemical characteristics of both the substance itself as well as any traces characteristic of its origin or processes (i.e. impurities). These characteristics include chemical identity, relative concentrations, stereochemistry, crystal morphology, and any other property which is a selective identifier. Impurities may arise from the synthetic process, handling, equipment used, storage and transportation, etc. Impurities may be present as left-over starting materials, catalysts, or impurities originally present in starting materials. They may also be created as intermediates, byproducts, or degradation products imparted to the substance as a result of contact with specific materials or any other process that results in the presence of a compound that is not the substance itself. Due to this "chemical memory," the SAP may be used to associate a given substance with a specific origin, history, or process (i.e. synthesis route, event, manufacturer, batch, person, country of origin, etc.).

Attribution profiles have been examined for compounds belonging to a range of chemical classes, including explosives, nuclear materials, drugs, toners, inks and chemical warfare agents [1–8]. These studies rely on a variety of analytical detection techniques including infrared spectroscopy (IR), scanning electron microscopy (SEM), gas chromatography–mass spectrometry (GC–MS), liquid chromatography–mass spectrometry (LC–MS), nuclear magnetic resonance (NMR), thin layer chromatography (TLC) and inductively coupled plasma–mass spectrometry (ICP–MS). Generally, the amount of analytical information collected is too extensive to manually evaluate all of the possible contributing variables and to separate them from background, unrelated signals. Multivariate pattern recognition techniques, including principal components analysis (PCA), are useful for source attribution [9,10]. These techniques can be supervised (looking for an expected pattern) or unsupervised (looking for patterns to emerge). An important feature of the PCA approach is to reduce the dimensionality of the attribution

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doi:10.1016/j.forsciint.2011.09.024

profile from many different variables (i.e. peak areas of distinct compounds) to only a handful (3–4) of independent quantities.

Dust has several advantages as a collector of SAP information. Dust is ubiquitious in the indoor environment, eliminating the need to have a specific collection device in place at the time of chemical exposure. Collection of dust is uncomplicated. In addition, it is well documented that dust is an efficient collector of the semivolatile and nonvolatile organic chemicals and metals present in the indoor environment. Prevalent concentrations suggest that house dust is the main source of the exposure of young children to allergens, lead, and polybrominated diphenyl ethers (PBDEs) [11–17]. Dust is also a major in-home exposure source for pesticides, polyaromatic hydrocarbons (PAH), phthalates, alkylphenols, and their ethoxylates, arsenic, cadmium, chromium, mold, endotoxin, and bacteria [18–23]. Carpeting is a common dust reservoir and an efficient pesticide concentrator. Typically, pesticide concentrations in vacuum house dust are 10–100 times higher than those found in outdoor surface soil [24–26].

There is also evidence that dust slows the degradation process of many chemicals as compared to exposure in the open environment. Residues from pesticides discontinued long ago in the U.S. are still found in house dust. Chlordane (banned in 1988) was still detected in 38% of homes, and dichlorodiphenyltrichloroethane (DDT, discontinued in 1972) was still found in 70% of house dust samples collected from 1998 to 2001 [27]. Another example is the degradation of DDT to dichlorodiphenyldichloroethylene (DDE). The DDT:DDE ratio typically found in home dust samples is approximately 5:1 [28]. However, in soil samples, degradation is more advanced, with a typical DDT:DDE ratio of approximately 1.5:1 [29].

The overall goal of this work is to demonstrate that dust can yield meaningful information for the purpose of source attribution. For this proof-of-concept work, the organophosphate pesticide acephate and compounds related to chemical warfare agents (CWAs) were chosen as the chemical systems. Dust collected from storage sheds was loaded with different chemical profiles using an exposure chamber and extracted after a given period of time. Resulting GC–MS and/or LC–MS results were subjected to PCA to determine if different chemical sources could be distinguished and if extracts from the same chemical source could be associated with one another.

2. Materials and methods

2.1. Exposure chamber

A chamber was required to provide reproducible exposure of carpet and dust to aerosolized spray solutions containing the test chemical(s). To satisfy this requirement, an exposure chamber consisting of an 18″ acrylic cube with an open bottom was custom-built. A small fan (3″ square, Dayton Electric, 107 CFM AC AXIAL) was affixed to the inside roof of the chamber. The distance between the fan and the roof was approximately 2–4″ and adjusted before each set of experiments by spraying a dye solution and observing the resultant deposition pattern. A fixed needle guide was installed through one of the sides of the chamber approximately 1–1/8″ from the bottom. The needle guide set the angle of the aerosolizing needle at approximately 40° pointing upwards towards the fan. To accomplish aerosolization of the test solution a Penn-Century Microsprayer© was utilized (model 1A customized with no bend, length = 8″, mass median diameter = 28 μm).

For exposure experiments, the chamber with open-bottom was placed over an 18″ square of test carpet and dust. Approximately 4 mL of the spray solution was aerosolized, and the fan aided in both circulating the aerosolized droplets and directing them downward towards the test carpet and dust. Although some of the spray solution was deposited on the walls of the chamber, this does not affect the overall results because relative fidelity of the SAP is being tested, not absolute recovery. The fan, aerosolizing needle, and inside of the exposure chamber were cleaned in between spray solutions.

