Appendix 4

This appendix responds to comments provided by DC DOH on 23 specific chemicals. Some of DC DOH chemical-specific comments were made in the main body of the report, and some were made in the attachments. USACE has reviewed each of the 23 compounds identified by DC DOH in its comments; the resulting USACE responses are grouped into the following categories:

- Ubiquitous Chemicals
- Hydrocarbons and Combustion Products
- Natural Products
- Analytical Artifacts
- Other Chemicals

USACE maintains the following with regard to the compounds in question:

- 8 of the 23 compounds are likely to have originated as naturally occurring contaminants, or have a large number of industrial sources not associated with the AUES.
- 9 of the 23 compounds are either hydrocarbon constituents of fuels or are products of incomplete wood combustion in fireplaces and woodstoves.
- 3 of the 23 compounds are components of food items.
- 2 of the 23 compounds are almost certainly analytical artifacts.
- The remaining compound is a potential contaminant in a widely used adhesive component.
- None of the 23 compounds listed are experimental chemical warfare agents, and only two could be a precursor compound to a potential agent. Finally, all chemicals are present at levels likely to correspond to a *de minimis* risk.

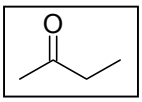
It is worth noting that USACE found several statements by DC DOH that mischaracterize the content of the standard references utilized to discuss the toxicity and potential health impacts of various compounds. The toxicological, production, and occurrence information used to address these chemical-specific comments by DC DOH in the following sections was collected primarily from the following sources:

- EPA Region III Risk-Based Concentration Table (October 2002 and April 2003). Available on line at http://www.epa.gov/reg3hwmd/risk/index.htm
- Hazardous Chemical Desk Reference (Sax, N. I.; Lewis, R. J., Van Nostrand Reinhold, NY, 1987
- Merck Index, (Merck & Co., Inc., Whitehouse Station, NJ)
- EPA, Office of Pollution Prevention and Toxics, Chemical Fact Sheets. Available on line at http://www.epa.gov/opptintr/chemfact/

Ubiquitous Chemicals

Of the 23 compounds listed in DC DOH's Tab B, 8 are likely either to have originated as naturally occurring chemicals or to have large potential sources not associated with the AUES. Furthermore, these chemicals appear likely to be ubiquitous contaminants in an urban residential environment.

2-Butanone

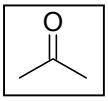


2-Butanone (CAS Registry No. 78-93-3), also known as Methyl Ethyl Ketone (MEK), occurs in the environment at low levels as a natural product (produced by some trees and found in small amounts in some fruits and vegetables). It occurs naturally and has been found in a number of foods and beverages, including Swiss cheese, cream, barley, bread, honey, oranges, black tea, rum, non-alcoholic beverages, and ice cream. It is also released to the air from car and truck exhausts. 2-Butanone is produced in large quantities for use in paints and other coatings, in adhesives, and as a cleaning agent. It is also found in cigarette smoke. Annual production in the United States in the late 1980s was on the order of 500-700 million pounds.

Tab B in the DC DOH report comments that 2-butanone is "toxic by ingestion and dermal, affects peripheral nervous system," citing *Hazardous Chemical Desk Reference* (Sax, N. I.; Lewis, R. J., Van Nostrand Reinhold, New York, 1987). This statement by DC DOH mischaracterizes the content of that reference. A complete reading of Sax and Lewis shows that 2-butanone is "moderately toxic by ingestion, skin contact, and intraperitoneal routes." The moderate toxicity is reflected in EPA Region III's risk-based concentration for residential soil. 2-Butanone was detected at levels ranging from 0.003 to 0.030 mg/kg at the OU4 residential properties, whereas EPA Region III has established a risk-based concentration for residential soil at 46,900 mg/kg. Because 2-butanone is a non-carcinogen, USACE screened the concentrations detected at OU4 using an adjusted risk-based concentration of 4,600 mg/kg.

2-Butanone is not listed on the AUES list of chemicals, and has never been considered either an experimental chemical warfare agent or an agent precursor compound. It is used extensively in industry and is potentially of natural origin. Given its use in consumer products, it is likely to be a ubiquitous contaminant in an urban residential environment.

