# **Soil and Groundwater Analysis**

# Volatile Organic Compounds (VOCs)

**VOCs should be evaluated at all petroleum related UST sites.** Soil Remediation Levels (SRLs) were established in 1997 and of the petroleum-related compounds of concern, only 4-ethyltoluene and propylene don't have SRLs. All petroleum-related compounds of concern should have been part of any UST investigation once the SRLs were adopted in 1997. Arizona Department of Health Services (ADHS) issued Information Update #52 in 1998 in regards to what compounds are to be reported using EPA Method 8260B. ADHS issued Information Update # 106 in 2010 regarding additions to the standard 8260 VOC list.

The ADHS issued Information Update #119 on May 15, 2014 to include the most recent additions to the 8260B target compound list. Currently, twenty four (24) compounds found in petroleum products are included in the 8260B target analyte list for both soil and groundwater. The entire 8260B compounds list needs to be reported by the laboratory. The six compounds identified with an asterisk (\*) may be reported as a tentatively identified compound (TIC), depending upon the laboratory used.

1,3-Butadiene*	Benzene	1,2-4-Trimethylbenzene	
n-butyl benzene	Toluene	1,3,5-Trimethylbenzene	
Sec-butyl benzene	Ethyl benzene	MTBE (methyl tert butyl ether)	
Tert-butyl benzene	Xylenes	1,2-DCA (1,2-dichloroethane)	
Carbon disulfide	Methyl cyclohexane*	Dicyclopentadiene*	
Cumene (Isopropyl benzene)	Naphthalene	n-Hexane	
Cyclohexane*	n-propylbenzene	p-isopropyl toluene	
4-ethyltoluene*	Propylene (Propene)*	EDB (1,2-dibromoethane/ethylene dibromide)	

# Where do you find some of these compounds?

Diesel fuel contains higher concentrations of 1,3-butadiene than gasoline.

# Leaded or regular gasoline - between 1920s and the early 1990s

Ethylene dibromide/1,2-dibromoethane (EDB)/1,2-dichloroethane (1,2-DCA) EDB and 1,2-DCA are lead scavengers which were added to prevent the build up of lead oxide deposits in internal combustible engines. EDB analysis in soil can be done using EPA Method 8260B. If the laboratory's reporting limit is not below the residential Soil Remediation Level of 0.29 mg/Kg, EPA Method 8011 should be used for analysis. EDB analysis in groundwater (source well and any wells with previous detections of EDB) should be conducted using EPA Method 504.1 or EPA Method 8011 to reach a reporting limit below the Aquifer Water Quality Standard (AWQS) of 0.05  $\mu$ g/L. EDB is persistent in groundwater due to the physical weathering process of both EDB and 1, 2-DCA, which is slow and can last decades and beyond.

Tetraethyl lead [TEL] is a component of leaded gasoline. The first ban of leaded gasoline occurred in 1985. Leaded gasoline was sold until approximately 1995 but it made up only 0.6% of total gasoline sales. TEL analysis is required for known or suspected (based on the year the UST was installed) leaded gasoline sites and aviation fuel sites. Tetraethyl lead has had a Soil Remediation Level since 1997 and should have been included in UST investigations for gasoline releases that occurred prior to 1995. Inorganic lead or toxicity characteristic leaching procedure (TCLP)

lead data is <u>not</u> acceptable to evaluate tetraethyl lead. There is no AWQS for tetraethyl lead and the AWQS for lead is <u>not</u> an acceptable regulatory standard for tetraethyl lead in groundwater.

# Unleaded gasoline-pre 2004

**Methyl tertiary butyl ether (MTBE)** was first used in 1979 in some gasoline blends, but in exceedingly small concentrations. In Arizona, MTBE was primarily used until approximately 2004 to satisfy the 1990 Clean Air Act amendments, which required oxygenated additives to reduce pollution from vehicle exhaust systems. By 2003, California banned MTBE and began using ethanol as the oxygenated additive. By 2004, Arizona was receiving over 60% of its gasoline from California.

# Unleaded gasoline releases- after approximately 2004

**Ethanol** is the current oxygenated additive in gasoline (E10, E15, E20, E85, E95 fuels) and is miscible in water unlike conventional petroleum fuels. Ethanol can be analyzed as part of EPA Method 8260B, but the laboratory detection limit in groundwater may be too high to give consistent, quantitative results. If requested, the laboratory can modify EPA Method 8260B by following the method as defined by the EPA in the SW-846 8000 series methods dated December 1996 or later updates. Most of the modifications are for instrument calibration. Dissolved gases which include methane, ethane and ethylene can be analyzed in groundwater by using the Standard Operating Procedure for method RSK-175 which was developed by the EPA Robert S. Kerr Research Laboratory. Aqueous samples are analyzed for the dissolved gases using a headspace Gas Chromatography/Flame Ionization Detection (GC/FID) technique. This data provides additional information to support the presence of ethanol in the groundwater since methane concentrations increase as ethanol degrades. Methane generation may be delayed for months to years after the gasoline release and may persist for years after the ethanol is no longer present in the groundwater.

# Premium and super (mid) grades of unleaded gasoline contain dicyclopentadiene.

# Polycyclic aromatic hydrocarbons (PAHs)

**PAHs should be evaluated for all gasoline, diesel, aviation gas (not Jet A), waste oil and unknown contaminant sources**. Analyze for PAHs using EPA Method 8310 or Method 8270C-SIM. Many of the PAHs may or may not be present at detectable levels in gasoline or diesel. As mentioned in the ADHS' Information Update #119, the following PAHs have SRLs, so they are to be reported.