2.2. Dust

Dust was collected from two separate storage sheds in Pine Bluff, Arkansas in quantities of approximately 100 g (shed 1) and 300 g (shed 2). The dust was sieved with a stainless steel US standard number 40 sieve (Fisher Scientific, nominal opening 425 μm). The fractions with smaller particulate size were retained for experimentation. The pH of both dust sources was approximately 8 as measured from a 1 g/mL solution in water. Dust from the two sheds was blended at a 50:50 ratio for acephate experiments prior to deposition on the carpet. Due to concern about exhausting the supply of dust, it was blended at a 15:85 (shed 1:shed 2) ratio for all CWA experiments. Dust was deposited onto carpet purchased from a local hardware store (Beaulieu Solutions, Walnut Ridge commercial loop).

2.3. Acephate

The goal of this work was to demonstrate that chemicals could be distinguished by their SAP after being deposited on dust. The specific sources of the test material are not critical, as long as they are shown to have distinguishable source attribution profiles. Therefore, three distinct sources of technical-grade acephate were obtained from proprietary suppliers and used without further purification. The identity and purity (~97%) was confirmed prior to use by GC–MS. Furthermore, it was confirmed that the three different acephate sources contained distinct SAP. The three acephate sources will be referred to throughout this article as "acephate A," "acephate B," and "acephate C."

2.4. Acephate exposure experiments

Carpet squares (18″ × 18″) were prepared and subdivided into three 6″ × 18″ strips. Dust (approximately 7 g) was evenly deposited onto each 18″ × 18″ carpet square using a sifter. A total of 4 mL of a 10% acephate solution in water was aerosolized using the exposure chamber as described above. The carpet squares were stored for either 1, 24, or 72 h inside of a loosely sealed cardboard box that was kept in a laboratory fume hood. Different acephate sources were stored in separate boxes. At the designated time, the dust on a single carpet strip (6″ × 18″) was collected using the high volume small surface sampler (HVS3) vacuum cleaner. The HVS3 has been shown previously to generate excellent, repeatable, and sensitive detection results for pesticides and semivolatile organic contamination [30]. A total of three strips per acephate source and per time point were collected, each from a separate carpet square. Their position in the carpet square (left, middle, or right) was randomized. This resulted in a total of nine strips per acephate source, with three strips at each time point for each acephate source. The vacuum was cleaned with acetone between collections and blank dust collected to ensure carryover was not contributing to the analytical results. Furthermore, blank dust was collected at each time point to ensure cross-contamination of volatile species was not occurring. Extraction proceeded with 20 mL of dichloromethane for every 1 g of dust collected. The average amount of dust collected from each carpet strip was 1 g. Samples were sonicated for 20 min, centrifuged, and filtered prior to analysis.

A portion of each of the left-over acephate feed solutions was extracted with dichloromethane (DCM) at a 1:100 ratio immediately following the initial exposure of the test carpet and dust. These solutions were sonicated for 20 min, centrifuged, and filtered, and are referred to as recovery standards (RS). The feed solutions (FS) were analyzed as standards with no sonication or filtration at a concentration of 1 mg/mL in DCM.

A semi-volatile internal standard mixture consisting of dichlorobenzene-D4, naphthalene-D8, and acenaphthene-D10 was added to each sample prior to analysis. Analysis proceeded via GC–MS (Agilent 7890A/5925C inert XL EI/CI) with a RTX-5Sil MS column (30 m × 0.32 mm, 0.5 μm film thickness). A Siltek-coated gooseneck glass liner with glass wool (4 mm ID) was used. Triplicate splitless 1-μL injections were used and data averaged. The oven was initially held at 50 °C for 0.5 min, ramped at 10 °C/min to 270 °C, then ramped at 50 °C/min to 320 °C. A Dean Switch with RXI guard columns (1.3 m × 0.18 mm, FID and 2.4 m × 0.18 mm, MS) was used to divert the eluent to a Flame Ionization Detector (FID) from 0 to 6 min and 17.1 to 18.15 min. The first divert window was to minimize solvent exposure to the MS source. The second divert window was used to avoid sending acephate to the MS detector since its concentration is much higher than the compounds being monitored. The MS was operated in selected-ion monitoring (SIM) mode with electron impact ionization. A minimum of two ions were monitored for each compound.

2.5. CWA-related compounds

The following neat chemicals were purchased from Sigma–Aldrich (St. Louis, MO) and used without further purification: *O*-ethyl methylphosphonothioate (EMPTA), *N*,*N*-diisopropylmethylamine (DIPMA), *N*,*N*-diisopropylethylamine (DIEA), diisopropylamine (DIPA), diethyl aniline (DEA), diethyl ethyl phosphonate (DEEP), trimethyl phosphite (TMP), dimethyl hydrogen phosphite (DMHP), diethyl hydrogen phosphite (DEHP), and triethyl phosphate (TEP). Ethyl methylphosphonate (EMPA) and diisopropyl methylphosphonate (DIMP) were purchased from Cerilliant (Round Rock, TX) as 1000 μg/mL standards in methanol, and used without further purification.

Solutions with varying relative levels of compounds were prepared in water as summarized in Tables 1 and 2. In order to minimize hydrolysis, an intermediate solution was prepared in acetone and the diluted by a factor of 20 into water just prior to the exposure experiments. The VX profiles were included in the same solution with the corresponding G-agent profiles (i.e. VX (A) and G (A) profiles