Acetone



Acetone (CAS Registry No. 67-64-1) is a manufactured chemical that is also found naturally in the environment. It occurs naturally in plants and trees at low concentrations. Low levels of acetone are normally present in the body from the breakdown of fat; the body can use it in normal processes to make sugar and fat. It is present in vehicle exhaust, tobacco smoke, and landfill sites. Acetone is used to make plastic, fibers, drugs, and other chemicals. It is also sold commercially as a solvent and in such consumer products as nail polish remover. The reported total production volume of acetone in the United States was 2.3 billion pounds in 1990. Industrial processes contribute more acetone to the environment than natural processes.

Acetone was detected at levels ranging from 0.027 to 0.120 mg/kg, whereas EPA Region III has established a risk-based concentration for residential soil at 7,800 mg/kg. Because acetone is a non-carcinogen, USACE screened the concentrations detected at OU4 using an adjusted risk-based concentration of 780 mg/kg.

Acetone is not listed on the AUES list of chemicals and has never been considered an experimental chemical warfare agent, although it can be an agent precursor compound. It is used extensively in industry and is potentially of natural origin. Given its use in consumer products, it is likely to be a ubiquitous contaminant in an urban residential environment.

Carbon Disulfide

Carbon disulfide (CS_2, CAS Registry No. 75-15-0) is a natural product of anaerobic biodegradation. It is also used to manufacture viscose rayon, cellophane, carbon tetrachloride, dyes, and rubber. Some solvents, waxes, and cleaners contain carbon disulfide. It is also used as an insecticide. In 1985, commercial production was estimated to be 315 million pounds.

Carbon disulfide was detected at levels ranging from 0.008 to 0.170 mg/kg, whereas EPA Region III has established a risk-based concentration for residential soil at 7,800 mg/kg. Because carbon disulfide is a non-carcinogen, USACE screened the concentrations detected at OU4 using an adjusted risk-based concentration of 780 mg/kg.

Carbon disulfide is listed on the AUES list of chemicals, but it has never been considered either an experimental chemical warfare agent or an agent precursor compound. It is used extensively in industry, is potentially of natural origin, and is likely to be a ubiquitous contaminant in an urban residential environment.

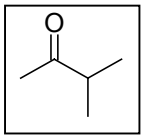
Chloromethane

Chloromethane (CH_3Cl, CAS Registry No. 74-87-3), also known as methyl chloride, is both an anthropogenic and naturally occurring chemical. Anthropogenic sources include industrial production, polyvinyl chloride burning, and wood burning; natural sources include the oceans, microbial fermentation, and biomass fires (e.g., forest fires, grass fires). Other sources of exposure to methyl chloride include cigarette smoke, polystyrene insulation, aerosol propellants, and chlorinated swimming pools. Chloromethane is produced industrially; 994 million pounds were produced in 1994.

Chloromethane was detected at levels ranging from 0.001 to 0.007 mg/kg, whereas EPA Region III has established a risk-based concentration for residential soil at 49 mg/kg. Because chloromethane is a carcinogen, USACE screened the concentrations detected at OU4 using an unadjusted risk-based concentration of 49 mg/kg. (Note: In 2003, the EPA eliminated the risk-based concentration for chloromethane in soil.)

Chloromethane is not listed on the AUES list of chemicals and has never been considered either an experimental chemical warfare agent or an agent precursor compound. It is used extensively in industry, is potentially of natural origin, and is likely to be a ubiquitous contaminant in an urban residential environment.

3-Methyl-2-Butanone

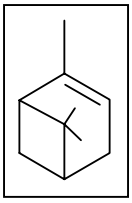


3-methyl-2-butanone (CAS Registry No. 563-80-4) is also known as Methyl Isopropyl Ketone (MIPK). The analysis indicates that there is sufficient evidence to make a tentative identification of MIPK as present in some of the samples. MIPK is used as an intermediate in the synthesis of other chemicals and as an industrial solvent. It may also find some use as a solvent in specialty coatings applications, such as nitrocellulose lacquers. It can be used as an MEK substitute. No production data for MIPK were readily available.