Acenaphthene	Dibenz[ah]anthracene	Pyrene	Benzo(k)fluoranthene
Benzo(b)fluoranthene	Indeno [1,2,3-cd] pyrene	Anthracene	
Chrysene	Benz(a)anthracene	Napthalene	
Fluorene	Fluoranthene	Benzo(a)pyrene	

# **Inorganic Metals**

**Waste oil, and unknown UST content sites should be evaluated for certain inorganic metals.** The Resource Conservation and Recovery Act (RCRA) 8 metals by EPA Method 6010 etc. should be evaluated. The eight metals are: arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver.

<u>Note:</u> The petroleum product stored in USTs may have changed over the systems' lifetime. All petroleum-related analyses should be performed if UST history is not thoroughly known.

#### Geochemical parameters- Natural Attenuation in Groundwater

Because the natural attenuation rate includes the rates of processes other than biodegradation, *i.e.*, dispersion, sorption, dilution, volatilization, advection, geochemical indicators may be used to demonstrate the potential for biodegradation in groundwater.

The collection of the following geochemical data reflects the state of those metabolic steps in the reduction of organic molecules for energy and biomass production: *dissolved oxygen* (aerobic electron acceptor); *nitrate* (facultative anaerobic electron acceptor); *sulfate* (anaerobic electron acceptor), *manganese* (Mn+2, reduced form of anaerobic electron acceptor Mn+4), *ferrous iron* (Fe+2, reduced form of anaerobic electron acceptor Fe+3); *methane* (refractory anaerobic product); and *redox potential* (reflects the relative incidence of biological activity).

# **Soil Vapor Analysis**

ADEQ's Soil Vapor Guidance document dated April 2017 is available on our webpage.

# Volatile Organic Compounds

ADHS issued the most recent information update in November 2011 for compounds to be added to the EPA Method TO-15 (the original list was dated July 1999). The compounds listed need to be included on the EPA Method TO-15 target compound list. The laboratory may need to report some of the compounds as a TIC (tentatively identified compound). All TO-15 target compounds need to be reported. All TICs need to be reported which will include the leak detection tracer compound (1,1-difluoroethane also known as 1,1-DFA).

Acetone	4-Ethyltoluene	Trichlorotrifluoroethane (F-113)	
Dichlorodifluoromethane (F-12)	Bromodichloromethane	Methyl cyclohexane	
Dichlorotetrafluoroethane (F-114)	Cis-1,2-Dichloroethene	n-octane	
Isopropyl alcohol (2-propanol)	Cyclohexane	Nonane	
Propene (Propylene)	Dibromochloromethane	Isopropyl benzene (Cumene)	
1,2-4-Trimethylbenzene	Ethyl Acetate	n-propyl benzene	
1,2-Dichlorobenzene	Heptane	Tert-butyl benzene	
1,3,5-Trimethylbenzene	Tetrahydrofuran	Sec-butyl benzene	
1,3-Dichlorobenzene	Trans-1,2-Dichloroethene	n-butyl benzene	
Trans-1,3-Dichloropropene	Trichlorofluoromethane (F-11)	Naphthalene	
		Ethanol (most unreported analyte)	

# Fixed Gases

For suspected releases related to operating service stations (or to assist is differentiating a new release from an older release), soil vapor samples can be analyzed for fixed gases (methane, oxygen, nitrogen, carbon dioxide and carbon monoxide) by EPA Method 3C or equivalent.

# **General Information**

# **Field Protocols**

#### <u>Soil</u>

Soil samples for VOC analyses must be field preserved per EPA Method 5035 or subsampled using an Encore<sup>®</sup> or Terracore<sup>™</sup> type sampling device. Soil samples are <u>not</u> to be submitted to a laboratory in brass sleeves or glass jars for VOC analysis.

Soil sample collection should begin between 0 and 10 feet to evaluate for possible ingestion and dermal contact risk. **PAHs and TEL samples do not need to be collected at each depth that VOC samples are collected.** For PAH and TEL, collect additional samples at lithology changes, the deepest sample depth and also at the highest PID readings, at a minimum.

# **Groundwater**

Compliance sampling is required for LUST case closure evaluation. For compliance sampling, groundwater wells must be purged and appropriately sampled (low flow is an option). Compliance sampling may not be necessary during the monitoring phase of a project. This decision is project-specific and should be discussed with the ADEQ project manager.

If groundwater has recently been treated with oxidizing agents, most laboratories recommend collecting the samples in un-preserved Volatile Organic Analysis (VOA) vials to limit matrix interference and compound recovery problems due to the oxidizing agents. The holding time is seven (7) days for these unpreserved samples. Unpreserved samples can always be collected from wells if the holding time can be met.

Each sample matrix set should include duplicate samples (10% of total sample number). The appropriate blank sample(s) [equipment or trip blanks] should be collected as appropriate for the project.

# **Laboratory Information**

# Chain of Custody forms

The chain of custody form should indicate EPA Method 8260B (Arizona Full List) plus TICs or the target analyte list should be submitted along with the chain of custody form so the laboratory reports the correct data set.

# **Detection limits**

For all data sets, the laboratory should be reporting both the reporting level (RL) and the method detection limit (MDL). If the compound is present below the RL but above the MDL, the laboratory should report the concentration as estimated and use the EPA flag of "J" and/or the ADEQ data qualifier of E4 on another appropriate data qualifier. The laboratory detection limits and/or the reporting limits need to be below the lowest applicable regulatory standard. Data is to be reported as less than values, not as 'Non Detect'.

# Laboratory certification

The laboratory must be certified by ADHS for applicable method(s) and laboratory certification must be valid on the analysis date.