The MIPK concentration was estimated at levels ranging from 0.002 to 0.040 mg/kg; EPA Region III has not established a risk-based concentration for MIPK. Given its structural similarity to MEK, it likely corresponds to a *de minimis* risk.

MIPK is not listed on the AUES list of chemicals and has never been considered either an experimental chemical warfare agent or an agent precursor compound. It is used extensively in industry and is likely to be a ubiquitous contaminant in an urban residential environment.

2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene



2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene (CAS Registry No. 80-56-8) is also known as α-pinene. The analysis indicates that there is sufficient evidence to make a tentative identification of α-pinene as present in some of the samples. α-Pinene is a monoterpene that is a major component of wood turpentine; it is obtained from the resinous sap of pine trees by steam distillation. Terpenes are widely used as solvents for paints, protective coatings, polishes, and waxes; flavorings; deodorants; and medicines (as in the treatment of acne). α-Pinene is continuously emitted into the atmosphere from all plants, mainly from conifers. Estimates of biogenic and anthropogenic emissions indicate that all human exposure to α-pinene is essentially from biogenic sources. No production data for α-pinene were readily available.

The α-pinene concentration was estimated at levels ranging from 0.010 to 0.080 mg/kg; EPA Region III has not established a risk-based concentration for α-pinene. Based on toxicity data for laboratory mammals (LD_{50} of 3,700 mg/kg), this concentration is not anticipated to present any adverse health effects. In addition, α-pinene is recognized as a food additive by the U.S. Food and Drug Administration.

α-Pinene is not listed on the AUES list of chemicals, although turpentine is listed (α-pinene is a component of turpentine). α-Pinene has never been considered either an experimental chemical warfare agent or an agent precursor compound. It is of natural origin, is used extensively in industry, and is likely to be a ubiquitous contaminant in an urban residential environment.

Dichlorodifluoromethane

The DC DOH's Tab B lists "dichlorofluoromethane," whereas the USACE report indicates that dichlorodifluoromethane (CCl_2F_2, CAS Registry No. 75-71-8) was found in samples from the site. Dichlorodifluoromethane is also known as CFC-12. Because it is an ozone-depleting chemical, production of CFC-12 was halted on 1 January 1996. However, prior to being banned, it was used as a refrigerant in domestic and automobile air conditioners, aerosol propellant, foam-blowing agent, and solvent, as well as in the manufacture of fluoropolymers. Peak annual production in the United States was over 500 million pounds.

The CFC-12 concentration was estimated at levels ranging from 0.067 to 0.160 mg/kg; EPA Region III has established a risk-based concentration for CFC-12 in residential soil at 16,000 mg/kg. Because CFC-12 is a non-carcinogen, USACE screened the concentrations detected at OU4 using an adjusted risk-based concentration of 1,600 mg/kg. As an indicator of the non-toxic nature of CFC-12, it is noted that existing stocks continue to be used as propellants in bronchial dilator pharmaceutical preparations.

CFC-12 is not listed on the AUES list of chemicals and has never been considered either an experimental chemical warfare agent or an agent precursor compound. It is almost certainly unrelated to AUES activities; the compound was only discovered in the late 1920s and the first patent application for the manufacture of CFC-12 was filed on 5 April 1930 (Midgley et al., *Manufacture of aliphatic fluoro compounds*, U.S. Patent 1,930,129). It has been used extensively in industry and consumer products and is likely to be a ubiquitous contaminant in an urban residential environment.

Carbonyl Sulfide

Carbonyl sulfide (COS, CAS Registry No. 463-58-1) is also known as carbon oxide sulfide. The analysis indicates that there is sufficient evidence to make a tentative identification of carbonyl sulfide as present in some of the samples. Carbonyl sulfide is a gas at normal temperatures and pressures. It is used as an intermediate in the synthesis of organic sulfur compounds and alkyl carbonates. The compound can be released to the atmosphere naturally from marshes, soils, and deciduous and coniferous trees. It can also be released to the ambient environment as a result of the combustion of sulfur-containing fuels. Anthropogenic emissions have been estimated to be less than one-third of natural emissions.

The carbonyl sulfide concentration was estimated at levels ranging from 0.006 to 0.010 mg/kg; EPA Region III has not established a risk-based concentration for carbonyl sulfide. Based on data summarized by the EPA's Office Pollution Prevention and Toxics (1994), this concentration in soil is not anticipated to present any adverse health effects.

Carbonyl sulfide is not listed on the AUES list of chemicals and has never been considered either an experimental chemical warfare agent or an agent precursor compound. It is used extensively in industry, is potentially of natural origin, and is likely to be a ubiquitous contaminant in an urban residential environment.

Hydrocarbons and Combustion Products

Of the 23 compounds listed in DC DOH's Tab B, 9 are either hydrocarbon constituents of fuels—such as gasoline (octane, *E*-2-octene, 3-methyleneheptane)—or are aldehydes (acetaldehyde, hexanal, 5-methylhexanal, octanal, pentanal, 14 octadecenal). Aldehydes are formed as a result of incomplete wood combustion in fireplaces, woodstoves, forest fires, and wildfires. They are also produced during pulp and paper production and emitted from stationary internal combustion engines and turbines, vehicle exhaust, and wastewater processing. The analysis indicates that there is sufficient evidence to make a tentative identification of these compounds as present in some of the samples.

These compounds are not listed on the AUES list of chemicals and they have never been considered either an experimental chemical warfare agent or an agent precursor compound. They are mostly of natural origin and used to a minor degree in industry; some are components of gasoline and other fuels. They are likely to be a ubiquitous contaminant in an urban residential environment. Estimated concentrations are given in Table App.4-1.

Table App.4-1: Estimated Concentrations of Hydrocarbons and Combustion Products

Compound	Synonym	CAS Registry No.	Estimated concentration (µg/kg)
Octane		111-65-9	8-20
E-2-octene	Trans-2-octene	13389-42-9	7-60
3-methyleneheptane	2-ethyl-1-hexene	1632-16-2	6-10
Acetaldehyde		75-07-0	4-40
Hexanal		66-25-1	10-100
5-methylhexanal		1860-39-5	3-10
Octanal		124-13-0	4-20
Pentanal isomer 1		NA	3-30
14 octadecenal		NA	180

In Tab B, DC DOH states that acetaldehyde "causes respiratory paralysis" and cites the Ninth Edition of the Merck Index. This statement mischaracterizes the content of that reference and fails to take into account the concentration of the chemical reported at the OU4 properties. The Merck Index entry for acetaldehyde notes that "large doses may cause death by respiratory paralysis" and provides an oral LD_{50} of 1.9 g/kg in laboratory rats; this roughly corresponds to a dose of 140 g for 70 kg human. At soil concentrations of 0.040 mg/kg, acute poisoning would require consumption of over 3,000 metric tons of soil. Although children are potentially more susceptible, they would still need to consume many times their body weight in contaminated soil in order to experience toxic effects. EPA Region III does not list an RBC for acetaldehyde in soil, likely because it is essentially non-toxic by ingestion as demonstrated by its use as a flavoring agent. Acetaldehyde is a by-product of yeast production and is a naturally occurring compound in wine, bread, soy sauce, and other yeast-fermented products.

Tab B in the DC DOH report states that octane is an "asphyxiant and blister agent" and cites Sax and Lewis. This statement mischaracterizes the content of the reference. Sax and Lewis write that octane "may act as a simple asphyxiant." Elsewhere, the reference describes the action of a simple asphyxiant as "excluding O_2 from the lungs. The effect of simple asphyxiant gases is proportional to the extent to which they diminish the amount (partial pressure) of O_2 in the air that is breathed." Parts per million levels in soil will not significantly diminish the amount of oxygen in the air that is breathed. Similarly, Sax and Lewis write that "human dermal exposure to undiluted octane for five hours resulted in blister formation." This effect is unrelated to the class of chemical warfare agents classified as blister agents and is very unlikely to occur at the levels found in the samples.

Tab B of the DC DOH's comments states that hexanal is "toxic [by] ingestion and inhalation, (acrid smoke)," citing Sax and Lewis. This statement mischaracterizes the content of that reference. Sax and Lewis write that hexanal is "mildly toxic" and "when heated to decomposition, it emits acrid smoke and fumes." The oral LD_{50} for hexanal in laboratory rats is 4,890 mg/kg, which corresponds to a dose of 342 grams (0.8 lb) for an adult human. At soil concentrations on the order of 0.100 mg/kg, acute poisoning would require consumption of over 3,000 metric tons of soil.

Natural Products

Of the 23 compounds listed in Tab B of the DC DOH's comments, 3 are major components of a number of food items, are likely to have originated as naturally occurring contaminants, or have large potential sources that are not associated with the AUES.

Hexadecanoic Acid

Hexadecanoic acid (CAS Registry No. 57-10-3) is also known as palmitic acid. The analysis indicates that there is sufficient evidence to make a tentative identification of this compound as present in some of the samples.

The DC DOH's Tab B confuses "hexadecanoic acid" with "decanoic acid." The DC DOH material on hexadecanoic acid indicates that "decanoic acid is a poison (acrid smoke)." Decanoic acid (chemical formula $C_{10}H_{20}O_2$) is a different chemical compound than hexadecanoic acid (chemical formula $C_{16}H_{32}O_2$). Sax and Lewis have an entry under "palmitic acid" that indicates that it is a poison by the intravenous route; the substance is essentially non-toxic by the oral route. Sax and Lewis also write that when heated to decomposition, it emits acrid smoke and irritating fumes; the relevance of smoke generation, as cited in the DC DOH report, to parts per billion levels in soil is unclear. Palm oil contains 44 percent palmitic acid esters; other natural

oils contain significant quantities of palmitic acid esters. Enzymatic digestion of the oil produces the free acid.

The palmitic acid concentration was estimated at levels ranging from 0.089 to 0.670 mg/kg. EPA Region III has not established a risk-based concentration for palmitic acid, most likely because it is essentially non-toxic and is a major component of many food items.

Palmitic acid is not listed on the AUES list of chemicals and has never been considered either an experimental chemical warfare agent or an agent precursor compound. It is of natural origin, is used extensively in industry, and is likely to be a ubiquitous component of the environment.

Oleic Acid

Oleic Acid (CAS Registry No. 112-80-1) is also known as Z-9- octadecenoic acid. The analysis indicates that there is sufficient evidence to make a tentative identification of this compound as present in some of the samples.

The DC DOH's Tab B states that oleic acid is a "poison and skin irritant," citing Sax and Lewis. This statement mischaracterizes the content of that reference. Sax and Lewis write that oleic acid is a "poison by intravenous route;" they also cite toxicological data for laboratory rats indicating an intravenous LD_{50} of 2,400 µg/kg versus an oral LD_{50} of 74 g/kg; this indicates that oleic acid is 30,000 times less toxic by ingestion. Olive oil contains 55-85 percent oleic acid esters. Extra virgin olive oil can have up to 1 percent free oleic acid, virgin between 1 and 3 percent free oleic acid. Other natural oils contain significant quantities of oleic acid esters. Enzymatic digestion of these oils produces the free acid.

The oleic acid concentration was estimated at levels ranging from 0.130 to 4.20 mg/kg; EPA Region III has not established a risk-based concentration for oleic acid, most likely because it is essentially non-toxic and is a major component of many food items.

Oleic acid is listed on the AUES list of chemicals, but it has never been considered either an experimental chemical warfare agent or an agent precursor compound. It is of natural origin, is used extensively in industry, and is likely to be a ubiquitous component of the environment.

1-Eicosanol

The analysis indicates that there is sufficient evidence to make a tentative identification of 1-eicosanol (CAS Registry No. 629-96-9) as present in some of the samples. 1-Eicosanol is used by plants and animals to make wax, which is a mixture of esters of long-chain alcohols and long-chain carboxylic acids. The alcohol has been found in the secretions from the abdominal tips of queen bees, and beeswax samples have included eicosyl hexadecanoate and eicosyl octadecanoate. It is also present in plant waxes, including Jojoba wax.

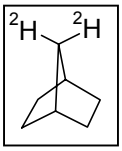
The 1-eicosanol concentration was estimated at levels ranging from 0.190 to 0.200 mg/kg. EPA Region III has not established a risk-based concentration for 1-eicosanol, most likely because it is essentially non-toxic and is a major component of a number of natural products.

1-Eicosanol is not listed on the AUES list of chemicals and has never been considered either an experimental chemical warfare agent or an agent precursor compound.

Analytical Artifacts

Of the 23 compounds listed in the DC DOH's Tab B, 2 are likely to be analytical artifacts—false positives—because they are not present in the soil samples collected from the OU4 residential locations. These compounds are unlikely to be present in the soil at AUES.

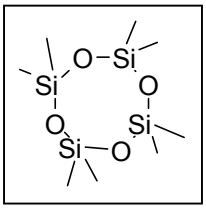
Bicyclo[2.2.1]heptane-7,7-d



Bicyclo[2.2.1]heptane-7,7-d is almost certainly a misidentified substance or an analytical artifact. The analysis indicates that this is a tentatively identified compound (TIC). In practice, TICs result from analyses using gas chromatography/mass spectrometry (GC/MS) when a compound not on the target analyte list is detected. The instrument compares the pattern of ions produced in the MS part of the instrument with a computer library and tentatively identifies the compound with the library spectrum that provides the best match. In this case, the best match apparently was an isotopically-labeled compound that is unlikely to occur outside a laboratory. It almost certainly would not result from AUES activities, as isotopically labeled compounds did not become common research tools until well after World War II. Isotopically labeled compounds have never been considered either experimental chemical warfare agents or agent precursor compounds.

It is possible that identification could be made by an analyst reviewing the reconstructed ion chromatogram from the data package. However, it is very likely that this is a monoterpene (similar in structure to α-pinene) of some sort; a more specific identification may not be possible. Given that the concentration of this compound is estimated at 0.006 to 0.050 mg/kg, further effort at identification may not be reasonable.

Octamethylcyclotetrasiloxane

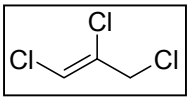


Octamethylcyclotetrasiloxane (CAS Registry No. 556-67-2) is an analytical artifact. Traditional polysiloxane-type GC column stationary phases degrade at elevated temperatures. The degradation process is well documented and consists of the thermal rearrangement of the siloxane backbone to produce cyclosiloxanes, such as octamethylcyclotetrasiloxane. These compounds are volatile and elute from the column as column "bleed". The estimated concentrations reported (0.003 to 0.010 mg/kg) are typical of column bleed; the likelihood that this substance was present in the samples as taken is very small. Where octamethylcyclotetrasiloxane is a suspected contaminant, the analysis must be performed using an extra-low bleed capillary column to avoid this potential for interference.

Other Chemicals

There was only one chemical that could not be characterized within the other groups listed above.

1,2,3-Trichloropropene



The analysis indicates that there is sufficient evidence to make a tentative identification of 1,2,3-trichloropropene (CAS Registry No.96-19-5) or a similar compound as present in some of the samples. 1,2,3-Trichloropropene is generally found as a contaminant of epichlorohydrin, which is used in turn to manufacture glycerin and unmodified epoxy resins.

The 1,2,3-trichloropropene concentration was estimated at levels ranging from 0.100 to 0.280 mg/kg, whereas EPA Region 3 has established a risk-based concentration for residential soil at 390 mg/kg. Because 1,2,3-trichloropropene is a non-carcinogen, USACE screened the concentrations detected at OU4 using an adjusted risk-based concentration of 39 mg/kg.

1,2,3-trichloropropene is not listed on the AUES list of chemicals; 1,2,3-trichloropropane, which is on the list, is a different substance. 1,2,3-Trichloropropene has never been considered an experimental chemical warfare agent, although it can be an agent precursor compound.